

## The multipole-extracted adiabatic-nuclei approximation for electron-molecule collisions

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An extension of the adiabatic-nuclei approximation appropriate for electron collisions with polar molecules is discussed. The method will find most useful application, but is not restricted, to molecules with large permanent dipole moments. Treatment of molecules with small or negligible dipole moments but significant quadrupole moments and/or dipole polarizabilities is also within its purview. The essence of the method consists of extracting the effects of the long-range interactions from the usual adiabatic-nuclei expressions, and reintroducing them in the laboratory frame in a self-consistent manner. The first Born approximation is the simplest, but not the only possible, vehicle for this approach. The method is closely related to the angular frame-transformation method. Illustrative applications are presented.

### I. INTRODUCTION

The adiabatic-nuclei (AN) approximation<sup>1,2</sup> for electron-molecule collisions has been widely used<sup>3</sup> in scattering calculations for nonpolar molecules. The prescription for computing a rovibrational cross section in this approximation can be written

$$\frac{d\sigma(vj \rightarrow v'j')}{d\Omega} = \frac{k_{v',j'}}{k_{v,j}} \sum_{l_t} C(jj'l_t) \frac{d\sigma^{l_t}(v \rightarrow v')}{d\Omega}, \quad (1)$$

where  $k_{vj}$  and  $k_{v',j'}$  are the initial and final momenta of the scattered electron,  $C(jj'l_t)$  is a purely algebraic coefficient, and  $d\sigma^{l_t}(v \rightarrow v')/d\Omega$  is a differential cross section partial in the angular momentum  $l_t$  transferred during the collision.<sup>4</sup> The channel momenta are related to the total rovibrational energies of the molecular states by

$$k_{v',j'}^2 - k_{vj}^2 = 2(\epsilon_{vj} - \epsilon_{v',j'}). \quad (2)$$

The notation  $v \rightarrow v'$  in  $d\sigma^{l_t}(v \rightarrow v')/d\Omega$  indicates that vibrational transitions are to be taken into account in obtaining this quantity. This could be achieved in a variety of ways, ranging in sophistication from full vibrational close coupling<sup>5</sup> in a molecular body-fixed coordinate frame to use of the adiabatic nuclear vibration approximation.<sup>6</sup> In any case,  $d\sigma^{l_t}(v \rightarrow v')/d\Omega$  is ultimately obtained by a transformation from the body-fixed to laboratory-fixed coordinate frames.

In a subsequent discussion, reference to the body

frame should be taken to imply neglect of the rotational, but not necessarily the vibrational Hamiltonian in the scattering calculations. Irrespective of the treatment of vibration, the effects of rotational dynamics are incorporated explicitly in (1) only through the algebraic factor and the kinematic ratio  $k_{v',j'}/k_{vj}$ . The algebraic factor has the general property that it yields unity when summed over all final rotor state quantum numbers  $j'$ . Assuming the kinematic ratio constant with respect to  $j'$ , the total cross section thus has the well-known property that is independent of the initial rotor state.<sup>3</sup>

The form of the cross section given by (1) includes an implicit average over all initial, and sum over all final, degenerate magnetic substates. This is not an essential feature of the approximation, since (1) could be expressed more generally so as to allow for this additional "resolution" of magnetic transitions. Likewise, the cross section  $d\sigma^{l_t}(v \rightarrow v')/d\Omega$  represents a quantity that can, in principle, be computed for any molecular system, since  $l_t$  is a quantity that represents the dynamical effects of the collision process on the scattered electron. For transitions involving a  ${}^1\Sigma$  state of a linear molecule,  $C(jj'l_t)$  takes the simple form<sup>1</sup>

$$C(jj'l_t) = C(jl_t j'; 00)^2, \quad (3)$$

where  $C(\dots)$  is a Clebsch-Gordon coefficient.

Chang and Temkin<sup>1</sup> demonstrated the utility of the AN approximation, and illustrated its application, by showing that the results of elaborate

laboratory-frame calculations of cross sections for rotational transitions in  $H_2$  bear a mathematical relationship among themselves consistent with (1) and (3). This demonstration has been recently buttressed by Shimamura,<sup>7</sup> who showed that inclusion of the kinematic ratios (not emphasized in the earlier<sup>1</sup> comparison) yields even better results near rotational thresholds, as predicted.<sup>2</sup> These demonstrations may not be held completely convincing, of course, as they involved only the integrated cross sections, which are perhaps least sensitive to any breakdown of the AN approximation. No direct comparison, at the level of near-threshold differential cross sections computed with and without the AN approximation, and with a fairly realistic representation of the interaction potential, has yet been published for any molecule.<sup>8</sup>

The essential criterion for validity of the AN approximation is often stated as the requirement that the interaction time be short compared with the typical period of molecular motion (rotation or vibration). It may therefore fail for highly excited rotational states and near thresholds. It is also widely viewed as being much less valuable for polar than nonpolar molecules, owing to the fact that large impact parameters (used loosely here to indicate angular momenta or radial distance) dominate the interaction. For  $l_t = 1$ , which is dominated by the dipole interaction, (1) diverges in the forward direction and the integral cross section is infinite.<sup>9</sup> It has been suggested<sup>10</sup> that a complete and accurate specification of cross sections for polar molecules, particularly near thresholds, may require an approach with at least the sophistication of the radial frame-transformation method.<sup>11</sup> The AN approximation has, however, been found useful in a number of limited cases for polar molecules, especially away from thresholds and for cross sections that are not dominated by forward (large impact parameter) scattering.<sup>9</sup>

There is reason to believe, however, that the AN approximation may, with very simple modification, be of great value in studying electron collisions with any molecule for which there is a significant long-range component to the interaction. We refer to a method recently suggested<sup>12,13</sup> for obtaining total (summed over all final rotor states) vibrationally elastic cross sections, by correcting a simple expression<sup>3</sup> for this cross section in the laboratory-frame first Born approximation (FBA), using the results of calculations carried out completely in the body frame. This method permits the inclusion of the effects of the rotational Hamiltonian for those

large impact parameters for which the AN approximation breaks down, but for which the FBA may be valid. The method discussed in Sec. II is a straightforward extension and generalization of this approach. The extension amounts to providing a prescription for obtaining individual rovibrational cross sections, instead of just the total. The generalization amounts to removing the restriction to the FBA for the dipole potential as the vehicle for the method.

The essential hypothesis of the method is that the differential cross section for some rovibrational transition can be separated into two terms [see (7) and (8)] that are treated independently. The first term represents a quantity calculated in the laboratory frame with full account being taken of the rovibrational dynamics, but for which a relatively unsophisticated and economical approach may be adequate. The second term represents a quantity calculated in the body frame, with the usual approximations for the rovibrational dynamics, but with arbitrarily sophisticated techniques otherwise. To the extent that the first term can be obtained with relative ease, and the second with the simplification of the factorization (1), the method permits the full power of the AN approximation to be brought to bear on polar molecules. Moreover, to the extent that the interactions dominating near-threshold collisions can be incorporated in the first term, the method may be found useful over a broader range of collision energy than the original AN approximation.

## II. THE MULTIPOLE-EXTRACTED ADIABATIC-NUCLEI APPROXIMATION

Let us assume first that *no* approximations are made with respect to the rovibrational dynamics, and that all calculations are carried out in the laboratory frame. The differential cross section for scattering into polar angle  $\theta$  is often expressed as a Legendre expansion

$$\frac{d\sigma(vj \rightarrow v'j')}{d\Omega} = \frac{1}{4k_{vj}^2} \sum_{\lambda} A_{\lambda}(vj \rightarrow v'j') P_{\lambda}(\cos\theta). \quad (4)$$

The coefficients  $A_{\lambda}$  depend explicitly only on products of elements of the transition matrix  $\vec{T}$  and algebraic factors. Their precise definition is not of interest here, but it involves (in principle) infinite sums over the angular momenta  $l$  and  $l'$  that characterize the elements of  $\vec{T}$ . The integral cross

section involves only  $A_0$ , and the momentum-transfer cross section only  $A_0$  and  $A_1$ .

