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Angular Dependence of Scattering Products in Electron-Molecule Resonant Excitation and in Dissociative Attachment

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For the processes mentioned in the title, the general rearrangement formalism of a previous paper is applied with specific consideration to the effect of molecule orientation on the electronic matrix elements and on the total and differential cross sections. Formulas are given for two cases: when one can and when one cannot treat the effect of rotation as a semiclassical orientation average. A short discussion is given of selection rules and of the use of these formulas in (a) *ab initio* calculation of the cross section, (b) approximate prediction of angular dependence, and (c) parametrization of experimental data.

INTRODUCTION

The process of dissociative attachment (DA) and pure resonant scattering of an electron from a diatomic molecule have been theoretically described in an extremely simple way in I.[1] The key simplification was the definition of the Q, the resonant part of Hilbert space, as that part of the total electronic-nuclear function space which has an electronic component (independent of the nuclear part) identical with the electronic wave function for the resonant state ϕ_r. In the Born-Oppenheimer separation, the function ϕ_r and Q depend parametrically on the internuclear distance R. The formalism does not depend on which of the many methods for the calculation of electronic resonant states is used to get the ϕ_r, which for the purpose of this paper we assume known. It is shown in I that, for all processes in which one of the channels involves an asymptotic free electron, the T matrix for the process, and therefore the cross section, depend on the matrix element $a_p{}^+$ which couples P to Q space, as defined in I-4.[1] The matrix element $a_p{}^+$ in turn depends on the resonant electronic state ϕ_r, the Hamiltonian, and the initial or final (as the case may be) potential-scattering wave function. This latter function is assumed, with much justification from experiment, to be separable (in the adiabatic sense) into an electronic part ϕ_{ad}, about which we make no assumptions for the present, and a nuclear part, which we assume to be exactly that of the target molecule [Eq. (I.5.1)]. The dependence of the electronic matrix element on orientation was not made explicit in I; this we do in Sec. I of this paper. In Sec. II we derive formulas for the total and differential dissociative attachment cross section; and in Sec. III we do the same for the resonant part of the electron-molecule vibrational excitation cross section. In Sec. IV we discuss the application of these formulas to relevant problems.

I. THE ELECTRONIC MATRIX ELEMENT

In I.5.2 the matrix element $a_p{}^+(\vec{\mathrm{R}})$ is given in the adiabatic approximation as

$$a_p{}^+(\vec{\mathrm{R}}) = V_{\bar{a}}(\vec{\mathrm{R}})\chi_v(R)Y_{JM}(\hat{R})/R, \tag{1}$$

where $\chi_v(R)$ and $Y_{JM}(\hat{R})$ are the target vibration and rotation states, respectively. $V_{\bar{a}}(\vec{\mathrm{R}})$, the basic *electronic* matrix element which directly links P to Q space, is central to this paper. It is defined by

$$V_{\bar{a}}(\vec{\mathrm{R}}) = \int d\vec{\mathrm{r}}\ \phi_r{}^*(\vec{\mathrm{r}}, R)H_{\mathrm{el}}\,\phi_{\mathrm{ad}}{}^+(\mathrm{r}, \vec{\mathrm{R}}), \tag{2}$$

$\vec{\mathrm{r}}$ being the electronic coordinates. The dependence of $V_{\bar{a}}$ on orientation comes from the dependence of ϕ_{ad} on the incident-electron momentum vector $\vec{\mathrm{k}}$ and the subsequent expression of $\vec{\mathrm{k}}$ in a coordinate system with a polar axis along the internuclear direction (see Fig. 1). This dependence can be made by expressing $\phi_{\mathrm{ad}}{}^+$ in integral-equation form and then expanding the asymptotic part of $\phi_{\mathrm{ad}}{}^+$; thus

$$\begin{aligned}\phi_{\mathrm{ad}}{}^+ &= (1+G_pV)\,e^{i\vec{\mathrm{k}}\cdot\vec{\mathrm{r}}_e}\,\phi_T(\vec{\mathrm{r}}_T, R)\\ &= \sum_{L=0}^{\infty} i^L(2L+1)(1+G_pV)j_L(kr)\\ &\quad\times\phi_T(\vec{\mathrm{r}}_T, R)P_L(\cos\hat{\vec{\mathrm{k}}}\cdot\hat{\vec{\mathrm{r}}}_e)\\ &= 4\pi\sum_{L=0}^{\infty}\sum_{\mu=-L}^{L} i^L(1+G_pV)\phi_T(\vec{\mathrm{r}}, R)\\ &\quad\times j_L(kr_e)Y_{L\mu}{}^*(\hat{\mathrm{k}})Y_{L\mu}(\hat{r}_e).\end{aligned} \tag{3}$$

