

## Scattering of low-energy electrons by polar molecules: An analytic approach

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(Received 22 September 1997; revised manuscript received 11 March 1998)

The scattering of low-energy electrons by polar molecules is considered. The excitation to the rotational states in the sudden approximation and the effect of the Coulomb dipole force to all orders are taken into account. Analytic expressions for the scattering amplitudes are obtained. These are valid for arbitrarily large dipole moments of the molecule. Differential and momentum-transfer cross sections have been calculated for several molecules and compared with experimental data, with the Born approximation and with coupled-channels calculations. [S1050-2947(98)01208-6]

PACS number(s): 34.80.Bm, 34.80.Gs

### I. INTRODUCTION

The fact that polar molecules are present in very different scenarios of scientific interest makes the scattering of electrons by this kind of molecules an interesting and relevant problem that has been studied for many years [1,2]. The dominant interaction in this process is the long-range dipole interaction, which implies the coupling of many excited states. In principle, one has to solve the associated coupled-channels problem. However, this is a tremendous task (if possible to solve) and several approximations have been used to bring the problem to sizable dimensions [3,4]. Instead of going to the detail of solving the coupled-channels problem by making more or less sophisticated approximations, it is interesting to have simple analytic formulas that describe appropriately the scattering of electrons by polar molecules. These formulas should provide one not only with useful estimates of different magnitudes of interest (such as differential, momentum-transfer, and integrated cross sections) but also give a qualitative and even quantitative picture in order to check more fundamental and complex calculations. The simplest and best known analytic formula is the point-dipole Born approximation (BA) [1]. However, it is known that it gives a poor estimate of the scattering of electrons by strongly polar molecules. The reason is that the long-range dipole force, when treated only to first order, does not give accurate results.

In this spirit, a previous paper [5] was published in which analytic formulas for the scattering of electrons by polar diatomic molecules were obtained. In that work the structure of the molecule was described using the vibron model [6,7], which considers both rotations and vibrations. The scattering problem was solved analytically by making use of the fact that the electric dipole potential has the same radial dependence as the centrifugal potential ( $1/r^2$ ). The scattering amplitudes were obtained by using the stationary phase approximation and an asymptotic expansion of Legendre functions. The expressions obtained in [5] were extremely simple, and they were in good agreement with the experimental data and more sophisticated calculations. However, there were some limitations in that treatment. It was restricted to diatomic molecules. Since the vibron model describes vibrations and

rotations of the molecule, both were treated in the same footing. Thus, the use of the sudden approximation implied neglecting not only the rotational energies of the molecule but also the much higher vibrational ones. This is unsatisfactory and unnecessary since the dominant aspect of molecular structure, affecting low-energy electron scattering by polar molecules is the rotation of the molecule, while vibrations play a minor role. On the other hand, the use of the stationary phase approximation made that the expressions obtained in [5] were not valid for small dipole moments and scattering angles. Thus, the Born approximation could not be obtained in the limit of weak coupling. Finally, the asymptotic expansion used for the Legendre functions led to unphysical results for backward angle scattering.

In this paper we improve the results of [5]. We consider separately the effect of rotational and vibrational degrees of freedom, to concentrate on the rotations. The approximation made in the previous paper for calculating the scattering amplitudes is improved, avoiding the need for the stationary phase approximation. Thus, the Born approximation is obtained from our present results in the limit of weak coupling. In addition, better approximations are used for the Legendre functions. Our results can be applied to arbitrary polyatomic molecules because they only depend on the static dipole moment of the molecule. The paper is structured as follows: in Sec. II, we discuss the solution of the coupled-channel equations. In Sec. III analytic expressions for the scattering amplitudes and differential cross sections are derived. Section IV is devoted to making comparisons of the results obtained in the previous section with other calculations and experimental data for differential and momentum-transfer cross sections. The summary and conclusions are presented in Sec. V.

### II. COUPLED-CHANNEL EQUATIONS

Let us consider by definiteness a diatomic molecule. The state can be characterized in terms of the interatomic distance  $\tilde{\xi}$ . If the interaction between vibrational and rotational degrees of freedom can be ignored the wave function factorizes,

$$\Psi_{KIM}(\vec{\xi}) = \Phi_K(\xi) Y_{IM}(\hat{\xi}), \quad (1)$$

where  $K$  is a vibrational quantum number, indicating the number of nodes of the radial wave function,  $I$  is the angular momentum of the molecular state, and  $M$  is its projection on a given axis.

The dominant dipole interaction between the electron and the molecule depends on the internal coordinate of the molecule ( $\vec{\xi}$ ) and on the relative electron-molecule coordinate ( $\vec{r}$ ) and is given by

$$V(\vec{r}, \vec{\xi}) = \frac{4\pi}{3} \frac{\xi e_{ef} e}{r^2} \sum_{\mu} Y_{1\mu}^*(\hat{r}) Y_{1\mu}(\hat{\xi}), \quad (2)$$

where  $e_{ef}$  is the effective charge of each one of the atoms in the molecule.

The basis for coupled-channel calculations is given by  $|KI LJ M_J\rangle$ , where  $L$  is the angular momentum of the electron with respect to the molecule while  $J$  and  $M_J$  are the total angular momentum and its projection on a given axis, respectively. The matrix elements of the interaction  $V(\vec{r}, \vec{\xi})$  in this basis are

$$\begin{aligned} \langle KI LJ M_J | V(\vec{r}, \vec{\xi}) | K' I' L' J M_J \rangle \\ = \frac{4\pi}{3} \frac{e_{ef} e}{r^2} W(IL I' L'; J1) (L \| Y_1 \| L') \\ \times (I \| Y_1 \| I') (-1)^{L'+I+J} \int d\xi \Phi_K^*(\xi) \xi \Phi_{K'}(\xi). \end{aligned} \quad (3)$$

It can be defined  $\xi_0$  as

$$\xi_0 = \int d\xi \Phi_0^*(\xi) \xi \Phi_0(\xi), \quad (4)$$

so  $\xi_0$  is the average interatomic distance in the vibrational ground state and

$$\begin{aligned} \int d\xi \Phi_K^*(\xi) \xi \Phi_{K'}(\xi) &= \int d\xi \Phi_K^*(\xi) \xi_0 \Phi_{K'}(\xi) \\ &+ \int d\xi \Phi_K^*(\xi) (\xi - \xi_0) \Phi_{K'}(\xi) \\ &= \xi_0 \delta_{KK'} + \xi_{KK'}. \end{aligned} \quad (5)$$

In general  $\xi_{KK'} \ll \xi_0$ . In the harmonic limit,  $\Phi_K(\xi)$  are har-

monic oscillator wave functions on the variable  $(\xi - \xi_0)$  and  $\xi_{KK'} = \delta_{KK'} \pm 1 \sqrt{\max(K, K') a_0 / \sqrt{2}}$ , where  $a_0$  is the oscillator length.