For polar molecules these sums can be very slowly convergent, owing to the contributions from large angular momenta, and many values of  $\lambda$  may also be required. This is analogous to the complete divergence that characterizes the AN approximation. Since the FBA for the elements of  $\vec{T}$  becomes exact in the limit of large angular momenta, for example,  $l(l') \geq l_B$ , Crawford and Dalgarno<sup>14</sup> suggested use of the alternate, but *completely equivalent*, formulas (here generalized to include vibrational transitions)

$$\frac{d\sigma}{d\Omega}(vj \rightarrow v'j') = \frac{d\sigma^{\text{FBA}}}{d\Omega}(vj \rightarrow v'j') + \Delta \frac{d\sigma}{d\Omega}(vj \rightarrow v'j'), \quad (5)$$

where

$$\begin{aligned} \Delta \frac{d\sigma}{d\Omega}(vj \rightarrow v'j') &= \frac{1}{4k_{vj}^2} \sum_{\lambda} [A_{\lambda}(vj \rightarrow v'j') \\ &\quad - A_{\lambda}^{\text{FBA}}(vj \rightarrow v'j')] P_{\lambda}(\cos\theta). \quad (6) \end{aligned}$$

The first term in (5) is the FBA for the cross section, for which simple closed-form expressions are available,<sup>3</sup> and the second term in (6) is its partial-wave representation. Expressions for the elements of  $\vec{T}$  in the FBA are also available.<sup>15</sup> Aided by cancellation, the sum over  $\lambda$  in (6) now converges much more rapidly and terminates (to some specified accuracy) at  $\lambda_{\text{max}}$ . More importantly, contributions to *any*  $A_{\lambda}$  and  $A_{\lambda}^{\text{FBA}}$  for  $l(l') \geq l_{\text{max}} = l_B + \lambda$  cancel identically ( $A_{\lambda}$  couples elements of  $\vec{T}$  differing in  $l$  by not more than  $\lambda$ ). Therefore elements of  $\vec{T}$  are required for the limited range  $l(l') \leq l_B + \lambda_{\text{max}}$ , and all sums terminate rapidly and gracefully.

At this point the closure formulas [(5) and (6)] are simply a powerful, numerical device involving no additional assumptions except the ultimate validity of the FBA, and have been extensively used as such. The expressions labeled FBA in (5) and (6) are not restricted to the dipole interaction, although this is the most problematic case, and could be generalized to go beyond the FBA without destroying the identity of (4) and (5). It is required only that the first term in (5) and the second term in (6) be formally identical, and that the elements of  $\vec{T}$  used to calculate the two terms in (6) approach the same limit for large angular momenta. Viewed solely as extensions to a numer-

ical device, these may not offer significant advantage, merely trading more effort in one place for less in another. We note, however, that the closure formulas have effectively separated the cross section into small and large angular momentum components. It is also true, if less obvious, that contributions from large radial distances cancel in (6). Thus even if the AN approximation is clearly invalid for (4), it may be appropriate to consider its possible validity for (6). To the extent that the range of small impact parameters contributing to (6) is reduced by going beyond the FBA for the dipole interaction, the AN approximation becomes more attractive. To the extent that the first term in (5) becomes more exact, (6) also becomes relatively smaller and any errors associated with the AN approximation become less significant. This last point is particularly relevant near threshold, where the FBA for the long-range interactions must ultimately become correct if the cross section is dominated by an entrance or exit channel with finite angular momentum.

The multipole-extracted adiabatic-nuclei (MEAN) approximation consists, therefore, of the replacement of (5) and (6) by

$$\frac{d\sigma(vj \rightarrow v'j')}{d\Omega} = \frac{d\sigma^{\text{APP}}(vj \rightarrow v'j')}{d\Omega} + \Delta \frac{d\sigma}{d\Omega}(vj \rightarrow v'j'), \quad (7)$$

where

$$\Delta \frac{d\sigma}{d\Omega}(vj \rightarrow v'j') = \frac{k_{v'j'}}{k_{vj}} \sum_{l_t} C(jj'l_t) \Delta \frac{d\sigma^{l_t}}{d\Omega}(v \rightarrow v'), \quad (8)$$

and

$$\begin{aligned} \Delta \frac{d\sigma^{l_t}}{d\Omega}(v \rightarrow v') &= \frac{1}{4k_v k_{v'}} \sum_{\lambda} [B_{\lambda}(v \rightarrow v', l_t) \\ &\quad - B_{\lambda}^{\text{APP}}(v \rightarrow v', l_t)] P_{\lambda}(\cos\theta). \quad (9) \end{aligned}$$

The coefficients  $B_{\lambda}$  and  $B_{\lambda}^{\text{APP}}$ , like their analogs in (6), depend explicitly only on elements of  $\vec{T}$  (now calculated in the body frame) and algebraic factors. The quantities labeled APP (approximate) in (7) and (9) are obtained for the same approximate interaction potential, including the dominant long-range interactions, but without and with, respectively, the AN approximation. The first term in (9) is precisely  $d\sigma^{l_t}(v \rightarrow v')/d\Omega$  in (1), the momenta  $k_v$  and  $k_{v'}$  being related by (2) without the rotation-

al contributions. If the vibrational Hamiltonian is also neglected in the body-frame calculations, and we consider only electronically elastic scattering, then  $k_v k_{v'}$  is replaced by  $k^2$ .

Since in arriving at (9), the AN approximation has been adopted for *both* terms in (6), we may still assume that there exists some  $l_B$  such that the elements of  $\vec{T}$  used to calculate the coefficients  $B_\lambda$  and  $B_\lambda^{\text{APP}}$  are effectively identical for  $l(l') \geq l_B$ . Thus the sum over  $\lambda$  in (9) still terminates at some  $\lambda_{\text{max}}$ , and the contributions to  $B_\lambda$  and  $B_\lambda^{\text{APP}}$  still cancel for  $l(l') \geq l_{\text{max}} = l_B + \lambda$ . This cancellation is completely analogous to that which occurs in (6). The numerical convenience of the original closure formula is therefore preserved. This cancellation is, in fact, an essential ingredient for polar molecules. The body-frame coefficients are logarithmically divergent for *all*  $\lambda$  for  $l_t = 1$  for polar molecules, as shown in Appendix A. This behavior, in a partial-wave representation, is due to contributions from large angular momenta, for which the AN approximation is inappropriate. Since these contributions to  $B_\lambda$  and  $B_\lambda^{\text{APP}}$  ultimately becomes identical and cancel in (9), the *difference* converges for all  $\lambda$  for  $l_t = 1$ . These contributions are then effectively reintroduced through the first term in (7), with a correct treatment of the rovibrational dynamics.

