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Louis Biolsi Jr.
Missouri University of Science and Technology, biolsi@mst.edu

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Inelastic cross sections for molecules interacting through dipole and/or quadrupole potentials

Louis Biolsi

Department of Chemistry, University of Missouri-Rolla, Rolla, Missouri 65401
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Formal expressions for the lowest order inelastic contribution to the degeneracy averaged total cross section for both distinguishable and indistinguishable rigid diatomic molecules are obtained for molecules interacting through a multipole potential. Explicit expressions for the inleastic cross section are obtained for molecules interacting through permanent dipole–dipole, dipole–quadrupole, or quadrupole–quadrupole potentials. These results require the summation over only a single quantum number; the relative angular momentum quantum number. Thus, they are useful for analytic or numerical calculations.

I. INTRODUCTION

Consider a collision between rigid diatomic molecules a and b, separated by intermolecular distance r. The rotation R makes the intermolecular axis parallel to the space fixed z axis and, in a body fixed coordinate system, S_a and S_b are the rotations that bring the internuclear axes of molecules a and b, respectively, parallel to the intermolecular axis after the rotation R has been performed. A complete set of functions in the space of r, R, S_a, and S_b is provided by the spherical harmonics. Thus, the intermolecular potential can be written as

$$V(rS_aS_b) = \sum_{L_aL_b\nu_1} v(L_aL_b\nu_1 \mid r) Y(L_a, -\nu_1 \mid S_a) Y(L_b\nu_1 \mid S_b) .$$

(1)

Gioumousis and Curtiss[1] found certain restrictions on the expansion coefficient for a potential of this form. In particular,

$$v(L_aL_b\nu_1 \mid r) = 0 \quad \text{if } L_a \text{ is odd} ,$$

(2)

when molecule a is a homonuclear diatomic molecule. An exactly similar restriction holds if molecule b is homonuclear.

A restricted distorted wave expansion is obtained by considering a perturbation potential in which the unperturbed potential is taken to be the spherical approximation. Thus the expansion coefficient of the potential can be written as[2]

$$v(L_aL_b\nu_1 \mid r) = v^{(0)}(r)\delta(L_aL_b\nu_1 ; 000) + v^{(1)}(L_aL_b\nu_1 \mid r) ,$$

(3)

where $v^{(0)}(r)$ is the spherical term in the expansion. Also, if the interaction is between two electrostatic multipoles, the nonspherical expansion coefficient has the form[2]

$$v^{(1)}(L_aL_b\nu_1 \mid r) = \alpha(L_aL_b\nu_1)\phi(r) .$$

(4)

For such potentials there are restrictions on the potential and the possible quantum states for the lowest order nonspherical elastic and the lowest order inelastic contributions to the scattering cross section.[3]

Consider the interaction between two rigid diatomic molecules possessing permanent dipole and/or quadrupole moments. A general expression for the lowest order contribution to the total inelastic cross section for potentials having the characteristics defined by Eqs. (1), (3), and (4) is given by Eq. (43) in Ref. 4. However, this expression also accounts for nuclear spin. If nuclear spin is ignored, the result is

$$Q_{DA}^{22} = \Delta(\bar{\lambda}\lambda L)\Delta(l_a\bar{l}_aL_a)\Delta(l_b\bar{l}_bL_b)\Delta(L_aL_bL) \frac{4\pi k}{\bar{k}} \sum_{L_a L_b \nu_1 \nu_1' L \lambda \bar{\lambda}} (2\lambda+1)(2\bar{\lambda}+1) \frac{(2l_a+1)(2l_b+1)}{(2L_a+1)(2L_b+1)}$$

$$\times \begin{pmatrix} l_a & \bar{l}_a & L_a \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} l_b & \bar{l}_b & L_b \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} \lambda & \bar{\lambda} & L \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} L & L_a & L_a \\ 0 & -\nu_1 & \nu_1 \end{pmatrix} \begin{pmatrix} L & L_a & L_b \\ 0 & -\nu_1' & \nu_1' \end{pmatrix} \alpha(L_aL_b\nu_1)\, \alpha(L_aL_b\nu_1')^* f(\lambda\bar{\lambda} \mid k\bar{k}) f(\lambda\bar{\lambda} \mid k\bar{k})^*,$$

(5)

where

$$f(\lambda\bar{\lambda} \mid k\bar{k}) = -(-i)^\lambda \frac{2\mu}{\hbar^2} \int \chi_\lambda(k \mid r)\phi(r)\chi_\lambda(\bar{k} \mid r)\, r^2 dr .$$

(6)

The notation is explained in Ref. 4. This expression is somewhat simpler than the corresponding result given in Ref. 2; i.e., Eq. (83).

