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Algebraic-eikonal approach to electron-molecule scattering. II. Rotational and vibrational excitation of LiF and KI

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The algebraic-eikonal approach to electron-molecule scattering is further developed. A simple perturbation method is used to illustrate the coupling of vibrational bands. Furthermore, it is shown explicitly that the differential cross section summed over the final rotational states and averaged over the initial magnetic substates does not depend on the initial angular momentum. Finally this approach is applied to calculate the differential cross section for scattering electrons from the diatomic molecules LiF and KI.

I. INTRODUCTION

The scattering of medium-energy (5–50-eV) electrons from polar diatomic molecules is governed largely by the long-range dipole interaction between the incoming electron and the molecule.[1–9] This interaction leads to multistep processes which involve fully the rotational and vibrational degrees of freedom of the molecule. In principle the scattering equations can be solved in a full close-coupling calculation, but this is a prodigous numerical undertaking. However, for electron energies well above the rotational and vibrational excitation energies, simplifying procedures have been used based on the adiabatic (fixed-nucleus) approximation. This approximation has proven to be particularly useful for electron collisions with polar molecules. However, even in the fixed-nucleus approximation standard close-coupling calculations become very complex especially for larger (triatomic and polyatomic) molecules. It is therefore of great importance to find a simple prescription that both exploits the simplifications that arise from the dominance of the dipole interaction and at the same time incorporates the rotational-vibrational structure of the molecule at a level sufficient to calculate the cross sections of interest.

In Ref. 10 (hereafter referred to as BAS) we have proposed a new method to calculate cross sections for electron-molecule scattering. In this approach we combine an algebraic description of the molecular dynamics, the vibron model,[11–13] in the adiabatic approximation with eikonal scattering methods.[14] This algebraic-eikonal approach provides a simple method for describing electron-molecule scattering that is numerically efficient and presents a physically clear treatment of the scattering. In the algebraic-eikonal approach the full close-coupling calculation is done essentially in closed form treating both elastic and inelastic scattering to rotational and vibrational states on the same footing. In this paper we develop the method further and apply it to medium-energy electron scattering from LiF and KI.

In Sec. II we review the algebraic-eikonal approach. Section III describes a perturbation method for introducing coupling of vibrational bands that turns out to be an excellent approximation for the cases at hand. In Sec. IV we study the rotationally summed cross section. Since in most experiments the rotational states cannot be resolved it is of interest to study the differential cross section (DCS) summed over the final rotational states and averaged over the initial ones. We show that the algebraic techniques make such sums easy to perform and we show that in the limit of very large rotational bands the summed and averaged differential cross section is independent of the initial angular momentum.

In Sec. V we present our results. To get to the dynamics of our molecules we express the molecular energies given by the vibron Hamiltonian in terms of a Dunham expansion that has been fit to the molecular states. With the Hamiltonian parameters fixed we calculate electron scattering for LiF at 5.44 and 20.0 eV and for KI at 6.74 and 15.7 eV and compare with experimental data. The excitation of the first vibrational band is predicted to be four orders of magnitude smaller than the eikonal scattering in the ground-state band. We show that our results differ considerably from the first Born approximation and that the correct treatment of multistep processes (or equivalently the correct treatment of close coupling) is essential. In Sec. VI we conclude with some remarks about future extension of this work.

II. THE ALGEBRAIC-EIKONAL APPROACH

The vibron model[11–13] is an algebraic model of molecular dynamics realized in terms of four boson (or vibron) creation (annihilation) operators divided into a scalar boson with $L^{\pi}=0^{+}$, $s^{\dagger}$ (s) and the three components of a vector boson with $L^{\pi}=1^{-}$, $p_{\mu}^{\dagger}$ (p_{μ}); $\mu=1,0,-1$. For a diatomic molecule we take only one such set and then the dynamical group of the molecule is U(4) whose generators are the $4^2=16$ possible bilinear products of vibron creation and annihilation operators. The most general U(4) invariant Hamiltonian that contains no terms more than quadratic in the generators and that preserves spherical symmetry and parity invariance is

$$H_{\text{mol}}=H_0+A\hat{P}_4+B\hat{L}\cdot\hat{L}+\varepsilon\hat{n}_p+\delta\hat{n}_p^{\,2}\,, \tag{2.1}$$

where

$$
\begin{aligned}
\hat{P}_4 &= \tfrac{1}{4}(p^\dagger\cdot p^\dagger - s^\dagger s^\dagger)(\tilde{p}\cdot\tilde{p} - ss) \\
&= \tfrac{1}{4}[-\hat{D}\cdot\hat{D} - \hat{L}\cdot\hat{L} + \hat{N}(\hat{N}+2)] , \\
\hat{D}_\mu &= (s^\dagger\tilde{p} + p^\dagger s)^{(1)}_\mu , \\
\hat{L}_\mu &= \sqrt{2}(p^\dagger\tilde{p})^{(1)}_\mu , \\
\hat{n}_p &= p^\dagger\cdot\tilde{p} , \\
\hat{N} &= \hat{n}_p + \hat{n}_s = p^\dagger\cdot\tilde{p} + s^\dagger s , \\
\tilde{p}_\mu &= (-1)^\mu p_{-\mu} .
\end{aligned}
\tag{2.2}
$$

The s's and p's obey the usual boson commutation relations. H_0 depends only on N, the total number of bosons, which is conserved by H and therefore H_0 determines only the overall energy scale and will be dropped in the following.