The static dipole moment of the molecule is  $d_0 = \xi_0 e_{ef}$ , while  $d_{KK'} = \xi_{KK'} e_{ef}$  are the matrix elements of the dipole operator between different vibrational states. For an arbitrary polyatomic molecule,  $d_0$  is the static dipole moment and  $d_{KK'}$  describe the dipole matrix elements between vibrational states.

The matrix elements of the interaction can be partially diagonalized by using the tidal spin basis [8,9],

$$|KI NJ M_J\rangle = \sum_L (-1)^{I-N} \frac{\hat{I}}{\hat{J}} \langle IN L 0 | JN \rangle |KI LJ M_J\rangle, \quad (6)$$

giving

$$\begin{aligned} \langle KI NJ M_J | V(\vec{r}, \vec{\xi}) | K' I' N' J M_J \rangle \\ = \delta_{NN'} \frac{e(d_0 \delta_{KK'} + d_{KK'})}{r^2} \\ \times \frac{\hat{I}}{\hat{I}'} \langle I 0 1 0 | I' 0 \rangle \langle IN 1 0 | I' N \rangle. \end{aligned} \quad (7)$$

These matrix elements can be fully diagonalized with respect to the angular momentum variables by using the basis [10]

$$|Kx NJ M_J\rangle = \sum_I \frac{\hat{I}}{\sqrt{2}} d_{N0}^I(\arccos x) |KI NJ M_J\rangle, \quad (8)$$

where  $x$  is a continuous variable defined in the interval  $[-1, 1]$ . Note that with this transformation the initial basis characterized by a discrete variable  $I$  is changed to a new one characterized by a continuous label  $x$ . The states  $|Kx NJ M_J\rangle$  are orthogonal as shown in Appendix A.

The matrix elements of the interaction in this new basis  $|Kx NJ M_J\rangle$  are

$$\begin{aligned} \langle Kx NJ M_J | V(\vec{r}, \vec{\xi}) | K' x' N' J M_J \rangle &= \delta_{NN'} \frac{e(d_0 \delta_{KK'} + d_{KK'})}{r^2} \\ &\times \sum_{I'I''} \frac{\hat{I}^2}{2} \langle I 0 1 0 | I' 0 \rangle \langle IN 1 0 | I'' N \rangle d_{N0}^I(\arccos x) d_{N0}^{I''}(\arccos x'). \end{aligned} \quad (9)$$

Making first the sum with respect to  $I'$  and using the properties of the rotational matrices the following is obtained:

$$\begin{aligned} \sum_{I'} \langle I 0 1 0 | I' 0 \rangle \langle I N 1 0 | I' N \rangle d_{N0}^{I'}(\arccos x') \\ = d_{00}^1(\arccos x') d_{N0}^I(\arccos x'), \end{aligned} \quad (10)$$

and, since  $d_{00}^1(\beta) = \cos \beta$ , the matrix elements of Eq. (9) are finally written as

$$\begin{aligned} \langle Kx NJ M_J | V(\vec{r}, \vec{\xi}) | K' x' N' J M_J \rangle \\ = \delta_{NN'} \frac{e(d_0 \delta_{KK'} + d_{KK'})}{r^2} x \delta(x - x'). \end{aligned} \quad (11)$$

It is worth noting that in Ref. [5] discrete eigenvalues of the dipole operator were found. This was due to the fact that in the vibron model, used to describe the molecular structure in that paper, the model space for the molecular states is finite. Here a continuum of eigenvalues for the dipole operator is obtained since all possible values of  $I$  are considered.

So far, the matrix elements of the potential have been evaluated. In order to formulate the coupled equations, one needs to have the matrix elements of the kinetic energy and of the molecular Hamiltonian. These matrix elements become diagonal when two approximations are made:

(i) Centrifugal-sudden or isocentrifugal approximation: the centrifugal potential  $(\hbar^2/2\mu r^2)L(L+1)$  is substituted by an average value  $(\hbar^2/2\mu r^2)\bar{L}(\bar{L}+1)$ , where  $\bar{L}$  is taken as  $(L_i + L_f)/2$ . This approximation requires the introduction of a factor  $2/\pi$  on the dipole potential [4,11]. Thus, the tidal spin  $N$  is conserved.

(ii) Rotational-sudden approximation: the rotational energies are ignored, so the orientation of the molecule, characterized by  $x$ , is fixed during the scattering process.