Here G_p is the total Green's function; V is the electron target interaction, ϕ_T is the unperturbed electronic wave function of the target; and $\vec{\mathrm{r}}_T$ and $\vec{\mathrm{r}}_e$ are the target and incident electron coordinates, respectively. Also j_L, P_L, and $Y_{L\mu}$ are the Bessel function, Legendre polynomial, and spherical harmonic, respectively.[2] Since $\vec{\mathrm{r}}_e$ is to be integrated over in Eq. (2), it must be relative to the body-fixed polar axis $\vec{\mathrm{R}}$ as are all other electrons. This latter statement means that $\hat{\mathrm{k}}$ is the unit vector in the incident direction expressed in

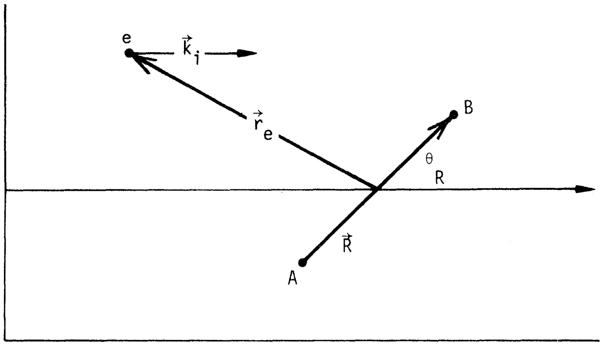

FIG. 1. The vectors which characterize dissociative attachment. The incident electron momentum is $\vec{k}_i$. The vector $\vec{R}$ is the molecular axis, joining the atoms A and B. Its angular coordinates θ_R and ϕ_R (not shown) are defined relative to the $\vec{k}_i$ axis. The coordinates $\vec{r}_e$ of the incident electron are then defined relative to the molecular $\vec{R}$ axis (with origin at the center of nuclear charge).

the body-fixed coordinates. In integrating Eq. (2), the conservation of axial orbital angular momentum restricts the sum over μ to values that satisfy

$$\mu = \Lambda_r - \Lambda_T \ , \tag{4}$$

where Λ_T and Λ_r are the target and resonant axial orbital angular momenta, respectively. These are algebraic quantities and may be either positive or negative. The general form of $V_{\bar{a}}(\vec{R})$ is therefore

$$V_{\bar{a}}(\vec{R}) = (4\pi)^{\frac{1}{2}} \sum_{L=|\mu|}^{\infty} V_{L|\mu|}(R) Y_{L\mu}{}^*(\hat{k}) \tag{5}$$

In practice $V_{L'|\mu|}(\vec{R})$ is calculated by taking the scalar product of Eq. (5) with $Y_{L'\mu'}(\hat{k})$.

In homonuclear diatomics, L is further restricted to even or odd values, according as ϕ_T and ϕ_r have the same or opposite parity. The obvious selection rules for spin ($S_r = S_T \pm \frac{1}{2}$ must also be obeyed. Less obvious is the fact that if both resonance and target are Σ states, then both states, for an allowed transition, must have the same parity for reflection in a plane containing the molecular axis. This is true since the only part of the plane wave absorbed is σ and this is "plus." With these considerations, $a_p{}^+$ can be written in the form

$$a_p{}^+(\vec{R}) = (4\pi)^{1/2} \sum_{L=|\mu|}^{\infty} V_{L|\mu|}(R) \chi_v(R) \times R^{-1} Y_{JM}(\vec{R}) Y_{L\mu}{}^*(\vec{k}) \ . \tag{6}$$