The vibron Hamiltonian for a diatomic molecule has two interesting dynamical subgroups. If $\varepsilon=\delta=0$, H_{mol} has O(4) symmetry and the molecular states are specified by N, the total number of bosons; l, the angular momentum (and m); and by σ, a quantum number that can be related to the usual vibrational label v by $v=(N-\sigma)/2$. In this limit the molecular energies are given in closed form by the expression

$$
E_{\sigma l} = \tfrac{1}{4}A(N-\sigma)(N+\sigma+2) + Bl(l+1) . \tag{2.3}
$$

In the large-N limit the O(4) Hamiltonian corresponds to the Morse oscillator.[13,15] The other dynamical symmetry, U(3), arises if $A=0$. In this case the states are labeled by N, l, m, and n, the number of p bosons. The energy eigenvalues are given by

$$
E_{nl} = \varepsilon n + \delta n^2 + Bl(l+1) . \tag{2.4}
$$

In this case the large-N limit corresponds to the three-dimensional anharmonic oscillator.[13,15] Given the success of the Morse oscillator for the description of diatomic molecules we expect that for realistic cases the vibron Hamiltonian will be close to that of the O(4) limit.

To study electron scattering from a diatomic molecule we write the Hamiltonian of the electron-molecule system as

$$
H = \frac{\mathbf{p}^2}{2m} + H_{\mathrm{mol}} + V(\mathbf{r}) , \tag{2.5}
$$

where the first term is the kinetic energy of the projectile electron, the second term is the vibron Hamiltonian of Eq. (2.1), and the third term represents the coupling between the electron and the molecule. It should be recalled that in the algebraic description, the molecular degrees of freedom are carried by the boson operators. We assume that the incoming electron couples only to the molecule's dipole moment and write

$$
\begin{aligned}
V(\mathbf{r}) &= \alpha(r)\hat{\mathbf{r}}\cdot\hat{D} , \\
\alpha(r) &= -\frac{ed}{r^2+R_0^2} ,
\end{aligned}
\tag{2.6}
$$

where $\hat{D}$ is the dipole operator of Eq. (2.2), $\mathbf{r}$ is the electron coordinate measured from the center of the molecule, and $\alpha(r)$ goes like r^{-2} for large r (dipole coupling) but is cutoff or damped at small r to suppress the nonphysical singularity at the origin in a modest attempt to represent some of the short-range electron-molecule dynamics.

The essence of the eikonal treatment of scattering is to realize that the electron kinetic energy is large compared with the coupling energy to the molecule. If we also assume it is large compared with the molecular energies carried in H we can easily obtain an eikonal scattering amplitude in closed form. This adiabatic assumption is equivalent to the fixed-nucleus approximation of more conventional treatments. The algebraic-eikonal scattering amplitude for scattering from an initial molecular state N,v_i,l_i,m_i to N,v_f,l_f,m_f and from electron momentum $\mathbf{k}_i$ to $\mathbf{k}_f$ ($\mathbf{q}=\mathbf{k}_f-\mathbf{k}_i$) is given by

$$
\begin{aligned}
A_{fi}(q) &= \frac{k_i}{2\pi i}\int d^2b\, e^{i\mathbf{q}\cdot\mathbf{b}} \\
&\qquad \times \langle N,v_f,l_f,m_f \,|\, e^{i\chi(\mathbf{b})}-1 \,|\, N,v_i,l_i,m_i\rangle , \\
\chi(\mathbf{b}) &= g(b)\hat{b}\cdot\hat{D} , \\
g(b) &= -\frac{m_e}{\hbar^2 k_i}\int_{-\infty}^{\infty} dz\,\alpha(r)\frac{b}{r} .
\end{aligned}
\tag{2.7}
$$

This reduces the solution of the scattering problem to a two-dimensional integral over the impact parameter $\mathbf{b}$. The transition matrix elements

$$
\begin{aligned}
&\langle N,v_f,l_f,m_f \,|\, e^{ig(b)\hat{\mathbf{b}}\cdot\hat{D}} \,|\, N,v_i,l_i,m_i\rangle \\
&\quad = e^{i(m_i-m_f)\phi}\sum_m d^{(l_f)}_{m_f m}(\pi/2)\,d^{(l_i)}_{m_i m}(\pi/2)\sum_\sigma c^{v_f}_\sigma(l_f)\,c^{v_i}_\sigma(l_i)\langle N,\sigma,l_f,m \,|\, e^{ig(b)\hat{D}_z} \,|\, N,\sigma,l_i,m\rangle ,
\end{aligned}
\tag{2.8}
$$

with $\hat{\mathbf{b}}=(\phi,\theta=\pi/2,\psi=0)$ are representation matrix elements of the dipole operator and can be derived using standard group-theoretic techniques.[10,16] The occurrence of the representation matrix in Eq. (2.7) is typical of these algebraic-eikonal approaches, but appears to be the first case beyond the familiar Wigner D functions of rotation theory of these matrices in physics. The scattering amplitude in Eq. (2.7) contains the coupling between molecular states to all orders and is completely equivalent to a close-coupling calculation within the framework of the adiabatic-eikonal approximation.

III. PERTURBATIVE TREATMENT OF VIBRATIONAL COUPLING

It has been shown that the Morse oscillator potential gives a relatively good description of the spectrum of diatomic molecules. Therefore we expect the physically interesting diatomic molecules to be near the O(4) limit which in the large-N limit corresponds to the Morse oscillator. However, in the exact O(4) limit the dipole operator does not couple vibrational bands and hence only in-band transitions would be permitted in our treatment of electron-molecule scattering. In this section we will use first-order perturbation theory to illustrate the mechanism of vibrational excitation in the algebraic-eikonal approach.