Under these circumstances the coupled equations can be written as

$$\begin{aligned} \left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{\hbar^2}{2\mu} \frac{\bar{L}(\bar{L}+1)}{r^2} + \frac{2}{\pi} \frac{ed_0}{r^2} x + \epsilon_K - E \right] \\ \times \phi_K^{\bar{L}N_x}(r) + \sum_{K'} \frac{2}{\pi} \frac{ed_{KK'}}{r^2} x \phi_{K'}^{\bar{L}N_x}(r) = 0. \end{aligned} \quad (12)$$

Note that  $\epsilon_K$  is the vibrational energy. Thus, one has as many coupled equations as vibrational states. Rotational excitations should in general be more important than vibrational ones since  $d_0 \gg d_{KK'}$ . The solution of Eq. (12) can be written asymptotically as

$$\phi_K^{\bar{L}N_x}(r) = h_{\bar{L}}^{(-)}(k_K r) + \sum_{K'} S_{KK'}^{\bar{L}x} h_{\bar{L}}^{(+)}(k_{K'} r) \sqrt{\frac{k_{K'}}{k_K}}. \quad (13)$$

The numerical solution of these equations is difficult. However, defining

$$\frac{\hbar^2}{2\mu} \bar{L}(\bar{L}+1) + \frac{2}{\pi} ed_0 x = \frac{\hbar^2}{2\mu} \Gamma(\Gamma+1), \quad (14)$$

the following equation is obtained:

$$\begin{aligned} \left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{\hbar^2 \Gamma(\Gamma+1)}{2\mu r^2} + \epsilon_K - E \right] \phi_K^{\bar{L}N_x}(r) \\ + \sum_{K'} \frac{2ed_{KK'}}{\pi r^2} x \phi_{K'}^{\bar{L}N_x}(r) = 0. \end{aligned} \quad (15)$$

The solution of this equation can be written asymptotically as

$$\phi_K^{\bar{L}N_x}(r) = h_{\Gamma}^{(-)}(k_K r) + \sum_{K'} \tilde{S}_{KK'}^{\Gamma x} h_{\Gamma}^{(+)}(k_{K'} r) \sqrt{\frac{k_{K'}}{k_K}}, \quad (16)$$

where  $\tilde{S}_{KK'}^{\Gamma x}$  is induced only by the coupling potential. Comparing expressions (13) and (16) it is easy to obtain

$$S_{KK'}^{\bar{L}x} = \exp\left[2i(\Gamma - \bar{L}) \frac{\pi}{2}\right] \tilde{S}_{KK'}^{\Gamma x}. \quad (17)$$

Note that in this expression the effects of the rotation appear in the exponential factor. The effects of the vibrations are characterized by  $\tilde{S}_{KK'}^{\Gamma x}$ . This comes from the solution of Eq. (15) containing as many channels as vibrational states considered and including explicitly the excitation energies.

For a rigid molecule, the vibrations are neglected. In that case,  $d_{KK'} = 0$ ,  $\tilde{S}_{KK'}^{\Gamma x} = \delta_{KK'}$ , and only the states of the vibrational ground-state band are populated. Taking  $C = (2\mu/\hbar^2)ed_0$ , one gets  $S_{00}^{\bar{L}x} = \exp[i\pi(\Gamma - \bar{L})]$ , where

$$(\Gamma - \bar{L}) = \sqrt{(\bar{L} + 1/2)^2 + \frac{2Cx}{\pi}} - (\bar{L} + 1/2). \quad (18)$$

Thus, an analytic expression for the  $S$  matrix in a basis characterized by the orientation  $x$  and, implicitly, by the tidal spin  $N$ , has been obtained. It is straightforward to derive the  $S$  matrix in the standard basis by considering the basis transformations given in Eqs. (6) and (8).

### III. EVALUATION OF SCATTERING AMPLITUDES AND CROSS SECTIONS

Once the  $S$  matrix is known, the scattering amplitude is given by

$$A(Cx, \theta) = \frac{1}{2ik} \sum_L (2L+1) P_L(\cos \theta) (S^L - 1). \quad (19)$$

The evaluation of Eq. (19) is complicated because it involves an infinite sum of oscillating terms that decrease very slowly with  $L$ . In order to find an approximate expression for it, the following approximations are done, introducing the continuous variable  $\lambda = \bar{L} + 1/2$ ,

$$P_L(\cos \theta) \approx J_0(\lambda \theta) \frac{\theta/2}{\sin(\theta/2)}, \quad (20)$$

$$S^{Lx} \approx \exp\left[i \frac{Cx}{\lambda}\right], \quad (21)$$

$$\sum_{L=0}^{\infty} \approx \int_0^{\infty} d\lambda. \quad (22)$$

With these approximations Eq. (19) becomes

$$A(Cx, \theta) \approx \frac{1}{2ik} \int_0^{\infty} 2\lambda J_0(\lambda \theta) \frac{\theta/2}{\sin(\theta/2)} \left( \exp\left[i \frac{Cx}{\lambda}\right] - 1 \right) d\lambda. \quad (23)$$

This integral can be expressed as

$$\begin{aligned} A(Cx, \theta) &\approx \frac{1}{2ik\theta \sin(\theta/2)} \int_0^{\infty} t J_0(t) \left( \exp\left[i \frac{Cx\theta}{t}\right] - 1 \right) dt \\ &= \frac{Cx}{2k \sin(\theta/2)} I(Cx\theta), \end{aligned} \quad (24)$$

where  $I(z)$  is a function satisfying  $I(0) = 1$ , and

$$(izI(z))'' = - \int_0^{\infty} J_0(t) \exp\left[i \frac{z}{t}\right] \frac{dt}{t}. \quad (25)$$

This last integral can be evaluated and expressed in terms of Bessel and Kelvin functions [12],

$$(izI(z))'' = -2J_0\left(\sqrt{2z} \exp\left[-i \frac{\pi}{4}\right]\right) K_0\left(\sqrt{2z} \exp\left[-i \frac{\pi}{4}\right]\right). \quad (26)$$

Then, the following expression for  $I(z)$  can be obtained by using recursion relations,

$$\begin{aligned} I(z) &= 2J_1\left(\sqrt{2z} \exp\left[-i \frac{\pi}{4}\right]\right) K_1\left(\sqrt{2z} \exp\left[-i \frac{\pi}{4}\right]\right) \\ &= 2i[\text{ber}_1(\sqrt{2z}) + i \text{bei}_1(\sqrt{2z})] \\ &\quad \times [\text{ker}_1(\sqrt{2z}) - i \text{kei}_1(\sqrt{2z})], \end{aligned} \quad (27)$$

where  $\text{ber}_1$ ,  $\text{bei}_1$ ,  $\text{ker}_1$ , and  $\text{kei}_1$ , are Kelvin functions as defined in [12].