In some cases[3] the first non-symmetry-forbidden term of Eq. (6) may be adequate to describe the scattering. By analogy with Rydberg states, for which one-center expansions are common, and whose orbital structure is similar to that of single-particle resonances, one expects this adequacy to be general for resonant-continuum transitions where one can qualitatively envision a single electron leaving the resonant system without subsequent major changes in the structure of the target core. Low-energy single-particle resonance[4] processes which fit this approximation will be discussed in Sec. IV. The ability to retain the first symmetry term in (6) will be seen to introduce enormous simplifications into the formulas. At low energy there is actually a second reason why we could hope to be able to use this approximation. This reason is related to the fact that at low energy the amplitudes of the various sperical components in a plane wave decrease rapidly with increasing L. As a result, even if the expansion of ϕ_r in spherical harmonics does not converge rapidly, ϕ_{ad} in Eq. (2) will cause the integral to weight the lower moments of ϕ_r more heavily. This will give the same effect after integration as a rapidly converging one-center expansion of ϕ_r. In fact, this second reason gives us some hope that one-center expansions of core-excited resonances, where rapid convergence is problematic, might be useful. The possibility of predicting the angular dependence from the electronic configuration of the resonance will certainly be enhanced by this second effect.

II. DISSOCIATIVE ATTACHMENT

The T matrix for dissociative attachment is given by

$$T_{\text{DA}} = \langle \zeta^-(\vec{R}) a_p{}^+(\vec{R}) \rangle_R = (4\pi)^{1/2} \sum_{L=|\mu|}^{\infty} \int \zeta^-(\vec{R}) V_{L|\mu|}(R) \chi_v(R) R^{-1} Y_{J_i M_i}(\hat{R}) Y_{L\mu}{}^*(\hat{k}) d^3R \ , \tag{7}$$

where i refers to "initial" target state and $\zeta(\vec{R})$ is the unbound nuclear-motion state associated with the motion of the nuclei in the complex potential set up (in the Born-Oppenheimer sense) by the complex molecular electronic energy. (See I, Sec. IV). The equation for $\zeta^{\pm}(\vec{R})$ is

$$[T_R + V_f(R) + \Delta(R) - \tfrac{1}{2} i \Gamma(R) - E] \zeta^{\pm}(\vec{R}) = 0 \ . \tag{8}$$

The approximate locality and spherical symmetry of the Δ and Γ are derived in Appendix A, where the conditions for these to hold are established. The state $\zeta^+(\vec{R})$ approaches a plane (plus outgoing) wave advancing in the direction of the final relative momentum vector and is given by

$$\zeta^+(\vec{R}) = \sum_{J,M} i^J (4\pi)^{1/2} Y_{JM}{}^*(\hat{R}) Y_{JM}(\Omega_{\vec{K}}) e^{i\bar{\delta}_J} \chi_J(k,R)/R \ , \tag{9}$$

where $\bar{\delta}_J = \delta_J + (i\rho_J)/2$ is complex, and χ_J is normalized, according to I-5.6 and I-5.7, respectively. $\Omega_{\vec{K}}$ is as the solid angle about the relative momentum vector $\vec{K}$. For the orientation vector $\vec{R}$ and the solid angle subtending the detector, $\Omega_{\vec{K}}$ the polar axis as taken along the direction of the incident electron $\vec{k}_i$.

Substitution of Eq. (9) into (7) will give the desired angular dependence of the T matrix. Before doing this, however, we must pause and introduce the assumption which is basic to the treatment of this paper. This assumption is that the rotation of the molecule is *quasiclassical* in the sense that the rotational levels are very closely spaced, or equivalently, that the frequency of rotation $\omega_r = \hbar(J + \frac{1}{2})/MR^2$ is small (as compared with the frequencies of vibrational or electronic motion). This assumed slow variation of the rotational or centrifugal energy with J then implies that the wave functions $\chi_J(R)$ will vary slowly with J, and so we may replace the subscript J with an average value J_r characteristic of a range of J's. This allows us to take χ_{J_r} outside the summation in (9) and write

$$\zeta^+(R) = (4\pi)^{1/2} \exp(i\bar{\delta}_{J_r}) i^{J_r} \chi_{J_r}(R) R^{-1} \sum_{JM} Y_{JM}{}^*(\hat{R}) Y_{JM}(\Omega_K)$$

$$= (4\pi)^{1/2} \exp(i\bar{\delta}_{J_r}) i^{J_r} \chi_{J_r}(R) R^{-1} \delta(\hat{R} - \Omega_K) \tag{10}$$