The simplest way to include mixing between the vibrational bands with $\Delta v = \pm 1$ is to take $\delta = 0$ in Eq. (2.1) and treat ε to first order. Consider a state labeled by the vibrational quantum number v [in the O(4) limit $v = (N-\sigma)/2$]. To first order we write for the state function, in terms of the O(4) basis states,

$$|N,v,l,m\rangle = |N,\sigma = N-2v,l,m\rangle + \sum_{\sigma' \neq \sigma} a_{\sigma\sigma'}(l)\,|N,\sigma',l,m\rangle , \tag{3.1}$$

and for the energies

$$E_{vl} = E^{(0)}_{\sigma l} + E^{(1)}_{\sigma l} ,$$

$$E^{(0)}_{\sigma l} = \tfrac{1}{4} A (N-\sigma)(N+\sigma+2) + Bl(l+1) , \tag{3.2}$$

$$E^{(1)}_{\sigma l} = \langle N,\sigma,l,m \mid \varepsilon \hat{n}_p \mid N,\sigma,l,m \rangle$$

$$= \begin{cases} \varepsilon \left[\tfrac{1}{2}(N-1) + \dfrac{l(l+1)(N+2)}{2\sigma(\sigma+2)} \right], & \sigma = N-2v \neq 0 \\ \varepsilon \tfrac{3}{4} N, \quad \sigma = 0 . \end{cases}$$

The mixing amplitude is given by

$$a_{\sigma\sigma'}(l) = \frac{\langle N,\sigma,l,m \mid \varepsilon \hat{n}_p \mid N,\sigma',l,m \rangle}{E^{(0)}_{\sigma l} - E^{(0)}_{\sigma' l}} \tag{3.3}$$

which can be evaluated to give[13]

$$\begin{aligned} a_{\sigma,\sigma'=\sigma+2}(l) &= \frac{-\varepsilon}{4A(\sigma+2)^2} \left[\frac{(\sigma+l+2)(\sigma+l+3)(\sigma-l+2)(\sigma-l+1)(N-\sigma)(N+\sigma+4)}{(\sigma+1)(\sigma+3)} \right]^{1/2} , \\ a_{\sigma,\sigma'=\sigma-2}(l) &= \frac{\varepsilon}{4A\sigma^2} \left[\frac{(\sigma+l)(\sigma+l+1)(\sigma-l)(\sigma-l-1)(N-\sigma+2)(N+\sigma+2)}{(\sigma-1)(\sigma+1)} \right]^{1/2} . \end{aligned} \tag{3.4}$$

The scattering amplitude, Eq. (2.7), can be calculated in first-order (in ε) perturbation theory using the wave functions of Eqs. (3.1), (3.3), and (3.4). The transition matrix element appearing in the right-hand side of Eq. (2.8) is an O(4) representation matrix element, which has been derived in closed form in the Appendix of BAS, Eq. (A10). A simpler but equivalent expression can be obtained using the isomorphism $O(4) \approx SU(2)_1 \otimes SU(2)_{2'}$

$$\langle N,\sigma,l_f,m \mid e^{ig(b)\hat{D}_z} \mid N,\sigma,l_i,m \rangle$$

$$= \sum_{\mu} \langle \sigma/2,\mu,\sigma/2,m-\mu \mid l_f,m \rangle \times \langle \sigma/2,\mu,\sigma/2,m-\mu \mid l_i,m \rangle e^{ig(b)(2\mu-m)} . \tag{3.5}$$

For in-band rotational transitions we take $v' = v$ and $\sigma = N-2v$, while for vibrational transitions we have $v' = v \pm 1$. These transitions amplitudes are linear in ε and to this order σ can only change by 2.

In Sec. V we compare calculations of vibrational excitation in electron scattering done to all orders in ε with perturbation treatments based on results of this section. As we shall see the first-order results agree very well with the exact values even when the dimensionless parameter that controls the size of the perturbation is rather large.

IV. THE SUMMED CROSS SECTION

With present experimental techniques it is not possible (except for H_2) to resolve individual rotational transitions (and sometimes not even vibrational excitations). To compare theoretical calculations and experimental data the quantity of interest in electron-molecule scattering is therefore the differential cross section summed over the final rotational states and averaged over the initial m states. In this section we will use the vibron model to show that in the limit of many molecular bound states (large N) this summed and averaged DCS is independent of the angular momentum of the initial molecular state.

The differential cross section for an electron of momentum $\mathbf{k}_i$ scattering through transfer $\mathbf{q}$ and exciting a diatomic molecule from an initial vibrational state v_i to a final vibrational state v_f, averaged over the initial (m_i) and summed over the final rotational states (l_f,m_f), is given by

$$\frac{d\sigma}{d\Omega}(q) = \frac{2}{2l_i+1} \sum_{m_i} \sum_{l_f,m_f} |A_{fi}(q)|^2 . \tag{4.1}$$