In order to check the approximations proposed in Eqs. (20)–(22) the modulus of the ratio of expressions (19) to (23), for different values of  $Cx$ , are presented in Fig. 1. It can be observed that the approximations are rather good, specially for small scattering angles.

Two limits can be obtained for  $I(z)$ . One is the Born approximation, which corresponds to  $z \ll 1$  and gives  $I^{(\text{BA})}(z) = 1$ . The other one, valid for  $z \gg 1$ , is the evaluation of the integral in the stationary phase approximation (SPA), which gives  $I^{(\text{SPA})}(z) = -i\sqrt{1/2z} \exp(2i\sqrt{z})$ . The Born approximation is better for  $z < 1/2$  and the SPA is better for  $z > 1/2$ . This is clearly shown in Fig. 2.

The scattering amplitudes  $A(Cx, \theta)$  correspond to a certain molecular orientation  $x$  and, implicitly, to a tidal spin  $N$ .

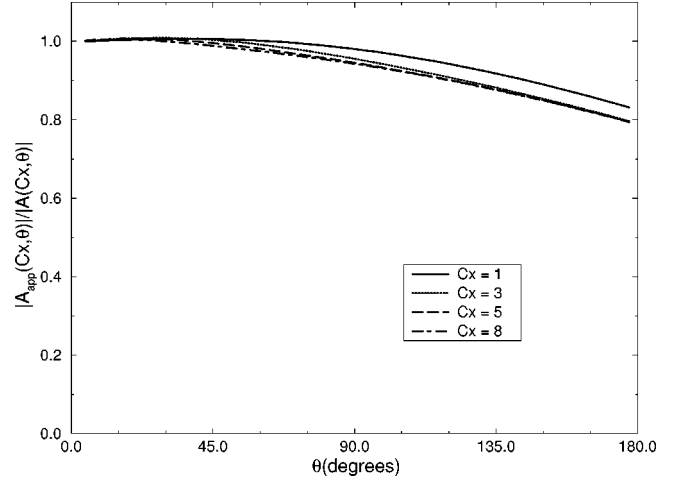


FIG. 1. Modulus of the ratio of the approximate expression for the scattering amplitude (23) to the ‘‘exact’’ expression (19), for different values of  $Cx$ .

References [8,9] can be followed in order to obtain the physical scattering amplitudes from a molecular state  $|IM\rangle$  to another one  $|I' M'\rangle$ ,

$$\begin{aligned} \langle I' M' | A(\theta) | IM \rangle \\ = \sum_N d'_{M'N} \left( \frac{\pi + \theta}{2} \right) \langle I' N | A(\theta) | IN \rangle d'_{MN} \left( \frac{\pi + \theta}{2} \right), \end{aligned} \quad (28)$$

where  $N$  is the tidal spin, which is conserved in the collision. Using the basis  $|x\rangle$  the matrix element  $\langle I' N | A(\theta) | IN \rangle$  can be evaluated,

$$\begin{aligned} \langle I' N | A(\theta) | IN \rangle &= \frac{\hat{I}I'}{2} \int_{-1}^1 dx d'_{N0}(\arccos x) d'_{N0}(\arccos x) \\ &\quad \times A(Cx, \theta). \end{aligned} \quad (29)$$

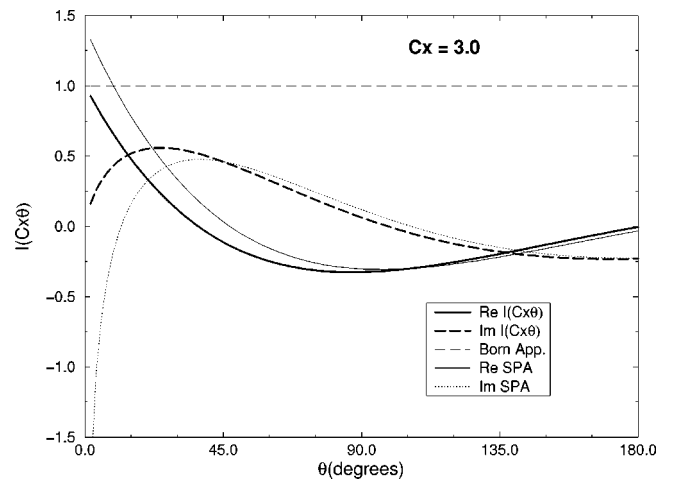


FIG. 2.  $I(Cx\theta)$ , Eq. (27), vs the angle  $\theta$  for a value of  $Cx = 3.0$ . Real and imaginary parts of  $I(Cx\theta)$  are plotted separately and compared with Born approximation and stationary phase approximation (SPA). Similar results are obtained for other values of  $Cx$ .

Using the properties of the rotational matrices,

and calling

$$d_{N0}^I(\arccos x)d_{N0}^{I'}(\arccos x) = \sum_{\lambda} d_{00}^{\lambda}(\arccos x)(-1)^N \times \langle IN I' - N | \lambda 0 \rangle \langle I 0 I' 0 | \lambda 0 \rangle, \quad (30)$$

$$I_{\lambda}(C\theta) = \frac{1}{2} \int_{-1}^1 dx P_{\lambda}(x) x I(C\theta, x) \quad (31)$$

the expression (28) can be computed [note that  $d_{00}^{\lambda}(\arccos x) = P_{\lambda}(x)$ ],

$$\langle I' M' | A(\theta) | IM \rangle = \frac{1}{2} \sum_{\lambda} \sum_N d_{M'N}^{I'} \left( \frac{\pi + \theta}{2} \right) \langle IN I' - N | \lambda 0 \rangle (-1)^N \times d_{MN}^I \left( \frac{\pi + \theta}{2} \right) \hat{I} \hat{I}' \langle I 0 I' 0 | \lambda 0 \rangle \frac{C}{k \sin(\theta/2)} I_{\lambda}(C\theta). \quad (32)$$

This can be rewritten by using again the properties of the rotational matrices as

$$\langle I' M' | A(\theta) | IM \rangle = \frac{1}{2} \sum_{\lambda\mu} d_{\mu 0}^{\lambda} \left( \frac{\pi + \theta}{2} \right) (-1)^{M'} \hat{I} \hat{I}' \langle I 0 I' 0 | \lambda 0 \rangle \times \langle IM I' - M' | \lambda \mu \rangle \frac{C}{k \sin(\theta/2)} I_{\lambda}(C\theta). \quad (33)$$