The approximation labeled APP in (7) and (9) may be freely chosen. It may be as elaborate and "exact" as desired, indeed in the limit of an exact treatment the second term in (7) would vanish. For highly polar molecules it may be necessary to go beyond the FBA for the dipole interaction, owing to the importance of second-order effects, or to the breakdown of quantum-mechanical unitarity. To the extent that the latter effect will appear in both in the first term in (7) and the second term in (9), its pernicious consequences may be mitigated. The next level of approximation might involve, for example, the unitarized Born approximation<sup>16</sup> or semiclassical perturbation theory.<sup>17</sup> One approach that will *not* work is exact solutions for the point dipole rotator, since the first term in (7) cannot, except in limited circumstances, be defined in this approximation.<sup>18</sup> If one goes beyond the FBA, the first term in (7) may require, for its evaluation, the original closure formulas [(5) and (6)]. It is obvious that the simplest approximation consistent with accurate results is desirable. It may well be that the FBA is entirely adequate for most purposes.

The MEAN approximation is closely related to

the angular frame-transformation method.<sup>13</sup> This method, like the radial frame-transformation method,<sup>11</sup> is designed to take maximum advantage of the Born-Oppenheimer separation of electronic and nuclear coordinates. It is based on a partition of space into two (or more) regions of angular momenta, rather than radial distance, and on the hypothesis that for a limited range of small angular momenta a body-frame treatment may be adequate, but that for large angular momenta a complete treatment of the rovibrational dynamics in the laboratory frame may be required. One can also view this as a separation into two regions of the polar scattering angle.<sup>7,13</sup> The precise point of "best" interface between the two regions is no less ambiguous than that between the two regions in the radial frame-transformation method. The angular frame-transformation method has been applied recently with apparent success.<sup>13,19,20</sup>

In this method the elements of  $\vec{T}$  obtained in the body frame are geometrically transformed<sup>11</sup> to the laboratory frame and augmented by additional elements of  $\vec{T}$  obtained directly in the laboratory frame, again by a procedure as elaborate as required. Then the closure formulas [(5) and (6)] are applied. Specializing to the FBA for APP in (7) and (9), it is clear that the essential difference with the MEAN approximation is the adoption of the AN approximation for the second term in (6) in the latter. This additional approximation is actually an improvement in one important sense, since when the approximation APP becomes quite good, as near threshold, the two terms in (9) may tend to cancel, whereas the two terms in (6) may not. This situation is analogous to calculations of atomic or molecular transition energies, where it is important to maintain the same level of approximation in both the initial and final states, even if one knows how to do much better for one or the other.

Since the MEAN approximation may find useful application even quite near threshold and/or for highly excited rotational states, let us consider the mechanics of such calculations in a little detail. It is not possible, for example, to rigorously identify  $k^2$  (for  $k_v = k_{v'} = k$ ) in (9), and by implication in the body-frame calculations themselves, with either  $k_{vj}^2$  or  $k_{v,j'}^2$ . For many applications, as in the examples presented in Sec. III, it may be adequate to identify  $k^2$  with the kinetic energy of the electron relative to the initial (or final) rotor state. At a minimum, this achieves a crude approximation to inclusion of the average effect of rotational kinetic energy, i.e., should be superior to identifying  $k^2$

with the electron kinetic energy relative to the ground rotor state. Very near threshold, however, a more precise resolution of this essential ambiguity may be of some consequence. One reasonable possibility is suggested by comparing (8) with (9) and (6), and equating the factors explicitly dependent on the channel momenta. This gives  $k^2 = k_{vj}k_{v,j}$ , the geometric mean, and was suggested by Nesbet<sup>21</sup> as a crude variant of his general energy-modified adiabatic approximation. One advantage of this choice is that threshold in the final results ( $k_{v,j} \rightarrow 0$ ) is unambiguously associated with threshold in the body-frame calculations ( $k \rightarrow 0$ ). This also achieves a crude approximation to the average effect of rotational kinetic energy. The computational prescription thus implied is a

$$k_{lJm_l v}^2 = 2(E - \epsilon_v) - 2\mathcal{B} \sum_j \left[ \frac{2j+1}{2J+1} \right] C(jlJ; 0m_l)^2 j(j+1), \quad (10)$$

where  $E$  is the total system energy,  $\epsilon_v [\simeq \omega(v + \frac{1}{2})]$  is the vibrational energy,  $\mathcal{B}$  is the rotational constant of the molecule (in a.u.),  $J$  is the total angular momentum, and  $m_l$  is the projection of the angular momentum of the scattered electron. This reduces to<sup>23</sup>

$$k_{lJm_l v}^2 = 2(E - \epsilon_v) - 2\mathcal{B} [l(l+1) + J(J+1) - 2m_l^2]. \quad (11)$$

The scattering equations now depend on  $J$  as well as  $m_l$ , but remain uncoupled in both. Since the last two terms in (11) can be incorporated into  $k^2$ , the additional calculations required for all  $J$  of interest actually amount to no more than an adequate range of values of

$$k_{lJm_l v}^2 \equiv 2(E - \epsilon_v) - 2\mathcal{B} [J(J+1) - 2m_l^2],$$

with nondegenerate channel energies related by

$$k_{l' J m_l v}^2 - k_{l J m_l v}^2 = 2\mathcal{B} [l(l+1) - l'(l'+1)]. \quad (12)$$

With this modification, the definitions of (8) and (9) must be appropriately generalized, but this should present no essential difficulty.

### III. ILLUSTRATIVE APPLICATIONS

The most severe test of the MEAN approximation will be near thresholds. Without two sets of calculations near threshold, one involving the MEAN approximation and one not, it can be tested by seeking to determine if the results of a set of calculations (or measurements) *not* involving the

set of calculations in the body frame for a range of  $k^2$ , these being interpolated at the discrete values of the product  $k_{vj}k_{v,j}$ , as necessary, for use in (8) and (9).

The body-frame calculations can also be improved, in addition to just conveniently and reasonably interpreted, without going beyond the context of the AN approximation. Choi and Poe<sup>22</sup> suggested that the simplifications of the usual body-frame, fixed-nuclei approach could be retained while still including in the scattering equations the major part of the rotational kinetic energy. For a  $^1\Sigma$  state of a linear molecule this " $l_z$ -conserving" modification amounts (to lowest order) to replacing  $k^2$  by the diagonal channel energies

approximation satisfy the relationships suggested by (7)–(9), as was originally done for the AN approximation.<sup>1,7</sup> Only one such set of calculations for a polar molecule is available, those of Chandra<sup>15</sup> for CO. These results include cross sections for elastic scattering, excitation, and momentum transfer involving several low-lying rotational states of the ground vibrational state.

The mechanics of the test involve using the angular-integrated equivalents of (7)–(9) to define  $\Delta\sigma^{l'}$  in terms of Chandra's results for  $\sigma(0 \rightarrow j)$ , using  $\Delta\sigma^{l'}$  to predict values for  $\bar{\sigma}(1 \rightarrow j)$ , and then comparing the latter with Chandra's results. In making this comparison we will use the simplest approximation for APP, namely, the FBA, and this only for the dipole potential. This should constitute, then, a rather severe test. Using (3) for  $j=0$ , we have simply

$$\Delta\sigma^{l'} = \frac{k_0}{k_{l'}} \sigma(0 \rightarrow l').$$

Taking these to correspond to the *same* incident electron energy  $E_0 (= \frac{1}{2}k_0^2)$  relative to any other initial state, the relationships between  $\bar{\sigma}(1 \rightarrow j)$  and  $\sigma(0 \rightarrow j)$  that follow are

$$\bar{\sigma}(1 \rightarrow 1) = \sigma(0 \rightarrow 0) + \frac{2}{5} \frac{\bar{k}_1}{k_2} \sigma(0 \rightarrow 2), \quad (13a)$$

$$\bar{\sigma}(1 \rightarrow 2) = \sigma^{\text{FBA}}(1 \rightarrow 2) + \frac{2}{3} \frac{\bar{k}_2}{k_1} [\sigma(0 \rightarrow 1) - \sigma^{\text{FBA}}(0 \rightarrow 1)] + \frac{3}{7} \frac{\bar{k}_2}{k_3} \sigma(0 \rightarrow 3), \quad (13b)$$

