Towards Realistic Correlated Electronic Dynamics: New Developments in the Modeling of Harmonic Bath Models and Many Body Dispersion Interactions

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Towards Realistic Correlated Electronic Dynamics: New Developments in the Modeling of Harmonic Bath Models and Many Body Dispersion Interactions

A DISSERTATION PRESENTED

BY

THOMAS MARKOVICH

TO

THE DEPARTMENT OF CHEMICAL PHYSICS

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Towards Realistic Correlated Electronic Dynamics: New Developments in the Modeling of Harmonic Bath Models and Many Body Dispersion Interactions

ABSTRACT

In this work we develop and characterize tools to compute realistic environmental models and accurate molecular structures, with the ultimate goal of enabling accurate correlated electronic dynamics.

The procedure to compute environmental models starts with ab inito molecular dynamics, from which an autocorrelation function is computed. In this work we introduce super-resolution as a technique for recovering high resolution bath models from one quarter of the data that the Fourier transform requires. We further characterize the method and the closely related compressed sensing, to better understand transferability to other problems in chemistry. While work remains to improve upon our factor of four undersampling, we are optimistic that super-resolution will provide a path forward to computing accurate environmental models.

To accurately model the structure and energetics of many materials, particularly those in condensed phase, it is frequently necessary to include dispersion in density functional theory (DFT) calculations. One of the most accurate techniques for including dispersion in DFT is the many-body dispersion (MBD) model, which models the dispersion energy as the correlation energy of an auxiliary quantum harmonic oscillator system. In this work we present gradients of MBD model with respect to the ions, unit cell parameters, and the charge density, which yield the forces, cell stresses, and dispersion potential respectively. To make the MBD model applicable to a wide range of systems, we develop an efficient implementation of the MBD gradients and energies within the Quantum ESPRESSO, FHIaims, Octopus, and QChem software packages. We present results for gradient and unit cell optimizations for a wide range of systems, and find good agreement with reference values. In addition, we characterize the MBD’s dependence on both the application of MBD self consistently and the inclusion of the Hirshfeld volume gradients and find both are important for accurate forces. We present a framework for combining the MBD model with new exchange correlation functionals and provide this fitting data for twenty-four DFT exchange-correlation functionals. While significant work
still remains in further benchmarking the MBD model, we are encouraged by current results.
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Modeling dynamical processes such as energy transfer and chemical binding have received renewed interest in recent years, due to the increased computational power available to more accurately and efficiently simulate these processes. In order to provide a more accurate model of laboratory experiments, it is often important to perform simulations of either solvated or solid-state materials. Because these condensed phase materials require treating a computationally intractable number of degrees of freedom, approaches that depend on the open quantum systems formalism are frequently employed. These approaches separate the large system into two subsystems. A small system to be treated explicitly, and a much larger system to be averaged over and modeled as a set of harmonic oscillators. We typically refer to the larger system as a harmonic bath. With this partitioning in hand, the equation of motion is typically referred to as the master equation.

In recent years, the open quantum formalism has proved to be vital for the accurate description of energy transfer in excitonic systems, electron transport through molecular bridges, and charge transport in organic molecules. Unfortunately, most of these cases require that we construct a model Hamiltonian in an appropriate, general, electronic basis, thereby ignoring the electronic correlations. The implicit assumption in the construction of this model Hamiltonian is that the electronic problem has been solved. While possible for some systems, this assumption represents a significant limitation on the application of the open quantum systems formalism to an arbitrary system. In Chapter 2, we present a polaron transformed open quantum systems formalism that treats the full many-body many-electron problem. By making use of the polaron transformation, we combine the electron correlation and system-bath coupling into a single perturbation theory. This allows us to directly simulate the role of environmental factors such as solvation, nuclear vibrations, and finite temperature effects on electronic decay. We neglected the structure of the spectral density by opting for a simplistic Ohmic peak for the simulations in Chapter 2. While this allowed us to explore the results in our proof of principle, we observed during the course of the research that the electronic dynamics are sensitive to the choice of spectral density and molecular geometry. With the observation that
the spectral density and molecular geometry are vital to any correlated electron master equation, the remainder of the dissertation will focus on developing tools to construct spectral densities and geometries.

1.1 \( L_1 \) Methods

A spectral density that includes specific information about the bath, such as normal modes and lifetimes is termed “atomistic.” The procedure to compute atomistic spectral densities first starts with a molecular dynamics (MD) simulation of our system of interest. At every time step, a time dependent density functional theory (TDDFT) calculation is done to obtain the energy gap between the groundstate and first excited state. With energy gaps at every time step, we compute the energy gap correlation function, take the Fourier transform, and weight by a harmonic prefactor. Due to the Shannon-Nyquist sampling theorem, a 50 picosecond MD-TDDFT simulation, with a time step of 0.5 femtoseconds, is necessary to provide sufficient resolution. This procedure frequently requires millions of CPU hours. Because one of the significant bottle necks enters through the restrictions in place from the Shannon-Nyquist sampling theorem, the use of novel signal processing techniques that bypass the Shannon-Nyquist sampling theorem provide a promising path forward. The two novel signal processing techniques that we will consider are compressed sensing and super-resolution. Compressed sensing and super-resolution have found applications in fields as disparate as modern spectroscopy, partial differential equations, radar, modern imaging, and medicine.

We begin by defining the traditional problems of spectral decomposition and spectral parameter estimation, which are ubiquitous in the physical sciences. The traditional technique used to solve these problems is the Fourier transform, which decomposes a time series into its conjugate domain:

\[
\hat{f}(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{i\omega t} f(t) \, dt.
\]  

(1.1)

In spite of the Fourier transform’s many successes, it has a fundamental resolution termed the Nyquist limit or the Shannon-Nyquist theorem. If we assume that we sample regularly in time with sample spacing of \( \Delta t \), then the largest frequency that can be resolved is \( 1/2\Delta t \). Additionally, if we sample for \( N \) seconds, the best possible frequency resolution that we can recover is \( 1/2N \).

In situations where collecting data is difficult, it is often desirable to recover signals with resolution better than what is allowed by the Nyquist limit. While not explicitly possible within the framework of the Fourier transform, new methods have emerged. Two of these methods, compressed sensing and super-resolution, have found applications in fields as disparate as modern spectroscopy, partial differential equations, radar, modern imaging, and medicine.
super-resolution are closely related and claim to provide exact reconstruction of a signal that is proportional to the information in the signal. Both methods provide such guarantees when it is known that the signal of interest is sparse in some basis. That is, if we know the signal is sparse in some basis, and we can sample in the conjugate basis, it is possible to recover sub-Nyquist resolution with very few samples.

In the remainder of this section, we will present a mathematical introduction to compressed sensing and super-resolution. While we will specialize our discussion to Fourier matrices, it is important to note that this is without loss of generality.

When recast as a matrix equation, the Fourier transform is done by solving

\[ \mathcal{F}x = b, \] (1.2)

where \( \mathcal{F} \) is a square \( n \times n \) matrix, and that the frequencies are spaced according to the Nyquist condition, \( x \) is the frequency representation of the signal, and \( b \) is the time representation of the signal. In this situation, our goal is to find the signal’s frequency representation given the sampled points. In the situation that \( \mathcal{F} \) is square, we can solve this problem through exact matrix inversion or more numerically stable techniques.

Suppose, however, that one would like to recover the same signal but with fewer sampled points. This will require \( b \) be a vector of length \( m \) and \( \mathcal{F} \) is a matrix of size \( m \times n \). In this situation, we now have an underdetermined set of linear equations, and thus, we require an extra constraint to choose a specific vector from the nullspace. In general, this is not a well posed problem.

However, if we know that the signal should only have \( k \) nonzero frequencies, and \( k \ll n \), it is possible to beat the Nyquist condition by using compressed sensing or super-resolution – the two signal processing methods studied in this dissertation. Both compressed sensing and super-resolution simply need to find the sparsest possible vector while still satisfying the matrix equation, \( \mathcal{F}x = b \). Put concretely,

\[ \arg\min_x \|x\|_0 \text{ subject to } \|b - \mathcal{F}x\|_2, \] (1.3)

where \( \|x\|_0 \) is the zero-norm, which counts the number of nonzero elements of the vector. This optimization problem is computationally intractable because minimizing the zero-norm carries a combinatorial computational complexity. By lifting the zero-norm to the one-norm, however, we can make the problem tractable [29, 30]. That is, the following minimization problem is soluble in polynomial time:

\[ \arg\min_x \|x\|_1 \text{ subject to } \|b - \mathcal{F}x\|_2, \] (1.4)
Both compressed sensing and super-resolution share the same optimization problem, with the primary
difference between the two methods being the difference in sampling technique.\cite{27,28} Compressed sensing
explicitly requires randomly sampled data, whereas super-resolution provides theoretical guarantees for
uniformly sampled data.

To provide a strong intuition for the convergence properties of $L_1$, we first consider a situation where
$m = 1$, and $n >> m$. In this situation, $\mathcal{F}x = b$ is extremely underdetermined and will admit a solution that is
highly likely to be inconsistent with the full data. Adding a second point is highly unlikely to provide
exactly enough information to find the exact solution. This trend continues until a critical number of
elements are observed. Once the critical number of observations is reached, a phase transition occurs and $L_1$
methods provide exact reconstruction.\cite{31}

For compressed sensing, this phase transition has been proven to occur at $m^*_{cs}$, where $m^*_{cs}$ is given by:

$$
m^*_{cs} \approx \mu^2 k \ln n,
$$

(1.6)

where $\mu$ is the incoherence parameter given by

$$
\mu = \sqrt{n} \max_{ij} \left| \langle \phi_i, \psi_j \rangle \right|,
$$

(1.7)

where $\phi_i$ is the Fourier basis and $\psi_j$ is the conjugate basis.\cite{33,34} We see from Equation (1.6), that $m^*$ occurs
at a position which depends linearly on $k$, the number of nonzero elements $x$.

For super-resolution, this phase transition has been proven to occur when the minimum sampling density,$\Delta(T)$ is given by

$$
\frac{1}{N} \Delta(T) \geq \frac{1.87}{f_c},
$$

(1.8)

where $f_c$ is the maximum frequency cutoff, and $N$ is the number of sampled points. Using a factor called the
super-resolution factor, $SRF$, given by

$$
SRF = \frac{N}{2f},
$$

(1.9)
Chapter 1. Introduction

we can recast Equation (1.8) as simply $4 \times SRF$.

Due to numerical noise, it is typically impossible to solve the optimization problem given in Equation (1.4) exactly. In practice, we typically solve the following optimization problem

$$\arg\min_x \|x\|_1 \text{ subject to } \|b - \mathcal{F}x\|_2 < \eta,$$  

(1.10)

where $\eta$ is termed the “denoising” parameter and typically takes on values between $10^{-4}$ and $10^{-8}$.\cite{4}

While we have only considered the Fourier basis in the above exposition, many possible bases exist such as random delta functions,\cite{35} random Gaussians,\cite{36} random wavelets,\cite{32} and many others. In fact, for a basis to be useful within the framework of compressed sensing or super-resolution it must satisfy the restricted isometry property (RIP).\cite{32,37}

The RIP condition, require that for some given isometry constant, $\delta_s$, that:

$$(1 - \delta_s) \|x\|_2^2 \leq \|\mathcal{F}x\|_2^2 \leq (1 + \delta_s) \|x\|_2^2.$$  

(1.11)

Said intuitively, RIP requires that under a sparsifying transform, the pairwise distances in both the original and the sparsified space are preserved. If RIP is satisfied, it ensures that the matrix is close to orthogonal.\cite{37}

Of particular interest to the construction of spectral densities is the basis of random Lorentzians. Each basis function corresponds to a damped oscillator with a specific frequency and lifetime, which allows for the direct extraction of physically relevant parameters from physical simulations.

1.2 Many Body Dispersion

Because the electronic dynamics are sensitive to accurate geometries, a reliable and accurate \textit{ab initio} method to predict geometries is required. While sophisticated wave-function techniques such as coupled cluster or configuration interaction are capable of providing such a method, their poor computational scaling places systems with more than one hundred atoms or systems in condensed phase out of reach. Kohn-Sham density functional theory (DFT) provides an alternative method for providing an \textit{ab initio} description of matter, with favorable computational scaling.\cite{38,43}

While DFT is in principle exact with proper choice of exchange correlation (XC) functional which governs electron-electron interaction, approximations must be made. The success of DFT can be largely attributed to remarkable accuracy offered by very simple approximations to the XC functional, which make systems of thousands of atoms tractable. The most commonly used approximations, which include the local density approximation (LDA),\cite{44} the generalized gradient approximation (GGA),\cite{45,55} or the hybrid

\(
1.2. Many Body Dispersion

approximation, all make the assumption that electron-electron correlation is inherently local. For the remainder of this discussion, we will refer to all three approximations as semi-local. Semi-local DFT has been successful in describing the energetics, structure, and function of a broad range of materials.

In spite of semi-local DFT’s success, one of its most significant failures is the inability to model long-range electron-electron correlation, which we will call dispersion interactions. Dispersion interactions originate from the collective non-local correlated motion of electrons, and as a result are inherently quantum mechanical. Dispersion interactions are present in many gas-phase molecular systems, solvated molecules, and solid state organic crystals, among many others. Therefore, an accurate treatment of dispersion interactions is vital to further improve DFT.

To motivate the need for dispersion corrections, we consider the cases of DNA binding and the graphite crystal structure. In the case of DNA binding, adenine and thymine are in a hydrogen-bonded motif, semi-local DFT successfully predicts binding. In this configuration, the binding occurs due to simple electrostatics, and thus, semi-local DFT has no problem because the failure to describe long range electron-electron correlation is irrelevant to the structure and function. By contrast, we observe that when adenine and thymine are stacked in a cofacial binding motif, semi-local DFT incorrectly predicts that the DNA base pairs should not bind. We know, however, from the structure of DNA, that such binding should happen. Such a fundamental failure in the description of the structure and function of DNA is illustrative but not unique. In the case of graphite, we observe that uncorrected semi-local DFT tends to significantly underbind graphite. Indeed, a unit cell optimization of graphite using one of the most commonly used GGA XC functionals, PBE, predicts that graphite should spontaneously decompose into graphene sheets. With dispersion corrections, however, we are able to recover the experimental unit cell.

Following the classification of Klimeš et al., we will provide a brief introduction to the most frequently used techniques for modeling dispersion interactions within the DFT framework. Klimeš et al. suggested a tiered hierarchy of dispersion interaction approximation schemes in analogy to the “Jacob’s ladder” categorization of successively improving XC functional approximation.

1.2.1 Step One - Ground

While the need for a long-range dispersion correction to semi-local DFT has been established, there are some semi-local functionals that can provide an accurate short range description of dispersion. That is, the XC functional still predicts an exponentially decaying asymptotic tail, but through cancellation of error and other inaccuracies, provides an adequate short range description. One of the earliest such examples is that of
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LDA, which is well known to mimic dispersion through spurious exchange binding. In fact, LDA is capable of binding the graphite unit cell. Unfortunately, LDA is incapable of providing accurate energetics or consistent structural results.

Other XC functionals, such as the “Minnesota functionals”\textsuperscript{[65,66]}, machine-learned functionals\textsuperscript{[67–69]} or the long-range corrected functionals are constructed by minimizing, as a function of free parameters, the average error in predicted energies across a range of atoms and molecules. These functionals attempt to include short range dispersion by including dispersion bound data in the functional fitting test set. While this provides a description of dispersion, these functionals still predict the incorrect asymptotic tail and can frequently suffer from other problems, such as oscillatory potential energy surfaces.

1.2.2 Step Two - Simple Pairwise Corrections

London’s original description of the dispersion interaction between two rare gas atoms by second order perturbative expansion of the Coulomb interaction, which yields

\[
E_{AB}^{\text{disp}} = -\frac{C_{6}^{AB}}{R_{AB}^{6}},
\]

where \( R_{AB} \) is the distance between the two atoms, and \( C_{6}^{AB} \) is the general dispersion coefficient.\textsuperscript{[70]} For rare-gas atoms in particular, London found the dispersion coefficient to be

\[
C_{6}^{AB} = \frac{3}{2} \frac{I_{A}I_{B}}{I_{A} + I_{B}} \alpha_{A} \alpha_{B},
\]

where \( I \) is the first ionization potential, and \( \alpha \) is the dipole polarizability. Unfortunately, computing dispersion coefficients in general proves to be a difficult problem. Indeed, London to arrive at Equation (1.13), he had to make significant assumptions about the electronic structure including that the electron density was isotropic. While plausible for rare-gas dimers, such assumptions are difficult to justify in molecular systems.

Using London’s original expression given in Equation (1.12), we observe that the energy diverges for small interatomic distances. For this reason, it is necessary to add a damping that depends on the interatomic distance to eliminate the divergence. The pairwise energy expression, including this damping function, is given by:

\[
E_{AB}^{\text{disp}} = -\sum_{AB} f(R_{AB}) \frac{C_{6}^{AB}}{R_{AB}^{6}},
\]
Methods in “step two” use pre-tabulated $C_6$ coefficients, that are arrived at through either experimental data, functional fitting, or some combination of the two. Because these dispersion coefficients are pre-tabulated, they cannot describe differences in chemical environment such as coordination or solvation. This can introduce quite significant errors because the difference between the dispersion coefficients for $sp$ and $sp^3$ hybridized carbon can be as large as 35%. In addition, because this method is still based on second order perturbation theory, at the dipole-dipole level of approximation, we neglect all higher-order multipole and multi-body dipole effects.

In spite of these problems, methods in “step two”, which include Grimme’s DFT-D2 have been incredibly successful due in large part to the near trivial computational cost, and reasonable level of accuracy for many simple systems.

With a dispersion energy in hand, the total energy is found by:

$$E_{\text{total}} = E^{DFT} + E^{\text{disp}}. \quad (1.15)$$

### 1.2.3 Step Three - Environmentally Dependent Pairwise Corrections

One of the significant problems with the methods in “step two” is the lack of system-dependent information built into the dispersion coefficients. The methods in “step three” seek to provide a path forward by including such chemical information, while still maintaining the computational advantages afforded by the pairwise energy expression.

The simplest of these methods is the DFT-D3 method of Grimme et al., which captures the chemical environment by pre-tabulating dispersion coefficients for a range of coordination numbers. These dispersion coefficients are found through a fitting process over a large training set. During a dispersion calculation, the coordination number of each atom will be calculated and the corresponding dispersion coefficient will be obtained from the lookup table. This method has supplanted DFT-D2 because the additional computational cost is negligible, and the DFT-D3 energetics provide significant improvement upon those given by DFT-D2. DFT-D3, however, is not capable of accurately modeling dispersion in systems where coordination number is unclear or when other environmental effects such as an electric field are present.

The Exchange Dipole Model (XDM) seeks to compute the dispersion coefficients by considering the XC hole. The exchange-correlation hole is averaged to provide an anisotropic charge density, from which the $C_6$ coefficient is calculated. This technique is outperformed almost uniformly by DFT-D3, and carries a
computational cost on par with hybrid density functionals.\cite{2009-Curro.338B,2010-Curro.338E}

Seeking a more clear path forward towards building in chemical information, Tkatchenko and Scheffler (TS) proposed a method where dispersion coefficients are found by weighting accurate reference atom polarizabilities by the ratio of an atomic volume in a molecule to that in a vacuum.\cite{2009-Tkatchenko.16264,2009-Tkatchenko.16265} The atomic volume in a molecule is referred to as the effective volume, and computed through the Hirshfeld partitioning scheme. This technique of reweighting is predicated on the approximation that polarizabilities are proportional to the atomic volume. The TS method is capable of providing extremely accurate energetics at modest computational cost. Additionally, because the Hirshfeld partitioning procedure provides explicit density dependence, it is possible to compute the dispersion potential to provide dispersion specific corrections to the Fock matrix.

Notably, all three methods in step three still assume that interactions are pairwise, and depend in some fashion on reference data.

### 1.2.4 Step Four - Long-Range Kernel Methods

In an attempt to stay within the DFT framework, and to avoid tabulating reference data, the methods in “step four” attempt to treat the dispersion energy as a nonlocal correlation energy given by

\[
E^{nl} = \int \int d\mathbf{r}_1 \, d\mathbf{r}_2 \, n(\mathbf{r}_1)n(\mathbf{r}_2)\Phi(\mathbf{r}_1, \mathbf{r}_2),
\]

where \(\Phi(\mathbf{r}_1, \mathbf{r}_2)\) is the nonlocal kernel constructed to provide the corrected asymptotic dependence, and \(n(\mathbf{r})\) is the charge density. Methods in step four include vdW-DF\cite{2001-Boer.13517,2003-Boer.2259} and VV10.\cite{2011-Chen.14249,2012-Chen.606}\cite{2012-Chen.606,2011-Chen.14249,2011-Chen.14249,2011-Chen.14249,2011-Chen.14249} While originally computationally expensive due to the double integration, a decade of work has significantly improved the efficiency through memoization, resolution of the identity approximations, and obtaining analytical expressions for specific integrals.

While these methods are capable of providing an accurate model for dispersion interactions without requiring reference data, they still assume that all interactions are pairwise. Critically, these long-range kernel methods are unable to model the presence of a dielectric slab without explicitly modeling the dielectric itself.
1.2.5 **Step Five - Many-body Methods**

While popular and successful for a wide range of systems, we now know that pairwise methods can provide quantitative and qualitative failures for the binding energies of host-guest complexes, layered 2D materials, cohesive properties of molecular crystals, among many others. Each of these cases requires the treatment of the true many-body nature of these dispersion interactions to properly explain the structure, function, and stability of complexes.

There are three different but closely related many-body effects that are important to consider – the non-additivity of polarizability, electrodynamic screening, and many-body dipole-dipole interaction effects. There are two distinct ways to include these effects: either through use of the random phase approximation (RPA) XC functional, or through the use of an effective Hamiltonian.

The RPA XC functional provides a direct path to an asymptotically correct XC functional that includes all orders of long-range many body interactions, with no reference data required. The RPA XC functional, however, is extremely computationally expensive and difficult to converge. In solid state calculations, for example, RPA frequently requires k-grids an order of magnitude larger than the DFT itself.

The technique of constructing effective Hamiltonians, by contrast, can be significantly cheaper. Within this framework, quantum harmonic oscillators (QHOs) are used to model the charge fluctuations which give rise to dispersion interactions. Because they are treated as QHOs, the Hamiltonian is quadratic, so the correlation energy can be found through exact diagonalization. This model is almost as old as quantum mechanics itself, and has been rediscovered many times. The principle difficulty with this model is the selection of parameters for each QHO. In the many body dispersion (MBD) method, these parameters are chosen in exactly the same way as they are in TS. With the TS level parameters in hand, the oscillators are screened using a Dyson-type screening equation, and then the full interacting Hamiltonian is diagonalized. The MBD method is provably equivalent to RPA within the dipolar limit. While the MBD method still suffers from the need for a large amount of reference data, it provides a path forward to accurately modeling the true many body nature of systems. The dispersion-based sections of this dissertation will focus on extensions of the MBD method.

1.3 **Outline**

In Chapter 2 we seek to motivate the remainder of the dissertation by introducing a correlated electronic master equation. While a proof of principle, we compare favorably across a range of model systems.
Chapter 1. Introduction

In Chapter 3, we apply super-resolution to achieve the goal of sub-Nyquist resolution in resolving spectral densities for use in open quantum systems simulations. Through the use of super-resolution, we are able to recover a spectral density with a quarter of the data that provides qualitatively excitonic dynamics.

In Chapter 4, we present a comparison between super-resolution, compressed sensing, and the filter diagonalization method to better understand the performance of these techniques for a broad range of noise models and signal types. We evaluate and present the performance of each method for the task of signal reproduction for a benchmark set of signals commonly used in the signal processing literature. In Chapter 5, we justify our study and methodology.

In Chapter 6, we present the analytical energy gradients in gas phase for the MBD model. We present a detailed and self-contained introduction to the MBD model, and present results for structure optimizations in the benzene dimer, a set of tri-peptide complexes, and a super-molecular complex. In addition, we prove the importance of including all implicit derivatives.

In Chapter 7, we extend upon the work of Chapter 6 to apply the MBD gradients solid state. In addition to the ionic gradients, we also present the cell forces, and the self-consistent derivatives. We discuss the details of our implementation, including parallelization scheme.

In Chapter 8, we extend upon the work in Chapter 7 to implement both Ewald summation and reciprocal space sampling. We present new formulas for all relevant gradients, and present convergence results. In addition, we present the first MBD “band structures,” and briefly discuss the MBD quasi-particles, termed “disperons.”

In Chapter 9, we extend the MBD model for use with DFT functionals other than PBE. MBD as a theory has only one adjustable parameter, which is the range-separation parameter. The range-separation parameter needs to be fit for each functional before MBD can be used. We present a framework for performing this fitting, and results for 24 different DFT functionals. Additionally, we present what appears to be a general equation for any GGA functional.

Finally, in Chapter 10, we present current preliminary work and future directions.
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Part I

Polaron Transformed Nonadiabatic Dynamics
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A Correlated-Polaron Electronic Propagator: Open Electronic Dynamics Beyond the Born-Oppenheimer Approximation

Apart from minor modifications, this chapter originally appeared as:


Abstract

In this work we develop an approach to treat correlated many-electron dynamics dressed by the presence of a finite-temperature harmonic bath. Our theory combines a small polaron transformation with the second-order time-convolutionless master equation and includes both electronic and system-bath correlations on equal footing. Our theory is based on the ab initio Hamiltonian and is therefore well-defined apart from any phenomenological choice of basis states or electronic system-bath coupling model. The equation-of-motion for the density matrix which we derive includes non-Markovian and non-perturbative bath effects and can be used to simulate environmentally broadened electronic spectra and dissipative dynamics which are subjects of recent interest. The theory also goes beyond the adiabatic Born-Oppenheimer approximation but with computational cost scaling like the Born-Oppenheimer approach. We perform example propagations with a developmental code, thus demonstrating the treatment of electron-correlation.
in absorption spectra, vibronic structure, and decay in an open system. An untransformed version of the theory is also presented to treat more general baths and larger systems.

2.1 INTRODUCTION

The small-polaron transformation of the electronic Hamiltonian was originally developed in the 1960s\cite{91}, and more recently revived\cite{92,93} in the many-electron context. It is a classic example\cite{94} of the utility of canonical transformations in quantum physics. While its usefulness is well-established\cite{94}, yet it is also experiencing renewed interest\cite{95,96,97,98}.

In particular, second-order master equations in the polaron frame afford good results in all bath strength regimes\cite{99,100} employing the variational technique of Harris and Silbey\cite{102}. In the many-electron case, there has also been some recent pioneering work towards developing random-phase approximation equations\cite{92,93}. The electronic structure community has also produced some related work\cite{103,108}, including phenomenologically damped response theory\cite{109}.

In this paper we formulate and implement a correlated many-electron master equation that overcomes several limitations of the adiabatic Born-Oppenheimer approximation and includes effects such as excited-state lifetimes and vibronic structure. The basic goal of our method is to produce electronic spectra for small molecules that include the effects of coupling to an environment. With continued development, our formalism could describe environmental localization of electronic states and the decay of quantum entanglement in correlated electronic systems.

The theory we present exploits the polaron transformation to combine both electron correlation and system-bath couplings in a single perturbation theory. In the transformed frame, high-rank quantum expressions are dressed by environmental factors which cause them to decay during dynamics. This introduces the possibility for environmentally induced decay of the correlations in
an electronic system, thereby making the problem computationally more tractable. We also discuss how a general one-particle perturbation to the electronic system may be treated in a closely related untransformed version of the theory. Physically relevant coupling models of this form are numerous, and several examples include nuclear motion coupled to electronic degrees of freedom, Coulomb coupling to a nearby nanoparticle surface, the electromagnetic vacuum, solvation effects, and perhaps even Coulomb coupling to surrounding molecules in a condensed phase.

The present method is distinguished from previous work by a few characteristic features. Unlike virtually all master equation approaches, it treats the dynamics without assuming the many-body problem of the electronic system to be solved. The reason being that, in general, the appropriate basis of a few electronic states to prepare a master equation cannot be found a priori. As a result, this theory begins from a system-bath Hamiltonian which is well-defined and atomistic in terms of single-electron states and employs a non-Markovian equation of motion (EOM) in place of phenomenological damping. Conveniently, we find that high-rank operator expressions responsible for the computational intractability of exact, closed, many-particle quantum mechanics are multiplied by factors which exponentially vanish in many circumstances.

We demonstrate the implementation of the formalism in a pilot code and apply it to calculate some dynamic properties of model small molecules. The spectra produced by the electron correlation theory are shown to compare favorably to related methods in the adiabatic limit. Vibronically progressed spectra are shown to be produced by the dressed theory and a Markovian version is applied to a basic model of electronic energy transport between chromophores. Finally the undressed, uncorrelated theory is used to simulate the ultraviolet absorption spectrum of 1,1-difluoroethylene and compared with available experimental data.
### 2.2 Theory

#### 2.2.1 Hamiltonian

As in the work of references,\textsuperscript{92,93} we use the non-relativistic \textit{ab initio} many-electron Hamiltonian with a Holstein-type\textsuperscript{114} (linear) coupling to a bath of non-interacting bosons (summation over repeated indices is implied throughout this paper unless stated otherwise), given by

\begin{equation}
\hat{H} = \hat{F} + \hat{V} + \hat{H}_{\text{b}} + \hat{H}_{\text{el}-\text{b}} = f_p^q a^\dagger_q a_p + V_{pq}^r s^\dagger_r a_p a_q + \omega_k b^\dagger_k b_k + a^\dagger_p a_p M^p_k (b^\dagger_k + b_k) . \tag{2.1}
\end{equation}

Here, \( a^\dagger_s \) creates an electron in the single-particle basis state \( s \), while \( b^\dagger_k \) creates a bosonic bath particle in the \( k^{th} \) mode. \( \hat{F} \) is the Fock operator of the reference determinant, and \( \hat{V} \) is the two-electron part of the electronic Hamiltonian in the same single-particle basis. The third term is the boson Hamiltonian, \( \hat{H}_{\text{b}} \) and the last term is the coupling of the electronic system to the bath. For a general bath mode with dimensionless displacement \( Q_k \), the bi-linear coupling constant \( M^p_k \), is related to the derivative of the orbital energy via \( M^p_k = \omega_k^{-1} \frac{df^p_k}{dQ_k} \) (no summation over \( p \) and \( q \) implied). In the following discussion, we will assume the one-electron parts of \( \hat{H} \) and \( \hat{F} \) to be diagonal in the (canonical) one-electron basis with eigenvalues \( \epsilon_p = f^p_p \).

We now introduce the displacement operator,

\begin{equation}
\exp[\hat{S}] = \exp[a^\dagger_p a_p M^p_k (b^\dagger_k - b_k)] \tag{2.2}
\end{equation}

\begin{equation}
\tilde{M}^k_p = M^k_p / \omega_k , \tag{2.3}
\end{equation}

which generates the polaron transformation. Since the operator \( \hat{S} \) is anti-Hermitian, it generates a unitary transformation of the electron-boson Hamiltonian \( \hat{H} \rightarrow \tilde{H} = e^{-\hat{S}} \hat{H} e^{\hat{S}} \). Explicitly, the
polaron transformed Hamiltonian is given by

\[
\hat{H} = \tilde{F} + \hat{H}_{\text{int}},
\]

(2.4)

where the one-particle part of the transformed Hamiltonian is given by

\[
\tilde{F} = \tilde{F}_{\text{cle}} + \hat{H}_{\text{boson}} = (\varepsilon_p - \lambda_p) a_p^\dagger a_p + \omega_k b_k^\dagger b_k,
\]

(2.5)

and we have introduced the reorganization energy \( \lambda_p = \sum_k M_p^k / \omega_k \). The transformed electron-electron interaction is given by

\[
\hat{H}_{\text{int}} = \tilde{V}^{rs}_{pq} a_s^\dagger a_q^\dagger a_r a_p X_s^\dagger X_q^\dagger X_r X_p,
\]

(2.6)

where the transformed matrix elements are

\[
\tilde{V}^{rs}_{pq} = V^{rs}_{pq} - 2(\omega_k \tilde{M}_r^k \tilde{M}_s^k) \delta_{ps} \delta_{qr} (1 - \delta_{sr}),
\]

(2.7)

and we have defined the bath operators \( \hat{X}_p \) as

\[
\hat{X}_p = \exp[\tilde{M}_k^p (b_k^\dagger - b_k)].
\]

(2.8)

For future reference it will also be useful to define dressed electronic creation and annihilation operators, denoted by \( \tilde{a}_s^\dagger \equiv a_s^\dagger X_s^\dagger \) and \( \tilde{a}_s \equiv a_s X_s \).

The key feature of the polaron transformation is that \( \hat{H} \) has no electron-phonon coupling term. As a result, the two-electron and electron-boson parts of the original Hamiltonian are combined into a single term which now couples two dressed electrons and two dressed bosons (Eq. 2.6). One
Figure 2.1: A schematic representation of the polaron transformation. One-electron energies of the underlying Hamiltonian take the form of displaced parabolas coupled to the Coulomb interaction $V$. In the transformed frame, the boson effects are absorbed into a $\tilde{V}$, which depends on the boson operators, $\hat{X}$. This makes $\tilde{V}$ effectively time-dependent via the bath correlation function $B(t)$.

should intuitively imagine the situation depicted in Fig. 2.1 where two displaced electronic energy surfaces are dragged into alignment by the polaron transformation thus altering the coupling region between them which now absorbs the electron-boson coupling. In what follows, our expressions will be derived in the interaction picture with respect to Eq. 2.6 and then switched to the Schrödinger picture. The harmonic nature of the bosons means that the correlation functions of $\hat{X}$ operators (in any combination and at multiple times) can be given as simple functions of $\omega_p, \tilde{M}$ and $\beta = k_b T$. The transformed electron-boson problem takes the form of the usual many-electron problem with a time-dependent electron-electron interaction. This allows us to harness powerful methodologies that stem from two distinct areas of research: quantum master equations and quantum chemistry methods. We exploit this feature to produce a model of electronic dynamics which treats system-bath dynamics and correlation effects within the same perturbation theory.
Chapter 2. A Correlated-Polaron Electronic Propagator: Open Electronic Dynamics Beyond the Born-Oppenheimer Approximation

2.2.2 ELECTRONIC DYNAMICS

Having reviewed the polaron transformation in the previous section, we now combine it with the time-convolutionless perturbation theory (TCL)\textsuperscript{117,118} to arrive at the central theoretical result of this manuscript. Our goal is to derive an equation-of-motion for a dressed particle-hole excitation operator, which we denote \( \tilde{o}_i^a \) (here \( i, j, k \ldots \) are zeroth-order occupied levels and \( a, b, c \ldots \) are unoccupied). We consider only the particle-hole part of the density matrix, commonly referred to as the Tamm-Dancoff approximation\textsuperscript{119,120} (TDA), to simplify the derivation of our equations and avoid the possible issues associated with the non-linearity of the other blocks.\textsuperscript{121}

To derive Fock-space expressions,\textsuperscript{122} it is convenient to assume that the initial equilibrium state is the canonical Hartree-Fock (HF) determinant \( i.e. \) the initial density matrix is \(|\Psi(0)\rangle\langle\Psi(0)| \approx |0\rangle\langle0|\), with being \(|0\rangle\) the HF determinant. This assumption relies on two approximations: 1) the first excited-state energy of the systems we will study is much larger than \( k_B T \), so that the system is effectively in the ground-state and 2) the initial state of the system is weakly correlated and hence dominated by a single Slater determinant. Assumption 1 is clearly valid for the small molecular systems we will study, while assumption 2 requires more care and the effects of initial correlations are discussed in detail in Section II. E. We define projection operators:

\[
\mathcal{P} \tilde{\mathcal{A}} = \mathcal{P}_F(\text{Tr}_b(\tilde{\mathcal{A}})) \times \langle X^+ ... X \rangle_{b,eq}, \text{ and } Q = \mathcal{K} - \mathcal{P}.
\]

(2.9)

where \( \mathcal{P}_F \) is a Fock space projector onto maps between single-electron \( \{a^\dagger a\} \) operators like the typical projector of a partitioned electron-correlation perturbation theory \( i.e. \):

\[
\mathcal{P}_F(\mathcal{L}_1 : o^a \rightarrow \eta^a) = \mathcal{L}_1
\]

(2.10)

\[
\mathcal{P}_F(\mathcal{L}_{\geq 2} : o^a ... a^b \rightarrow \eta^{a'b'}) = 0.
\]

(2.11)
This partitioning is consistent with the perturbative ordering of $\hat{H}$ by powers of $\tilde{V}$. We treat the description of the many-electron state in terms of only one-body operators (neglecting all higher density matrices) on the same footing as tracing over the bath degrees of freedom, so both phenomena are easily incorporated in the same master equation.

The effective Liouvillian becomes time-dependent due to the polaron transformation. Consequently, there exists no simple analytical formula for its Fourier transform. Instead, we must give a differential representation of the EOM for a particle-hole excitation, which can then be integrated numerically. Given these projectors, the time-convolutionless perturbation theory (TCL) over the space of $\mathcal{P}$ is:

$$\frac{d}{dt} \mathcal{P} \tilde{\sigma}(t) = \left( \mathcal{P} \mathcal{L}(t) \mathcal{P} + \int_0^t ds \mathcal{P} \mathcal{L}(t) \mathcal{Q} \mathcal{L}(s) \mathcal{P} \right) \tilde{\sigma}(t) + \mathcal{I}(t). \quad (2.12)$$

This is written in the interaction picture where $\mathcal{L} = -i[\tilde{V}(t), \cdot]$. The first term above is the uncorrelated part of the evolution, the second is a homeogenous term reflecting correlation between the system and the bath, and the last term is an inhomogeneity reflecting correlations of the initial state. The interaction picture perturbation is:

$$\tilde{V}(t) = (\tilde{V}^{pq}_{rs} e^{i\tilde{\Delta}^{pq}_{rs}} a_q^+ a_p^+ a_r a_s) \times \left( X_q^+(t) X_r^+(t) X_p(t) X_s(t) \right), \text{ where } \Delta^{\partial\partial \cdots}_{\alpha\beta \cdots} = (\varepsilon_q + \varepsilon_r + \cdots - \varepsilon_p - \varepsilon_s - \cdots).$$

Expanding the first term over the one-particle space and moving into the Schrödinger picture we obtain (left arrows, $\leftarrow$, are used to indicate the contribution of a term to $d\tilde{\sigma}/dt$):

$$\frac{d}{dt} \mathcal{P} \tilde{\sigma}_v^u(t) \leftarrow -i(\varepsilon_u - \varepsilon_v + \tilde{V}^{vp}_{us} B^{vs}_{pu}(t, t)) \tilde{\sigma}_p^v(t) \quad (2.13)$$

---

*Usually the TCL is applied to a phenomenological density operator and 1-body Liouvillian. Here we will apply it to a one-particle transition density operator. The projection operator technique and quantum Ehrenfest theorem required for the TCL both carry over.

†Since the perturbation is a two-particle operator, we cannot trivially diagonalize the first order term, as one does when working with tight-binding type Hamiltonians.

‡We leave $X$ operators in the interaction picture while pulling electronic operators into the Schrödinger picture throughout the text.
Chapter 2. A Correlated-Polaron Electronic Propagator: Open Electronic Dynamics Beyond the Born-Oppenheimer Approximation

We have introduced a shorthand for the correlation function $B^{(a\dagger),(a)}_{(a\dagger),(a)}$ (lower time, upper time):

$$B^{mnop}_{pqrs}(t,s) = \langle X^\dagger_m(s)X^\dagger_n(s)X_p(s)X^\dagger_q(t)X^\dagger_r(t)X_s(t) \rangle. \quad (2.14)$$

Term (2.13) is comparable in dimension and physical content to the response matrices of configuration interaction singles (CIS) with an attached, time-local boson correlation function. Because all arguments have the same time-index, $B$ only applies a real factor ($\sim 1$ as $\tilde{M} \rightarrow 0$) to values of the interaction and thus introduces no new time-dependence. The indices of the boson correlation function and their order, are simply read-off the $\tilde{V}$ integral they multiply.

The second homogeneous term introduces bath correlation functions between boson operators occurring at different times ($t$ and $s$) according to

$$\frac{d}{dt}P \partial^b_v(t) \leftarrow \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^t ds(P\mathcal{L}(t)Q\mathcal{L}(s)P\partial(t)) \quad (2.15)$$

$$= -[\check{V}_{pq}^r(t), Q[\int_{t_0}^t B^{ab,xy}_{rs,qp}(t,s)\check{V}_{xy}^{ab}(s)ds, \partial^a_m(t)]] \quad (2.16)$$

Moving the electronic part into the Schodinger picture and rearranging this becomes:

$$= -[\check{V}_{pq}^r(t), Q[\check{V}_{xy}^{ab}, \partial^a_m]] e^{i(\Delta^{ab}_n)^t} e^{i(\Delta^{ab}_m)^t} \int_{t_0}^t B^{ab,xy}_{rs,qp}(t,s) e^{i(\Delta^{ab}_s)^t} ds \quad (2.17)$$

Expanding the commutators in Eq. (2.17) applying Wick’s theorem to remove the many vanishing terms, and enforcing the connectivity constraint, one obtains many topologically distinct terms. In our implementation this is done automatically before the execution of a simulation. The terms are easily related to terms which occur in the expansion of the second-order Fermion propagator (SOPPA) and diagonalization-based excited-state theories like configuration interaction singles with perturbative doubles (CISD(D)). Since we employ the time-convolutionless
2.2. Theory

perurbation theory, the oscillating $e^{i\Delta t}$ factors are different than those which occur in
Rayleigh-Schrödinger perturbation theories (in the energy-domain denominator $\frac{1}{\omega - \Delta}$) and warrants
further study. We sum terms from a hole $\rightarrow$ particle excitation which is obtained by multiplying
both sides of Equation (2.12) on the left with $(a_i^\dagger d_i)^\dagger$ and applying Wick’s theorem

$$\dot{\hat{O}}_i^a(t) \leftrightarrow \tilde{V}_{ba}^{ij} \tilde{V}_{cj}^{bd} \tilde{a}_i^\dagger e^{i(\Delta_{bd})t} \int_{t_0}^t B_{a_{j,bd}}^{b_{d,cj}}(t,s) e^{i(\Delta_{cj})s} ds. \quad (2.18)$$

This term has six indices overall, but can be factorized as follows:

$$\dot{\hat{O}}_i^a(t) \leftarrow \dot{I}_i^a(t) \hat{a}_i^a \ \text{where:} \ \dot{I}_i^a(t) = \tilde{V}_{ba}^{ij} \tilde{V}_{cj}^{bd} e^{i(\Delta_{bd})t} \int_{t_0}^t B_{a_{j,bd}}^{b_{d,cj}}(t,s) e^{i(\Delta_{cj})s} ds \quad (2.19)$$

The calculation of $\dot{I}_i^a$ scales fifth order with the number of single electron states, and linearly with
the number of bath modes (which go into the calculation of $B(t)$). This low scaling with number of
bath modes is inherited from the approach of Silbey,\textsuperscript{102} Jang\textsuperscript{97} and Nazir\textsuperscript{129} The algebraic version
of the second term in Fig. 2.2 is:

$$\dot{\hat{O}}_k^b(t) \leftrightarrow \tilde{V}_{ab}^{ij} \tilde{V}_{cj}^{ab} \tilde{a}_i^\dagger e^{i(\Delta_{ab})t} \int_{t_0}^t B_{ij,ak}^{ab,cj}(t,s) e^{i(\Delta_{cj})s} ds \quad (2.20)$$

This term is sixth order with the size of the system, with the boson correlation function preventing
a desirable factorization of the V-V contractions. Fourteen sixth-or-less-order terms are found
which couple hole-particle excitations to each other; skeletons\textsuperscript{130} of these are shown
diagrammatically in Fig. 2.2 with explicit expressions for each of these terms given in the
supplementary information. We should note that our formalism lacks several terms which occur in
the SOPPA because of the $Q$ projector and the absence of $V_i o_{vac} o V_i$ ordered terms that are invoked
in the formal expansion of the time-ordered exponential.

As described so-far the EOM is not time-reversible even when $\hat{M} = 0$ because neither the
homogenous term nor the normal excitation operator take the form of an anti-Hermitian matrix.\footnote{This same issue occurs in SOPPA and CIS(D). Since CIS(D) is derived from diagonalization of the response matrix, this problem appears as a non-Hermitian effective response matrix instead of time-irreversibility, but these issues are the same.}

We remedy this by adding the terms which result from the normal excitation’s operator’s Hermitian conjugate, \textit{i.e.:} the indices of the vacuum and \( o \) are swapped, and the signs of \( \Delta_v \) and prefactor are flipped and the new term is added to the other perturbative terms. For example, Term $2.20$ becomes the following two terms:

\[
\begin{align*}
\frac{\dot{\delta}_{k}^{b}}{2} & = -\frac{1}{2} \tilde{\chi}_{ij} V_{c j} \delta_{k}^{b} \int_{t_0}^{t} B_{ij, ak}^{c b}(t, s)(e^{i(\Delta_{ab}^{c})(t-s)}) ds \\
\frac{\dot{\delta}_{l}^{c}}{2} & = -\frac{1}{2} \tilde{\chi}_{ik} V_{l j} \delta_{l}^{c} \int_{t_0}^{t} B_{ij, ak}^{b c}(t, s)(e^{i(\Delta_{ab}^{c})(t-s)}) ds.
\end{align*}
\]

Upon making this modification, the linear response spectrum of the adiabatic model is not significantly altered, but the adiabatic norm conservation is enforced and changes by less than 1 percent after 1700 a.u. in the case of $H_4$ with 4$^{th}$ order Runge-Kutta and a timestep of 0.05 a.u.

### 2.2.3 Dipole Correlation Function

Like any canonical transformation,\cite{131} the polaron transformation preserves the spectrum of the overall electron-phonon Hamiltonian but the statistical meaning of the state related to a particular eigenvalue is changed. In other words, the operators of our theory are different objects from the
2.2. Theory

adiabatic Fock space. To lowest order in system-bath coupling, electronic observables like the time-dependent dipole correlation function, which predicts the results linear optical experiments, can be obtained by generating the transformed property operator $\tilde{\mu} = e^{\tilde{S}} \mu e^{-\tilde{S}} = \mu^I a_i^\dagger a_j X^I X_j$.

Within the Condon, approximation the dipole correlation function is then the product of the electronic trace and bath trace over the $\hat{X}$ operators introduced in $\tilde{\mu}$. This adds a bath correlation function to the usual observable. Taking all the relevant expectation values gives the following explicit numerical formula for the dipole moment expression:

$$C_{d-d}(t) = \sum_{i,j,ab} \{ \mu_{ia} \tilde{\sigma}_{ia}(t) \mu_{jb} \tilde{\sigma}_{jb}(0) \} \cdot [\text{Tr}_B \{ X^I_a(t) X^I_b(0) X^I_j(t) X^I_j(0) \}].$$

This expression for the dipole-dipole correlation function assumes that the bath remains at equilibrium. CIS likewise only offers a zeroth-order oscillator strength. The spectra in this work are generated by “kicking” the electronic system with the dipole operator instantaneously and Fourier transforming the resulting dipole-dipole oscillations.

2.2.4 Untransformed Version

Because of the polaron transformation, the above formalism is accurate in the strong bath regime with diagonal system-bath couplings. To treat an off-diagonal, weak coupling, one can develop the complementary untransformed theory. With a bi-linear system-bath coupling of the form:

$$H_{sb} = \sum_{ij} a_i^\dagger a_j M_{ij}^I (b_i^\dagger + b_k^\dagger),$$

the development of an uncorrelated particle-hole equation of motion follows similarly to the one described above and described with $\tilde{H}_{sb}$ taking the place of $\tilde{V}$. The untransformed version also makes it possible to introduce an Ehrenfest scheme for the nuclear bath which may be pursued in
The projector of the untransformed version is simply the equilibrium trace over the \( b \) operators. The time convolutionless (TCL) produces second-order contribution of the form:

\[
\dot{\hat{o}}(t) \leftarrow \int_{t_0}^{t} [H_{sb}(t), [H_{sb}(s), \dot{\hat{o}}(t)]] ds.
\]

(2.24)

which after translation into the Schrödinger picture and application of Wick’s theorem produces several terms similar to the following:

\[
\dot{\hat{o}}_a(t) \leftarrow M^{1,j}_k M^{m,j}_k \rho^j_m(t) e^{i\Delta h s} \int_{t_0}^{t} e^{i\Delta s} C(t-s) ds
\]

(2.25)

The correlation function \( C_m(t) = \langle b_m^\dagger(t) b_m(0) \rangle \) is given by the usual formula:

\[
\begin{align*}
\text{Re}(C(\tau)) &= \sum_i \coth \left( \frac{\beta \omega_i}{2} \right) \cos (\omega_i \tau) \\
\text{Im}(C(\tau)) &= \sum_i \sin (\omega_i \tau).
\end{align*}
\]

(2.26)

These contributions to the equations of motion scale with the 4th order of the system size and they are two-orders of magnitude cheaper than the transformed version. They can be combined with just the uncorrelated part of the particle-hole equation of motion, or added to the correlation terms developed above with the bath factor removed. To treat a continuous bath of oscillators, one can introduce a continuous parameterization of \((M_k)^2 = J(\omega) / \omega^2 = \frac{n_i}{\omega} e^{-\omega / \omega_k}\) as an ohmic spectral density under the assumption that the coupling to the continuous bath is the same for every state up to a factor.

Furthermore, we find that the reorganization energy is given by \( \lambda_i = \omega_i d_i^2 \) which can be subtracted from the original Hamiltonian.

---

\(^4\text{Given in the supplementary material.}\)
2.2. Theory

2.2.5 Initial Correlations

In the above we have expanded on existing master equations by giving the electronic system a many-body Hamiltonian with Fermionic statistics. We have also improved upon typical electronic response theories by incorporating bath dynamics but we have assumed that the initial state was a single determinant and employed the corresponding Wick’s theorem. These approximations are made in many other treatments of electronic spectra\cite{110, 134, 135} and are acceptable for situations where a molecule begins in a nearly determinantal state. Optical absorption experiments of gapped small molecules belong to this regime. To rigorously study electron transport in a biased junction\cite{136} or otherwise more exotic initial state, one needs to treat the initial correlations,\cite{137,140} as in the non-equilibrium Green’s function (NEGF) method.\cite{141,143} These methods first propagate an initial determinant in imaginary time\cite{139} thermalizing and correlating the system before the dynamics, but numerical applications of the NEGF formalism require storage and manipulation of a state variable with three indices, \( G_{pq}(\omega) \), and are usually limited to small systems\cite{144} and short times. We can similarly perform an imaginary time propagation and have performed some exploratory calculations which are described in Section 2.6.

Instead of performing an imaginary time integration one can replace the usual Wick’s theorem and build the theory beginning from a state which is already correlated. Extended normal ordering\cite{145} makes it possible to take expectation values with a multi-configurational reference function via a generalization of Wick’s theorem\cite{146}. Using the extended normal ordering technique, the expressions of the present paper can be promoted to treat a general initial state directly, so long as the density operator of that state is known. This approach would eliminate the need for any adiabatic preparation of the initial state, but would generate more complex equations and is a matter for future work.

\footnote{A related technique was recently developed for the Green’s function.\cite{147}}
For weakly correlated systems it’s reasonable to keep the approximation that the usual Wick’s theorem applies to the initial state of the electronic system, and instead of adiabatically preparing an initial state, choose a perturbative approximation to the correlated part of the initial state, \( \tilde{Q}_0(0) = \int_{-\infty}^{0} ds L(s) \tilde{\phi}(0) \), and then treat the first inhomogenous term of the master equation:

\[
\mathcal{I}(t) = \mathcal{P} L(t) \int_{-\infty}^{0} ds L(s) \tilde{\phi}(0).
\]

The bath parts of the inhomogenous term are known to be relatively unimportant from studies of tight-binding Hamiltonians, and only slightly perturb the results of a propagation for short times so we will not include them.