With this expression the unpolarized cross sections can be evaluated as

$$\frac{d\sigma_{I \rightarrow I'}}{d\Omega} = \frac{1}{2I+1} \sum_{MM'} |\langle I' M' | A(\theta) | IM \rangle|^2 = \frac{1}{2I+1} \frac{C^2}{4k^2 \sin^2(\theta/2)} \sum_{\lambda} \hat{I}^2 \hat{I}'^2 \langle I 0 I' 0 | \lambda 0 \rangle^2 |I_{\lambda}(C\theta)|^2. \quad (34)$$

In the limit of small angles, or small dipole moments,  $C\theta \rightarrow 0$  and the function  $I(C\theta, x)$  can be approximated by 1. Then, the only nonvanishing  $I_{\lambda}(C\theta)$  is for  $\lambda=1$  and gives  $I_1 = 1/3$ . Thus, in this case the result obtained is

$$\frac{d\sigma_{I \rightarrow I'}}{d\Omega} \approx \frac{C^2}{36 k^2 \sin^2(\theta/2)} \hat{I}'^2 \langle I 0 I' 0 | 1 0 \rangle^2, \quad (35)$$

which coincides with the plane-wave Born approximation, in the sudden limit.

#### IV. APPLICATIONS

Generally, the difference in excitation energy of the rotational states of a molecule is so small that experimental measurements can only give the summed cross sections to all the states in a rotational band. This can be done analytically using Eq. (34), and the quasielastic (QE) or vibrational-elastic differential cross sections are given by

$$\frac{d\sigma^{\text{QE}}}{d\Omega} = \sum_{I'} \frac{d\sigma_{I \rightarrow I'}}{d\Omega} = \frac{C^2}{4k^2 \sin^2(\theta/2)} \sum_{\lambda} \hat{\lambda}^2 |I_{\lambda}(C\theta)|^2. \quad (36)$$

Note that this expression is independent on the initial state  $I$ . Besides, it is convenient to write

$$F(C\theta) = \sum_{\lambda} \hat{\lambda}^2 |I_{\lambda}(C\theta)|^2 = \int_0^1 |I(yx)|^2 x^2 dx, \quad (37)$$

where  $I(z)$  is given in Eq. (27). Note that  $x$  is the cosine of the angle between the position of the electron and the symmetry axis of the molecule. Expression (36) indicates that the quasielastic cross section is related to the average of the cross section for fixed orientations. In the Born approximation,  $F(C\theta) = 1/3$ , and

$$\frac{d\sigma_{\text{BA}}^{\text{QE}}}{d\Omega} = \frac{C^2}{12k^2 \sin^2(\theta/2)}. \quad (38)$$

In Fig. 3 the contributions of each multipolarity to the quasielastic cross section are presented. Note that, for low  $C\theta$ , the dipole contribution dominates. However, as  $C\theta$  increases, other multipoles play an important role. A similar result was obtained in [5], where the stationary phase approximation was used for the evaluation of the scattering amplitudes.

In Figs. 4, 5, and 6 experimental data of strongly polar diatomic molecules, LiF ( $d_0 = 6.58$  D) and KI ( $d_0 = 10.82$  D), are compared with our calculations. In these figures the results of a plane-wave Born approximation are also shown. In Figs. 4(a), 5(a), and 6(a) the experimental data are nor-

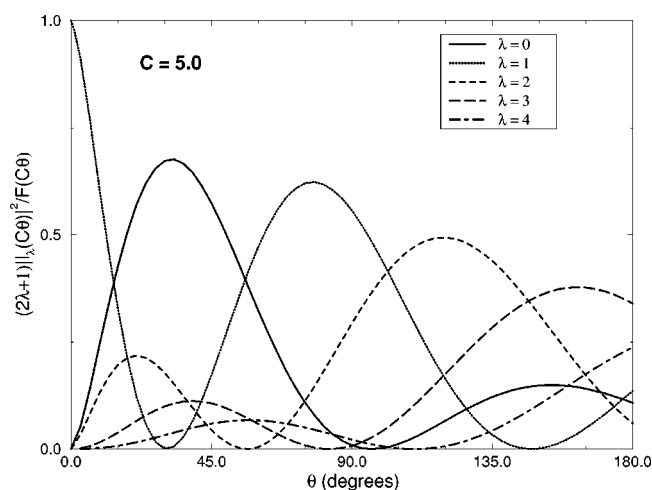


FIG. 3. Contribution of each multipolarity, given by the proper combination of Eqs. (31) and (37), to the quasielastic cross section as a function of the angle,  $\theta$ , for a value  $C=5.0$ .

malized to our results at  $40^\circ$ . In Figs. 4(b), 5(b), and 6(b) our calculations together with existing calculations using other models are plotted. Here the normalization of the data given by Collins and Norcross [1] has been kept. The calculations presented in these figures are the following:

SE: Coupled-channel calculations with a realistic interaction and a local exchange potential derived assuming that the electrons in the molecule form a free Fermi gas [1].

DCO: Coupled-channel calculations with dipole forces characterized by a form factor  $(1/r^2)\{1 - \exp[-(r/r_0)^6]\}$ . The cutoff radius  $r_0$  is taken as  $0.5a_0$  for LiF and  $0.9a_0$  or  $1.35a_0$  for KI [1].

Note that in our formulation the energy dependence is a trivial factor  $1/E$ , while the dependence on the dipole moment  $d_0$  is included in the dimensionless parameter  $C$ . For low values of  $C\theta$  the Born approximation is obtained, but important deviations from it are expected for  $e$ -LiF and  $e$ -KI scattering cross sections. The experimental data, as well as more sophisticated coupled-channel calculations, agree with our calculations for small angles. For large angles, however, important deviations are found. These are due to the effect of exchange forces, other multipoles, and deviations of the  $1/r^2$  form of the dipole form factors. Our results also compare well with the previous work [5], except at angles close to  $0^\circ$  or  $180^\circ$ , where the stationary phase approximation done in [5] is not valid.

