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Threshold laws for collisional reorientation of electronic angular momentum

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It is shown that the velocity dependence of cross sections for projection-changing transitions in collisions of paramagnetic atoms or molecules with structureless targets near threshold has the form $v^{2\Delta m}$ when Δm is even and $v^{2(\Delta m+1)}$ when Δm is odd, where Δm is the change in the projection quantum number and v is the relative velocity.

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Recent advances in experiments on ultracold atoms and the generation of ultracold molecules [1–7] have stimulated research on collisions near energy thresholds. A general technique for the production of ultracold atoms and molecules is the buffer gas loading method developed by Doyle and co-workers [6,7]. These experiments are based on collisional equilibration of the translational energy of atoms or molecules in elastic collisions with cold buffer gas atoms and the subsequent trapping of cooled molecules in a magnetic field. This technique can be applied to atoms and molecules with nonzero magnetic moments. The atoms or molecules are trapped in the state with a particular projection of total electronic angular momentum. The transitions for which there is a change of the projection remove the atoms or molecules from the trap. The behavior of the cross sections for the projection-changing transitions at very low energies is critical and we discuss it here. We derive threshold laws for the energy dependence of cross sections for projection flipping in paramagnetic atoms or molecules in collisions with structureless targets.

Wigner presented threshold laws for elastic and inelastic cross sections [8] and showed that the cross section for an exothermic inelastic process increases inversely as the velocity v as v tends to zero producing a finite rate coefficient at zero temperature. He did not consider explicitly scattering in which the only change during the collision is in the projection quantum number m along a space-fixed axis. The state with a defined space-fixed projection of the angular momentum $|jm\rangle$ does not correspond to a state with a specific orbital angular momentum l . We consider here the behavior of the projection-flipping cross sections in the absence of the magnetic field when there is no energy defect between the states with different electronic angular-momentum projections.

The total angular momentum of an atom or a molecule j can be written as the vector sum of the spin angular momentum s and the angular momentum N describing the rotational motion of molecules or the orbital motion of electrons [9]: $\hat{j} = \hat{s} + \hat{N}$. In the quantum mechanical formalism of Arthurs and Dalgarno [10], the scattering T matrix is obtained for

total angular momentum J and total energy from the solution of the following system of coupled differential equations:

$$\left[\frac{d^2}{dR^2} + k_{j(Ns)}^2 - \frac{l(l+1)}{R^2} \right] F_{jl}^J(R) = 2\mu \sum_{j'l'} \langle Jj(Ns)l | \hat{V} | Jj'(N's')l' \rangle F_{j'l'}^J(R), \quad (1)$$

where R is the center-of-mass separation between the colliding particles, $k_{j(Ns)} = \mu v$, μ is the reduced mass of the collision complex, v is the relative collision velocity of the open-shell atom or molecule in the state with the angular momentum j , l is the orbital angular momentum for the collision, and $\langle Jj(Ns)l | \hat{V} | Jj'(N's')l' \rangle$ are the elements of the interaction potential coupling matrix. The Hamiltonian matrix is assumed to be diagonal in the $|Jj(Ns)l\rangle$ representation when $R = \infty$ [10]. If the interaction potential for the atom-molecule or atom-atom interaction is expanded in a Legendre series, the interaction potential matrix elements can be written as follows [11]:

$$\begin{aligned} \langle Jj(Ns)l | \hat{V} | Jj'(N's')l' \rangle &= \sum_{\lambda} V_{\lambda} (-1)^{2j'+J+s+\lambda} [(2l+1) \\ &\times (2l'+1)(2j+1)(2j'+1)(2N+1)(2N'+1)]^{1/2} \\ &\times \begin{Bmatrix} N & j & s \\ j' & N' & \lambda \end{Bmatrix} \begin{Bmatrix} j & l & J \\ l' & j' & \lambda \end{Bmatrix} \\ &\times \begin{pmatrix} l & \lambda & l' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} N & \lambda & N' \\ 0 & 0 & 0 \end{pmatrix}, \end{aligned} \quad (2)$$

where V_{λ} are the terms of the Legendre expansion and the symbols in the curly brackets and parentheses are $6j$ and $3j$ symbols. The T -matrix elements or the probability amplitudes for transitions between the states with defined values of internal and orbital angular momenta can be computed from the solution of Eqs. (1) with the usual boundary conditions. The cross sections for the transitions changing the projection of $\hat{j}$ with respect to an axis fixed in space are given by the following equation:

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$$\sigma_{jm \rightarrow j'm'} = \frac{\pi}{k_j^2} \sum_{J_1} \sum_{J_2} \sum_l \sum_{m_l} \sum_{l'} \sum_{m_{l'}} T_{jl \rightarrow j'l'}^{J_1*} T_{jl \rightarrow j'l'}^{J_2} \times \sum_{M_1} \sum_{M_2} \begin{bmatrix} j & l & J_1 \\ m & m_l & M_1 \end{bmatrix} \begin{bmatrix} j & l & J_2 \\ m & m_l & M_2 \end{bmatrix} \times \begin{bmatrix} j' & l' & J_1 \\ m' & m_{l'} & M_1 \end{bmatrix} \begin{bmatrix} j' & l' & J_2 \\ m' & m_{l'} & M_2 \end{bmatrix}, \quad (3)$$

where m , m_l , and M denote the space-fixed projections of j , l , and J , respectively, and the symbols in the square brackets are the Clebsch-Gordan coefficients. To derive Eq. (3) we used the same approach as in Refs. [10,12] with the assumption that collisions occur with random initial direction relative to the quantization axis. Because the cross sections for the projection-flipping transitions (3) are expressed in terms of the T -matrix elements for the transitions between different orbital angular-momentum (l) states, we begin by considering the selection rules for l transitions.

One or another of the $3j$ symbols

$$\begin{pmatrix} N & \lambda & N' \\ 0 & 0 & 0 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} l & \lambda & l' \\ 0 & 0 & 0 \end{pmatrix}$$

vanishes for odd λ except when N and l both change by odd integers and for even λ except when N and l both change by even integers or zero. Thus there is no coupling between even and odd l for the same N and the T -matrix elements connecting even and odd l states in the same state N vanish. Cross section (3) for the j -projection change is determined by the sum over the T -matrix elements for the transitions that preserve the parity of the angular-momentum states l .

Wigner [8] showed that in the limit of zero relative velocity the square of the $T_{jl \rightarrow j'l'}$ matrix element varies as

$$|T_{jl \rightarrow j'l'}|^2 \sim v^{2l+2l'+2}. \quad (4)$$

When v is small the cross section for the projection-flipping transitions will be dominated by the $T_{jl \rightarrow j'l'}$ matrix element for the lowest values of l and l' for which the transition is possible. The products

$$\begin{bmatrix} j & l & J \\ m & m_l & M \end{bmatrix} \begin{bmatrix} j & l' & J \\ m' & m_{l'} & M \end{bmatrix}$$

in Eq. (3) vanish if $l=l'=0$ and $m \neq m'$. The threshold cross section for the $|jm\rangle \rightarrow |jm \pm \Delta m\rangle$ transition is, therefore, determined by the scattering of higher partial waves. The recoupling coefficients in Eq. (3) determine the threshold behavior of the projection-flipping cross section, which is dependent on the value Δm by which the projection of $\hat{j}$ is changed. The corresponding products of the Clebsch-Gordan coefficients

$$\begin{bmatrix} j & l & J \\ m & m_l & M \end{bmatrix} \begin{bmatrix} j & l' & J \\ m \pm \Delta m & m_{l'} & M \end{bmatrix}$$

FIG. 1. Cross sections as functions of energy for projection-changing transitions in collisions of $O(^3P_{j=2, m=2})$ with ^4He : circles, $\Delta m=1$, diamonds, $\Delta m=2$, triangles, $\Delta m=3$, squares, $\Delta m=4$. The slopes of the lines are 2 (circles and diamonds) and 4 (squares and triangles). The corresponding rate coefficients are given by the following expressions (in $\text{cm}^3 \text{sec}^{-1}$): $5.14 \times 10^{-9} T^{5/2}$ for $\Delta m=1$; $8.93 \times 10^{-11} T^{5/2}$ for $\Delta m=2$; $9.40 \times 10^{-9} T^{9/2}$ for $\Delta m=3$; $1.68 \times 10^{-9} T^{9/2}$ for $\Delta m=4$.