It is interesting to note that with the addition of this inhomogenous term, there is a correspondence between the present theory and a model of electronic linear response derived from an effective Hamiltonian, CIS(D). The CIS(D) excited states are the eigenvectors of a frequency dependent matrix, \( A_{ai,bj}^{\text{CIS(D)}}(\omega) \), with the dimension of the particle-hole space:

\[
A_{ai,bj}^{\text{CIS(D)}}(\omega) = \hat{\mathcal{H}}^{\text{CIS}} - \frac{\mathcal{P} \hat{V} Q \mathcal{P} \hat{P}}{(\Delta - \omega)} + \mathcal{P} \hat{V} \hat{T}_2^2 \mathcal{P}.
\]

In the above equation \( \hat{T}_2 \) is the second-order excitation operator from Møller-Plesset perturbation theory. These terms correspond respectively to the Fourier transform of our \( \mathcal{P} \hat{V} \mathcal{P} \), \( \mathcal{P} \hat{V} Q \mathcal{P} \), and \( \mathcal{I}(t) \) terms with different denominators. This correspondence suggests the present method should produce linear response spectra of quality similar to CIS(D), which is usually slightly better than TDDFT. Because the formalism is somewhat involved and many approximations have been made, we have summarized the limitations of this work in a table (2.1) with references that point to possible improvements. The formalism is now developed to the point where particle-hole excitations can be usefully propagated and the main features of the approach can be demonstrated.
2.3 Results

Approximation Extension

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<td>(</td>
<td>\Psi_{eq}\rangle \approx</td>
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<td>Second-Order in (\tilde{V})</td>
<td>\text{TCL-4}\cite{147}</td>
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<td>(\langle \mu(t) \rangle \approx Tr(\tilde{\mu} \cdot \tilde{\sigma}(t)))</td>
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<td>TDA</td>
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<td>Orbital relaxation</td>
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Table 2.1: Limitations of this work and how they may be relaxed. Orbital relaxation isn’t really an approximation, per-se, but would be beneficial for the results of the perturbation theory.

in calculations.

2.3 Results

2.3.1 Adiabatic (\(\bar{M} \rightarrow 0\)) Spectrum

To incorporate both bath and electron correlation effects it was necessary to write down a second-order, time-local EOM for electronic dynamics based on the time-convolutionless perturbation theory which we will call "2-TCL". The zeroth order poles of the correlation terms in this theory differ from those which occur in other second-order theories of electronic response (SOPPA\cite{148}, ADC(2)\cite{132}, CIS(D)\cite{135} and CC2\cite{134}) which arise from perturbative partitioning of what is essentially an energy-domain propagator matrix. Interestingly, the denominator of the present theory is naturally factorized and in the adiabatic limit all terms can be evaluated to fifth order time, unlike Rayleigh-Schodinger perturbation theory which requires a denominator factorization approximation to avoid a 6-index denominator.\cite{128} To verify that the electronic part of this work is indeed a reasonable model of electronic dynamics and check our implementation (signs, factors etc.) it is useful to compare an adiabatic spectrum (\(\bar{M} \rightarrow 0\)) to one arising from exact diagonalization. We have coded the above formalism into a standalone extension of the Q-Chem package\cite{149} from which we take the results of some other standard models. The particle hole equation of motion is integrated with the Runge-Kutta 4\textsuperscript{th} / 5\textsuperscript{th} method with an adaptive time step.
Chapter 2. A Correlated-Polaron Electronic Propagator: Open Electronic Dynamics Beyond the Born-Oppenheimer Approximation

Propagations in all three directions are followed at once and the resulting time dependent dipole tensor is Fourier transformed to produce the spectra presented below in Figure 2.3. Bath integrals are calculated with 3rd-order Gaussian quadrature with the same time-step as the electronic Runge-Kutta integration, or integrated analytically in the adiabatic limit. The exact results and moments shown below come from the PSI3\textsuperscript{150} program package.

To check the adiabatic theory, we present calculations of dipole spectra on the $H_4$ and BH$_3$ molecules\textsuperscript{**}. In both cases the molecules have been stretched from their equilibrium bond lengths to a geometry where correlation effects are stronger\textsuperscript{151} and excitations are anomalously low-in-energy because of near degeneracy of the single-particle levels. We prepared the minimal basis molecule of H$_4$ in a density excited by the dipole operator, and propagated it for 250 a.u. The dipole-dipole correlation functions $C_{\alpha\beta}(t) = \langle \mu_\alpha(t) \mu_\beta(0) \rangle$ were collected during the simulation and Fourier transformed. The real part of this spectrum of spherically-averaged dipole oscillations is compared against stick spectra with the height given by the transition moment at the poles of an exact adiabatic calculation within this basis, and related theories. One sees that the propagator of the present work is a meaningful correction to CIS, moving poles away from the green positions towards the blue (Fig. 2.3). The excited state near 12.52eV in H$_4$ has increased in energy from the green position of 11.54eV toward the exact pole at 13eV. A more strongly correlated state just below this is unresolved. This is likely because the dipole moment operator doesn’t couple the reference determinant to this multi-configurational state. The higher energy peak of the spectrum is brought into good agreement with the exact result. Similar performance is seen in the case of a distorted BH$_3$ molecule, albeit with corrections of the higher energy peaks near 23eV being too small.

\textsuperscript{**}Coordinates: ((B(Å) H: -1, 0, 0; H: 1, 0, 0; H: -2.17557, 1.61803, 0; H: 2.17557, 1.61803, 0) and (B (Å): -0.26429,0.47149,0 H: 0.84371, 0.47149, -0.40000; H: -0.81829, 1.43104, 0.4; H: -0.81829, -0.48807,0.4)
2.3. Results

Figure 2.3: Left: Adiabatic dipole absorption spectra of H\textsubscript{4} in the minimal basis, CIS which is a part of the first term in 2.12 CIS(D), and the present theory. Numbers indicate maxima in eV and horizontal axis is given in Hartree. The largest maxima have been normalized to the same value. Right: adiabatic 2-TCL applied to the BH\textsubscript{3} molecule. The placement of red peaks nearer to blue than green indicates success as a perturbation theory. The atomic geometries (given in a footnote, are also shown).

2.3.2 Vibronic Features

The spectra of Markovian system-bath perturbation theories take the form of Lorentzians\textsuperscript{113} at the poles of the response matrix. Because the present theory is non-Markovian it should be capable of yielding new poles off of the main transitions. To evaluate this effect we add a strong bath oscillator at 1600 cm\textsuperscript{-1} and calculate the absorption spectra. We choose this bath oscillator at high energies to observe vibronic peaks in a reasonable amount of the propagation time (1700 a.u.), and choose a correspondingly high temperature (4397.25 K) so that there are several peaks in the progression which should take-on a Boltzmann-ian shape. The resulting absorption spectrum is pictured in Figure 2.4 with a close up of the promised progression. It is relevant to wonder whether the vibronic peaks are simply the result of the bath displacement operators present in the dipole correlation function expression or the result of the polaron density matrix dynamics. Simply eliminating the bath-correlation function from the dipole expression and generating the same spectrum, a vibronic progression still results, indicating that it is the non-Markovian dynamics of
the system operators which provides the vibronic progression. It is important to note that, while the vibronic progression is due to the non-Markovian dynamics of the system, the bath still does evolve according to its equilibrium propagator to produce both the peak structure and its broadening.

2.3.3 ENERGY TRANSPORT AND MARKOVIAN EVOLUTION

The continuous integration of the rank-6 bath correlation tensors required for the non-Markovian propagation shown in Figure 2.4 is a rather costly proposition for larger systems. This is especially true if one would like to study incoherent electronic energy transport which takes place in times on the order of picoseconds, roughly a million times more than the electronic timestep required to integrate Eq. (2.12) for a typical molecule. A useful approximation to overcome this is a Markov approximation, by which we mean taking the limit of the integral to infinity for each term, such as:

$$R_{ij,ok}^{ab,cj} \to \lim_{t \to \infty} \int_0^t B_{ij,ok}^{ab,cj}(t,s)(e^{i\Delta_{ab}(t-s)})ds,$$

where $R$ is now a factor replacing the integral expression. Each term possesses its own $R$ tensor but they only need be calculated once. Numerically, this limit can be taken in the case of a continuous
2.3. Results

Figure 2.5: Adiabatic linear response spectrum of a minimal model of transport between electronically excited states, two H\textsubscript{2} molecules in the D\textsubscript{2h}\textsuperscript{152} basis.

super-ohmic bath with cutoff frequency $\omega_c$ by introducing a cutoff time $t_c$, above which the bath correlation function is assumed to be equal to its equilibrium value, which is a good approximation for $\beta \omega_c (t_c)^2 >> 2$.

We have used the letter $R$ to suggest the analogy between this time-independent rate tensor and that occurring in the Redfield theory,\textsuperscript{153,154} although in this theory there are 28 such fifth and sixth rank tensors. These tensors also differ because they use the transformed rather than the bare correlation function. The value of the integral above only depends on the values of a Laplace-transformed $B(\omega) = \int_0^\infty e^{i\omega t} B(t, 0) \, dt$ at the zeroth order electronic frequencies ($\Delta$). The Markovian rate matrix can then be calculated once in sixth order time giving effective kinetic rates which include the effects of correlation and bath coupling. These can be used to calculate dynamics at a drastically reduced fourth order cost (since the perturbative EOM then takes the form of a single matrix product with time-independent effective Hamiltonian) or diagonalized directly to obtain spectra. The frequency independent nature of this term means that no new peaks can appear due to correlation or system-bath coupling. Only damping of the dynamics between correlation and bath shifted CIS-like poles leading to Lorentzian spectra can be expected within the confines of this Markovian approximation.
To give an example of how this methodology could be applied to the transfer of electronic energy, we examine two hydrogen molecules separated by several bond lengths in a DZ basis. The basis has been expanded to allow for the induced dipole moment between the two molecules. Since these two molecules are well separated and fixed at nearly their Born-Oppenheimer minima there is no longer any strong correlation or spin-frustration in this system. The adiabatic linear response spectrum is shown in Fig. (2.5), again showing good agreement with the stick spectra emerging from exact diagonalization as in $H_4$. The CIS states of this pair of molecules are well-localized. The splitting between the two peaks around 18eV corresponds to a weak coupling between them, and a distortion to the molecule on the right which has been imposed to lower the energy of the state localized on that side so that a bath can induce transfer of population. We initialize the pair of molecules into an even superposition of their excited states and couple a 2831cm$^{-1}$ oscillator at 273.0K to the HOMO, HOMO-1, LUMO and LUMO+1 with dimensionless $\tilde{M}$’s of (0.025, 0.05, .165, and .055) respectively. Over the course of $\approx$60fs (Fig. 2.6), the overlap of the time-dependent state with the higher energy state 0 has halved the overlap with the lower energy state has grown, and the overall norm of the state has decreased by about 10 percent, corresponding to non-radiative decay. The rapid, small beating between the states, which corresponds to what a tight binding-model would call the coherence between 0 and 1 is not well captured in the Tamm-Dancoff approximation because we have neglected the block which couples the particle-hole excitation to its conjugate.

2.3.4 UNTRANSFORMED AND UNCORRELATED VERSION

The transformed version of the theory has several interesting formal advantages, but to treat larger systems or off-diagonal system-bath couplings we have also presented the untransformed version of our theory which is similar to a propagation of the CIS wave-function with dissipative bath.

---

\[11\] Coordinates: (Bohr) H: -.45 0. 0.0; H: .45 0. 0.0; H -0.48296291 0. 5.0; H 0.48296291 0. 5.2588190)
2.3. Results

Figure 2.6: Transfer of probability between H₂ molecules in the DZ basis. After being initialized in a transition density which is the superposition of the adiabatic states at 17.3 and 18.1 eV, probabilities relaxation proceeds because of interaction with the bath. To zeroth-order in bath coupling State 1 is localized on the left, undistorted H₂, and State 0 is localized on the right, distorted H₂.

terms. Even in our relatively rudimentary code it is possible treat much larger systems with the undressed version especially if the electron correlation terms are neglected. To demonstrate the idea we have simulated the ultraviolet photoabsorption spectrum of 1,1-difluoroethylene [155]. We will compare the result of an untransformed calculation (Fig. 2.7) with available experimental data for the valence $\pi \rightarrow \pi^*$ transition. Bath bosons are positioned at the frequencies of the resolved vibronic peaks, the C=C stretch at 0.214eV, the CF₂ symmetric mode at .114eV, and the CH₂ rocking mode at .162eV. We have also added a super-ohmic spectral (n=3) density with coupling constant $\alpha = 0.01$ and cutoff frequency of 5580 cm⁻¹. Because of a mixture of basis limitations and the absence of electron correlation the simulated absorption is centered an electron-volt higher in energy than the gas-phase experiment, but both transitions appear in a qualitatively similar way. The somewhat irregular vibronic progression of the experimental peak hints at the limitations of approximating the nuclear degrees of freedom as a harmonic bath. This suggests that in future work it may be interesting to explore more accurate ways to calculate $\langle b^\dagger(t)b(0)\rangle$ for example by

---

[155] Geometry (Angstrom): F: 0.979002, -0.062874, -0.111271; C, 2.253554, 0.247708, -0.293548; F: 2.903831, -0.802928, -0.770347; C: 2.791571, 1.423625, -0.041291; H: 3.843081, 1.582482, -0.222345; H: 2.177490, 2.222097, 0.344802, Basis: 6-31+G* on C, 3-21G on all other atoms
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Figure 2.7: Experimental and simulated UV absorption cross-section of 1,1-difluoroethlyene in the region dominated by the $\pi \to \pi^*$ transition produced by 1500 a.u. of propagation at 303K. The untransformed version of the theory is employed and correlation terms are neglected.

propagating frozen gaussians in an Ehrenfest-type\textsuperscript{156} scheme.
2.4 Conclusion

In this paper we have presented a model of correlated electronic dynamics that is transformed by a bosonic bath. This allows us to study the effects of environmental dephasing on electronic excited states without assuming a reduced model for the electrons and their coupling to each other. Intriguingly, factors appear in the theory which damp high-rank operator expectation values. The possibility of exploiting this damping to reduce the cost of high-level electronic structure is interesting. \[157\] The adiabatic limit of the propagation developed here offers a useful correction to the placement of electronic energies. The linear-response spectrum of the complete model has been shown to exhibit vibronic structure. A Markovian, Tamm-Dancoff approximation to the energy transport problem has been examined, leading to bath-induced transfer of electronic energy between \( H_2 \) molecules, although coherence decay cannot yet be captured because several off-diagonal blocks of the transition density matrix have been neglected in the EOM of this initial work. The untransformed version of this formalism could be made efficient enough to study non-linear optical experiments via propagation. \[158\]-\[160\]

We note that, in contrast to Heller’s method for time-dependent absorption spectroscopy, we do not require that the 3N electronic degrees of freedom be represented by a single (i.e., frozen) surface parameterized by the nuclei. In cases where the electronic dynamics are of interest like those examined above, Heller-type dynamics are unable to provide much insight. Unlike Heller’s approach, however, our approach requires a harmonic approximation to the nuclear correlation function. In future work, we intend to combine Heller’s correlation function with the undressed theory to produce a model which has all the many-electron details and also the nuclear dynamics beyond the Harmonic approximation. Indeed, to include the second half to this theory, it is important to provide nuclear dynamics, perhaps with Heller-type, Ehrenfest, or molecular dynamics. Accurate protocols for providing a per-orbital spectral density must be developed and
the accuracy of the resulting lineshapes and lifetimes must be assessed. Simply projecting the
orbital energy gradient onto the normal modes of the molecule is an obvious choice, but it would
be more appealing to treat the influence of the surrounding molecules in a similar way. The
Tamm-Dancoff equations of motion provided in this work propagates only one-block of a much
larger transition density matrix which must be treated to capture coherence phenomena between
particles among themselves (and holes). The treatment of a thermalized initial condition is an
interesting, but computationally demanding question. The payoff for developing these additional
features would be a more realistic treatment of the electronic excited states that can be offered in
the adiabatic picture. These states would be naturally localized with a size depending on the
vibronic structure and temperature and evolve and relax irreversibly.

2.5 APPENDIX: EXPRESSIONS FOR THE CORRELATION FUNCTIONS AND FACTORIZATION

Time-ordered harmonic correlation functions (HCF’s) of all orders of the type \( \langle \hat{X}^{\dagger} ... \hat{X}^{\dagger} \rangle \) were
made available in Dahmoky’s pioneering work\(^{23}\) by expanding the exponentials in \( \hat{X} \) as power
series in \( \hat{A} = (\hat{b}_k e^{i \omega_k t} - \hat{b}_k^{\dagger} e^{-i \omega_k t}) \) and applying Wick’s theorem to the resulting \( \hat{A} \) operator strings
paying careful attention to the combinatorial statistics. Since we employ a master equation theory
rather than a Green’s function theory, our version of the HCF depends on the sign of \((t - s)\) but is
otherwise the same after making the simplifications which appear in our second order theory.

\[
B_{p_1 q_1; p_2 q_2}(s, t) = \langle \hat{X}_{p_1}^{\dagger}(t) \hat{X}_{p_2}^{\dagger}(t) \hat{X}_{p_4}(t) \hat{X}_{q_1}^{\dagger}(s) \hat{X}_{q_2}^{\dagger}(s) \hat{X}_{q_4}(s) \rangle =
\exp\left\{ - \sum_m \frac{1}{2} \Coth(\beta \omega_m/2) \tilde{M}_{p_1 p_2 q_1 q_2}^{(m)} \right\} \cdot \exp\left\{ - \sum_m (\tilde{M}_{p_3 p_4}^{(m)}(m) \tilde{M}_{q_3 q_4}^{(m)}(m)) F_m(t - s) \right\}
\]

where: \( F_m(t) = \Coth(\beta \omega_m/2) \Cos(\omega_m t) - i \Sin(\omega_m t) \) (2.30)
Here we use an abbreviated notation (the same as $\Delta$), $\tilde{M}_{ij...}^{ab} (s) = (\tilde{M}_{ij}^{ab} + \tilde{M}_{ij}^{ba} - \tilde{M}_{ij}^{ai} - \tilde{M}_{ij}^{ja} ... )$. The correlation function above includes the equilibrium value of the HCF. The qualitative behavior of the real part of bath integrals in terms like Equation (2.20) governs the relaxation process and is worth commenting upon here. If $\omega_s \sim \Delta > 0$ at time $s$, and $\tilde{M}_{at} \tilde{M}_{at} < 0$, then the sum over all terms $\text{Re}(B(t))$ is negative (causing relaxation) for a time on the order of $1/(\omega_s - \Delta_s)$, after which it oscillates. If $\Delta < 0$ then relaxation occurs if $\tilde{M}_{at} \tilde{M}_{at} > 0$. In most applications of master equations a single, positive, spectral density is assumed for all states which basically parameterizes $\tilde{M}_{at} \tilde{M}_{at}$ as a function of $\omega$. This approximation is more than a mere convenience: If $\tilde{M}$ is assigned generally and different states are allowed to couple to a single frequency with different strengths it is quite easy for some elements of the EOM to have $\tilde{M}_{at} \tilde{M}_{at} > 0$ thus causing exponential growth in the Markovian limit and at short times.

To treat a continuous number of bath oscillators one can introduce a continuous parameterization of $\tilde{M}$ called the spectral density, $J_i(\omega), \tilde{M}_{i\omega a} = \int_0^\infty J_i(\omega) / \omega \delta (\omega - \omega_a) d\omega$. The renormalization of the electronic integrals is clear given this form. With a relatively simple functional form for $J$, such as a super ohmic spectral density with cutoff parameter $\omega_c$,

$$J_i(\omega) = \frac{\eta_i \omega^3}{\omega_c} e^{-\omega / \omega_c},$$

the time dependence of of correlation function $B(t, s)$ can be analytically calculated to a good approximation. So long as $\omega_c$ is the same for all single-electron states, and only $\eta_i$ changes the whole formalism works identically with $\sqrt{\eta_i}$ taking the role of $\tilde{M}_{i\omega_c}$. We note that the requirement that the correlation function be easily integrable is only a pre-requisite for the polaron transformation. If only the time-convolutionless equation of motion is used, any correlation function which is known can be easily incorporated.

Without further approximation a sixth-order number of $B$’s must be calculated and integrated (in our code a third order Gaussian Quadrature with the electronic time-step was found sufficient), since at least two indices are shared between each $\tilde{V}$. Consider the cost limiting term Eq. (2.20). It
would be advantageous to evaluate the implied sum over $c$ and make a 5-index intermediate, since then the remaining indices are also a fifth order loop, unfortunately the HCF depends on index $c$.

On the other hand, *High-rank operator strings are exponentially damped by the presence of this HCF* in the Markovian limit. It seems likely that this feature could be used as a new locality principle which would lift the curse of dimensionality in the strong bath regime.

**ACKNOWLEDGEMENTS**

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## 2.6 Supplementary

### 2.6.1 Treatments of Initial Correlations.

We have mentioned three methods for treating the initial correlations of the system, of these We have implemented (Fig. 2.8) an imaginary time propagation, and perturbative inhomogenous term. In the former case, we still employ Runge-Kutta integration, but decrease the timestep to 0.0125 for the initial imaginary time-portion of the propagation in the interval $[-\beta, 0]$, which is roughly 1156 a.u. When $T=0$ is reached the state is renormalized and propagated for 2 au. in the presence of a dipole field. Finally the real-time integration begins and dipole oscillations are collected and transformed as usual. This result yields a much-improved peak near 0.7 $E_h$ where the adiabatic spectrum in Fig. 2.3 was much too small. The relative intensities of the peaks at .45 and .85 $E_h$ are also made qualitatively correct. The addition of the perturbative inhomogenous term does not seem to improve the spectrum significantly although again the peak near 0.7 is enhanced.
2.6. Supplementary

2.6.1.1 Undressed Bath Terms:

Here we have simply tabulated the output of our code which evaluates the double commutator:

\[ \langle \sigma^\dagger [H_{sb}(t), [H_{sb}(s), \sigma(t)]] \rangle \]
\[o_0^1 \leftarrow M_{hh}^{2,0}(t) M_{hh}^{3,2}(s) o_3^1 e^{i(\Delta s)} \int_{0}^{t} e^{i(\Delta s)} C(t - s) ds\]

\[o_0^1 \leftarrow -M_{hh}^{2,0}(t) M_{pp}^{1,3}(s) o_2^1 e^{i(\Delta s)} \int_{0}^{t} e^{i(\Delta s)} C(t - s) ds\]

\[o_0^1 \leftarrow -M_{hp}^{2,3}(t) M_{pp}^{3,0}(s) o_2^1 e^{i(\Delta s)} \int_{0}^{t} e^{i(\Delta s)} C(t - s) ds\]

\[o_0^1 \leftarrow -M_{hp}^{2,3}(t) M_{ph}^{1,2}(s) o_0^1 e^{i(\Delta s)} \int_{0}^{t} e^{i(\Delta s)} C(t - s) ds\]

\[o_0^1 \leftarrow -M_{hp}^{1,2}(t) M_{ph}^{3,0}(s) o_2^1 e^{i(\Delta s)} \int_{0}^{t} e^{i(\Delta s)} C(t - s) ds\]

\[o_0^1 \leftarrow -M_{pp}^{1,2}(t) M_{pp}^{2,3}(s) o_3^1 e^{i(\Delta s)} \int_{0}^{t} e^{i(\Delta s)} C(t - s) ds\]

\[o_0^1 \leftarrow M_{hp}^{2,3}(t) o_0^1 M_{ph}^{1,2}(s) e^{i(\Delta s)} \int_{0}^{t} e^{i(\Delta s)} C(t - s) ds\]

\[o_0^1 \leftarrow M_{hp}^{2,3}(t) o_2^1 M_{ph}^{3,0}(s) e^{i(\Delta s)} \int_{0}^{t} e^{i(\Delta s)} C(t - s) ds\]

\[o_0^1 \leftarrow -M_{hp}^{2,3}(t) o_0^1 M_{ph}^{1,2}(s) e^{i(\Delta s)} \int_{0}^{t} e^{i(\Delta s)} C(t - s) ds\]

\[o_0^1 \leftarrow -M_{hp}^{2,3}(t) o_2^1 M_{ph}^{3,0}(s) e^{i(\Delta s)} \int_{0}^{t} e^{i(\Delta s)} C(t - s) ds\]

\[o_0^1 \leftarrow M_{hp}^{2,3}(t) o_0^1 M_{ph}^{1,2}(s) e^{i(\Delta s)} \int_{0}^{t} e^{i(\Delta s)} C(t - s) ds\]

\[o_0^1 \leftarrow -M_{hp}^{2,3}(t) o_2^1 M_{ph}^{3,0}(s) e^{i(\Delta s)} \int_{0}^{t} e^{i(\Delta s)} C(t - s) ds\]

\[o_0^1 \leftarrow M_{hp}^{2,3}(t) o_0^1 M_{ph}^{1,2}(s) e^{i(\Delta s)} \int_{0}^{t} e^{i(\Delta s)} C(t - s) ds\]

\[o_0^1 \leftarrow M_{hp}^{2,3}(t) M_{ph}^{3,0}(s) e^{i(\Delta s)} \int_{0}^{t} e^{i(\Delta s)} C(t - s) ds\]

\[o_0^1 \leftarrow M_{hp}^{2,3}(t) M_{ph}^{3,0}(s) e^{i(\Delta s)} \int_{0}^{t} e^{i(\Delta s)} C(t - s) ds\]

\[o_0^1 \leftarrow M_{hp}^{2,3}(t) M_{ph}^{3,0}(s) e^{i(\Delta s)} \int_{0}^{t} e^{i(\Delta s)} C(t - s) ds\]

\[o_0^1 \leftarrow M_{hp}^{2,3}(t) M_{ph}^{3,0}(s) e^{i(\Delta s)} \int_{0}^{t} e^{i(\Delta s)} C(t - s) ds\]

\[o_0^1 \leftarrow M_{hp}^{2,3}(t) M_{ph}^{3,0}(s) e^{i(\Delta s)} \int_{0}^{t} e^{i(\Delta s)} C(t - s) ds\]

\[o_0^1 \leftarrow M_{hp}^{2,3}(t) M_{ph}^{3,0}(s) e^{i(\Delta s)} \int_{0}^{t} e^{i(\Delta s)} C(t - s) ds\]

\[o_0^1 \leftarrow M_{hp}^{2,3}(t) M_{ph}^{3,0}(s) e^{i(\Delta s)} \int_{0}^{t} e^{i(\Delta s)} C(t - s) ds\]

\[o_0^1 \leftarrow M_{hp}^{2,3}(t) M_{ph}^{3,0}(s) e^{i(\Delta s)} \int_{0}^{t} e^{i(\Delta s)} C(t - s) ds\]

\[o_0^1 \leftarrow M_{hp}^{2,3}(t) M_{ph}^{3,0}(s) e^{i(\Delta s)} \int_{0}^{t} e^{i(\Delta s)} C(t - s) ds\]

\[o_0^1 \leftarrow M_{hp}^{2,3}(t) M_{ph}^{3,0}(s) e^{i(\Delta s)} \int_{0}^{t} e^{i(\Delta s)} C(t - s) ds\]

\[o_0^1 \leftarrow M_{hp}^{2,3}(t) M_{ph}^{3,0}(s) e^{i(\Delta s)} \int_{0}^{t} e^{i(\Delta s)} C(t - s) ds\]
2.6 Supplementary

2.6.1.2 SECOND ORDER SYSTEM-BATH CORRELATION TERM

\[
\begin{align*}
o_0^1 &\leftarrow -\frac{1}{4} V_{hhpp}^{2,3,0,4} (t) V_{pphh}^{5,4,2,3} (s) o_5^2 e^{i(\Delta t)} \int_{t_0}^{t} e^{i(\Delta t)} C(t-s) ds \\
o_0^1 &\leftarrow \frac{1}{4} V_{hhpp}^{2,3,0,4} (t) V_{pphh}^{5,1,2,3} (s) o_2^4 e^{i(\Delta t)} \int_{t_0}^{t} e^{i(\Delta t)} C(t-s) ds \\
o_0^1 &\leftarrow \frac{1}{2} V_{hhpp}^{2,3,0,4} (t) V_{pphh}^{4,1,3,5} (s) o_2^3 e^{i(\Delta t)} \int_{t_0}^{t} e^{i(\Delta t)} C(t-s) ds \\
o_0^1 &\leftarrow \frac{1}{4} V_{pphh}^{2,3,5,4} (t) V_{pphh}^{5,4,0,3} (s) o_0^2 e^{i(\Delta t)} \int_{t_0}^{t} e^{i(\Delta t)} C(t-s) ds \\
o_0^1 &\leftarrow \frac{1}{4} V_{pphh}^{2,3,5,4} (t) V_{pphh}^{5,1,2,3} (s) o_2^4 e^{i(\Delta t)} \int_{t_0}^{t} e^{i(\Delta t)} C(t-s) ds \\
o_0^1 &\leftarrow \frac{1}{2} V_{pphh}^{2,1,4,3} (t) V_{pphh}^{5,4,0,3} (s) o_0^2 e^{i(\Delta t)} \int_{t_0}^{t} e^{i(\Delta t)} C(t-s) ds \\
o_0^1 &\leftarrow \frac{1}{4} V_{pphh}^{2,1,4,3} (t) V_{pphh}^{5,4,2,5} (s) o_0^2 e^{i(\Delta t)} \int_{t_0}^{t} e^{i(\Delta t)} C(t-s) ds \\
o_0^1 &\leftarrow \frac{1}{4} V_{pphh}^{2,1,4,3} (t) V_{pphh}^{5,4,0,5} (s) o_0^2 e^{i(\Delta t)} \int_{t_0}^{t} e^{i(\Delta t)} C(t-s) ds \\
o_0^1 &\leftarrow \frac{1}{2} V_{pphh}^{2,3,5,4} (t) o_3 V_{pphh}^{4,1,0,2} (s) e^{i(\Delta t)} \int_{t_0}^{t} e^{i(\Delta t)} C(t-s) ds \\
o_0^1 &\leftarrow \frac{1}{4} V_{pphh}^{2,3,5,4} (t) o_3 V_{pphh}^{4,1,2,3} (s) e^{i(\Delta t)} \int_{t_0}^{t} e^{i(\Delta t)} C(t-s) ds \\
o_0^1 &\leftarrow \frac{1}{4} V_{pphh}^{2,3,5,4} (t) o_5 V_{pphh}^{4,4,0,2} (s) e^{i(\Delta t)} \int_{t_0}^{t} e^{i(\Delta t)} C(t-s) ds \\
o_0^1 &\leftarrow \frac{1}{4} V_{pphh}^{2,3,5,4} (t) o_0 V_{pphh}^{4,4,0,2} (s) e^{i(\Delta t)} \int_{t_0}^{t} e^{i(\Delta t)} C(t-s) ds \\
o_0^1 &\leftarrow \frac{1}{4} V_{pphh}^{2,3,5,4} (s) o_0 V_{pphh}^{4,1,2,3} (t) e^{i(\Delta t)} \int_{t_0}^{t} e^{i(\Delta t)} C(t-s) ds \\
o_0^1 &\leftarrow \frac{1}{4} V_{pphh}^{2,3,5,4} (s) o_3 V_{pphh}^{4,4,0,2} (t) e^{i(\Delta t)} \int_{t_0}^{t} e^{i(\Delta t)} C(t-s) ds \\
\end{align*}
\]
Chapter 2. A Correlated-Polaron Electronic Propagator: Open Electronic Dynamics Beyond the Born-Oppenheimer Approximation

(a continuation of terms in the ph–ph block of the second order term.)

\[
\begin{align*}
o_5^1 & \leftarrow \frac{1}{4} V_{hhpp}^{2.3.0.4} (t) V_{phhh}^{5.4.2.3} (s) o_0^1 e^{i(A_{22}^{(2)})t} \int_{t_0}^{t} e^{i(A_{32}^{(2)} s)} C(t-s) ds \\
o_5^2 & \leftarrow \frac{1}{4} V_{hhpp}^{2.3.0.4} (t) V_{phhh}^{5.1.2.3} (s) o_0^1 e^{i(A_{22}^{(2)})t} \int_{t_0}^{t} e^{i(A_{32}^{(2)} s)} C(t-s) ds \\
o_5^3 & \leftarrow \frac{1}{4} V_{hhpp}^{2.3.0.4} (t) V_{phph}^{5.1.3.5} (s) o_0^1 e^{i(A_{22}^{(2)})t} \int_{t_0}^{t} e^{i(A_{32}^{(2)} s)} C(t-s) ds \\
o_5^4 & \leftarrow \frac{1}{4} V_{hhpp}^{2.3.5.4} (t) V_{pphp}^{5.4.0.3} (s) o_0^1 e^{i(A_{22}^{(2)})t} \int_{t_0}^{t} e^{i(A_{32}^{(2)} s)} C(t-s) ds \\
o_5^5 & \leftarrow \frac{1}{4} V_{hhpp}^{2.3.5.4} (t) V_{pphh}^{5.1.2.3} (s) o_0^1 e^{i(A_{22}^{(2)})t} \int_{t_0}^{t} e^{i(A_{32}^{(2)} s)} C(t-s) ds \\
o_5^6 & \leftarrow \frac{1}{2} V_{hhpp}^{2.1.4.3} (t) V_{phhh}^{5.4.0.2} (s) o_0^1 e^{i(A_{22}^{(2)})t} \int_{t_0}^{t} e^{i(A_{32}^{(2)} s)} C(t-s) ds \\
o_5^7 & \leftarrow \frac{1}{4} V_{hhpp}^{2.1.4.3} (t) V_{pphp}^{5.4.3.2.5} (s) o_0^1 e^{i(A_{22}^{(2)})t} \int_{t_0}^{t} e^{i(A_{32}^{(2)} s)} C(t-s) ds \\
o_5^8 & \leftarrow \frac{1}{4} V_{hhpp}^{2.1.4.3} (t) V_{pphp}^{5.4.3.0.5} (s) o_0^1 e^{i(A_{22}^{(2)})t} \int_{t_0}^{t} e^{i(A_{32}^{(2)} s)} C(t-s) ds \\
o_5^9 & \leftarrow \frac{1}{2} V_{hhpp}^{2.1.4.3} (t) o_0^1 V_{pphh}^{5.4.1.0.2} (s) o_0^1 e^{i(A_{22}^{(2)})t} \int_{t_0}^{t} e^{i(A_{32}^{(2)} s)} C(t-s) ds \\
o_5^{10} & \leftarrow \frac{1}{4} V_{hhpp}^{2.1.4.3} (t) o_0^1 V_{phhh}^{5.4.1.2.3} (s) o_0^1 e^{i(A_{22}^{(2)})t} \int_{t_0}^{t} e^{i(A_{32}^{(2)} s)} C(t-s) ds \\
o_5^{11} & \leftarrow \frac{1}{4} V_{hhpp}^{2.3.0.4} (t) o_0^1 V_{pphh}^{5.4.0.2} (s) o_0^1 e^{i(A_{22}^{(2)})t} \int_{t_0}^{t} e^{i(A_{32}^{(2)} s)} C(t-s) ds \\
o_5^{12} & \leftarrow \frac{1}{4} V_{hhpp}^{2.3.0.4} (t) o_0^1 V_{pphh}^{5.4.0.2} (s) o_0^1 e^{i(A_{22}^{(2)})t} \int_{t_0}^{t} e^{i(A_{32}^{(2)} s)} C(t-s) ds
\end{align*}
\]

(2.33)
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Part II

Compressed Sensing
Accelerating the Computation of Bath Spectral Densities with Super-resolution

Apart from minor modifications, this chapter originally appeared as:

“Accelerating the Computation of Bath Spectral Densities with Super-resolution”. Thomas Markovich, Samuel M. Blau, John Parkhill, Christoph Kreisbeck, Jacob N. Sanders, Xavier Andrade, Alán Aspuru-Guzik

ABSTRACT

Quantum transport and other quantum phenomena are typically modeled by coupling the system of interest to an environment, or bath, held at thermal equilibrium. Realistic bath models are at least as challenging to construct as models for the actual quantum systems themselves, since they must incorporate the many degrees of freedom that interact with the system on a wide range of timescales. Because of computational limitations, the environment is often modeled by simple functional forms, with a few parameters fit to experiment to yield semi-quantitative results. Growing computational resources have enabled the construction of more realistic bath models from molecular dynamics (MD) simulations. In this paper we develop a numerical technique to construct these atomistic bath models with improved accuracy and decreased cost. We apply a novel signal processing technique, known as super-resolution, combined with a dictionary of physically-motivated bath modes to derive spectral densities from MD simulations. Our approach
reduces the required simulation time and provides a more accurate spectral density than can be obtained via standard Fourier transform methods. Moreover, the spectral density is provided as a convenient closed-form expression which yields an analytic time-dependent bath kernel. Exciton dynamics of the Fenna-Matthews-Olsen light-harvesting complex are simulated with a second order time-convolutionless master equation, and spectral densities constructed via super-resolution are shown to reproduce the dynamics using only a quarter of the amount of MD data.

3.1 INTRODUCTION

Irreversible processes such as solvation, energy transfer, and chemical binding have received renewed interest in recent years. Because these processes involve large systems with many degrees of freedom, the typical approach to studying these processes is the open quantum systems formalism in which the degrees of freedom are partitioned into a system of interest and a bath held at thermal equilibrium. It is commonly assumed that the system only couples weakly to the bath, making the precise nature of the bath a secondary concern in the physical theory. For example, in studying the energy transfer dynamics in a system of chromophores embedded in a protein framework, each chromophore is individually coupled to many thousands of atoms in the protein, but the system-bath formalism dramatically simplifies all of these couplings in order to make the dynamics tractable. Renewed interest in the strong and intermediate coupling regions, which are relevant for energy transfer in the exciton dynamics of light-harvesting complexes, has lead to various studies on the precise influence of the bath on the higher systems. Higher order phonon processes, non-Markovian effects, and structures in the exciton-phonon coupling change the energy transfer. Thus, details in the bath are relevant and need to be taken into account in more realistic simulations. Accordingly, our goal in this paper is to apply a recent signal-processing technique known as super-resolution to obtain realistic
atomistic models of environments containing thousands of atoms at feasible computational expense. With these atomistic bath models in hand, one can begin to evaluate the importance of a realistic bath model in a physical theory.

In the approach to open quantum systems employed in our work, we model the bath by an ensemble of noninteracting harmonic oscillators. The central mathematical object of such a model is the spectral density, $J(\omega)$, which gives the frequency-dependent strength of the system-bath coupling. The spectral density can be understood as the density of bath oscillator states at each frequency. Owing to computational limitations, most studies of open quantum systems assume an extremely simple functional form for the spectral density, such as a single broad peak covering all relevant excitonic transitions of the system. With the goal of providing more physically accurate bath models and dynamics, Valleau et al. have previously obtained atomistic spectral densities for the FMO complex from combined Molecular Dynamics (MD) and time-dependent density functional theory (TDDFT) simulations. However, the difficulty of this more realistic approach is the high computational cost of running expensive TDDFT calculations at every step in a MD simulation. In order to obtain a spectral density of sufficient resolution, the MD-TDDFT simulation must be run for over 40 picoseconds (ps), which may become computationally intractable for larger systems.

To make progress we first observe that a typical vibrational bath is not an arbitrary function but rather a relatively sparse collection of damped harmonic oscillators. Sparsity enables us to apply a novel numerical technique known as super-resolution in order to reconstruct the spectral density from much shorter MD-TDDFT simulations. Super-resolution has been applied to a broad range of scientific problems, including image and video compression, image denoising, astronomy, microscopy, and medical imaging. To our knowledge, this paper is the first application of super-resolution to quantum dynamics. Super-resolution provides a provably
convergent algorithm for the reconstruction of signals from limited time-domain measurements using a total variation minimization procedure. Super-resolution is also related to compressed sensing.\cite{19,20,24,27,201–208} Compressed sensing is a technique designed to recover sparse signals from randomly-sampled data by minimizing the $L_1$ norm of an underdetermined system of linear equations. Compressed sensing works by finding the sparsest signals consistent with the underdetermined system of equations and this usually involves an optimization problem. Despite its success for many applications, the $L_1$-norm minimization of compressed sensing can result in spurious signals as it only emphasizes the sparsity of the solution. Super-resolution is a numerical method that shares the spirit of compressed sensing. The difference between super-resolution and compressed sensing stems from both the choice of the objective function and sampling technique. It was developed to recover sparse signals from nonrandomly undersampled data. By minimizing the $L_1$-norm of the gradient of the function in addition to the $L_1$ norm of the function itself, super-resolution allows for smoother solutions to the sampling problem.\cite{28,209,210}

Because of there is a wealth of experimental and theoretical data to compare calculated results with,\cite{7,129,166,169,172,174,177–180,182,183,185,188,192,211–218} we apply super-resolution to the FMO light-harvesting complex of \textit{C. tepidium}, but, we should emphasize that this technique is broadly applicable. While this paper focuses on a vibrational bath which perturbs the energies of molecular electronic states, the techniques we introduce are generic for any model of a bath which is based on time-correlation functions.

### 3.2 Super-resolution of Spectral Densities

In this section, we briefly review the procedure for simulating the dynamics of open quantum systems and computing spectral densities from combined MD-TDDFT simulations. We then apply the theory of super-resolution to accelerate and improve the accuracy of these computations.
Computing spectral densities from atomistic calculations, rather than from semi-empirical functional forms, enables the inclusion of molecular vibrations and other physical effects (such as solvation effects) to produce a more realistic bath model. Super-resolution, in turn, makes the construction of these atomistic bath models more computationally feasible.

Armed with our more realistic bath model, we will employ a second-order time-convolutionless master equation (TCL-2) to simulate the dynamics of FMO monomer, allowing us to evaluate the physical impact of different approximations to the spectral density. TCL-2 includes non-Markovian effects up to second order in the system-bath coupling. By comparing TCL-2 with exact methods like the hierarchical equations of motion (HEOM) we show that most of the relevant effects of the structured spectral density of the FMO complex are captured by TCL-2. Here we use TCL-2, since it is numerically more tractable than HEOM, in particular for structured spectral densities where HEOM becomes cumbersome and requires a high performance GPU implementation. We employ the equation of motion:

\[
\frac{d \rho_I(t)}{dt} = -\frac{i}{\hbar} [H_I, \rho_I] - \frac{1}{\hbar^2} \sum_n \int_0^t d\tau D_n(t-\tau) [H_{In}(t), [H_{In}(\tau), \rho_I(t)]]
\]  

\[
D_n(t) = \int_0^\infty d\omega J_n(\omega) \left[ \coth\left( \frac{\hbar \omega \beta}{2} \right) \cos(\omega t) - i \sin(\omega t) \right].
\]

where \(H\) is the system Hamiltonian, \(\rho\) is the system density matrix, \(D\) is our bath kernel, the subscript \(I\) indicates that we are using the interaction picture, the summation runs over all sites, and \(J(\omega)\) is the spectral density computed via super-resolution. The bath kernel is heavily dependent on our spectral density, causing it to play a central role in our dynamics. Therefore, a more physical bath picture should provide more physically intuitive dynamics.

In our atomistic bath model, molecular vibrations in the environment (e.g. a protein framework or solvation effects) create fluctuations in the energy gaps between the ground and excited states of the system (e.g. a set of chromophores). These time-dependent energy gaps are computed from...
3.2. Super-resolution of Spectral Densities

TDDFT calculations run for each of the chromophores at each step of the MD simulation. The key object in the computation of spectral densities is the correlation function of the energy gap time series,

\[ C(t) = \text{Tr}_{\rho_b}[\hat{\Delta}(t)\hat{\Delta}(0)\rho_b], \]  

(3.3)

where \( \hat{\Delta}(t) \) is the time-dependent energy gap between the ground and the first excited state of the system (as calculated with TDDFT), \( \rho_b \) is the density matrix of the bath at thermal equilibrium, and \( C(t) \) is the correlation function obtained after tracing over all the modes of the bath. We discretize this equation by using an unbiased autocorrelation function,

\[ C_k = \frac{1}{N - k} \sum_{i=1}^{N-k} (\Delta_i - \bar{\Delta})(\Delta_{i+k} - \bar{\Delta}), \]  

(3.4)

where \( \bar{\Delta} \) is the mean energy gap and \( i \) and \( k \) denote discrete time indices. Note that \( C_k \) involves comparing energy gaps that are \( k \) time steps apart (\( \Delta_i \) and \( \Delta_{i+k} \)), and \( N - k \) is the total number of included comparisons.

The frequency-dependent spectral density, \( J(\omega) \), is typically obtained by computing the Fourier transform of the correlation function. From the definition of \( C_k \) above, it is easy to check that the correlation function is real and symmetric (i.e. \( C_k = C_{N-k} \)), which implies that the Fourier transform should be real and symmetric as well. Because quantum mechanical spectral densities must instead be antisymmetric and obey detailed balance, it is necessary to introduce a prefactor that enforces these two properties. Many choices are possible, but Valleau et al. have previously shown that a harmonic prefactor, \( \beta \hbar \omega / 2 \), produces the most physical temperature dependence. With this choice, the spectral density becomes the cosine transform

\[ J(\omega) = \frac{\beta \hbar \omega}{2} \int_{-\infty}^{\infty} \cos(\omega t)C(t)dt, \]  

(3.5)
which characterizes the frequency-dependent coupling strength of the system to all of the nuclear vibrational modes.

The standard approach to performing this integral is the fast Fourier transform. Unfortunately, the fast Fourier transform requires sampling on a uniform grid at the Shannon sampling rate. This means that a relatively long time series, \( C(t) \), must be computed in order to obtain good resolution of the spectral density in the frequency domain.\(^8\) Given the computational cost of MD simulations, and the even greater expense of running TDDFT calculations on top of these simulations, any method which can reduce the required length of the time series \( C(t) \) unplugs the computational bottleneck in deriving physically accurate atomistic spectral densities. That is our main goal in this paper.

While reducing the amount of time required to reproduce \( J(\omega) \) we also choose a basis of functions which has a convenient physical form. When decomposed into a basis of damped cosines,

\[
g_{ij}(t) = e^{-\gamma t} \cos(\Omega_j t),
\]

the function \( C(t) \) is smooth and sparse. This allows for the use of the machinery of super-resolution.

To apply the super-resolution method, we discretize in time and cast our task as an inversion problem

\[
C_k = \lambda_{ij} e^{-\gamma t} \cos(\Omega_j t_k),
\]

where we seek the basis expansion coefficients \( \lambda_{ij} \) and have assumed Einstein summation convention over repeated indices. This can be rewritten as

\[
C_k = A_{ijk} \lambda_{ij},
\]
3.2. Super-resolution of Spectral Densities

where

$$A_{ijk} = e^{-\gamma t_i} \cos(\Omega_j t_k)$$  \hspace{1cm} (3.9)

is a matrix of damped cosines, and $\lambda_{ij}$ is the set of basis coefficients we seek to recover.

The central idea of super-resolution is that the sparsity of $\lambda_{ij}$ enables its full recovery even when the system $C_k = A_{ijk} \lambda_{ij}$ is underdetermined, which is to say the number of time samples $C_k$ is significantly smaller than the number of total expansion coefficients $\lambda_{ij}$ we seek to recover. Hence, we can recover the expansion coefficients on a dense grid of frequencies $\Omega_j$ and damping coefficients $\gamma_i$ from even fewer time samples $C_k$. Of the many possible solutions to our underdetermined system, super-resolution simply selects a balance between the smoothest and sparsest (with an emphasis on smoothness) set of basis expansion coefficients. Formally, this is done by finding the vector $\lambda_{ij}$ that minimizes

$$\arg\min_{\lambda_{ij}} \left\{ ||\nabla \lambda_{ij}||_1 + \mu ||\lambda_{ij}||_1 \right\}$$ \hspace{1cm} (3.10)

subject to $||A_{ijk} \lambda_{ij} - C_k||_2 < \eta$,

where the subscript 1 represents the $L_1$ norm (sum of absolute values), $\mu$ represents a sparsity penalty, $\nabla \lambda_{ij}$ represents the total variation norm, and $\eta$ represents the solution tolerance. By minimizing $||\nabla \lambda_{ij}||_1$, or total variation term, we are enforcing smoothness in the time domain on the reconstructed signal. This throws out the “peaky” solutions that can appear with compressed sensing. The total variation norm also provides us with a provably exact technique for recovering peak position at the expense of peak amplitude, which solves one of main the issues seen previously with compressed sensing.

Recovering the expansion coefficients $\lambda_{ij}$ in this manner by solving an underdetermined matrix inversion problem takes advantage of the natural sparsity of the problem and, as we will see in the
next section, enables the construction of a well-resolved spectral density with far less time-domain data. Even more attractive, with the $\lambda_{ij}$ coefficients in hand, it is possible to construct an analytical representation of the spectral density by taking the cosine transform of the basis functions $g_{ij}(t)$ and applying the appropriate prefactors:

$$J(\omega) = \frac{\lambda_{ij}}{\sqrt{\pi}} \left( \frac{\beta \hbar \gamma_i}{\gamma_i^2 + (\omega - \Omega_j)^2} + \frac{\beta \hbar \gamma_i}{\gamma_i^2 + (\omega + \Omega_j)^2} \right),$$  \hspace{1cm} (3.11)

where the Einstein summation convention has again been assumed. This is an analytical representation of the spectral density in Drude-Lorentz form, and it explicitly provides the oscillation frequencies which characterize the system-bath coupling. We note that the Drude-Lorentz basis naturally provides us with a width parameter, $\gamma$, that can be understood as the lifetime of oscillations in the bath. This is seen by examining the time dependent formula, Equation (3.7), where this $\gamma$ parameter determines the strength of damping. It is important to note that in the limit as $\gamma \to 0$, we recover the cosine basis in the time domain and a Dirac delta distribution in the frequency domain. By using this super-resolution technique in concert with the Drude-Lorentz basis, we see that we can recover a small set of peaks with physically-relevant information. Additionally, the parameters that characterize the Drude-Lorentz spectral densities can be input directly into both TCL-2 and HEOM without any additional parameter fitting or numerical integration.

### 3.3 Numerical Methods

We employ the proposed Drude-Lorentz super-resolution method described above and apply it to a monomer of the Fenna-Matthews-Olsen (FMO) photosynthetic energy transfer complex of the green-sulfur bacterium *C. tepidium*. The FMO monomer is a system of seven chlorophyll molecules which are excitonically coupled to each other, as well as to the vibrations of the atoms in
Figure 3.1: Comparison of the spectral density for site 1 of the FMO complex as a function of time and technique for spectral density recovery. Compared to the fast Fourier transform at 40 ps, much of the fine structure is easily recovered by super-resolution in the Drude-Lorentz basis, even with significant undersampling by a factor of four.

Figure 3.2: Comparison of the coherences between excitonic eigenstates 1 and 3 as a function of time and technique for spectral density recovery. Compared to the fast Fourier transform at 40 ps, the 10 ps Drude-Lorentz decomposition introduces a slight shift in oscillation frequency, but nevertheless yields more accurate dynamics than the equivalently-sampled fast Fourier transform at 10 ps.
Figure 3.3: Comparison of the populations for sites 1-3 as a function of time and technique for spectral density recovery. Compared to the fast Fourier transform at 40 ps, the 10 ps Drude-Lorentz decomposition recovers the overall shape and provides much more faithful dynamics than the equivalently-sampled fast Fourier transform at 10 ps.
the protein framework. It functions as a molecular excitonic wire, passing excitons from the light harvesting antenna complex to the reaction center, where a biochemical cascade is initiated.

To create spectral densities for the FMO complex, we use the MD-TDDFT results of Shim et al. The calculations were done in an isothermal-isobaric ensemble at 77 K using the AMBER force field. These calculations began with a 2 ns equilibration before performing the production computations. The production steps ran for a total of 40 picoseconds with a 2 femtosecond timestep, and the optical gap was calculated for each fragment every 4 femtoseconds using TDDFT with the BLYP functional in the 3-21G basis set in Q-Chem.