If we had put (9) into (7) and integrated on $\hat{R}$, only those terms in (9) would contribute to (7) that have J values of $|L + J_i|$, $|L + J_i| - 2, \ldots, |L - J_i|$. This result is due to well-known properties of the spherical harmonics and is independent of χ_J. There exists a set of terms in (9) whose radial parts $\chi_J(R)$ can be modified to $\chi_{J_r}(R)$ without affecting the result, simply because these terms do not contribute at all to the integral in Eq. (7). The terms that *do* contribute are expected to have a limited range of J values; $J_i \pm 5$ for given J_i. This can be safely said from the all calculational experience on one-center expansion calculations of both ground and excited states of diatomic molecules, and is in accordance with the general expectation that the change in J is small for low-energy electron scattering. If we can justify replacing J by J_r in this limited range of allowed χ_J, we have achieved our object. In Eq. (8) the J dependence of χ_J is due to the centrifugal potential, which is proportional to $J(J+1)/2I$, I being the moment of inertia of the system. Now the assumed small spacing of the levels immediately guarantees that the variation of the centrifugal potential in this limited range will likewise be small.

In this centrifugal term, which is essentially the energy of rotation, it makes little difference if J is changed to an average J_r, provided the difference itself is small compared to any one of the two quantities $E - [V_f(R) + \Delta(R)]$ and $\Gamma(R)/2$ in Eq. (8). Since $E - [V_f(R) + \Delta(R)]$ is the relative kinetic energy of the dissociating nuclei and $\Gamma(R)$ is the electronic width of the resonance, we see that Eq. (10) can be used when either of the following conditions exist:

(*i*) The rotational energy spacing is small compared with the relative nuclear kinetic energy (for R values in the Franck–Condon regions of the ground state and energetically accessible target states).

(*ii*) The rotational energy spacing is small compared to the width; or, equivalently, the period of rotation is big compared to the lifetime of the resonance.

Assumption (*i*) is the usual spectroscopic assumption which permits us to drop rotation-vibration interaction and to treat the motion in the R coordinate as occurring for a fixed orientation. Assumption (*ii*) states that if the whole process takes place in a time much shorter than the period of rotation, then the molecule can be considered to have a fixed orientation during the process. In both cases the fixed-orientation concept leads to the δ function in Eq. (10). In general, one need only worry about satisfying assumption (*i*) if one has reason to think that $V_f + \Delta$ is either a very shallow bound potential or a very flat repulsive potential in the Franck-Condon region, and even if this were the case one would further have to argue that the lifetime of the resonance was long compared to the rotational period. To our knowledge no resonance state has yet been reported that does not seem to satisfy (*i*) or (*ii*) or both. In the following, the cross section is derived both for the case where (10) is valid and the case where it is not. The formulas for the latter case are more complicated in form, and they hide the similarity between the expressions for the rigorous and the phenomenologically derived cross section.[5] If one cannot use (10) (or does not use it) one must also consider nuclear spin and the Konig-type selection rules.[6]

For the case where Eq. (10) is valid, T_{DA} in Eq. (7) becomes, after integrating over angles $\hat{R}$,

$$T_{\mathrm{DA}} = 4\pi \exp(-i\bar{\delta}_{J_r})(-i)^{J_r} \chi_{J_r}{}^*(R) \chi_\nu(R) \sum_{L=|\mu|}^{\infty} V_{L|\mu|}(R) Y_{J_i M_i}(\Omega_K) Y_{L\mu}{}^*(\Omega_K) . \tag{11}$$

Here, before integration, the $Y_{L\mu}(\hat{k})$ with polar axis $\vec{R}$ was expressed in terms of $Y_{L\mu}{}'(\hat{R})$ with polar axis $\vec{k}$, using $\theta_R = \theta_k$ and $\phi_R = -\phi_k$, with the result that

$$Y_{L\mu}(\hat{k}) = Y_{L\mu}{}^*(\hat{R}) \tag{12}$$

The angular dependence of Eq. (11) tells us, as expected in the slow rotation aproximation implicit in the use of Eq. (10), that only those molecules contribute to DA at angle θ_K which are initially oriented (at the time of collision) along Ω_K.