and

$$\bar{\sigma}(1 \rightarrow 3) = \frac{3}{5} \frac{\bar{k}_3}{k_2} \sigma(0 \rightarrow 2) + \frac{4}{9} \frac{\bar{k}_3}{k_4} \sigma(0 \rightarrow 4), \quad (13c)$$

etc. Of these only (13b) differs in any respect from the prescription of the original AN approximation. The momenta in (13a)–(13c) are related to the electron kinetic energy  $E_0$  by, for state  $j=0$ ,

$$k_j = \{2[E_0 - \mathcal{B}j(j+1)]\}^{1/2} \quad (14a)$$

and, for state  $j=1$ ,

$$\bar{k}_j = (2\{E_0 - \mathcal{B}[j(j+1) - 2]\})^{1/2}, \quad (14b)$$

where  $\mathcal{B} = 8.75 \times 10^{-6}$  a.u. All cross sections in the Born approximation are computed using<sup>3</sup>

$$\sigma_1^{\text{FBA}}(j \rightarrow j') = \frac{8\pi}{3k^2} D^2 \frac{j_{>}}{2j+1} \ln \frac{(k+k')}{|k-k'|}, \quad (15)$$

where  $D = 0.044$  a.u.,  $j_{>}$  is the larger of  $j$  and  $j'$ , and  $k(k') = k_j(k_{j'})$  for  $j=0$  and  $=\bar{k}_j(\bar{k}_{j'})$  for  $j=1$ .

The results are compared with  $\sigma(1 \rightarrow j)$  in Figs. 1 and 2. Note that the latter are for an electron incident on state  $j=1$  with energy  $\frac{1}{2}k_1^2$ , not  $E_0$ . The difference is negligible except at the lowest energies. Two approximations to (7)–(9) are also shown. One involves using only the algebraic factors in (13a)–(13c), i.e., neglecting the kinematic ratios, and the Born corrections in (13b). The second includes, in addition, only the kinematic ratios. Curves were drawn through the results as a visual aid. Also shown are the results using the FBA for the transitions  $1 \rightarrow 2$  and  $1 \rightarrow 3$ . The latter was computed using<sup>3</sup>

$$\sigma_1^{\text{FBA}}(j \rightarrow j') = \frac{16\pi}{45} Q^2 C(j2j'; 00)^2 \frac{k_{j'}}{k_j}, \quad (16)$$

where  $Q = 1.547$  a.u. From the form of (16), and the fact that  $k_0 = \bar{k}_1$ , it follows that FBA corrections to (13a) and (13c) would cancel. Only if (16) is generalized<sup>24</sup> to include the effect of the anisotropic polarizability would any difference from (13a) and (13c) arise. This effect is less than 3% of (16) below 0.01 eV.

The AN approximation for the transitions  $1 \rightarrow 1$  and  $1 \rightarrow 3$ , and the MEAN approximation for the

transition  $1 \rightarrow 2$ , would appear to be extremely good. At the lowest energy, the collision energy is still approximately five times the excitation energy for the transition  $1 \rightarrow 2$  and twice that for the transition  $1 \rightarrow 3$ . At lower energies the first Born approximation appears to be entirely adequate, but comparisons at lower energies would be needed to confirm this. A similar comparison may be made using (13a)–(13c) for the momentum-transfer cross section. Such a comparison has, in fact, already been made<sup>7</sup> for energies above 0.05 eV, with only the algebraic factors included. For lower energies the kinematic ratios become important, and, for  $\bar{\sigma}_m(1 \rightarrow 2)$ , the Born corrections. Agreement equally impressive as that shown in Figs. 1 and 2 is obtained.

To illustrate more direct application of the method we use preliminary results of a detailed study that is in progress of electron scattering by HCl. The interaction potential and computational algorithm used to solve the body-frame scattering equations have been previously described.<sup>19</sup> A general computer program<sup>25</sup> has been written to compute both  $B_\lambda(v \rightarrow v', l_t)$  and  $B_\lambda^{\text{FBA}}(v \rightarrow v', l_t)$ , given as input a set of elements of  $\vec{T}$  from the scattering calculations. These are augmented, as necessary, for higher symmetries and angular momenta by internally generated elements of  $\vec{T}$  in the unitarized Born (BII) and first Born approximations. The coefficients  $B_\lambda^{\text{FBA}}(v \rightarrow v', l_t)$  can be made to include the effect of long-range quadrupole and polarizability, in addition to dipole, interactions if desired. The generation of these coefficients and their convergence properties are discussed in Appendix B.

Typical results are shown in Table I. (The discussion hereafter refers to vibrationally elastic scattering; the indices  $v$  are suppressed.) For  $l_t = 1$  and  $\lambda \geq 10$  the coefficients cancel to high precision. Since the  $B_\lambda(1)$  and  $B_\lambda^{\text{FBA}}(1)$  are formally divergent, their values are very dependent on the choice of  $l_{\text{max}}$  but their *difference* is quite well converged. Here we took  $l_B = 19$ , and hence convergence in this difference was achieved with  $l_{\text{max}} \simeq 19 + \lambda$  in

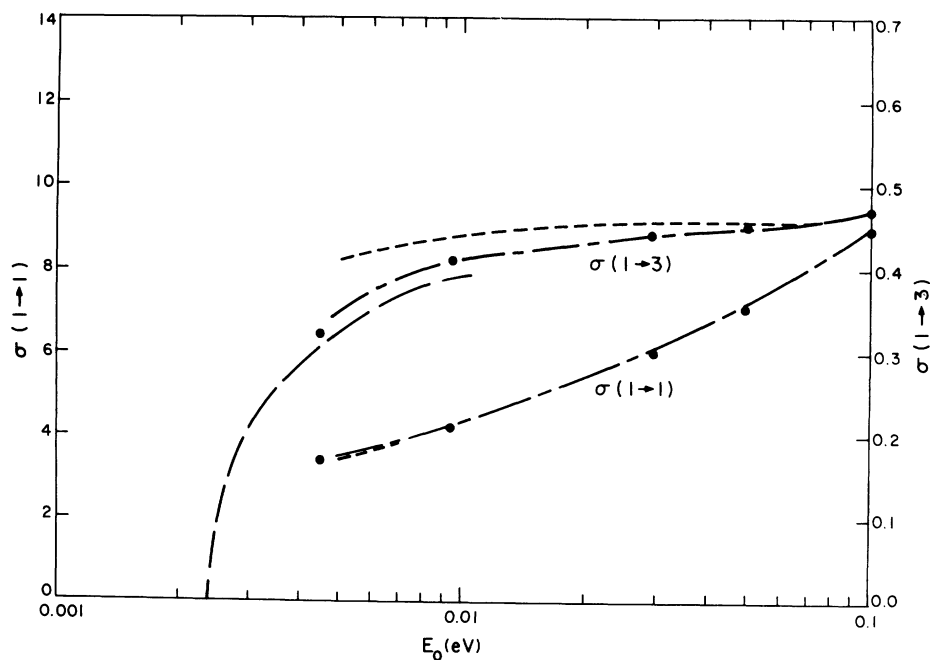


FIG. 1. Comparison of cross sections (in  $\text{\AA}^2$ ) for two transitions in CO. The solid points are from the calculations of Chandra,<sup>15</sup> the --- curve is drawn through the results obtained using those of Chandra for the transition  $0 \rightarrow j$  and the adiabatic-nuclei approximation. The - - - curve includes only the algebraic factors in (13a) and (13c). The - · - curve is the first Born approximation for the cross section  $\sigma(1 \rightarrow 3)$ .