To perform super-resolution numerically, we require an algorithm which minimizes the total variation norm to solve the minimization problem described by Equation (3.10). In our implementation, we use the two step iterative shrinkage thresholding (TwIST) algorithm, which combines computational efficiency with strong convergence. To construct the measurement matrix $A$ described in Equation (3.9), we must select a grid of possible frequencies ($\{\Omega_j\}$) and linewidths ($\{\gamma_i\}$). In our implementation, we use a grid of frequencies ranging from 0 to 2000 cm$^{-1}$ in 2 cm$^{-1}$ intervals, and a grid of linewidths ranging from 0 to 160 cm$^{-1}$ in 6 cm$^{-1}$ intervals. We assume that our calculations are converged when $\eta < 10^{-7}$ (in Equation (3.10)), or the solution vector remains constant for 100 iterations. Finally, we perform an $L_2$ minimization of $A_{ijk}\hat{\lambda}_{ij} - C_k$ while freezing the recovered nonzero basis functions, thus allowing us to further minimize the error. We refer to this procedure as debiasing because it partly removes the bias towards sparsity and smoothness introduced by the $L_1$ minimization. This debiasing procedure reduces our solution tolerance to $\eta < 10^{-9}$, allowing convergence to a better solution. It is important to note that, in general, the super-resolution technique is robust to an over-complete basis.
3.4 **RESULTS**

Fig. 3.1 shows the results of employing the Drude-Lorentz super-resolution method to recover the spectral density for site 1 of FMO. The figure compares Drude-Lorentz super-resolution with 10 ps of MD to a standard fast Fourier transform approach with both 10 and 40 ps of MD. We take the fast Fourier transform with 40 ps of MD as our standard for comparison. By comparing the two methods with 10 ps of MD, it is clear that super-resolution resolves more features of the spectral density than the standard fast Fourier transform from the same amount of time-domain data. Moreover, super-resolution captures most of the features of the fast Fourier transform with the full 40 ps of MD: we see the expected CO stretch at 1600 cm\(^{-1}\), which we attribute to the amides in the protein scaffold, as well as all of the other major peaks in the spectral density. We attribute a significant amount of the error in our spectral density reconstruction to the fact that the truncated MD series does not explore the phase space as thoroughly in only 10 ps.

For completeness we present the results for sites two-seven in Figs. 3.4-3.9. The figure compares the spectral densities obtained with super-resolution in the Drude-Lorentz basis using 10ps of data, to those obtained with 10ps and 40ps of data using the fast Fourier transform. We observe that super-resolution has similar resolving power to site one for sites two-seven. In addition, we observe that super-resolution is capable of recovering an accurate reorganization energy. We have presented a comparison between previously published Drude-Lorentz spectral parameters and the ones recovered through our new technique in Table 3.1. We are particularly encouraged by the similar levels of sparsity between the hand-fit results and our own.

The Drude-Lorentz basis also provides significant sparsity gains in comparison to the cosine basis: we require only 56 Drude-Lorentz peaks to create the spectral density given in Fig. 3.1 whereas. This sparsity provides a significant computational advantage for excitonic propagation in both hierarchical equations of motion (HEOM) and second order time-convolutionless master
3.4. Results

Equation (TCL-2) approaches because the propagations scale factorially and linearly, respectively, as a function of the number of peaks included. In the excitonically accessible regime of 0-540 cm\(^{-1}\), we recover only 20 Drude-Lorentz peaks, and six of them have amplitudes that are two orders of magnitude smaller than the rest. These Drude-Lorentz peaks can be entered directly into master equation simulations, including HEOM codes, without the need to perform any intermediate fitting. In summary, super-resolution yields a well-resolved spectral density using less time-domain data than is required by the standard fast Fourier transform approach and precludes the need for additional fitting.

As mentioned above, the TCL-2 propagation of the exciton dynamics of the FMO complex, with the Hamiltonian coming from, was carried out using the Drude-Lorentz spectral densities obtained from super-resolution. We propagated 1 ps of dynamics and obtained the populations of sites 1-3, as well as the coherence between sites 1 and 3.

Fig. 3.2 shows the coherence between excitonic eigenstates 1 and 3 as a function of time. Compared to the 40 ps fast Fourier transform, we see that the 10 ps Drude-Lorentz super-resolution more faithfully reproduces the coherence dynamics than the 10 ps fast Fourier transform, both in terms of the oscillation frequency and the overall damping. The fast Fourier transform with 10 ps of MD data introduces serious overdamping as well as a significant shift in oscillation frequency. In contrast, the Drude-Lorentz expansion with 10 ps of MD data introduces only a small shift in oscillation frequency, resulting in more accurate coherence dynamics overall. We attribute most of the discrepancies to slight relative differences in the reorganization of each site between spectral densities constructed with 10 and 40 ps of MD data. It appears that while the oscillations are extremely sensitive to the relative reorganization energies between the sites, the damping is more dependent on the fine structure of the spectral densities. The Drude-Lorentz super-resolution (10 ps MD-TDDFT data) reproduces the coherence life-times obtained by fast
Chapter 3. Accelerating the Computation of Bath Spectral Densities with Super-resolution

Fourier transform using all 40 ps of MD-TDDFT data – representing a factor of four improvement.

The contrast between these two approximation techniques becomes even more significant when we simulate dynamics beginning with an exciton fully localized on site 1. In Fig. 3.3, we have plotted the populations of the first three sites as a function of time. The Drude-Lorentz expansion with 10 ps of MD yields good qualitative agreement with our standard of comparison. The fast Fourier transform on 10 ps overestimates population transfer to site 3 at short times and grows much more quickly from there, whereas the Drude-Lorentz expansion slightly under predicts the population transfer at long times. We attribute these errors in the asymptotic behavior to slight differences in the reorganization energies for the spectral densities of each of the sites, since each site is embedded in a different environment, the reorganization process of the individual pigments is different. This sensitivity affects overall dissipation and even small changes in the spectral density of the Drude-Lorentz expansion (10 ps) when compared to the standard of comparison affects energy relaxation. Beyond that, the Drude-Lorentz expansion is capable of reproducing the oscillations at 0.2 and 0.4 ps in the data for sites 1 and 2 whereas the fast Fourier transform reproduces them less faithfully. In summary, the Drude-Lorentz super-resolution technique provides us with much more physical behavior.

3.5 CONCLUSIONS

We have shown that the Drude-Lorentz super-resolution method provides significant computational advantages for the construction of atomistic bath models. In particular, the super-resolution calculations require only 10 ps of MD-TDDFT simulations to obtain reasonable atomistic spectral densities and system dynamics; this is one quarter the amount of data needed in standard fast Fourier transform-based calculations. Ultimately, this will permit the use of more physically accurate calculations or larger systems. Given the computational expense of running
TDDFT calculations at every MD simulation step, we believe that the super-resolution method will enable the treatment of larger systems than previously thought possible.

One of the most significant advantages of our super-resolution method is the decomposition of these atomistic spectral densities into a naturally-sparse basis of Drude-Lorentz oscillators. This makes it easy to perform fast master equation simulations within either the TCL-2 or HEOM formalisms by exploiting analytic integrals of the spectral density. Beyond this, we also directly extract physically important parameters such as the coherence lifetimes of all the oscillators in the bath. In the future, it is easy to imagine turning this technique on its head to create new spectral densities in a constructive fashion from a set of Drude-Lorentz oscillators.

3.6 Supplementary Information
Chapter 3. Accelerating the Computation of Bath Spectral Densities with Super-resolution

Figure 3.4: Comparison of the spectral density for site 2. We assume our basis to compare against is the fast Fourier transform at 40 ps and can see that much of the fine structure is easily recovered by super-resolution in the Drude-Lorentz basis, even with significant undersampling.

Figure 3.5: Comparison of the spectral density for site 3. We assume our basis to compare against is the fast Fourier transform at 40 ps and can see that much of the fine structure is easily recovered by super-resolution in the Drude-Lorentz basis, even with significant undersampling.
Figure 3.6: Comparison of the spectral density for site 4. We assume our basis to compare against is the fast Fourier transform at 40 ps and can see that much of the fine structure is easily recovered by super-resolution in the Drude-Lorentz basis, even with significant undersampling.

Figure 3.7: Comparison of the spectral density for site 5. We assume our basis to compare against is the fast Fourier transform at 40 ps and can see that much of the fine structure is easily recovered by super-resolution in the Drude-Lorentz basis, even with significant undersampling.
Figure 3.8: Comparison of the spectral density for site 6. We assume our basis to compare against is the fast Fourier transform at 40 ps and can see that much of the fine structure is easily recovered by super-resolution in the Drude-Lorentz basis, even with significant undersampling.

Figure 3.9: Comparison of the spectral density for site 7. We assume our basis to compare against is the fast Fourier transform at 40 ps and can see that much of the fine structure is easily recovered by super-resolution in the Drude-Lorentz basis, even with significant undersampling.
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*Table 3.1:* Comparison of \( \mathcal{L}_2 \) fits done by Kreisbeck et al. against ours in the excitonically accessible region.
3.7 ACKNOWLEDGEMENTS

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Benchmarking Compressed Sensing, Super-Resolution, and Filter Diagonalization

Apart from minor modifications, this chapter originally appeared as:

“Benchmarking Compressed Sensing, Super-Resolution, and Filter Diagonalization”, Thomas Markovich, Samuel M. Blau, Jacob N. Sanders, Alán Aspuru-Guzik

Abstract

Signal processing techniques have been developed that use different strategies to bypass the Nyquist sampling theorem in order to recover more information than a traditional discrete Fourier transform. Here we examine three such methods: filter diagonalization, compressed sensing, and super-resolution. We apply them to a broad range of signal forms commonly found in science and engineering in order to discover when and how each method can be used most profitably. We find that filter diagonalization provides the best results for Lorentzian signals, while compressed sensing and super-resolution perform better for arbitrary signals.

4.1 Introduction

The reconstruction of frequency-resolved spectra from limited and undersampled measurements in the time domain is a significant problem throughout the physical sciences. The standard approach to solving such a problem is the discrete Fourier transform which decomposes a time series in
terms of its component frequencies (or, more generally, decomposes a series into its conjugate domain). The discrete Fourier transform offers two major advantages: no \textit{a priori} knowledge about the signal is required and the computation can be implemented very efficiently via the fast Fourier transform. Unfortunately, a major disadvantage is that the discrete Fourier transform imposes a natural bound on the maximum frequency resolution possible given the nature of the time series, known as the Shannon-Nyquist condition.\textsuperscript{8}

A natural question to ask is whether the Shannon-Nyquist condition can be bypassed by exploiting any additional knowledge we may have about the signal. Recent advances in signal processing have provided many such techniques for leveraging additional \textit{a priori} knowledge about the signal to improve reconstruction. Our goal in this paper is to compare three such methods, filter diagonalization,\textsuperscript{203,232,235} compressed sensing,\textsuperscript{14,17,19,27,201,203,237} and super-resolution,\textsuperscript{8,11,19} against a series of test signals in order to understand their relative strengths and weaknesses. Our comparison will be based on a subset of the signals contained in the Sparco toolbox,\textsuperscript{238} a Gaussian, a sum of random Lorentzians, and the Jacob’s Ladder signal.\textsuperscript{232} The Sparco toolbox provides a standard set of signal processing benchmarks while the other signals are commonly encountered throughout the physical sciences.

Filter diagonalization is one of the earliest techniques for bypassing the Shannon-Nyquist condition and it assumes that the time series is generated by an underlying dynamical system with a frequency spectrum modeled by a sum of Lorentzians. It attempts to express the frequency spectrum as a sum of Lorentzian peaks by finding the optimal frequencies, linewidths, and intensities that fit the time series. Filter diagonalization has been applied to a broad range of signals that vary from NMR spectra\textsuperscript{232,235} to scattering data\textsuperscript{234} and image analysis.\textsuperscript{233}

More recently $\mathcal{L}_1$ minimization techniques, such as compressed sensing and super-resolution, have also been proposed as an alternative technique for sampling below the rate imposed by the
Nyquist-Shannon condition. Rather than assuming a particular kind of underlying dynamical system, these techniques simply assume that the signal is sparse in some \textit{a priori} known basis. The two methods differ in both sampling strategy and the particular optimization problem to be solved. Compressed sensing is designed to recover sparse frequency spectra (or other signals) by randomly undersampling data over the entire time domain, and then minimizing the $L_1$ norm of an underdetermined system of linear equations. Compressed sensing has been successfully applied to data acquisition in many different areas, including the improvement of the resolution of medical magnetic-resonance imaging and the experimental study of atomic and quantum systems.

Super-resolution is a related technique that shares the spirit of compressed sensing, but with a different sampling technique. Super-resolution was developed to recover sparse frequency spectra (or other signals) from regularly sampled data over a short segment of the time domain. It provides a provably convergent algorithm for the reconstruction of signals from these limited time-domain measurements by using a total-variation minimization procedure. Like compressed sensing, super-resolution has been applied to a broad range of scientific problems, including image and video compression, image denoising, atomistic modeling of open quantum systems, astronomy, microscopy, and medical imaging.

The goal of this paper is to elucidate the strengths and weaknesses of the aforementioned signal processing techniques to provide a clear and coherent aid in choosing a method. To achieve this we will first introduce the theory that underlies each method and outline our procedure for benchmarking the methods. Then, we will introduce the test signals and compare the performance of each method on each signal. Finally, we will present some general conclusions.
4.2 Theory

4.2.1 Discrete Fourier Transform

The Fourier transform is a cornerstone method in signal processing as it provides a technique for decomposing an arbitrary function of time into its component frequencies:

\[
\hat{f}(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{i\omega t} f(t) \, dt.
\]  

(4.1)

When treating a problem numerically we often only have access to the values of the signal \( f(t) \) on an equally-spaced \( N \)-point grid. Accordingly, we discretize the continuous Fourier transform to obtain the discrete Fourier transform:

\[
\hat{f}(\omega_j) = \frac{1}{\sqrt{N}} \sum_{j} f(t_j) e^{i\omega_j t_j}.
\]  

(4.2)

which can be reformulated as a matrix multiplication according to:

\[
\hat{f}_i = \sum_j F_{ij} f_j,
\]  

(4.3)

where \( f_j = f(t_j) \), \( \hat{f}_i \equiv \hat{f}(\omega_k) \), and \( F_{ij} \) is the Fourier operator. Here we have assumed a uniform frequency grid with a spacing of \( f_s/N \), a time sampling rate of \( \Delta t \), where the maximum frequency that can be sampled is \( 1/\Delta t \), \( N \) is the number of time points, and \( T \) is the time length of the signal.

The Nyquist-Shannon sampling theorem states that if a function is band limited with maximum frequency \( \Omega \), it is completely characterized with a uniform series of time points spaced by \( 1/2\Omega \). It is often more convenient to use the converse statement in signal reconstruction which claims that the with a sampling rate of \( \Delta t \) the maximum frequency that can be recovered is \( 1/2\Delta t \). This is a direct consequence of discretizing the Fourier transform. A major disadvantage of the discrete
Chapter 4. Benchmarking Compressed Sensing, Super-Resolution, and Filter Diagonalization

Fourier transform is that a long and uniformly-sampled time series is required to obtain good resolution in the frequency domain.

4.2.2 $\ell_1$ MINIMIZATION

$\ell_1$ minimization methods, including compressed sensing and super-resolution, have emerged as a powerful technique for bypassing the constraint of the Shannon-Nyquist theorem in the special case where the signal is known to be sparse in a particular basis.

To illustrate this, suppose we have an unknown function $f(t)$ that we wish to recover with as few samples as possible. Suppose further that we can find a set of basis functions $\{g_j(t)\}$ such that $f(t)$ is sparse when expanded in this basis. That is,

$$f(t) = \sum_j \lambda_j g_j(t), \quad (4.4)$$

where most of the $\lambda_j$ expansion coefficients are equal to zero (or near zero). Our goal is to find the set of coefficients $\{\lambda_j\}$, since this would in turn identify the function $f(t)$. All we know a priori is that most of the $\lambda_j$ are zero. We do not know which of them are zero and we do not know their values in general. By sampling $f(t)$ at a set of points $\{t_i\}$, we can obtain a set of linear equations,

$$f_i = \sum_j \lambda_j g_{ij}, \quad (4.5)$$

where $f_i \equiv f(t_i)$ and $g_{ij} \equiv g_j(t_i)$, and our goal is to solve these equations for the set of coefficients $\{\lambda_j\}$. While the $t$ variable suggests discretization in time, we are free to sample the signal in any domain. Since we are trying to obtain accurate resolution by taking as few time samples as possible, in general this system of equations will be underdetermined and we must impose additional constraints to pick out the desired solution.
In $\mathcal{L}_1$ optimization methods, including compressed sensing and super-resolution, the desired solution to the underdetermined system of equations given in Equation 4.5 is chosen by solving the following $\mathcal{L}_1$ minimization problem:

$$\arg\min_{\lambda_j} ||\lambda_j||_1 \text{ subject to } ||f_i - \sum_j \lambda_j g_{ij}||_2 < \eta,$$  \hspace{1cm} (4.6)

where $\eta$ is a small thresholding parameter. In this minimization problem, the $\mathcal{L}_1$ norm serves as a proxy for the sparsity-enforcing $\mathcal{L}_0$ norm by selecting the sparsest set of coefficients $\{\lambda_j\}$ such that the system of equations in Equation 4.5 are satisfied to within $\eta$. It is important to note that each $g_j(t)$ should be normalized to unity so that no single basis function is privileged.

Compressed sensing and super-resolution differ in the sampling strategy, which, in turn, is often determined by computational and experimental constraints. Compressed sensing addresses the case where the value of the function $f(t)$ is sampled at random points $\{t_i\}$ over the entire domain. This random sampling of points $f_i$ ensures that each point provides the maximum possible amount of information for the reconstruction of the signal. A key result from compressed sensing is that the number of time samples $f_i$ which must be measured for accurate recovery scales roughly with the sparsity of the basis expansion (i.e. the number of nonzero $\lambda_j$), rather than the total size of the basis expansion (i.e. the total number of $\lambda_j$).

A related method to compressed sensing is super-resolution. Unlike compressed sensing, which applies to randomly-sampled data, super-resolution applies to data that is regularly sampled on a short segment of the time domain. It has been proven that super-resolution enables the recovery of signals with frequencies at one quarter of the Shannon-Nyquist condition reliably.

A major advantage of both compressed sensing and super-resolution is that we can recover $f(t)$ in any basis in which the signal is sparse. The methods work with bases as varied as wavelets, \cite{241,242} treelets, \cite{243} geometric harmonics, \cite{244} and polynomials. \cite{227,228} All that is required is
Chapter 4. Benchmarking Compressed Sensing, Super-Resolution, and Filter Diagonalization

that we know the sparse basis ahead of time. Although this may seem like a strong restriction, for many scientific problems physical intuition often leads to a sparse basis. One does not need to pick the optimal basis; any reasonably sparse basis will work. Moreover, both compressed sensing and super-resolution are robust to choosing an overcomplete basis, which allows for a lot more freedom in finding a sparse basis.

For example, in computational chemistry, we are often interested in resolving spectra which are known to be sparse directly in the frequency domain (i.e. the spectrum is mostly zero except for a few sharp frequency peaks). In this case, we might choose a basis of complex exponentials $g_j(t) = \frac{1}{2\pi} e^{i\omega_j t}$. After time sampling, the matrix $g_{ij} = \frac{1}{2\pi} e^{i\omega_j t}$ simply becomes an undersampled set of rows of the discrete Fourier transform matrix. Once the sparse coefficients $\lambda_j$ have been found by solving Equation 4.6, the final spectrum may be plotted as

$$\hat{f}(\omega) = \sum_j \lambda_j \hat{g}_j(\omega) = \sum_j \lambda_j \delta(\omega - \omega_j),$$

(4.7)

Other similar bases commonly used when applying compressed sensing or super-resolution to Fourier analysis are sine functions $g_j(t) = \frac{1}{2\pi} \sin(\omega_j t)$ and cosine functions $g_j(t) = \frac{1}{2\pi} \cos(\omega_j t)$.

To take another common example in the physical sciences, we often find damped oscillatory signals which may be expressed as a sum of damped cosines:

$$g_{jk}(t) = e^{-\gamma t} \cos(\omega_j t).$$

(4.8)

Compressed sensing and super-resolution are easily adapted to this overcomplete basis and, once
the sparse coefficients $\lambda_{jk}$ have been found via Equation 4.6, the final spectrum may be plotted as

$$
\hat{f}(\omega) = \sum_{j,k} \lambda_{jk} g_{jk}(\omega)
$$

$$
= \sum_{j,k} \frac{\lambda_{jk}}{\sqrt{2\pi}} \left( \frac{\gamma_k}{\gamma_k^2 + (\omega - \omega_j)^2} + \frac{\gamma_k}{\gamma_k^2 + (\omega + \omega_j)^2} \right).
$$

In short, compressed sensing and super-resolution both enable the recovery of an undersampled signal by using a customized, sparse basis that is appropriate to the problem at hand. The choice of technique typically depends on which sampling method is easier to perform: random sampling over the entire time domain is appropriate for compressed sensing, while regular sampling over a short part of the time domain is appropriate for super-resolution.

4.2.3 Filter Diagonalization

Filter diagonalization is another approach to circumvent the Shannon-Nyquist condition. Inspired by quantum mechanics, the method assumes that the signal $f(t)$ to be recovered is generated by the time evolution of a unitary propagator,

$$f(t) = (\Phi_0, e^{-i\hat{H}t} \Phi_0).$$

If we sample $f(t)$ on an equally-spaced grid $t_n = n\tau$, we can discretize this equation as

$$f(t_n) = (\Phi_0, e^{-i\hat{H}\tau} \Phi_0).$$
where $\hat{U} = e^{-i\hat{\Omega}\tau}$ is the unitary propagator. By expanding the propagator in terms of its eigenvalues and (possibly complex) eigenvectors,

$$e^{-i\hat{\Omega}\tau} = \sum_j e^{-i\omega_j \tau} |u_j\rangle \langle u_j|,$$

(4.12)

and substituting this expansion into Equation 4.11, we obtain

$$f(t_n) = \sum_j |(u_j, \Phi_0)|^2 e^{-i\omega_j n\tau},$$

(4.13)

which is the equation for a Lorentzian signal with (possibly damped) frequencies $\omega_j$ and amplitudes $\lambda_j = |(u_j, \Phi_0)|^2$. Hence, resolving a signal $f(t)$ into a sum of Lorentzian peaks is reduced to the standard linear algebra problem of finding the eigenvalues and eigenvectors of the propagator $\hat{U} = e^{-i\hat{\Omega}\tau}$.

The key insight of filter diagonalization is that the propagator to be diagonalized, $e^{-i\hat{\Omega}\tau}$, may be expressed entirely in terms of time samples of the signal $f(t)$.

A common approach is to write the propagator in a so-called Krylov basis,

$$\Psi_k = \sum_{n=0}^{N} \left( \frac{\hat{U}}{z_k} \right)^n \Phi_0,$$

(4.14)

where $z_k = e^{-i\nu_k \tau}$ is a complex value chosen along the unit circle. By selecting the $\nu_k$ close to the frequencies we wish to resolve, it is possible to filter $f(t)$ and recover only those frequency components near the $\nu_k$; this is where the name filter diagonalization comes from. It is important to include more basis vectors $|\Psi_k\rangle$ than there are frequencies we wish to resolve.

Expressing the propagator in the Krylov basis yields

$$U_{kk'} = (\Psi_k, \hat{U} \Psi_{k'}) = \sum_{n=0}^{N} \sum_{n'=0}^{N} f_{n+n'+1} z_k^{-n} z_{k'}^{-n'},$$

(4.15)
which is expressed completely in terms of time samples of the signal. Because the Krylov basis is not orthonormal, we also need the overlap matrix,

\[ S_{kk'} = (\Psi_k, \Psi_{k'}) = \sum_{n=0}^{N} \sum_{n'=0}^{N} f_{n+n'} z_k^n z_{k'}^{-n'}, \quad (4.16) \]

after which the eigenvalues and eigenvectors of \( \hat{U} \) may be found by solving the generalized eigenvalue problem,

\[ UB_j = u_j S B_j. \quad (4.17) \]

For computational efficiency, the double sums in Equations 4.15 and 4.16 are rewritten as single sums, as shown in. With the eigenvalues \( u_j \) and eigenvectors

\[ u_j = \sum_k B_{kj} \Psi_k, \quad (4.18) \]

in hand, the frequencies \( \omega_j \) and amplitudes \( \lambda_j \) in the signal \( f(t) \) may be reconstructed according to the formulas

\[ u_j = e^{-i\omega_j \tau}, \quad \text{and} \quad (4.19) \]

\[ \lambda_j = \left| (u_j, \Phi_0) \right|^2 = \left| \sum_k B_{kj} (\Psi_k, \Phi_0) \right|^2. \quad (4.20) \]

Because the Krylov basis is often close to becoming linearly dependent, we include a numerical conditioning step to remove possible spurious frequencies. In particular, we select a value of \( p \) and resolve the generalized eigenvalue equation with \( \hat{U}^{p+1} \) and \( \hat{U}^p \) (used in place of \( \hat{U} \) and \( \hat{S} \)). We remove the eigenvalues that are not shared in the two spectra, and then select a filtering grid with frequencies \( v_j \) located only at the nonspurious eigenvalues. We rerun filter diagonalization one more time on this adaptive frequency grid, and these are the results we report below.
While this technique was initially derived with quantum mechanics in mind, it is not limited to such applications. Indeed, with generalizations such as 2D filter diagonalization and multi-resolution filter diagonalization, the method has been expanded to be applicable to a broad range of signals.

4.3 METHODS

As our goal in this paper is to compare the performance of compressed sensing, super-resolution, and filter diagonalization in recovering sparse signals, we began by obtaining a series of sparse signals from the Sparco toolkit, which is a well-known set of sparse signals used for benchmarking various signal processing techniques. We also generated a few other signals of interest to highlight particular properties of each technique. Unless otherwise stated, each signal began as a continuous function of time \( f(t) \) and, to generate a discrete time series, we sampled \( f(t) \) at 4096 time points ranging uniformly from \( t = 0 \) to \( t = 1 \) second. This gave a grid separation of \( \frac{1}{4096} \) seconds, with a maximum recoverable frequency of 2048 Hz.

For each sparse signal processing method, we varied how many of the 4096 time points we sampled (in increments of 64) and investigated the dependence of the recovery error on the extent of undersampling. As a measure of the recovery error, we employed the relative 2-norm error over all 4096 time points (regardless of the extent of undersampling):

\[
\text{Recovery Error} = \frac{\sum_{i=1}^{4096} |f_{\text{recovered}}(t_i) - f_{\text{original}}(t_i)|^2}{\sum_{i=1}^{4096} |f_{\text{original}}(t_i)|^2},
\]

We consistently obtained similar results with the 1-norm error and the \( \infty \)-norm error, but the 2-norm error has the advantage that, by Parseval’s theorem, it is the same whether it is measured in the time domain or the frequency domain. Therefore, we adopted the 2-norm as our primary benchmark. In some instances, filter diagonalization has been marketed as a parameter estimation
4.3. Methods

For compressed sensing and super-resolution, we attempted to recover each signal in an appropriate sparse basis. The basis used depends on the signal and is discussed in the individual sections below. Because super-resolution requires a grid of equally spaced sample points, we began our analysis by examining the full signal and computing the errors. We then repeated our analysis for the signal by successively undersampling in powers of two, taking care to ensure that our sample points were always equally spaced. In contrast, our analysis with compressed sensing involved randomly selecting the same number of points that were included in the super-resolution analysis at each step.

For filter diagonalization, we used the same regular sampling strategy as for super-resolution, and we monitored the recovery error as a function of the sampling. Filter diagonalization requires specifying a grid of frequencies on which we expect the components of the signal to lie, so we specified a frequency range of 0 kHz to 20 kHz. To find the appropriate grid density and number of frequencies, we tuned these two parameters for optimal reconstruction with the full time signal and assumed these parameters would be valid for the entire numerical experiment. To ensure the robustness of our results, we also performed the analysis from 0 to 5, 10, 50, 100, 200, and 500 kHz, with a similar density of frequencies.

From a numerics standpoint, compressed sensing and super-resolution require a fast, memory-efficient $L_1$ solver. For all results in this paper, we implemented the two step iterative shrinkage/thresholding (TwIST) algorithm in Python. Our TwIST solver is capable of solving arbitrary optimization problems given a measurement matrix, signal vector, and objective function, and gives numerically identical answers to the Matlab version for a wide range of test
Figure 4.1: (a) Time series consisting of a Gaussian given by Equation 4.22 centered at $t = 0$ with standard deviation $\sigma = 0.4$. (b) Comparison of the relative 2-norm error in the reproduction of a Gaussian signal as a function of undersampling between compressed sensing, super-resolution, and filter diagonalization.

signals, including all those in this paper.

We implemented filter diagonalization in Python, performing all required matrix diagonalizations using the zgeev function from LAPACK. We benchmarked our implementation against Harminv, a freely-available C++ implementation based on the methods described in, and found that they give the same answers to within numerical precision for a wide range of signals, including all of those presented in this paper.

4.3.1 GAUSSIAN SIGNAL

We begin with one of the most ubiquitous signals throughout signal processing, a simple Gaussian centered at time $t = 0$ with $\sigma = 0.4$ (Figure 4.1a).

$$f(t) = e^{-\frac{t^2}{0.4^2}}.$$  \hspace{1cm} (4.22)

To recover this signal with compressed sensing and super-resolution, we employ a basis of displaced Gaussians

$$g_{jk}(t) = e^{-\frac{(t-t_j)^2}{0^2}}.$$  \hspace{1cm} (4.23)

with 100 centers $t_j$ ranging uniformly from 0 to 1, and 100 standard deviations $\sigma_k$ also ranging
uniformly from 0 to 1, for a total of 10,000 different basis functions. It is clear that the function we hope to recover, $f(t)$, is sparse in this basis. 

Figure 4.1b compares the performance of compressed sensing, super-resolution, and filter diagonalization in recovering the Gaussian signal. Compressed sensing and super-resolution both converge quickly to the correct signal, and as more time-domain information is sampled, the signal becomes more obviously composed of a single Gaussian. Moreover, compressed sensing converges more quickly than super-resolution, indicating that randomly sampling over the entire time domain provides more complete information about the overall shape of the signal than sampling uniformly with a coarse grid. Both compressed sensing and super-resolution recover a single strongly converged, correct, peak with amplitude 1 and a few spurious peaks with amplitudes smaller than $10^{-6}$. This represents a small numerical instability in our implementation of TwIST but these spurious features are easy to identify and disregard.

By contrast, filter diagonalization fails to converge completely because it attempts to recover the Gaussian as a sum of Lorentzian peaks, rather than taking advantage of the natural sparsity of the signal in a Gaussian basis. This example highlights the basis set agnosticism of the $\ell_1$ minimization techniques, which is one of their principal advantages.

### 4.3.2 Sparco Problem 1

For our second signal, we consider a sinusoid that is “disrupted” by two Heaviside step functions (Figure 4.2a).

$$f(t) = 4\sin(4\pi t) - \Theta(t - 0.3) - \Theta(0.72 - t), \quad (4.24)$$

one of the earliest signals used to benchmark wavelet and compressed sensing techniques.\textsuperscript{27,24,52,17} This signal is Problem 1 in the Sparco toolbox of sparse signals.\textsuperscript{238}

To recover this signal via compressed sensing and super-resolution, we employ a composite
basis of sine functions and Heaviside step functions

\[ g_j(t) = \sin(\omega_j t) \quad (4.25) \]
\[ h_j(t) = \Theta(t - t_j), \quad (4.26) \]

with the spectral spacing \( \omega_j \) of the sine functions ranging uniformly from 0 to 4096\( \pi \) kHz in units of \( \frac{\pi}{10} \) kHz, and the unit steps \( t_j \) of the Heaviside step functions ranging uniformly from 0 to 1 second in units of 0.01 seconds. While either basis \( g_j(t) \) or \( h_j(t) \) by itself would provide a complete basis for recovery of the signal \( f(t) \) (to within numerical precision), the function \( f(t) \) would not be sparse in either basis on its own. On the other hand, there is no problem in \( \mathcal{L}_1 \) minimization techniques with using the combined basis, which affords the additional advantage that \( f(t) \) is sparse in this combined basis. However, when building a composite basis with different functional forms, it is important to ensure that each basis function is normalized to the same value, for which we chose unity.

Figure 4.2b compares the performance of compressed sensing, super-resolution, and filter diagonalization in recovering the signal \( f(t) \). For super-resolution and filter diagonalization, both
of which involve regular sampling over a coarse time domain grid, most of the initial error simply comes from the fact that the methods cannot reproduce aspects of the signal that have not been sufficiently sampled.

Super-resolution and compressed sensing are able to identify that the signal has some underlying sine structure, but initially fails to recognize the exact position of the step functions. As more samples are included in the analysis, both techniques are able to quickly converge to the exact location of the step function. This convergence leads to a very sharp phase transition characteristic of an $\mathcal{L}_1$ analysis, and represents the minimum amount of information required to exactly reproduce the full signal. This phase transition is a well known aspect of $\mathcal{L}_1$ minimization techniques, and provides a useful and valid check on convergence and accuracy.

This stands in contrast to filter diagonalization, which attempts to match the Heaviside step functions by creating a signal that contains exponentially growing components, eventually resulting in an explosion of error. To better understand this behavior, we varied the magnitude of the Heaviside step functions, but found that the creation of an exponentially growing signal persisted even when the Heaviside step function was 0.1% of the amplitude of the oscillating sine wave.

Not surprisingly, compressed sensing fares better than both super-resolution and filter diagonalization. This is easily explained by the fact that compressed sensing randomly samples the entire domain, so it can quickly “recognize” all features of the signal and recover them accurately. After roughly one sixty fourth of the signal has been sampled, the error changes only marginally, and this effect is robust across different runs of random sampling.
Figure 4.3: (a) The combination of three cosines and random spikes in the time domain as described in Equation (4.27). (b) Comparison of the 2-norm recovery error for the Problem 5 from the Sparco toolbox as a function of undersampling for compressed sensing, super-resolution, and filter diagonalization. We attribute the large error peaks found by filter diagonalization to the recovery of spurious exponentially divergent solutions.

4.3.3 Sparco Problem 5

For our third signal, we consider the sum of three cosines with the addition of 40 spikes at random time points \( \{ t_i \} \) (Figure 4.3a),

\[
    f(t) = 2\cos(2\pi t) + 3\cos(9\pi t) - \cos(20\pi t) + \sum_i \alpha_i \delta(t-t_i),
\]

where \( \delta(t-t_i) \) is regarded here as the Kronecker delta function (equal to 1 at the time point \( t = t_i \), 0 otherwise) and \( \alpha_i \) is a uniform random number between 0 and 1. This signal is Problem 5 in the Sparco toolbox of sparse signals, and including it in our comparison is particularly useful for benchmarking the ability of compressed sensing, super-resolution, and filter diagonalization to deal with random noise.

To recover this signal via compressed sensing and super-resolution, we employ a cosine basis:

\[
    g_j(t) = \cos(\omega_j t),
\]

with the spectral spacing \( \omega_j \) of the cosine functions ranging uniformly from 0 to \( 4096\pi \) kHz in
4.3. Methods

units of $\frac{\pi}{10}$ kHz. Note that we do not include Kronecker delta functions $\delta(t - t_i)$ in our basis, since our goal is to see whether our signal processing methods can recover the underlying cosine functions despite the random noise.

As shown in Figure 4.3b, both compressed sensing and super-resolution successfully recover the underlying cosine functions in spite of the noise peaks (the noise peaks simply get absorbed into the denoising parameter $\eta$). As expected, compressed sensing recovers the signal with less sampling than super-resolution, since randomly sampled points over the entire time domain effectively contribute more information than regularly sampled points over that same time domain.

In contrast, filter diagonalization does not include a robust denoising procedure, and the method struggles with the Kronecker delta peaks because they represent sharp deviations from the underlying cosine signal. In particular, in attempting to match the Kronecker delta peaks, filter diagonalization creates a signal that contains exponentially growing components rather than exponentially damped Lorentzians. In summary, compressed sensing and super-resolution both pick out the underlying cosine signals by denoising the Kronecker delta peaks, whereas filter diagonalization does not.

4.3.4 JACOB’S LADDER

Next, we consider a time series devised by some of the original developers of filter diagonalization for benchmarking sparse signal processing techniques. This signal is known as Jacob’s Ladder, and it consists of a very large number of Lorentzian peaks (Figure 4.4a):

\[
 f_n = \sum_{m=0}^{49} e^{-1.8m\pi^2 \times 10^{-4} n} \left[ \cos(1.8m\pi 2 \times 10^{-4} 2500n) + \cos(1.8m\pi 2 \times 10^{-4} 2487.5n) + \cos(1.8m\pi 2 \times 10^{-4} 2475.0n) \right].
\]
In this experiment, we created a signal with 1000 data points that ranged, uniformly, from 0 to 1 seconds using the formula in Equation (4.29). We first analyzed this signal with a numerical implementation of filter diagonalization using a frequency range of 0 kHz to $\pi$ kHz and assumed that we had a maximum of 4500 frequencies in our signal.

We started by performing the filter diagonalization analysis with the above frequency grid using the entire signal, and used the recovered frequencies and expansion coefficients to construct the recovered signal. This allowed us to compute the 2-norm error between the recovered signal and the exact signal over the entire range. We then repeated the analysis, while successively undersampling, first taking every second point, then every fourth, fifth, eighth, tenth, twentieth, twenty-fifth, fortieth, fiftieth, and finally, hundredth. We then performed the same analysis with super-resolution and compressed sensing. Because compressed sensing involved random sampling, we took care to randomly sample the same number of points that were included in the super-resolution analysis at each step.

In order to perform the $L_1$ analysis we examined the functional form and the signal itself and concluded that it should be sparse in the basis of damped oscillators. Thus we constructed such a basis with a spectral spacing of 0.01 Hz and a maximum of $4\pi$ Hz. We also scanned exponential
decay parameters ranging from 0 to \( \pi \) Hz in steps of 0.01 Hz. For the super resolution analysis, we performed the same time addition procedure that was performed with filter diagonalization. We began the compressed sensing analysis by picking 50 random time points, and at each subsequent step an additional 50 random points were taken from those remaining until we were sampling the full signal.

From the errors given in Figure 4.4b both compressed sensing and super resolution converge to a better answer more rapidly than filter diagonalization. We attribute these errors to the recovery of exponentially divergent solutions but we have no way of accounting for the difference between our results and those obtained elsewhere. Our working theory is a sensitivity of filter diagonalization to the frequency grid and parameter choice, and we have not found the correct combination of parameters that allows us to completely recover the desired signal. This suggests that our implementation, as well as our standard of comparison suffered from significant numerical instability. We are unsure whether this is explained better by fundamental instabilities in the method at hand, or simply instabilities in the current implementations.

By contrast, super-resolution and compressed sensing do not suffer from these same problems. Many current methods are extremely stable. These techniques only include the basis functions that are explicitly chosen. Unfortunately, we are limited to the recovery of Lorentzian parameters (frequency and line-width), that are on the grid, which requires a sufficiently dense set of parameters for accurate recovery. As a result, \( \mathcal{L}^1 \)-optimization methods become more and more memory intensive as the number of basis functions increases.

4.3.5 Sum of Random Lorentzians

For the final comparison, we created a sum of twenty random damped cosines:

\[
    f(t) = \sum_{n=1}^{20} e^{-\gamma_n t} \cos \omega_n t, \tag{4.30}
\]
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Figure 4.5: (a) Combination of twenty random damped cosines as described in Eq. (4.30). (b) Comparison among compressed sensing, super-resolution, and filter diagonalization of the 2-norm error in the reproduction of the combination of random damped cosines as a function of undersampling. We attribute the large error peaks found by filter diagonalization to the recovery of spurious exponentially divergent solutions.

with \( \gamma_n \) drawn from a uniform random distribution ranging from 0 to 20 Hz and \( \omega_n \) ranging from 0 to 50\( \pi \) Hz. This type of autocorrelation signal is ubiquitous not only in chemistry applications, but in signal processing at large.

To recover this signal via compressed sensing and super-resolution, we employ a basis of damped cosine functions:

\[
g_{jk}(t) = e^{-\gamma_k t} \cos(\omega_j t). \tag{4.31}
\]

Here, the spectral spacing \( \omega_j \) ranges uniformly from 0 to 40\( \pi \) Hz in steps of \( \pi/24 \) Hz and the damping parameters \( \gamma_k \) ranges uniformly from 0 to 20 Hz in steps of 1/2 Hz. For filter diagonalization, we selected a frequency range from 0 to 100\( \pi \) Hz and chose a basis of 1200 frequencies. This was chosen because it gave near perfect reconstruction of the full signal, while bases smaller than this were prone to numerical instability.

As shown in Figure 4.5b, both compressed sensing and super-resolution successfully recover the underlying damped cosine structure but is restricted to the functions on the grid. This is the most
significant source of error. As expected, compressed sensing recovers the signal with less sampling than super-resolution, since randomly sampled points over the entire time domain effectively contribute more information than regularly sampled points over a short time.

In contrast, filter diagonalization can recover off-grid frequencies extremely efficiently. Because of this, the final errors should be smaller than the errors from both compressed sensing and super resolution. Unfortunately, we encountered significant stability issues during many of our decompositions that resulted in exponentially growing solutions. These solutions gave $\ell_2$ errors on the order of $10^4$ at times (note that we have chosen to only plot a few orders of magnitude in Figure 4.5b) While filter diagonalization is capable of giving a much better answer, the technique is significantly more sensitive to slight deviations in the operational parameters chosen.

4.4 CONCLUSIONS

In conclusion, we have performed a broad comparison of three different signal processing techniques that attempt to “beat” the Shannon-Nyquist limit. With prior information about a reasonable basis for one’s signal, $\ell_1$ minimization techniques provide a robust and faithful reproduction of the signal. We emphasize that the difference between super-resolution or compressed sensing is simply a choice of sampling procedure and normally is determined by the data acquisition technique.

Additionally, we found that if the signal at hand was Lorentzian, filter diagonalization was capable of significantly outperforming both compressed sensing and super resolution because of its ability to sample off the grid. Even still, the technique was sensitive to a broad range of parameters, which were capable of making it divergent if chosen incorrectly. Given enough tuning and the appropriate signal form, however, filter diagonalization is the superior method for these types of signals.
4.5 ACKNOWLEDGEMENTS

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Response to: “Comment on Benchmarking Compressed Sensing, Super-Resolution, and Filter Diagonalization”

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INTRODUCTION

Signal processing is ubiquitous in the physical sciences. Traditionally, most signal processing has been performed with some sort of Fourier analysis, which is naturally limited by the Shannon-Nyquist condition. This condition places significant and strict limits on the frequency resolution based on both the frequency of sampling and length of time observed in the time domain. Often, we desire better resolution that what is guaranteed by the Shannon-Nyquist sampling theorem. To achieve this end, many techniques have been proposed. Three of the most prominent techniques are the Filter Diagonalization Method (FDM), Super-Resolution (SR) sampling, and Compressed or Compressive-Sensing (CS). In our recently published work, we set out to compare each of these methods for the purpose of data-fitting on a small test set of representative signals. These signals were intended to test the ability of the three methods to fit
data in the presence of kicks, jumps, and Gaussian broadening. This work was recently criticized by Professor Vladimir Mandelshtam, one of the developers of the FDM methodology. We welcome these criticisms as ultimately discussion is what ensures science moving forward. In his comment, Professor Mandelshtam raised many concerns, which can be separate into five separate thrusts:

1. Our implementation of the Filter Diagonalization Method (FDM) is incorrect.

2. Parseval’s equality does not apply for the systems that we have considered.

3. FDM is only intended for parameter estimation, and thus, comparison of the total quality of reproduction is an invalid metric.

4. FDM is not well suited for extrapolation.

5. Our signals are incorrectly described and the signals provide an unfair comparison.

We will respond to each argument below.

5.1 Our Implementation of Filter Diagonalization

As described in the paper, our implementation of FDM used adaptive gridding. We chose to use adaptive gridding because it appeared to be a mathematically mature technique, and our search of the FDM literature did not indicate numerical issues. The only freely available code we found with an FDM implementation was the Harminv code, developed by Steven G Johnson[248]. We thoroughly checked our implementation against his and verified that it provided good agreement.

We have decided to open source our entire test-suite of signals, as well as all the code associated with the project so that the accuracy of the reproductions can be tested and verified. This will be freely available on github[249]. All of our code is in Python, and we have included Jupyter notebooks that reproduce the plots of the paper. We welcome exploration of the code. We also welcome any new results computed with any private implementations of FDM as a follow-up to this paper.
5.2 Parseval’s Equality

Professor Mandelshtam argues that Parseval’s equality does not hold for any of the signals studied in our paper, and does not allow us to be able to compare spectral errors based on time reproduction errors. We disagree with this statement, because Parseval’s theorem applies to not only continuous Fourier transforms but also discrete-time Fourier transforms and discrete-time discrete-frequency Fourier transforms. Furthermore, he seems to claim that over-complete basis sets cannot be subject to Parseval’s equality. We will first prove that over-complete basis sets can obey Parseval’s equality, and then we will prove Parseval’s theorem for the discrete case.

Let us begin by defining a function, \( f(t) \), which is square integrable. Parseval’s theorem tells us that

\[
\int_{-\infty}^{\infty} dt |f(t)|^2 = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega |\hat{f}(\omega)|^2. \tag{5.1}
\]

If we then define a function, \( \tilde{f}(t) \), which is also square integrable, we can also compute the \( L^2 \) error between the two functions in the following way

\[
\int_{-\infty}^{\infty} dt |f(t) - \tilde{f}(t)|^2 = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega |\hat{f}(\omega) - \hat{\tilde{f}}(\omega)|^2. \tag{5.2}
\]

Without loss of generality, we can define \( \tilde{f}(t) \) as

\[
\tilde{f}(t) = \sum_n c_n \phi_n(t), \tag{5.3}
\]

where \( c_n = (f, \phi_n) \), and the set of functions, \( \phi \) are assumed to be square integrable as well. Substituting our expression for \( \tilde{f}(t) \) into equation (5.4), we arrive at

\[
\int_{-\infty}^{\infty} dt \left| f(t) - \sum_n (f, \phi_n) \phi_n(t) \right|^2 = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \left| \hat{f}(\omega) - \sum_n (f, \phi_n) \hat{\phi}_n(\omega) \right|^2. \tag{5.4}
\]
5.2. Parseval’s equality

Rearranging the sum, we obtain

\[ \int_{-\infty}^{\infty} dt \left| \sum_n f(t) - (f, \phi_n) \phi_n(t) \right|^2 = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \left| \sum_n \hat{f}(\omega) - (f, \phi_n) \hat{\phi}_n(\omega) \right|^2. \] (5.5)

Clearly, this will still satisfy Parseval’s theorem. We are confident that the equality holds, because each substitution was performed identically on both sides of the equation. Note, we have made no claim about the overlap of the \( \phi \) functions, aside from the restriction that they be square integrable. This is, in general, no more severe than the restrictions placed on the original Fourier transform itself. For each of the different signals considered in our paper, we picked a different series of signals in the time domain and each was square-integrable over the domain of consideration.

We next turn our attention to the discrete version of Parseval’s theorem. One of the critiques was that Parseval’s theorem provides no guarantees in the finite-sampling discrete case. We have chosen to prove the discrete version of Parseval’s theorem below for clarity and completeness. Note, the discrete version of Parseval’s theorem only applies to the observed data-range.

Let’s begin by assuming that we can define a signal given by the function \( f \) on a grid of points, with the \( n^{th} \) point given by \( t_n \). The function evaluated at the \( t_n \) point will referred to as \( f(t_n) \). Then, the discrete Fourier transform of a signal, given by \( \hat{f}(k) \) is defined as

\[ \hat{f}(k) = \sum_{n=0}^{N-1} f(t_n)e^{i2\pi kn/N}, \] (5.6)

Then, we wish to prove Parseval’s equality, which requires computing \( |\hat{f}(k)|^2 \), which is computed via:

\[ \sum_j |\hat{f}(k_j)|^2 = \sum_{j} \sum_{m=0}^{N-1} \overline{f^*(t_m)} \sum_{n=0}^{N-1} f(t_n)e^{-i2\pi kj_m/N}e^{i2\pi kj_n/N}. \] (5.7)
Rearranging, we obtain

$$\sum_j |\hat{f}(k_i)|^2 = \sum_{m=0}^{N-1} f^*(t_m) \sum_{n=0}^{N-1} f(t_n) \sum_j e^{-i2\pi k_i j_m/N} e^{i2\pi k_i j_n/N}. \quad (5.8)$$

The sum of exponentials becomes:

$$\sum_j e^{-i2\pi k_i j_m/N} e^{i2\pi k_i j_n/N} = \frac{e^{2\pi i(m-n)} - 1}{e^{2\pi i(m-n)/N} - 1}, \quad (5.9)$$

which reduces to

$$N \delta_{mn}. \quad (5.10)$$

We can substitute this back into equation (5.8)

$$\sum_j |\hat{f}(k_i)|^2 = \sum_{m=0}^{N-1} f^*(t_m) \sum_{n=0}^{N-1} f(t_n) N \delta_{mn}. \quad (5.11)$$

Collapsing the Kronecker delta, we obtain

$$\sum_j |\hat{f}(k_i)|^2 = \sum_{n=0}^{N-1} f^*(t_n) f(t_n) N, \quad (5.12)$$

which simplifies to:

$$\sum_j |\hat{f}(k_i)|^2 = N \sum_{n=0}^{N-1} |f(t_n)|^2, \quad (5.13)$$

This completes the proof of Parseval’s equality for discrete signals. Note, we are free to define our function without loss of generality. For all signals considered in the paper, we have defined the function as the difference between the exact function and some function found via data-fitting.

It is important to note that while we were using Compressed Sensing, Super Resolution, and Filter Diagonalization to expand into some basis, the ultimate goal is to explore the signals in the
conjugate domains of time and frequency. Because we know the analytic Fourier transforms for each of the bases considered in our paper, and because the basis functions are all square integrable, computing the time-domain reconstruction error is clearly a valid metric for assessing overall errors in the spectral domain.

5.3 Parameter Estimation

The goal of our original study was to explore efficient ways to accurately fit correlation functions, so that we could use the recovered parameters in excitonic simulations. During the course of peer review, we were asked to compare FDM to our methods. As we performed a more thorough comparison, and wanted to explore the data-fitting features and observed instability further, we ultimately performed the published comparisons.

While we did evaluate the various methods on their performance for data fitting, we have observed that the reported $\mathcal{L}_2$ errors provide a lower bound for the parameter errors. This can be seen by first starting with the following definition of a Lorentzian:

$$L(\omega; \gamma, \Omega) = \frac{1}{2\pi} \left( \frac{\gamma}{\gamma^2 + (\omega - \Omega)^2} \right), \quad (5.14)$$

where $\gamma$ and $\Omega$ are related to the width and position of the lorentzian respectively. We can then define perturbations $\delta$ and $\sigma$ in each parameter, such that

$$L(\omega; \gamma - \delta, \Omega - \sigma) = \frac{1}{2\pi} \left( \frac{\gamma - \delta}{(\gamma - \delta)^2 + (\omega - \Omega - \sigma)^2} \right). \quad (5.15)$$
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If we compute the $L_2$ error of perturbations with respect to $\delta$ and $\sigma$, we arrive at

$$
||L(\omega; \gamma, \Omega) - L(\omega; \gamma - \delta, \Omega - \sigma)|| = 
\left( \int d\omega \left| \frac{1}{2\pi} \left( \frac{\gamma}{\gamma^2 + (\omega - \Omega)^2} \right) \right| - \frac{1}{2\pi} \left( \frac{\gamma - \delta}{(\gamma - \delta)^2 + (\omega - \Omega - \sigma)^2} \right) \right)^{1/2}.
$$

(5.16)

This integral reduces to:

$$
L_2 = \sqrt{\frac{(2\gamma - \delta)(\delta^2 + \sigma^2)}{8\pi\gamma(\gamma - \delta)(4\gamma^2 - 4\gamma\delta + \delta^2 + \sigma^2)}}.
$$

(5.17)

We have plotted the $L_2$ error due to perturbations, $\sigma$, in frequency offset, $\Omega$, in Figure 5.1. The plot shows the errors as a function of $\sigma$ for a Lorentzian with $\gamma = 10$ and $\Omega = 10$. As is clearly seen, the $L_2$ norm provides a lower bound for spectral errors in the spectral offset.

![Figure 5.1](image)

**Figure 5.1:** We present a plot of the two different error metrics plotted against the size of the perturbation, $\sigma$, in the spectral position parameter $\Omega$ as defined in Equation (5.15). The $L_2$ error is given by Equation (5.17) and the Parameter Error is given by $|\sigma|$. We see that the $L_2$ error provides a rigorous lower bound to the spectral parameter error.