are nonvanishing only if the transitions changing the projection of $\hat{j}$ by Δm are accompanied by the same changes of the projection of l according to the relation $m_{l'} - m_l = \mp \Delta m$, which must hold for the transition from a state m to the state $m \pm \Delta m$. The change of the orbital angular-momentum projection by Δm is allowed for the transitions between the states for which

$$l + l' = \Delta m \quad (5)$$

when Δm is even and for which

$$l + l' = \Delta m + 1 \quad (6)$$

when Δm is odd. The contributions from transitions corresponding to larger values of $l + l'$ fall off more rapidly with decreasing relative velocity v . Combining the results of Eqs. (5), (6), and (4) and noting factor $1/v^2$ in the cross section (3), we obtain the following threshold law for the $|jm\rangle \rightarrow |jm \pm \Delta m\rangle$ cross sections for even Δm :

$$\sigma_{jm \rightarrow jm \pm \Delta m} \sim v^{2\Delta m}, \quad (7)$$

and for Δm odd,

$$\sigma_{jm \rightarrow jm \pm \Delta m} \sim v^{2(\Delta m + 1)}. \quad (8)$$

Expression (7) recovers the Wigner law for elastic scattering when $\Delta m=0$.

The functional forms of cross sections (7) and (8) determine the limiting temperature dependence of the corresponding rate coefficients as follows:

$$R_{m \rightarrow m'}(T) = \left(\frac{8k_B T}{\pi \mu} \right)^{1/2} \int_0^\infty \sigma_{m \rightarrow m'} e^{-E/k_B T} \frac{E dE}{(k_B T)^2} \\ = A \left(\frac{8}{\pi \mu} \right)^{1/2} (k_B T)^{a+1/2} (a+1)!, \quad (9)$$

where $a = \Delta m$ if Δm is even and $a = \Delta m + 1$ if Δm is odd, $A = \sigma_{m \rightarrow m'}/E^a$ is a proportionality constant, k_B is the Boltzmann constant, and E is the collision energy.

To demonstrate that Eqs. (7) and (8) hold for low-energy scattering, we present in Fig. 1 cross sections for various $(j=2, m=2) \rightarrow (j=2, m')$ transitions in collisions of $O(^3P_{j=2})$ with ^4He as functions of collision energy. The calculations are performed with realistic interaction potentials as described earlier [13]. The three electronic states of oxygen corresponding to $j=0, 1$, and 2 were included in the computations. In order to verify the accuracy of our results, we repeated the calculations directly in the uncoupled space-fixed basis $|jm_j\rangle|lm_l\rangle$ and confirmed that the cross sections of Fig. 1 are converged to within an uncertainty of 1%. The $(j=2, m=2) \rightarrow (j=2, m'=1)$ and $(j=2, m=2) \rightarrow (j=2, m'=0)$ cross sections are proportional to v^4 and the $(j=2, m=2) \rightarrow (j=2, m'=-1)$ and $(j=2, m=2) \rightarrow (j=2, m'=-2)$ cross sections are proportional to v^8 , as predicted.

To summarize, we have derived the threshold laws for the projection-changing transitions in collisions of paramagnetic

atoms or molecules with structureless targets. We show that the projection-changing transitions cannot be induced by s -wave collisions if the orbital angular momentum for the collision remains unchanged. Thus the transitions $(l=1) \rightarrow (l'=1)$ and $(l=0) \rightarrow (l'=2)$ determine the limiting cross section for a collision in which m changes by 1 or 2. The numerical results show that the dominant contribution to the $\Delta m=1$ transitions is from the $(l=1) \rightarrow (l'=1)$ cross section, while the $\Delta m=2$ transitions are predominantly determined by the $(l=0) \rightarrow (l'=2)$ scattering.

Our derivations apply to scattering for which the Wigner law (4) is valid for $l \rightarrow l'$ transitions. If the colliding particles interact through a long-range potential $-C_s/R^s$, the asymptotic form of the scattering wave function is modified by the $1/R^s$ term and the cross section for a single-channel scattering in the state with angular momentum l follows the Wigner law only if $l < (s-3)/2$ [14]. When $l > (s-3)/2$, the square of the T -matrix element varies as $|T_{l \rightarrow l}|^2 \sim v^{2s-4}$ independently of l . Whether or not long-range potentials modify the threshold behavior of off-diagonal T -matrix elements in a multichannel collision remains to be explored.

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