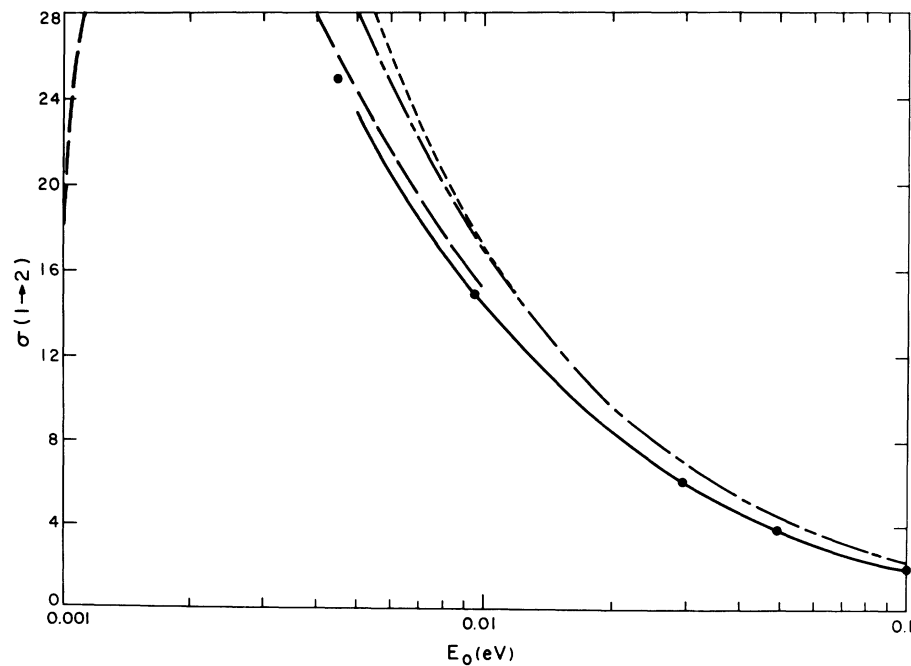


FIG. 2. Same as Fig. 1 for the transition  $1 \rightarrow 2$ . The solid curve includes the first Born approximation corrections as in (13b).

TABLE I. The coefficients  $B_\lambda(0 \rightarrow 0, l_t)$  and  $B_\lambda^{\text{FBA}}(0 \rightarrow 0, 1)$  for scattering by HCl at 11.0 eV. The first three columns are for  $l_t = 1$ .

$\lambda$	$B_\lambda$	$B_\lambda^{\text{FBA}}$	$l_t$	$B_0$	$B_1$
0	1.408	2.092	0	14.87	20.57
1	2.939	4.551	2	2.061	0.5279
2	5.363	6.221	3	0.2337	0.0036
3	6.859	7.459	4	1.246	-0.0230
4	8.365	8.442	5	0.07239	-0.09256
5	8.746	9.214	6	0.004869	-0.005580
6	9.811	9.852			
7	10.35	10.36			
8	10.78	10.78			
9	11.11	11.11			

this case. The very compact set of results in Table I are adequate to define [using (3), (7)–(9), and the appropriate FBA cross sections] integral, momentum-transfer, and energy-loss cross sections through contributions with  $l_t \leq 6$  for any  $j$  and  $j'$ .

With the assumption that  $k_{j'}/k_j$  is effectively constant, these can be summed over  $j'$  for any  $j$ , yielding results that depend on  $j$  only through the FBA cross sections. The total integrated cross section is simply obtained, for example, by adding to (15),

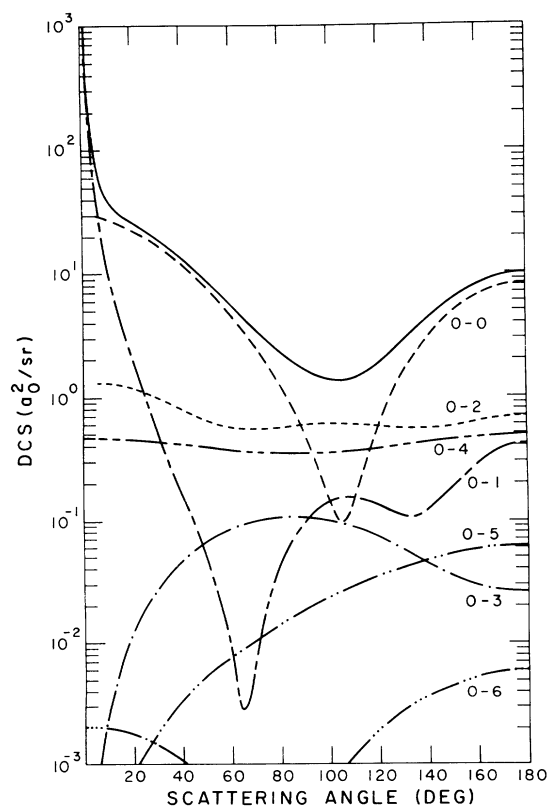


FIG. 3. Differential cross sections for transitions from the  $j=0$  state in vibrationally elastic scattering by HCl at 11.0 eV.

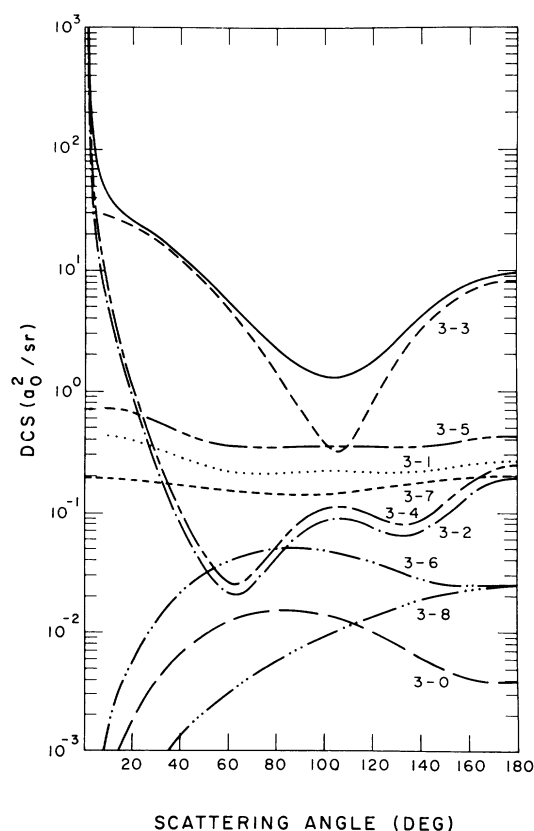


FIG. 4. Same as Fig. 3 for the  $j=3$  state.



summed over  $j'$  for any  $j$ , the correction

$$\Delta\sigma_I = \frac{\pi}{k^2} \left[ \sum_{l_t} B_0(l_t) - B_0^{\text{FBA}}(1) \right]. \quad (17)$$

The correction to the FBA for the total rotational energy-loss cross section is also independent<sup>26</sup> of  $j$ , and takes the simple form<sup>23</sup>

$$\Delta\sigma_S = \frac{\pi}{k^2} \sum_{l_t} \mathcal{B} l_t(l_t + 1) [B_0(l_t) - B_0^{\text{FBA}}(l_t) \delta_{1,l_t}]. \quad (18)$$

Note that there is no contribution for  $l_t = 0$ , since this contributes only to rotationally elastic scattering.