The scattering amplitude $A_{fi}(q)$ is defined in Eq. (2.7). For the physically interesting cases the vibron Hamiltonian is close to that of the O(4) limit. For simplicity we will therefore assume that the molecular eigenstates have O(4) symmetry. Since in the O(4) limit the dipole operator is diagonal in the vibrational quantum number $v = (N-\sigma)/2$ the sum over the final rotational states can be done by closure to yield

$$\frac{d\sigma}{d\Omega}(q)=\frac{k_i^2}{2\pi^2}\int d^2b_1\int d^2b_2 e^{i\mathbf{q}\cdot(\mathbf{b}_1-\mathbf{b}_2)}\frac{1}{2l_i+1}\sum_{m_i}\langle N,\sigma,l_i,m_i\,|\,1+e^{ig(b_1)\hat{\mathbf{b}}_1\cdot\hat{D}}e^{-ig(b_2)\hat{\mathbf{b}}_2\cdot\hat{D}}$$

$$-e^{ig(b_1)\hat{\mathbf{b}}_1\cdot\hat{D}}-e^{-ig(b_2)\hat{\mathbf{b}}_2\cdot\hat{D}}\,|\,N,\sigma,l_i,m_i\rangle\ . \tag{4.2}$$

This matrix element does not depend on N and can be evaluated in closed form using the results of BAS. However, for $l_i/\sigma \ll 1$ and $g\sigma$ finite, we can obtain a very simple result for the summed and averaged DCS. In this limit, the first term in the sum in the matrix element in (4.2) can be written as a single exponential since the neglected commutator is of order l_i/σ. We have

$$\langle N,\sigma,l_i,m_i\,|\,e^{ig(b_1)\hat{\mathbf{b}}\cdot\hat{D}}e^{-ig(b_2)\hat{\mathbf{b}}_2\cdot\hat{D}}\,|\,N,\sigma,l_i,m_i\rangle\approx\langle N,\sigma,l_i,m_i\,|\,e^{i[g(b_1)\hat{\mathbf{b}}_1-g(b_2)\hat{\mathbf{b}}_2]\cdot\hat{D}}\,|\,N,\sigma,l_i,m_i\rangle\ . \tag{4.3}$$

Thus all the matrix elements are of the form

$$I=\frac{1}{2l_i+1}\sum_{m_i}\langle N,\sigma,l_i,m_i\,|\,e^{ig(b)\hat{\mathbf{b}}\cdot\hat{D}}\,|\,N,\sigma,l_i,m_i\rangle=\frac{1}{2l_i+1}\sum_{m_i}\langle N=\sigma,\sigma,l_i,m_i\,|\,e^{ig(b)\hat{D}_z}\,|\,N=\sigma,\sigma,l_i,m_i\rangle\ , \tag{4.4}$$

which can be evaluated easily using the isomorphism $O(4)\approx SU(2)_1\otimes SU(2)_2$,

$$I=\frac{1}{2l_i+1}\sum_{m_i}\sum_{\mu}\langle\sigma/2,\mu,\sigma/2,m_i-\mu\,|\,l_i,m_i\rangle^2\cos[(2\mu-m_i)g(b)]\ . \tag{4.5}$$

For $l_i/\sigma \ll 1$ this sum can be done using an asymptotic from the Clebsch-Gordon coefficient to give

$$I=\frac{\sin[g(b)\sigma]}{g(b)\sigma}=j_0(g(b)\sigma)\ . \tag{4.6}$$

Thus in the limit $l/\sigma \ll 1$ with $g\sigma$ finite the summed and averaged DCS does not depend on the initial angular momentum of the molecule. Using $\bar{g}(b)=g(b)\sigma$ and introducing polar coordinates in (4.2) we can write

$$\frac{d\sigma}{d\Omega}(q)=\frac{k_i^2}{2\pi^2}\int b_1db_1d\phi_1\int b_2db_2d\phi_2 e^{iq(b_1\cos\phi_1-b_2\cos\phi_2)}$$

$$\times[1+j_0(\{[\bar{g}(b_1)]^2+[\bar{g}(b_2)]^2-2\bar{g}(b_1)\bar{g}(b_2)\cos(\phi_1-\phi_2)\}^{1/2})-j_0(\bar{g}(b_1))-j_0(\bar{g}(b_2))]\ . \tag{4.7}$$

We note that for finite values of N the DCS of Eq. (4.1) can be calculated numerically and compared with the large-N result. For typical dipolar couplings, and $N=\sigma=50$ and initial angular momentum $l_i \le \sigma/3$, the fractional rms deviation of the two sums is less than 0.01 while for $l_i \le \sigma/4$ it is less than 0.005. From a numerical point of view it is difficult to calculate the four-dimensional integral of (4.7) because of the rapidly oscillating integrand. We have found it more efficient to calculate the individual cross sections and sum them directly, but since we have proven that the result is independent of the initial angular momentum l_i in our calculation we make the simplifying choice of $l_i=0$.

Another way to show that the summed and averaged DCS is independent of the initial angular momentum is by using coherent states. In this method the connection with the classical rotor is immediately evident. Following the notation of the Appendix of BAS, Eq. (4.4) can be written as

$$I=\frac{1}{4\pi}\frac{(\sigma-l_i)!(\sigma+l_i+1)!}{\sigma!\sigma!(2l_i+1)}\sum_{m_i}\int d\Omega Y^*_{l_im_i}(\Omega)\int d\Omega' Y_{l_im_i}(\Omega')\langle[\sigma],\alpha(\Omega)\,|\,e^{ig(b)\hat{D}_z}\,|\,[\sigma],\alpha(\Omega')\rangle\ , \tag{4.8}$$

where $\hat{\boldsymbol{\Omega}}=(\theta,\phi)$ is the "direction" of the coherent state. The action of $\exp(ig\hat{D}_z)$ on the coherent state is

$$e^{ig(b)\hat{D}_z}\,|\,[\sigma],\alpha(\Omega')\rangle=e^{i\beta\sigma}\,|\,[\sigma],\alpha(\Omega'')\rangle\ , \tag{4.9}$$

with

$$\alpha(\Omega'')=e^{-i\beta}\alpha(\Omega')\ ,$$
$$\beta=\arctan\{\cos\theta'\tan[g(b)]\}\ . \tag{4.10}$$