We have plotted the $L_2$ error due to perturbations, $\delta$, in the Lorentzian width parameter, $\gamma$, in Figure 5.2. The plot shows the errors as a function of $\sigma$ for a Lorentzian with $\gamma = 10$ and $\Omega = 10$. As can clearly be see, the $L_2$ norm provides a lower bound for almost the entire region. The only area where the $L_2$ norm exceeds that of the parameter error is when $\delta$ is 9.9996, or when there is a 99.996% error in the width parameter for the presented $\gamma$ and $\Omega$ values. More generally, this
crossover occurs for:

\[ \delta > \frac{3\gamma}{2} - \frac{\sqrt{2\pi\gamma^3 + 1}}{2\sqrt{2\pi\sqrt{\gamma}}}. \]  

(5.18)

In the instance where the error in the width parameter is higher than 99%, either error metric is capable of providing an accurate description of the performance of the method.

Figure 5.2: We present a plot of the two different error metrics plotted against the size of the perturbation, \( \delta \), in the spectral width parameter \( \gamma \) as defined in Equation (5.15). The \( L^2 \) error is given by Equation (5.17) and the Parameter Error is given by \(|\delta|\). We see that the \( L^2 \) error provides a lower bound to the spectral parameter error until the error in the spectral parameter is 99.996%.

5.4 Extrapolation

We agree that the extrapolation problem is difficult, and one where none of FDM, SR, or CS perform well. Because of this, we have chosen to only run numerical experiments involving interpolation.

5.5 Signal Description and Signal Choice

We agree with Professor Mandelshtam’s observations. For the signal that was constructed as a sum of randomly constructed Lorentzians, we had an error in our formula. We generated them with random amplitudes as well as random parameters. The formula should read:

\[ f(t) = \sum_n \hat{\lambda}_n e^{-\eta t} \cos(\Omega t). \]  

(5.19)
Chapter 5. Response to: “Comment on Benchmarking Compressed Sensing, Super-Resolution, and Filter Diagonalization”

We apologize for the error.

Prof Mandelshtam took particular issue with our use of a Gaussian function as a test. We included this test for two main reasons. First, many of the correlation functions we are interested in are frequently given some sort of gaussian broadening in the time domain. When we initially observed the relatively poor performance of FDM, we wanted to explore whether this was due to an inability for the method to handle a Gaussian signal or not. By contrast, because both CS and SR can work with heterogeneous and over-complete bases, we felt that it was an entirely fair test. Beyond this, however, a Gaussian is a very simple model frequently used in signal processing. The authors have occasionally even heard it referred to as the “harmonic oscillator” of signal processing.

CONCLUSIONS

We have addressed all the concerns of Professor Mandelshtam regarding our manuscript. We believe it stands as a valid benchmark for the community. Furthermore, we have released our code using an open-source license for achieving reproducibility and transparency. In addition, we have provided mathematical reasons for the use of our error metrics.

5.6 ACKNOWLEDGEMENTS

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Part III

Many Body Dispersion
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Analytical Nuclear Gradients for the Range-Separated Many-Body Dispersion Model of Noncovalent Interactions

Apart from minor modifications, this chapter originally appeared as:

“Analytical nuclear gradients for the range-separated many-body dispersion model of noncovalent interactions”. Martin A. Blood-Forsythe, Thomas Markovich, Robert A. DiStasio Jr., Roberto Car, and Alán Aspuru-Guzik
‡ These authors contributed equally to this work.

ABSTRACT

Accurate treatment of the long-range electron correlation energy, including van der Waals (vdW) or dispersion interactions, is essential for describing the structure, dynamics, and function of a wide variety of systems. Among the most accurate models for including dispersion into density functional theory (DFT) is the range-separated many-body dispersion (MBD) method [A. Ambrossetti et al., J. Chem. Phys. 140, 18A508 (2014)], in which the correlation energy is modeled at short-range by a semi-local density functional and at long-range by a model system of coupled quantum harmonic oscillators. In this work, we develop analytical gradients of the MBD energy with respect to nuclear coordinates, including all implicit coordinate dependencies arising from the partitioning of the charge density into Hirshfeld effective volumes. To demonstrate the
efficiency and accuracy of these MBD gradients for geometry optimizations of systems with intermolecular and intramolecular interactions, we optimized conformers of the benzene dimer and isolated small peptides with aromatic side-chains. We find excellent agreement with the wavefunction theory reference geometries of these systems (at a fraction of the computational cost) and find that MBD consistently outperforms the popular TS and D3(BJ) dispersion corrections. To demonstrate the performance of the MBD model on a larger system with supramolecular interactions, we optimized the $\text{C}_{60} \@ \text{C}_{60} \text{H}_{28}$ buckyball catcher host–guest complex. Finally, we find that neglecting the implicit nuclear coordinate dependence arising from the charge density partitioning, as has been done in prior numerical treatments, leads to an unacceptable error in the MBD forces, with relative errors of $\sim 20\%$ (on average) that can extend well beyond 100%.

6.1 INTRODUCTION

A theoretically sound description of noncovalent interactions, such as hydrogen bonding and van der Waals (vdW) or dispersion forces, is often crucial for an accurate and reliable prediction of the structure, stability, and function of many molecular and condensed-phase systems.\textsuperscript{58–61} Dispersion interactions are inherently quantum mechanical in nature since they originate from collective non-local electron correlations. Consequently, they pose a significant challenge for electronic structure theory and often require sophisticated wavefunction-based quantum chemistry methodologies for a quantitatively (and in some cases qualitatively) correct treatment. Over the past decade, this challenge has been addressed by a number of approaches seeking to approximately account for dispersion interactions within the hierarchy of exchange-correlation functional approximations in Kohn-Sham density functional theory (DFT),\textsuperscript{66,71–78,80–88,250–280} which is arguably the most successful electronic structure method in widespread use today throughout chemistry, physics, and materials science.\textsuperscript{281}
Chapter 6. Analytical Nuclear Gradients for the Range-Separated Many-Body Dispersion Model of Noncovalent Interactions

Based on a summation over generalized interatomic London ($C_6/R^6$) dispersion contributions, the class of pairwise-additive dispersion methods provide a simple and computationally efficient avenue for approximately incorporating these ubiquitous long-range interactions within the framework of DFT. (See Ref. 64 for a recent and comprehensive review of dispersion methods in DFT.) Although these pairwise-additive methods are capable of reliably describing the dispersion interactions in many molecular systems, it is now well known that both quantitative and qualitative failures can occur, as demonstrated recently in the binding energetics of host-guest complexes, conformational energetics in polypeptide $\alpha$-helices, cohesive properties in molecular crystals, relative stabilities of (bio)-molecular crystal polymorphs and interlayer interaction strengths in layered materials, to name a few.

In each of these cases, the true many-body nature of dispersion interactions becomes important, whether it is due to beyond-pairwise contributions to the dispersion energy, such as the well-known three-body Axilrod-Teller-Muto (ATM) term, or the non-additivity of the dynamic polarizability. One of the most successful models for incorporating these many-body effects into DFT is the many-body dispersion (MBD) model of Tkatchenko et al., which approximates the long-range correlation energy via the zero-point energy of a model system of quantum harmonic oscillators (QHOs) coupled to one another in the dipole approximation. The correlation energy derived from diagonalizing the corresponding Hamiltonian of these QHOs is provably equivalent to the random-phase approximation (RPA) correlation energy (through the adiabatic-connection fluctuation-dissipation theorem). The MBD model has consistently provided improved qualitative and quantitative agreement with both experimental results and wavefunction-based benchmarks. Notably, MBD correctly predicts the experimentally known relative stabilities of the molecular crystal polymorphs of glycine and aspirin, which pairwise methods fail to do. Refs. 279 and 295.
offer recent perspectives on the role of non-additive dispersion effects in molecular materials and the key successes of the MBD model.

In this work, we seek to extend the applicability of the MBD model by deriving and implementing the analytical gradients of the range-separated many-body dispersion (MBD@rsSCS) energy with respect to nuclear coordinates, thereby enabling efficient geometry optimizations and molecular dynamics simulations at the DFT+MBD level of theory. This paper is principally divided into a theoretical derivation of the analytical forces in the MBD model (Sec. 6.2), and a discussion of the first applications of these analytical MBD forces to the optimization of isolated molecular systems (Sec. 6.4). In Secs. 6.2.1 and 6.2.2, we start by presenting a self-contained summary of the MBD framework to clarify notation and highlight the different dependencies of the MBD energy on the nuclear coordinates. We then derive analytical nuclear gradients of the MBD@rsSCS correlation energy (Sec. 6.2.3). In Sec. 6.3 and Sec. 6.7.9 of the accompanying Electronic Supplementary Information (ESI)*, we give computational details. Subsequently, we demonstrate the importance of MBD forces for several representative systems encompassing inter-, intra-, and supra-molecular interactions (Secs. 6.4.1 and 6.4.3). We finally examine the role of the implicit nuclear coordinate dependence that arises from the partitioning of the electron density into effective atomic volumes (Sec. 6.4.4) and conclude with some final remarks on potential avenues for future work.

6.2 Theory

6.2.1 Notation employed in this work.

As the theory comprising the MBD model has evolved over the past few years, several notational changes have been required to accommodate the development of a more complete formalism that

*Electronic Supplementary Information (ESI) available: The ESI contains additional derivation details, a comprehensive symbol glossary, and Cartesian coordinates for all structures considered in this work.
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accounts for the various contributions to the long-range correlation energy in molecular systems and condensed-phase materials. In this section, we provide a current and self-contained review of the MBD@rsSCS model followed by a detailed derivation of the corresponding analytical nuclear gradients (forces). Our discussion most closely follows the notation employed in Refs. [279,280].

To assist in the interpretation of these equations, we have also furnished a glossary of symbols utilized in this work as part of the ESI. For a more thorough discussion of the MBD model (including its approximations and physical interpretations), we refer the reader to the original works [273,280] as well as a recent review [279] on many-body dispersion interactions in molecules and condensed matter.

Throughout this manuscript, all equations are given in Hartree atomic units ($\hbar = m_e = e = 1$) with tensor (vector and matrix) quantities denoted by bold typeface. In this regard, one particularly important bold/normal typeface distinction that will arise below is the difference between the $3 \times 3$ dipole polarizability tensor,

$$\alpha = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix}, \quad (6.1)$$

and the “isotropized” dipole polarizability, a scalar quantity obtained via

$$\alpha = \frac{1}{3} \text{Tr} [\alpha]. \quad (6.2)$$

The Cartesian components of tensor quantities are indicated by superscript Latin indices $ij$, i.e., $T^{ij}$ is the $(i, j)^{th}$ component of the tensor $T$. Likewise, Cartesian unit vectors are indicated by $\{\hat{e}_i, \hat{e}_j\}$. Atom (or QHO) indices are denoted by subscript Latin indices $abc$. The index $p$ will be used as a dummy index for summation. The imaginary unit is indicated with blackboard bold typeface, $i$, to distinguish it from the Cartesian component index $i$. Quantities that arise from the
solution of the range-separated self-consistent screening (rsSCS) system of equations introduced by Ambrosetti et al.\textsuperscript{280} will be denoted by an overline, \textit{i.e.}, \( \bar{X} \). For brevity we will refer to the MBD@rsSCS model (which has also been denoted as MBD* elsewhere) as simply MBD throughout the manuscript.

The MBD model requires keeping track of several different quantities that are naturally denoted with variants of the letter “\( R \)”, so we highlight these quantities here for the benefit of the reader. Spatial position, such as the argument of the electron density, \( \rho(\mathbf{r}) \), is indicated by \( \mathbf{r} \). The nuclear position of an atom \( a \) (or QHO mapped to that atom) is indicated by \( \mathbf{R}_a \). The internuclear vector is denoted \( \mathbf{R}_{ab} = \mathbf{R}_a - \mathbf{R}_b \), such that the internuclear distance is given by \( R_{ab} = \| \mathbf{R}_{ab} \| \). It follows that the \( i \)th Cartesian component of this internuclear vector is \( R_{ab}^i \). Finally, the effective vdW radius of an atom \( a \) is indicated by \( R_{vdW}^a \).

The dependence of the long-range MBD correlation energy, \( E_{MBD} \), on the underlying nuclear positions, \( \{ \mathbf{R} \} = \mathbf{R}_a, \mathbf{R}_b, \mathbf{R}_c, \ldots \), will arise both \textit{explicitly} through the presence of internuclear distance terms, \( R_{ab} \), and \textit{implicitly} through the presence of effective atomic volume terms, \( V_a = V_a[\{ \mathbf{R} \}] \), obtained \textit{via} the Hirshfeld partitioning\textsuperscript{297} of \( \rho(\mathbf{r}) \) (see Sec. 6.2.2.1). As such, these distinct types of dependence on the nuclear positions will be clearly delineated throughout the review of the MBD model and the derivation of the corresponding MBD nuclear forces below. For notational convenience, we will often use \( \partial_c \) rather than \( \nabla_{\mathbf{R}_c} \) to indicate a derivative with respect to the nuclear position of atom \( c \).

6.2.2 Review of the Many-Body Dispersion (MBD) Model.

The MBD formalism is based on a one-to-one mapping of the \( N \) atoms comprising a molecular system of interest to a collection of \( N \) QHOs centered at the nuclear coordinates, each of which is characterized by a \textit{bare} isotropic frequency-dependent dipole polarizability, \( \alpha_a(i\omega) \). Derived from the electron density, \textit{i.e.}, \( \alpha_a = \alpha_a[\rho(\mathbf{r})] \), these polarizabilities describe the unique local chemical
Chapter 6. Analytical Nuclear Gradients for the Range-Separated Many-Body Dispersion Model of Noncovalent Interactions

environment surrounding a given atom by accounting for hybridization (coordination number), Pauli repulsion, and other non-trivial exchange-correlation effects (see Sec. [6.2.2.1]). To account for anisotropy in the local chemical environment as well as collective polarization/depolarization effects, the solution of a range-separated Dyson-like self-consistent screening (rsSCS) equation is used to generate screened isotropic frequency-dependent dipole polarizabilities for each QHO, \( \alpha_a \) (see Sec. [6.2.2.2]). The MBD model Hamiltonian is then constructed based on these screened frequency-dependent dipole polarizabilities. Diagonalization of this Hamiltonian couples this collection of QHOs within the dipole approximation, yielding a set of interacting QHO eigenmodes with corresponding eigenfrequencies \( \{ \lambda \} \). The difference between the zero-point energy of these interacting QHO eigenmodes and that of the input non-interacting modes \( \{ \omega_a \} \), is then used to compute the long-range correlation energy at the MBD level of theory (see Sec. [6.2.2.3]), i.e.,

\[
E_{MBD} = \frac{1}{2} \sum_{p=1}^{3N} \sqrt{\lambda_p} - \frac{3}{2} \sum_{a=1}^{N} \omega_a. \tag{6.3}
\]

6.2.2.1 THE MBD STARTING POINT: BARE DIPOLE POLARIZABILITIES.

Mapping the \( N \) atoms comprising a molecular system of interest onto a collection of \( N \) QHOs is accomplished via a Hirshfeld partitioning of \( \rho(\mathbf{r}) \), the ground state electron density. Partitioning \( \rho(\mathbf{r}) \) into \( N \) spherical effective atoms enables assignment of the bare frequency-dependent dipole polarizabilities \( \alpha_a(i\omega) \) used to characterize a given QHO. Within the MBD formalism, this assignment is given by the following 0/2-order Padé approximant applied to the scalar dipole polarizabilities:

\[
\alpha_a(i\omega) = \frac{\alpha_a(0)}{1 - (i\omega/\omega_a)^2}, \tag{6.4}
\]

\[\text{\footnotesize \cite{297}}\]

Although there are numerous schemes for partitioning the electron density, the Hirshfeld prescription (Ref. [297] has been shown to result in atomic partitions that most closely resemble the densities of the corresponding free (isolated) atoms (by minimizing the Kullback-Leibler entropy deficiency of information theory) cf. Ref. [298].
in which $\alpha_a(0)$ is the static dipole polarizability and $\omega_a$ is the characteristic excitation (resonant) frequency for atom $a$. The dependence of the bare frequency-dependent dipole polarizability in Eq. (6.4) on $\rho(r)$ is introduced by considering the direct proportionality between polarizability and atomic volume,\textsuperscript{83} an approach that has been very successful in the Tkatchenko-Scheffler (TS) dispersion correction,\textsuperscript{83} \textit{i.e.},

$$\alpha_a[\rho(r)](0) = \left( \frac{V_a[\rho(r)]}{V_{a,\text{free}}} \right) \alpha_{a,\text{free}}(0) = \left( \frac{\int dr w_a(r)\rho(r)r^3}{\int dr \rho_{a,\text{free}}(r)r^3} \right) \alpha_{a,\text{free}}(0), \quad (6.5)$$

in which $V_{a,\text{free}}$ and $\alpha_{a,\text{free}}$ are the volume and static dipole polarizability of the free (isolated) atom in vacuo, respectively, obtained from either experiment or high-level quantum mechanical calculations. \textit{Explicit} dependence on $\rho(r)$ resides in the effective “atom-in-a-molecule” volume, $V_a[\rho(r)]$, obtained \textit{via} Hirshfeld partitioning\textsuperscript{297} of $\rho(r)$ into atomic components, in which the weight functions,

$$w_a(r) = \frac{\rho_{a,\text{free}}(r)}{\sum_b \rho_{b,\text{free}}(r)}, \quad (6.7)$$

are constructed from the set of spherical free atom densities, $\{\rho_{b,\text{free}}(r)\}$. At present, we compute the Hirshfeld partitioning and subsequently the MBD energy and forces as an \textit{a posteriori} update to the solution of the non-linear Kohn-Sham equations, \textit{i.e.} without performing self-consistent updates to $\rho(r)$. Future work will address the impacts of computing the Hirshfeld partitioning iteratively\textsuperscript{300} and using the MBD potential to update the Kohn-Sham density self-consistently. In this regard, recent work on the self-consistent application of the TS method indicates that self-consistency can have a surprisingly large impact on the charge densities, and corresponding work functions, of metallic surfaces,\textsuperscript{301} so we anticipate that self-consistent MBD will be particularly interesting for the study of surfaces and polarizable low-dimensional systems.
For later convenience, we rewrite Eqs. (6.4) and (6.5) to collect all quantities that do not implicitly depend on the nuclear coordinates through $V_a[\rho(r)]$ into the quantity $Y_a(i\omega)$:

$$\alpha_a[\rho(r)](i\omega) = \left[ \frac{1}{1 - (i\omega/\omega_a^{\text{free}})^2} \alpha_a^{\text{free}}(0) \right] V_a[\rho(r)]$$

$$\equiv Y_a(i\omega) V_a[\rho(r)]. \quad (6.8)$$

$$\alpha_a[\rho(r)](i\omega) V_a[\rho(r)]$$

$$\equiv Y_a(i\omega) V_a[\rho(r)]. \quad (6.9)$$

### 6.2.2.2 RANGE-SEPARATED SELF-CONSISTENT SCREENING (rsSCS).

Let $A$ be a $3N \times 3N$ block diagonal matrix formed from the frequency-dependent polarizabilities in Eq. (6.8): **

$$A(i\omega) = \bigoplus_{b=1}^{N} \alpha_b(i\omega) = \text{diag}[\alpha_1, \alpha_2, \ldots, \alpha_N]. \quad (6.10)$$

This quantity will be referred to as the bare system dipole polarizability tensor. For a given frequency, range-separated self-consistent screening (rsSCS) of $A(i\omega)$ is then accomplished by solving the following matrix equation (see the ESI for the detailed derivation of Eq. (6.12)):

$$\overline{A} = A - AT_{\text{SR}} \overline{A}$$

$$\Rightarrow \overline{A} = \left[ A^{-1} + T_{\text{SR}} \right]^{-1}, \quad (6.12)$$

where $T_{\text{SR}}$ is the short-range dipole–dipole interaction tensor, defined below in Sec. 6.2.2.4 Eq. (6.36). The matrix $\overline{A}$ is the (dense) screened non-local polarizability matrix, sometimes called the relay matrix. ††

Partial internal contraction over atomic sub-blocks of $\overline{A}$ yields the screened and anisotropic atomic polarizability tensors (the corresponding molecular polarizability is obtained by total

---

**The dipole polarizability tensor $\alpha_a$ for a given atom or QHO is formed by populating the diagonal elements ($\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$) with the isotropic dipole polarizability in Eq. (6.8).

††At this point, it is very important to note a difference in the notation relative to Refs. 279 & 276: our matrix $\overline{A}$ is equivalent to their $B$ or $B$, which was keeping with Thole’s original notation for the relay matrix (Ref. 302).
6.2. Theory

internal contraction), i.e.,

\[
\overline{\alpha}_a(i\omega) = \sum_{b=1}^{N} \overline{\lambda}_{ab}(i\omega).
\]

(6.13)

The static “isotropized” screened polarizability scalars, \(\overline{\alpha}_a(0)\), that appear in the MBD Hamiltonian in Eq. (6.18) and Sec. 6.2.2.3 below are then calculated from \(\overline{\alpha}_a(0)\) via

\[
\overline{\alpha}_a(0) = \frac{1}{3} \text{Tr} \left[ \overline{\alpha}_a(0) \right]
\]

(6.14)

as described above in Eq. (6.2). Note that Eqs. (6.12-6.13) can be solved at any imaginary frequency, \(i\omega\), so we do not require the Padé approximant given in Eq. (6.4) to bootstrap from \(\overline{\alpha}_a(0)\) to \(\overline{\alpha}_a(i\omega)\). However, the relationship between \(\overline{\alpha}_a\) and \(\overline{C}_{6,aa}\), given in Eq. (6.16), is one that is derived from the Padé approximant for the bare polarizability \(\alpha(i\omega)\).

In the non-retarded regime, the Casimir-Polder integral relates the effective \(C_{6,ab}\) dispersion coefficient to the dipole polarizabilities of QHOs \(a\) and \(b\) via the following integral over imaginary frequencies:

\[
C_{6,ab} = \frac{3}{\pi} \int_0^{\infty} d\omega \ \alpha_a(i\omega) \alpha_b(i\omega).
\]

(6.15)

By solving Eqs. (6.12-6.13) on a grid of imaginary frequencies \(\{iy_p\}\), a set of screened effective \(C_6\) coefficients, \(\overline{C}_6\), can be determined by a Gauss-Legendre quadrature estimate of the integral in Eq. (6.15). The screened QHO characteristic excitation frequency, \(\overline{\omega}_a\), is then calculated as

\[
\overline{\omega}_a = \frac{4}{3} \frac{\overline{C}_{6,aa}}{[\overline{\alpha}_a(0)]^2} = \frac{4}{3} \sum_p g_p \left[ \frac{\overline{\alpha}_a(iy_p)}{\overline{\alpha}_a(0)} \right]^2,
\]

(6.16)

where \(g_p\) and \(y_p\) are the quadrature weights and abscissae, respectively. Scaling of the usual Gauss-Legendre abscissae from \([-1, 1]\) to the semi-infinite interval \([0, \infty)\) is discussed in the accompanying ESI.
6.2.2.3 THE MBD MODEL HAMILTONIAN.

The central concept in the MBD model is the Hamiltonian for a set of coupled QHOs that each fluctuate within an isotropic harmonic potential \( U(x_a) = \frac{1}{2}m_a\omega_a^2 x_a^2 \), and acquire instantaneous dipole moments, \( d_a = q_a x_a \), that are proportional to the displacement, \( x_a \), from the equilibrium position and charge, \( q_a \), on each oscillator. This Hamiltonian defines the so-called coupled fluctuating dipole model (CFDM)\(^\text{304}\) and is given by:

\[
\mathcal{H}_{\text{CFDM}} = -\sum_{a=1}^{N} \frac{1}{2} \nabla_x^2 x_a + \sum_{a=1}^{N} \frac{1}{2} m_a\omega_a^2 x_a^2 + \sum_{a>b} N d_a^\dagger T_{ab} d_b, \tag{6.17}
\]

where \( T_{ab} \) is the dipole–dipole interaction tensor that couples dipoles \( a \) and \( b \).

In the range-separated MBD model,\(^\text{280}\) \( T \) is replaced by a long-range screened interaction tensor, \( T_{LR} \) (as defined in Sec. 6.2.2.4 and Eq. (6.38) below), and the fluctuating point dipoles are replaced with the Gaussian charge densities of QHOs, with effective masses \( m_a = (\overline{\alpha}_a(0) \overline{\omega}_a)\) obtained from their respective static polarizabilities and excitation frequencies. The corresponding range-separated MBD model Hamiltonian is therefore:\(^\text{280}\)

\[
\mathcal{H}_{\text{MBD}} = -\sum_{a=1}^{N} \frac{1}{2} \nabla_{\mu_a}^2 \mu_a + \sum_{a=1}^{N} \frac{1}{2} \overline{\omega}_a^2 \mu_a^2 + \sum_{a>b} N \overline{\alpha}_a \overline{\omega}_b \sqrt{\overline{\alpha}_a(0) \overline{\alpha}_b(0)} \mu_a^\dagger T_{LR}^{ab} \mu_b, \tag{6.18}
\]

in which \( \mu_a = \sqrt{m_a} \xi_a \) is the mass-weighted dipole moment\(^\text{f}\) of QHO \( a \) that has been displaced by \( \xi_a \) from its equilibrium position. The first two terms in Eq. (6.18) represent the kinetic and potential energy of the individual QHOs, respectively, and the third term is the two-body coupling due to the long-range dipole–dipole interaction tensor, \( T_{LR}^{ab} \), defined below in Eq. (6.38).

\(^\text{f}\)Since each QHO is assigned a unit charge (\( e = 1 \)), the dipole moment \( \mu \) is thereby equivalent to the displacement vector \( \xi \).
By considering the single-particle potential energy and dipole–dipole interaction terms in Eq. (6.18), we can construct the $3N \times 3N$ MBD interaction matrix, which is comprised of $3 \times 3$ subblocks describing the coupling of each pair of QHOs $a$ and $b$:

$$C_{ab}^{MBD} = \delta_{ab} \omega_a^2 + (1 - \delta_{ab}) \omega_a \omega_b \sqrt{\sigma_a(0) \sigma_b(0)} T_{ab}^{LR},$$

(6.19)

where $\delta_{ab}$ is the Kronecker delta between atomic indices.

The eigenvalues $\{ \lambda_p \}$ obtained by diagonalizing $C_{ab}^{MBD}$ correspond to the interacting (or “dressed”) QHO modes, while $\omega_a$ correspond to the modes of the non-interacting reference system of screened oscillators. The MBD correlation energy is then evaluated via Eq. (6.3) as the zero-point energetic difference between the interacting and non-interacting modes.

For periodic systems, all instances of the dipole–dipole interaction tensor would be replaced by

$$T_{ab} \rightarrow T_{ab} + \sum_{b'} T_{ab'},$$

(6.20)

where the sum over $b'$ indicates a lattice sum over the periodic images of atom $b$. Since this is an additive modification of $T$, it will not qualitatively modify the expressions for the analytical nuclear derivatives of the MBD energy. Hence, the derivation of the nuclear forces presented herein (and the accompanying chemical applications) will focus on non-periodic (or isolated) systems. We note in passing that the current implementation of the MBD energy and nuclear forces in QUANTUM ESPRESSO (QE) is able to treat both periodic and non-periodic systems. In this regard, a forthcoming paper will describe the details of the implementation and discuss the subtleties required to make the computation of well-converged MBD nuclear forces efficient for periodic systems.
6.2.2.4 The range-separated dipole–dipole interaction.

Prior to range-separation, the $3 \times 3$ sub-block $T_{ab}$ of the dipole–dipole interaction tensor $T$, which describes the coupling between QHOS $a$ and $b$, is defined as:

$$T_{ab} = \nabla_{\mathcal{R}_a} \otimes \nabla_{\mathcal{R}_b} v_{ab},$$

(6.21)

where $v_{ab}$ is the frequency-dependent Coulomb interaction between two spherical Gaussian charge distributions. This frequency-dependent interaction arises due to the fact that the ground state of a QHO has a Gaussian charge density:

$$v_{ab}(\mathcal{R}_{ab}, i\omega) = \frac{\text{erf}[\zeta_{ab}(i\omega)]}{R_{ab}},$$

(6.22)

where $R_{ab} = \|\mathcal{R}_a - \mathcal{R}_b\|$, 

$$\zeta_{ab}(i\omega) \equiv \frac{R_{ab}}{\Sigma_{ab}(i\omega)}$$

(6.23)

and

$$\Sigma_{ab}(i\omega) = \sqrt{\sigma_a(i\omega)^2 + \sigma_b(i\omega)^2}$$

(6.24)

is the effective correlation length of the interaction potential defined by the widths of the QHO Gaussians (see Eq. (6.25), below). As such, the dependence of $T$ on both the frequency and (implicitly) on the nuclear coordinates originates from $\Sigma_{ab}(i\omega)$ (see also Eqs. (6.8)-(6.9)).

In terms of the bare dipole polarizability, the width of the QHO ground-state Gaussian charge
density is given by:

\[ \sigma_a(i\omega) = \left[ \frac{i}{3} \sqrt{\frac{2}{\pi}} \alpha_a(i\omega) \right]^{1/3} \]
\[ = \left[ \frac{i}{3} \sqrt{\frac{2}{\pi}} \chi_{a}(i\omega) \right]^{1/3} [V_a]^{1/3}, \quad (6.25) \]

where \( \alpha_a(i\omega) = \frac{1}{3} \text{Tr} [\alpha_a] \) is the “isotropized” bare dipole polarizability and Eq. (6.9) was used to make the effective volume dependence more explicit.

The Cartesian components of the dipole–dipole interaction tensor in Eq. (6.21) (with all QHO indices and frequency-dependence of \( \zeta \) suppressed) are given by:

\[ T_{ij}(i\omega) = \left[ \text{erf}[\zeta] - \frac{2\zeta}{\sqrt{\pi}} \exp \left[ -\zeta^2 \right] \right] T_{ij}^{\text{dip}} + \frac{4}{\sqrt{\pi}} \frac{R^i R^j}{R^3} \zeta^3 \exp \left[ -\zeta^2 \right], \quad (6.27) \]

where \( R^i = R_{ab} \cdot \hat{e}_i \) is the \( i^{th} \) Cartesian component of \( R_{ab} \), and \( T_{ij}^{\text{dip}} \) is the frequency-independent interaction between two point dipoles:

\[ T_{ij}^{\text{dip}} = -\frac{3R^i R^j + R^2 \delta_{ij}}{R^3}, \quad (6.28) \]

with \( \delta_{ij} \) indicating the Kronecker delta between Cartesian indices.

The range-separation of the dipole–dipole interaction tensor is accomplished by using a Fermi-type damping function:

\[ f(Z_{ab}) = \left[ 1 + \exp \left[ -Z_{ab} \right] \right]^{-1}, \quad (6.29) \]

which depends on \( Z_{ab} \), the ratio between \( R_{ab} \), the internuclear distance, and \( S_{ab} \), the scaled sum of
the effective vdW radii of atoms $a$ and $b$, $R_{vdW}^a$ and $R_{vdW}^b$:

\[
Z_{ab} = 6 \left[ \frac{R_{ab}}{S_{ab}} - 1 \right] 
\]

\[
S_{ab} = \beta \left[ R_{vdW}^a + R_{vdW}^b \right]. 
\]

Here, the range-separation parameter $\beta$ is fit once for a given exchange-correlation functional by minimizing the energy deviations with respect to highly accurate reference data.\(^{280}\) The short- and long-range components of the dipole–dipole interaction tensor in Eq. (6.27) are then separated according to:

\[
T_{SR} = [1 - f(Z)] T 
\]

and

\[
T_{LR} = f(Z)T. 
\]

However, at long-range, the frequency-dependence in $T$ dies off quickly, so when evaluating the MBD Hamiltonian we replace Eq. (6.33) with the approximation

\[
T_{LR} \approx f(Z)T_{dip} 
\]

which is equivalent to taking $\text{erf} [\zeta] \approx 1$ and $\exp [-\zeta^2] \approx 0$ in Eq. (6.27) and (6.33). This has the added benefit of improved computational efficiency since special functions such as the error function and exponential are relatively costly to compute. As shown in Fig. 6.6 in the ESI, these approximations are exact to within machine precision for $\zeta > 6$, and thus in practice by the time $f(Z)$ has obtained a substantial value, the frequency dependence in $T$ has vanished, thereby justifying Eq. (6.34).

The rsSCS procedure described in Sec. 6.2.2.2 adds a further subtlety in that it modifies the
effective vDW radii in the definition of the $S_{ab}$ and $Z_{ab}$ quantities above (see Refs. [273, 279] for a more detailed discussion of these definitions). For the short-range interaction tensor (i.e., the tensor used in the rsSCS procedure) the damping function utilizes effective vDW radii calculated at the Tkatchenko-Scheffler (TS) level [83].

\[ \mathcal{R}_{a}^{\text{vdW,TS}} \equiv \left( \frac{V_{a}}{V_{a}^{\text{free}}} \right)^{1/3} \mathcal{R}_{a}^{\text{vdW,free}} \]  

(6.35)

where $\mathcal{R}_{a}^{\text{vdW,free}}$ is the free-atom vDW radius defined in Ref. [83] using an electron density contour, not the Bondi [307] radius that corresponds to the “atom-in-a-molecule” analog of this quantity. To indicate that the TS-level effective vDW radii are being used, the argument of the damping function for the short-range interaction tensor, used in Eqs. (6.11, 6.12), will be denoted with $Z^{\text{TS}}$ (cf. Eqs. (6.35, 6.30, 6.31)):

\[ T_{SR} = \left[ 1 - f \left( Z^{\text{TS}} \right) \right] T. \]  

(6.36)

For the long-range dipole–dipole interaction tensor used in the MBD Hamiltonian in Eq. (6.18), the damping function utilizes the self-consistently screened effective vDW radii [273],

\[ \mathcal{R}_{a}^{\text{vdW}} \equiv \left( \frac{\bar{\alpha}_{a}(0)}{\alpha_{a}^{\text{free}}(0)} \right)^{1/3} \mathcal{R}_{a}^{\text{vdW,free}}, \]  

(6.37)

wherein the ratio $\bar{\alpha}(0)/\alpha^{\text{free}}(0)$ takes the place of $V/V^{\text{free}}$ thereby still exploiting the proportionality between polarizability and volume. [89, 279] To indicate that the screened effective vDW radii are being used, the argument of the damping function for the long-range interaction tensor will be denoted with $\mathcal{Z}$ (cf. Eqs. (6.37, 6.30, 6.31)):

\[ T_{LR} = f \left( \mathcal{Z} \right) T_{\text{dip}}. \]  

(6.38)
With the above definitions in hand, we are now ready to proceed with the derivation of the analytical derivatives of the MBD correlation energy with respect to the nuclear (or nuclear) position $\mathbf{R}_c$ of an arbitrary atom $c$. These MBD forces are added to the DFT-based forces. As mentioned above in Sec. 6.2.1, two distinct types of nuclear coordinate dependence will arise: explicit dependence through $\mathbf{R}_{ab} = \mathbf{R}_a - \mathbf{R}_b$ and implicit dependence through $V[\{\mathbf{R}\}]$ (as moving a neighboring atom $c$ will slightly alter the effective volume assigned to atom $a$). Future work will address the effects of the MBD contribution to the exchange-correlation potential when applied self-consistently, which will ultimately impact $\rho(\mathbf{r})$. Our current work neglects these effects, and computes MBD as an \textit{a posteriori} correction to DFT, \textit{i.e.}, non-self-consistently.

Having carefully separated out the implicit dependence on $V[\{\mathbf{R}\}]$ in the relevant quantities above, the derivation proceeds largely by brute force application of the chain and product rules. The derivative of the MBD correlation energy given in Eq. (6.3) is governed by:

$$\partial_c E_{\text{MBD}} = \frac{1}{2} \sum_{p=1}^{3N} \partial_c \sqrt{\lambda_p} - \frac{3}{2} \sum_{a=1}^{N} \partial_c \overline{\alpha}_a,$$

(6.39)

hence requiring derivatives of the screened excitation frequencies, $\overline{\alpha}_a$, as well as the eigenvalues, $\lambda_p$, of the $C^{\text{MBD}}$ matrix. Since $C^{\text{MBD}}$ is real and symmetric, it has $3N$ orthogonal eigenvectors. We therefore do not concern ourselves here with repeated eigenvalues (see the ESI for a more detailed
discussion) and take derivatives of \( \lambda_p \) as:

\[
\frac{\partial}{\partial c} \lambda_p = \frac{\partial \lambda_p}{2 \sqrt{\lambda_p}}
\]  

(6.40)

\[
\partial_c \lambda_p = \left[ \chi^T \partial_c C^{MBD} \chi \right]_{pp}
\]  

(6.41)

\[
\Rightarrow \sum_{p=1}^{N} \frac{\partial}{\partial c} \lambda_p = \frac{1}{2} \text{Tr} \left[ \Lambda^{-1/2} \chi^T \partial_c C^{MBD} \chi \right].
\]  

(6.42)

where \( \chi \) is the matrix of eigenvectors of \( C^{MBD} \) and \( \Lambda = \text{diag}[\lambda_p] \) is the diagonal matrix of eigenvalues. To evaluate this last line we require the derivative of the \( ab \) block of \( C^{MBD} \) (cf. Eq. (6.19)),

\[
\partial_c C^{MBD}_{ab} = 2 \delta_{ab} \overline{\omega}_a \partial_c \overline{\omega}_a + (1 - \delta_{ab}) \left[ \overline{\omega}_a \partial_c \overline{\omega}_b + \overline{\omega}_b \partial_c \overline{\omega}_a \right] \sqrt{\overline{\alpha}_a(0) / \overline{\alpha}_b(0)} T^{LR}_{ab}
\]  

(6.43)

\[
+ (1 - \delta_{ab}) \overline{\omega}_a \overline{\omega}_b \sqrt{\overline{\alpha}_a(0) / \overline{\alpha}_b(0)} \frac{\overline{\alpha}_a(0) \partial_c \overline{\alpha}_a(0) + \overline{\alpha}_b(0) \partial_c \overline{\alpha}_b(0)}{2 \sqrt{\overline{\alpha}_a(0) \overline{\alpha}_b(0)}} T^{LR}_{ab}
\]  

To proceed any further we now need the derivatives of \( \overline{\omega} \), \( \overline{\alpha} \), and \( T^{LR} \). From Eq. (6.16), we find that the derivative of the screened excitation frequency, \( \overline{\omega} \), requires us to evaluate derivatives of \( \overline{\alpha}(i \omega) \) (with \( \overline{\omega}(0) \) as a specific case) as follows:

\[
\partial_c \overline{\omega} = \frac{8}{\pi} \sum_{p=1}^{n} g_p \left[ \frac{\overline{\alpha}_a(i \omega_p) \partial_c \overline{\alpha}_a(i \omega_p)}{[\overline{\alpha}_a(0)]^2} - \frac{[\overline{\alpha}_a(i \omega_p)]^2 \partial_c \overline{\alpha}_a(0)}{[\overline{\alpha}_a(0)]^3} \right].
\]  

(6.44)

The derivative of the screened polarizability, \( \overline{\alpha} \), Eq. (6.14), is calculated from the “isotropized” partial contraction of \( \overline{\Lambda} \) (with the frequency dependence suppressed):

\[
\partial_c \overline{\alpha} = \frac{1}{3} \text{Tr} \left[ \sum_{b=1}^{N} \partial_c \overline{\alpha}_{ab} \right].
\]  

(6.45)
Using Eq. (6.12) and (6.36) and expanding the derivative of the inverse of a non-singular matrix, we have

\[ \partial_c \overline{A} = - \overline{A} \left[ -A^{-1} [\partial_c A] A^{-1} + \partial_c T_{SR} \right] \overline{A}. \]  

(6.46)

Using Eqs. (6.9) and (6.10), we compute \( \partial_c A \) as:

\[ \partial_c A = \bigoplus_{a=1}^{N} \text{diag} [\Gamma_a \partial_c V_a]. \]  

(6.47)

In Eq. (6.47) we have terminated the chain-rule with \( \partial_c V_a \), which has remaining *implicit* dependence on the nuclear coordinates. We regard \( \partial_c V_a \) as one of our three fundamental derivatives since the Hirshfeld partitioning is typically computed separately from the rest of the MBD algorithm. Discussion of how to compute \( \partial_c V_a \) may be found in the ESI.

In considering the derivatives of the dipole–dipole interaction tensors, we will encounter both implicit and explicit nuclear position dependence through \( \zeta_{ab} \), Eq. (6.23). The derivatives of \( T_{SR} \), Eq. (6.36), and \( T_{LR} \), Eq. (6.38), are fairly complicated, so it will help to consider first the damping function, \( f \), in isolation. Here,

\[ \partial_c f(R_{ab}) = \frac{\exp[-Z_{ab}]}{[1 + \exp(-Z_{ab})]^2} \partial_c Z_{ab}, \]  

(6.48)

\[ \partial_c Z_{ab} = 6 \frac{[\partial_c R_{ab} - R_{ab} \partial_c S_{ab}]}{S_{ab}^2 S_{ab}^2}, \]  

(6.49)

\[ \partial_c S_{ab} = \beta \left[ \partial_c R_{vdW}^a + \partial_c R_{vdW}^b \right], \]  

(6.50)

where \( \partial_c R_{ab} \) is calculated as

\[ \partial_c R_{ab} = \nabla_{R_{ab}} \|R_{ab}\| = (\delta_{ac} - \delta_{bc}) \frac{R_{ab}}{\|R_{ab}\|}, \]  

(6.51)

and the effective vdW radii have only implicit nuclear coordinate dependence. For the gradient of
6.2. Theory

\( T_{SR} \), Eq. (6.36), we require the derivative of the TS-level effective vdW radii, Eq. (6.35):

\[
\partial_c R_{\text{vdW},TS} = \frac{R_{\text{vdW}}^{\text{free}}}{[V_a^{\text{free}}]^{1/3}} \frac{\partial_c V_a}{3 [V_a]^{2/3}},
\]

while for the gradient of \( T_{LR} \), Eq. (6.38), we require the derivative of the screened effective vdW radii, Eq. (6.37):

\[
\partial_c R_{\text{vdW}} = \frac{R_{\text{vdW}}^{\text{free}}}{[\alpha_a^{\text{free}}(0)]^{1/3}} \frac{\partial_c \tau_a(0)}{3 [\tau_a(0)]^{2/3}},
\]

which was evaluated using Eqs. (6.45)-(6.47).

In the following we suppress the \( a, b, c \) QHO indices where possible so that the Cartesian indices \( i, j \) are highlighted. First we consider the derivative of \( T_{\text{dip}} \), Eq. (6.28), which is given by:

\[
\partial T_{\text{dip}}^{ij} = -3 \left[ \frac{\delta_{ij}}{R^4} \partial R + \frac{R^2 \partial R^i + R^2 \partial R^j}{R^5} - \frac{5R^2R^i}{R^5} \partial R^i \right],
\]

where \( \partial R^i \) is evaluated as:

\[
\partial_c R_{ab}^i = \nabla_{\mathcal{R}} ((\mathcal{R}_a - \mathcal{R}_b) \cdot \mathbf{\hat{e}_i}) = (\delta_{ac} - \delta_{bc}) \mathbf{\hat{e}_i},
\]

Since the long-range dipole–dipole interaction tensor is approximated with the frequency-independent \( T_{\text{dip}} \) (thereby eliminating \( \zeta \)), Eqs. (6.48)-(6.53) and (6.54) provide us with all of the quantities needed to evaluate \( \partial_c T_{LR} \) as:

\[
\partial_c T_{ab,LR}^{ij} = T_{ab,\text{dip}}^{ij} \partial_c f \left( Z_{ab} \right) + f \left( Z_{ab} \right) \partial_c T_{ab,\text{dip}}^{ij},
\]

The derivative of \( T_{SR} \) is more complex since \( T \) depends on \( \zeta \):

\[
\partial_c T_{ab,SR}^{ij} = -T_{ab}^{ij} \partial_c f \left( Z_{ab}^{TS} \right) + \left[ 1 - f \left( Z_{ab}^{TS} \right) \right] \partial_c T_{ab}^{ij},
\]
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in which the derivative of $T_{ij}$ is given below (see the ESI for a detailed derivation):

\[
\partial T_{ij} = -3 \left[ \text{erf} [\zeta] - \frac{h(\zeta)}{2\zeta} \right] \partial T_{ij}^{\text{dip}} \\
+ \zeta h(\zeta) \left[ -\frac{1}{3} \frac{\partial T_{ij}^{\text{dip}}}{\partial R} - \frac{\delta_{ij}}{R^4} \frac{\partial R}{\partial R} \right] \\
+ \left[ T_{ij}^{\text{dip}} + \frac{R^i R^j}{R^5} \left[ 3 - 2\zeta^2 \right] \right] h(\zeta) \partial \zeta,
\]  

(6.58)

wherein we have defined the following function for compactness,

\[
h(\zeta_{ab}) \equiv \frac{4 \zeta_{ab}^2}{\sqrt{\pi}} \exp \left[ -\zeta_{ab}^2 \right].
\]  

(6.59)

The derivative of $\zeta_{ab}$ is given by (with QHO indices restored to express $\partial_c \zeta_{ab}$ from Eq. (6.24)):

\[
\partial_c \zeta_{ab} = \frac{\zeta_{ab}}{R_{ab}} \partial_c R_{ab} - \frac{\zeta_{ab}^3}{R_{ab}^2} \left[ \sigma_a \partial_c \sigma_a + \sigma_b \partial_c \sigma_b \right].
\]  

(6.60)

where $\partial_c \sigma_a$ is computed from Eq. (6.26) as

\[
\partial_c \sigma_a = \left[ \frac{1}{3} \sqrt{\frac{2}{\pi}} \gamma_a \right]^{1/3} \frac{\partial V_a}{3 [V_a]^{2/3}}.
\]  

(6.61)

We have now reduced the analytical nuclear derivative of the MBD correlation energy to quantities that depend on three fundamental derivatives: $\partial_c R_{ab}$, $\partial_c R_{ab}^i$, and $\partial_c V_a$. The expressions for $\partial_c R_{ab}$ and $\partial_c R_{ab}^i$ have been given above in Eqs. (6.51) and (6.55), and are straightforward to implement. The computation of $\partial_c V_a$ is outlined briefly in the ESI.
6.3 Computational Details

We have implemented the MBD energy and analytical nuclear gradients (forces) in a development version of QUANTUM ESPRESSO v5.1 (QE). A forthcoming publication will discuss the details of this implementation, including the parallelization and algorithmic strategies required to make the method efficient for treating large-scale condensed-phase systems.

All calculations were performed with the Perdew, Burke, and Ernzerhof (PBE) exchange-correlation functional and Hamann-Schlueter-Chiang-Vanderbilt (HSCV) norm-conserving pseudopotentials. As a point of completeness, it should be noted that in QE the Hirshfeld partitioning has only been implemented for norm-conserving pseudopotentials, and thus the MBD method cannot presently be used with ultrasoft pseudopotentials or projector-augmented wave methods. To ensure a fair comparison with our implementation of the MBD model, all TS calculations were performed as a posteriori corrections to the solution of the non-linear Kohn-Sham equations, i.e. we turned off the self-consistent density updates from TS. Additional computational details, including detailed convergence tolerances and basis sets are given in Sec. 6.7.9 of the ESI. For comparison with the D3(BJ) dispersion correction of Grimme et al. (hereafter abbreviated as D3) we also optimized structures using ORCA v3.03. We used the atom-pairwise version of D3(BJ) since only numerical gradients were available for the three-body term.

6.4 Results and Discussion

To verify our implementation of the MBD energy in QE, we compared against the implementation of the MBD@rsSCS model in the FHI-AIMS code and find agreement to within $10^{-11}$ E$_h$. We next verified our implementation of the analytical gradients by computing numerical derivatives via the central difference formula and find agreement within the level of expected error.
given the finite spacing between the grid points describing $\rho(\mathbf{r})$ and error propagation of finite differences of the Hirshfeld effective volume derivatives.

To demonstrate the efficiency and accuracy of the analytical MBD nuclear gradient, we performed geometry optimizations on representative systems for intermolecular interactions (benzene dimer), intramolecular interactions (polypeptide secondary structure), and supramolecular interactions (buckyball catcher host-guest complex). We subsequently examined the importance of the implicit nuclear coordinate dependence that arises from the Hirshfeld effective volume gradient $\partial V$ in the computation of the MBD forces.

6.4.1 INTERMOLECULAR INTERACTIONS: STATIONARY POINTS ON THE BENZENE DIMER POTENTIAL ENERGY SURFACE.

As the prototypical example of the $\pi-\pi$ interaction, there have been a large number of theoretical studies on the benzene dimer using very high-level wavefunction theory methods. Since the intermolecular attraction between the benzene dimer arises primarily from a balance between dispersion interactions and quadrupole-quadrupole interactions (depending on the intermolecular binding motif), the interaction energy is quite small ($\sim 2 - 3$ kcal/mol) and the potential energy surface (PES) is very flat. Consequently, resolving the stationary points of this PES is quite challenging for both theory and experiment. The prediction of the interaction energy in the benzene dimer represents a stringent test of the ability of a given electronic structure theory method to capture and accurately describe non-bonded intermolecular interactions. Historically, three conformers of the dimer have received the most attention, namely the “sandwich,” “parallel-displaced,” and “T-shaped” structures. Using the high-level benchmark interaction energy calculations as a guide, several studies have used a variety of more approximate methods to examine the PES more broadly. By scanning the PES of the benzene dimer with DFT-based symmetry adapted perturbation theory (DFT-SAPT), Podeszwa et al. identified 10
stationary points, i.e., either minima (M) or saddle points (S) of the interaction energy (see Fig. 6.1). Most wavefunction studies of the benzene dimer PES have used a fixed monomer geometry, assuming that the weak interactions will produce very little relaxation of the rigid monomer. Using the highly accurate fixed benzene monomer geometry of Gauss and Stanton, Bludský et al. performed counterpoise-corrected geometry optimizations of these 10 configurations at the PBE/CCSD(T) level of theory, with an aug-cc-pVDZ basis set. The resulting geometries are among the largest molecular dimers to be optimized with a CCSD(T) correction to date and represent the most accurate available structures for the dimer of this classic aromatic system. As a first application of the MBD analytical nuclear gradients derived and

![Figure 6.1: Top: Graphical depictions of the 10 configurations that correspond to stationary points on the benzene dimer PES, following the nomenclature of Podeszwa et al. (Mn = minima; Sn = saddle points). Left: Change in inter-monomer distance, $R$, relative to the PBE/CCSD(T) reference for geometries optimized with PBE+vdW methods: MBD (shown in blue), TS (shown in yellow) and D3 (shown in green). PBE+MBD consistently predicts the correct inter-monomer distance. For the stacked configurations (M1, S4, S7, and S8) PBE+TS shortens the inter-monomer distance, while for T-shaped configurations (M2, S1, S2, S3, S5, and S6) the inter-monomer distance is elongated. For all configurations except the stacked S7 and S8 structures PBE+D3 predicts too long an inter-monomer distance. Right: Root-mean-square-deviations (RMSD) in Å between the PBE+vdW and PBE/CCSD(T) optimized geometries of these 10 benzene dimer configurations. The RMSD between the PBE+MBD and reference PBE/CCSD(T) geometries (shown in blue) are uniformly small and consistent across all minima and saddle points on the benzene dimer PES. For several Mn and Sn configurations, the PBE+D3 optimized geometries (shown in green) agree quite well with the PBE/CCSD(T) reference, while the PBE+TS optimized geometries (shown in yellow) have more significant deviations.

implemented in this work, we performed geometry optimizations on these 10 benzene dimer
configurations at the PBE+MBD, PBE+TS, and PBE+D3 levels of theory. All of the geometry optimizations performed herein minimized the force components on all atomic degrees of freedom according to the thresholds and convergence criteria specified in Sec. 6.7.9 of the ESI (i.e., frozen benzene monomers were not employed in these geometry optimizations). The root-mean-square-deviations (RMSD in Å) between the PBE+MBD, PBE+TS, and PBE+D3 optimized geometries with respect to the reference PBE/CCSD(T) results are depicted in Fig. 6.1.

From this figure, it is clear that the PBE+MBD method, with a mean RMSD value of 0.01 Å (and a vanishingly small standard deviation of $3 \times 10^{-4}$ Å) with respect to the reference PBE/CCSD(T) results, was able to provide uniformly accurate predictions for the geometries of all of the benzene dimer configurations considered. These findings are encouraging and consistent with the fact that the PBE+MBD method yields significantly improved binding energies for the benzene dimer as well as a more accurate quantitative description of the fractional anisotropy in the static dipole polarizability of the benzene monomer. This is also consistent with the finding of von Lilienfeld and Tkatchenko that the three-body ATM term contributes ~ 25% of the binding energy of the benzene dimer in the parallel displaced configuration.