Differential cross sections for several transitions are shown in Figs. 3 and 4. The partial cross section for  $l_t = 0$  is seen to dominate at all but quite small angles. It also dominates the total integrated cross section. The shape of the cross sections for particular values of  $\Delta j$  differ noticeably for initial  $j = 0$  and 3. This is because, for example, the  $0 \rightarrow 1$  transition involves only  $l_t = 1$ , whereas the  $3 \rightarrow 4$  transition involves  $l_t = 1, 3, 5$ , and 7. The total differential cross sections for initial states  $j = 0$  and 3 do not, however, differ significantly except for  $\theta \lesssim 2^\circ$ , reflecting the high ratio of impact energy to rotational spacing.

Another example of preliminary results from the HCl work is given in Table II. The third column contains results for  $\Delta B_\lambda(2) \equiv B_\lambda(2) - B_\lambda^{\text{FBA}}(2)$ , obtained with elements of  $\vec{T}$  from the scattering calculations for  $l(l') \leq 10$  and  $m_l \leq 4$ , augmented by elements of  $\vec{T}$  in the B II approximation for all scattering symmetries,  $m_l$ , and angular momenta up to  $l_B = 26$  and elements of  $\vec{T}$  in the FBA up to  $l_{\text{max}} = 26 + \lambda$ . The fourth column contains results for the same quantity, but with B II  $\vec{T}$  matrices for all  $l(l') < l_B$ . In both cases, the B II  $\vec{T}$  matrices included dipole and quadrupole terms. We note first the rather surprising result that the B II approximation appears to be *worse* than the FBA in general, since many of the corrections  $\Delta B_\lambda^{\text{B II}}(2)$  are larger than the corrections  $\Delta B_\lambda(2)$ . This suggests a subtle interference between second-order contributions from the dipole interaction incorporated in  $\Delta B_\lambda^{\text{B II}}(2)$  and the short-range effects incorporated, in addition, in  $\Delta B_\lambda(2)$ .

Both columns are seen to decrease, but slowly, as  $\lambda$  increases, and to approach equality for  $\lambda > 10$ . Thus many values of  $\lambda$  (in this case  $\lambda \sim 30$ ), and hence a large value of  $l_{\text{max}}$ , are required to achieve good numerical convergence of large- and small-angle differential cross sections using either  $\Delta B_\lambda(2)$

or  $\Delta B_\lambda^{\text{B II}}(2)$ . This compromises the utility of the MEAN approximation to some extent. If, however, the B II approximation were to be used for APP in (7) and (9) the issue would become the  $\lambda$  dependence of the difference  $\Delta B_\lambda(2) - \Delta B_\lambda^{\text{B II}}(2)$ , and hence a much smaller value of  $l_{\text{max}}$  would be adequate for convergence. The more elaborate treatment of the first term in (7) thereby required should present no essential difficulty. This illustrates not only the potential value of upgrading the approximation APP, but also the fact that it may be required in only very limited circumstances. In this case, for example, the results for  $\lambda = 0$  and 1, hence the partial integral and momentum-transfer cross sections, for  $l_t = 2$  are well converged for  $l_{\text{max}} \simeq 27$ .

Consider now the second column of Table II. These coefficients were obtained, as noted above, with  $l_{\text{max}} = 26 + \lambda$ , i.e.,  $l_{\text{max}}$  increasing with  $\lambda$  and including all scattering symmetries with  $m_l \leq l_{\text{max}}$ . The values of  $B_0^{\text{FBA}}(2)$  is quite accurate (the exact result is  $6.2604 \times 10^{-2}$ ), but the values of  $B_\lambda^{\text{FBA}}(2)$  for  $\lambda > 0$  should vanish, and would do so if we took  $l_{\text{max}} = \infty$  for all  $\lambda$ . This follows directly from the fact that the differential cross section in the FBA for a pure quadrupole interaction is isotropic.<sup>3</sup> It is clear, however, that convergence to this limit is quite slow. In fact, it appears that  $B_\lambda^{\text{FBA}}(2)$  approaches a nearly constant value as  $\lambda$  becomes large. Thus were these values of  $B_\lambda^{\text{FBA}}(2)$  used to construct the differential cross section, the result

TABLE II. Coefficients  $\Delta B_\lambda(0 \rightarrow 0, 2)$  and  $\Delta B_\lambda^{\text{B II}}(0 \rightarrow 0, 2)$ , as defined in the text, for scattering by HCl at 0.3 eV.  $B_\lambda^{\text{FBA}}(0 \rightarrow 0, 2)$  contains only quadrupole contributions.

$\lambda$	$B_\lambda^{\text{FBA}}(\times 100)$	$\Delta B_\lambda(\times 100)$	$\Delta B_\lambda^{\text{B II}}(\times 100)$
0	6.2533	-0.6091	1.2180
1	-0.0204	-0.2245	-0.1137
2	-0.0322	0.4726	0.3020
3	-0.0429	0.5134	0.2994
4	-0.0523	0.5199	0.3717
5	-0.0609	0.4069	0.4084
6	-0.0684	0.4663	0.4206
7	-0.0752	0.4101	0.4181
8	-0.0813	0.2610	0.4074
9	-0.0868	0.3220	0.3918
10	-0.0915	0.3442	0.3735
11	-0.0959	0.3319	0.3535
12	-0.0997	0.3143	0.3326

would become progressively *worse*, particularly in the forward direction, as more terms were included in the Legendre expansion.

The use of a partial-wave expansion to compute the differential cross section in the FBA for the pure quadrupole interaction is obviously less than cunning. Our point is, however, that if the real interaction potential is such that the differential cross section is dominated, or very strongly influenced, by the long-range quadrupole interaction, then the effort to achieve convergence by straightforward calculation of the coefficients  $B_\lambda(2)$  might be extraordinarily, and needlessly, difficult. This fact was, of course, appreciated by the authors<sup>14</sup> of the original laboratory-frame closure formulas [(5) and (6)], and was apparently found useful by Chandra<sup>15</sup> in calculations of differential cross sections for transitions with  $\Delta j=2$  in CO. We only wish to emphasize here that the body-frame analog of the closure formulas, as incorporated in the MEAN approximation, offers similar computational advantages.

The MEAN approximation might also be extremely useful in the analysis of experimental data. Shimamura has shown<sup>27</sup> how state-to-state rotational cross sections can be extracted from unresolved energy-loss spectra. This technique takes advantage of the fact that the rotationally dependent terms in (1) are easily averaged over the initial rotational distribution of the target molecules. The cross sections partial in  $l_i$  in (1) can then be used as a relatively small set of free parameters in a least-squares fit to the observed data. Generalizing this idea to the MEAN approximation, the average over initial states need only take account, in addition, of the first term in (7), which is trivial if the FBA is used for APP. The partial cross sections  $\Delta\sigma^{l_i}(v \rightarrow v')/d\Omega$  in (8) then become the free parameters in the fit. Measurements of this type near threshold for vibrational excitation might contribute to the understanding of the dynamics involved in observed<sup>28</sup> threshold resonances in many molecules.

#### IV. CONCLUDING REMARKS

In the interests of future tests of the MEAN approximation, those carrying out elaborate calculations of the type performed by Chandra for CO are strongly encouraged to provide results for enough rotor-state transitions that tests such as illustrated here can be performed. We also encourage those working in the fixed-nuclei approximation to pro-

vide their results in the form of the *partial* cross sections  $\Delta\sigma^{l_i}(v \rightarrow v')/d\Omega$ , not just total (summed over all  $l_i$ ) as is often done. This will not only provide for future tests of the approximation, but, should it prove useful, also permit the calculation of cross sections for arbitrary rotor states. The HCl calculations, used here only to illustrate application of the approximation, are being refined and carried out to quite low energies with both of these ends in view.