The interaction between two nonoverlapping permanent charge distributions is discussed in Ref. 5(a). Upon using those results, it can be shown that[3,5a]

$$\alpha(L_aL_b\nu_1) = [(L_a + \mid \nu_1 \mid)! (L_a - \mid \nu_1 \mid)! (L_b + \mid \nu_1 \mid)! (L_b - \mid \nu_1 \mid)!]^{-1/2}$$

and, using the relation between the Jacobi polynomials and the irreducible representations[5b] and the relation between the 3-j coefficients and the irreducible representations, it can be shown that

$$\alpha(L_aL_b\nu_1) = \alpha_0 \begin{pmatrix} L_a & L_b & L_a+L_b \\ -\nu_1 & \nu_1 & 0 \end{pmatrix} ,$$

(7)

where

$$\alpha_0 = \frac{(-1)^{L_a+L_b}}{(L_a+L_b)!} \sqrt{\frac{(2L_a+2L_b+1)(2L_a+2L_b)!}{(2L_a)!(2L_b)!}} \; . \tag{8}$$

When this is substituted into Eq. (5) and the summation properties of the 3-j coefficients are used, the result is

$$Q_{DA}^{22} = \Delta(\bar\lambda\lambda; L_a+L_b)\Delta(l_a\bar l_a L_a)\Delta(l_b\bar l_b L_b)\frac{4\pi k}{k}(2l_a+1)(2l_b+1)\sum_{L_a L_b}\alpha_0^2[(2L_a+1)(2L_b+1)(2L_a+2L_b+1)]^{-1}$$

$$\times\begin{pmatrix}l_a & \bar l_a & L_a\\ 0 & 0 & 0\end{pmatrix}^2\begin{pmatrix}l_b & \bar l_b & L_b\\ 0 & 0 & 0\end{pmatrix}^2\sum_{\lambda\bar\lambda}(2\lambda+1)(2\bar\lambda+1)\begin{pmatrix}\lambda & \bar\lambda & L_a+L_b\\ 0 & 0 & 0\end{pmatrix}^2 f(\lambda\bar\lambda|k\bar k)f(\lambda\bar\lambda|k\bar k)^* \; . \tag{9}$$

Notice that the number of summations has been reduced from seven to four.

II. DIPOLE-DIPOLE INTERACTIONS

For dipole–dipole interactions, $L_a = L_b = 1$. Thus, using Eq. (2), both molecules must be heteronuclear. It is possible that $L_a = 0$ and $L_b = 2$ or vice versa. However, then one of the molecules would have a spherically symmetric charge distribution. This situation would represent an induced interaction between a spherically symmetric charge distribution and a permanent dipole, not an interaction between two permanent dipoles.

The properties of the 3-j coefficients[6] constrain the values of $\bar\lambda$ to $\lambda+2$, λ, and $\lambda-2$. Condon and Shortley[7] tabulate the 3-j coefficients with one index equal to 2. When these values are substituted into Eq. (9), the result is

$$Q_{DA}^{22}(\mu_a, \mu_b) = \Delta(\bar\lambda\lambda 2)\Delta(l_a\bar l_a 1)\Delta(l_b\bar l_b 1)\frac{2\pi k}{3k}(2l_a+1)(2l_b+1)\begin{pmatrix}l_a & \bar l_a & 1\\ 0 & 0 & 0\end{pmatrix}^2\begin{pmatrix}l_b & \bar l_b & 1\\ 0 & 0 & 0\end{pmatrix}^2\sum_\lambda\left(\frac{\lambda(\lambda+1)(2\lambda+1)}{(2\lambda-1)(2\lambda+3)}\right.$$

$$\times f(\lambda\bar\lambda|k\bar k)f(\lambda\bar\lambda|k\bar k)^* + \frac{3\lambda(\lambda-1)}{2(2\lambda-1)}\left[f(\lambda-2,\lambda|k\bar k)f(\lambda-2,\lambda|k\bar k)^* + f(\lambda,\lambda-2|k\bar k)f(\lambda,\lambda-2|k\bar k)^*\right]\Bigg) \; . \tag{10}$$

Only one summation remains. This is essentially the same result as that obtained by Olmsted and Curtiss,[8] except that they calculated the moments of the degeneracy averaged differential cross section.