With a mean RMSD value of $0.03 \pm 0.01$ Å and $0.05 \pm 0.02$ Å respectively, the PBE+D3 and PBE+TS methods both yielded a less quantitative measure of the benzene dimer geometries with respect to the reference PBE/CCSD(T) data. Of the 7 benzene dimer configurations for which the PBE+TS RMSD values were greater than 0.05 Å (namely M2, S1, S3, S4, S6, S7, and S8), it is difficult to identify a shared intermolecular binding motif among them. Interestingly, PBE+D3 seems to fare better on sandwiched geometries and it is only the T-shaped S4 and S6 which have RMSDs above 0.05 Å.

However, analysis of the inter-monomer distance (see Fig. 6.1) reveals that PBE+TS tends to shorten the inter-monomer distance $R$ for sandwich geometries (M1, S4, S7, and S8) by an average...
of 0.03 Å relative to the PBE/CCSD(T) results, while it elongates the inter-monomer distance by an average of 0.09 Å for T-shaped structures. The dispersive interaction between the stacked structures (S7 and S8) is stronger than that of the parallel displaced structures (M1 and S4), so PBE+TS shortens the inter-monomer distance more significantly for S7 and S8. Likewise, these are the only two structures for which PBE+D3 shortens the inter-monomer distance. For all other geometries PBE+D3 elongates the inter-monomer distance by an average of 0.06 Å. For both sandwich and T-shaped structures, PBE+MBD performs much more consistently, elongating the inter-monomer distance by a scant $5 \times 10^{-3}$ Å and $1 \times 10^{-3}$ Å for sandwich and T-shaped configurations, respectively.

We note that RMSD values in the range of 0.03–0.08 Å, and errors on the inter-monomer distances of 0.05-0.15 Å, in the geometries of small molecular dimers (as found here with the PBE+TS and PBE+D3 methods) are not unacceptably large in magnitude; however, these differences will become even more pronounced as the sizes and polarizabilities of the monomers continue to increase. In this regime, the MBD method—by accounting for both anisotropy and non-additivity in the polarizabilities as well as beyond-pairwise many-body contributions to the long-range correlation energy—is expected to yield accurate and consistent equilibrium geometries for such systems. As such, the combination of DFT+MBD has the potential to emerge as a computationally efficient and accurate electronic structure theory methodology for performing scans of high-dimensional PESs for molecular systems whose overall stability is primarily dictated by long-range intermolecular interactions.

### 6.4.2 Intramolecular Interactions: Secondary Structure of Polypeptides

As a second application, we considered the intramolecular interactions that are responsible for the secondary structure in small polypeptide conformations. In particular, we studied 76 conformers of 5 isolated polypeptide sequences (GFA, FGG, GGF, WG, and WGG), which are comprised of the
following four amino acids: glycine (G), alanine (A), phenylalanine (F), and tryptophan (W). This set of peptide building blocks includes the simplest amino acids, glycine and alanine (with hydrogen and methyl side chains, respectively), as well as the larger aromatic amino acids, phenylalanine and tryptophan (with benzyl and indole side chains, respectively). Although each of these polypeptides are relatively small (with 34-41 atoms each), a significant amount of conformational flexibility is present due to the non-trivial intramolecular binding motifs found in these systems, such as non-bonded side chain–backbone interactions and intramolecular hydrogen bonding. In fact, it is the presence of these interactions that leads to the formation of \( \alpha \)-helices and \( \beta \)-pleated sheets—the main signatures of secondary structure in large polypeptides and proteins.

Following a benchmark study by Valdes et al.\textsuperscript{338} in which the geometries of these 76 conformers were optimized using second-order Møller-Plesset perturbation theory (MP2)\textsuperscript{339} within the resolution-of-the-identity approximation (RI-MP2) and the fairly high-quality cc-pVTZ atomic orbital basis set,\textsuperscript{343} we performed geometry optimizations on this set of conformers with several vdW-inclusive DFT approaches, namely, PBE+D3, PBE+TS, and PBE+MBD. All of the geometry optimizations performed in this section minimized the force components on all atomic degrees of freedom according to the thresholds and convergence criteria specified in the ESI Sec. 6.7.9. Treating the MP2 geometries as our reference, Fig. 6.2 displays box-and-whisker plots of the distributions of root-mean-square deviations (in Å) obtained from geometry optimizations employing the aforementioned vdW-inclusive DFT methodologies.

Here we find that the PBE+MBD method again yields equilibrium geometries that are consistently in significantly closer agreement with the reference MP2 data than both the PBE+TS and PBE+D3 methodologies. For instance, the RMSDs between the PBE+MBD and MP2 conformers are smaller than 0.12 Å for all but one GGF conformer (34: GGF04), with an overall mean RMSD value of 0.07 ± 0.03 Å. In contrast to the intermolecular case of the benzene dimer,
the PBE+TS method performs significantly better than PBE+D3 on the same benchmark set of polypeptides, with overall mean RMSD values of 0.11 ± 0.07 Å and 0.20 ± 0.17 Å, respectively. In this regard, the whiskers in Fig. 6.2 extend to RMSD values that are within 1.5 times the interquartile range (i.e., following the original, although arbitrary, convention for determining outliers suggested by Tukey\textsuperscript{344}), which highlights the fact that there are several conformers for which both PBE+TS and PBE+D3 predict equilibrium geometries that are significantly different than MP2.

Although MP2 is the most economical wavefunction-based electronic structure method that can describe dispersion interactions, MP2 tends to grossly overestimate $C_6$ dispersion coefficients and hence the binding energies of dispersion-bound complexes such as the benzene dimer\textsuperscript{345}. Since PBE+MBD should bind less strongly than MP2, we expect the side-chain to backbone distance to elongate slightly for bent conformers. Conformers where the side chain is extended away from the backbone are expected to show less deviation between MP2 and PBE+MBD as the side-chain to backbone dispersion interaction will be less significant in determining the geometry of the conformer.

![Box-and-whisker plots showing the distribution of root-mean-square-deviations (RMSDs) in Å between 76 conformers of 5 isolated small peptides optimized with PBE+MBD (blue), PBE+TS (yellow) and PBE+D3 (green) compared against the MP2 reference geometries of Ref. \textsuperscript{338}. Whiskers extend to data within 1.5 times the interquartile range.\textsuperscript{344} Note the need for a broken axis to show the largest RMSDs of PBE+D3. PBE+MBD consistently outperforms both PBE+TS and PBE+D3 in terms of yielding optimized geometries closer to the MP2 reference. Median (maximum) values are: 0.06 (0.28) Å for PBE+MBD, 0.09 (0.52) Å for PBE+TS, and 0.14 (1.10) Å for PBE+D3.](image-url)
Aside from the noticeable outliers, the structural deviations in most of the conformers correspond to small rotations or deflection of terminal groups and side chains due to dispersion-based interactions, in contrast to the backbone which is constrained by non-rotatable bonds. In Fig. 6.3 we present representative overlays of this rearrangement, showing the MP2 (blue), PBE+MBD (red), and PBE+D3 (yellow) geometries. In a) structure 17 (GFA03) is a conformer for which both PBE+MBD and PBE+D3 give small/moderate RMSDs with MP2. Both PBE+MBD and PBE+D3 open the cleft between the alanine and phenylalanine, also causing the amine on the backbone to slightly rotate. The relative positioning of these structures is expected, given the tendency of MP2 to over-bind dispersion interactions and the tendency of PBE+D3 to under-bind. In b) structure 48 (WG03), again shows PBE+MBD agreeing well with MP2, but slightly opening the backbone-side chain distance. However, PBE+D3 is disastrous for this structure, yielding an RMSD of 1.10 Å due to large rotations in both the backbone and indole side-chain.

Structures where the side-chain lies farther off to the side of the backbone, such as 4 (FGG215) shown in panel d), show the smallest RMSDs between the PBE+MBD and reference MP2 geometries with the PBE+MBD geometry lying almost exactly on top of the MP2 geometry. However, FGG215 is again a structure where D3 does poorly with respect to the MP2 geometry, this time rotating the benzyl side-chain away from the terminal glycine, yielding an RMSD of 0.64 Å.

The structure for which the PBE+MBD method has the largest RMSD, at 0.28 Å, is 34 (GGF04), shown in panel c). As opposed to opening a cleft like in GFA03, PBE+MBD rotates the phenylalanine and alanine groups together. This rotation occurs because the terminal hydrogen on the glycine is attracted to the π-system on the phenylalanine. The rigid nature of the glycine combined with the rotatable bond in the phenylalanine, forces the phenylalanine to slightly rotate.
6.4. Results and Discussion

Figure 6.3: Overlays of the structures obtained from geometry optimization with MP2 (blue), PBE+MBD (red), and PBE+D3 (yellow). In both a) GFA03 and b) WG03, the MBD correction opens the cleft between the backbone and aromatic side-chain as MP2 tends to over-bind dispersion interactions. c) In GGF04, PBE+MBD rotates the phenylalanine and alanine groups together. d) In FGG215, since the side-chain is farther away from the backbone, PBE+MBD matches the MP2 geometry almost exactly.
in response. The motion of the middle glycine solely attempts to minimize molecular strain from these other two interactions. Both PBE+TS and PBE+D3 methods show a similar rotation for this structure, though PBE+D3 rotates the structure even farther than PBE+MBD. This concerted rotation is associated with a very flat potential energy surface, as indicated by the fact that a second optimization run with the same tolerances resulted in a slightly greater rotation.

Following Valdes et al., we classified the structures by the existence of an intramolecular hydrogen-bond between the –OH of the terminal carboxyl group and the C=O group of the preceding residue. The mean RMSD is strongly influenced by the high outliers, so the median RMSD is a more representative measure for comparing these two groups of conformers. The median RMSD for CO$_2$H$_{free}$ (CO$_2$H$_{bonded}$) structures is: 0.06 (0.07) Å for PBE+MBD, 0.09 (0.09) Å for PBE+TS, and 0.14 (0.14) Å for PBE+D3. Overall, we find that the presence of this intramolecular hydrogen bond does not strongly correlate with which structures deviate more from the MP2 geometries. This finding was somewhat unexpected since Valdes et al. asserted that dispersion interactions are more important in determining the structure of the CO$_2$H$_{free}$ family of conformers due to tendency of the peptide backbone to lie over the aromatic side chain.

Overall, we find excellent agreement between the MP2 and PBE+MBD geometries. Where PBE+MBD deviates, we find agreement with physical and chemical intuition when we take into account the well known over-binding for dispersion interactions present in MP2. The agreement between PBE+MBD and MP2 geometries is in marked contrast to the inconsistent performance of PBE+D3 and PBE+TS, which both yielded numerous outliers. Although computational cost is not directly comparable between a Gaussian-type-orbital code and a planewave code, we are greatly encouraged by the accuracy of our PBE+MBD geometry optimizations since such calculations with a generalized gradient approximation functional like PBE are substantially cheaper than with RI-MP2.
6.4.3 **Supramolecular Interactions: The Buckyball Catcher Host–Guest Complex.**

Noncovalent interactions are particularly important in supramolecular chemistry, where non-bonded interactions, including dispersion, stabilize molecular assemblies. The large size of supramolecular host-guest complexes typically places them outside the reach of high-level quantum chemical methodologies and necessitates the use of DFT for geometry optimizations and energy computations. However, the large polarizable surfaces that interact in these systems requires a many-body treatment of dispersion to achieve a chemically accurate description of supramolecular binding energies. The C$_{60}$ “buckyball catcher” host–guest complex (also referred to as C$_{60}$@C$_{60}$H$_{28}$) in particular has received considerable attention as a benchmark supramolecular system in the hope that it is prototypical of dispersion-driven supramolecular systems, and it has been studied extensively both experimentally and theoretically. The C$_{60}$ buckyball catcher (denoted as 4a by Grimme) is one of the most well studied members of the S12L test set of noncovalently bound supramolecular complexes.

Much of the past computational work has focused on modeling the interaction energy of the C$_{60}$ buckyball catcher and comparing these results to the experimental data on thermodynamic association constants that have been extracted from titration experiments. This complex is a challenging system for most dispersion correction methods since the three-body term contributes approximately 10% of the interaction energy. Motivated by this large contribution of beyond-pairwise dispersion, we optimized the C$_{60}$@C$_{60}$H$_{28}$ complex with PBE+MBD, PBE+TS and PBE+D3 to see how significantly many-body effects impact the geometry. Containing 148 atoms, this system also represents a structure that would be too large to optimize with numerical MBD gradients or high-level wavefunction based methodologies. All theoretical calculations
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Table 6.1: Selected distances of DFT gas-phase optimized geometries of the C_{60}@C_{60}H_{28} host–guest complex and conformer a of the host alone compared to X-ray crystal structures of C_{60}@C_{60}H_{28}·2PhMe \textsuperscript{169} and the unsolvated buckyball catcher \textsuperscript{169}. The TPSS functional does not identify conformer a, so these entries are left blank.

<table>
<thead>
<tr>
<th>Method</th>
<th>Complex R_c (Å)</th>
<th>Complex R_p (Å)</th>
<th>Complex R_t (Å)</th>
<th>Host a R_p (Å)</th>
<th>Host a R_t (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE+MBD</td>
<td>8.312</td>
<td>12.992</td>
<td>6.303</td>
<td>13.263</td>
<td>6.394</td>
</tr>
<tr>
<td>TPSS+D3</td>
<td>8.392</td>
<td>12.748</td>
<td>6.288</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>TPSS+D3\textsuperscript{a}</td>
<td>8.361</td>
<td>12.822</td>
<td>6.303</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>B97-D\textsuperscript{b}</td>
<td>8.335</td>
<td>12.798</td>
<td>6.299</td>
<td>11.152</td>
<td>6.216</td>
</tr>
<tr>
<td>M06-2L\textsuperscript{c}</td>
<td>8.136</td>
<td>12.703</td>
<td>6.382</td>
<td>11.844</td>
<td>6.322</td>
</tr>
<tr>
<td>X-ray\textsuperscript{d,e}</td>
<td>8.484(3)</td>
<td>12.811(4)</td>
<td>6.418(5)</td>
<td>9.055(2)</td>
<td>6.44(3)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Ref. [354], \textsuperscript{b} Ref. [348], \textsuperscript{c} Ref. [351], \textsuperscript{d} Ref. [347], \textsuperscript{e} Ref. [350]

reported herein are for an isolated, i.e. gas-phase, host-guest complex at the classical equilibrium geometry at zero temperature, while the experimental values listed in Table 6.1 correspond to X-ray determined crystal structures measured at finite temperature. Since the base of the buckyball catcher host is quite flexible,\textsuperscript{348} we expect the packing environment in the solid state to potentially impact the reported conformation.

The buckyball catcher host is made of a tetrabenzocyclooctatetraene (TBCOT) tether and two corannulene pincers (cf. Fig. 6.10 in the ESI and Fig. 6.4 herein). The conformation of the catcher is determined by a competition between the attractive dispersion interactions between the corannulene pincers and the strain induced by deformation of the TBCOT tether.\textsuperscript{338} The two lowest energy “open” conformers of the catcher have the corannulene bowls in a convex–convex “catching” motif or in a convex–concave “waterwheel” motif; following the notation of Refs. \textsuperscript{347,348,352} we term the “catching” motif a and the “waterwheel” motif b.

To compare the size of the cleft between the corannulene pincers when the buckyball catcher is optimized with various DFT+vdW methods, we report the distance between the most separated carbon atoms of the central five-membered rings of both corannulene subunits as a measure of the
size of the cleft; we denote this distance as $R_p$ (cf. Fig. 6.4). Closing of the cleft tends to be accompanied by outward deflection of the TBCOT tether, so we also measure the distance between terminal carbons on the tether; we denote this distance as $R_t$ (cf. Fig. 6.4). Likewise, we measure the distance between the centroid of the $C_{60}$ and the plane that bisects the TBCOT tether at the base of the buckyball catcher (cf. Fig. 6.4); we denote this distance as $R_c$. Interestingly, several of the functionals that have been used to study the buckyball catcher do not identify all four conformers. Notably, TPSS-D3 is prone to drive conformer a to a closed variant that has $R_p = 5.53$ Å. With regard to the balance between dispersion and strain, conformer a results when the $C_{60}$ is removed from the pincers and the host is allowed to relax. We will focus our discussion on the relaxed conformer a and the optimized complex, but we also provide optimized structures of conformer b in the ESI.

Upon optimization with PBE+MBD we find that the corannulene pincers deflect outward, as seen by the increased $R_p$ distance relative to the starting TPSS+D3/def2TZVP geometry from the S12L dataset. The $R_p$ distance predicted by PBE+MBD is larger than other results from vdW-inclusive functionals (see Table 6.1), which may be consistent with previous reports of three-body and higher order terms substantially decreasing the binding energy of the $C_{60}@C_{60}H_{28}$ host–guest complex. However, this deflection is accompanied by a reduction of the buckyball–catcher distance $R_c$, which would suggest a tighter binding. Just as with the reduced cleft distances in the peptides and the inter-monomer distance in the benzene dimer, we find that the host–guest distance predicted by PBE+MBD ($R_c = 8.31$ Å) is smaller than that predicted by PBE+D3 ($R_c = 8.45$ Å) and PBE+TS ($R_c = 8.36$ Å). For comparison, we also optimized the complex with TPSS+D3/def2TZVP and found a buckyball–catcher distance of $R_c = 8.39$ Å, which is slightly larger than the $R_c = 8.36$ Å in the previously reported TPSS+D3/def2TZVP geometry in the S12L dataset. These results are reported in Table 6.1 together with a comparison to previous
Figure 6.4: Overlay between the geometry of the C\(_{60}\)@C\(_{60}\)H\(_{28}\) host–guest complex optimized with PBE+D3 (red) and PBE+MBD (blue). The distance, \(R_c\), between the C\(_{60}\) centroid and the plane bisecting the tetrabenzozycclooctatetraene (TBCOT) tether (transparent green) is reduced from 8.45 Å with PBE+D3 to 8.31 Å with PBE+MBD. The green arrow shows that the \(R_t\) distance is measured between terminal carbon atoms on the TBCOT tether. The yellow arrow shows that the \(R_p\) distance is measured between the most separated carbon atoms of the central five-membered rings of both corannulene subunits. \textbf{Inset:} The 2D molecular structure of the C\(_{60}\)H\(_{28}\) buckyball catcher host, with corannulene subunits shown in blue and the TBCOT tether shown in red. Atoms used to define the \(R_t\) and \(R_p\) distances are marked in green and yellow respectively. The black dot shows the centroid of the four atoms on the TBCOT tether used to define the \(R_c\) distance.
vdW-inclusive DFT results and the corresponding distances from the X-ray determined crystal structures.

The X-ray structure for the complex is taken from $\text{C}_{60}@\text{C}_{60}\text{H}_{28}$ co-crystallized with two disordered toluene molecules, *i.e.* $\text{C}_{60}@\text{C}_{60}\text{H}_{28}\cdot 2\text{PhMe}$.[347] In the solid state, the fullerenes form columns along the $a$-axis, while the buckyball catcher aligns back-to-back in the $bc$-plane. These back-to-back interactions have fewer atoms that are in van der Waals contact, but could still push the corannulene units together slightly. Zabula *et al.* recently obtained an X-ray crystal structure of the unsolvated buckyball catcher which adopts an inter-locked structure similar to conformer *a*.[350] This inter-locked structure provides an attractive vdW interaction between corannulene units, which causes the cleft to close ($R_p = 9.055(2)$ Å), with a corresponding outward deflection of the TBCOT tether ($R_t = 6.44(3)$ Å).

Perhaps the most unusual trend in Table 6.1 is the substantial opening of the cleft between the corannulene subunits, and the accompanying outward deflection of the TBCOT tether, when the isolated host is optimized with the PBE+MBD method. Comparing the $R_p$ and $R_t$ distances, we find an ordering of PBE+MBD > PBE+TS > PBE+D3. Mück-Lichtenfeld *et al.* previously found that the TBCOT tether is quite flexible, resulting in a shallow bending potential (see Fig. 2 of Ref. 348) as the $R_p$ distance is varied; using the B97-D functional and 6-31G* basis set, the energy of conformer *b* varies by only $\sim 1.3$ kcal/mol as $R_p$ is scanned from 10-14 Å.[348] Comparing the energy of the buckyball catcher in the strained conformer that it adopts when hosting the buckyball, to its energy when fully relaxed, we see that at the PBE+D3/def2TZVP level this strain energy is 1.02 kcal/mol. This is consistent with the shallow bending potential found by Mück-Lichtenfeld *et al.* Given how flat this PES is, it is less surprising that the three vdW corrections considered give such different relaxed $R_p$ distances for the isolated host.

The structure of the $\text{C}_{60}$ buckyball does not vary significantly between different vdW-inclusive
functionals. The PBE+MBD optimized structure of \( C_{60} \) has C-C bond lengths of 1.45192(5) \( \text{\AA} \) for bonds within five-membered rings (fusing pentagons and hexagons), and 1.39804(3) \( \text{\AA} \) for bonds fusing hexagonal rings; which compares favorably to the well known gas-phase electron diffraction results of 1.458(6) \( \text{\AA} \) and 1.401(10) \( \text{\AA} \). This result is consistent with the short-range behavior of the range-separated PBE+MBD method, which essentially reduces to the bare PBE functional and does a good job of predicting C-C bond lengths.

On the whole we find that the PBE+MBD method yields structures that are comparable to other vdW-inclusive functionals but deviates more significantly from the X-ray determined crystal structure than the PBE+D3 results. Since we do not have an experimentally determined gas-phase structure or a wavefunction theory reference for the \( C_{60} @ C_{60} H_{28} \) host–guest complex, the deviation of the gas-phase PBE+MBD optimization from the experimental crystal structure should not be taken as a benchmark comparison. Future work will address the optimization of this full crystal structure.

In light of the lack of high-level wavefunction-based geometries to compare against, we conclude with a few comments about the computational efficiency of our method. Starting from the TPSS/def2TZVP structures from the S12L dataset, we were able to optimize the 148-atom complex with the PBE+MBD method in 68 BFGS steps in about 415 cpu hours, while the PBE+D3 optimization in ORCA took 34 BFGS steps in about 450 cpu hours. Given that ORCA uses redundant internal coordinates for geometry optimizations and the D3 correction is almost instantaneous to calculate, it is worth noting that the Cartesian coordinates optimization in QE with the much more costly MBD correction is roughly competitive.

\[143\]

\[143\]The PBE+MBD optimization was run in about 2.75 hours on 170 Intel Xeon E5-2680 processors while the PBE+D3 optimization was run in about 14 hours on 32 AMD Opteron 6376 Abu Dhabi processors.
6.4. Results and Discussion

6.4.4 The Importance of $\partial V$.

Our derivation of the nuclear MBD forces placed considerable emphasis on the importance of including the implicit coordinate dependence arising from the gradients of the Hirshfeld effective atomic volumes. To test how large of a contribution that the $\partial V$ terms make to the MBD forces, we re-optimized the benzene dimers, this time setting $\partial V = 0$ explicitly. As shown in Fig. 6.7 in the ESI, neglect of the Hirshfeld volume gradients does not have a large impact for this system, in which the dispersion forces are intermolecular; the mean RMSD becomes $(16 \pm 5) \times 10^{-4}$ Å. This result is expected for this system because the Hirshfeld effective atomic volumes only change when nearest neighbor atoms are moved. Not only is the benzene monomer fairly rigid, but the range separation employed in MBD means that the long-range tensor $T_{LR}$, and correspondingly the MBD correction, is largely turned off within the benzene monomer (see Fig. 6.6 in the ESI).

![Figure 6.5: Left: Gaussian kernel density estimate of the distributions of the norm $\| \cdot \|$ of MBD forces $F_{MBD}$ acting on each atom at the optimized geometries of 76 tripeptide structures. In blue, the MBD forces were computed with full Hirshfeld gradients ($\| F \|$); in yellow, the forces were computed with the Hirshfeld gradients $\partial V$ set to zero ($\| F_{\partial V=0} \|$). Right: Gaussian kernel density estimate of the distribution of relative percentage error $\| \Delta F \|/\| F \|$ where $\Delta F \equiv F - F_{\partial V=0}$ is the error incurred by setting the Hirshfeld gradients to zero. The distribution is peaked at approximately 20% but extends to values much greater than 100%.

We expect a larger impact from Hirshfeld volume gradients for systems that are flexible and large enough for the damping function to have “turned on” the MBD correction. The case of polypeptide intramolecular dispersion interactions matches both of these criteria. We computed the MBD forces on the final optimized geometries of all 76 peptide structures and analyzed the atom...
by atom difference in the forces computed with and without the Hirshfeld volume gradients. As shown in Figure 6.5, neglect of the Hirshfeld gradient causes a significant shift in the distribution of the MBD forces in the peptides, with a tendency to increase the forces from the lower peak from $\sim 2 \times 10^{-4} \text{Eh/a.u.}$ to $\sim 4 \times 10^{-4} \text{Eh/a.u.}$. Comparing the Cartesian components of the MBD forces across all atoms in all 76 structures we find that the deviations between MBD forces with and without the Hirshfeld volume gradients $(\mathbf{F} - \mathbf{F}_{\partial V=0})$ are approximately normally distributed with zero mean and a standard deviation of $2 \times 10^{-4} \text{Eh/a.u.}$ (see Fig. 6.8 in the ESI). This leads to the norm of the force difference $(\Delta \|\mathbf{F} - \mathbf{F}_{\partial V}\|)$ having a mean of $(3.2 \pm 1.7) \times 10^{-4} \text{Eh/a.u.}$, and a mean of the difference of norms of $\|\mathbf{F}\| - \|\mathbf{F}_{\partial V=0}\| = (-5 \pm 17) \times 10^{-5} \text{Eh/a.u.}$ Overall, neglect of the Hirshfeld gradients increases forces and causes a long-tailed distribution of relative error, that is peaked at $\sim 20\%$, but extends up to $400\%$. This large distribution of relative errors has the potential to significantly impact the deterministic nature of ab initio molecular dynamics (AIMD) simulations run at the MBD level of theory that do not properly account for the analytical gradients of the Hirshfeld effective volumes. Given that this error would accumulate at every time step, combined with the fact that the MBD correction was found to be quite important in the geometry optimizations of the systems considered herein, we find the neglect of the Hirshfeld effective volume gradients to be an unacceptable approximation in AIMD. This finding is particularly true for large flexible molecular systems with significant intramolecular dispersion interactions since this error can cooperatively increase along any extended direction, i.e., along an alkane chain or polypeptide backbone.

6.5 CONCLUSIONS AND FUTURE RESEARCH

By developing analytical energy gradients of the range-separated MBD energy with respect to nuclear coordinates, we have enabled the first applications of MBD to full nuclear relaxations. By
treated the gradients of the MBD energy correction analytically, rather than numerically, we have reduced the number of self-consistent calculations that must be performed from $2 \times (3N - 6)$ to 1, enabling treatment of much larger systems. Our derivation and implementation includes all implicit coordinate dependencies arising from the Hirshfeld charge density partitioning. In the isolated molecule optimizations that we considered herein, the implicit coordinate dependencies that arise from the Hirshfeld volume gradients resulted in significant changes to the MBD forces. The long-tailed distribution of relative error that we observed indicates that any future AIMD simulations employing MBD forces must include full treatment of the Hirshfeld volume gradients, or the accumulation of error will negatively impact the simulation dynamics. Our careful treatment of these volume gradients paves the wave for future work to address how a self-consistent implementation of the MBD model will impact the electronic band structures of layered materials and intermolecular charge transfer couplings in molecular crystals. A fully self-consistent treatment of MBD will likely be required for energy conservation in AIMD simulations.

Consistent with previous findings that a many-body description of dispersion improves the binding energies of even small molecular dimers, we find that MBD forces significantly improve the structures of isolated dispersively bound molecular systems displaying both intermolecular and intramolecular interactions. We find excellent agreement between PBE+MBD optimized structures and reference PBE/CCSD(T) and MP2 geometries. Notably, PBE+MBD consistently outperformed the pairwise PBE+D3(BJ), and effectively pairwise PBE+TS optimizations.

The first applications of MBD forces in this paper were restricted to gas-phase systems because computation of MBD gradients in the condensed phase, where periodic images of the unit cell must be considered, is substantially more challenging from a computational perspective. Converging the MBD energy in the condensed phase is demanding (from both the memory and computational point of view) due to a real-space supercell procedure that is required to support
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long-wavelength normal modes of $\mathbf{C}^{MBD}$. A forthcoming publication will describe the details of our implementation of MBD forces for periodic systems, including careful treatment of parallelization and convergence criteria.
6.6. Acknowledgments

Since MBD forces are very efficient to evaluate for gas-phase molecules, we are eager to explore the application of MBD to AIMD simulations. Many-body effects have previously been shown to be significant in modeling solvation and aggregation in solution and can lead to soft collective fluctuations that impact hydrophobic association and the entropic stabilization of hydrogen-bonded molecular crystals. We therefore anticipate that our many-body forces will be of interest for solvated simulations, such as estimates of the thermodynamic properties of metabolites and modeling novel electrolytes.

6.6 Acknowledgments

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6.7 Supplementary Information

6.7.1 Length Scale of Damping

Figure 6.6: Left: Contours at $10^{-6}$ for damping functions $\exp[-\zeta^2]$ (purple) and $(1 - f[Z])$ (orange), with $||R||$ relative to the atom marked in red. Damping parameters $\Sigma \approx 1.03$ and $S \approx 2.96$ (cf. Eqs. (6.24) and (6.31)) were computed for a graphene nanoflake with the PBE functional. Right: Comparison of the three damping functions with the same $10^{-6}$ contour indicated. The rapid decay of $\exp[-\zeta^2]$ relative to the Fermi damping function demonstrates that the short-range dipole-dipole interaction tensor $T_{SR}$ reduces to the frequency-independent $T_{df}$ well before the long-range tensor $\tilde{T}_{LR}$ has been fully “turned on” by the Fermi damping function (cf. Eqs. (6.27, 6.28, 6.36, 6.38)).
Computational methods and results for the interaction energies of CHF₃/CF₃Cl complexes were previously developed in Quantum ESPRESSO (QE) by R. A. DiStasio Jr. A subroutine of the TSVDW module computes the Hirshfeld partitioning into effective atomic volumes, \( V_a \), and the derivatives of that volume, \( \partial V_a \). The Hirshfeld effective charge density of atom \( a \) is:

\[
\rho_{\text{eff}}^a(r) = w_a(r) \rho(r) = \frac{\rho_{\text{free}}^a(||r-R_a||)}{\rho_{\text{sad}}(r)} \rho(r),
\]

(6.62)

where \( \rho(r) \) is the total molecular charge density and \( \rho_{\text{sad}}(r) = \sum_b \rho_{\text{free}}^b(||r-R_b||) \) is the sum of free-atom densities. The effective volume is then:

\[
V_a = \int dr \frac{\rho_{\text{free}}^a(r)}{||r-R_a||^3} \rho_{\text{eff}}^a(r).
\]

(6.63)

Integrations on spherical atomic domains, such as in Eq. (6.63), are computed on subsets of the real-space mesh. Using reference data for the free atom volumes, the radial grid cutoff value is determined for each species such that the free atom volume obtained by numerical integration up to this cutoff does not deviate from the reference value by more than 1.0%. The effective volume derivative is evaluated as

\[
\partial_c V_a = \frac{\rho_{\text{free}}^c(||r-R_c||) \rho(r)}{\rho_{\text{sad}}(r)} - \frac{\rho(r)}{\rho_{\text{sad}}(r)} \delta_{ca}\int dr \frac{\rho_{\text{free}}^c(||r-R_c||)}{||r-R_c||} \partial_c \rho_{\text{free}}^c(r).
\]

(6.64)

\[
\partial_c \rho_{\text{eff}}^a(r) = \frac{\rho_{\text{free}}^c(||r-R_c||)}{\rho_{\text{sad}}(r)} \rho(r) - \frac{\rho(r)}{\rho_{\text{sad}}(r)} \delta_{ca}\int dr \frac{\rho_{\text{free}}^c(||r-R_c||)}{||r-R_c||} \frac{\partial_c \rho_{\text{free}}^c(r)}{dr}.
\]

(6.65)

Note that the free-atom density is spherically symmetric, which is why we reduce \( \partial_c \rho_{\text{free}}^c(||r-R_c||) \) to a spherical coordinate derivative \( \partial_c \rho_{\text{free}}^c/\partial r \). Likewise, Eq. (6.63) is evaluated
by mapping the radial form of $\rho_{a}^{\text{eff}}$ to a linear/equispaced grid, which is then interpolated using cubic splines. After interpolation, the derivative $\partial_{r}\rho_{a}^{\text{eff}}$ at each grid point is evaluated by numerical differentiation using Bickley’s 7-point formula.\[363\]

### 6.7.3 Repeated Eigenvalues of $C^{\text{MBD}}$

In considering the derivative of $\lambda_{p}$, in Eq. (6.42) we assumed that $C^{\text{MBD}}$ had $3N$ distinct eigenvalues. Due to numerical perturbations it is somewhat unlikely for $C^{\text{MBD}}$ to have repeated eigenvalues, but we cannot assume this $a$ priori. The procedure for taking derivatives of repeated eigenvalues of a real, symmetric matrix, like $C^{\text{MBD}}$, is essentially first order perturbation theory where the perturbation is the action of the derivative operator $\partial_{c}$. Eigenvalue degeneracies are lifted by diagonalizing the perturbation in the degenerate subspace. See Friswell\[364\] or Andrew $et$ $al.$\[365\] for a more algorithmic discussion of repeated eigenvalue derivatives. Since $C^{\text{MBD}}$ is real and symmetric, it is guaranteed to be diagonalizable with orthogonal eigenvectors.

### 6.7.4 Importance of $\partial V$

#### 6.7.4.1 Benzene Dimer

To analyze the importance of $\partial V$, we re-optimized the benzene dimer structures with $\partial V$ terms set explicitly to zero. As shown in Fig. 6.7, setting $\partial V = 0$ slightly degrades the consistency of the PBE+MBD optimized geometries, but the final RMSDs are still quite good (all $< 0.025$ Å). The optimization of M1 with $\partial V = 0$ proved numerically unstable, and was unable to converge, so M1 is not included in the figure. The fact that the Hirshfeld gradients have a negligible impact on the benzene dimer optimizations is expected since the Hirshfeld effective atomic volumes only change when nearest neighbor atoms are moved. In addition to being quite rigid, the benzene monomer is small enough that the range-separated MBD correction is largely turned off within the length scale.
of the monomer, which is where the Hirshfeld gradients could matter.

![Figure 6.7](image-url)

**Figure 6.7**: Root-mean-square-deviations (RMSD) in Å between the PBE+MBD and PBE/CCSD(T) optimized geometries of 9 benzene dimer configurations using the full MBD gradient (shown in blue), and the approximation where $\partial V$ contributions are set explicitly to zero (shown in grey).

### 6.7.4.2 Polypeptides

We also performed single-point calculations on the optimized geometries of all 76 polypeptide structures to compare the MBD forces computed with and without the $\partial V$ contributions. The peptide structures are much more flexible than the benzene monomer and also have the opportunity for cooperative addition of the Hirshfeld volume gradients along the chain, *i.e.* the local Hirshfeld volume gradients acting at the nearest neighbor level can propagate along the peptide chain and result in a larger change. In Fig. 6.8, we visualize the deviation between the forces computed with full Hirshfeld volume gradients and those computed with $\partial V = 0$ in several ways: difference of individual force components $\Delta F_i = F_i - F_i, \partial V = 0$, norm of the difference of forces $\|F - F, \partial V = 0\|$, relative percentage error $\|\Delta F\|/\|F\|$, and distributions of the norms of forces $\|F\|$ vs. $\|F, \partial V = 0\|$.
Figure 6.8: Gaussian kernel density estimates of the distributions of MBD forces acting on each atom at the optimized geometries of 76 polypeptide structures. a)-c.) Difference of the force components $\Delta F_i = F_i - F_{i,\partial V=0}$, with a normal distribution $\mathcal{N}(0,0.2)$ and dotted line indicating zero mean superposed for reference. d.) Norm of the difference of forces, $\|\Delta F\| = \|F - F_{\partial V=0}\|$, with the dotted line indicating that the peak occurs at $\sim 0.3 \times 10^{-3}$ Eh/a.u.
Figure 6.9: Left: Gaussian kernel density estimate of the distributions of the norm \(|\cdot|\) of TS forces \(\mathbf{F}_{TS}\) acting on each atom at the optimized geometries of 76 polypeptide structures. In blue, the TS forces were computed with full Hirshfeld gradients (\(\mathbf{F}\)); in yellow, the forces were computed with the Hirshfeld gradients \(\partial V\) set to zero (\(\mathbf{F}_{\partial V=0}\)). Right: Gaussian kernel density estimate of the distribution of relative percentage error \(|\Delta \mathbf{F}|/|\mathbf{F}|\) where \(\Delta \mathbf{F} \equiv \mathbf{F} - \mathbf{F}_{\partial V=0}\) is the error incurred by setting the Hirshfeld gradients to zero. The distribution is peaked at approximately 32% but extends to values near 100%.
6.7.5 **Structure of the C\textsubscript{60}@C\textsubscript{60}H\textsubscript{28} Buckyball Catcher Host–Guest Complex**

In Fig. 6.10 the 2D molecular structure of the buckyball catcher host and the 3D structure of the C\textsubscript{60}@C\textsubscript{60}H\textsubscript{28} host–guest complex with the three distances R\textsubscript{c}, R\textsubscript{p}, and R\textsubscript{t} are highlighted. For each DFT-vdW optimized structure of the host, we report the R\textsubscript{p} and R\textsubscript{t} distances. All geometry optimizations of the C\textsubscript{60}@C\textsubscript{60}H\textsubscript{28} buckyball catcher host–guest complex started from the TPSS+D3/def2-TZVP structures in the S12L set.\textsuperscript{354} We optimized the complex, guest C\textsubscript{60}, and conformers a and b of the host. Structures of the complex, guest C\textsubscript{60}, and host optimized with other functionals and vdW correction schemes can be found in the supplemental information of the following references: Ref. \textsuperscript{354}: TPSS+D3/def2-TZVP, Ref. \textsuperscript{348}: B97-D/TZVP, Ref. \textsuperscript{351}: M06-2L/MIDI!.

**Figure 6.10:** **Left:** 2D structure of the ‘buckyball catcher’ C\textsubscript{60}H\textsubscript{28}. The central tetrabenzo["c,g]cyclooctatetraene (TBCOT) tether (red) links the two corannulene bowls (blue). The orange circles mark the four atoms used to define the R\textsubscript{t} distance between the back ends of the TBCOT tether. The green circles mark the four atoms used to define the plane from which the distance to the C\textsubscript{60} centroid, R\textsubscript{c}, is measured. The purple circles mark the two atoms used to define the R\textsubscript{p} distance (C10e and C10e’ in the notation of Ref. \textsuperscript{352}), which are the most separated atoms of the central five-membered rings of both corannulene subunits. **Right:** 3D structure of the C\textsubscript{60}@C\textsubscript{60}H\textsubscript{28} complex with the three distances R\textsubscript{c}, R\textsubscript{p}, and R\textsubscript{t} highlighted.
6.7.6 SELF-CONSISTENT SCREENING

Self-consistent screening (SCS) is accomplished by solving the following non-homogeneous system of linear equations at a given complex frequency $i\omega$ (Eq. (17) in DiStasio et al.):\[ \alpha_a(i\omega) = \alpha_a(i\omega) - \alpha_a(i\omega) \sum_{b \neq a}^N T_{ab} \bar{\alpha}_a(i\omega). \] \tag{6.66}

To accomplish a range-separated self-consistent screening (rsSCS), we replace $T$ with $T_{SR}$ (see Ref. 280). Eq. (6.66) can then be written as a matrix equation as:

\[ \bar{\Lambda} = \Lambda - \Lambda T_{SR} \bar{\Lambda}. \] \tag{6.67}

Note that $\zeta_{pp} = 0$ so $T_{pp} = 0$ naturally (see Eq. (6.27)). Thus, the sum $\sum_{b \neq a} T_{ab} \bar{\alpha}_a$ is accomplished by the product $T_{SR} \bar{\Lambda}$. Rearranging Eq. (6.67) and then left multiplying by $\Lambda^{-1}$ gives:

\[ \Lambda^{-1} + \Lambda T_{SR} \bar{\Lambda} = \Lambda \] \tag{6.68}

\[ \Lambda^{-1} \left[ \Lambda^{-1} + T_{SR} \bar{\Lambda} \right] = \Lambda^{-1} \Lambda \] \tag{6.69}

\[ \left[ \Lambda^{-1} + T_{SR} \right] \Lambda^{-1} = \Lambda^{-1} \] \tag{6.70}

Left multiplying by the inverse of the bracketed quantity yields:

\[ \bar{\Lambda} = \left[ \Lambda^{-1} + T_{SR} \right]^{-1} \] \tag{6.71}
6.7.7 Derivation of $\partial T_{ij}$

To break the derivative of $T_{ij}$ into smaller pieces, we define some convenience functions:

\[
U \equiv \text{erf}[\zeta] - \frac{2}{\sqrt{\pi}} \zeta \exp[-\zeta^2] \\
W_{ij} \equiv \left( \frac{R^i R^j}{R^5} \right) \frac{4}{\sqrt{\pi}} \zeta^3 \exp[-\zeta^2] \\
T_{\text{dip}}^{ij} \equiv -3 \left( \frac{R^i R^j}{R^5} \right) + \frac{\delta_{ij}}{R^3}.
\]

So in terms of these functions, $T_{ij}$ is:

\[
T_{ij} = U T_{\text{dip}}^{ij} + W_{ij}
\]

\[
\Rightarrow \partial T_{ij} = U \partial T_{\text{dip}}^{ij} + T_{\text{dip}} \partial U + \partial W_{ij}
\]

The derivative of $T_{\text{dip}}^{ij}$ is given in Eq. (6.54). Note that we can write $\partial \left( \frac{R^i R^j}{R^5} \right)$ in terms of $\partial T_{\text{dip}}^{ij}$ as:

\[
\partial \left( \frac{R^i R^j}{R^5} \right) = -\frac{1}{3} \partial T_{\text{dip}}^{ij} - \frac{\delta_{ij}}{R^3} \partial R
\]

So the derivatives of $U$ and $W_{ij}$ are:

\[
\partial U = \frac{4}{\sqrt{\pi}} \zeta^2 \exp[-\zeta^2] \partial \zeta
\]

\[
\partial W_{ij} = \left( \frac{R^i R^j}{R^5} \right) \left[ 3 - 2 \zeta^2 \right] \frac{4}{\sqrt{\pi}} \zeta^2 \exp[-\zeta^2] \partial \zeta
\]

\[
+ \frac{4}{\sqrt{\pi}} \zeta^3 \exp[-\zeta^2] \left( -\frac{1}{3} \partial T_{\text{dip}}^{ij} - \frac{\delta_{ij}}{R^3} \partial R \right)
\]
Now define \( h(\zeta) \equiv \frac{4}{\sqrt{\pi}} \zeta^2 \exp \left[ -\zeta^2 \right] \).

\[
\Rightarrow \partial U = h(\zeta) \partial \zeta \\
\Rightarrow \partial W^{ij} = \left( \frac{R^i R^j}{R^5} \right) [3 - 2\zeta^2] h(\zeta) \partial \zeta + \zeta h(\zeta) \left( -\frac{1}{3} \partial T^{ij}_{\text{dip}} - \frac{\delta_{ij}}{R^4} \partial R \right) \tag{6.80}
\]

In terms of \( h(\zeta) \) we can then write \( \partial T^{ij} \) as:

\[
\partial T^{ij} = \left[ \text{erf}[\zeta] - \frac{1}{2} h(\zeta) \right] \partial T^{ij}_{\text{dip}} + \zeta h(\zeta) \left( -\frac{1}{3} \partial T^{ij}_{\text{dip}} - \frac{\delta_{ij}}{R^4} \partial R \right) \\
+ \left[ T_{\text{dip}} + \left( \frac{R^i R^j}{R^5} \right) [3 - 2\zeta^2] \right] h(\zeta) \partial \zeta \tag{6.81}
\]

Where the derivative of \( \zeta_{ab} \) is in Eq. (6.60).

### 6.7.8 Scaling of Gauss-Legendre Quadrature

To transform Gauss-Legendre quadrature from the interval \( x_p \in [-1, 1] \), to the semi-infinite interval \( y_p \in [0, \infty) \), we map the abscissa \( x_p \) and weights \( w_p \) with an algebraic scaling:

\[
y_p \in [0, \infty) \quad y_p = L \frac{(1 + x_p)}{(1 - x_p)} \quad x_p \in [-1, 1] \tag{6.83}
\]

\[
g_p = -\frac{2L}{(1 - x_p)^2} w_p \tag{6.84}
\]

There are many different possible transformations to \([0, \infty)\), but the algebraic mapping is quite robust for quadrature of functions \( f(x) \) that decay algebraically in \(|x|\) as \( x \to \infty \). Since the isolated atom dynamic polarizability is expected to decay as \( \alpha(i\omega) \propto 1/\omega^2 \) we found the algebraic scaling to be preferable, although other choices such as \( y_p = L \tan \left( \frac{\pi}{2} \left( \frac{x_p + 1}{2} \right) \right) \) also perform well. Since the number of Gauss-Legendre quadrature points, \( n \), determines the number of self-consistent screening computations that must be performed to determine \( \bar{w}_a \), the computational
cost (and numerical error) of evaluating the MBD correlation energy can be varied by adjusting the number of quadrature points. The quadrature error is also sensitive to the scale factor \( L \).

Based on the available atomic dynamic polarizability reference data in Derevianko et al. \(^{367}\) and the free atom reference quantities used in the TS method,\(^{83}\) our quadrature method should be able to integrate a response function for excitation frequencies in the range of \( \omega_0 \sim 0.06 \) (K) to \( \omega_0 \sim 1.2 \) (Ne). In optimizing the number of Gauss-Legendre points, \( n \), and the scale factor, \( L \), we used the Casimir-Polder integral for a single excitation frequency dipole oscillator as a trial function with \( \omega_0 \) varying in the range \([10^{-2}, 10^{2}]\).

\[
C_6(\omega_0) = \frac{3}{\pi} \int_0^\infty \left[ \frac{f}{(\omega_0^2 - (i\omega)^2)} \right]^2 d(i\omega) = \frac{3}{4} \frac{f^2}{\omega_0^3}
\] (6.85)

Using this trial function, we choose \( n = 20 \) quadrature points and a scale factor \( L = \frac{6}{10} \), which gives integration with a relative error less than \( 10^{-6} \) for all excitation frequencies in the range \([0.07, 5]\) and also performed well in self-consistent screening computations across a range of isolated atomic systems.

6.7.9 ADDITIONAL COMPUTATIONAL DETAILS

All geometry optimizations were performed using the quasi-Newton Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm\(^{368,371}\) with default parameters.

6.7.9.1 QUANTUM ESPRESSO

Cartesian coordinate geometry optimizations in QUANTUM ESPRESSO (QE)\(^{21}\) were performed in the PWSCF module in large simple cubic unit cells. Table 6.2 gives details of the convergence tolerances, kinetic energy wavefunction cutoffs, and unit cell sizes used for each system. Since QE uses Rydberg energy units (1 Ry = \( \frac{1}{2} \) \( E_h \)), we report the tolerances in these units. The PBE
Table 6.2: Convergence tolerances and unit cell sizes used in PWscf geometry optimizations, reported in Rydberg atomic units (1 Ry = $\frac{1}{2}$ $E_h$)

<table>
<thead>
<tr>
<th></th>
<th>Benzene Dimer</th>
<th>Peptides</th>
<th>C$_{60}$ Catcher</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{scf}}$ (Ry)</td>
<td>$10^{-8}$</td>
<td>$10^{-8}$</td>
<td>$10^{-8}$</td>
</tr>
<tr>
<td>$E_{\text{cut}}$ (Ry)</td>
<td>400</td>
<td>145</td>
<td>110</td>
</tr>
<tr>
<td>$E_{\text{tot}}$ (Ry)</td>
<td>$10^{-8}$</td>
<td>$5 \times 10^{-7}$</td>
<td>$5 \times 10^{-7}$</td>
</tr>
<tr>
<td>$F_{\text{tot}}$ (Ry/$a_0$)</td>
<td>$10^{-4}$</td>
<td>$5 \times 10^{-4}$</td>
<td>$5 \times 10^{-4}$</td>
</tr>
<tr>
<td>Cell Size ($a_0$)</td>
<td>30</td>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td>Grid Spacing (Å)</td>
<td>0.04</td>
<td>0.07</td>
<td>0.12</td>
</tr>
</tbody>
</table>

functional was used with Hamann-Schlueter-Chiang-Vanderbilt (HSCV) norm-conserving pseudopotentials obtained from the FPMD pseudopotential repository (and converted to UPF format using a modified version of QSO2UPF v1.2). All QE calculations were run at the $\Gamma$ point using a charge density cutoff of $\rho_{\text{cut}} = 4E_{\text{cut}}$. PBE+MBD jobs used 20 quadrature points for the Casimir-Polder integration. To ensure a fair comparison with our implementation of the MBD model, all TS calculations were performed as a posteriori corrections to the solution of the non-linear Kohn-Sham equations, i.e. we turned off the self-consistent density updates from TS. In Fig. 6.11 we present the results of convergence testing with respect to the kinetic energy cutoff in the planewave basis set expansion, showing that the total energy per atom was converged to better than 0.3 meV/atom for each system.

6.7.9.2 ORCA

Redundant internal coordinate geometry optimizations in ORCA v3.03 were performed with the PBE functional with the atom-pairwise version of the D3 dispersion correction of Grimme et al., using Becke-Johnson (BJ) damping. ORCA v3.03 implements D3 in the DFTD3 v2.1R6 software, which does not contain analytical gradients of the three-body term. The geometric counterpoise correction (gCP) of Kruse et al. was employed in all ORCA calculations. We employed the Ahlrichs def2-TZVP basis set coupled with an auxiliary Ahlrichs TZVP basis.
Table 6.3: Convergence tolerances used in ORCA geometry optimizations, reported in Hartree atomic units

<table>
<thead>
<tr>
<th></th>
<th>Benzene Dimer</th>
<th>Peptides</th>
<th>C₆₀ Catcher</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{scf}}$ ($E_h$)</td>
<td>$10^{-8}$</td>
<td>$10^{-8}$</td>
<td>$10^{-8}$</td>
</tr>
<tr>
<td>$E_{\text{tot}}$ ($E_h$)</td>
<td>$10^{-6}$</td>
<td>$5 \times 10^{-6}$</td>
<td>$10^{-6}$</td>
</tr>
<tr>
<td>$F_{\text{Max}}$ ($E_h/a_0$)</td>
<td>$10^{-4}$</td>
<td>$3 \times 10^{-4}$</td>
<td>$10^{-4}$</td>
</tr>
<tr>
<td>$F_{\text{RMS}}$ ($E_h/a_0$)</td>
<td>$3 \times 10^{-5}$</td>
<td>$10^{-4}$</td>
<td>$3 \times 10^{-5}$</td>
</tr>
<tr>
<td>Max Disp. ($a_0$)</td>
<td>$10^{-3}$</td>
<td>$4 \times 10^{-3}$</td>
<td>$10^{-3}$</td>
</tr>
<tr>
<td>RMS Disp. ($a_0$)</td>
<td>$6 \times 10^{-4}$</td>
<td>$2 \times 10^{-3}$</td>
<td>$6 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

All calculations used “tight” SCF tolerances; calculations on the benzene dimer and C₆₀ catcher used “tight” optimization tolerances, while those of the peptides used default optimization tolerances. Table 6.3 lists the tolerances corresponding to these two settings.
Figure 6.11: Convergence of the total energy per atom with respect to kinetic energy wavefunction cutoff ($E_{\text{cut}}$) of the planewave basis expansion for Left: simulations of the $C_{60}$ catcher complex, Right: the benzene dimer (M1 configuration).
Self-consistent Calculation of the Ionic Forces and Unit Cell Stresses for the Many-Body Dispersion Model

This work will be submitted for publication with modifications as:

‡ These authors contributed equally to this work.