The differential cross section $\sigma_{\mathrm{DA}}(\Omega)$ follows immediately from (11) using (I-3.13). We must sum over the final state Λ_r and average over the initial state Λ_T. **Further,** averaging over the degenerate M_i states then eliminates the $Y_{J_i M_i}$ factors by means of the **sum** rule (Unsold's theorem), leaving

$$\sigma_{\mathrm{DA}}(\Omega_K)=\left(\frac{\pi}{k_i}\right)^2 \sum_{M_i=J_i}^{J_i}\frac{1}{2J_i+1}\,\frac{1}{2}\sum_{\Lambda_T,\,\Lambda_r} g\,|\,T_{\mathrm{DA}}(M_i,\ldots)|^2$$

$$=(4\pi^3/k_i^2)\exp(-\rho_{J_r})\sum_{\Lambda_r}\left|\sum_{L=|\mu|}^{\infty}(\chi_{J_r}V_{L|\mu|}\chi_v)Y_{L\mu}{}^*(\Omega_K)\right|^2 . \tag{13}$$

Here the inner product signifies $\int_0^\infty dR$, and g is the spin weighting factor. In the final form of Eq. (13) the sum over Λ_T, which gives two equivalent terms, is eliminated in favor of the $+|\Lambda_T|$ term with a factor of 2. Equation (4), which determines μ, therefore assumes the more special form

$$\mu=\Lambda_r-|\Lambda_T|\,. \tag{4'}$$

Equation (4′) remains the operational definition for μ in subsequent equations, for the same reason. When applicable, the one-center approximation gives a simple approximate formula

$$\sigma_{\mathrm{DA}}(\Omega_K)\simeq(4\pi^3/k_i^2)\exp(-\rho_{J_r})g\,|(\chi_{J_r}V_{L_0|\mu_0|}\chi_v)|^2|Y_{L_0\mu_0}(\Omega_K)|^2 . \tag{14}$$

Here L_0 is the lowest allowed value of L and $\mu_0=|\Lambda_T|-|\Lambda_r|$. If we use the approximation that replaces the continuum nuclear motion wave function by a distorted δ function [see Eq. (I.5.14)], Eq. (14) becomes

$$\sigma_{\mathrm{DA}}(\Omega_K)\simeq(4\pi^3/k_i^2)\exp(-\rho_{J_r})g(\Gamma_{\overline{a}}/\Gamma_d)|\tilde{\chi}_v(x_E-ig)|^2|Y_{L_0\mu_0}(\theta_K)|^2 , \tag{14'}$$

where the various quantities Γ_d, $\tilde{\chi}_v$, and x_E were defined in I. $\Gamma_{\overline{a}}$ is given by analogy with the corresponding quantity of I by $\Gamma_{\overline{a}}=2\pi|V_{L_0\mu_0}|^2$ and is identical with $\Gamma_{\overline{a}}$ of I when $L_0=0$. See also Eq. (A6). Equation (14) predicts that, for the one-term cases, the DA products are expected to have an angular distribution relative to $\vec{k}_i$, which is the same as the partial wave absorbed from the continuum by the target in forming the resonance.

The total scattering cross section is easily obtained from (13) by integration over Ω_K (using the orthonormality of spherical harmonics):

$$\sigma_{\mathrm{DA}}^{\mathrm{tot}}=\frac{4\pi^3}{k_i^2}g\exp(-\rho_{J_r})\sum_{\Lambda_r}\sum_{L=|\mu|}^{\infty}|\int dR\,\chi_{J_r}{}^*(R)V_{L|\mu|}(R)\chi_v(R)|^2=\sigma_{\mathrm{capt}}\exp(-\rho_{J_r}) \tag{15}$$

Again μ is given by (4′). Equation (15) exhibits the noninterference of partial waves as well as the phenomenological form.[5]

Again, using the semiclassical approximation (I-5.14) for the radial integral in (15), reduces it to the familar form

$$\sigma_{\mathrm{DA}}^{\mathrm{tot}}=(4\pi^3/k_i^2)g\exp(-\rho_{J_r})(\Gamma_{\overline{a}}/\Gamma_d)|\chi_{v,J_r}(x_E-ig)|^2 , \tag{15'}$$

where now

$$\Gamma_{\overline{a}}=2\pi\sum_{\Lambda_r}\sum_L|V_{L|\mu|}(R_E)|^2=2\pi(|V_{\overline{a}}(\vec{R}_E)|^2)_{\mathrm{av}}.$$

The average here signifies an average over the angles $\hat{R}$ as well as over Λ_r. Equation (15) is therefore identical with the corresponding Eq. (I-5.19) of I for the total cross section with the following, somewhat expanded, definitions in terms of the angles and states of rotation:

(a) The capture width $\Gamma_{\overline{a}}$ is now defined as above in terms of the angular and orientation *average* of $|V_{\overline{a}}(\vec{R})|^2$, and

