

## Low-energy electron scattering from CO

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The scattering of electrons from carbon monoxide has been studied in the framework of a previously proposed pseudopotential method. It is found that the single-center expansion of the continuum electron orbital about the center of mass of the molecule is very well converged when the two noncoincident nuclear singularities and the nonlocal exchange interactions are properly taken into account in the scattering equations. An analytical proof has been given to show that unlike the total cross section, the momentum-transfer cross section in the fixed-nuclei approximation is finite even for polar molecules. The calculated results of the momentum-transfer cross section for  $e^-$ -CO scattering in the energy range between 0.1 and 10.0 eV are in good accord with the experimental measurements.

### I. INTRODUCTION

During the last few years it has been established very well that because of the presence of a permanent dipole moment, which gives rise to a long-range  $r^{-2}$  interaction potential, the scattering of electrons from polar molecules in the approximation in which the frame of reference attached to the molecule is fixed (fixed-nuclei approximation<sup>1</sup>) does not give finite total cross section.<sup>2</sup> Because the time-averaged field of a rotating dipole is zero, therefore, in order to obtain the finite results, one has to include the rotational motion of the nuclei in the scattering equations. (This means that the adiabatic-nuclei theory<sup>3</sup> cannot be used as well.) Electron-polar-molecule scattering should, therefore, be studied in a space-fixed frame of reference using the formulation, for example, of Arthurs and Dalgarno<sup>4</sup> when the diatomic molecular target is in its  $^1\Sigma$  electronic state and the motion of the nuclei has been taken into account.

As a result of the multicenter nature of molecular targets it becomes almost impossible, except for some lighter systems<sup>3</sup> like  $H_2^+$  and  $H_2$ , to include properly the nuclear singularities and the exchange effects in the Schrödinger equation if the electron-molecule problem has been formulated in a space-fixed frame of reference to include the vibration and/or rotation of the nuclei. However, in the molecular core region, the highly anisotropic short-range interaction potential terms are so strong that they will completely dominate the effects of the nuclear vibration/rotation on the incident electron's motion. But away from the molecular core, where the short-range potential terms and the exchange effects vanish, the interaction between the motions of the nuclei and the incident electron will be quite important.

On the basis of these physical considerations Fano<sup>5</sup> has proposed a frame-transformation theory for electron-molecule scattering. We think that

$e^-$ -CO scattering should be studied<sup>6</sup> in the framework of frame-transformation theory.

A successful application of the frame-transformation theory to electron-molecule scattering problems will very much depend upon the accuracy to which the nuclear singularities and the exchange effects have been included in the scattering equations to be solved in the inner molecular core region in a fixed-nuclei approximation. Traditionally speaking there have been two views of how to overcome the problems associated with the presence of more than one nuclei in molecular targets. Whereas the two nuclear centers in diatomic molecules provide a natural choice for the use of spheroidal coordinates, the simplifications to be gained from a single-center treatment are tempting enough to encourage the formulation and the computation of the problem by using the spherical polar coordinates with the center of mass of the molecule taken to be the origin of the coordinate system.

A recent calculation by Darewych *et al.*<sup>7</sup> for positron scattering from the hydrogen molecule has shown that the use of these two different coordinate systems gives almost identical results. The use of the spheroidal coordinates becomes quite difficult if one is trying to work with systems heavier than  $H_2^+$ . On the other hand, by employing the spherical coordinate system one is essentially trying to represent the highly anisotropic molecular field and the nuclear singularities by a series centered at the center of mass of the molecule. As regard to the convergence of this expansion, a successful application of the modified pseudopotential method proposed by Burke and the present author<sup>8</sup> to  $e^-$ - $N_2$  scattering has shown that good convergence can be obtained in the single-center expansion of the bound and continuum molecular orbitals (MO's) and the multipole expansion of the molecular charge distribution.

In a recent communication<sup>9</sup> we have reported an application of this pseudopotential method to  $e^-$ -CO

scattering. The results of that calculation indicated that the single-center expansion of the continuum electron orbital does not converge, at least for scattering in the  $^2\Sigma$  state of the  $e^- + \text{CO}$  system. Since CO is a heteronuclear molecule, therefore, not having a center of symmetry, we felt this was the reason for the lack of convergence. Specifically, since the ground-electronic-state configuration of CO is

$$(1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4)^1 \Sigma,$$

containing five bound orbitals of  $\sigma$  symmetry to which the continuum orbital is to be orthogonalized for scattering in the  $^2\Sigma$  state, we thought at that time that these two effects—two noncoincident nuclear singularities and the orthogonalization to five bound orbitals—cause severe distortion of the continuum wave function. And this nonphysical distortion of the wave function was basically responsible for the nonconvergence of the single-center expansion.

In the course of our subsequent studies we have found an error in a paper published by Faisal,<sup>10</sup> who derived an expression for the multipole expansion of the electron-molecule static potential. After making this correction in the program written by Faisal and Tench<sup>11</sup> the multipole expansion of the static potential for  $e^-$ -CO scattering was calculated again. As the new corrected potential is very much different than the old one, we therefore also redid our whole calculation of  $e^-$ -CO scattering using a program of mine.<sup>12</sup> This time we found that the eigenphase sum and hence the single-center expansion did converge also for scattering in the  $^2\Sigma$  state when the continuum orbital is orthogonalized to the five bound orbitals of CO. Therefore, in Sec. II we point out this mistake in Faisal's paper<sup>10</sup> and present the new calculated correct static potential.

Garrett<sup>2(a)</sup> has shown that the divergence in the total cross section for scattering of electrons from polar molecules in the fixed-nuclei approximation is due to the large contributions coming from distant collisions in the forward direction. Since the definition of the momentum-transfer cross section involves a weighting factor  $(1 - \cos\theta)$ , which will remove the contributions from forward scattering, it was expected that the momentum-transfer cross section is finite even for polar molecules in a molecule-fixed frame of reference. However, this finiteness will depend upon the asymptotic behavior ( $l \sim \infty$ ) of the angular distribution. In Sec. III we shall show, making use of the expression for angular distribution derived in BC in the fixed-nuclei approximation, that only a finite number of partial waves contribute to the momentum-transfer cross section averaged over

all molecular orientations. Therefore, the momentum-transfer cross section is finite even for polar molecules in the fixed-nuclei approximation. The various results to demonstrate the convergence of the single-center expansion in  $e^-$ -CO scattering and the calculated momentum-transfer cross section are presented in Sec. IV. The usefulness of the single-center expansion for studying the electron-molecule scattering in general is briefly discussed in the concluding section.