In the large-σ limit with $\bar{g}=g\sigma$ finite, $\Omega''=\Omega'$, and the matrix element in Eq. (4.8) reduces to

$$\langle[\sigma],\alpha(\Omega)\,|\,[\sigma],\alpha(\Omega')\rangle e^{i\beta\sigma}\ . \tag{4.11}$$

The overlap of the coherent states with directions $\hat{\boldsymbol{\Omega}}$ and $\hat{\boldsymbol{\Omega}}'$ in Eq. (4.11) can be expressed in terms of a sum over Legendre polynomials as

$$\langle [\sigma],\alpha(\Omega) \,|\, [\sigma],\alpha(\Omega') \rangle$$

$$= [\tfrac{1}{2}(1+\hat{\boldsymbol{\Omega}}\cdot\hat{\boldsymbol{\Omega}}')]^{\sigma}$$

$$= \sum_{k=0}^{\sigma} \frac{\sigma!\sigma!(2k+1)}{(\sigma-k)!(\sigma+k+1)!} P_k(\hat{\boldsymbol{\Omega}}\cdot\hat{\boldsymbol{\Omega}}') \,. \tag{4.12}$$

Combining Eqs. (4.8)–(4.12) we see that in the large-σ limit Eq. (4.12) reduces to

$$I = \frac{1}{2l_i+1} \sum_{m_i} \int d\Omega' Y^*_{l_i m_i}(\Omega') Y_{l_i m_i}(\Omega') e^{i\beta\sigma}$$

$$\rightarrow \tfrac{1}{2} \int d\cos\theta' e^{ig(b)\sigma\cos\theta'} = j_0(g(b)\sigma) \,, \tag{4.13}$$

which confirms Eq. (4.6) and establishes the independent on l_i. It is interesting to note in passing that Eq. (4.12) can be used to show that in the large-σ limit the overlap of the two coherent states reduces to a delta function

$$\lim_{\sigma\to\infty} \langle [\sigma],\alpha(\Omega) \,|\, [\sigma],\alpha(\Omega') \rangle = \frac{4\pi}{\sigma} \delta(\Omega-\Omega') \,. \tag{4.14}$$

If the fundamental amplitude is diagonal in Ω a very simple proof of the independence from initial l_i can be given. For example, consider a rigid rotor molecule. In the adiabatic approximation we can write the scattering cross section between specific states of the rotor as

$$\frac{d\sigma(l_i,m_i \to l_f,m_f;q)}{d\Omega} = \left| \int d\Omega\, Y^*_{l_f m_f}(\Omega) \langle \mathbf{k}_f,\Omega \,|\, T \,|\, \mathbf{k}_i,\Omega \rangle Y_{l_i m_i}(\Omega) \right|^2 , \tag{4.15}$$

where $\hat{\boldsymbol{\Omega}}$ is again the "direction" of the rotor in space, and the essence of the adiabatic approximation is the assumption that the t matrix is diagonal in Ω. For the summed and averaged DCS the sum over the final rotational states can be done simply by closure to yield

$$\frac{d\sigma}{d\Omega}(q) = \frac{1}{2l_i+1} \sum_{m_i} \int d\Omega\, Y^*_{l_i m_i}(\Omega) \times | \langle \mathbf{k}_f,\Omega \,|\, T \,|\, \mathbf{k}_i,\Omega \rangle |^2 Y_{l_i m_i}(\Omega)$$

$$= \frac{1}{4\pi} \int d\Omega\, | \langle \mathbf{k}_f,\Omega \,|\, T \,|\, \mathbf{k}_i,\Omega \rangle |^2 , \tag{4.16}$$

which clearly does not depend on the initial state.

V. RESULTS

As an illustration of our method we present some results for the rotationally summed and averaged cross sections for electrons scattered from the molecules LiF and KI. The parameters in the vibron Hamiltonian (2.1) can be determined either by fitting the molecular spectra directly or by rewriting the energy eigenvalues in the form of a Dunham expansion,[17] a form which was introduced as early as 1932 to parametrize the coupling between vibrational and rotational degrees of freedom. The Dunham expansion writes the energy in terms of the angular momentum l and the vibrational quantum number v as

$$E_{vl} = \sum_{i,j} Y_{ij}(v+\tfrac{1}{2})^i [l(l+1)]^j \,. \tag{5.1}$$

The coefficients Y_{ij} are tabulated by Huber and Herzberg[18] for a wide class of diatomic molecules. For the vibron Hamiltonian we take the form discussed in Sec. III. In first-order perturbation theory the energy eigenvalues are then given by Eq. (3.2). Expanding Eq. (3.2) in v/N and comparing coefficients of (5.1) and (3.2) the parameters in the vibron Hamiltonian can be related directly to the Dunham coefficients

$$\begin{aligned} Y_{00} &= -A\frac{2N+3}{4} \,, \\ Y_{10} &= A(N+2) \,, \\ Y_{20} &= -A \,, \\ Y_{01} &= \varepsilon\frac{(N+2)(N-4)}{2N^3} + B \,, \\ Y_{11} &= \varepsilon\frac{2(N+2)}{N^3} \,. \end{aligned} \tag{5.2}$$

The first term Y_{00} contributes only to the binding energy. In Table I we show the Hamiltonian parameters for the molecules LiF and KI based on the Dunham coefficients for these molecules given by Huber and Herzberg.[18] For N we have taken the nearest integer value. A measure of the deviation from the O(4) limit is given by $\varepsilon/(N-1)A$ which is 0.14 for LiF and -0.07 for KI. To fix the electron-molecule interaction, the coupling constant $\bar{d}$ of BAS is taken to be equal to the static dipole moment of the molecule, $\bar{d}=6.58$ D for LiF and $\bar{d}=10.82$ D for KI.