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#### APPENDIX A: DIVERGENCE OF THE $B_\lambda$ COEFFICIENTS FOR THE DIPOLE INTERACTION

The fact that  $B_0(0 \rightarrow 0, 1)$  is singular for even an exact treatment of short-range interactions for polar molecules is well known.<sup>29</sup> It has also been shown,<sup>30</sup> using explicit expressions for the elements of  $\vec{T}$  in the FBA, that  $B_\lambda^{\text{FBA}}(0 \rightarrow 0, 1)$  can be written in terms of the same logarithmically divergent sum for  $\lambda=0$  and 1. It follows that  $B_\lambda(0 \rightarrow 0, 1)$  is also divergent for  $\lambda=0$  and 1, but that the fixed-nuclei momentum-transfer cross section, which is  $\alpha [B_0(0 \rightarrow 0, 1) - \frac{1}{3}B_1(0 \rightarrow 0, 1)]$ , is finite since the divergent terms can be made to cancel. A general proof that  $B_\lambda^{\text{FBA}}(v \rightarrow v', 1)$  is divergent for all  $\lambda$  follows from the observation that the FBA differential cross section in the fixed-nuclei approximation is<sup>3</sup>  $\alpha (1 - \cos\theta)^{-1}$ , the coefficients of an expansion of which in Legendre polynomials can be written

$$\begin{aligned} \frac{1}{2}(2\lambda + 1) \lim_{z \rightarrow 1} \int_{-1}^1 P_\lambda(x)(z-x)^{-1} dx \\ = (2\lambda + 1) \lim_{z \rightarrow 1} Q_\lambda(z), \end{aligned}$$

where  $z$  is not on the real axis between  $-1$  and  $1$ . The functions  $Q_\lambda(z)$  are just the associated Legendre functions of the second kind, of zero order.<sup>31</sup> These are singular at  $z=1$ , behaving as

$$\frac{1}{2}P_\lambda(z)\ln[(1+z)/(1-z)] + \dots$$

Now  $B_\lambda(v \rightarrow v', 1)$  can always be decomposed as

$$\bar{B}_\lambda(v \rightarrow v', 1) + B_\lambda^{\text{FBA}}(v \rightarrow v', 1) - \bar{B}_\lambda^{\text{FBA}}(v \rightarrow v', 1),$$

where the overbar indicates that  $\bar{B}_\lambda$  and  $\bar{B}_\lambda^{\text{FBA}}$  are

expressed as partial-wave sums and evaluated for all  $l(l') \leq l_{\text{max}}$ , beyond which all contributions cancel. Since the first and third of these terms are finite,  $B_\lambda(v \rightarrow v', 1)$  must diverge logarithmically for all  $\lambda$ .

## APPENDIX B: GENERATION OF THE $B_\lambda$ COEFFICIENTS: THE $l_t$ -REDUCED $\vec{T}$ MATRIX

Specializing to collisions with a  $^1\Sigma$  state of a linear molecule, the coefficients  $B_\lambda(v \rightarrow v', l_t)$  can be written<sup>32</sup>

$$\begin{aligned} B_\lambda(v \rightarrow v', l_t) = & (-1)^{l_t + \lambda} \sum_{l_1} \sum_{l_2} \sum_{l'_1} \sum_{l'_2} \sum_{m_1} \sum_{m_2} [(2l_1 + 1)(2l_2 + 1)(2l'_1 + 1)(2l'_2 + 1)]^{1/2} i^{l_1 - l'_1 - l_2 + l'_2} \\ & \times C(l_1 l_2 \lambda; 00) C(l_1 l_2 \lambda; 00) W(l_1 l_2 l'_1 l'_2; \lambda l_t) \\ & \times (-1)^{m_1 + m_2} C(l_1 l_1 l_t; m_1 - m_1) C(l_2 l_2 l_t; m_2 - m_2) T_{vl_1, v' l'_1}^{m_1} (T_{vl_2, v' l'_2}^{m_2})^*, \end{aligned} \quad (\text{B1})$$

where  $W(\dots)$  is a Racah coefficient. It is convenient to introduce the  $l_t$ -reduced  $\vec{T}$  matrix<sup>33</sup>

$$T_{vl, v' l'}^l \equiv \sum_{m_l} (-1)^{m_l} C(l l' l_t; m_l - m_l) T_{vl, v' l'}^{m_l}, \quad (\text{B2})$$

which remains symmetric under interchange of indices. If now (B1) is rewritten using (B2), we see that the sum over  $m_l$  need actually be done only once, rather than twice for each value of  $\lambda$ . This results in a dramatic computational simplification.

The  $l_t$ -reduced  $\vec{T}$  matrix is also extremely useful in accessing the point at which the results of the scattering calculations have reached agreement with the FBA, i.e., in identifying  $l_B$ . Since this point will depend weakly on  $m_l$ , it introduces no serious restriction to demand that this limit be reached, for a given set  $(l, l')$  for all  $m_l$ . Then we can compare elements of  $\vec{T}^l$ , rather than  $\vec{T}^{m_l}$ , from the FBA and from more elaborate calculations. Consider a potential that behaves asymptotically as

$$V(r, R) \underset{r \rightarrow \infty}{\sim} -\frac{\alpha_0(R)}{2r^4} + \frac{D(R)}{r^2} P_1 + \left[ \frac{Q(R)}{r^3} - \frac{\alpha_2(R)}{2r^4} \right] P_2, \quad (\text{B3})$$

where  $\alpha_0(R)$ ,  $\alpha_2(R)$ ,  $D(R)$ , and  $Q(R)$  are the molecular isotropic and anisotropic polarizabilities, and dipole and quadrupole moments, respectively, which depend parametrically on the internuclear separations  $R$ . Taking known expressions<sup>30,34</sup> for the elements of  $\vec{T}^{m_l}$  in the FBA for the potential (B3), and using these in (B2) with the orthogonality relation

$$\sum_{m_l} C(l l' l_t; m_l - m_l) C(l l' n; m_l - m_l) = \delta_{l, n} \delta(l l' l_t), \quad (\text{B4})$$

we ultimately obtain for the various terms in (B3)

$$T_{vl, v' l'}^l(\alpha_0) = -2\pi i k^2 \langle v | \alpha_0 | v' \rangle (-1)^l \frac{1}{[(2l + 3)(2l - 1)](2l + 1)^{1/2}} \delta_{l, 0} \delta_{l, l'}, \quad (\text{B5})$$

$$T_{vl, v' l'}^l(D) = 2i \langle v | D | v' \rangle (-1)^l (3l >)^{-1/2} \delta_{l, 1} \delta_{l', l \pm 1}, \quad (\text{B6})$$

$$T_{vl,v'l'}^{l_i}(Q) = 2ik \langle v | Q | v' \rangle (-1)^l \left\{ \frac{1}{[30(2l_{>} - 1)l_{>}(l_{>} - 1)]^{1/2}} \delta_{l',l \pm 2} - \frac{(2l+1)^{1/2}}{[5(2l+3)(2l-1)(l+1)l]^{1/2}} \delta_{l,l'} \right\} \delta_{l,2}, \quad (\text{B7})$$

and

$$T_{vl,v'l'}^{l_i}(\alpha_2) = -\frac{\pi k^2}{\sqrt{5}} \langle v | \alpha_2 | v' \rangle (-1)^l \left\{ \frac{[6l_{>}(l_{>} - 1)]^{1/2}}{[2(2l_{>} + 1)(2l_{>} - 3)(2l_{>} - 1)]^{3/2}} \delta_{l',l \pm 2} - \frac{2[l(l+1)]^{1/2}}{(2l+1)^{1/2}[(2l+3)(2l-1)]^{3/2}} \delta_{l,l} \right\} \delta_{l,2}. \quad (\text{B8})$$

The case  $l'=l=0$  is excluded in (B5) because the Born integral is divergent, is excluded in (B7) and (B8) by the triangular rule. In (B6)–(B8)  $l_{>}$  is the larger of  $l$  and  $l'$ . If both  $Q$  and  $\alpha_2$  are nonzero, then (B7) and (B8) must be added.