## II. STATIC POTENTIAL FOR $e^-$ -CO SCATTERING

Harris and Michels<sup>13</sup> have developed the formulas for the linear displacement of a Slater-type atomic orbital (STAO). Faisal<sup>10</sup> has used these formulas to expand a normalized MO, which is a linear combination of STAO's centered at the two nuclei of the molecule, about the center of mass of the molecule. These single-center expansions of the MO's are then used to obtain an expression for the multipole expansion of the static potential for a closed-shell diatomic molecule. There is an error in Eq. (17) of Ref. 10, in which the contribution to the static potential coming from the two nuclei is given. The corrected form of this equation, in Faisal's notation, should read as follows:

$$\begin{aligned} & -\frac{Z_A}{r_{A,N+1}} - \frac{Z_B}{r_{B,N+1}} \\ & = -\sum_{\lambda=0}^{\infty} \left[ (-1)^\lambda Z_A \left( \frac{r_A^\lambda}{r_{>}^{\lambda+1}} \right)_A + Z_B \left( \frac{r_B^\lambda}{r_{>}^{\lambda+1}} \right)_B \right] P_\lambda(\cos\theta). \end{aligned} \quad (2.1)$$

(Here the internuclear axis is the polar axis with the center of mass of the molecule its origin. The angle  $\theta$  is defined with respect to this axis in a counterclockwise direction from end B to A of the molecule.<sup>10</sup>) A comparison of this relation with that given by Faisal<sup>10</sup> will show that the phase factor  $(-1)^\lambda$  multiplies the second term on the right-hand side in curly brackets in Eq. (17) of his paper. Although it will not make any difference in case of even  $\lambda$  values, this correction will be very important for odd  $\lambda$  values. The method described by Faisal<sup>10</sup> has been programmed by Faisal and Tench<sup>11</sup> to calculate the single-center expansion of MO's and the multipole expansion of the electrostatic potential for a closed-shell diatomic system. We have made this correction in their program.

When the molecular axis is taken as the polar axis with the center of mass of the molecule as the origin, the single-center expansion of a bound

MO can be written as

$$\phi_\alpha(\vec{r}) = r^{-1} \sum_{l \geq |m|} U_l^{m\alpha}(r) Y_{lm\alpha}(\hat{r}), \quad (2.2)$$

and the multipole expansion of the molecular static potential is given by

$$V(\vec{r}) = \sum_{\lambda \geq 0} V_\lambda(r) P_\lambda(\cos \theta), \quad (2.3)$$

where  $\theta$  is the polar angle of the point  $\vec{r}(r, \theta, \phi)$  measured from the molecular axis. In Eqs. (2.2) and (2.3) the summation indices  $l$  and  $\lambda$  will have both even and odd positive integral values for heteronuclear molecules. [But for homonuclear molecules, while  $\lambda$  will have only even values,  $l$  will be even for  $g$ -symmetry orbitals and odd for  $u$ -symmetry orbitals.] These two expansions for the CO molecule were obtained, as in BCG, from the two-center wave function of McLean and Yoshimine<sup>14</sup> for an equilibrium internuclear separation  $R_0 = 2.132$  a.u. In order to give an idea of the behavior of the multipole terms  $V_\lambda$  in Eq. (2.3) we had shown them in BCG for a few even and odd  $\lambda$  values in two different figures. Since the correction given in Eq. (2.1) will effect only the odd multipole terms, therefore, in Fig. 1 we show only the  $\lambda = 1, 3, 15$  terms to compare them with those given in BCG (Fig. 2). We see that these terms are now attractive at the position of the oxygen nucleus and repulsive at the carbon nucleus. While in the previous case these terms went from repulsive to attractive in going from the oxygen to the carbon nucleus.

Gianturco and Tait<sup>15</sup> in their paper on  $e^-$ -CO scattering have given tables of the multipole terms  $V_\lambda$  based on the old program of Faisal and Tench.<sup>11</sup>

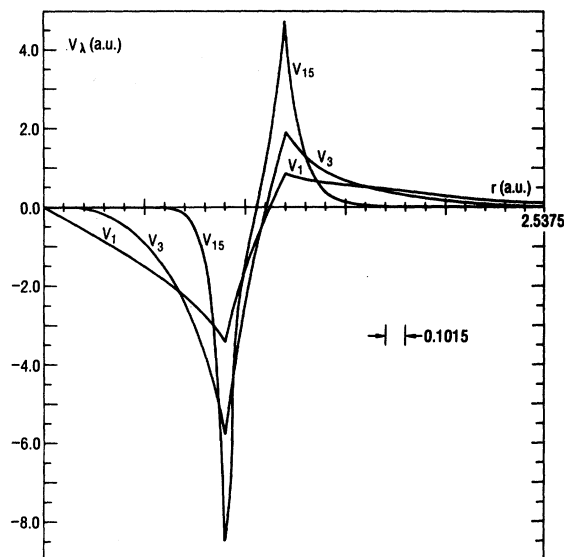


FIG. 1. Multipole coefficients  $V_\lambda$  from expansion (2.3) of the  $e^-$ -CO static potential.

For the sake of completeness, we tabulate the correct values of these terms in Table I.

### III. MOMENTUM-TRANSFER CROSS SECTION

The expression for the angular distribution of electrons scattered from a diatomic molecule in the fixed-nuclei approximation and averaged over all molecular orientations was derived in (BC-28).<sup>16</sup> In order to simplify this expression further we here write it first in  $3-j$  and  $6-j$  symbols,

$$\frac{d\bar{\sigma}}{d\Omega'} = \frac{1}{4k^2} \sum_{L=0}^{\infty} A_L(k) P_L(\cos \theta'), \quad (3.1)$$

TABLE I. Coefficients  $V_\lambda$  (a.u.) from the multipole expansion (2.3) of the static potential. For typographical simplicity the exponents of ten have been written as superscripts.