(b) the centrifugal energy, E_J, which in both papers enters into the definition of ρ, χ_v and the x_E (see I-5.22), is here interpreted as $E_{J_r}\simeq E_{J_i}$, characteristic of the small range of accessible final J's. Therefore, while the present paper supplements I by giving the correct angular distribution for $\sigma_{\mathrm{DA}}(\theta)$ through Eqs. (13) and (14), it makes no change in the formulas (I-5.19 and 5.24) for the *total* cross section. What it does, as mentioned in (a) and (b) is to clarify and make explicit the angular and rotational averages which are implied, and to improve the derivation of the parametric forms.

When the slow-rotation approximation cannot be made, Eq. (9) must be substituted into (7) to give

$$T_{\mathrm{DA}}=(4\pi)^{1/2}\sum_{L=|\mu|}^{\infty}\int dR\sum_J(-i)^Je^{-i\overline{\delta}_J}\chi_J{}^*(R)V_{L|\mu|}(R)\chi_v(R)\int d\hat{R}\,Y_{J,M-\mu}{}^*(\hat{R})Y_{L,\mu}{}^*(\hat{R})Y_{J_i,M_i}(\hat{R})Y_{J,M-\mu_i}(\Omega_K).$$

$$= (4\pi)^{1/2} \sum_{L=|\mu|} \sum_{J} (-i)^{J} e^{-i\bar{\delta}_J} \int dR \chi_J{}^*(R) V_{L|\mu|}(R) \chi_v(R) \left[\frac{(2J+1)(2J_i+1)}{2L+1}\right]^{1/2}$$

$$\times C(LJ_iJ; -\mu, M_i, M_i-\mu) C(LJ_iJ; 000) Y_{J, M_i-\mu}(\Omega_K) , \tag{16}$$

where the $C(ll_2l_3; mm_2m_3)$ are the Clebsch-Gordan coefficients.[2]

An interesting set of very general selection rules for rotational excitation can be derived from either Eqs. (16) or (18). Three cases are worth considering. The first is the case of a homonuclear diatomic molecule with isotopically identical nuclei. Here the center of mass [the usual origin for the rotational functions], and the center of charge [the usual origin for the one-center expansions of $V_{\overline{a}}(\vec{R})$] are the same. This allows for straightforward integration of the integral over R in (16). For parity-conserving (-breaking) transitions, only even (odd) L values are retained, with the result that when all allowed L are considered, only even (odd) ΔJ values are allowed. This result is completely consistent with the Konig[6] selection rules, since we already noted the selection rule $\Sigma_T{}^{\pm} \longleftrightarrow \Sigma_r{}^{\pm}$. Second, for heteronuclear molecules, the absence of inversion symmetry results in all ΔJ being allowed, even if the center for the expansion is chosen as the center of mass and not the usual (and here different) center of charge. Third, for homonuclear molecules with isotopically different nuclei, the parity will allow only even or odd terms in the expansion of $V_{\overline{a}}(\vec{R})$ about the center of charge. The difference between the first and third cases will again be that in the third case the centers of charge and mass will not be the same. To evaluate the integral in Eq. (16), the necessary re-expansion of the spherical harmonics of $V_{\overline{a}}(\vec{R})$ about the center of mass causes all L to reappear and, in principle, allows all ΔJ. If, in the homonuclear isotopically different molecule, the nuclei have similar masses, then the transitions that are allowed in the isotopically similar case are expected to be the strongest. The general expression for the differential scattering cross section is, using Eq. (16),

$$\sigma(\Omega_K) = \sum_{\Lambda_r} \frac{\pi^2}{k_i{}^2} \sum_{M_i=-J_i}^{J_i} \frac{1}{2J+1} g |T_{\mathrm{DA}}|^2 . \tag{17}$$

Since in general no simplification can be worked on (17) we will not write a more explicit form. To simplify (17) special approximations, such as restricting ΔJ to one even or odd value (0 or 1), can be made. But only the approximation of slow rotation, which is generally valid for resonances, gives essential simplifications.