III. DIPOLE-QUADRUPOLE INTERACTIONS

Consider the interaction between the permanent dipole moment of molecule a with the permanent quadrupole moment of molecule b. Thus, $L_a = 1$ and $L_b = 2$ and, using Eq. (2), molecule a must be heteronuclear. In this case $\bar\lambda$ is restricted to $\lambda+3$, $\lambda+1$, $\lambda-1$, and $\lambda-3$. The 3-j coefficients with one index equal to 3 are tabulated.[9] When these values are substituted into Eq. (9), the result is

$$Q_{DA}^{22}(\mu_a, Q_a) = \Delta(\bar\lambda\lambda 3)\Delta(l_a\bar l_a 1)\Delta(l_b\bar l_b 2)\frac{\pi k}{18k}(2l_a+1)(2l_b+1)\begin{pmatrix}l_a & \bar l_a & 1\\ 0 & 0 & 0\end{pmatrix}^2\begin{pmatrix}l_b & \bar l_b & 2\\ 0 & 0 & 0\end{pmatrix}^2$$

$$\times\sum_\lambda\left(\frac{5\lambda(\lambda-1)(\lambda-2)}{(2\lambda-1)(2\lambda-3)}\left[f(\lambda-3,\lambda|k\bar k)f(\lambda-3,\lambda|k\bar k)^* + f(\lambda,\lambda-3|k\bar k)f(\lambda,\lambda-3|k\bar k)^*\right]\right.$$

$$+\frac{3\lambda(\lambda+1)(\lambda-1)}{(2\lambda-3)(2\lambda+3)}\left[f(\lambda-1,\lambda|k\bar k)f(\lambda-1,\lambda|k\bar k)^* + f(\lambda,\lambda-1|k\bar k)f(\lambda,\lambda-1|k\bar k)^*\right]\Bigg) \; . \tag{11}$$

Also consider the interaction of the dipole moment of molecule a with the quadrupole moment of molecule b and the dipole moment of molecule b with the quadrupole moment of molecule a. The summation over λ in Eq. (11) is unchanged, but the term in front of the summation is replaced by

$$\Delta(\bar\lambda\lambda 3)\frac{\pi k}{18k}(2l_a+1)(2l_b+1)\left[\Delta(l_a\bar l_a 1)\Delta(l_b\bar l_b 2)\begin{pmatrix}l_a & \bar l_a & 1\\ 0 & 0 & 0\end{pmatrix}^2\begin{pmatrix}l_b & \bar l_b & 2\\ 0 & 0 & 0\end{pmatrix}^2 + \Delta(l_a\bar l_a 2)\Delta(l_b\bar l_b 1)\begin{pmatrix}l_a & \bar l_a & 2\\ 0 & 0 & 0\end{pmatrix}^2\begin{pmatrix}l_b & \bar l_b & 1\\ 0 & 0 & 0\end{pmatrix}^2\right] \; . \tag{12}$$

IV. QUADRUPOLE-QUADRUPOLE INTERACTIONS

For quadrupole–quadrupole interactions, $L_a = L_b = 2$ and, using Eq. (2), both molecules can be either heteronuclear or homonuclear. In this case $\bar\lambda$ is restricted to $\lambda+4$, $\lambda+2$, λ, $\lambda-2$, and $\lambda-4$. The 3-j coefficients with one index equal to 4 are easily evaluated.[6] When these values are substituted into Eq. (9), the result is

$$Q_{DA}^{22}(Q_a, Q_b) = \Delta(\bar\lambda\lambda 4)\Delta(l_a\bar l_a 2)\Delta(l_b\bar l_b 2)\,\frac{7\pi k}{720\bar k}\,(2l_a+1)(2l_b+1)\begin{pmatrix} l_a & \bar l_a & 2 \\ 0 & 0 & 0 \end{pmatrix}^2\begin{pmatrix} l_b & \bar l_b & 2 \\ 0 & 0 & 0 \end{pmatrix}^2$$

$$\times \sum_\lambda \left(\frac{35\lambda(\lambda-1)(\lambda-2)(\lambda-3)}{4(2\lambda-1)(2\lambda-3)(2\lambda-5)}\,[f(\lambda,\lambda-4|k\bar k)f(\lambda,\lambda-4|k\bar k)^* + f(\lambda-4,\lambda|k\bar k)f(\lambda-4,\lambda|k\bar k)^*]\right.$$

$$+\frac{5\lambda(\lambda+1)(\lambda-1)(\lambda-2)}{(2\lambda+3)(2\lambda-1)(2\lambda-5)}\,[f(\lambda,\lambda-2|k\bar k)f(\lambda,\lambda-2|k\bar k)^* + f(\lambda-2,\lambda|k\bar k)f(\lambda-2,\lambda|k\bar k)^*]$$

$$\left.+\frac{9\lambda(\lambda+1)(\lambda+2)(\lambda-1)(2\lambda+1)}{2(2\lambda-1)(2\lambda-3)(2\lambda+3)(2\lambda+5)}\,f(\lambda\lambda|k\bar k)f(\lambda\lambda|k\bar k)^*\right)\,. \qquad (13)$$