$r$ (a.u.)	$V_0$	$V_1$	$V_2$	$V_3$	$V_4$	$V_{10}$	$V_{15}$
0.203	-1.945	-5.664 <sup>-1</sup>	-3.683 <sup>-1</sup>	-5.550 <sup>-2</sup>	-1.874 <sup>-2</sup>	-2.047 <sup>-6</sup>	-1.135 <sup>-9</sup>
0.406	-2.130	-1.180	-1.492	-4.463 <sup>-1</sup>	-3.004 <sup>-1</sup>	-2.125 <sup>-3</sup>	-3.801 <sup>-5</sup>
0.609	-2.422	-1.882	-3.424	-1.526	-1.535	-1.273 <sup>-1</sup>	-1.743 <sup>-2</sup>
0.9135	-3.105	-3.400	-8.434	-5.826	-8.625	-8.526	-8.524
1.218	-2.066	8.455 <sup>-1</sup>	-5.723	1.938	-5.540	-4.895	4.727
2.03	-3.033 <sup>-1</sup>	2.946 <sup>-1</sup>	-5.714 <sup>-1</sup>	1.814 <sup>-1</sup>	-2.483 <sup>-1</sup>	-1.256 <sup>-2</sup>	9.879 <sup>-4</sup>
2.842	-4.787 <sup>-2</sup>	7.314 <sup>-2</sup>	-4.371 <sup>-2</sup>	2.466 <sup>-3</sup>	-2.386 <sup>-3</sup>	-1.273 <sup>-4</sup>	3.480 <sup>-6</sup>
4.872	-5.933 <sup>-4</sup>	5.483 <sup>-3</sup>	1.197 <sup>-2</sup>	-6.798 <sup>-3</sup>	3.470 <sup>-3</sup>	1.664 <sup>-6</sup>	-8.622 <sup>-10</sup>
6.902	-1.005 <sup>-5</sup>	2.227 <sup>-3</sup>	4.678 <sup>-3</sup>	-1.911 <sup>-3</sup>	7.048 <sup>-4</sup>	5.703 <sup>-8</sup>	-1.298 <sup>-11</sup>
10.15	-2.254 <sup>-8</sup>	1.020 <sup>-3</sup>	1.479 <sup>-3</sup>	-4.127 <sup>-4</sup>	1.041 <sup>-4</sup>	9.995 <sup>-10</sup>	-3.796 <sup>-14</sup>

where

$$A_L(k) = (-1)^L (2L+1) \sum_{\substack{l_1 l_2 l_1' l_2' \\ m_1 m_2 n}} i^{l_1 - l_1' - l_2 + l_2'} (-1)^{m_1 + m_2 + n} (2n+1) [(2l_1+1)(2l_1'+1)(2l_2+1)(2l_2'+1)]^{1/2} \\ \times \begin{pmatrix} l_1 & l_2 & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1' & l_2' & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_1' & n \\ -m_1 & m_1 & 0 \end{pmatrix} \begin{pmatrix} l_2 & l_2' & n \\ -m_2 & m_2 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & L \\ l_2' & l_1' & n \end{pmatrix} T_{l_1 l_1' l_2 l_2'}^{m_1 m_2 n} T_{l_2 l_2' l_1 l_1'}^{m_2 m_1 n} \quad (3.2)$$

and  $\Omega'(\theta', \phi')$  defines the direction of scattering in a space-fixed frame of reference. By making use of the relation<sup>17</sup>

$$\sum_{\beta_3 \beta_3} (-1)^{\alpha_3 + \beta_3 + \alpha_1 + \beta_1} (2\beta_3 + 1) \begin{pmatrix} b_1 & a_2 & b_3 \\ \beta_1 & \alpha_2 & \beta_3 \end{pmatrix} \begin{pmatrix} a_1 & b_2 & b_3 \\ \alpha_1 & \beta_2 & -\beta_3 \end{pmatrix} \begin{pmatrix} a_1 & a_2 & a_3 \\ b_1 & b_2 & b_3 \end{pmatrix} = \sum_{\alpha_3} \begin{pmatrix} a_1 & a_2 & a_3 \\ \alpha_1 & \alpha_2 & \alpha_3 \end{pmatrix} \begin{pmatrix} b_1 & b_2 & a_3 \\ \beta_1 & \beta_2 & -\alpha_3 \end{pmatrix},$$

one will readily find that Eq. (3.2) becomes

$$A_L(k) = (2L+1) \sum_{\substack{l_1 l_2 l_1' l_2' \\ m_1 m_2}} i^{l_1 - l_1' - l_2 + l_2'} [(2l_1+1)(2l_1'+1)(2l_2+1)(2l_2'+1)]^{1/2} \\ \times \begin{pmatrix} l_1 & l_2 & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1' & l_2' & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & L \\ m_1 & -m_2 & m_2 - m_1 \end{pmatrix} \begin{pmatrix} l_1' & l_2' & L \\ m_1 & -m_2 & m_2 - m_1 \end{pmatrix} T_{l_1 l_1' l_2 l_2'}^{m_1 m_2} T_{l_2 l_2' l_1 l_1'}^{m_2 m_1} \quad (3.3)$$

The total cross section in the fixed-nuclei approximation is given by (BC-29)

$$\bar{\sigma}_T = \int \frac{d\bar{\sigma}}{d\Omega'} d\Omega' = \frac{\pi}{k^2} A_0 = \frac{\pi}{k^2} \sum_m \sum_{l_1 l_2 \geq m} |T_{l_1 l_2}^m|^2, \quad (3.4)$$

and the momentum-transfer cross section

$$\bar{\sigma}_M = \int \frac{d\bar{\sigma}}{d\Omega'} (1 - \cos \theta') d\Omega'$$

becomes

$$\bar{\sigma}_M = \frac{\pi}{k^2} (A_0 - \frac{1}{3} A_1), \quad (3.5)$$

where, from Eq. (3.3),

$$\frac{1}{3} A_1 = \sum_{m_1 m_2} \sum_{l_1 l_2 l_1' l_2'} \left\{ i^{l_1 - l_1' - l_2 + l_2'} [(2l_1+1)(2l_1'+1)(2l_2+1)(2l_2'+1)]^{1/2} \right. \\ \left. \times \begin{pmatrix} l_1 & l_2 & 1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1' & l_2' & 1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & 1 \\ m_1 & -m_2 & m_2 - m_1 \end{pmatrix} \begin{pmatrix} l_1' & l_2' & 1 \\ m_1 & -m_2 & m_2 - m_1 \end{pmatrix} T_{l_1 l_1' l_2 l_2'}^{m_1 m_2} T_{l_2 l_2' l_1 l_1'}^{m_2 m_1} \right\} \quad (3.6)$$