Due to the orthonormality of the spherical harmonics, the *total* scattering cross section for the "fast rotation" case is considerably easier to compute, and is given by

$$\sigma_{\mathrm{DA}}{}^{\mathrm{TOT}} = \sum_{\Lambda_r} \frac{4\pi^3}{k^2} \sum_{M_i=-J_i}^{J_i} \sum_{L=|\mu|}^{\infty} \sum_{L'=|\mu|}^{\infty} \sum_{J} g e^{-\rho_J} \frac{2J+1}{[(2L+1)(2L'+1)]^{1/2}} \int dR \chi_J{}^* V_{L|\mu|} \chi_v$$

$$\times \int dR \chi_J V_{L'|\mu|} \chi_v{}^* C(LJ_iJ; -\mu, M_i, M_i-\mu) C(L'J_iJ; -\mu, M_i, M_i-\mu) C(LJ_iJ; 000) C(L'J_iJ; 000) , \tag{18}$$

where μ is given by (4′). Again, general simplifications are not possible.

III. ANGULAR DISTRIBUTION OF THE SCATTERED ELECTRON IN PURE RESONANT VIBRATIONAL EXCITATION

For many processes in low-energy-electron diatomic-molecule scattering, the resonant, as opposed to the potential, scattering dominates the scattering process. Such a process is one in which significant vibrational excitation occurs and momentum transfer considerations make large "single-collision" potential-scattering contributions less improbable.[3] A commonly studied process is the vibrational excitation of the ground states of such molecules as N_2, and CO, and (to a lesser degree) H_2. We here derive formulas for the angular distributions expected in such processes.

The transition matrix for the general electron scattering resonant process is given as

$$T = \langle a_{p_f} - g_F a_{p_i}{}^+ \rangle , \tag{19}$$

where i and f indicate initial and final states, respectively, a_p has been discussed in Sec. I, and g_F is the Green's function of the nuclear motion in the complex potential field, i.e.,

$$g_F = (E - T_R - V_f - \Delta + i\Gamma/2)^{-1} \tag{20}$$

The $\hat{k}_f$ in a_p, and $\hat{k}_i$ in $a_p{}^+$ are the angles of k_f and k_i, respectively, relative to the polar axis along $\vec{R}$. It is, of course, the transformation to a common coordinate system, usually with the polar axis along

$\vec{k}_i$ that introduces explicitly the observed scattering angle. Since a_p has already been evaluated it remains to evaluate g_F. To do this we use the approximations (i) and (*ii*) of Sec. II (the slow rotation approximation). Again we stress that these approximations are quite unrestrictive, in that for all (experimentally and theoretically) known molecular resonant states (i) or (ii) or both easily hold. Again we use the results of Appendix A, and take Δ and Γ to be local functions of scalar R only. g_F is now evaluated in the spectral representation of the nuclear motion operator as

$$g_f(\vec{R}\,|\,\vec{R}') = \sum_{JM} Y_{JM}(\hat{R}) Y_{JM}(\hat{R}') \Bigg(\sum_v \frac{\chi_{vJ}(R) R^{-1} \chi_{vJ}^*(R')(R')^{-1}}{E - [E_\gamma(R_0) + E_{vJ} + E_J] + i\Gamma^{vJ}/2} + \int dE_k \chi_J(kR) \chi_J^*(kR')(E - E_k)^{-1} e^{-\rho_J(E_k)} \Bigg) , \tag{21}$$

where $E_i = \hbar^2 k^2 / 2M$. The first term in the large parenthesis in Eq. (21) exists only for resonant states which allow bound nuclear motion, while the second term represents unbound motion and is common to all types of nuclear potential functions. $\chi_{vJ}(R)$ is the bound nuclear motion vibration state and $\chi_J(kR)$ is its continuum analog Eq. (9). The denominator of the first term of (21) is written with the understanding that the ground state of the target is taken as the zero of energy. $E_\gamma(R_0) + E_{vJ} + E_J$ is defined for the resonant state whose equilibrium distance is R_0. The second subscript on E_{vJ} indicates *that* we have not yet dropped the J dependence of radial nuclear motion. Γ^{vJ} is $\Gamma(R)$ averaged over the J dependence of $\chi_{vJ}(R)$. The real part of E_k is the energy at the classical turning point of the potential relative to the ground state. Without further approximation it is clear that if the experimental resolution were sufficiently narrow and the width were less than the rotational spacing (both conditions are unrealistic especially the former), one would observe a resonance for each rotation-vibration state. The angular dependence would then clearly change with energy, each peak having a dependence on L_i, L_f (in a_p) J_i and J_f. The limited ΔJ values (small) would generally give several peaks starting at each E_{v0} value. For widths larger than the rotational spacings, one would have an overlapping-resonance problem and would see a peak for the cross section as a function of energy at each E_{v0}, broadened, and perhaps structured, by being the envelope of several rotational resonances. The peaks would also have complicated angular dependences, depending on which E giving the peak was fixed when the angle was changed. Fortunately none of these complications seem necessary since the slow rotation assumption seems valid. With this assumption, one can replace the J on χ_{vJ} and $\chi_J(kR)$ with J_γ. This, of course, allows us to drop the J on Γ^{vJ} and E_{vJ}. Moreover, with the slow rotation assumption, the energy changes due to changes of rotation state are consistently assumed to be small compared with other changes and, more weakly, compared to Γ^v. Therefore $E_J - E_{Ji}$ can be dropped from the denominator of the first term of Eq. (21). The slow rotation assumption now allows us to apply closure to the rotation states in g_F and obtain