ABSTRACT

Dispersion interactions are ubiquitous in nature, and extremely important for explaining the structure and function of many systems, from soft matter to surfaces and solids. Due to their long-range and scaling with system size, dispersion interactions can prove particularly important in modeling nanostructured systems where reduced dimensionality creates large polarizable surfaces. Standard pairwise approximations are insufficient for such systems, and the true non-additive and many-body character of dispersion plays a crucial role. The many-body dispersion (MBD) method of Tkatchenko and co-workers [A. Tkatchenko et al., Phys. Rev. Lett. 108, 236402 (2012); A. Ambrossetti et al., J. Chem. Phys. 2014, 140, 18A508] seeks to address this behavior by computing the full many-body correlation energy for a fictitious set of coupled quantum harmonic oscillators.
that mimic the fluctuations of the real polarizable valence-electron density. Much of the work on MBD, to date, has focused on the energetics of various molecules and materials, with all necessary gradient information being obtained through numeric differentiation. We recently presented an implementation of the relevant analytic gradients with respect to nuclear displacements, cell parameters, and nuclear densities, which permitted fast and accurate unit cell optimizations of many condensed phase systems. We demonstrate the method on a range of dispersion bound and hydrogen bonded crystals, and show excellent agreement with experimental data.

7.1 Introduction

Although weak, dispersion interactions are ubiquitous, and they are important for explaining the structure, properties, and function of many systems, from soft matter to surfaces and solids.\[58,61\] Indeed, these interactions are important for explaining the cohesion energy of organic molecular crystals,\[285,289\] DNA binding,\[62\] workfunctions of metal surfaces,\[301\] the conformations of supermolecular systems,\[283\] the properties of van der Waals (vdW) heteromaterials,\[291,379\] and many other physical systems. Due to their long-range and scaling with the size of an electronic system, dispersion interactions can be particularly important for accurately modeling interactions in quasi-2D systems where reduced dimensionality creates large polarizable surfaces.\[280\] Given their importance, improving the accuracy and efficiency of techniques for representing these interactions has been a long standing focus area in electronic structure theory.

However, the long-range of dispersion interactions makes the correlation kernels used in semi-local density functional theory (DFT) wholly unsuitable for an accurate picture. Many highly accurate wavefunction theory methods, such as coupled cluster, accurately capture dispersion, but the computational cost of such methods makes them prohibitively expensive for periodic systems and more than \(\sim 50\) atoms in gas phase. Seeking a balance of computational cost and accuracy, a
common approach has been to add semi-empirical dispersion corrections to DFT that rely on pairwise approximations. For many systems, the pairwise approximation breaks down, and the true non-additive many-body character of dispersion plays a crucial role.

Graphene, for instance, has an extended polarizable $\pi$-system that is able to support large collective dipole modes. A pairwise description of dispersion is inherently incapable of capturing these extended fluctuations. The many-body dispersion (MBD) method of Tkatchenko et al. seeks to model this behavior by computing the full many-body correlation energy for a fictitious set of coupled fluctuating dipoles that mimic the fluctuations of the real polarizable electron density. By using a screened dipole-dipole interaction and assigning effective atomic polarizabilities with the Tkatchenko-Scheffler (TS) scheme, the MBD method is one of the most accurate and efficient methods for treating systems where pairwise theories fail.

To date, much of the work on MBD has focused on the energetics of various molecules and materials, with any gradient information being obtained through numeric differentiation. We recently presented an implementation of the relevant analytic gradients of the MBD energy with respect to nuclear displacements, which permitted fast and accurate geometry optimizations of many gas-phase systems. For systems such as the benzene dimer, it was shown that MBD gradients enabled the recovery of highly accurate wavefunction theories at a fraction of the cost.

In the present work we describe an efficient implementation of the MBD energy and analytic gradients with respect to ionic positions, cell parameters, and electronic density, which has enabled their application to simulations of condensed phase systems. In particular, the inclusion of the functional derivative of the MBD energy with respect to the electronic density, sometimes called the wavefunction force, allows the inclusion of MBD self-consistently. This in turn allows the exploration of vdW-corrected charge densities. The infinite periodicity of solids, in contrast to isolated gas-phase systems, raises several issues for the computation and convergence of MBD.
energies and forces. In particular, the supercell procedure required to support long wavelength collective dipole modes has been discussed only briefly in other treatments of MBD in its range-separated form.\cite{280} We discuss this procedure in detail and discuss our approach for parallelizing MBD for periodic systems.

The remainder of this paper is organized as follows: Section II will provide a brief introduction to the MBD formalism and gradients; Section III will contain a discussion of our new implementation and the parallelism necessary for optimizing periodic structures; Section IV will present the results of detailed convergence testing and the first application of molecular dynamics with MBD forces; and in Section V we present our conclusions and future outlook.

7.2 Overview of Many-Body Dispersion

We present here a brief overview of range-separated MBD as it applies to condensed phase systems to support the later discussion of our new implementation. This paper is a follow-up to a recent detailed derivation of analytic energy gradients for range-separated many-body dispersion, and we refer the reader to that work, as well as the original papers on MBD,\cite{273,279,280} for a more in-depth discussion of the notation and physical interpretation of various quantities. All equations are given in Hartree atomic units, \((\hbar = m_e = e = 1/4\pi\varepsilon_0 = 1)\).

Fitz London described dispersion interactions as a set of fluctuating dipoles, which create instantaneous weakly attractive forces.\cite{70} This model has proved useful in reasoning about dispersion interactions. In a similar vein, MBD describes dispersion interactions by constructing a fictitious system of quantum harmonic oscillators (QHO) to model collective oscillations in the real electronic charge density. Each atom \(p\) is assigned a single isotropic oscillator with an excitation frequency, \(\omega_a\) and dynamic polarizability, \(\alpha_a(i\omega)\). These two parameters \(\{\omega_a, \alpha_a\}\) completely characterize the QHO assigned to each atom, and are assigned to atoms in the
Chapter 7. Self-consistent Calculation of the Ionic Forces and Unit Cell Stresses for the
Many-Body Dispersion Model

simulation cell using the Tkatchenko-Scheffler (TS) scheme.\textsuperscript{[83]} The TS scheme takes in reference
free-atom polarizabilities and re-scales by $V_{\text{eff}}/V_{\text{free}}$, the ratio of the Hirshfeld effective atomic
volume\textsuperscript{[297]} to the isolated atom volume. TS-level polarizabilities are then self-consistently
screened (SCS) to take into account the anisotropy and electrodynamic screening of the local
chemical environment.\textsuperscript{[273]}

The set of screened oscillators \{\overline{\alpha}_a, \overline{\alpha}_d\} are then fully coupled with the long-range
dipole-dipole interaction, $T_{LR}$, where an overline indicates quantities that have been screened. The
corresponding interaction Hamiltonian, $C_{\text{MBD}}$ is then diagonalized, and the eigenvalues, $\lambda_i$,
describe the collective oscillations dressed by the many-body dipole interaction. We refer to these
as the interacting modes. The MBD correlation energy is then computed as the difference between
the zero-point energies of the interacting and non-interacting modes:

$$E_{\text{MBD}} = \frac{1}{2} \sum_{i=1}^{3N} \sqrt{\lambda_i} - \frac{3}{2} \sum_{p=1}^{N} \overline{\alpha}_p.$$  \hspace{1cm} (7.1)

In discussing our implementation, we will refer to the first term as the interacting energy, since it
requires diagonalizing the many-body interaction Hamiltonian, and the second term as the
non-interacting energy, since it can be computed from the non-interacting screened oscillators.

For an $N$ atom system, the interaction Hamiltonian $C_{\text{MBD}}$ is a $3N \times 3N$ matrix, composed of
$3 \times 3$ sub-blocks, which describe the coupling between each pair of atoms $p$ and $q$. The diagonal of
$C_{\text{MBD}}$ is constructed from the potential energy of the screened oscillators, while the off-diagonal
elements describe the coupling due to dipole-dipole interactions:

$$C_{\text{MBD}}^{ab} = \delta_{ab} \overline{\alpha}_a^2 + (1 - \delta_{ab}) \overline{\alpha}_a \overline{\alpha}_b \sqrt{\overline{\alpha}_a^0 \overline{\alpha}_b^0} T_{LR}^{ab},$$ \hspace{1cm} (7.2)

where $\overline{\alpha}_a$ is the screened static polarizability and $T_{LR}$ is the long-range part of the dipole-dipole
interaction tensor given in Equation (7.5). The eigenvectors of $C_{ab}$ describe the normal modes of this system system of coupled oscillators. Periodicity introduces the need to consider periodic interactions in computing both the dipole-dipole tensor and the normal modes. To allow for long wavelength normal modes, it is usually necessary to construct a supercell from the simulation unit cell. This supercell is extremely important for converging the MBD energy in a condensed phase system and significantly increases the computational cost.

7.2.1 RANGE-SEPARATION

The dipole-dipole interaction tensor $T$ is range-separated with a Fermi-type damping function $f(Z)$ to avoid double counting the correlation energy at short range where a semi-local exchange correlation functional is expected to perform well. The argument of this Fermi function, $Z_{ab} = 6[R_{ab}/S_{ab} − 1]$, is computed using the ratio of the inter-atomic separation, $R_{ab} = ||R_a − R_b||$, to $S_{ab}$, the scaled sum of effective van der Waals radii (see Ref. [5] for more detail). The Coulomb interaction in the MBD model takes on the form

$$T_{ab}(\omega) = \nabla_{R_a} \otimes \nabla_{R_b} \left[ \frac{\text{erf}[\zeta_{ab}(i\omega)]}{R_{ab}} \right],$$

(7.3)

where the error function arises from the overlap between two Gaussian charge densities. To model the local chemical environment, the screening procedure makes use of the short-range dipole-dipole interaction tensor $T_{SR}$:

$$T_{ab}^{SR}(\omega) = [1 − f(Z_{ab})]T_{ab}(\omega)$$

(7.4)

where $\zeta_{ab}(i\omega) ≡ R_{ab}/\Sigma_{ab}(i\omega)$, where $\Sigma_{ab}(i\omega)$ is the frequency-dependent length scale of the screened Coulomb potential describing the interaction between the Gaussian groundstate charge
densities of the QHOs. The frequency dependence arises from the fact that the width of the QHO ground state depends on the dynamic atomic polarizability, \( \alpha(i\omega) \).

The long-range tensor \( T_{LR} \) uses a similar damping function, but its argument \( Z_{ab} \) is constructed from screened effective van der Waals radii, and the frequency-independent point-dipole interaction \( T_{dip} \) is used since at long-range all frequency dependence in Eq. (7.3) falls off and the interaction reduces to the usual \( 1/R_{ab} \) Coulomb potential. The form of these tensors is:

\[
T_{LR}^{ab} = f(Z_{ab})T_{dip}
\]

\[
T_{dip}^{ij} = \left[ \frac{-3R_{ij}^iR_{ij}^j + R_{ij}^2\delta_{ij}}{R_{ab}^5} \right],
\]

where \( i, j \) superscripts indicate Cartesian components.

### 7.2.2 MBD Gradients

While periodicity introduces relatively little complexity in the computation of an MBD energy, aside from converging the dipole-dipole tensor, it provides us with not only the ionic derivatives given by \( \partial E_{MBD}/\partial R_i \), but also the unit cell derivatives given by \( \partial E_{MBD}/\partial h_{\gamma\sigma} \). In addition, the functional derivatives of the energy with respect to the electron density, \( n(r) \), given by \( \delta E_{MBD}/\delta n(r) \) can be computed using the equations below.

In Ref. 5 where we considered ionic derivatives for gas phase systems, we reported detailed expressions for \( \partial E_{MBD}/\partial R_{i} \) in terms of two fundamental partial derivatives \( \partial R_{i}^{j} \) and \( \partial V_{a}^{eff} \), where \( V_{a}^{eff} \) is the effective atomic volume from a Hirshfeld partitioning of the electronic density,

\[
V_{a}^{eff} = \int d\mathbf{r} \frac{n_{a}^{\text{free}}(||\mathbf{r} - \mathbf{R}_a||)}{\sum_b n_{b}^{\text{free}}(||\mathbf{r} - \mathbf{R}_b||)} n(r).
\]

For later convenience it is useful to define the sum of free atom densities as
7.2. Overview OF Many-Body Dispersion

\[ n_{SAD}(\mathbf{r}) = \sum_b n_b^{\text{free}}(||\mathbf{r} - \mathbf{R}_b||) \] and the effective density as
\[ n_a^{\text{eff}}(\mathbf{r}) = \left[ n_a^{\text{free}}(||\mathbf{r} - \mathbf{R}_a||)/n_{SAD}(\mathbf{r}) \right] n(\mathbf{r}). \]

For brevity, we will report only the key partial derivatives below, and refer the reader to Ref. 5 for a more thorough description of the equations. The distance \( R_{ab'} \) between atom \( a \) and atom \( b' \), where \( b' \) is a periodic image of \( b \) is given by

\[ R_{ab'}^i = R_{ab}^i + \sum_{j=1}^{3} h_{ij}n_j \] (7.8)

where \( h \) is the matrix of unit cell vectors, and \( n \) is the vector specifying the periodic image in terms of unit cell translations. With this definition in mind, the relevant derivatives of the internuclear vector \( R_{ab} \) are:

\[ \frac{\partial R_{ab}^i}{\partial R_{ab}^j} = (\delta_{ps} - \delta_{qs}) \] (7.9)

\[ \frac{\partial R_{ab}^i}{\partial h_{js}} = \delta_{jp}X_{ab}^{\sigma} \] (7.10)

\[ \delta \frac{\partial R_{ab}^i}{\partial n(\mathbf{r})} = 0, \] (7.11)

where \( X_{ab} \) is fractional coordinate defined by \( X_{ab} = h^{-1}R_{ab} \).

MBD’s other fundamental derivatives enter through an implicit nuclear coordinate dependence occurring in the Hirshfeld effective atomic volumes. Computing these derivatives can be quite expensive, but we previously showed that neglecting this term can lead to forces which are as much as 200% relative error\(^5\). The ionic derivative of the Hirshfeld volume is given by

\[ \frac{\partial V_a^{\text{eff}}}{\partial R_{ab}^i} = \int d\mathbf{r} \frac{3}{||\mathbf{r} - \mathbf{R}_a||} \frac{\partial n_a^{\text{eff}}(\mathbf{r})}{\partial R_{ab}^i} - 3\delta_{pp} \int d\mathbf{r} (\mathbf{r} - \mathbf{R}_a)||\mathbf{r} - \mathbf{R}_a|| n_a^{\text{eff}}(\mathbf{r}). \] (7.12)
\[
\frac{\partial n^{\text{eff}}(r)}{\partial R_i^a} = \left[ \frac{n_a^{\text{free}}(||r - R_u||) n(r)}{(n_{\text{SAD}}(r))^2} - \frac{n(r)}{n_{\text{SAD}}(r)} \delta_{ps} \right] \\
\times \left[ \frac{r - R_u}{||r - R_u||} \right] \frac{\partial n_a^{\text{free}}(r)}{\partial r}.
\] (7.13)

where \(n^{\text{eff}}(r)\) is the effective atomic density and \(n^{\text{free}}(r)\) is the free atomic density. Hirshfeld volumes have implicit dependence on the unit cell vectors through the distance away from each nucleus. We can then use the chain rule to calculate the derivative of the Hirshfeld volumes

\[
\frac{\partial V^{\text{eff}}_a}{\partial h_{\gamma\sigma}} = \sum_b \frac{\partial ||r - R_b||}{\partial h_{\gamma\sigma}} \frac{\partial V^{\text{eff}}_a}{\partial ||r - R_b||}.
\] (7.14)

Transforming to fractional coordinates using the unit-cell relation \(r = ho\) gives:

\[
\frac{\partial V^{\text{eff}}_a}{\partial h_{\gamma\sigma}} = \int dr \, n(r) \left[ \gamma^{\gamma\sigma}_a + \sum_{q \neq p} \gamma^{\gamma\sigma}_b \right].
\] (7.15)

For convenience, we have defined \(\gamma^{\gamma\sigma}_a\) and \(\gamma^{\gamma\sigma}_b\) as

\[
\gamma^{\gamma\sigma}_a = \frac{(r - R_u)^{\gamma}(x - X_u)^{\sigma}}{n_{\text{SAD}}} \left[ 3n_a^{\text{free}} + ||r - R_u|| \frac{\partial n_a^{\text{free}}(r)}{\partial r} \left( 1 - \frac{n_a^{\text{free}}}{n_{\text{SAD}}} \right) \right],
\] (7.16)

and

\[
\gamma^{\gamma\sigma}_b = -\frac{(r - R_b)^{\gamma}(x - X_b)^{\sigma}}{(n_{\text{SAD}})^2} n_a^{\text{free}} \frac{\partial n_a^{\text{free}}(r)}{\partial r},
\] (7.17)

where the subscript on each free atom density corresponds to the subscript on each atomic position vector, \(R\), and we have suppressed the \(r = ||r - R_u||\) argument for each free-atom density.

Finally, the functional derivative of the Hirshfeld volume is given by:

\[
\frac{\delta V^{\text{eff}}_a [n(r)]}{\delta n(r)} = \int dr \, ||r - R_u||^3 \frac{n_a^{\text{free}}(r)}{n_{\text{SAD}}(r)}.
\] (7.18)
Note, for the functional derivatives, the derivative reduces to:

$$\frac{\delta E_{MBD}}{\delta n(r)} = \sum_a \frac{\delta E_{MBD}}{\delta V_a^{\text{eff}}} \frac{\delta V_a^{\text{eff}}}{\delta n(r)}$$

(7.19)

because the $R_{ab}$ derivatives are exactly zero.

This derivative can be added to the Kohn-Sham potential to provide the dispersion correction to the Fock matrix. By adding in this correction, we ensure that we will only need to consider the Hellman-Feynman forces, because our converged density is guaranteed to be a stationary point of the total Hamiltonian. By neglecting this contribution, it is possible to observe drift because the forces computed at the end of each SCF cycle will be missing the density response term. While this term is commonly neglected, we find that it can be non-negligible for molecular dynamics trajectories.

7.3 IMPLEMENTATION

Broadly stated, the MBD algorithm begins by initializing arrays with free atom quantities. These quantities are used to compute the TS-level frequency dependent quantities by weighting the free atom quantities by the effective Hirshfeld volumes. The TS-level quantities are computed on an imaginary frequency grid to perform range-separated screening. The non-interacting energy requires $\overline{\omega}_d$, a screened excitation frequency, which is computed from the screened dynamic polarizabilities via the Casimir-Polder integral for the effective $C_6$ coefficient.

$$\overline{\omega}_d = \frac{4 C_{6,pp}}{3 |\overline{\omega}_a|^2} = \frac{4}{\pi} \left( \int_{0}^{\infty} \overline{\alpha}_a(i\omega) \overline{\alpha}_a(i\omega) \, d(i\omega) \right)^2$$

(7.20)

Since this integral does not have an analytic solution, we numerically evaluate it with Gauss-Legendre quadrature algebraically scaled to the semi-infinite interval $[0, \infty)$ with scaling
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Parameter $L = 0.6$.

$$\bar{\omega}_a = \frac{4}{\pi} \sum_{k=1}^{n} g_k \left[ \frac{\alpha_a(iy_k)}{\alpha_a^0} \right]^2$$  \hspace{1cm} (7.21)

where $g_k$ and $y_k$ are the quadrature weights and abscissae respectively.

After self-consistent screening, the running quadrature sums for $\bar{\omega}$ and $\partial \bar{\omega}$ are updated. At the end of the frequency integration loop, the final screened excitation frequencies are summed to give the non-interacting energy and forces. The interacting energy and forces are then computed using the screened quantities. Finally, the MBD energy and forces are computed by taking the difference between interacting and non-interacting quantities.

Since the computation of the MBD energy and gradients entails several layers of nested subroutines and requires mixed parallelization strategies, we present a flowchart in Figure 7.1 that graphically shows program flow. The blue boxes in Figure 7.1 denote parallelization over atom components, and the orange boxes denote parallelization over independent dipole tensors. These two separate, but complementary, strategies will be discussed in the remainder of this section, where we provide an indepth discussion of each algorithmic step.

The rate limiting step of our serial implementation involved the convergence of each $3 \times 3$ dipole tensor. While each the calculation of a single dipole tensor takes $10^{-6}$ seconds, periodic convergence of a single dipole tensor often required as many as $10^5$ function calls. This, coupled with the super-lattice construction for real-space periodic convergence, which requires the computation of a quadratic number of these subblocks represents a significant computational bottleneck. Fortunately, the independent subblock structure of both the Hamiltonian, $C_{MBD}$, and the screened-polarizability relay matrix, $\mathbf{K}$, can be leveraged for parallel algorithms. We distribute the dipole tensors evenly among MPI tasks, and converge each one in an embarrassingly parallel fashion. Because these pairs are indexed $a,b$ to indicate the atom-atom pair for the dipole tensor, we term this “ab-parallelism.” Our second parallelization strategy is referred to as “s-parallelism,”
because it is simply the parallelization over force components. Mixing parallelization types requires sending each MPI task the appropriate force components for every ab-pair. This means that every MPI task involved in the ab-parallelism will send to every MPI task involved in the s-parallelization scheme. Each dipole tensor is small in memory, so we can distribute their computations without concern for their communication overhead when they are sent back to the relevant computational nodes. With converged dipole tensor blocks on the relevant computational nodes, we diagonalize the matrix and compute the relevant forces. Finally, we synchronize the forces to all MPI processes through an all-to-all reduction of a floating point vector of size $3N$. The flowchart in Figure 7.1 describes our implementation.

This parallel implementation has been incorporated in our gradients code in a development version of the QUANTUM ESPRESSO v5.2 (QE) software package, which was chosen for its preexisting implementation of the Hirshfeld partitioning and its derivatives. We have written the code in a modular fashion to allow ease of incorporation into other packages: the only necessary inputs are the Hirshfeld volumes, Hirshfeld volume derivatives, lattice vectors, and atomic coordinates. At the time of writing, this module has additionally been incorporated into the OCTOPUS, Q-CHEM, and FHI-aims software packages. We will release this code in an upcoming version of QE, as well as a standalone code with a Python wrapper. In this work, we have also generalized the Hirshfeld implementation in QE which is limited to unit cells that are large-enough to encompass all the free atomic densities in their minimum images.

7.3.1 Initialization and Component Decomposition

We begin by initializing arrays with free atom quantities and Hirshfeld effective volumes, and assigning force components to each MPI process. The free atom quantities are found in a precomputed lookup table, and the Hirshfeld effective volumes and their derivatives are computed using the code in the TS-vdW module of QE. Because each component is independent,
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Figure 7.1: Parallelization flowchart for our MBD correlation energy and forces implementation. Note, the split parallelization over pairs and forces. This is done because the converging all forces for a single dipole-dipole tensor requires limited extra computation.

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Assign force components to each MPI process. Section 7.3.1

\[ c = \{1, 2, 3\} \quad \text{and} \quad \{4, 5, 6\} \]

Compute the unique \(a, b\) pairs

\[ a, b = \{1, 2, 3\} \quad \text{Converge each set of } T_{SR}(i\omega) \quad \text{and } \partial T_{SR}(i\omega) \quad \text{tensors} \]

\[ a, b = \{4, 5, 6\} \quad \text{Converge each set of } T_{SR}(i\omega) \quad \text{and } \partial T_{SR}(i\omega) \quad \text{tensors} \]

\[ a, b = \{7, 8, 9\} \quad \text{Converge each set of } T_{SR}(i\omega) \quad \text{and } \partial T_{SR}(i\omega) \quad \text{tensors} \]

Construct and invert \(\mathbf{A}\) and compute \(\partial_c \mathbf{A}\)

Compute \(\bar{\tau}, \partial_c \bar{\tau}, \bar{\omega}, \text{ and } \partial_c \bar{\omega}\)

Construct supercell, and unique \(a, b\) pairs for supercell. Section 7.3.2.1

\[ p, q = \{1, 2, 3\} \quad \text{Converge } T_{LR} \quad \text{and } \partial T_{LR} \quad \text{tensors} \quad [10] \]

\[ p, q = \{4, 5, 6\} \quad \text{Converge } T_{LR} \quad \text{and } \partial T_{LR} \quad \text{tensors} \quad [10] \]

\[ p, q = \{7, 8, 9\} \quad \text{Converge } T_{LR} \quad \text{and } \partial T_{LR} \quad \text{tensors} \quad [10] \]

Construct \(C_{ab}\) and \(\partial C_{ab}\) [12]

Compute interacting energy and forces [13]
communication is limited to synchronizing the force vector of size $3N$ across all processes. This parallelization scheme is represented in the flowchart with the blue boxes. In instances where there are more MPI processes than atoms, only the first $3N$ processes are given force components. In the event that the number of force components is larger than the number of MPI ranks, work is split up equally.

With these basic building blocks in hand, we perform the self-consistent screening (SCS) procedure to compute the screened frequencies and polarizabilities. We will make use of the Casimir-Polder integral, which will require numerical quadrature for the evaluation. Ultimately we want to compute the screened polarizabilities, which are found by constructing a relay matrix, $\bar{A}$, and inverting it. This construction begins with the computation of frequency dependent polarizabilities,

$$\alpha_a[\rho(r)](i\omega) = \left[\frac{1}{1 - (i\omega/\omega^\text{free}_a)^2} \frac{\alpha^\text{free,0}_a}{V^\text{free}_a}\right] V_a[\rho(r)], \quad (7.22)$$

QHO ground state charge density widths,

$$\sigma_a(i\omega) = \left[\frac{1}{3} \sqrt{\frac{2}{\pi}} \alpha_a(i\omega)\right]^{1/3}, \quad (7.23)$$

and effective van der Waals radii,

$$\mathcal{R}^\text{vdW,TS}_a[\rho(r)] \equiv \left(\frac{V_a[\rho(r)]}{V^\text{free}_a}\right)^{1/3} \mathcal{R}^\text{vdW,free}_a, \quad (7.24)$$

at the TS level for each quadrature frequency.

The screening subroutine builds the TS-level matrices $A_{TS}$ and $T_{SR}$ and solves for the screened polarizability through matrix inversions. Derivatives of all quantities are computed as they become available, and collected in a manner that avoids extra loops. We have employed s-parallelism over force components for $\partial_c A$, and ab parallelism for $T_{SR}$ and $\partial_c T_{SR}$. For a force calculation when $3N$
cores are used, each core has two matrix multiplies and one matrix inversion to compute at every quadrature point. In our numerical tests we find that this is not a numerically limiting step.

The elements of $T_{SR}^{ij}(i_\omega)$ are computed using

$$T_{SR}^{ij}(i_\omega) = (1 - f(Z)) \left( \text{erf}[\zeta] - \frac{2}{\sqrt{\pi}} \exp\left[-\zeta^2\right]\right) T_{dip}^{ij} + \frac{4}{\sqrt{\pi}} \frac{R_i R_j}{R^5} \zeta^3 \exp\left[-\zeta^2\right]$$

(7.25)

where

$$T_{dip}^{ij} = -\frac{3R_i R_j + R^2 \delta_{ij}}{R^5}. \quad (7.26)$$

In computing the elements of $T_{SR}$ we account for interactions with periodic images of atoms in the simulation unit cell by considering the coupling between atom $p$ and all of the periodic images $b'$ of atom $b$,

$$T_{SR}^{ab} \to T_{SR}^{ab} + \sum_{b'} T_{SR}^{ab'} \quad (7.27)$$

and similarly for the forces,

$$\partial T_{SR}^{ab} \to \partial T_{SR}^{ab} + \sum_{b'} \partial T_{SR}^{ab'}. \quad (7.28)$$

We sum over all periodic images $a'$ by adding successive shells of the simulation unit-cell (see Fig. 7.2a), until each $3 \times 3$ $ab$ sub-block of the tensor is converged to within a tolerance, $\delta$, (typically $10^{-5}$ or $10^{-6}$):

$$\| T_{SR}^{ab} \|_{\text{max}} = \max \left\{ |T_{ij}^{p a'}| \right\} \leq \delta, \quad (7.29)$$

where $\| \cdot \|_{\text{max}}$ is the max norm, i.e. the element-wise infinity norm. Once the max norm falls below $\delta$, we assume that we have reached convergence.

We perform this analysis in lieu of an energy convergence cutoff, which would be prohibitively expensive given that each energy computation requires a full matrix diagonalization in addition to lattice summation of both the short and long-range dipole tensors.
The error function in Eq. (7.3) gives rise to terms proportional to $\zeta \exp[-\zeta^2]$ and $\zeta^3 \exp[-\zeta^2]$ in $T_{SR}$. These terms and the exponential in the Fermi damping function, raise an important numerical consideration, namely, avoiding arithmetic underflow. For numerical stability, we therefore evaluate the Fermi damping function as:

$$1 - f(Z_{ab}) = \begin{cases} 
1 - [1 + \exp[-Z_{ab}]]^{-1} & Z_{ab} < 35 \\
0 & Z_{ab} \geq 35 
\end{cases} \quad (7.30)$$

and likewise for $f(Z)$. The cutoff $Z \geq 35$ is chosen since $f(Z) = 1$ to within machine precision ($\epsilon_{\text{mach}} \approx 2 \times 10^{-16}$) for $Z \geq 36$. Similarly, we evaluate the frequency-dependent terms in Eq. (7.3) in such a way that:

$$T = \begin{cases} 
T(i\omega) & \zeta < 6 \\
T_{\text{dip}} & \zeta \geq 6. 
\end{cases} \quad (7.31)$$

In addition to being sound numerically, this has a substantial computational benefit since the exponential and error function are both substantially more expensive than floating point multiplication or division and $T_{SR}$ is called on the order of $10^7 - 10^8$ times in a typical condensed phase MBD computation.

Note that since $T_{SR}$ is damped by the Fermi function, the underflow condition (Eq. (7.30)) often occurs within the simulation cell or within only a few periodic images. For instance, in graphene $S_{ab} = 2.96$, so the underflow condition $Z \geq 35$ corresponds to $R_{ab} \geq 20.7 \text{ Å}$. Before underflow is reached, the Fermi function becomes competitive with the max norm tolerance $\delta$, e.g. for graphene $f(Z) \leq 10^{-6}$ when $R_{ab} \geq 9.8 \text{ Å}$, which means we cut off lattice summation for $T_{SR}$ at shorter length scales than the underflow condition.

Even with these cutoffs, the convergence of each $T_{SR}$ block is the most computationally intensive part of the SCS loop. Because each block can be computed independent of one another,
we perform MPI parallelization over each $3 \times 3$ sub-block using the “ab-parallelization” strategy. These sub-blocks are distributed to the MPI ranks associated with each derivative component in the s-parallelism scheme. It is important to note that while the force component based parallelization cannot utilize more than $N$ processes, the ab parallelization can.

### 7.3.1.1 SCS: Contraction and Isotropization

We compute $\overline{A}(iy_k)$ and $\partial \overline{A}(iy_k)$ at each quadrature point using

$$
\overline{A}(iy_k) = \left[ A_{T3}^{-1}(iy_k) - T_{LR} \right]^{-1}.
$$

These matrices are contracted to scalar quantities to update the $\overline{w}$ and $\partial \overline{w}$ running sums.

While some quadrature schemes omit a point at $y_k = 0$, it is important to involve this frequency in the frequency loop even if not included in the integration, so that we can capture the static polarizability, $\overline{\alpha}^0$. During the course of the calculation, it is important to check whether the static polarizabilities have a negative component. If even one element of $\overline{\alpha}^0$ becomes negative, the MBD calculation is terminated immediately. This indicates that a “polarization catastrophe” has occurred. Typically this indicates that at least two nuclei significantly overlap in their QHO radii, and the geometry should be checked, but it can also occur with a poorly converged charge density.

At the end of the frequency integration loop, we have the final $\overline{w}$s, and $\partial \overline{w}$s, which yield the non-interacting energy and forces through summation.

### 7.3.2 Interacting Energies

With the computation of the non-interacting energies completed, our next task is to construct the Hamiltonian matrix elements that result from projecting the Hamiltonian into our non-interacting Gaussian basis. Construction of the Hamiltonian starts with converging the dipole-dipole
interaction tensor for all atom-atom pairs, as given in Equation (7.2). The converged dipole-dipole
tensors and the previously computed frequencies and polarizabilities are used to fill the upper
triangle of the Hamiltonian. Finally, the interacting energy is found by summing the square-root of
the eigenvalues and the interacting gradients are computed with

\[ \partial E_{\text{int}} = \sum_i (S^T \partial C_{ab} S)_{ii}, \quad (7.33) \]

where \( S \) is the matrix of eigenvectors.

Since these interacting modes can be thought of as normal modes of the dipole-dipole
Hamiltonian, we will need to construct a supercell that supports long wavelength, delocalized,
 modes. While performing this procedure in k-space will be investigated in future work, we present
the real-space construction in this work.

7.3.2.1 SUPERCELL

We now turn our attention to the construction of the supercell that is used to build \( C^\text{MBD} \) and \( \mathbf{T}_{\text{LR}} \).

Because the MBD theory seeks to model the dispersion energy through a set of coupled oscillators,
it is necessary to converge the MBD “polarization modes”. While we have no easy way to know
the longest possible normal mode present in the system, we have empirically observed 0.3 Å⁻¹ to
be the longest relevant wavelength. The longest described wavelength is computed as \( \frac{2\pi}{\min(\vert a \vert, \vert b \vert, \vert c \vert)} \).

If the longest wavelength normal mode described by the simulation cell is less than the desired
wavelength, a supercell is constructed from the simulation cell to capture the long wavelength
normal modes of \( C^\text{MBD} \). The supercell is constructed by tiling the simulation cell into the positive
octant as shown in Figure 7.2 c. The number of tilings in each direction are chosen by taking the
integer ceiling of the supercell cutoff $r_s$ divided by the lattice vector lengths:

\[
\begin{align*}
n_a &= \left\lceil \frac{r_s}{\|a\|} \right\rceil \\
n_b &= \left\lceil \frac{r_s}{\|b\|} \right\rceil \quad (7.34) \\
n_c &= \left\lceil \frac{r_s}{\|c\|} \right\rceil.
\end{align*}
\]

Some materials have marked anisotropy in terms of which crystallographic directions support collective dipole modes most strongly, often due to a layered structure. In graphite $\|c\|$ is larger than $\|a\|$, so this tiling scheme will result in more copies of the unit cell in the $ab$-plane. However, as the supercell size is increased, it will tend toward equal side-lengths, while maintaining the angular parameters of the simulation unit cell, in contrast to a spherical cutoff construction. Since we do not know \textit{a priori} which crystal directions will support the most important long wavelength normal modes, this tendency of the supercell toward equal side lengths is beneficial.

While we have no rigorous relationship between $r_s$ and the numerical uncertainty in the MBD energy, we have observed that $r_s$ values of $10-20$ Å are typically sufficient to converge the MBD energy to within about $10^{-4} E_h$ (10 meV) for 3D systems. However 2D systems, such as graphene, can support much longer wavelength collective dipole oscillations, and may require a $r_s$ as large as hundred Angstroms to appropriately resolve all modes. The drastic difference in required supercell size between two and three dimensions is attributed to the disorder that is introduced by coupling to the out-of-plane atoms.

Computation of the interacting energy proceeds by taking the screened static polarizability $\overline{\alpha}(0)$, the screened frequencies $\overline{\omega}$, and the converged long range dipole-dipole tensors to construct screened vdW radii and the MBD interaction matrix $C^{\text{MBD}}$ which is diagonalized to yield the interacting modes. The calculation of the interacting forces is split equally over each node according to the force-map described previously. Then forces are then synchronized to all nodes
7.3. Implementation

with an all-to-all summation. This corresponds to sending a single vector of $3N$ floating point numbers between all MPI-ranks, which is a negligible communication cost.

7.3.3 Generalize of Hirshfeld Implementation in QE

In QE and other condensed-phase simulation packages, the real space representation is typically restricted to the unit cell due to the translation symmetry. The free atomic density, however, is non-periodic and typically extends a radial distance (e.g. $\sim 4.2$ Å for Carbon) farther than a typical unit can encompass. Restricting the integration domain in Eq. (7.7), Eq. (7.12), and Eq. (7.15) to the unit cell $\Omega$ could be insufficient.

In this generalization, we choose a radius $R_d$ such that the sphere spanned by $R_d$ around each nucleus is sufficient to cover its free atomic density. From all periodic unit cell images

$$\Omega(n_a, n_b, n_c) = \{ r + n_a a + n_b b + n_c c | r \in \Omega \},$$

where $a$, $b$, and $c$ are lattice parameters and $n_a$, $n_b$, and $n_c$ integers representing a periodic cell image. We construct a sphere $S_d$ from the body center of the unit cell with radius $R_d$ and search for all of its overlapping periodic cell images $K$ such that for all $(n_a, n_b, n_c) \in K$, $\Omega(n_a, n_b, n_c)$ has non-vanishing overlap with $S_d$ and for all $(n_1, n_2, n_3) \notin K$, $\Omega(n_1, n_2, n_3)$ has vanishing overlap with $S_d$. The integration domain is then extended from the unit cell $\Omega$ to

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**Figure 7.2:** a) Lattice summation over the successive shells of the unit cell to converge $T_{SR}$. Periodic images of the central green atom are numbered with their shell index. b) Lattice summation over successive shells of a $2 \times 2$ supercell to converge $T_{LR}$. Periodic images of the atom marked in green are shown in yellow and numbered with their shell index. c) Schematic showing that a $3 \times 3$ supercell (grey) is built by tiling the unit cell (blue) into the positive octant, and will allow for longer wavelength normal modes.
cell to the union of all the overlapping periodic images generated by $K$. Such generalization then allows one to use unit cells much smaller than the size of the free atomic densities of its comprising atoms.

7.4 RESULTS

7.4.1 QUADRATURE CONVERGENCE

Using this scaling factor, we have explored the energy convergence as a function of number of quadrature points, taking as references the MBD correlation energy computed with 450 quadrature points. In Figure 7.3, we present a plot of the convergence.

![Figure 7.3: Convergence of the total MBD correlation energy as a function of the number of quadrature points. The energy converges to machine precision around 30 quadrature points.](image)

The correlation energy appears to converge to machine precision with approximately 30 quadrature points, with the rest of the fluctuations attributed to numerical noise. Indeed, to achieve convergence of $10^{-12}E_h$, we see that we only need 20 quadrature points. We recommend using 20 quadrature points because it presents a nice default balance of accuracy and efficiency, and have set this as the default value in the code. It may be desirable to use fewer quadrature points for larger clusters, or gas phase systems, where the Casimir-Polder integral is a more significant part of the computation cost.
7.4. Results

7.4.2 \( \delta \) Convergence

We present the convergence of our energy as a function of \( \delta \) in Figure 7.4. These numerical tests were run on a graphite unit cell with quadrature size, supercell cutoff, and DFT convergence thresholds kept constant for all calculations. The shoulder on the left-hand side of the figure corresponds to cutoffs that don’t add any new unit cells when converging \( T_{LR} \). After roughly a cutoff of \( \delta = 10^{-4} \), every order of magnitude of cutoff appears to yield an order of magnitude of energy accuracy. While we only present results for water, similar trends are seen in other systems. The implementation allows us to set a desired energy cutoff, and force the algorithm satisfy it. This stands in contrast to many previous schemes, which required the user to set a fixed cutoff distance heuristically. Our implementation has set \( \delta = 10^{-6} \) as the default cutoff, which is used unless otherwise stated.

![Figure 7.4: Absolute error in the total MBD correlation energy as a function of changing the max-norm cutoff \( \delta \) for a periodic simulation of strained water. The dotted line shows a linear relationship with slope 0.6.](image)

7.4.3 Supercell Convergence

The convergence with respect to the supercell size is more difficult to automate, however, because bigger unit cells cannot simply be added onto old ones as a test for convergence. This results in a significant adjustable parameter. We have explored the convergence of the MBD energy
as a function of super-cell size, and present the results for graphite in Figure 7.5.

![Graph showing convergence of total MBD correlation energy](image)

**Figure 7.5:** Convergence of the total MBD correlation energy as a function of supercell cutoff $r_s$ in graphite.

The results seem to indicate that the MBD energy approaches the correct value within $2 - 5 \times 10^{-3}$ $\text{E}_\text{h}$ within the first 10 Å tiling, but is still trending downwards. These fluctuations occur on the scale of hundredths of a milliHartree, which can usually be neglected. The super-lattice construct significantly increases the computational cost of the algorithm, because it both increases the number of dipole-dipole tensors to construct and the size of the matrix to diagonalize.

While this works for small to medium sized systems, we anticipate needing to implement distributed matrix operations if we want to continue to use a real-space construction and treat systems with more than 500 atoms. This is because computational and memory costs are dominated by the super-lattice interaction matrix. In future work we will explore k-point sampling of the energy instead of constructing the real-space supercell to converge these long range modes.

We previously asserted that this supercell construction dominates the computational cost of MBD in the condensed phase. We are now able to make this statement more concrete. Because the system is periodic, the tiled atoms will have the same polarizabilities and characteristic frequencies as their counterparts in the original unit cell. There are $N_{sc} = n_a \times n_b \times n_c \times N$ atoms in the supercell, where $N$ is the number of atoms in the unit cell and $N_{sc}$ is the number of atoms in the
7.5 Finite Difference: Ionic and Unit Cell Forces

supercell. Given that matrix diagonalization generally scale as $N^3$, the super-lattice construction carries an asymptotic computational cost of $\mathcal{O}(9N_{sc}^3)$ and a memory cost of $\mathcal{O}(9N_{sc}^2)$. The memory cost for the ionic forces on the $N$ atoms in the original unit cell is then $\mathcal{O}(9N_{sc}^2 \times 3N)$. For moderately sized systems, this memory cost is not a problem for our implementation when run on computer clusters with 32GB or more of available memory per node. This memory cost can represent a significant problem for smaller computer clusters.

7.5 Finite Difference: Ionic and Unit Cell Forces

To demonstrate the correctness of our implementation, we compare the analytically computed MBD ionic forces those computed with a two point central difference stencil, and a finite displacement of $10^{-4}$ a.u. We present results in Table 7.1 for a graphite system. These calculations were performed with a kinetic energy cutoff of $E_{\text{cut}} = 80$ Ry on a 4 atom graphite unit cell with experimentally derived unit cell parameters.

In Table 7.2 we present a comparison of our analytical gradients to the finite differenced values for an example graphite. As before, we computed these with a two point central difference stencil and a finite displacement of $10^{-4}$ a.u. These calculations were performed with $E_{\text{cut}} = 80$ Ry on a 4 atom graphite unit cell with experimentally derived unit cell parameters. The finite differences of the unit cell parameters require not only perturbing the unit cell vectors, but also scaling the nuclear positions by the new, perturbed, unit cell vectors. This was done by storing the fractional coordinates, and converting back to the Cartesian representation after perturbation.
Chapter 7. Self-consistent Calculation of the Ionic Forces and Unit Cell Stresses for the Many-Body Dispersion Model

Table 7.1: Comparison between the MBD ionic forces in graphite computed with finite differences (FD) and analytically (A). The difference between them is given as $\Delta \equiv F_A - F_{FD}$. All force components are stated in Hartree atomic units. The finite differences were computed using a two point central difference, and a displacement of $10^{-4} \ a_0$. The $s$ index corresponds to the atom being perturbed, and the $i$ index corresponds to the Cartesian direction of displacement.

<table>
<thead>
<tr>
<th>s</th>
<th>i</th>
<th>Finite Difference</th>
<th>Analytic</th>
<th>$\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>4.7611E-006</td>
<td>4.7620E-006</td>
<td>5.3E-011</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>8.2142E-006</td>
<td>8.2141E-006</td>
<td>4.6E-011</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>0.0000</td>
<td>3.2136E-014</td>
<td>3.2E-014</td>
</tr>
<tr>
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<td>1</td>
<td>6.4397E-005</td>
<td>6.4397E-005</td>
<td>4.6E-011</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>4.8977E-005</td>
<td>4.8977E-005</td>
<td>8.4E-011</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>6.6613E-011</td>
<td>2.4900E-013</td>
<td>6.6E-011</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>4.7328E-006</td>
<td>4.7328E-006</td>
<td>4.3E-011</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>8.2326E-006</td>
<td>8.2326E-006</td>
<td>3.7E-011</td>
</tr>
<tr>
<td>3</td>
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<td>2.9710E-014</td>
<td>2.2E-011</td>
</tr>
<tr>
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<td>7.4614E-005</td>
<td>7.4614E-005</td>
<td>5.4E-011</td>
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<tr>
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<td>3.1280E-005</td>
<td>3.1280E-005</td>
<td>2.9E-011</td>
</tr>
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<td>3</td>
<td>4.4409E-011</td>
<td>2.7285E-014</td>
<td>4.4E-011</td>
</tr>
</tbody>
</table>

Table 7.2: Comparison between the MBD unit cell forces in graphite computed with finite differences (FD) and analytically (A). The difference between them is given as $\Delta \equiv F_A - F_{FD}$. All cell force components are stated in Hartree atomic units ($E_h = a_0$). The finite differences were performed with a two point central difference, and a displacement of $10^{-4} \ a_0$. The $s$ index corresponds to the cell parameter being perturbed, and the $i$ index corresponds to the Cartesian direction of displacement.

<table>
<thead>
<tr>
<th>s</th>
<th>i</th>
<th>Finite Difference</th>
<th>Analytic</th>
<th>$\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>2.3685E-003</td>
<td>2.3684E-003</td>
<td>1E-11</td>
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<td>2</td>
<td>3.0580E-003</td>
<td>3.0580E-003</td>
<td>2E-11</td>
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<tr>
<td>1</td>
<td>3</td>
<td>2.2204E-011</td>
<td>-4.0808E-015</td>
<td>-2E-15</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1.3676E-003</td>
<td>1.3676E-003</td>
<td>4E-11</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>2.5614E-003</td>
<td>2.5614E-003</td>
<td>5E-11</td>
</tr>
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<td>3</td>
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<td>4E-11</td>
</tr>
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<td>6.1401E-015</td>
<td>6E-15</td>
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<tr>
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<td>2</td>
<td>0.0000</td>
<td>-2.7180E-015</td>
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</tr>
<tr>
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<td>3</td>
<td>5.4211E-004</td>
<td>5.4211E-004</td>
<td>4E-11</td>
</tr>
</tbody>
</table>

We note excellent agreement between both the finite differenced and analytically calculated ionic and unit cell forces. With the exception of forces like $s = 4, i = 3$ for the ionic forces, or $s = 3, i = 2$ for the unit cell forces, which are both numerical zeros, we observe relative errors below of less than 0.01%. In fact, in most cases, the forces agree to all presented digits.
Our code is distributed with tests that will check the finite differences for every individual subroutine to identify when errors have been introduced, either through new development or numerical instabilities due to other libraries our code depends on.

### 7.5.1 Importance of Self Consistency

We begin by exploring the effects of applying MBD self consistently. We present the difference between the PBE+MBD self consistent density and the PBE density for the graphite unit cell in Figure [7.6](#). This density was computed with a cutoff energy of $E_{\text{cut}} = 120\text{Ry}$ with a convergence criterion of $10^{-8}\text{Ry}$.

![Graphite Unit Cell Diagram](image)

**Figure 7.6**: The relative difference between the PBE+MBD self consistent density and the PBE density for the graphite unit cell. We see electron density being “pushed” into the inter-layer region of space. This difference density integrates to $0.05e^{-}$ of charge.

We first integrated the difference density, and found that MBD “pushes” $0.05\ e^{-}$ into the inter-layer region. This is not an insignificant change and can renormalize the Hartree contribution, which changed from 13.37173769\text{Ry} when computed with MBD applied self consistently to 13.35427157\text{Ry}. While a 0.1% change in the Hartree contribution is small, it represents energetic changes significantly larger than the convergence threshold.

In Table [7.4](#) that self consistency matters in computing the unit cell stresses.
Chapter 7. Self-consistent Calculation of the Ionic Forces and Unit Cell Stresses for the Many-Body Dispersion Model

<table>
<thead>
<tr>
<th>s</th>
<th>i</th>
<th>SC</th>
<th>NonSC</th>
<th>Δ</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>1</td>
<td>2.82899E-03</td>
<td>2.82624E-03</td>
<td>2.8E-06</td>
</tr>
<tr>
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<td>1.23009E-05</td>
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<tr>
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<td>3</td>
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<tr>
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<td>3.27374E-03</td>
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<tr>
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<tr>
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</tr>
<tr>
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<td>3</td>
<td>5.13030E-04</td>
<td>5.10240E-04</td>
<td>2.8E-06</td>
</tr>
</tbody>
</table>

**Table 7.3:** Comparison between the MBD unit cell forces in graphite when computed with MBD applied self consistently (SC) and non-self consistently (NonSC). The difference between them is given as $\Delta \equiv F_{SC} - F_{NonSC}$. All cell force components are stated in Hartree atomic units ($E_h/a_0$).

We observe agreement to within $10^{-6}E_h$ for graphite with the exception of element (2,2). In spite of the fact that most of the observed errors are on the order of $10^{-6}$, we observe that this still represents approximately a 0.1% relative error. With this in mind, we recommend that all optimizations be performed with MBD applied self consistently.

### 7.5.2 Importance of Self $\partial V_{eff}$

It has frequently been argued that neglecting the implicit dependence of the Hirshfeld volumes on the both unit cell vectors and ionic coordinates is a valid approximation. Given that computing the gradients of the Hirshfeld volumes is multiple orders of magnitude more expensive than computing the Hirshfeld volumes themselves, it would be advantageous to be able to neglect the implicit dependence. In Table 7.4, we present a comparison of the unit cell forces when with and without the implicit dependence taken into account.
7.5. Finite Difference: Ionic and Unit Cell Forces

<table>
<thead>
<tr>
<th>s</th>
<th>i</th>
<th>Full</th>
<th>(\partial V_{eff} = 0)</th>
<th>(\Delta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>2.82624E-03</td>
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<tr>
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<td>0.0</td>
<td>1.2E-05</td>
</tr>
<tr>
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<td>0.0</td>
<td>9.7E-09</td>
</tr>
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<td>-1.76000E-08</td>
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<td>1.8E-09</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>1.76000E-08</td>
<td>0.0</td>
<td>1.8E-09</td>
</tr>
<tr>
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<td>3</td>
<td>5.10240E-04</td>
<td>3.80387E-4</td>
<td>1.3E-04</td>
</tr>
</tbody>
</table>

Table 7.4: Comparison between the MBD unit cell forces in graphite when computed with all implicit derivatives, referred to as the “full derivative”, and with \(\partial V_{eff} = 0\). The difference between them is given as \(\Delta \equiv F_{\text{Full}} - F_{\partial V_{eff}=0}\). All cell force components are stated in Hartree atomic units \((E_h/a_0)\).

We observe that such neglect can result in relative errors as large as 50%. While this is only one system, this matches well with the results from similar gas-phase studies. Because of this, we recommend always computing the full implicit dependence, and have set this as the default value in our implementation.

7.5.3 Unit Cell Optimizations: Graphite

We have chosen to study the graphite unit cell because it is a crystal made of two dimensional graphene layers almost entirely held together by dispersion interactions. Because of this, the unit cell of graphite is difficult to obtain from first principles calculations. In fact, functionals like PBE predict that graphite will spontaneously exfoliate into individual graphene sheets. Recently it has been shown that by including the dispersion effects through the Random-Phase Approximation, it is possible to obtain a unit cell in good agreement with the experimental one. Since MBD is formally equivalent to RPA, this suggests that MBD is capable of capturing such effects as well.

We have performed this optimization with PBE+MBD with MBD applied self consistently, using a cutoff energy of 120\(R_y\), a 10\(\AA\)MBD supercell, and \(\delta = 10^{-6}\). The optimization was performed using BFGS, with a target pressure of 0.0kPa, and a convergence threshold of 10\(^{-3}\) kPa.
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Because Graphite can be pictured as an “A-B” stacked set of graphene sheets, the only significantly variable unit cell parameter is the layer spacing. We present these results in Table 7.5.

<table>
<thead>
<tr>
<th>Method</th>
<th>d(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp</td>
<td>3.3360(5)</td>
</tr>
<tr>
<td>PBE+MBD</td>
<td>3.36</td>
</tr>
<tr>
<td>PBE+RPA</td>
<td>3.34</td>
</tr>
<tr>
<td>PBE+TS</td>
<td>3.38</td>
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<td>PBE+D2</td>
<td>3.23</td>
</tr>
<tr>
<td>PBE</td>
<td>4.90</td>
</tr>
</tbody>
</table>

Table 7.5: Comparison between the recovered layer spacing in the graphite unit cell.