The divergence in the total cross section for polar molecules in the fixed-nuclei approximation comes from the fact that the values of the matrix elements  $T_{l_1 l_2}^m$  fall off so slowly even for higher values of  $l_1$  and  $l_2$  that the sum over  $l_1, l_2$  in Eq. (3.4) does not converge. (We will show in the Appendix that this series indeed has a logarithmic divergence.) But for the higher values of the angular momenta it is only the long-range dipole interaction potential which will essentially determine the scattering. For such high values of  $l_1$  and  $l_2$  one can adequately use the Born approximation to

calculate the  $T$  matrix.<sup>2(a)</sup>

Let us assume that for values of  $l_1, l_2, l_1', l_2'$  higher than, say,  $\bar{l}$  one can replace the close-coupling  $T$ -matrix elements in Eqs. (3.4) and (3.6) by their Born-approximation values. Then Eq. (3.5) can be decomposed as

$$(k^2/\pi) \bar{\sigma}_M = (A_0^{(i)} - \frac{1}{3} A_1^{(i)}) + (B A_0^{(\infty)} - \frac{1}{3} B A_1^{(\infty)}), \quad (3.7)$$

where

$$A_0^{(i)} = \sum_m \sum_{l_1 l_2 \geq m}^{\bar{l}} |T_{l_1 l_2}^m|^2, \quad (3.8a)$$

and

$${}^B A_0^{(\infty)} = \sum_m \sum_{l_1 l_2 > \bar{l}}^{\infty} |{}^B T_{l_1 l_2}^m|^2. \quad (3.8b)$$

Similarly

$$\frac{1}{3} A_1^{(i)} = \sum_{m_1 m_2} \sum_{l_1 l_2 l_1' l_2'}^{\bar{l}} \left\{ \dots \right\} \quad (3.9a)$$

and

$$\frac{1}{3} {}^B A_1^{(\infty)} = \sum_{m_1 m_2} \sum_{l_1 l_2 l_1' l_2' > \bar{l}}^{\infty} \left\{ \dots \right\}. \quad (3.9b)$$

The curly brackets in Eqs. (3.9) represent the terms which are enclosed in the curly brackets in Eq. (3.6). A left superscript  $B$  in Eqs. (3.8b) and (3.9b) means that the  $T$ -matrix elements obtained from the Born approximation have been used. We have given a proof in the Appendix to show that

$${}^B A_0^{(\infty)} - \frac{1}{3} {}^B A_1^{(\infty)} = 0. \quad (3.10)$$

Therefore Eq. (3.7) now becomes

$$\bar{\sigma}_M = (\pi/k^2) (A_0^{(i)} - \frac{1}{3} A_1^{(i)}). \quad (3.11)$$

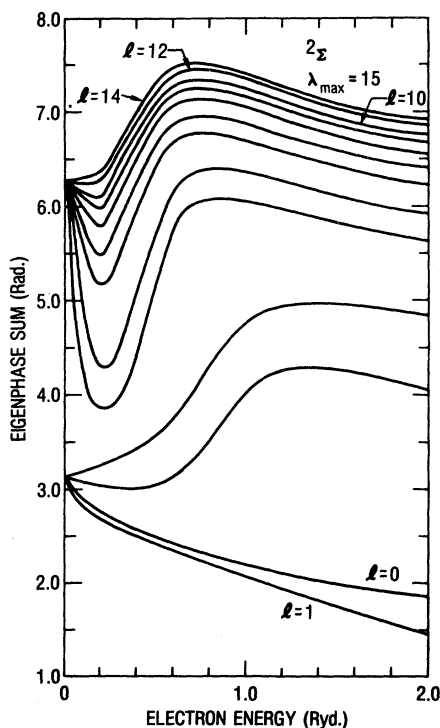


FIG. 2. Convergence of the eigenphase sum with the number of  $l$  values retained in the single-center expansion (BC-9) of the continuum electron orbital for scattering in  ${}^2\Sigma$  state. The value of  $\lambda_{\max} = 15$  was kept fixed in Eq. (2.3) and the orthogonalization to the bound orbitals has not been included.

Hence, in the fixed-nuclei approximation of electron-molecule scattering only a finite number of the lower angular momentum values contribute to the momentum-transfer cross section averaged over all molecular orientations. Therefore the momentum-transfer cross section in a molecule-fixed frame of reference is finite even for polar molecules.

#### IV. RESULTS

The first thing to consider is the convergence of the single-center expansion (BC-9) of the continuum orbital and the multipole expansion (2.3) of the static potential. Note that in these two equations  $l$  and  $\lambda$  will have both even and odd positive integral values. As usual we look at the behavior of the eigenphase sum, Eq. (BC-39), as a function of energy, which is obtained by diagonalizing the  $K$  matrix computed by solving the coupled Eqs. (BC-10).

The eigenphase sums from the solution of the homogeneous Eqs. (BC-10) (with right-hand side equal to zero) for scattering in  ${}^2\Sigma$  and  ${}^2\Pi$  states of the  $e^- + \text{CO}$  system are shown in Figs. 2 and 3,

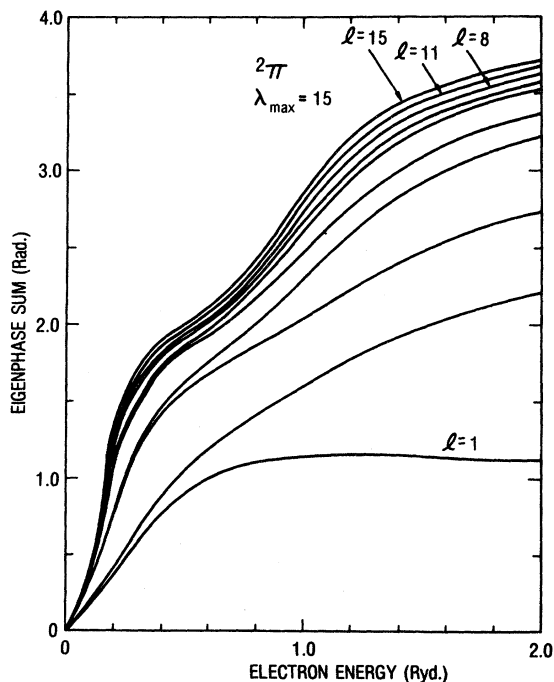


FIG. 3. Convergence of the eigenphase sum with the number of  $l$  values retained in the single-center expansion (BC-9) of the continuum electron orbital for scattering in the  ${}^2\Pi$  state. The value of  $\lambda_{\max} = 15$  was kept fixed in Eq. (2.3) and the orthogonalization to the bound orbitals has not been included.