In order to test our model for smaller dipole moments and show its ability to treat polyatomic molecules, we have chosen the cases of  $H_2O$  and  $NH_3$ . They have dipole moments of  $d_0=1.471$  D and  $1.844$  D, respectively. Experimental data with fixed normalization and theoretical variational calculations for low-energy electron scattering from those targets are available ([15,16] for  $H_2O$  and [17,18] for  $NH_3$ ). In Figs. 7 and 8 the differential cross sections for  $e^-H_2O$  and  $e^-NH_3$  at 2.2 and 2 eV, respectively, are shown. It can be seen that there is a reduction of the experimental cross section at small angles with respect to the Born approximation. This reduction is reproduced by our calculation. At larger angles, exchange forces and other short-range interactions, which are not considered in our calculations, produce an increase in the cross section, specially in the  $H_2O$  case. The agreement in

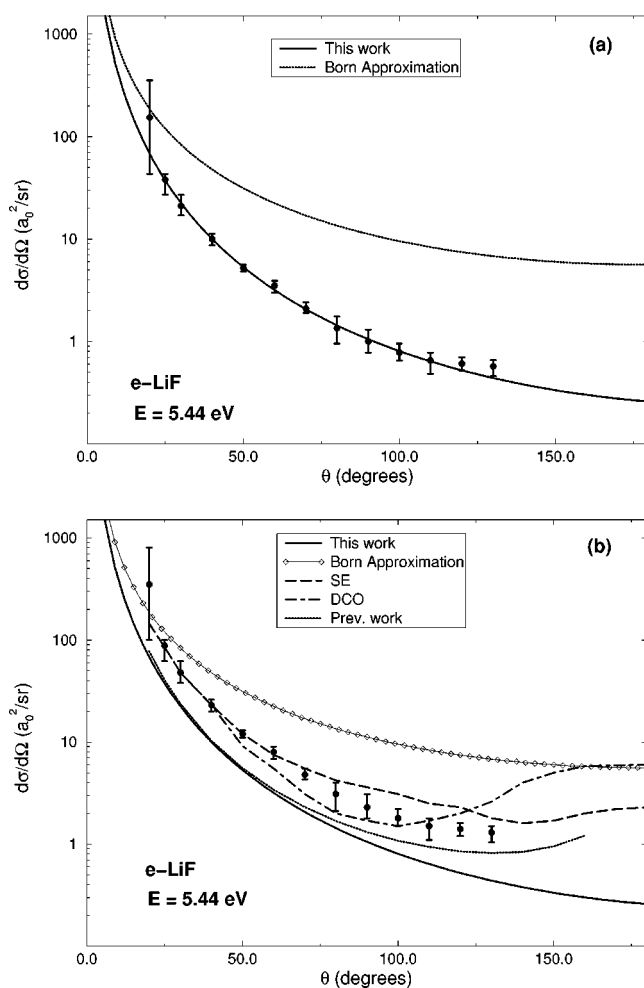


FIG. 4. The quasielastic differential cross sections for electron scattering off LiF at 5.44 eV. The experimental data are taken from Ref. [13]. In (a) the experimental data are normalized to our results at  $40^\circ$ . In (b) the experimental data are normalized to the coupled channels results by Collins and Norcross [1] (SE and DCO lines).

the case of  $NH_3$  is remarkable.

Looking carefully at the behavior of the cross sections at very small angles, it seems that the coupled-channel calculations get closer to the Born approximation than to our calculations. This is surprising in principle, because our calculations are more accurate than the Born approximation. However, due to the difficulty of performing coupled-channel calculations for large partial waves, the  $S$  matrix in the coupled-channel calculations cited in [1] for LiF and KI are substituted by the Born approximation expression for large angular momenta. A similar treatment is made for  $NH_3$  in [18]. Thus, the agreement between coupled-channel calculations and Born approximation at small angles may be artificial, and our results would indicate the actual trend of a full coupled-channel study. In the case of  $H_2O$ , the contribution of large partial waves is neglected in the calculation by Brescansin *et al.* [16]. Thus its cross section for small scattering angles is not shown in Fig. 7.

It is worth noting that our calculations can be used in a hybrid model to obtain the  $S$  matrix for large partial waves while for low partial waves the explicit coupled-channel calculations can be performed. In this way it is expected that the results for small scattering angles will be more accurate than

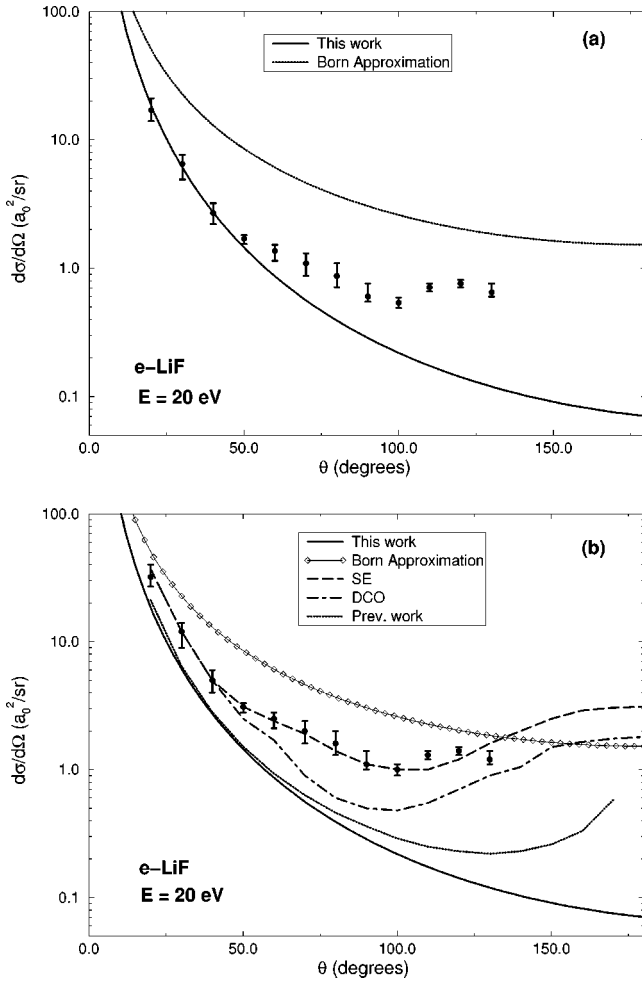


FIG. 5. Same as Fig. 4 but for electron scattering off LiF at 20.0 eV.

using the Born approximation for large partial waves.