In Figs. 1 and 2 we compare the cross sections for excitation of the ground-state band ($v=0\to v'=0$) and the first excited vibrational band ($v=0\to v'=1$) in LiF by electrons of energy 5.44 and 20.0 eV, respectively, with the measurements of Vuscovic *et al.*[19] We have normalized the experimental data to our absolute calculations at $\theta=40°$. At the lower energy the agreement between our calculation and the data is very good except at the larger angles (where the eikonal approximation has doubtful validity in any case). At the higher energy the discrepancy between data and calculation shows up at a smaller angle

TABLE I. Parameters in the vibron Hamiltonian for the molecules LiF and KI.

	N	A (cm^{-1})	B (cm^{-1})	ε (cm^{-1})	δ (cm^{-1})
LiF	113	7.929	0.792	127.268	0
KI	325	0.574	0.082	-13.882	0

($\lesssim 60°$) but a comparable momentum transfer. The large angles correspond to short distances or small impact parameter and our discrepancies there reflect our neglect of certain molecular electronic structure effects in the dynamics. Of these, exchange is probably the most important.[1,5] We are presently working to include the effects of exchange in the algebraic-eikonal approach. Note in Figs. 1 and 2 that we predict the differential cross section for vibrational excitation ($v=0 \rightarrow v'=1$) to be about 4 orders of magnitude smaller than the rotationally elastic scattering. We know of no measurement of this cross section.

The good agreement of the calculated and measured differential cross sections at small angles is due to the dominance of dipole coupling at large impact parameters. In our calculation this is included to all orders. In Fig. 3 we show the same LiF calculation at 5.44 eV compared with just the Born approximation. We see that only at the very smallest angles ($\lesssim 25°$) do the born and full calculation agree. Thus the correct summing of multistep processes or equivalently the correct treatment of close coupling in our calculation is essential for its agreement with the data. Also shown in Fig. 3 are the various partial cross sections for exciting the molecular ground state in the ground-state rotational band. Notice that the rotationally summed differential cross section (labeled total on the figure) really is a sum of many parts, and that the true elastic contribution ($0^+ \rightarrow 0^+$) and first excited-state ($0^+ \rightarrow 1^-$) contributions drop off quite quickly with an-

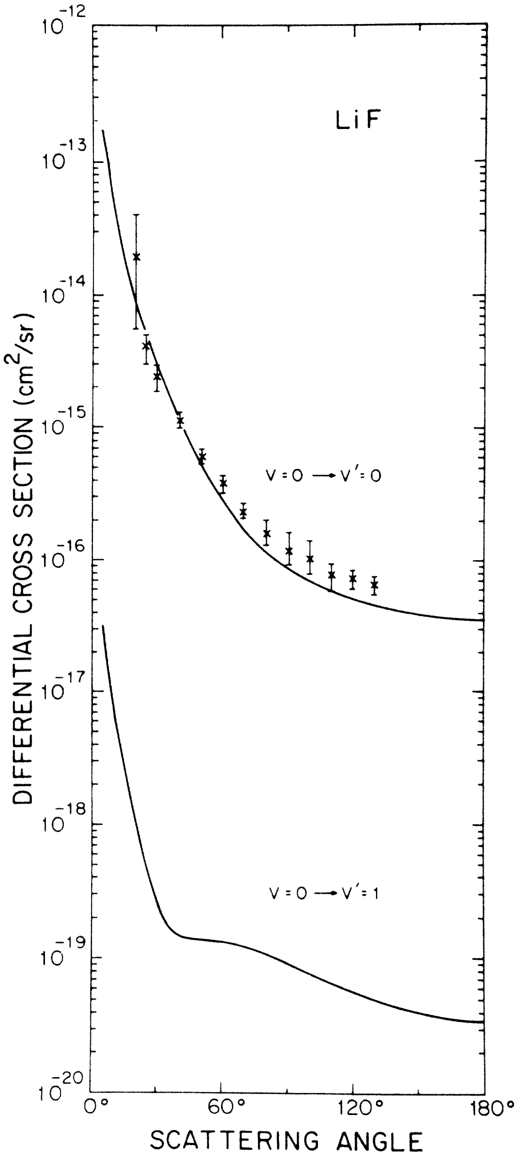

FIG. 1. Differential cross section for vibrationally elastic ($v=0 \rightarrow v'=0$) and inelastic ($v=0 \rightarrow v'=1$) excitation of LiF by 5.44-eV electrons. The experimental data (Ref. 19) are normalized to our results at 40°.