respectively. These figures show the results as the number of partial waves in Eq. (BC-9) is increased but keeping  $\lambda_{\max} = 15$ , i.e., 16 terms ( $\lambda = 0, 1, \dots, 15$ ), in expansion (2.3). We notice that the eigenphase sum is beginning to converge after solving 15 coupled homogeneous equations ( $l_{\max} = 14$  for  ${}^2\Sigma$  and  $l_{\max} = 15$  for  ${}^2\Pi$ ). We also find that these results are quite different than those given in BCG (Figs. 3 and 4). To consider the convergence in  $\lambda_{\max}$ , we plot in Fig. 4 the eigenphase sums for  $\lambda_{\max} = 15, 20$ , and 24 obtained by solving 15 coupled homogeneous equations. These results indicate that without orthogonalization while only 16 values ( $\lambda = 0, \dots, 15$ ;  $\lambda_{\max} = 15$ ) are sufficient for the  ${}^2\Pi$  state, 21 values ( $\lambda_{\max} = 20$ ) are required for the  ${}^2\Sigma$  state.

Now we consider the convergence when the orthogonalization of the continuum orbital to the bound orbitals of the appropriate symmetry has been carried out and thus solve the coupled inhomogeneous equations (BC-10). From our previous experience of  $e^- - N_2$  scattering, we expect that the orthogonalization should increase the rate of con-

vergence. In Figs. 5 and 6 we present, respectively, the eigenphase sums for scattering in  ${}^2\Sigma$  and  ${}^2\Pi$  states. Here, as in Figs. 2 and 3, the maximum value of  $\lambda$  in Eq. (2.3) is 15 but the values of  $l$  are progressively increasing. We notice that the rate of convergence has now certainly improved and in no case is it required to keep more than 15 values of  $l$  in the single-center expansion (BC-9). To emphasize it again, unlike in BCG (Fig. 7), the  ${}^2\Sigma$  eigenphase sum does converge when the orthogonalization of the continuum orbital to the five bound orbitals of  $\sigma$  symmetry is included. [Actually in BCG we found that the eigenphase sum in this case was diverging with the inclusion of higher values of  $l$  in expansion (BC-9).] As regards the

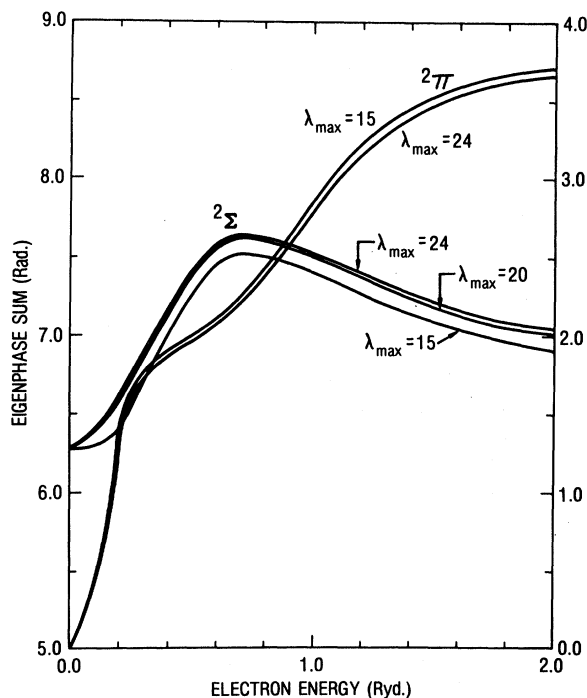


FIG. 4. Convergence of the eigenphase sum with the number of terms retained in the multipole expansion (2.3) of the static potential for scattering in  ${}^2\Sigma$  and  ${}^2\Pi$  states without orthogonalization to the bound orbitals. First 15 values of  $l$  were included in the single-center expansion (BC-9) for both states. The left- and right-hand scales are, respectively, for  ${}^2\Sigma$  and  ${}^2\Pi$  states.

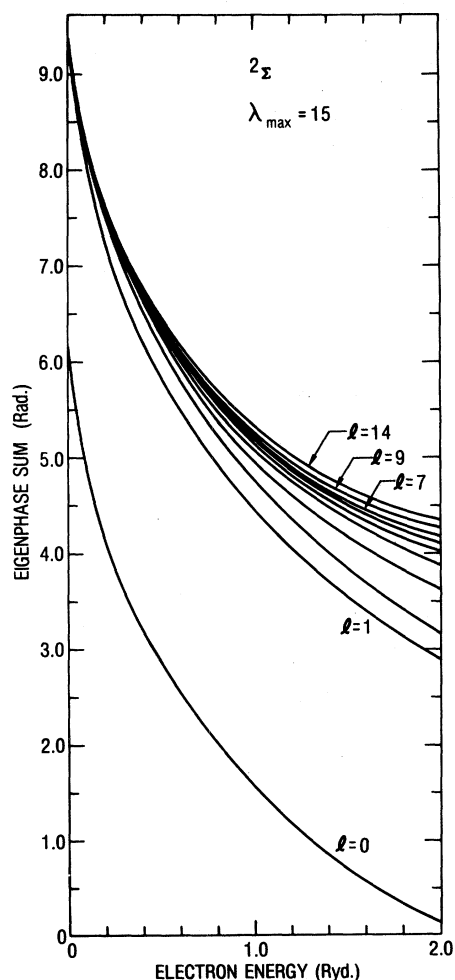


FIG. 5. Convergence of the eigenphase sum with the number of  $l$  values retained in the single-center expansion (BC-9) of the continuum electron orbital for scattering in the  ${}^2\Sigma$  state. The value of  $\lambda_{\max} = 15$  was kept fixed in Eq. (2.3) and the orthogonalization to the bound orbitals has been included.

convergence in the multipole expansion (2.3) when the orthogonalization to the bound orbitals is included, good convergence is obtained even for  $\lambda_{\max}=15$  both in  $^2\Sigma$  and  $^2\Pi$  states, keeping only 15 terms in the single-center expansion (BC-9).

It is well known that the CO molecule, being iso-electronic to  $N_2$ , exhibits a  $^2\Pi$  resonance<sup>18</sup> at about 1.75 eV. Therefore another interesting feature of these new results is that the orthogonalization has removed (Fig. 5) the unphysical resonance from the  $^2\Sigma$  state which was present in Fig. 2. At the same time  $^2\Pi$  eigenphase sum shows a resonance behavior, although at a higher energy. All these results are obtained simply by using the static potential and the orthogonalization of the continuum orbital to the occupied bound orbitals of the same symmetry. These calculations do not involve any free parameter.