Given the values of the vibrational integrals, (B5)–(B8) are easily evaluated, and can be compared with results obtained for (B2) using elements of  $\vec{T}^{l_i}$  from a body-frame scattering calculation. This greatly simplifies the identification of  $l_B$ , since only a few values of  $l_i$ , rather than perhaps many values of  $m_l$ , need be considered. It is also important to note that all possible values of  $m_l$  are included in the results (B5)–(B8). Thus, calculated values of  $T_{vl,v'l'}^{l_i}$  to be compared with (B5)–(B8) must also be summed over all possible  $m_l$ . This is

obviously a formal requirement on the sums over  $m_{l_1}$  and  $m_{l_2}$  in (B1). Its importance can be appreciated by noting that all  $m_l$  contribute with roughly equal weight to (B5)–(B8), i.e., the  $B_\lambda$  coefficients cannot be converged with respect to angular momentum contributions by taking the sums in (B1) to large  $l$  without simultaneously including all possible  $m_l$ . It is easy to show that (B4), incompletely summed over  $m_l$ , will yield a result quite different from unity, typically in error by a factor of 2 for maximum  $m_l \simeq \max(l, l')/2$ . In addition, an incomplete sum will introduce incorrect nonzero contributions, e.g., to  $l_i = 0, 4, \dots$ , for the quadrupole and anisotropic polarizability interactions, and to  $l_i = 3, 5, \dots$  for the dipole interaction.

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<sup>1</sup>E. S. Chang and A. Temkin, Phys. Rev. Lett. **23**, 399 (1969).

<sup>2</sup>E. S. Chang and A. Temkin, J. Phys. Soc. Jpn. **29**, 172 (1970).

<sup>3</sup>See the review by N. F. Lane, Rev. Mod. Phys. **52**, 29 (1980).

<sup>4</sup>U. Fano and D. Dill, Phys. Rev. A **6**, 185 (1972).

<sup>5</sup>N. Chandra and A. Temkin, Phys. Rev. A **13**, 188 (1976); J. Chem. Phys. **65**, 4537 (1976); Phys. Rev. A **14**, 507 (1976).

<sup>6</sup>R. J. W. Henry and E. S. Chang, Phys. Rev. A **5**, 276 (1972); F. H. M. Faisal and A. Temkin, Phys. Rev. Lett. **28**, 203 (1972).

<sup>7</sup>I. Shimamura, in *Proceedings of the Symposium on Electron-Molecule Collisions*, edited by I. Shimamura and M. Matsuzawa (University of Tokyo, Tokyo, 1979), p. 13.

<sup>8</sup>Such a comparison is in progress: A. N. Feldt and M. A. Morrison, Bull. Am. Phys. Soc. **25**, 1114 (1980).

<sup>9</sup>See, for example, the review by Y. Itikawa, Phys. Rep. **46**, 117 (1978).

<sup>10</sup>N. Chandra and F. A. Gianturco, Chem. Phys. Lett. **24**, 326 (1974); Vo Ky Lan, M. Le Dourneuf, and B. I. Schneider, in *XI ICPEAC Abstracts*, edited by K. Takayanagi and N. Oda (The Society for Atomic Collision Research, Japan, 1979), p. 290.

<sup>11</sup>E. S. Chang and U. Fano, Phys. Rev. A **6**, 173 (1972).

<sup>12</sup>I. I. Fabrikant Zh. Eksp. Teor. Fiz. **71**, 148 (1976) [Sov. Phys.—JETP **44**, 77 (1976)]; A. S. Dickinson, J. Phys. B **10**, 967 (1977).

<sup>13</sup>L. A. Collins and D. W. Norcross, Phys. Rev. A **18**, 467 (1978).

<sup>14</sup>O. H. Crawford and A. Dalgarno, J. Phys. B **4**, 494 (1971).

<sup>15</sup>N. Chandra, Phys. Rev. A **16**, 80 (1977).

<sup>16</sup>N. T. Padial, D. W. Norcross, and L. A. Collins, J. Phys. B **14**, 2901 (1981).

<sup>17</sup>W. H. Miller and F. T. Smith, Phys. Rev. A **17**, 939 (1978).

- <sup>18</sup>W. R. Garrett, *Phys. Rev. A* **23**, 1737 (1981).
- <sup>19</sup>L. A. Collins, R. J. W. Henry and D. W. Norcross, *J. Phys. B* **13**, 2299 (1980). Polarization was neglected in the calculations whose results are used in the present paper.
- <sup>20</sup>J. Siegel, J. L. Dehmer, and D. Dill, *J. Phys. B* **13**, L215 (1980); *Phys. Rev. A* **23**, 632 (1981).
- <sup>21</sup>R. K. Nesbet, *Phys. Rev. A* **19**, 551 (1979).
- <sup>22</sup>B. H. Choi and R. T. Poe, *Phys. Rev. A* **16**, 1831 (1977).
- <sup>23</sup>D. W. Norcross, *Phys. Rev. A* (in press).
- <sup>24</sup>A. Dalgarno and R. J. Moffett, *Proc. Natl. Acad. Sci., India*, **33**, 511 (1963).
- <sup>25</sup>N. T. Padial and D. W. Norcross (unpublished).
- <sup>26</sup>I. Shimamura, *Phys. Rev. A* **23**, 3350 (1981).
- <sup>27</sup>I. Shimamura, *Chem. Phys. Lett.* **73**, 328 (1980).
- <sup>28</sup>See K. Rohr, *J. Phys. B* **11**, 1849 (1978), and references therein.
- <sup>29</sup>W. R. Garrett, *Phys. Rev. A* **4**, 2229 (1971).
- <sup>30</sup>N. Chandra, *Phys. Rev. A* **12**, 2342 (1975).
- <sup>31</sup>*Handbook of Mathematical Functions*, U.S. Natl. Bur. Stand. (Appl. Math. Ser. No. 55), edited by M. Abramowitz and I. A. Stegun (U. S. GPO, Washington, D. C., 1964), pp. 332–335.
- <sup>32</sup>See, for example, the presentation of R. J. W. Henry [*Comput. Phys. Commun.* **10**, 375 (1975)], which differs from (B1) in several minor respects. His expression includes the additional factor from (3) and is summed over  $l_i$ . It also omits the factor  $i^{l_1 - l'_1 - l_2 + l'_2}$ , i.e., implicitly adopts the phase convention that preserves time-reversal invariance in the partial-wave expansion of the total wave function [R. Huby, *Proc. Phys. Soc. (London)* **67A**, 1103 (1954)]. It is required only that the phase convention used in the scattering calculations and the phase factor in (B1) be consistent. Henry's expression and code also incorrectly omit the factor  $(-1)^{l_i}$  in (B1).
- <sup>33</sup>A similar reduction for laboratory-frame  $\vec{T}$  matrices was suggested by N. Chandra [*J. Phys. B* **8**, 1338 (1975)].
- <sup>34</sup>M. A. Morrison, N. F. Lane, and L. A. Collins, *Phys. Rev. A* **15**, 2186 (1977).