We are encouraged by the fact that PBE+MBD provides answers in good agreement with experiment and RPA, while being significantly cheaper than RPA. We do observe a minor contraction in the unit cell, and we attribute this to the lack of temperature in our geometry optimization in comparison to the X-Ray crystal structure which was taken at 4.2K.

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the STC Center for Integrated Quantum Materials, NSF Grant No. DMR-1231319. All opinions expressed in this paper are the authors’ and do not necessarily reflect the policies and views of DOE, ORAU, ORISE, or NSF.
Towards an Efficient Implementation of Range-Separated Many-Body Dispersion Model of Noncovalent Interactions in Condensed Phase Systems

This work will be submitted for publication with modifications as:


‡ These authors contributed equally to this work.

8.1 INTRODUCTION

Correctly describing dispersion interactions in molecular and condensed phase has proven to be vital in describing the energetics, structure, and function of systems as diverse as peptide complexes, super-molecular complexes, organic crystals, and stacked monolayers. In fact, due to the scaling of dispersion interactions with system size and asymptotic behavior, they can be important for modeling many condensed phase materials. In the London description of dispersion, dispersion interactions arise from the correlated electronic motion resulting in
8.1. Introduction

instantaneous attractive dipole forces.

Given their importance, any theoretical technique used to model materials where dispersion interactions could be present should be capable of providing an accurate description of dispersion. While wavefunction techniques such as configure interaction or coupled cluster can provide such a description, their computational cost and scaling preclude their application from all but the smallest molecules. Density functional theory (DFT), by contrast, is computationally efficient and computational cost can scale linearly with system size. Unfortunately, treating dispersion interactions within the DFT framework has proven difficult due to their highly delocalized, correlated, and long-range nature. In an effort to ameliorate such a failing, it is common to add a correction to the energy at the end of a DFT calculation. The most popular of such approaches is the addition of an empirical pairwise correction.

However, due to the many-body character of many dispersive interactions, especially in condensed phase, pairwise methods frequently provide an incomplete description of the relevant physics\(^{296}\). For example, pairwise methods will fail to capture the many-body nature for a 2D system such as graphene with a large delocalized \(\pi\)-system. The many-body dispersion (MBD) method of Tkatchenko \textit{et al.} provides a way forward by modeling these fluctuations through the construction of an auxiliary harmonic oscillator system\(^{273,279,280}\). Then, the dispersion energy is given by the correlation energy of the harmonic oscillator system. Consequently, the method has cubic asymptotic scaling – the same asymptotic scaling as empirical methods intended to capture three-body interactions.

To date, MBD has proven to be remarkably successful for describing the energetics of various molecules and materials. We have recently presented an implementation of the relevant analytical ionic gradients, cell gradients, and wavefunction forces of the MBD energy in both solid state and gas phase\(^3\). For systems such as a tri-peptide complex, MBD provided accurate corrections to the
geometry in agreement with the geometries obtained from MP2. Beyond this, for graphite, PBE+MBD obtained a graphite unit cell which was in agreement with experimental data.

Motivated by the previous successes of MBD for both accurately describing energetics and optimizations, we have worked to make the method more efficient and thus, applicable, to a broader class of systems. In the present work we describe an efficient implementation of the MBD energy and analytical ionic gradients, cell gradients, and wavefunction forces. Our implementation makes use of Ewald summation and reciprocal space sampling to provide significant computational savings over our previous supercell based implementation.

The remainder of this paper is organized as follows: In Section II we provide a brief introduction to the theory of MBD and describe our reciprocal space sampling and Ewald summation modifications to the theory; Section III contains a derivation of the MBD forces, unit cell vectors, and wavefunction forces; Section IV presents results of detailed convergence studies; Section V presents unit cell optimization results; and Section VI summarizes our conclusions and further research.

8.2 Theory: MBD Energy

The MBD model treats the dipole oscillations, which provide the basis for the London picture of dispersion, as a set of coupled quantum harmonic oscillators (QHO). Each atom has a single QHO with unit charge, a characteristic frequency, a scalar dipole polarizability, and they interact through the Coulomb interaction. In our parameterization, the polarizability plays the role of the mass for each QHO. These parameters are found by weighting the free-atom parameters by the Hirshfeld volumes. This Hirshfeld based parameterization provides an ab initio framework for selecting the parameters for the MBD model to make it quantitatively accurate. The effects of local electrodynamic screening and the anisotropy of the chemical environment are included in the
MBD model by solving the Dyson-like self consistent screening equation to compute the screened
dynamic polarizabilities. These dynamic polarizabilities are used to compute screened atomic
quantities, which parameterize the MBD Hamiltonian. The dispersion energy is then given by
taking the difference in the zero-point energies of the interacting and non-interacting oscillator
systems.

Our modifications to the MBD model only affect the long-range contribution and the interacting
energy. We refer the reader to Refs. [276,280] for a detailed discussion of the MBD model and Refs.
[5] for a detailed derivation of the MBD forces, including both the self consistent screening and
range separation aspects of the theory. In the remainder of this section we provide a brief
introduction to the MBD model, with a thorough discussion of our modifications to the model. Our
proposed modifications leave the model epistemologically unchanged, and provide significant
computational savings to make a wide range of materials simulatable that were previously out of
reach.

Throughout this manuscript, all equations are given in Hartree atomic units with vector, matrix,
and tensor quantities typeset in bold typeface. For example, the nuclear position vector will be
typeset as \( \mathbf{r} \), whereas the norm of the nuclear position vector will be typeset as \( r \). We will use the \( \mathbf{r \cdot r} \)
notation to indicate outer products. For periodic summation, we use the vector \( \mathbf{g} \), such that

\[
\mathbf{r}_{AB} = \mathbf{r}_A - \mathbf{r}_B + \mathbf{g},
\]

where \( \mathbf{r}_A \) is the nuclear position vector for atom \( A \), \( \mathbf{r}_B \) is the nuclear position vector for atom \( B \), and
\( \mathbf{g} \) is the periodic summation vector given by

\[
\mathbf{g} = \mathbf{a} \mathbf{n}.
\]
We will use the notation that \( \mathbf{a} \) is the matrix of lattice vectors with each lattice vector as a column, and \( \mathbf{n} \) is periodic index in each lattice vector direction. We will have two different reciprocal space vectors, \( \mathbf{q} \) and \( \mathbf{G} \); \( \mathbf{q} \) corresponds vectors sampled from the first Brillouin zone of which there are an uncountably infinite number of vectors, and \( \mathbf{G} \) corresponds to vectors sampled from all but the first Brillouin zone of which there are a countably infinite number of vectors. Both \( \mathbf{q} \) and \( \mathbf{G} \) are constructed through linear combinations of reciprocal space vectors. The symbol \( \mathbf{i} \) denotes the unit imaginary number, \( \mathbf{I} \) denotes the identity tensor, \( \delta_{ij} \) is the Kronecker delta for indices \( i \) and \( j \), and \( \delta(x) \) is the “Dirac delta function”, which will treat as an indicator function. Finally, a bar over top a quantity such as \( \bar{\alpha}_A(i\omega) \) indicates that this is a screened polarizability.

The MBD procedure begins by weighting free-atom quantities by the ratio of Hirshfeld volumes to free atom volumes. From this weighting procedure, we can get approximate polarizabilities, frequencies, and van der Waals radii. We term these weighted quantities “Tkatchenko-Scheffler” quantities, indicated by a superscript \( TS \), because they are the starting point for the Tkatchenko-Scheffler method\(^{[83]} \). The MBD model starts with \( TS \) level data and screens it by solving a Dyson-like self consistent screening equation to obtained screened dynamic polarizabilities, \( \bar{\alpha}(i\omega) \), for each QHO

\[
\bar{\alpha}_A(i\omega) = \alpha_A^{TS}(i\omega) - \sum_B \alpha_A^{TS}(i\omega) T_{AB}^{SR} \bar{\alpha}_B(i\omega),
\]

(8.3)

where \( T_{AB}^{SR} \) is the short range screened dipole-dipole tensor. We refer the reader to Ref.\(^{[280]} \) for a more detailed discussion of \( T_{AB}^{SR} \). By inverting the 0/2 - order Padé approximant to the Casimir-Polder integral we have that \( \bar{\omega}_A \) is given by

\[
\bar{\omega}_A = \frac{4}{\pi} \int_0^\infty \frac{\bar{\alpha}_A(i\omega)^2 d\omega}{\bar{\alpha}_A(0)^2},
\]

(8.4)
where $\bar{\alpha}_A(i\omega)$ is the frequency dependent scalar dipole polarizability given in Eqn. (8.3). With the screened frequencies and polarizabilities in hand, we can calculate the energy of the “non-interacting” QHO system given by:

$$E_{\text{non-int}} = -\frac{3}{2} \sum_i \bar{\omega}_i.$$  \hfill (8.5)

The energy of the “interacting” QHO system is given by diagonalizing the MBD Hamiltonian

$$H = \sum_A \frac{1}{2} \nabla_{\xi_A}^2 + \sum_A \frac{1}{2} \bar{\omega}_A^2 \xi_A^2 + \frac{1}{2} \sum_{AB} \bar{\omega}_A \bar{\omega}_B \sqrt{\bar{\alpha}_A(0)\bar{\alpha}_B(0)} \xi_A T_{AB} \xi_B,$$  \hfill (8.6)

where $\xi_A$ defines the coordinate of motion for oscillator $A$ and $T$ is the dipole-dipole coupling matrix. It is convenient to project the Hamiltonian into the basis of the non-interacting Gaussians, giving the matrix elements

$$C_{AB} = \delta_{AB} \omega_A^2 + (1 - \delta_{AB}) \omega_A \omega_B \sqrt{\bar{\alpha}_A(0)\bar{\alpha}_B(0)} T_{AB}.$$  \hfill (8.7)

The computation of the MBD energy, then, reduces to a single matrix diagonalization. Because the MBD model treats the electronic system as a set of coupled harmonic oscillators, we compute all orders of dipole-dipole interaction by considering only dipole-dipole interactions through exact diagonalization. This is because the result of the diagonalization provides the polarization equivalent of “normal modes,” which we refer to as polarization waves.

Given that matrix diagonalization scales as $O(N^3)$, where $N$ is the number of atoms, this is an efficient procedure when compared with techniques like random phase approximation based functionals. In gas phase, this matrix diagonalization is the limiting step. In solid state, however, both converging the dipole tensors and the polarization waves by constructing super cells can make the MBD calculations cost-prohibitive. In this paper, we will provide techniques to alleviate these
computational bottle necks. The convergence of the dipole-dipole tensor will be handled by an Ewald transformation, and the convergence of the polarization waves will be treated by sampling in the first Brillouin Zone.

We first turn our attention to the Brillouin sampling of the MBD Hamiltonian to converge the polarization modes. By applying Bloch’s theorem to the Hamiltonian given in Equation (8.6), we obtain:

\[
H(q) = \sum_A \frac{1}{2} \nabla_A^2 + \sum_A \frac{1}{2} \omega_A^2 \xi_A^2 + \frac{1}{2} \sum_{AB} \omega_A \omega_B \sqrt{\alpha_A(0) \alpha_B(0)} \xi_A T_{AB}(q) \xi_B. \tag{8.8}
\]

If we perform the same projection as before, we obtain matrix elements

\[
C_{AB}(q) = \delta_{AB} \omega_A^2 + (1 - \delta_{AB}) \omega_A \omega_B \sqrt{\alpha_A(0) \alpha_B(0)} T_{AB}(q), \tag{8.9}
\]

which are now dependent on the reciprocal space vectors. The only \(q\) dependent quantity is the dipole-dipole tensor

\[
T_{AB}(q) = \sum_g T_{AB}^g e^{-i q \cdot (r_A - r_B + g)}, \tag{8.10}
\]

Our dipole-dipole tensor can be understood as a Bloch-weighted dipole-dipole tensor. This Hamiltonian is then diagonalized at every \(q\)-point, and the energy summed to allow the integration over the entire first Brillouin zone.

\[
E_{\text{int}} = \frac{1}{N_q} \sum_q E_{\text{int}}(q). \tag{8.11}
\]

Instead of creating a supercell, which carries a computational cost of \(\mathcal{O}(N^3(n_1 n_2 n_3)^3)\), where \(n_i\) is the size of the supercell in each direction, the reciprocal implementation carries a computational
cost of \((O)(N^3N_q)\), where \(N\) is the number of atoms and \(N_q\) is the number of vectors sampled in the reciprocal space. For small to medium unit cells, this represents a considerable computational savings.

We next turn our attention to the use of Ewald summation in the MBD model. Aside from converging the super-lattice, the other computationally intensive step in converging the MBD model is converging the pairwise dipole-dipole tensor in real-space. We have empirically observed that dipole cutoffs of 200 Å can be required to converge the MBD energy to \(10^{-6} \text{E}_h\). Given that the dipole-dipole tensor is only conditionally convergent, and because there are a cubically growing number of periodic images to sum over, the construction of a converged dipole-dipole tensor can represent as much as 40% of the overall run time for many of the crystals in the X23 set.

We accelerate this periodic summation through the Ewald summation procedure. The Ewald summation procedure divides the infinite periodic real-space summation of dipoles into two parts, one quickly converging real-space summation, and a second quickly converging reciprocal space summation. By summing the long-range contributions in the Fourier domain, we have greatly reduced the computational cost of converging the dipole-dipole tensor. Because the summation of dipoles does not explicitly converge in reciprocal space, it is necessary to perform the reciprocal space summation over Gaussian charge clouds, and the real-space summation over the point-dipoles minus the Gaussian clouds. This amounts to adding and subtracting the same value in two different representations.

The full expression for the dipole-dipole summation is given by:

\[
T_{AB}(q) = \sum_{|\mathbf{g}|<R_c} \left( \frac{r^2 I_B(r, \sigma) - 3rrC(r, \sigma)}{r^3} \right) e^{-i\mathbf{q} \cdot \mathbf{r}} + (f(r) - 1) \left( \frac{r^2 I - 3rr}{r^3} \right) e^{-i\mathbf{q} \cdot \mathbf{r}}
\]

\[
+ \frac{4\pi}{V_{uc}} \sum_{|\mathbf{G}|<G_c} (1 - \delta(k)) \mathbf{k} \mathbf{k} e^{-\frac{r^2}{4\epsilon^2} - i\mathbf{G}\cdot\mathbf{R}_{AB}} - \frac{4\beta^3}{3\sqrt{\pi}} \delta_{AB} \mathbf{I} + \frac{4\pi}{3V_{uc}} \mathbf{I} \delta(q),
\]

(8.12)
where $\delta(x)$ is understood as the Dirac delta. While not formally correct, the function operates as an indicator function over the norm of the reciprocal vector. Stated concretely, $\delta(q) = 1$ when $q = 0$ and 0 for all other values. The functions $B(r, \sigma)$ and $C(r, \sigma)$ are defined as

$$B(r, \sigma) = \text{Erfc}(\sigma R) + \frac{2\sigma R}{\sqrt{\pi}} e^{-\sigma^2 R^2}$$

(8.13)

$$C(r, \sigma) = 3\text{Erfc}(\sigma R) + \frac{2\sigma R}{\sqrt{\pi}} \left(3 + 2(\sigma R)^2\right) e^{-\sigma^2 R^2}.$$  

(8.14)

The $\sigma$ parameter, which controls the size of the Gaussian charge clouds, as well as the cutoff values $R_c$ and $G_c$ are given by

$$\sigma = \frac{2.5}{(V_{uc})^{1/3}},$$

(8.15)

$$R_c = \frac{6}{\sigma},$$

(8.16)

$$G_c = 10\sigma,$$

(8.17)

with $V_{uc}$ is defined as the unit cell volume, found by taking the determinant of the unit cell vector matrix. Finally, the reciprocal space vector that allows us to perform both reciprocal space sampling in the first Brillioun zone and reciprocal space summation for the Ewald summation is given by:

$$\hat{k} = \frac{G + q}{||G + q||}.$$  

(8.18)

Ewald summation always results in a crystal with metallic boundary conditions, which requires us to add the surface charge given by $4\pi/3V_{uc}$. The Ewald summation procedure presented above is written in generality for arbitrary $q$. If one desires to perform a non-reciprocal space calculation with Ewald summation, the $e^{-i\mathbf{q} \cdot \mathbf{r}}$ factor simply reduces to 1.
8.3 Theory: MBD Forces

With the energy defined, we now turn our attention to the gradients of the MBD energy. There are three possible gradients to compute: the gradient with respect to the ions, cell parameters, and electronic density. From the ion and cell gradients, we can relax the ions and unit cells, perform variable-cell molecular dynamics, or compute stresses. The derivative with respect to the electron density is understood as the dispersion potential, and can be added point-wise to the existing Kohn-Sham potential. By adding this correction at every self consistent field (SCF) step, we ensure that the density obtained is the fixed point of the full DFT+MBD Hamiltonian. Without this correction, we have observed forces and cell stresses require additional terms in addition to the Hellman-Feynman term to match finite differentiation.

With the energy expression given in Equation (8.11), the matrix elements given in Equation (8.9), and the Ewald summed dipole-dipole tensor given in Equation (8.12), we now turn our attention to the gradient expressions. We begin with the reciprocal space sampling and its effect on the gradients. Because the total interacting energy given in Equation (8.11) is found by summing together the q-point dependent energies, and differentiation is linear, the gradient will take the form:

\[
\partial E_{\text{int}} = \frac{1}{N_q} \sum_q \partial E_{\text{int}}(q)
\]

\[
= \frac{1}{N_q} \sum_q \sum_i \left[ S^\dagger \partial C_{ab}(q) S \right]_{ii},
\]

where \( S \) is the matrix of eigenvectors, and \( \{ \lambda_i \} \) is the set of eigenvalues. The explicit \( q \) dependence of \( C_{ab}(q) \) through an application of Bloch’s theorem to the dipole-dipole tensor. Using Equation

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we can express the derivative as:

$$\partial C_{AB}(q) = \delta_{AB} 2 \omega_A \partial \omega_B + (1 - \delta_{AB}) \left( (\bar{\omega}_A \bar{\omega}_B + \bar{\omega}_A \partial \bar{\omega}_B) \sqrt{\bar{\alpha}_A(0)\bar{\alpha}_B(0)} T_{AB}(q) \right. \right.$$  \(8.21\)

$$\left. - \bar{\omega}_A \partial \bar{\omega}_B \frac{(\partial \bar{\alpha}_A(0) \bar{\alpha}_B(0) + \bar{\alpha}_A(0) \partial \bar{\alpha}_B(0))}{2 \sqrt{\bar{\alpha}_A(0)\bar{\alpha}_B(0)}} T_{AB}(q) + \bar{\omega}_A \partial \bar{\omega}_B \sqrt{\bar{\alpha}_A(0)\bar{\alpha}_B(0)} \partial T_{AB}(q) \right).$$

Note, the only difference between this derivative and the previously reported reported derivatives is the presence of a \(q\) dependent dipole-dipole tensor. By taking the derivative of Equation (8.10), we observe that

$$\partial T_{AB}(q) = \sum_g \partial \left( T_{AB}^g \right) e^{-i q \cdot r_{AB}} - i \left( \partial q \cdot r_{AB} + q \cdot \partial r_{AB} \right) T_{AB}^{0g}.$$

(8.22)

where the superscript \(g\) is the vector sum index. The derivatives of \(T\) and \(R_{AB}^g\) have been previously reported and will not be reproduced here. The only remaining derivative is that of the reciprocal space vector. Clearly, \(q\) is invariant under ionic motion, which yields

$$\frac{\partial q}{\partial R_i^g} = 0.$$  \(8.23\)

Because \(q\) depends on the unit cell vectors, we observe that

$$\frac{\partial q^l}{\partial h_{\gamma,\tau}} = q^l a_{\gamma,j} \frac{q^j a_{\tau,i}}{2\pi},$$

(8.24)

where \(a\) is the matrix of unit cell vectors. We also note that the

$$\frac{\partial q^l}{\partial n(r)} = 0.$$  \(8.25\)

With these derivatives defined, we have provided a complete description of the information.
required to compute all MBD gradients with the standard dipole-dipole tensor that is converged through real-space summation.

We next turn our attention to the derivative of the Ewald summation version of the dipole-dipole tensor. Using the gradient of the matrix elements defined in Equation (8.21), we observe that because Ewald summation only changes the dipole-dipole tensor, the only new gradient to consider is that of the dipole-dipole tensor. To express the derivative, we first reformulate Equation (8.12) as

\[
T_{AB}(q) = \sum_{|g|<R_c} \Gamma(g) \frac{4\pi}{V_{uc}} \sum_{|G|<G_c} \Phi(G) - \Xi \delta_{AB} I + DI \delta(|q|). \tag{8.26}
\]

Using this definition, we see that

\[
\partial T_{AB}(q) = \sum_{|g|<R_c} \partial \Gamma(g) + \partial \left( \frac{4\pi}{V_{uc}} \sum_{|G|<G_c} \Phi(G) \right)
+ \frac{4\pi}{V_{uc}} \sum_{|G|<G_c} \partial \Phi(G) - \partial \Xi \delta_{AB} I + \partial DI \delta(|q|). \tag{8.27}
\]

Starting from left to right, we first observe that the gradient of \( \Gamma \) is given by:

\[
\partial \Gamma = \left( \frac{r I(2\partial r B(r, \sigma) + r \partial B(r, \sigma) \cdot r)}{r^5} - 3(\partial rr + r \partial r) C(r, \sigma) - 3rr \partial C(r, \sigma) \right) - 5\partial r \frac{r^2 B(r, \sigma) - 3rr C(r, \sigma)}{r^6}
+ \partial f(r) \frac{r^2 I - 3rr}{r^5} + (f(r) - 1) \left( \frac{2r \partial r I - 3r \partial r}{r^5} - 5\partial r \frac{r^2 I - 3rr}{r^6} \right) e^{-iq \cdot r} - i(\partial q \cdot r + q \cdot \partial r) \Gamma \tag{8.28}
\]

where \( \partial r \) and \( \partial r \) have been previously reported, \( \partial q \) is reported in Equation (8.19), \( \partial B(r, \sigma) \) is given by

\[
\partial B(r, \sigma) = -\frac{4}{\sqrt{\pi}} e^{-\frac{\sigma^2}{2}} \frac{\partial}{\partial r} e^{\frac{\sigma^2}{2}r^2} (\partial \sigma r + \sigma \partial r). \tag{8.29}
\]
and $\partial C(r, \sigma)$ is given as

$$\partial C(r, \sigma) = -\frac{8\sigma^4 r^4 e^{-\sigma^2 r^2} (\partial \sigma r + \sigma \partial r)}{\sqrt{\pi}}. \quad (8.30)$$

Using the definition of $\sigma$ given in Equation (8.15), we observe that

$$\partial \sigma = -\frac{2.5}{3(V_{UC})^{4/3}} \partial V_{UC}, \quad (8.31)$$

where $\partial V_{UC}$ for the ionic and cell gradients is given by

$$\frac{\partial V_{uc}}{\partial R_i} = 0 \quad (8.32)$$

and

$$\frac{\partial V_{uc}}{\partial a_{\gamma, \sigma}} = -V_{uc} a_{\gamma, \sigma}^{-1}. \quad (8.33)$$

To compute the derivative of the second term in Equation (8.27), we first need to consider the derivative of the prefactor, which is given by

$$\partial \left(\frac{4\pi}{V_{UC}}\right) = -\frac{4\pi}{V_{UC}^2} \partial V_{UC}. \quad (8.34)$$

Turning our attention to $\partial \Phi(G)$, we observe that the gradient is given by

$$\partial \Phi(G) = (\partial \hat{k} \hat{k} + \hat{k} \partial \hat{k}) e^{-\frac{i}{8\beta} e^{-iG \cdot r}} + \hat{k} \hat{k} \left(\frac{-8\beta^2 k \partial k + 8k^2 \beta \partial \beta}{18\beta^4}\right) e^{-\frac{i}{8\beta} e^{-iG \cdot r}} \quad (8.35)$$

$$-\hat{k} \hat{k} e^{-\frac{i}{8\beta} e^{-iG \cdot r}} (\partial G \cdot r + G \cdot \partial r),$$

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where $\partial G$ is calculated using Equations (8.25) and (8.24), $\partial q$ is given by

$$
\frac{\partial q}{\partial a_{\gamma,\tau}} = \frac{q\sum q' a_{\tau,i}}{2\pi q},
$$

(8.36)

$$
\frac{\partial q}{\partial R_i} \equiv 0,
$$

(8.37)

and

$$
\frac{\partial \hat{q}}{\partial R_i} \equiv 0,
$$

(8.38)

$$
\frac{\partial \hat{q}}{\partial a_{\gamma,\sigma}} = \frac{q\partial q - q\partial q}{q^2}.
$$

(8.39)

With the above derivatives, we have defined all the required components to implement the nuclear, ionic, and self-consistent gradients for the reciprocal space implementation using either real-space or Ewald summation to converge the dipole-dipole tensor.

8.4 Results

8.4.1 MBD Band Structures

Using the $q$-dependent MBD energy expression defined in Equation (8.11), we can plot the a band structure for the MBD Hamiltonian. This band structure provides us with insight into the $q$ dependence of the MBD energy. We can interpret this as the dispersion relationship of the MBD quasi-particles, which we term a “disperon.” In Figure 8.1 we present the band structures for graphene and the argon crystal.
Chapter 8. Towards an Efficient Implementation of Range-Separated Many-Body Dispersion Model of Noncovalent Interactions in Condensed Phase Systems

Figure 8.1: The MBD band structures for (a) graphene and (b) argon crystal. We note that for both graphene and argon, we observe what looks to be a Van Hove singularity.

Figure 8.2: The MBD band structures for (a) a linear argon chain and (b) two parallel linear argon chains.

We have plotted the band structure for an argon chain in Figure 8.2(a) and two parallel argon chains in Figure 8.2(b). We follow a linear path through the first Brillouin zone along the chain. The observed periodicity in Figure 8.2(a) is consistent with an atomic spacing of 2Å.

In all cases, we observe no obviously pathological states but find providing additional physical intuition difficult at this time. We note that we are unable to directly add the MBD band structure to the Kohn-Sham band structure, because the number of bands presented in each is different in general. Additionally, a quasiparticle basis needs to be in the right interaction basis, and we have no guarantee that the Kohn-Sham quasiparticles and disperons share such a basis.

The discontinuity at the $\Gamma$-point in the band structure of the argon crystal in Figure 8.2(b) is
interesting and warrants more study. At present, we have observed that including the Γ-point in crystal calculations can make calculations far more difficult to converge. If, instead, one were to add a constant shift to the Γ, we are able to skip such a discontinuity and therefore achieve convergence more readily.

8.4.2 Convergence

We next explore the convergence properties of the MBD with respect to the number of reciprocal vectors used in Figure 8.3 and the real-space summation cutoff in Figure 8.4.

We first consider the convergence of the MBD energy with respect to the size of the unit cell or number of k-points considered. In Figure 8.3a, we observe that both the supercell and the reciprocal space procedure both appear to converge with similar behaviors. This appears to be a general behavior for 1D and 2D materials. In Figure 8.3b we see that the supercell procedure struggles to converge in the case of the 3D argon crystal, whereas the reciprocal space sampling procedure converges quickly. While not plotted, we note that the forces and stresses have very similar convergence statistics. In addition the reciprocal space sampling approach is significantly cheaper computationally because we only have \( N_q N^3 \), where \( N \) is the numbers of atoms in the unit cell and \( N_q \) is the number of q-points, calculations to perform instead of \( N_{sl}^3 \), where \( N_{sl} \) is the number of atoms in a super lattice. With the observed rapid rate of convergence, as well as the significantly reduced computational time, we recommend using the reciprocal sampling technique for all but the largest unit cells. As a typical rule of thumb, we have found that MBD typically requires the same q-point density as the underlying DFT.

We next explore the convergence of the MBD energy as a function of dipole-dipole cutoff when compared to the Ewald summed variant of MBD. In Figure 8.4 we plot the convergence for an argon crystal with dipole-dipole real-space cutoffs ranging from 0Å-400Å. We observe the hallmark oscillatory convergence behavior that characterizes conditionally convergent sums like
Figure 8.3: Plots of the convergence of the MBD energy as a function of number of cells included. In (a) we consider a graphene sheet, and in (b) we consider the argon crystal.

8.4.3 Finite Differences: Ionic and Unit Cell Forces

To demonstrate the correctness of our implementation, we compare the analytically computed MBD ionic forces those computed with a two point central difference stencil, and a finite displacement of $10^{-5}$ a.u. We present results in Table 8.1 for a phosphorus system. These calculations were performed with a kinetic energy cutoff of $E_{\text{cut}} = 100$ Ry on a 4 atom phosphorus unit cell with experimentally derived unit cell parameters.
8.4. Results

Figure 8.4: Plots of the convergence of the MBD energy as a function of the real-space dipole dipole cutoff. We present a plot of the energy as a function of dipole-dipole cutoff length for distances (a) 0Å-200Å (b) 200Å-400Å. We observe the hallmark oscillatory pattern we expect to see for dipole-dipole interactions.

<table>
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<th>$i$</th>
<th>Finite Difference</th>
<th>Analytic</th>
<th>$\Delta$</th>
</tr>
</thead>
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Table 8.1: Comparison between the MBD ionic forces in phosphorus computed with finite differences (FD) and analytically (A). The difference between them is given as $\Delta = F_A - F_{FD}$. All force components are stated in Hartree atomic units. The finite differences were computed using a two point central difference, and a displacement of $10^{-5} a_0$. The $s$ index corresponds to the atom being perturbed, and the $i$ index corresponds to the Cartesian direction of displacement.

In Table 7.2 we present a comparison of our analytical gradients to the finite differenced values.
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for an example phosphorus system. As in Table 8.1, we computed these with a two point central difference stencil and a finite displacement of $10^{-5}$ a.u. These calculations were performed with $E_{\text{cut}} = 80$ Ry on a 4 atom phosphorus unit cell with experimentally derived unit cell parameters. The finite differences of the unit cell parameters require not only perturbing the unit cell vectors, but also scaling the nuclear positions by the new, perturbed, unit cell vectors. This was done by storing the fractional coordinates, and converting back to the Cartesian representation after perturbation.

<table>
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<td>-1.29065043e-09</td>
<td>1.64916894e-12</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>-6.66133815e-12</td>
<td>-1.17667294e-17</td>
<td>6.66132638e-12</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>-1.28563826e-09</td>
<td>-1.29065044e-09</td>
<td>-5.01218195e-12</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>2.15978969e-02</td>
<td>2.15978966e-02</td>
<td>-3.22067251e-10</td>
</tr>
</tbody>
</table>

Table 8.2: Comparison between the MBD unit cell forces in phosphorus computed with finite differences (FD) and analytically (A). The difference between them is given as $\Delta \equiv F_{A} - F_{FD}$. All force components are stated in Hartree atomic units. The finite differences were computed using a two point central difference, and a displacement of $10^{-5}$ a.u. The $s$ index corresponds to the atom being perturbed, and the $i$ index corresponds to the Cartesian direction of displacement.

We note excellent agreement between both the finite differenced and analyticly calculated ionic and unit cell forces. With the exception of forces like $s = 2, i = 1$ for the ionic forces, or $s = 3, i = 1$ for the unit cell forces, which are both numerical zeros, we observe relative errors below of less than 0.01%. In fact, in most cases, the forces agree to all presented digits.

Our code is distributed with tests that will check the finite differences for every individual subroutine to identify when errors have been introduced, either through new development or numerical instabilities due to other libraries our code depends on.
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Calibration of the Many-Body Dispersion Range-Separation Parameter

Apart from minor modifications, this chapter originally appeared as:


Abstract

Recent work has shown that a fully many-body treatment of noncovalent interactions, such as that given by the method of many-body dispersion (MBD), is vital to accurately modeling the structure and energetics of many molecular systems with density functional theory (DFT). To avoid double counting the correlation contributions of DFT and the MBD correction, a single-parameter range-separation scheme is typically employed. Coupling the MBD correction to a given exchange-correlation functional therefore requires calibrating the range-separation parameter. We perform this calibration for 24 popular DFT functionals by optimizing against the S66×8 benchmark set. Additionally, we report a linear equation that predicts near optimal range-separation parameters, dependent only on the class of the exchange functional and the value of the gradient enhancement factor. When a calibrated MBD correction is employed, most of the exchange-correlation functionals considered are capable of achieving agreement with CCSD(T)/CBS interaction energies in the S66×8 set to better than 1 kcal/mol mean absolute error.
9.1 Introduction

Noncovalent interactions, ranging from hydrogen bonding to weak van der Waals (vdW) forces, present significant challenges to quantum chemical modeling. The difficulty arises due to their many-body quantum nature and small energy scales (typically 5-10 kcal/mol for hydrogen bonds, 1-2 kcal/mol for van der Waals forces). As a result, while approximate density functional theory (DFT) can often predict the thermochemistry of organic compounds dominated by covalent interactions to within 1 kcal/mol ("chemical accuracy"), accurate prediction of noncovalent interactions within DFT remains a challenging task. At the same time, these noncovalent interactions play an important role in the energetics, structure, and function of a wide range of systems, including intermolecular interactions between small molecules, intramolecular interactions in biomolecules, and various properties of condensed phase systems such as, molecular crystals, and vdW layered materials.

The accurate treatment of noncovalent interactions within the framework of DFT is vital for reaching the goal of chemical accuracy for an ever-larger set of experimentally relevant systems. Many different methodologies have been developed to approximately treat noncovalent interactions within the DFT framework. Following the classification scheme of Klimeš (Ref. 64), these differing approaches can be categorized into four levels of approximation: I, II, III, and IV. Level I methods involve no explicit correction for noncovalent interactions. Instead, they are parameterized to reproduce experimental data but provide incorrect asymptotics. Level II methods (generally termed “DFT-D”) correct DFT functionals with pairwise-additive corrections employing empirical parameters that minimize average errors across large calibration sets. While extremely computationally efficient and enormously popular, DFT-D methods fail to capture the true many-body nature of dispersion, such as the $N$-body dipole terms, electrodynamic response screening effects, and the non-additivity of the dynamic polarizability.
Indeed, examples of the failings of pairwise methods are numerous, and include incorrect conformer ordering of polypeptide α-helices and organic crystal polymorphs, and poor characterization of the cohesive properties of molecular crystals, among others. Level III consists of non-local kernel-based methods such as vdW-DF and VV10. While these methods get the asymptotic behavior correct, they are unable to capture the presence of dielectrics and still rely on subtle pairwise dipole approximations (see Ref. for an explanation of how pairwise approximations appear in non-local kernel methods). Level IV methods treat the pairwise, beyond pairwise, and screening interactions on equal footing, thereby allowing an accurate description of a wider range of dispersively dominated systems with a high degree of confidence. The many-body dispersion (MBD) method discussed herein is one of the most computationally efficient methods at this level of approximation.

The MBD method treats the beyond-pairwise nature of dispersion through a model Hamiltonian that models each atom as a quantum harmonic oscillator, which is fully coupled to other atoms by a screened dipole interaction. The long-range correlation energy is then calculated from the difference between the zero-point energy of the coupled oscillator system and that of the uncoupled oscillators. The procedure of diagonalizing the Hamiltonian of these coupled oscillators is equivalent (through the adiabatic-connection fluctuation-dissipation theorem) to the random-phase approximation (RPA) correlation energy in the dipole limit.

To date, the MBD model has only been applied as a correction to the PBE, PBE0, and HSE exchange-correlation functionals. While these functionals have proved generally successful for a broad range of systems, many functionals exist that have been specifically designed to perform well for specific classes of molecules, or specific chemical applications such as thermochemistry, kinetics, or spectroscopy. Like other dispersion corrections, the MBD model employs a damping function to avoid double counting the
9.2 The MBD Method

correlation energy at short-range where the exchange-correlation functional is expected to give a
good description of correlation. The MBD range-separation parameter, $\beta$, which determines the
range of the damping function must be tuned carefully for each functional because the short-range
behavior of the exchange-correlation potential (particularly the repulsive exchange wall) will
dramatically impact the shape of a binding curve. In this work we extend the applicability of the
MBD model to other functionals by performing this calibration. We present the optimal
range-separation parameter for MBD, as well as benchmark results, for 24 popular
exchange-correlation functionals.

9.2 The MBD Method

The following is a brief introduction to the theory and notation of the MBD model. All equations
are given in Hartree atomic units ($\hbar = m_e = e = 1$) with tensor quantities denoted by bold typeface.
We refer the reader to Ref. [5] for a more detailed derivation and discussion of the equations
presented below. The canonical London approximation for dispersion interactions describes small
instantaneous oscillations of the charge density that induce local dipoles. As these dipoles oscillate
about their equilibrium positions, they interact through the Coulomb interaction. With this picture
in mind, modeling these density oscillations with quantum harmonic oscillators (QHO) provides a
physically intuitive description. One QHO is centered on each atomic nucleus, parameterized with
a frequency-dependent scalar dipole polarizability, $\alpha_a(i\omega)$, and a characteristic frequency, $\omega_a$,
where $a$ is an atomic/nuclear index. Here, the polarizability plays the role of the QHO mass and
the characteristic frequency is directly related to the strength of the QHO potential. These
parameters are determined by reweighting reference atomic polarizabilities by the ratio of the
Hirshfeld atomic volume\textsuperscript{[297]} to the free atom volumes for each atom. This captures effects of the
local chemical environment without introducing adjustable parameters. This partitioning is in
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contrast to methods such as DFT-D3, which seek to capture the local chemical environment from the geometry alone by parameterizing coordination numbers. Purely geometric approaches miss important density-dependent changes to the polarizability that can occur from solvation or the presence of external electric fields.

In addition to local changes to the atomic static polarizabilities, electrodynamic screening and the anisotropy of chemical bonds are modeled by solving a Dyson-like self-consistent screening equation to compute screened dynamic polarizabilities, \( \overline{\alpha}_a(i\omega) \), for each QHO. Using these screened polarizabilities, we compute the corresponding screened characteristic frequency, \( \omega_a \), for each QHO by numerical evaluation of the Casimir-Polder integral and inversion of a 0/2-order Padé approximant\(^{[299]} \) to the frequency dependence of the scalar dipole polarizability

\[
\omega_a = \left( \frac{4}{3} \left( \frac{1}{\overline{\alpha}(0)} \right)^2 \right) \left( \frac{3}{\pi} \int_0^\infty \overline{\alpha}_a(i\omega)^2 \, d\omega \right), \tag{9.1}
\]

The MBD model Hamiltonian for an \( N \) atom system is then constructed from these screened polarizabilities and excitation frequencies as

\[
H_{\text{MBD}} = -\sum_{a=1}^{N} \frac{1}{2} \nabla_a^2 \mu_a + \sum_{a=1}^{N} \frac{1}{2} \overline{\alpha}_a \mu_a^2 + \sum_{a>b} \overline{\alpha}_a \overline{\alpha}_b \sqrt{\overline{\alpha}_a(0) \overline{\alpha}_b(0)} \mu_a^i T_{\text{LR}}^{ab} \mu_b^i, \tag{9.2}
\]

where \( \mu_a \) is the polarizability-weighted displacement of the \( a \)th QHO, and \( T_{\text{LR}}^{ab} \) is the long-range component of the dipole-dipole interaction tensor. The first two terms can be identified as the base QHO Hamiltonian in polarization weighted coordinates, while the third term represents two-body coupling. This coupling is calculated from the long-range contribution to the dipole-dipole interaction tensor weighted by a Fermi-type damping function, so the \((i,j)\)th Cartesian component is:

\[
T_{\text{LR}}^{ab,ij} = \left[ \frac{1}{1 + \exp[-Z_{ab}]} \right] \frac{-3R_i^a R_j^b + \|R_{ab}\|^2 \delta_{ij}}{\|R_{ab}\|^5}, \tag{9.3}
\]
where
\[ Z_{ab} = 6 \left[ \frac{||R_{ab}||}{\beta (R_{vdW}^a + R_{vdW}^b)} - 1 \right] \]  

(9.4)
is the ratio between the internuclear distance, \( ||R_{ab}|| \), and the modified sum of the effective van der Waals (vdW) radii, \( R_{vdW} \), of atoms \( a \) and \( b \). The parameter \( \beta \) is an adjustable range-separation parameter that determines the length scale at which the damping function acts to “turn on” the MBD contribution. To prevent double counting of the correlation energy, the MBD correction should “turn on” only after the correlation contribution from the underlying DFT exchange-correlation functional becomes sufficiently small. \( \beta \) can be thought of as an inverse length scale. As \( \beta \to 0 \), the MBD contribution never turns off, and as \( \beta \to \infty \), the MBD contribution never turns on. While we are free to choose \( \beta \), it is typically fit once for a given exchange-correlation functional by minimizing the mean absolute error with respect to highly accurate reference data. This calibration has previously been done for PBE, PBE0, and HSE using as reference the S66×8 benchmark set, which is comprised of 528 interaction energies of 66 molecular dimers computed with CCSD(T) extrapolated to the complete basis-set limit.

Diagonalization of the interacting Hamiltonian produces \( 3N \) polarization normal modes with corresponding eigenfrequencies, \( \sqrt{\lambda_p} \). The MBD correlation energy is then computed from the difference of two zero point energies, the first obtained from summing these eigenfrequencies and the second from summing the screened characteristic frequencies of the uncoupled oscillators:

\[ E_{MBD} = \frac{1}{2} \sum_{p=1}^{3N} \sqrt{\lambda_p} - \frac{3}{2} \sum_{a=1}^{N} \sigma_a. \]  

(9.5)

Finally, \( E_{MBD} \) is applied as an additive correction to the DFT exchange-correlation energy, so the total energy is

\[ E_{total}(\beta) = E_{kinetic} + E_{XC} + E_{MBD}(\beta). \]  

(9.6)

As usual, the eigenvalues \( \lambda_p \) are the square of the frequencies, \( \sqrt{\lambda_p} \), associated with the normal modes.
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Because the MBD energy is a function of \( \beta \), we can straightforwardly minimize the deviation of the DFT+MBD total energy in equation (9.6) from a reference energy by varying \( \beta \).

9.3 Methods

9.3.1 MBD and DFT Energies

All DFT calculations were carried out in a development version of Octopus v5.0.0, in which we have implemented routines to compute the MBD energy as well as analytic nuclear gradients and analytic functional derivatives of the MBD energy. The Octopus package uses the LibXC library of exchange-correlation functionals, which provides access to many more functionals than are currently available in Quantum ESPRESSO, the other open-source quantum chemistry package that currently contains an implementation of the MBD correction. As an added benefit, Octopus’ use of real-space grids provides an efficient treatment of gas-phase molecules and other isolated systems.

When MBD is applied non-self-consistently it has no impact on the charge density. As a result, the Hirshfeld volumes do not depend on the range-separation parameter, \( \beta \), and may be saved to disk for each monomer and dimer in the calibration set. Thus, we optimized \( \beta \) by computing each interaction energy once per exchange-correlation functional and then applied MBD as an \( a \) \textit{posteriori} correction using a locally developed standalone MBD code that accepts \( \beta \) as an input parameter together with the atomic coordinates and Hirshfeld volumes. This scheme avoids unnecessary duplication of a large number of DFT single-point calculations.

9.3.2 Basis Sets

All calculations were run with Octopus’ built in library of Hartwigs-Goedeker-Hutter (HGH) dual space Gaussian norm-conserving pseudopotentials, on spherical atom grids of radius of
6 au with a grid spacing of 0.08 au. We tested these pseudopotentials, grid parameters, and grid shapes extensively to verify that they provided energies that agreed to better than 0.02 kcal/(mol·atom) with respect to all-electron Gaussian-type orbital (GTO) complete-basis set extrapolated calculations run in Q-Chem v4.1. We also explored the energy convergence of molecular single-point energies in Octopus for grid spacings ranging from 0.5 to 0.02 au, and observed that grid spacings ≤ 0.08 au provided convergence within 0.02 kcal/(mol·atom) of the value obtained by a quadratic extrapolation to the complete-basis set limit.

9.3.3 β Optimization

We determined the optimal range-separation parameter, $\beta_{\text{opt}}$, by computing the MBD energy over a grid of $\beta$ values between 0.35 and 1.19, with a spacing of 0.01. We have found that with $\beta$ values below 0.35, MBD becomes numerically unstable and yields imaginary frequencies when diagonalizing the interacting Hamiltonian. The optimal $\beta$ value was selected to minimize the mean absolute error with respect to CCSD(T)/CBS interaction energies from the S66×8_395_402 benchmark set of Řezáč. The S66×8 benchmark includes interaction energies for 66 molecular dimers designed to be representative of the types of noncovalent interactions that commonly occur in organic molecules and biomolecules, including electrostatic (hydrogen bonding) dominated, dispersion dominated (aromatic-aromatic, aromatic-aliphatic, and aliphatic-aliphatic), and mixed character interactions with a variety of bonding motifs for each interaction type. The S66×8 set systematically explores 8 points along the dissociation curves of each complex; by optimizing $\beta$ against a dataset that includes non-equilibrium geometries, we avoid introducing a bias towards equilibrium structures.

To determine the consistency of this optimal $\beta$ value across reference datasets, we also optimized $\beta$ against the revised S22_62_403 benchmarks of Sherrill and co-workers. The S22 dataset contains 22 small molecule dimers covering a mix of hydrogen bonded and dispersion
bound complexes, although it is somewhat weighted toward nucleic acid-like structures and less balanced in its coverage of interaction motifs than the S66 set\textsuperscript{402}. Results of optimizing $\beta$ against the S66 and S22 benchmarks are presented in the Supporting Information.

9.4 RESULTS AND DISCUSSION

To facilitate clarity, Table 9.10 of the Supporting Information provides a glossary that details the exchange and correlation functionals associated with each DFT functional abbreviation used in the following discussion of our results.

In Figure 9.1 we present a representative plot of the variation of the mean absolute error (MAE) as $\beta$ is scanned for five different DFT functionals that cover the diversity of exchange present in our 24 functional test suite: SVWN\textsuperscript{404,406}, PBE\textsuperscript{45,46}, OLYP\textsuperscript{230,231,407}, TPSS\textsuperscript{408,409}, and B97\textsuperscript{410}. We observe flat minima for PBE, TPSS, and B97 with a wide range of $\beta$ values resulting in $<1$ kcal/mol error. This behavior is representative of most functionals in the test suite. OLYP displays a narrower minima with an abrupt jump at $\beta = 0.42$. Unfortunately, we have no clear explanation for this behavior, though we note that similar discontinuities are observed for a few other functionals at the same $\beta$ value. We have tested our methods extensively and found them to produce no negative eigenvalues in the $\beta$ range of interest. We believe that this may be an artifact.
that results from coupling oscillators together that are too close to one another. It is well known
that LDA functionals exhibit spurious exchange binding that mimics an over-bound dispersive
attraction, but is entirely unphysical in its origin; therefore, adding a dispersion correction on top
of LDA is expected to degrade the performance of LDA functionals. This is consistent with the
behavior of SVWN observed in Figure 9.1 with the MAE decreasing monotonically as $\beta$
increases. We have confirmed that this monotonic trend continues out to $\beta = 10$ for LDA
functionals, consistent with $\beta \to \infty$ being optimal, i.e. turning off the MBD correction completely.

In Figure 9.2, we present the MAEs for our full collection of functionals, both with and without
the MBD correction. Table 9.1 provides a different view of these results, demonstrating the
fractional improvement in MAE that is offered by employing the optimized MBD correction. In
the Supporting Information, we present additional tabulations of the MAEs and mean absolute
relative errors (MAREs) for the S66×8, S66, and S22 benchmark sets in Tables 9.2–9.9. We have
found that with the exception of the two LDA functionals (SPZ and SVWN), the addition of MBD
greatly improves the performance of the functionals considered and most are able to achieve
“chemical accuracy” when paired with an optimized MBD.

In general, the functionals seem to require a larger $\beta_{\text{opt}}$ for systems with more hydrogen bonding
character than dispersion character. This implies that the underlying functional is providing a
better treatment of hydrogen bonding/electrostatic interactions than dispersion. Given that
hydrogen bonding is an exchange dominated effect, while dispersion interactions are correlation
dominated, it is unsurprising that a long-range correction to the correlation energy is not as
beneficial for hydrogen-bonded systems. There are two notable exceptions to this trend, for both
B97 and B97-3[111], which are both global hybrid functionals. $\beta_{\text{opt}}$ for dispersion is larger than $\beta_{\text{opt}}$
for hydrogen-bonded systems. It is hard to draw any general conclusions about global hybrids
from these results. However, for B97 and B97-3 specifically, this behavior is likely caused by an
overly repulsive exchange wall. Octopus’ implementation of exact exchange is inefficient enough that a wider survey of local and global hybrid functionals was computationally prohibitive.

In agreement with previous work, the optimal $\beta$ for PBE was found to be $0.83^{280}$ and produced an MAE of 0.37 kcal/mol against the S66×8 set, which is the smallest error in our simulations.

We next considered three PBE-like functionals, revPBE$^{47,48}$, PBE$_{\kappa=1}^{45,46,412}$, and optPBE$^{45,46,412}$, which were reparameterized to improve their short-range behavior. PBE$_{\kappa=1}$ and optPBE, were explicitly constructed to allow for the inclusion of noncovalent and long-range corrections such as MBD or D3 without double counting short-range correlation. revPBE, by contrast, was reparameterized to obey the Oxford-Lieb bound on the exchange-correlation energy$^{87}$.
9.4. Results and Discussion

cases, we find a smaller $\beta_{\text{opt}}$ than that of PBE. This agrees well with the observation that the gradient enhancement factors, $F_i(s)$, for revPBE, PBE$_{x=1}$, and optPBE were designed to be shorter range than PBE. Given that these functionals differ only slightly in the parameters of their exchange interaction, it is unsurprising that their average performances are quite similar, with optPBE, PBE$_{x=1}$, and revPBE having MAEs of 0.49, 0.42, and 0.71 kcal/mol respectively.

The next functional considered with PBE-like exchange was revTCA\textsuperscript{54}, which is the combination of a revised PBE exchange functional formulated to globally obey the Lieb-Oxford bound, and a correlation functional constructed to give zero correlation energy for hydrogenic atoms. While the uncorrected revTCA functional was among the worst of the functionals tested, yielding an MAE of 3.31 kcal/mol, revTCA+MBD was able to achieve an excellent MAE of 0.52 kcal/mol. Previous studies demonstrated that revTCA provides better predictions than PBE for several standard test properties such as barrier heights, atomization energies, and activation enthalpies, and performs comparably to revPBE\textsuperscript{54,55}. The similarity between revTCA and revPBE is reflected in their optimal $\beta$ values: 0.52 and 0.54 kcal/mol respectively. Across all binding motifs (see Table 9.8), we observe that revTCA has a similar optimal $\beta$ value to revPBE, but is slightly shorter range. This correlation in optimal range-separation across binding motifs suggests that the exchange walls described by these two functions is quite similar.

In the same PBE family, PBEsol\textsuperscript{49} was parameterized to perform more similarly to LDA functionals for condensed phase systems. This was achieved largely by damping the gradient enhancement factor at intermediate range to allow for LDA exchange to play a larger role. It is no surprise then that the $\beta_{\text{opt}}$ value for PBEsol is larger than that of PBE due to LDA’s spurious exchange binding. When the S66×8 set is segmented into binding motif subsets (see Table 9.8), we see that like LDA, uncorrected PBEsol sufficiently binds hydrogen-bonded complexes and thus the addition of MBD to PBEsol for these systems incurs additional error; this is reflected by the
negative Δ value in Table 9.1. It is notable that PBEsol+MBD’s performance on hydrogen-bonded systems is the only observed instance where MBD increases the MAE of a non-LDA functional.

Previous authors have found that the non-empirical PW86 exchange functional provides the best description of the repulsive part of the exchange potential relevant to van der Waals (vdW) interactions at short range. Because PW86 exchange avoids spurious exchange binding, it is therefore a good candidate for the foundation of a vdW corrected functional. Furthermore, PW86 has a revised variant, rPW86, which more correctly obeys the Lieb-Oxford bound and was constructed to offer improved performance with vdW corrections. Both PW86 and rPW86 achieve some of the lowest errors against the S66×8 set, with MAEs of 0.38 and 0.39 kcal/mol, respectively. We found that the optimized range-separation parameters differed by 0.01, with PW86 and rPW86 giving \( \beta_{\text{opt}} = 0.80 \) and 0.81, respectively. The similarity of these optimal \( \beta \) values to that of PBE is expected, given the similarity in the functional form of their exchange.