To calculate the momentum-transfer cross section in a molecule-fixed frame of reference in the fixed-nuclei approximation, averaged over all molecular orientations, which was shown in Sec. III to be finite for polar molecules, we first augment our static potential with the polarization potential exactly in the same form as was done in BC, i.e.,

$$V_{\text{pol}}(\vec{r}) = -(1/2r^4)[\alpha_0 + \alpha_2 P_2(\cos \theta)](1 - e^{-(r/r_0)^6}), \quad (4.1)$$

where  $\alpha_0=13.3$  a.u. and  $\alpha_2=2.4$  a.u. are, respectively, the spherical and nonspherical components

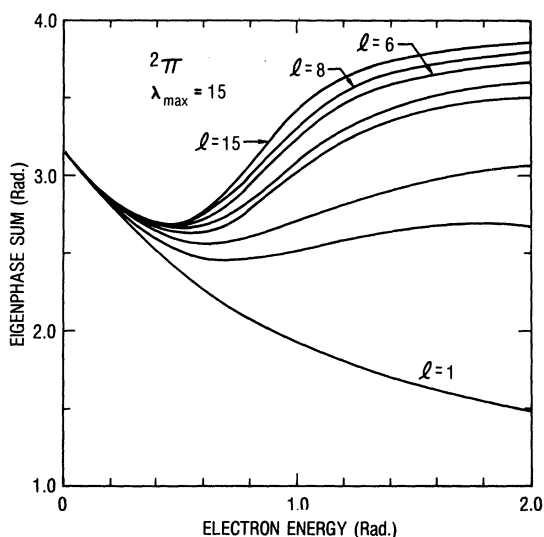


FIG. 6. Convergence of the eigenphase sum with the number of  $l$  values retained in the single-center expansion (BC-9) of the continuum orbital for scattering in the  $^2\Pi$  state. The value of  $\lambda_{\max}=15$  was kept fixed in Eq. (2.3) and the orthogonalization to the bound orbitals has been included.

of the polarizability of the CO molecule.<sup>19</sup> The value of the free parameter  $r_0=1.605$  a.u. was determined so that the resonance in the  $^2\Pi$  state occurred at about 1.75 eV. The final results for the  $^2\Sigma$ -,  $^2\Pi$ -, and  $^2\Delta$ -state eigenphase sums are shown in Fig. 7. In each case we have solved 15 coupled equations, i.e.,  $l_{\max}=14, 15$ , and 16, respectively, in Eq. (BC-9), and the 25 terms ( $\lambda_{\max}=24$ ) were kept in the multipole expansion (2.3). The ground-electronic-state configuration of the CO molecule has only the bound orbital of  $\sigma$  and  $\pi$  symmetry, therefore the continuum orbitals were orthogonalized to the bound orbitals only for scattering in  $^2\Sigma$  and  $^2\Pi$  states of the  $e^- + \text{CO}$  system.

Our results for the momentum-transfer cross section, which was calculated using Eq. (3.5), are shown in Fig. 8 (curve A). The contributions from 21 states ( $m=0, 1, \dots, 20$ ) of the  $e^- + \text{CO}$  system were included. Although the maximum value of  $l$

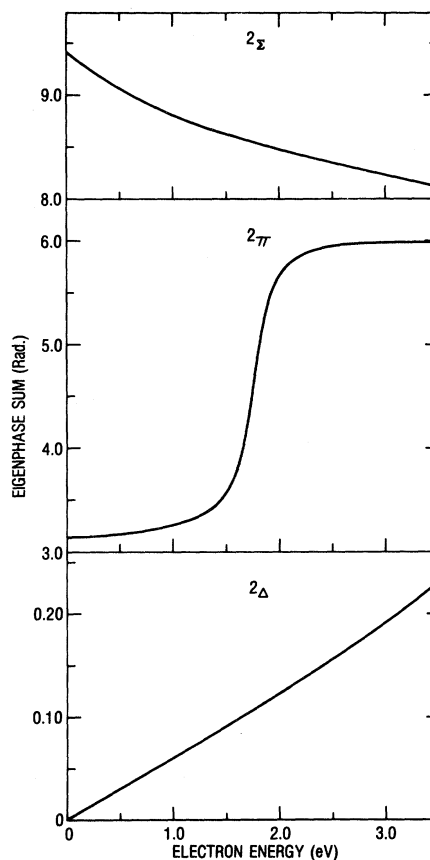


FIG. 7. Eigenphase sum for scattering in  $^2\Sigma$ ,  $^2\Pi$ , and  $^2\Delta$  states of the  $e^- + \text{CO}$  system calculated using the static-plus-polarization potential and including the orthogonalization to the bound orbitals of appropriate symmetry.

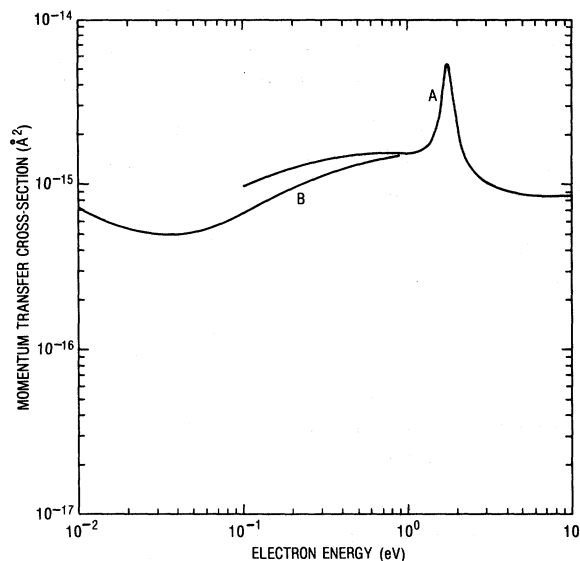


FIG. 8. Momentum-transfer cross section: theoretical results (curve A) and the experimental measurements (curve B) of Hake and Phelps (Ref. 21).

in Eq. (BC-9) was kept to 20, for any state of the  $e^- + \text{CO}$  system we keep only up to the maximum of 15 terms in this expansion. The experimental measurements of momentum-transfer cross section of Hake and Phelps<sup>20</sup> in the energy range from 0.01 to 1.0 eV are also shown in Fig. 8 (curve B). (The results shown by Hake and Phelps<sup>20</sup> in their paper above 1 eV were not obtained directly from the measurements.) In view of the fact that the theoretical results are obtained by using a single free parameter in the polarization potential, the over-all agreement between the theory and experiment is satisfactory.