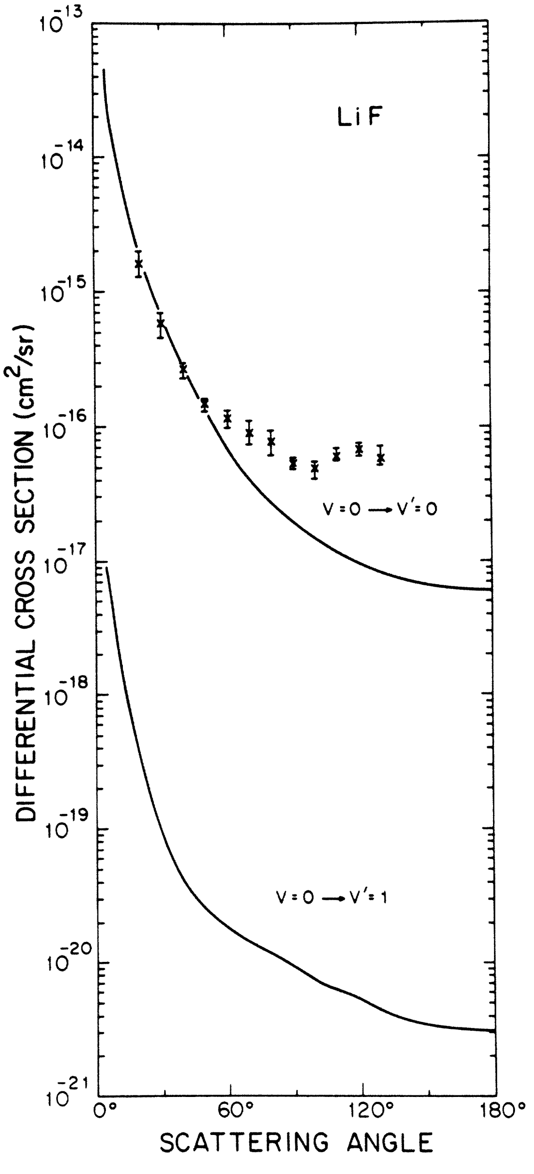

FIG. 2. As in Fig. 1, with electron energy 20.0 eV.

gle. Excitation of the higher rotational states is also a multistep process.

In Figs. 4 and 5 we show our calculations for KI interacting with electrons of 6.74 and 15.7 eV compared with the data of Rudge *et al.*[20] Once again the data are normalized to the absolute calculation at $\theta = 15°$. Most of the main features of the KI calculation are the same as for LiF. Also in this case the vibrational excitation is quite small. The calculation begins to disagree with the data at smaller angles in KI than in LiF. As before, better treatment of the larger angles depends on including more of the details of the short-range dynamics, particularly exchange and perhaps resonances.

We have carried out our calculations using the parameters of Table I in the vibron Hamiltonian. In addition we have performed a calculation in which the term proportional to ε in the vibron Hamiltonian Eq. (2.1) is treated in first-order perturbation theory as discussed in Sec. III. Even though in LiF the deviation from O(4) symmetry as measured by the parameter $\varepsilon/A(N-1)$ is of order 0.14, and even though such a large deviation will mean that a first-order perturbation theory treatment of the molecular energies or wave functions is not very good, we find that the difference between cross sections calculated in first or-

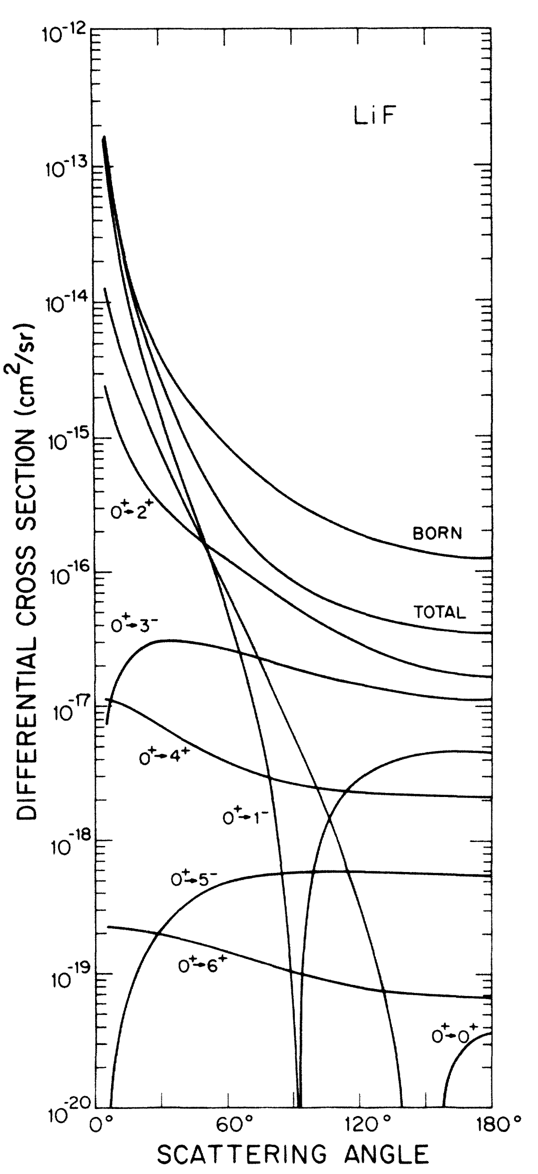

FIG. 3. Differential cross section for vibrationally elastic excitation of LiF by 5.44-eV electrons. The excitation to the individual final rotational states l_f as well as the Born term are shown explicitly.