The integrated cross section obtained from Eq. (36) diverges. This is related to the sudden approximation taken for the rotational states. However, the so-called momentum transfer cross section, defined as

$$\sigma_m = \int \left( \frac{d\sigma}{d\Omega} \right)_{QE} 2 \sin^2(\theta/2) d\Omega, \quad (39)$$

can be calculated and gives

$$\sigma_m = \frac{2\pi C^2}{4k^2} \int_0^\pi 2(\sin \theta) F(C\theta) d\theta. \quad (40)$$

This is to be compared with the result of the Born approximation,

$$\sigma_m = \frac{2\pi}{3k^2} C^2. \quad (41)$$

Note that, in general,  $\sigma_m k^2$  depends only on the dipole moment through the parameter  $C$ .

In Fig. 9 the values of  $\sigma_m E$  versus the dipole moment  $d_0$  are shown for different systems. Note that the Born approximation predicts a parabolic behavior, while our calculation shows that, for large  $d_0$ , the behavior is rather linear. This

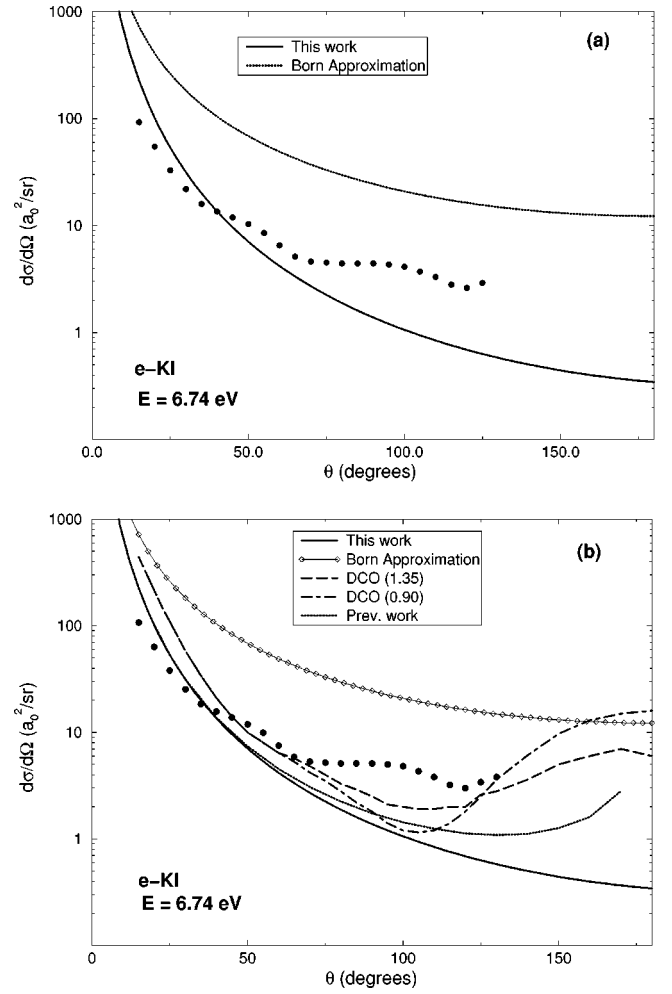


FIG. 6. Same as Fig. 4 but for electron scattering off KI at 6.74 eV. The data are taken from Ref. [14].

result is in accord with the trend of the data. Our calculation, however, underestimates the momentum transfer cross sections. This is partly due to the fact that in it only the Coulomb dipole interaction is considered. Short-range interac-

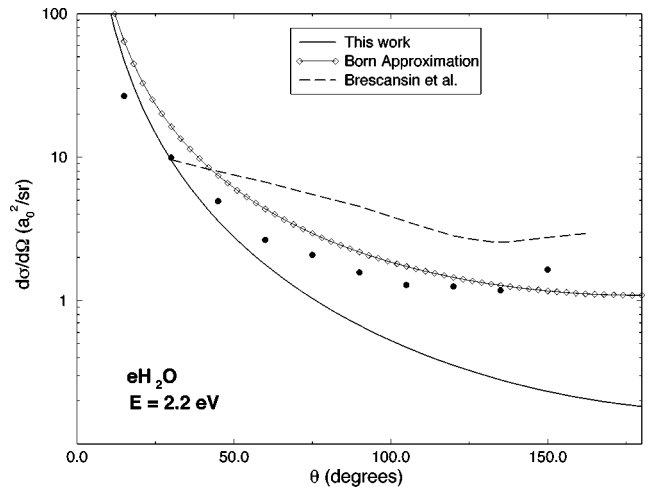


FIG. 7. The quasielastic differential cross sections for electron scattering off H<sub>2</sub>O at 2.2 eV. The experimental data are taken from Ref. [15]. Our calculation, the result of the variational approach of Ref. [16], and the Born approximation are shown.