We have discussed in the Introduction the fact that a complete and exact solution to the problem of  $e^-$ -polar-molecule scattering will require an application of the frame-transformation theory.<sup>6</sup> However, the present discussion of the convergence of the eigenphase sum in the molecule-fixed frame of reference has shown that to represent properly the nuclear singularities and other highly anisotropic short-range terms in the scattering equations, one has to consider at least 16 or 17 values of  $l$  in this (fixed-nuclei) approximation. Therefore the long-range electron-dipole interaction will dominate the scattering for values of  $l$  higher than 20. The contribution of these higher partial waves, for which one can use the Born approximation, to the momentum-transfer cross section is zero, Eq. (3.10). Nevertheless, one may argue that even for values of  $l$  lower than 20 the impact parameter may be so large that the

potential at these large distances may be smaller than the rotational terms in the Hamiltonian which are neglected in a molecule-fixed frame of reference. The value of  $l$ , say  $l_{\text{max}}$ , beyond which the nuclear rotation will seriously affect the fixed-nuclei results will depend upon the impact energy of the incident electron and the rotational level spacing of the molecule, and a rough estimate for it is given by<sup>21</sup>  $l_{\text{max}} \geq k^2/B$ , where  $B$  is the rotational constant ( $2.38 \times 10^{-4}$  eV for CO) of the target molecule. For the present investigation this gives  $l_{\text{max}} \geq (0.1 \text{ eV})/(2.38 \times 10^{-4} \text{ eV}) \approx 400$ , which is far greater than the value of  $l$  at which the momentum-transfer cross section is actually converged.

## V. CONCLUSION

The present calculations have proved two very important points. Firstly, the modified pseudo-potential method, which was proposed in BC, works very well to describe the scattering of electrons from closed-shell molecular systems in the fixed-nuclei approximation. Therefore this method can be easily used to solve the scattering equations in the inner molecular core region, where one is trying to study the  $e^-$ -molecule scattering in the context of the frame-transformation theory. The simplicity with which the exchange effects are included makes it feasible to apply this method to the scattering of electrons from nonlinear molecules.<sup>22</sup> The second point, which we think is quite important and has never been tested before, is that the single-center expansion of the molecular orbitals, whether bound or continuum, converges very well even for heavier systems. However, for molecular systems which are highly symmetric, e.g., homonuclear diatomic molecules, the number of terms to be contained to achieve this convergence in expansions (2.2) and (BC-9) will usually be smaller than that used for molecular systems which are not so symmetric, e.g., heteronuclear diatomic molecules. Therefore the rate of convergence of the single-center expansion will very much depend upon the symmetry properties of the molecular system under consideration.

Finally, we would like to point out that the conclusions of this paper will also affect the results of Ref. 6, which contains a preliminary report on an attempt to apply the frame-transformation theory to  $e^-$ -CO scattering. We hope to complete this study in the future.

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#### APPENDIX

The  $\underline{T}$ -matrix elements in the Born-approximation are given by<sup>23</sup>

$${}^B T_{ii'}^m = i4k \int_0^\infty j_l(kr) \langle lm | V | l'm \rangle j_{l'}(kr) r^2 dr, \quad (A1)$$

where  $j_l(x)$  is a spherical Bessel function of order  $l$ . For a dipole potential

$$V(\vec{r}) = (D/r^2) P_1(\cos \theta)$$

we have<sup>17</sup>

$$\langle lm | V | l'm \rangle = (-1)^m \frac{D}{r^2} [(2l+1)(2l'+1)]^{1/2} \times \begin{pmatrix} l & l' & 1 \\ -m & m & 0 \end{pmatrix} \begin{pmatrix} l & l' & 1 \\ 0 & 0 & 0 \end{pmatrix}. \quad (A2)$$

Here  $D$  is the dipole moment of the target molecule in a.u. After substituting (A2) into (A1) and making use of the relation<sup>24</sup>

$$\int_0^\infty j_n(x) j_m(x) dx = \frac{\sin(n-m)\pi/2}{n(n+1) - m(m+1)}, \quad (A3)$$

the expression for  ${}^B \underline{T}$ -matrix elements will become

$${}^B T_{ii'}^m = (-1)^m i4D [(2l+1)(2l'+1)]^{1/2} \times \begin{pmatrix} l & l' & 1 \\ -m & m & 0 \end{pmatrix} \begin{pmatrix} l & l' & 1 \\ 0 & 0 & 0 \end{pmatrix} \frac{\sin(l-l')\pi/2}{l(l+1) - l'(l'+1)}. \quad (A4)$$

The reader will notice that similar to the scattering from an inverse-cube-law field,<sup>25</sup> the  $\underline{T}$ -ma-

trix elements of Eq. (A4) are independent of the incident-electron energy although they have a more complicated dependence on the quantum numbers  $l$ ,  $l'$ , and  $m$ .

Now we substitute Eq. (A4) into (3.8b) and simplify it to the following form by using an orthogonality relation<sup>17</sup> of 3- $j$  symbols.

$${}^B A_0^{(\infty)} = \frac{16}{3} D^2 \sum_{l_1 l_2} (2l_1+1)(2l_2+1) \begin{pmatrix} l_1 & l_2 & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 \times \left( \frac{\sin(l_1-l_2)\pi/2}{l_1(l_1+1) - l_2(l_2+1)} \right)^2.$$

This expression is nonzero only for  $l_2 = l_1 + 1$ . Therefore one can write

$${}^B A_0^{(\infty)} = \frac{4}{3} D^2 \sum_l (2l+1) \left[ \frac{2l-1}{l^2} \begin{pmatrix} l & l-1 & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 + \frac{2l+3}{(l+1)^2} \begin{pmatrix} l+1 & l & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 \right].$$

Replacing 3- $j$  symbols by their values,<sup>17</sup> we finally get

$${}^B A_0^{(\infty)} = \frac{4}{3} D^2 \sum_l \left( \frac{1}{l} + \frac{1}{l+1} \right). \quad (A5)$$

Equation (A5) shows that the total cross section, which is proportional to  $A_0$ , diverges logarithmically for scattering of electrons from polar molecules in a molecule-fixed frame of reference.