Both PW91 and mPW91 functionals achieved MAEs of 1.25 and 2.30 kcal/mol respectively, while the MBD correction reduced these errors to an impressive 0.50 and 0.49 kcal/mol respectively. These errors being within 0.15 kcal/mol of the PBE+MBD results is perhaps unsurprising given the fact that PBE exchange was derived to be energetically similar to PW91 exchange. We observe that uncorrected PW91 performs well on the hydrogen-bonded subset and benefits by only a 0.1 kcal/mol reduction in MAE with the addition of MBD. By contrast, mPW91 provides a considerably worse description of hydrogen bonding and requires MBD to turn on much quicker, as indicated by \( \beta_{\text{opt}} = 0.77 \). Generally, the PW91 family of functionals performs quite well when corrected with MBD.

We found that of the functionals tested, those based on B88 exchange, including BOP, BPW91, BP86, and optB88 were among the worst functionals when corrected
with MBD. While optB88 and BP86 were able to achieve MAEs < 1 kcal/mol with an optimized MBD correction, BPW91 and BOP achieved MAEs of 1.02 and 1.15 kcal/mol, respectively.

Judging from the optimal $\beta$ values, all functionals based on B88 appear much shorter range than PBE, with BOP being the shortest at $\beta_{\text{opt}} = 0.42$ and optB88 the longest, with $\beta_{\text{opt}} = 0.65$. All of the B88-based functionals considered struggle with treating dispersion dominated complexes (see Table 9.8), while performing significantly better on other binding motifs. In the case of BOP, the poor treatment of the dispersion dominated dimers contributes the most to the overall error. The final functional that we considered with B88 exchange was XLYP, which uses a weighted combination of PW91 and B88 exchange. As such, it is unsurprising that the MAE for XLYP falls between that of PW91 and BP86. Indeed, the optimal $\beta$ for XLYP is in between that of BP86 and PW91, lying closer to BP86 due to the 72.2% B88 contribution to XLYP exchange.

We examined two functionals, OLYP and MOHLYP, that use Handy and Cohen’s OPTX exchange functional, and found that they were among the worst performers in the set, even with the MBD correction. The poor performance of these functionals is unsurprising given that OPTX has an overly repulsive short-range exchange potential; this is reflected in the very short range $\beta_{\text{opt}} \simeq 0.4$. OLYP attains a MAE of 4.29 kcal/mol, which is lowered to 1.21 kcal/mol with the application of MBD. The MOHLYP functional contains a scaled version of OPTX and obtained a MAE of 4.86 kcal/mol, which was reduced to 1.34 kcal/mol with MBD. Although the MBD correction provides a large fractional improvement of 3.5 and 3.6 for OLYP and MOHLYP respectively, they are still markedly inferior to the other LYP correlation based functional XLYP. MOHLYP was optimized for transition metal chemistry, emphasizing the role of d-orbital interactions at the cost of $\pi$-delocalized systems, which explains its generally poor performance on the S66×8 set. While this is a justifiable design for treating organometallic systems, this is the wrong set of physical approximations required to appropriately treat the systems in the S66×8 set.
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Even still, we find that MBD significantly improves MOHLYP’s treatment of dispersion interactions.

One of the most unusual functionals in our test set is the AM05 functional. AM05 was constructed to treat molecules and surfaces on the same footing as bulk solids. While AM05 has been remarkably successful in treating surfaces and solids, it has rarely been applied to molecules in the gas-phase. Achieving an MAE of 0.64 kcal/mol when dispersion corrected, AM05 is capable of high accuracy on molecular interaction energies. AM05 is notable as the functional with the largest spread in $\beta_{opt}$ values for the three binding motifs, ranging from 0.57 to 0.87. It is worth noting that the MBD optimization curve is particularly flat for AM05, indicating that the MBD contribution is a robust correction that is less sensitive to the particular form of AM05’s exchange potential than with other functionals.

We included two global hybrids in our set of functionals, B97 \cite{410} and B97-3 \cite{411}. B97 and B97-3 reached 0.55 and 0.68 kcal/mol MAE respectively when corrected with MBD. Both had MAEs $> 3$ kcal/mol prior to correction with MBD, resulting in an impressive fractional improvement of $\Delta = 5.7$. B97 and B97-3 have among the shortest range exchange, resulting in small $\beta_{opt}$ values of 0.50 and 0.45 respectively. The final functional tested using a B97-style series expansion of exchange, was HCTH/407, a heavily parameterized GGA functional \cite{418}. HCTH/407 performed the best of the three B97-style functionals with an MAE of 2.21 kcal/mol, but receives the smallest benefit from MBD, only lowering the MAE to 0.73 kcal/mol.

TPSS \cite{408, 409} was found to be one of the best performing functionals in our test set when corrected with MBD, with a total MAE of 0.44 kcal/mol, which is only 0.07 kcal/mol above PBE+MBD – an effectively negligible difference in overall performance. Split by category, we observe that TPSS+MBD performs among the best for dimers with hydrogen-bonded and “other” binding motifs, and acceptably well for dispersion-bound systems. MBD yields a remarkable
1200% improvement ($\Delta = 12$) for TPSS on hydrogen-bonded systems. We also observe very little spread in the $\beta_{\text{opt}}$ among the different classes of interaction motif. Because of this consistency in both $\beta_{\text{opt}}$ and accuracy between various classes of interactions, we believe that among the functionals tested, TPSS is the optimal one to be paired with MBD.

Throughout this discussion we have divided functionals according to the classification of the exchange functional because of the interplay between the repulsive exchange wall and the range-separation of the long-range correlation correction. This analysis is made more explicit by examining the behavior of the gradient enhancement factor of the exchange functional. In Figure 9.3 we plot the gradient enhancement factor $F_x$ evaluated at a reduced gradient, $s = 4$, against $\beta_{\text{opt}}$ for each functional. We have chosen $s = 4$ because this is close to the value of the reduced gradient in the intermolecular range where noncovalent interactions tend to dominate. We find that for the two different classes of gradient enhancement factor present (B97/OPTX-like and PBE-like), a

![Figure 9.3](image-url)

**Figure 9.3:** The GGA enhancement factor evaluated at a reduced gradient of $s = 4$ plotted against the associated optimal MBD range-separation parameter, $\beta_{\text{opt}}$. There are two broad groups of GGA functionals, with the first, shown in yellow, corresponding to exchange functionals with PBE style exchange, and the second, shown in blue, corresponding to those that with B97 style exchange.
linear fit determines near optimal $\beta$s. $\beta$ values determined in this manner are hereafter referred to as $\beta_{\text{fit}}$. We have evaluated the MAE for MBE@$\beta_{\text{fit}}$ for all GGA and global hybrid functionals in this study, and presented these results in green in Figure 9.2. Although the performance of MBD with an optimize $\beta$ is superior, if optimizing $\beta$ for your functional of choice is not an option, we have found that we are able to obtain much of the benefits of MBD using a $\beta_{\text{fit}}$ value. In many cases, we are able to reach chemical accuracy through this fitting process. We attribute much of this success to previously discussed the flat minima observed in the MAE curve when $\beta$ is varied. Indeed, the MAE across the S66×8 set typically only changes by 0.2 kcal/mol for as much as a 15% change in $\beta$ away from the minimum.

Overall, we find that the MBD model is able to compensate for the deficiencies of a variety of GGA and global hybrid functionals, with regard to their ability to describe noncovalent interaction energies. When the range-separation parameter is optimally tuned, many different functionals are able to achieve MAEs on the S66×8 set that are well below 1 kcal/mol. Given the flat minima and the diversity of the S66 test set, we expect that the optimal $\beta$ determined in this study will be transferable to a wide range of systems. Additionally, the general functional form that we have determined for $\beta_{\text{fit}}$, and the consistently high quality results that MBD@$\beta_{\text{fit}}$ achieves, provides us with a way forward to applying MBD to a broader range of DFT functionals. This is an encouraging result, given that this study has only considered a small subset of existing functionals.
Table 9.1: Fractional improvement ($\Delta$) in the mean absolute error (MAE) with respect to the S66×8 benchmark set when using the range-separated MBD correction at the optimal $\beta$ value, indicated by $\beta_{\text{opt}}$, is presented for the considered exchange-correlation functionals. $\Delta$ is computed as the ratio of the MAE for the uncorrected functional over that of the MBD corrected functional. For instances in which the MBD correction results in a worse MAE, $\Delta$ is computed as the negative ratio of the MBD corrected MAE over that of the uncorrected functional. In addition to considering the total S66×8 set, we independently optimized $\beta$ on three subgroups of complexes categorized by their dominant bonding motif: hydrogen bonds, dispersion, and other mixed character interactions.

<table>
<thead>
<tr>
<th>Functional</th>
<th>Total $\beta_{\text{opt}}$</th>
<th>$\Delta$</th>
<th>H-Bonds $\beta_{\text{opt}}$</th>
<th>$\Delta$</th>
<th>Dispersion $\beta_{\text{opt}}$</th>
<th>$\Delta$</th>
<th>Other $\beta_{\text{opt}}$</th>
<th>$\Delta$</th>
</tr>
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<tbody>
<tr>
<td>B97-3</td>
<td>0.45</td>
<td>5.7</td>
<td>0.44</td>
<td>11</td>
<td>0.55</td>
<td>4.5</td>
<td>0.42</td>
<td>6.1</td>
</tr>
<tr>
<td>B97</td>
<td>0.50</td>
<td>5.7</td>
<td>0.49</td>
<td>8.6</td>
<td>0.61</td>
<td>4.8</td>
<td>0.52</td>
<td>7.7</td>
</tr>
<tr>
<td>TPSS</td>
<td>0.56</td>
<td>6.6</td>
<td>0.57</td>
<td>12</td>
<td>0.48</td>
<td>6.0</td>
<td>0.49</td>
<td>8.0</td>
</tr>
<tr>
<td>MOHLYP</td>
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<td>0.45</td>
<td>4.5</td>
<td>0.39</td>
<td>3.8</td>
<td>0.39</td>
<td>4.7</td>
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<tr>
<td>OLYP</td>
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<td>0.49</td>
<td>5.0</td>
<td>0.41</td>
<td>4.1</td>
<td>0.39</td>
<td>4.9</td>
</tr>
<tr>
<td>BOP</td>
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<td>3.6</td>
<td>0.52</td>
<td>4.7</td>
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<td>4.4</td>
<td>0.40</td>
<td>6.0</td>
</tr>
<tr>
<td>BPW91</td>
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<td>0.62</td>
<td>3.6</td>
<td>0.43</td>
<td>6.3</td>
<td>0.42</td>
<td>5.8</td>
</tr>
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<td>0.55</td>
<td>8.1</td>
<td>0.43</td>
<td>4.6</td>
<td>0.42</td>
<td>5.7</td>
</tr>
<tr>
<td>revPBE</td>
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<td>4.4</td>
<td>0.59</td>
<td>6.6</td>
<td>0.43</td>
<td>5.7</td>
<td>0.44</td>
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<tr>
<td>XLYP</td>
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<td>5.0</td>
<td>0.52</td>
<td>6.5</td>
</tr>
<tr>
<td>BP86</td>
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<td>0.75</td>
<td>3.1</td>
<td>0.47</td>
<td>5.5</td>
<td>0.53</td>
<td>5.0</td>
</tr>
<tr>
<td>optB88</td>
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<td>3.4</td>
<td>0.79</td>
<td>2.5</td>
<td>0.49</td>
<td>5.3</td>
<td>0.57</td>
<td>4.6</td>
</tr>
<tr>
<td>optPBE</td>
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<td>4.8</td>
<td>0.75</td>
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<td>0.59</td>
<td>6.7</td>
<td>0.62</td>
<td>6.6</td>
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<tr>
<td>PBE$_{x=1}$</td>
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<td>0.74</td>
<td>5.1</td>
<td>0.60</td>
<td>6.4</td>
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<tr>
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<td>0.77</td>
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<td>0.57</td>
<td>6.8</td>
<td>0.64</td>
<td>7.1</td>
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<tr>
<td>AM05</td>
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<td>0.57</td>
<td>5.7</td>
<td>0.68</td>
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</tr>
<tr>
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<td>0.76</td>
<td>6.3</td>
</tr>
<tr>
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<td>0.81</td>
<td>4.4</td>
<td>0.95</td>
<td>3.1</td>
<td>0.75</td>
<td>8.5</td>
<td>0.77</td>
<td>6.1</td>
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<tr>
<td>PW91</td>
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<td>1.19*</td>
<td>1.2</td>
<td>0.83</td>
<td>5.0</td>
<td>0.91</td>
<td>3.3</td>
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<td>0.93</td>
<td>6.1</td>
<td>0.96</td>
<td>4.0</td>
</tr>
<tr>
<td>SVWN</td>
<td>1.19*</td>
<td>-1.3</td>
<td>1.19*</td>
<td>-1.1</td>
<td>1.19*</td>
<td>-1.7</td>
<td>1.19*</td>
<td>-1.4</td>
</tr>
<tr>
<td>SPZ</td>
<td>1.19*</td>
<td>-1.3</td>
<td>1.19*</td>
<td>-1.1</td>
<td>1.19*</td>
<td>-1.7</td>
<td>1.19*</td>
<td>-1.4</td>
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</tbody>
</table>

* Maximum value of $\beta$ considered. LDA functionals are expected to optimize to $\beta \to \infty$.  

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9.5 CONCLUSIONS

By determining the optimal value of the MBD range-separation parameter, $\beta$ for a range of functionals, we have enabled the further adoption of MBD as a highly accurate, low computational cost, correction for noncovalent interactions. Indeed, this work helps to ameliorate the common criticism that MBD is only applicable in conjunction with PBE or PBE0\cite{PBE0}. We have shown that with the optimal range-separation of MBD, most functionals can obtain chemical accuracy for the interaction energy on the S66×8 set. This provides a way forward towards more accurate predictions of the structure, energetics, and function of many systems previously inaccessible with uncorrected DFT.

While we have only tested a small subset of available GGAs, our linear equation provides a near-optimal $\beta$ parameter. In most cases, the MAE for functionals with the parameterized $\beta$ were still able to achieve an accuracy better than 1 kcal/mol. We recommend finding the optimal $\beta$ value through MAE minimization, but recognize that this may not be possible in all cases. For those instances, we have shown that parameterized $\beta$ values will provide suitable results.

While we have provided reliable fits for twenty four different functionals, and many of them were developed to treat specific classes of molecules or properties, we recommend using either PBE+MBD or TPSS+MBD as general purpose functionals. Not only are PBE and TPSS two of the most popular and well understood functionals with sound non-empirical derivations, we observed mean absolute errors of 0.37 kcal/mol and 0.44 kcal/mol with respect to S66×8 the CCSD(T)/CBS references for PBE+MBD and TPSS+MBD respectively. Additionally, their optimal range-separation values do not significantly depend on the type of noncovalent interaction, suggesting that the MBD correction to both functionals is quite transferable.

Future work will determine the optimal range separation parameter for a wider range of commonly used hybrids, meta-hybrids, and double hybrid functionals. Once a broader class of
functionals has been parameterized for use with MBD, it will be interesting to see how the
self-consistent application of MBD performs on the recently released 3B-69 benchmark set of
three-body interactions\cite{419}, which have called into question whether many-body induction is at the
root of many errors that were previously ascribed to dispersion. Because MBD can be applied
self-consistently, it would also be interesting to explore the effect of the MBD contribution to the
Kohn-Sham potential on the hole sum-rule. Such an analysis could provide new insights in
understanding the underlying physics that results from the inclusion of many-body dispersion
corrections to DFT.

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All opinions expressed in this paper are the authors’ and do not necessarily reflect the policies and
views of DOE, ORAU, ORISE, or NSF.

9.6  SUPPORTING INFORMATION

9.7  S22 BENCHMARK SET
Table 9.2: Mean absolute error (MAE) in kcal/mol with respect to Takatani’s revised S22 benchmark set\cite{Takatani2003} with the bare exchange-correlation functional and with the optimized range-separated MBD correction. $\beta_{\text{opt}}$ is the optimized MBD range-separation parameter.

<table>
<thead>
<tr>
<th>Functional</th>
<th>MAE (kcal/mol)</th>
<th>$\beta_{\text{opt}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B97-3</td>
<td>7.055</td>
<td>0.828</td>
</tr>
<tr>
<td>B97</td>
<td>5.766</td>
<td>0.768</td>
</tr>
<tr>
<td>TPSS</td>
<td>4.75</td>
<td>0.801</td>
</tr>
<tr>
<td>MOHLYP</td>
<td>8.15</td>
<td>2.921</td>
</tr>
<tr>
<td>OLYP</td>
<td>7.124</td>
<td>2.675</td>
</tr>
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<td>BOP</td>
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<td>BPW91</td>
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<td>revTCA</td>
<td>5.633</td>
<td>1.605</td>
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<td>revPBE</td>
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</tr>
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<td>1.109</td>
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<tr>
<td>PBE$_{K=1}$</td>
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<tr>
<td>mPW91</td>
<td>3.675</td>
<td>0.895</td>
</tr>
<tr>
<td>AM05</td>
<td>3.37</td>
<td>1.056</td>
</tr>
<tr>
<td>HCTH/407</td>
<td>3.949</td>
<td>0.828</td>
</tr>
<tr>
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<td>PW91</td>
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<td>PBEsol</td>
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<td>SPZ</td>
<td>2.065</td>
<td>2.789</td>
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</table>

* Maximum value of $\beta$ considered. LDA functionals are expected to optimize to $\beta \to \infty$. 

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9.7. S22 benchmark set

Table 9.3: Mean absolute relative percentage error (MARE) with respect to Takatani’s revised S22 benchmark set \(^{[29,30]}\) with the bare exchange-correlation functional and with the optimized range-separated MBD correction. \(\beta_{\text{opt}}\) is the optimized MBD range-separation parameter.

<table>
<thead>
<tr>
<th>Functional</th>
<th>MARE (%)</th>
<th>Bare</th>
<th>MBD</th>
<th>(\beta_{\text{opt}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>B97-3</td>
<td>124</td>
<td>18</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td>B97</td>
<td>102</td>
<td>18</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>TPSS</td>
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<td>17</td>
<td>0.51</td>
<td></td>
</tr>
<tr>
<td>MOHLYP</td>
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<td>51</td>
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<td></td>
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<tr>
<td>OLYP</td>
<td>150</td>
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<td>0.39</td>
<td></td>
</tr>
<tr>
<td>BOP</td>
<td>146</td>
<td>42</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>BPW91</td>
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<td>0.42</td>
<td></td>
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<td>revTCA</td>
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<td>31</td>
<td>0.42</td>
<td></td>
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<tr>
<td>revPBE</td>
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<td>27</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
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<td>25</td>
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<td></td>
</tr>
<tr>
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<tr>
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<tr>
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<td>0.62</td>
<td></td>
</tr>
<tr>
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</tr>
<tr>
<td>HCTH/407</td>
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<td>0.66</td>
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<tr>
<td>PW86</td>
<td>63</td>
<td>9</td>
<td>0.75</td>
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<tr>
<td>rPW86</td>
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<td></td>
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<tr>
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<td>0.95</td>
<td></td>
</tr>
<tr>
<td>SVWN</td>
<td>35</td>
<td>52</td>
<td>1.19*</td>
<td></td>
</tr>
<tr>
<td>SPZ</td>
<td>31</td>
<td>47</td>
<td>1.19*</td>
<td></td>
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</tbody>
</table>

* Maximum value of \(\beta\) considered. LDA functionals are expected to optimize to \(\beta \rightarrow \infty\).
Chapter 9. Calibration of the Many-Body Dispersion Range-Separation Parameter

9.8 S66 Benchmark Set

Table 9.4: Mean absolute error (MAE) in kcal/mol with respect to the S66 benchmark set[102] with the bare exchange-correlation functional and with the optimized range-separated MBD correction. $\beta_{\text{opt}}$ is the optimized MBD range-separation parameter.

<table>
<thead>
<tr>
<th>Functional</th>
<th>MAE (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bare</td>
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<tr>
<td>B97-3</td>
<td>3.86</td>
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<td>B97</td>
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<tr>
<td>TPSS</td>
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<td>MOHLYP</td>
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<td>OLYP</td>
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</tr>
<tr>
<td>BOP</td>
<td>4.15</td>
</tr>
<tr>
<td>BPW91</td>
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<td>revTCA</td>
<td>3.31</td>
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<tr>
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<tr>
<td>XLYP</td>
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<td>2.62</td>
</tr>
<tr>
<td>optB88</td>
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<tr>
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</tr>
<tr>
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</tr>
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<td>AM05</td>
<td>2.25</td>
</tr>
<tr>
<td>HCTC/407</td>
<td>2.21</td>
</tr>
<tr>
<td>PW86</td>
<td>1.76</td>
</tr>
<tr>
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<td>1.71</td>
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<tr>
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</tr>
<tr>
<td>PW91</td>
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</table>

* Maximum value of $\beta$ considered. LDA functionals are expected to optimize to $\beta \rightarrow \infty$. 
Table 9.5: Mean absolute relative percentage error (MARE) with respect to the S66 benchmark set with the bare exchange-correlation functional and with the optimized range-separated MBD correction. $\beta_{\text{opt}}$ is the optimized MBD range-separation parameter.

<table>
<thead>
<tr>
<th>Functional</th>
<th>Bare</th>
<th>MBD</th>
<th>$\beta_{\text{opt}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B97-3</td>
<td>146</td>
<td>47</td>
<td>0.46</td>
</tr>
<tr>
<td>B97</td>
<td>117</td>
<td>42</td>
<td>0.57</td>
</tr>
<tr>
<td>TPSS</td>
<td>117</td>
<td>28</td>
<td>0.53</td>
</tr>
<tr>
<td>MOHLYP</td>
<td>185</td>
<td>62</td>
<td>0.39</td>
</tr>
<tr>
<td>OLYP</td>
<td>163</td>
<td>58</td>
<td>0.40</td>
</tr>
<tr>
<td>BOP</td>
<td>161</td>
<td>45</td>
<td>0.40</td>
</tr>
<tr>
<td>BPW91</td>
<td>137</td>
<td>35</td>
<td>0.43</td>
</tr>
<tr>
<td>revTCA</td>
<td>127</td>
<td>43</td>
<td>0.47</td>
</tr>
<tr>
<td>revPBE</td>
<td>118</td>
<td>31</td>
<td>0.46</td>
</tr>
<tr>
<td>XLYP</td>
<td>112</td>
<td>30</td>
<td>0.57</td>
</tr>
<tr>
<td>BP86</td>
<td>110</td>
<td>30</td>
<td>0.55</td>
</tr>
<tr>
<td>optB88</td>
<td>113</td>
<td>33</td>
<td>0.55</td>
</tr>
<tr>
<td>optPBE</td>
<td>105</td>
<td>31</td>
<td>0.62</td>
</tr>
<tr>
<td>PBE$_\varepsilon = 1$</td>
<td>103</td>
<td>30</td>
<td>0.65</td>
</tr>
<tr>
<td>mPW91</td>
<td>94</td>
<td>21</td>
<td>0.63</td>
</tr>
<tr>
<td>AM05</td>
<td>104</td>
<td>31</td>
<td>0.66</td>
</tr>
<tr>
<td>HCTH/407</td>
<td>169</td>
<td>117</td>
<td>0.65</td>
</tr>
<tr>
<td>PW86</td>
<td>80</td>
<td>22</td>
<td>0.76</td>
</tr>
<tr>
<td>rPW86</td>
<td>80</td>
<td>24</td>
<td>0.76</td>
</tr>
<tr>
<td>PBE</td>
<td>76</td>
<td>23</td>
<td>0.80</td>
</tr>
<tr>
<td>PW91</td>
<td>58</td>
<td>30</td>
<td>0.88</td>
</tr>
<tr>
<td>PBEsol</td>
<td>55</td>
<td>19</td>
<td>0.95</td>
</tr>
<tr>
<td>SVWN</td>
<td>44</td>
<td>54</td>
<td>1.19*</td>
</tr>
<tr>
<td>SPZ</td>
<td>42</td>
<td>49</td>
<td>1.19*</td>
</tr>
</tbody>
</table>

* Maximum value of $\beta$ considered. LDA functionals are expected to optimize to $\beta \to \infty$. 
9.9 S66×8 BENCHMARK SET

Table 9.6: Mean absolute error (MAE) in kcal/mol with respect to the S66×8 benchmark set compounded with the bare exchange-correlation functional and with the optimized range-separated MBD correction. $\beta_{\text{opt}}$ is the optimized MBD range-separation parameter.

<table>
<thead>
<tr>
<th>Functional</th>
<th>Bare</th>
<th>MBD</th>
<th>$\beta_{\text{opt}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B97-3</td>
<td>3.86</td>
<td>0.68</td>
<td>0.45</td>
</tr>
<tr>
<td>B97</td>
<td>3.14</td>
<td>0.55</td>
<td>0.50</td>
</tr>
<tr>
<td>TPSS</td>
<td>2.90</td>
<td>0.44</td>
<td>0.56</td>
</tr>
<tr>
<td>MOHLYP</td>
<td>4.86</td>
<td>1.34</td>
<td>0.40</td>
</tr>
<tr>
<td>OLYP</td>
<td>4.29</td>
<td>1.21</td>
<td>0.41</td>
</tr>
<tr>
<td>BOP</td>
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<td>1.15</td>
<td>0.42</td>
</tr>
<tr>
<td>BPW91</td>
<td>3.33</td>
<td>1.02</td>
<td>0.53</td>
</tr>
<tr>
<td>revTCA</td>
<td>3.31</td>
<td>0.81</td>
<td>0.52</td>
</tr>
<tr>
<td>revPBE</td>
<td>3.13</td>
<td>0.71</td>
<td>0.54</td>
</tr>
<tr>
<td>XLYP</td>
<td>2.63</td>
<td>0.61</td>
<td>0.65</td>
</tr>
<tr>
<td>BP86</td>
<td>2.62</td>
<td>0.72</td>
<td>0.64</td>
</tr>
<tr>
<td>optB88</td>
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<td>0.75</td>
<td>0.65</td>
</tr>
<tr>
<td>optPBE</td>
<td>2.34</td>
<td>0.49</td>
<td>0.67</td>
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<tr>
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<td>0.42</td>
<td>0.68</td>
</tr>
<tr>
<td>mPW91</td>
<td>2.30</td>
<td>0.49</td>
<td>0.68</td>
</tr>
<tr>
<td>AM05</td>
<td>2.25</td>
<td>0.64</td>
<td>0.71</td>
</tr>
<tr>
<td>HCTC/407</td>
<td>2.21</td>
<td>0.73</td>
<td>0.67</td>
</tr>
<tr>
<td>PW86</td>
<td>1.76</td>
<td>0.38</td>
<td>0.80</td>
</tr>
<tr>
<td>rPW86</td>
<td>1.71</td>
<td>0.39</td>
<td>0.81</td>
</tr>
<tr>
<td>PBE</td>
<td>1.57</td>
<td>0.37</td>
<td>0.83</td>
</tr>
<tr>
<td>PW91</td>
<td>1.25</td>
<td>0.50</td>
<td>0.91</td>
</tr>
<tr>
<td>PBEsol</td>
<td>1.23</td>
<td>0.55</td>
<td>0.97</td>
</tr>
<tr>
<td>SVWN</td>
<td>1.49</td>
<td>1.88</td>
<td>1.19</td>
</tr>
<tr>
<td>SPZ</td>
<td>1.37</td>
<td>1.76</td>
<td>1.19</td>
</tr>
</tbody>
</table>

* Maximum value of $\beta$ considered. LDA functionals are expected to optimize to $\beta \rightarrow \infty$. 

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Table 9.7: Mean absolute relative percentage error (MARE) with respect to the S66×8 benchmark set with the bare exchange-correlation functional and with the optimized range-separated MBD correction. $\beta_{opt}$ is the optimized MBD range-separation parameter.

<table>
<thead>
<tr>
<th>Functional</th>
<th>Bare</th>
<th>MBD</th>
<th>$\beta_{opt}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B97-3</td>
<td>146</td>
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<td>0.46</td>
</tr>
<tr>
<td>B97</td>
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<td>42</td>
<td>0.57</td>
</tr>
<tr>
<td>TPSS</td>
<td>117</td>
<td>28</td>
<td>0.53</td>
</tr>
<tr>
<td>MOHLYP</td>
<td>185</td>
<td>62</td>
<td>0.39</td>
</tr>
<tr>
<td>OLYP</td>
<td>163</td>
<td>58</td>
<td>0.40</td>
</tr>
<tr>
<td>BOP</td>
<td>161</td>
<td>44</td>
<td>0.40</td>
</tr>
<tr>
<td>BPW91</td>
<td>137</td>
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<td>0.43</td>
</tr>
<tr>
<td>revTCA</td>
<td>127</td>
<td>43</td>
<td>0.47</td>
</tr>
<tr>
<td>revPBE</td>
<td>118</td>
<td>31</td>
<td>0.46</td>
</tr>
<tr>
<td>XLYP</td>
<td>112</td>
<td>30</td>
<td>0.57</td>
</tr>
<tr>
<td>BP86</td>
<td>110</td>
<td>30</td>
<td>0.55</td>
</tr>
<tr>
<td>optB88</td>
<td>113</td>
<td>33</td>
<td>0.55</td>
</tr>
<tr>
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<td>0.62</td>
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<td>0.65</td>
</tr>
<tr>
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<td>21</td>
<td>0.63</td>
</tr>
<tr>
<td>AM05</td>
<td>104</td>
<td>31</td>
<td>0.66</td>
</tr>
<tr>
<td>HCTH/407</td>
<td>169</td>
<td>117</td>
<td>0.65</td>
</tr>
<tr>
<td>PW86</td>
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<td>22</td>
<td>0.76</td>
</tr>
<tr>
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<td>23</td>
<td>0.80</td>
</tr>
<tr>
<td>PW91</td>
<td>58</td>
<td>30</td>
<td>0.88</td>
</tr>
<tr>
<td>PBEsol</td>
<td>55</td>
<td>19</td>
<td>0.95</td>
</tr>
<tr>
<td>SVWN</td>
<td>44</td>
<td>54</td>
<td>1.19</td>
</tr>
<tr>
<td>SPZ</td>
<td>42</td>
<td>49</td>
<td>1.19</td>
</tr>
</tbody>
</table>

* Maximum value of $\beta$ considered. LDA functionals are expected to optimize to $\beta \to \infty$. 
### Table 9.8: Mean absolute error (MAE) in kcal/mol with respect to subsets of the S66×8 benchmark set categorized by bonding motif, with the bare exchange-correlation functional and with the optimized range-separated MBD correction. $\beta_{opt}$ is the optimized MBD range-separation parameter.

<table>
<thead>
<tr>
<th>Functional</th>
<th>H-Bonded</th>
<th>Dispersion</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>B97-3</td>
<td>3.93 0.36 0.44</td>
<td>4.42 0.99 0.55</td>
<td>3.13 0.51 0.42</td>
</tr>
<tr>
<td>B97</td>
<td>3.00 0.35 0.49</td>
<td>3.80 0.80 0.61</td>
<td>2.54 0.33 0.52</td>
</tr>
<tr>
<td>TPSS</td>
<td>2.18 0.18 0.57</td>
<td>4.07 0.68 0.48</td>
<td>2.39 0.30 0.49</td>
</tr>
<tr>
<td>MOHLYP</td>
<td>3.88 0.86 0.45</td>
<td>6.52 1.70 0.39</td>
<td>4.09 0.87 0.39</td>
</tr>
<tr>
<td>OLYP</td>
<td>3.10 0.62 0.49</td>
<td>5.97 1.45 0.41</td>
<td>3.73 0.76 0.39</td>
</tr>
<tr>
<td>BOP</td>
<td>2.98 0.64 0.52</td>
<td>5.77 1.31 0.40</td>
<td>3.64 0.61 0.40</td>
</tr>
<tr>
<td>BPW91</td>
<td>2.08 0.58 0.62</td>
<td>4.88 0.77 0.43</td>
<td>2.99 0.52 0.42</td>
</tr>
<tr>
<td>revTCA</td>
<td>2.42 0.30 0.55</td>
<td>4.61 1.01 0.43</td>
<td>2.83 0.50 0.42</td>
</tr>
<tr>
<td>revPBE</td>
<td>2.17 0.33 0.59</td>
<td>4.44 0.78 0.43</td>
<td>2.72 0.38 0.44</td>
</tr>
<tr>
<td>XLYP</td>
<td>1.45 0.19 0.71</td>
<td>4.06 0.81 0.49</td>
<td>2.34 0.36 0.52</td>
</tr>
<tr>
<td>BP86</td>
<td>1.38 0.45 0.75</td>
<td>4.04 0.74 0.47</td>
<td>2.41 0.48 0.53</td>
</tr>
<tr>
<td>optB88</td>
<td>1.27 0.51 0.79</td>
<td>4.03 0.76 0.49</td>
<td>2.33 0.51 0.57</td>
</tr>
<tr>
<td>optPBE</td>
<td>1.29 0.35 0.75</td>
<td>3.60 0.54 0.59</td>
<td>2.11 0.32 0.62</td>
</tr>
<tr>
<td>PBE_{c=1}</td>
<td>1.33 0.26 0.74</td>
<td>3.51 0.55 0.60</td>
<td>2.06 0.26 0.63</td>
</tr>
<tr>
<td>mPW91</td>
<td>1.21 0.31 0.77</td>
<td>3.60 0.53 0.57</td>
<td>2.06 0.29 0.64</td>
</tr>
<tr>
<td>AM05</td>
<td>0.94 0.46 0.87</td>
<td>3.69 0.65 0.57</td>
<td>2.09 0.39 0.68</td>
</tr>
<tr>
<td>HCTC/407</td>
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<td>3.47 1.10 0.60</td>
<td>1.88 0.52 0.63</td>
</tr>
<tr>
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<td>1.70 0.27 0.76</td>
</tr>
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<td>1.66 0.27 0.77</td>
</tr>
<tr>
<td>PBE</td>
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<td>2.66 0.32 0.77</td>
<td>1.44 0.19 0.82</td>
</tr>
<tr>
<td>PW91</td>
<td>0.43 0.36 1.19*</td>
<td>2.23 0.45 0.83</td>
<td>1.06 0.32 0.91</td>
</tr>
<tr>
<td>PBEsol</td>
<td>0.70 0.74 1.19*</td>
<td>1.94 0.32 0.93</td>
<td>1.03 0.26 0.96</td>
</tr>
<tr>
<td>SVWN</td>
<td>2.66 2.93 1.19*</td>
<td>0.82 1.35 1.19*</td>
<td>0.93 1.28 1.19*</td>
</tr>
<tr>
<td>SPZ</td>
<td>2.49 2.76 1.19*</td>
<td>0.72 1.25 1.19*</td>
<td>0.83 1.18 1.19*</td>
</tr>
</tbody>
</table>

* Maximum value of $\beta$ considered. LDA functionals are expected to optimize to $\beta \to \infty$. 

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Table 9.9: Mean absolute relative percentage error (MARE) with respect to subsets of the S66×8 benchmark set, categorized by bonding motif, with the bare exchange-correlation functional and with the optimized range-separated MBD correction. $\beta_{\text{opt}}$ is the optimized MBD range-separation parameter.

<table>
<thead>
<tr>
<th>Functional</th>
<th>H-Bonded</th>
<th>Dispersion</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>B97-3</td>
<td>51 7 0.45</td>
<td>265 100 0.55</td>
<td>118 28 0.42</td>
</tr>
<tr>
<td>B97</td>
<td>39 7 0.50</td>
<td>215 89 0.63</td>
<td>92 20 0.53</td>
</tr>
<tr>
<td>TPSS</td>
<td>31 3 0.57</td>
<td>229 60 0.45</td>
<td>89 16 0.50</td>
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<tr>
<td>MOHLYP</td>
<td>55 13 0.41</td>
<td>350 127 0.39</td>
<td>144 38 0.39</td>
</tr>
<tr>
<td>OLYP</td>
<td>45 11 0.47</td>
<td>308 119 0.40</td>
<td>132 34 0.39</td>
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<tr>
<td>BOP</td>
<td>46 11 0.47</td>
<td>300 88 0.40</td>
<td>133 25 0.40</td>
</tr>
<tr>
<td>BPW91</td>
<td>35 11 0.57</td>
<td>259 56 0.43</td>
<td>112 22 0.42</td>
</tr>
<tr>
<td>revTCA</td>
<td>35 6 0.54</td>
<td>242 87 0.43</td>
<td>101 25 0.42</td>
</tr>
<tr>
<td>revPBE</td>
<td>33 6 0.56</td>
<td>217 52 0.43</td>
<td>100 21 0.45</td>
</tr>
<tr>
<td>XLYP</td>
<td>23 4 0.71</td>
<td>223 58 0.43</td>
<td>87 17 0.52</td>
</tr>
<tr>
<td>BP86</td>
<td>25 9 0.71</td>
<td>210 48 0.46</td>
<td>91 22 0.50</td>
</tr>
<tr>
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<td>24 9 0.73</td>
<td>223 58 0.50</td>
<td>89 22 0.50</td>
</tr>
<tr>
<td>optPBE</td>
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<td>211 64 0.59</td>
<td>79 17 0.63</td>
</tr>
<tr>
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<td>21 4 0.72</td>
<td>208 67 0.62</td>
<td>77 15 0.63</td>
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<tr>
<td>mPW91</td>
<td>20 5 0.75</td>
<td>185 39 0.58</td>
<td>75 14 0.64</td>
</tr>
<tr>
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<td>18 7 0.81</td>
<td>209 59 0.55</td>
<td>81 20 0.68</td>
</tr>
<tr>
<td>HCTH/407</td>
<td>18 11 0.76</td>
<td>397 285 0.60</td>
<td>81 40 0.64</td>
</tr>
<tr>
<td>PW86</td>
<td>12 4 0.92</td>
<td>160 42 0.74</td>
<td>66 14 0.76</td>
</tr>
<tr>
<td>rPW86</td>
<td>11 4 0.94</td>
<td>162 46 0.75</td>
<td>64 14 0.77</td>
</tr>
<tr>
<td>PBE</td>
<td>11 5 0.96</td>
<td>160 46 0.75</td>
<td>56 11 0.82</td>
</tr>
<tr>
<td>PW91</td>
<td>7 7 1.19</td>
<td>123 55 0.83</td>
<td>40 21 0.91</td>
</tr>
<tr>
<td>PBEsol</td>
<td>10 9 1.19</td>
<td>107 27 0.94</td>
<td>45 14 0.96</td>
</tr>
<tr>
<td>SVWN</td>
<td>35 39 1.19</td>
<td>58 76 1.19</td>
<td>39 45 1.19</td>
</tr>
<tr>
<td>SPZ</td>
<td>33 37 1.19</td>
<td>57 68 1.19</td>
<td>35 42 1.19</td>
</tr>
</tbody>
</table>

* Maximum value of $\beta$ considered. LDA functionals are expected to optimize to $\beta \to \infty$. 

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Chapter 9. Calibration of the Many-Body Dispersion Range-Separation Parameter

9.10 GLOSSARY

Table 9.10: Definition of abbreviations referring to the exchange-correlation functionals considered herein.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Exchange</th>
<th>Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>SVWN</td>
<td>Slater exchange</td>
<td>Vosko, Wilk, &amp; Nussair ’80, (RPA)</td>
</tr>
<tr>
<td>SPZ</td>
<td>Slater exchange</td>
<td>Perdew &amp; Zunger ‘81 local</td>
</tr>
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<td>Becke ‘88</td>
<td>B88 one parameter progressive</td>
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<td>Becke ‘88</td>
<td>Perdew ‘86</td>
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<tr>
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<td>Becke ‘88</td>
<td>Perdew &amp; Wang ‘91</td>
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Part IV

Future Directions and Conclusions
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While we have found MBD to be remarkably successful for predicting the energetics and structures of a wide range of materials, future development and characterization of the method is necessary.

10.1 MBD Calibration

At present, MBD has only been calibrated to work with twenty-six DFT functionals. With the exception of PBE0, MBD has not been parameterized for any hybrid, meta-hybrid, or double hybrid DFT functionals. Hybrid functionals have gained popularity in recent years due to their ability to reach chemical accuracy for a diverse set of molecular properties, including nonbonding interaction energies, thermodynamics, and kinetics. In future work, we propose calibrating the range separation parameter, $\beta$, for many hybrid, meta-hybrid, and double hybrid DFT functionals. This study would follow from the methodology we have defined in Chapter 9 and would provide the community with many more dispersion-corrected DFT functionals. With accurate range separation parameters in hand, a thorough benchmarking study would be valuable.

While grafting MBD onto currently existing functionals is appealing due to the simplicity of the approach and the promise of providing simple corrections to commonly used functionals such as the B3LYP, it is also possible to create a new functional that uses MBD as the long-range correlation. We are motivated by the observation that DFT functionals frequently depend on the cancellation of errors between the correlation and exchange functionals to arrive at
an accurate answer. This cancellation of errors explains why range-separated exact exchange can perform poorly when combined with an existing DFT functional. To remedy this, the correlation and exchange functionals should be derived in concert to obtain as much consistency between the two functionals.

With this goal in mind, we propose creating a new functional that combines range-separated MBD and range-separated exact exchange. We believe this has promise because both MBD and exact exchange are asymptotically correct for correlation and exchange, respectively. Unfortunately, MBD and exact exchange provide a poor description of the potential at short ranges. To this end, when combined with a DFT functional that has been derived to be explicitly short range, it may be possible to combine semi-local DFT’s success for short-range interactions with exact exchange and MBD’s success for long-range interactions. Because we are proposing using both range-separated MBD and exact exchange, we will need to perform a two-parameter optimization. While we can follow the procedure outlined in Chapter 9, it may be valuable to explore the parameter dependent effects on the f-sum rule. In preliminary tests on the hydrogen fluoride dimer, with crudely optimized range separation values, MBD appears to provide the compensatory pair to exact exchange as checked by various sum rules. This will need to be extensively studied and characterized.

10.2 MBD for Excited States

While MBD has thus far been applied as a correction to groundstates within the DFT framework, it is possible to apply MBD self-consistently to explore the effects of dispersion interactions on excited state electronic structure as well. Among Time Dependent Density Functional Theory’s (TDDFT) many short comings, we have empirically observed poor descriptions of charge transfer excitations, polarizabilities of large molecules and solids, and Rydberg states. All of these
failures can be partially viewed as the failing of DFT to provide an asymptotically correct charge density from which to perturb. Made more concrete, if we picture two benzene rings separated by a distance, \( R \), as shown in Figure 10.1, we know that the charge transfer energy within the single pole approximation is:

\[
E_{\text{ct}} = I_2 - A_1 - \frac{1}{R},
\]

(10.1)

where the subscripts serve as molecule identifiers. By contrast, the energy from TDDFT is given by

\[
E_{\text{CT}} = E_{1}^{\text{LUMO}} - E_{1}^{\text{HOMO}} - \int dr \phi_1^{\text{HOMO}}(r) \phi_2^{\text{LUMO}}(r) f_{\text{HXC}}(r, r') \phi_1^{\text{HOMO}}(r') \phi_1^{\text{LUMO}}(r'),
\]

(10.2)

where \( \phi(r) \) is the molecular orbital, the subscripts are molecular indices, and \( f_{\text{HXC}}(r, r') \) is the exchange correlation kernel. TDDFT typically underestimates the charge transfer energy due to DFT’s prediction of decaying charge densities, and the underestimation of the HOMO-LUMO gap. Because \( E^{\text{HOMO}}, E^{\text{LUMO}}, \phi^{\text{HOMO}}, \) and \( \phi^{\text{LUMO}} \) are all computed from the exchange-correlation potential, and have the most significant effect on the charge transfer energy, systematically correcting this would provide an efficient way to accurately calculate excited state spectra.

Moving beyond the single pole approximation, it has been observed that accurate descriptions of the exchange-correlation potential were far more important for the recovery of accurate excited state spectra. Baerends et al observed that a simple adiabatic local density approximation for the time dependent density functional kernel is sufficient for nonmetallic systems, so long as the
10.2. MBD for Excited States

Motivated by the observation that correcting the exchange-correlation potential in such a way as to provide asymptotically correct charge densities, MBD may provide improved performance for certain excited state spectra when applied as a self-consistent correction.

In a preliminary study, we first sought to study effects of MBD when applied self-consistently to the benzene dimer. The difference density between the PBE+MBD and PBE groundstate charge densities for the benzene dimer is presented in Figure 10.2. We have chosen to plot only the positive density, which provides a clear picture of where PBE+MBD “moved” the charge density to. We observe the charge density being pushed into the intramolecular and asymptotic regions. With Equation (10.2) in mind, this holds the promise of increasing the orbital overlap, and thus, causing the integral in Equation (10.2) to vanish far less quickly.

With these results in hand, we tested the calculation of an absorption spectrum within the Real Time TDDFT (RT-TDDFT) framework by applying MBD self-consistently at every electronic time step. The capability has been built into the OCTOPUS computer code, which is an efficient code for RT-TDDFT. As a proof of principle study, we configured two HF molecules in an...
Figure 10.3: Singlet absorption spectrum for an anti-symmetric hydrogen fluoride dimer separated by 2.8 Å. PBE+MBD is in blue and PBE is in red.

Figure 10.4: High harmonic generation spectrum for an anti-symmetric hydrogen fluoride dimer separated by 2.8 Å. PBE+MBD is in blue and PBE is in red.

anti-symmetric configure with 2.8 Å of separation. We computed the singlet absorption spectrum, given in Figure 10.3 and the high harmonic generation (HHG) spectrum, given in Figure 10.4. It is clear in these plots that the MBD correction has an effect. Indeed, we see a small red-shift in the absorption spectrum that corresponds nicely with the amplification of the integral in Equation (10.2). While the effects are small, their presence is encouraging and warrants further study. The role of dispersion in the HHG spectrum plotted in Figure 10.4 is more significant. We observe multiple order of magnitude deviations in the harmonics sixteen through nineteen. It is unclear if this corresponds to physical data because the experimental data is unavailable, but the
presence of non-negligible corrections is interesting. While these results are encouraging, further study is required to completely characterize the role of MBD in TDDFT.

One particularly exciting system to study with this technology is that of the well separated gold nanoparticles. It has recently been observed that these systems could be modeled with a Jellium model\textsuperscript{381}. However, due to the incorrect treatment of dispersion interactions, the absorption spectrum that was obtained struggled to accurately describe peak positions. Given that MBD was observed to provide a red shift in agreement with our physical intuition, it is possible that the MBD model could provide the relevant physics for these nanoparticles as well.

10.3 \textbf{INTERFACIAL EXCITONIC STUDIES}

Finally, the vision of this dissertation is to provide the tools to enable the accurate simulation of open system dynamics of electronic motion in condensed phase systems, such as the Tetracyanoquinodimethane(TCNQ)-Rubrene interface presented in Figure\textsuperscript{10.5}.\textsuperscript{135} The goal of such a study is to capture the timescales of electronic dynamics. To this end, we have developed the following pipeline to perform such studies. Because the goal is to study electron-hole separation, we will need to construct a unit cell the size of the exciton diffusion length. To achieve such a large system, we will construct a tight binding Hamiltonian for our original supercell and use that Hamiltonian to construct a large supercell. The tight binding Hamiltonian will be used in the dissipative electron-hole dynamics.

The first step clearly is to compute the structure of the interface. Given that the interface has significant $\pi$-orbital delocalization, the role of many-body dispersion effects may be quite significant. Therefore, performing a unit cell optimization with PBE+MBD will give a reliable unit cell for the rest of the calculation. With an accurate unit cell in hand, we will compute an electronic band structure. Because DFT has a well known to have the gap problem, it may be
necessary to correct the band-gap using GW calculations. 436,437

Using the charge density, potential, and band structure, we will use WANNIER90 438 to compute the maximally localized Wannier function (MLWF) representation of the charge density. 439–443 The MLWFs are very much like atomic orbitals, and can be interpreted as such. In addition to providing some sense of localization, they define a tight binding Hamiltonian. 444–446 Because the MLWFs are constructed so that they reproduce specific bands, it is necessary to create one set of MLWFs to reproduce the valence band, thereby giving you the hole-Hamiltonian, and another set of MLWFs to reproduce the conduction band, thereby giving you the electron-Hamiltonian. With the MLWFs in hand, it is possible to construct massive unit cells (many hundreds of unit-cell copies). Moreover, is possible to build real space disorder into this Hamiltonian by introducing noise (Gaussian or otherwise) in the real space copies.

With the Hamiltonian constructed, the spectral density needs to be considered. The simplest approximation would be to pick an ohmic spectral density, which is chosen to closely match the
vibrational density of states around the interface. If more details are desired, we can make use of
the technology outlined in Chapter 3 to generate an accurate spectral density with 5ps of AIMD of
fixed unitcell \textit{ab initio} molecular dynamics and TDDFT.

With both a Hamiltonian and spectral density in hand, we need to run the dissipative dynamics.
For a system of this size, an optimized TCL(2) code should still be possible on a large memory
node.
Conclusion

This dissertation consists of three parts, intended to develop a set of tools to make *ab initio* open quantum system dynamics in solvated and condensed matter systems possible. The first part developed the theory of polaron transformed open quantum system dynamics; the second focuses on accelerating the computation of spectral densities to better model environmental effects; and the third part presents nuclear gradients, cell stresses, and self consistent functional derivatives for the MBD model to provide deeper insight into the structure and energetics of solvated and condensed phase systems.

In Chapter 2, we presented the equation of motion for correlated electron nuclear dynamics within the second order time-convolutionless formalism. The nuclear and environmental effects enter through the spectral density, which provides a harmonic model for these interactions. While the study was a proof of principle, we observed excellent agreement between our method and both high-quality wave-function techniques and experimental data. Through exploration of the method, we observed that many systems are sensitive to minor changes in both the structure and the spectral density.

In Chapter 3, we presented a technique for generating faithful spectral densities that requires only one quarter of the data that traditional methods require. Spectral densities are computed by computing the Fourier transform of the HOMO-LUMO energy gap correlation function, where a HOMO-LUMO gap is computed at every time-step of a molecular dynamics simulation. Using
super-resolution, and adapting it to perform the first ever super-resolution calculations in nonorthogonal bases. We showed that our approximate spectral densities were capable of providing dynamics consistent to those generated with the full data. During the course of this study, we sought to compare the performance of super-resolution to other methods traditionally used to resolve signals beyond the nyquist-sampling theorem. We presented this work in Chapter 4 with Chapter 5 providing the more theoretical insight into our study methodology.

To develop tools to address the structure of solvated and condensed phase systems, where dispersion forces are vital, we developed an efficient implementation of the nuclear gradients, unit cell stresses, and self consistent derivatives. In Chapter 6 we presented the ionic derivative expressions and provided benchmark results across a wide range of systems. We were able to recover high-level wavefunction geometries using only PBE+MBD. In Chapter 7 we presented the expressions for the cell stresses and self consistent derivatives for the supercell variant of MBD. We found that the PBE+MBD forces and cell stresses were difficult to converge in solid state for some cases. This resulted in mixed results on our optimization test set. In addition, the supercell procedure proved to be computationally costly. Indeed, the MBD computational cost could dwarf the MBD for large supercell cutoffs.

In Chapter 8 we presented the MBD method in reciprocal space as a computationally efficient alternative to the supercell procedure. Through reciprocal space sampling, and ewald summation, we significantly reduced the overall computational effort required to compute the forces and stresses. Because if the efficiency gains, we were able to properly converge the forces and stresses for PBE+MBD on our test set, and were able to recover the experimental unit cells for many of the crystals under consideration. In addition, because we can parallelize over k-points, the computational cost of an MBD calculation with all gradients is typically equivalent to that of a single SCF calculation. This will make the MBD method more readily applicable to the simulation.
of large, condensed phase, materials.

In Chapter 9 we developed a methodology for combining the MBD model for dispersion interactions with new DFT functionals. This is done by minimizing as a function of $\beta$ the mean absolute error of DFT+MBD with reference to the CCSD(T) reference data on the S66×8 data set of molecular interactions. We performed this analysis for 24 different DFT functionals, and reported the optimal $\beta$ value for each. In addition, we also reported an approximate equation for the $\beta$ value, which gave near optimal results but requires running no calculations. This will allow the use of MBD with other DFT functionals, that may have been parameterized for specific systems or properties.

Finally, in Chapter 10 we outlined current preliminary research results and future research directions. We are particularly excited to understand the role of dispersion interactions in the excited state spectra of molecules and solids; and to explore the dissipative electronic dynamics of organic photovoltaic systems.


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