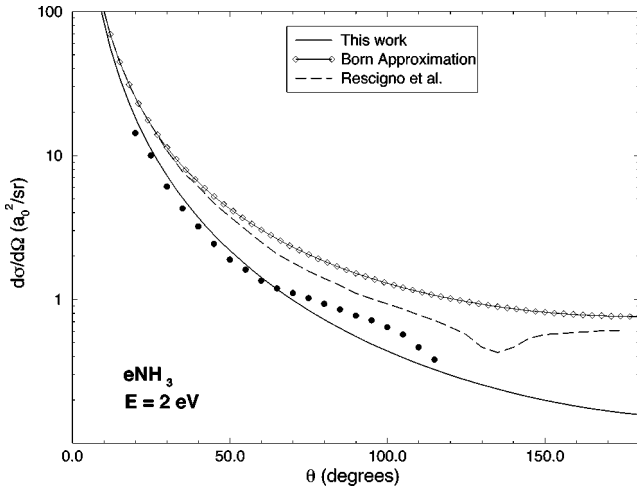


FIG. 8. The quasielastic differential cross sections for electron scattering off  $\text{NH}_3$  at 2.0 eV. The experimental data are taken from Ref. [17]. Our calculation, the result of the variational calculation of Ref. [18], and the Born approximation are shown.

tions, such as exchange forces or other multipoles, that are not included in our calculation contribute to  $\sigma_m E$ . Full dots are the experimental data corresponding to the cases discussed in this paper [Figs. 4(a), 5(a), 6(a), 7, and 8]. The global normalization of the data for LiF and KI is obtained by fitting them to our calculations.

## V. SUMMARY AND CONCLUSIONS

The scattering of electrons by polar molecules has been investigated, considering only the long-range Coulomb dipole potential, in the rotational sudden and centrifugal sudden approximations. The effect of molecular rotations has been separated from the effect of molecular vibrations in the coupled-channel system and in the expression of the scattering matrix. When the vibrations are neglected, an analytic

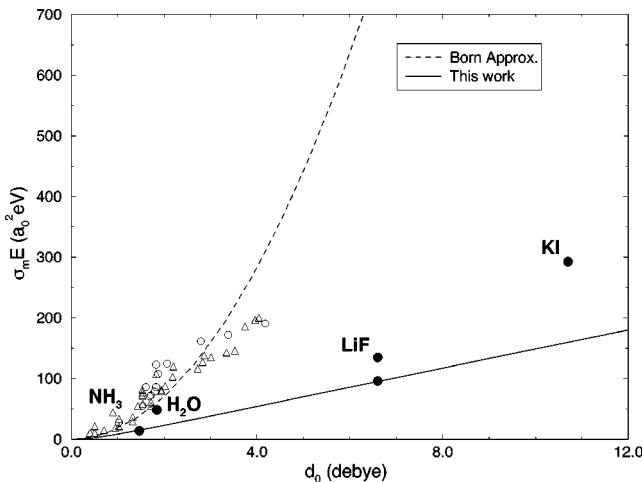


FIG. 9. Values of  $\sigma_m E$  vs the dipole moment  $d_0$  for different systems. The experimental data (open triangles and circles) are from thermal-energy swarm measurements [19]. Full dots are the experimental values for LiF (2 energies), KI,  $\text{H}_2\text{O}$ , and  $\text{NH}_3$ , which are extracted from the cases shown in Figs. 4(a), 5(a), 6(a), 7, and 8, respectively.

expression for the scattering matrix as a function of the partial wave has been obtained.

By integrating the contributions of all the partial waves, the scattering amplitudes as a function of the scattering angle have been evaluated. Closed analytical expressions have been obtained. These tend to the Born approximation for weak coupling, and to the stationary phase approximation for strong coupling.

Quasielastic differential cross sections and momentum transfer cross sections have been evaluated. They have been compared with experimental data and coupled-channel calculations. From this comparison it is found that the behavior of these magnitudes for low scattering angles is well described. At larger angles, the effect of other interactions not included in this treatment increases the cross sections.

This work can be useful to have a rapid estimate of the cross section based on Coulomb dipole interactions for electron on polar molecules, which, unlike the Born approximation, is valid for arbitrary values of the dipole moment of the molecule. It can be applied to arbitrary polyatomic molecules, provided that the static dipole moment is known. Besides, the  $S$  matrix given in this work can be used in a hybrid model for large partial waves while for low partial waves the explicit coupled channels calculations is performed. In this way the results for small scattering angles will be improved with respect to calculations using the Born approximation for large partial waves.

## ACKNOWLEDGMENTS

This work was supported in part by the Spanish DGICYT under Project No. PB95-0533, by the ISC program of the European Commission under Project No. CII\*-CT94-0072, and by the scientific cooperation agreement between the Spanish CICYT and the Italian INFN. We acknowledge useful discussions with A. Frank, R. Lemus, and M. A. Nagarajan.

## APPENDIX

In this appendix is shown the orthogonality condition for the states  $|Kx NJ M_J\rangle$  [Eq. (8)]. Starting with Eq. (8) and the well-known relation

$$\sum_{IM} Y_{IM}(\theta, \phi) Y_{IM}^*(\theta', \phi') = (\sin^{-1} \theta) \delta(\theta - \theta') \delta(\phi - \phi'), \quad (\text{A1})$$

the following is obtained:

$$\begin{aligned} \sum_{IM} \frac{\hat{I}^2}{4\pi} d_{M0}^I(\theta) e^{iM\phi} d_{M0}^I(\theta') e^{-iM\phi'} \\ = (\sin^{-1} \theta) \delta(\theta - \theta') \delta(\phi - \phi'). \end{aligned} \quad (\text{A2})$$

Multiplying this expression by  $\exp[-iN(\phi - \phi')]$  and integrating with respect to  $(\phi - \phi')$  between 0 and  $2\pi$ , only the term with  $M = N$  contributes in the left-hand side of the equation and one gets



$$\sum_I \frac{\hat{I}^2}{2} d_{N_0}^I(\theta) d_{N_0}^I(\theta') = (\sin^{-1} \theta) \delta(\theta - \theta') \\ = \delta(\cos \theta - \cos \theta'). \quad (\text{A3})$$

Finally, by using the relationship between the variables  $\theta$  and  $x$ ,

$$\sum_I \frac{\hat{I}^2}{2} d_{N_0}^I(\arccos x) d_{N_0}^I(\arccos x') = \delta(x - x'), \quad (\text{A4})$$

the orthogonality condition is obtained,

$$\langle Kx \ NJ \ M_J | Kx' \ NJ \ M_J \rangle = \delta(x - x'). \quad (\text{A5})$$

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