Now to evaluate the expression (3.9b), we first replace the  $\underline{T}$ -matrix elements by their Born values, Eq. (A1). The sum over  $m_1$  and  $m_2$  can be carried out with the help of the relation<sup>17</sup>

$$\sum_{\alpha_1 \alpha_2} (-1)^S \begin{pmatrix} a_1 & a_2 & a_3 \\ \alpha_1 & \alpha_2 & \alpha_3 \end{pmatrix} \begin{pmatrix} a_1 & b_2 & b_3 \\ \alpha_1 & \beta_2 & -\beta_3 \end{pmatrix} \begin{pmatrix} b_1 & a_2 & b_3 \\ -\beta_1 & \alpha_2 & \beta_3 \end{pmatrix} \begin{pmatrix} b_1 & b_2 & a_3 \\ \beta_1 & -\beta_2 & \alpha_3 \end{pmatrix} = (2a_3+1)^{-1} \begin{Bmatrix} a_1 & a_2 & a_3 \\ b_1 & b_2 & b_3 \end{Bmatrix},$$

where

$$S = (b_1 + b_2 + b_3) + (\beta_1 + \beta_2 + \beta_3),$$

to give

$${}^B A_1^{(\infty)} = 16D^2 \sum_{l_1 l_2 l_1' l_2'} i^{l_1 - l_1' - l_2 + l_2'} (2l_1+1)(2l_1'+1)(2l_2+1)(2l_2'+1) \times \begin{pmatrix} l_1 & l_2 & 1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1' & l_2' & 1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_1' & 1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & l_2' & 1 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} l_1 & l_2 & 1 \\ l_2' & l_1' & 1 \end{Bmatrix} \left( \frac{\sin(l_1-l_1')\pi/2}{l_1(l_1+1) - l_1'(l_1'+1)} \right) \left( \frac{\sin(l_2-l_2')\pi/2}{l_2(l_2+1) - l_2'(l_2'+1)} \right). \quad (A6)$$

Because of the selection rules imposed upon the values of the angular momenta by the 3- $j$  symbols, only one sum out of the four sums present in Eq. (A6) is independent. After doing some careful, but straight-

forward, algebra Eq. (A6) can be written in the following form:

$${}^B A_1^{(\infty)} = 4D^2 \sum_l \{X_1(l) + X_2(l) - [X_3(l) + X_4(l)]\}, \quad (\text{A7})$$

where

$$\begin{aligned} X_1(l) &= \frac{(2l-1)(2l+1)}{l} \begin{pmatrix} l & l-1 & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 \left[ \frac{(2l-3)(2l-1)}{l-1} \begin{pmatrix} l-1 & l-2 & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 \right. \\ &\quad \left. \times \left\{ \begin{matrix} l & l-1 & 1 \\ l-2 & l-1 & 1 \end{matrix} \right\} + \frac{(2l+1)(2l+3)}{l+1} \begin{pmatrix} l+1 & l & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 \left\{ \begin{matrix} l & l+1 & 1 \\ l & l-1 & 1 \end{matrix} \right\} \right], \\ X_2(l) &= \frac{(2l+1)(2l+3)}{l+1} \begin{pmatrix} l+1 & l & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 \left[ \frac{(2l-1)(2l+1)}{l} \begin{pmatrix} l & l-1 & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 \right. \\ &\quad \left. \times \left\{ \begin{matrix} l & l-1 & 1 \\ l & l+1 & 1 \end{matrix} \right\} + \frac{(2l+3)(2l+5)}{l+2} \begin{pmatrix} l+2 & l+1 & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 \left\{ \begin{matrix} l & l+1 & 1 \\ l+2 & l+1 & 1 \end{matrix} \right\} \right], \\ X_3(l) &= \frac{(2l-1)^2(2l+1)^2}{l^2} \begin{pmatrix} l & l-1 & 1 \\ 0 & 0 & 0 \end{pmatrix}^4 \left\{ \begin{matrix} l & l-1 & 1 \\ l & l-1 & 1 \end{matrix} \right\}, \end{aligned}$$

and

$$X_4(l) = \frac{(2l+1)^2(2l+3)^2}{(l+1)^2} \begin{pmatrix} l+1 & l & 1 \\ 0 & 0 & 0 \end{pmatrix}^4 \left\{ \begin{matrix} l & l+1 & 1 \\ l & l+1 & 1 \end{matrix} \right\}.$$

On substituting for the values<sup>17</sup> of the various 3-*j* and 6-*j* symbols present in these expressions, we find that

$$\begin{aligned} X_1(l) &= \left\{ \begin{matrix} l & l-1 & 1 \\ l-2 & l-1 & 1 \end{matrix} \right\} + \left\{ \begin{matrix} l & l+1 & 1 \\ l & l-1 & 1 \end{matrix} \right\} = \frac{1}{2l-1} + \frac{1}{2l+1}, \\ X_2(l) &= \left\{ \begin{matrix} l & l-1 & 1 \\ l & l+1 & 1 \end{matrix} \right\} + \left\{ \begin{matrix} l & l+1 & 1 \\ l+2 & l+1 & 1 \end{matrix} \right\} = \frac{1}{2l+1} + \frac{1}{2l+3}, \\ X_3(l) &= \left\{ \begin{matrix} l & l-1 & 1 \\ l & l-1 & 1 \end{matrix} \right\} = \frac{1}{l(2l-1)(2l+1)}, \end{aligned}$$

and

$$X_4(l) = \left\{ \begin{matrix} l & l+1 & 1 \\ l & l+1 & 1 \end{matrix} \right\} = \frac{1}{(l+1)(2l+1)(2l+3)}.$$

Therefore, Eq. (A7) becomes

$${}^B A_1^{(\infty)} = 4D^2 \sum_l \left( \frac{2}{2l+1} + \frac{1}{2l-1} + \frac{1}{2l+3} - \frac{1}{l(2l-1)(2l+1)} - \frac{1}{(l+1)(2l+1)(2l+3)} \right) = 4D^2 \sum_l \left( \frac{1}{l} + \frac{1}{l+1} \right). \quad (\text{A8})$$

Hence, in view of Eqs. (A5) and (A8), we have

$${}^B A_0^{(\infty)} - \frac{1}{3} {}^B A_1^{(\infty)} = 0, \quad (\text{A9})$$

which proves the statement made in Eq. (3.10).

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