V. INDISTINGUISHABLE MOLECULES

The Pauli principle must be invoked when indistinguishable molecules collide. In this case the lowest order inelastic contribution to the degeneracy averaged total cross section (including nuclear spin) is given by Eqs. (16) and (17) in Ref. 10. If nuclear spin is ignored, these equations reduce to

$$Q_{DA}^{22i(ID)} = \Delta(\bar\lambda\lambda; L_a+L_b)\,\frac{4\pi k}{\bar k}\,(2l_a+1)(2l_b+1)\sum_{L_aL_b}\alpha_0^2[(2L_a+1)(2L_b+1)(2L_a+2L_b+1)]^{-1}$$

$$\times\left[\Delta(l_a\bar l_a L_a)\Delta(l_b\bar l_b L_b)\begin{pmatrix} l_a & \bar l_a & L_a \\ 0 & 0 & 0 \end{pmatrix}^2\begin{pmatrix} l_b & \bar l_b & L_b \\ 0 & 0 & 0 \end{pmatrix}^2 + \Delta(l_b\bar l_a L_a)\Delta(l_a\bar l_b L_b)\begin{pmatrix} l_b & \bar l_a & L_a \\ 0 & 0 & 0 \end{pmatrix}^2\begin{pmatrix} l_a & \bar l_b & L_b \\ 0 & 0 & 0 \end{pmatrix}^2\right]$$

$$\times\sum_{\lambda\bar\lambda}(2\lambda+1)(2\bar\lambda+1)\begin{pmatrix} \lambda & \bar\lambda & L_a+L_b \\ 0 & 0 & 0 \end{pmatrix}^2 f(\lambda\bar\lambda|k\bar k)f(\lambda\bar\lambda|k\bar k)^* \qquad (14)$$

and

$$Q_{DA}^{22ii(ID)} = \delta(L_a+L_b; L_a'+L_b')\epsilon\Delta(\bar\lambda\lambda; L_a+L_b)\Delta(l_a\bar l_a L_a)\Delta(l_b\bar l_b L_b)\Delta(l_b\bar l_a L_a')\Delta(l_a\bar l_b L_b')\frac{4\pi k}{\bar k}(2l_a+1)(2l_b+1)$$

$$\times\sum_{L_aL_bL_a'L_b'}(-1)^{l_a+l_b+L_a+L_a'}\alpha_0\alpha_0'(2L_a+2L_b+1)^{-1}\begin{pmatrix} l_a & \bar l_a & L_a \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l_b & \bar l_b & L_b \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l_b & \bar l_a & L_a' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l_a & \bar l_b & L_b' \\ 0 & 0 & 0 \end{pmatrix}$$

$$\times\left[\begin{Bmatrix} \bar l_a & l_a & L_a \\ l_b & \bar l_b & L_b \\ L_a' & L_b' & L_a+L_b \end{Bmatrix} + \begin{Bmatrix} \bar l_a & l_b & L_a' \\ l_a & \bar l_b & L_b' \\ L_a & L_b & L_a+L_b \end{Bmatrix}\right]\sum_{\lambda\bar\lambda}(-1)^\lambda(2\lambda+1)(2\bar\lambda+1)\begin{pmatrix} \lambda & \bar\lambda & L_a+L_b \\ 0 & 0 & 0 \end{pmatrix}^2 f(\lambda\bar\lambda|k\bar k)f(\lambda\bar\lambda|k\bar k)^*\,, \qquad (15)$$

respectively, where $\epsilon = +1$ for bosons and $\epsilon = -1$ for fermions, and the quantities in braces are 9-j coefficients.

The first term in Eq. (14) is the "normal" result for the collision of distinguishable molecules; i.e., molecules in initial state $\bar l_a$, $\bar l_b$ go to final states l_a, l_b, and the second term is the exchange term; i.e., molecules in initial states $\bar l_a$, $\bar l_b$ go to final states l_b, l_a. Equation (15) is a purely quantum mechanical term and leads to quantum statistics effects. [11] Classically, this term oscillates rapidly with zero average value. [12]

Notice that the summation over λ and $\bar\lambda$ in Eq. (14) is the same as in Eq. (9) and the summation over λ and $\bar\lambda$ in Eq. (15) is the same as in Eq. (9), but multiplied by $(-1)^\lambda$. Thus, the summations over λ in Eqs. (10), (11), and (13) for the various multipole interactions between distinguishable molecules are also applicable when indistinguishable molecules collide.

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