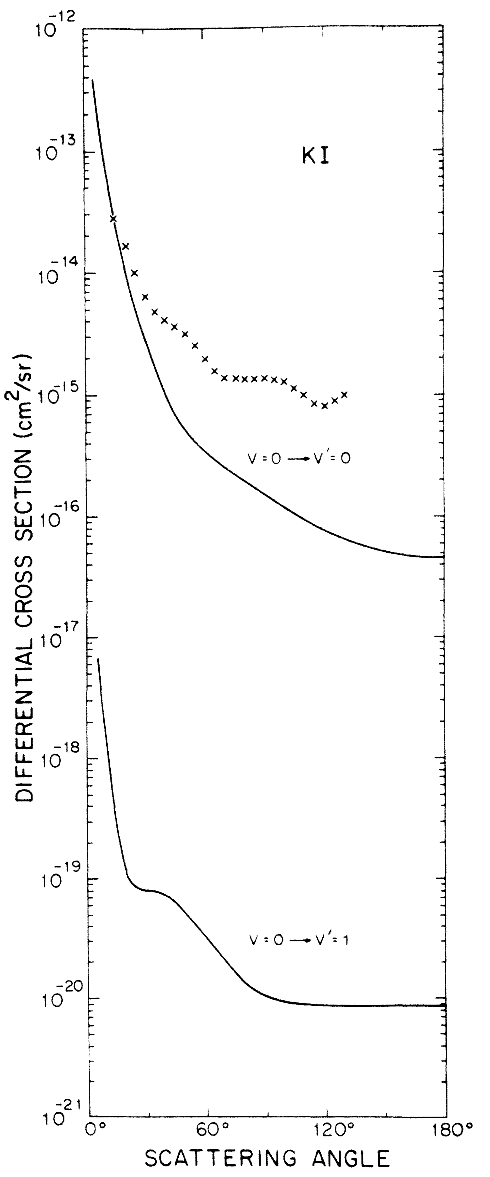

FIG. 4. Differential cross section for vibrationally elastic $(v=0 \to v'=0)$ and inelastic $(v=0 \to v'=1)$ excitation of KI by 6.74-eV electrons. The experimental data (Ref. 20) are normalized to our results at 15°.

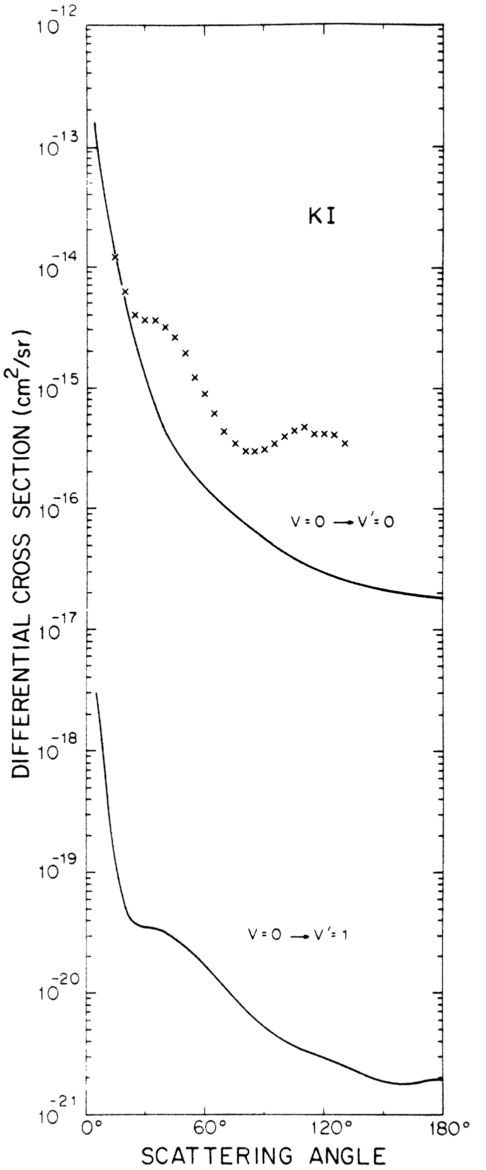

FIG. 5. As in Fig. 4, with electron energy 15.7 eV.

der and to all orders is so small as to be completely invisible in Figs. 1 and 2. The fractional rms deviation of the two calculations is of order 0.005. This shows that these scattering processes off polar molecules are largely dominated by multistep excitation mechanisms rather than by the details of the molecular wave functions. Since first-order perturbation theory works so well for coupling of the vibrational bands, the cross section for interband excitation is a direct measure of the value of $\varepsilon/A\,(N-1)$.

VI. CONCLUSION

We have shown that the algebraic-eikonal theory of medium-energy electron scattering from polar diatomic molecules gives a simple yet adequate treatment of the scattering for two typical examples, LiF and KI. In particular we have shown that the multistep or close-coupling mature of the dynamics is essential while details of the wave functions are less crucial. We have also seen that the algebraic approach makes it easy to develop a perturbative treatment of vibrational coupling and to do sums and averages of cross sections.

So far the short-range dynamics has been included only partially in our calculations. The neglect of the exchange potential is probably responsible for the discrepancy between our calculations and the data at large angles. We are presently working on a scheme to include exchange and related short-range dynamics in the algebraic approach. We are also looking at ways to make corrections to the adiabatic approximation which should allow us to at least estimate the order of magnitude of the corrections. Finally, but most importantly, we are working to extend those methods to triatomic and polyatomic molecules where the algebraic approach should have an even greater advantage over other methods. Preliminary results for HCN are most encouraging.

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