$$g_F(\vec{R}\,|\,\vec{R}') = g_{F_R}(R, R')\delta(\hat{R} - \hat{R}') , \tag{22}$$

where g_{F_R} is the term in large parentheses of Eq. (21). The only remaining J dependence implicit in the χ and the energies is an average value J_γ common to the range of states which contributed to g_F as in Sec. II. In practice, J_γ would be taken to be J_i. Even if $\Delta J = 0$ were forbidden [as in the case for homonuclear, isotopically identical nuclei, in molecules where the parities of the initial (final) and resonance electronic states are not the same as the final (initial) state] J_i would be the average final J.

We are now ready to insert (22) into Eq. (19) for T_{fi}. As mentioned, a_{pi} and implicitly a_{pf} are already given by Eq. (6). However there is a minor difference now which should be brought out. For the case of DA, the Λ values Λ_{Ti} and Λ_γ characterized the initial and final state respectively. Given Λ_{Ti} and Λ_γ, a unique value of μ was selected from the infinite number present in the plane wave in (3). For the present case of vibrational excitation it is Λ_{Tf} rather than Λ_γ which characterizes the final state. For a given Λ_{Ti} and Λ_{Tf}, two values of μ are selected from either the initial or final electron plane wave, each one giving one of the two values of Λ_γ, the intermediate-state angular-momentum projection. We must therefore sum over the two values of Λ_γ which contribute to T_{fi}. This means that in both a_{pi} and a_{pf} there is also an implied dependence on Λ_γ which therefore determines the μ values in the form

$$\mu_{i\gamma} = \Lambda_\gamma - |\Lambda_{Ti}|, \quad \mu_{f\gamma} = \Lambda_\gamma - \Lambda_{Tf} . \tag{23}$$

Again Λ_{Ti} is taken as positive for definiteness as in (4′) since the negative value produces the same final result.

When we now insert (22) into (19), integrate over $\vec{R}'$ using the delta function, and sum over the two intermediate values of Λ_γ, we have

$$T_{fi} = \int d\hat{R} J(\hat{R}) Y^*_{J_f M_f}(\hat{R}) Y_{J_i M_i}(\hat{R}) , \tag{24}$$

where R is relative to an axis along k_i and

$$J = 4\pi \sum_{\Lambda_r} \sum_{L_i = |\mu_{ir}|}^{\infty} \sum_{L_f = |\mu_{fr}|}^{\infty} (\chi V g V \chi)_{f,i} Y_{L_f \mu_{fr}}{}^{*}(\hat{k}_f) Y_{L_i |\mu_{ir}|}(\hat{k}_i) \tag{25}$$

and where

$$(\chi V g V \chi)_{f,i} = \int dR \int dR' \chi_{vf}{}^{*}(R) V^{*}_{L_f |\mu_{fr}|}(R)\, g_{F_R}(R, R') V_{L_i |\mu_{ir}|}(R') \chi_{vi}(R') \,. \tag{26}$$

The angles $\hat{k}_f$ and $\hat{k}_i$ are measured relative to $\bar{R}$. The reason for breaking up (24) as was done will be seen presently. (The Y_{J_i} and Y_{J_f} terms will drop out of the suitably averaged differential cross section.)

Equation (24) may now be substituted directly into Eq. (I-3.15) for the differential cross section. Again, after summing and averaging over those final and initial states respectively which are not observable in a standard experiment, we find

$$\sigma_{fi}(\Omega) = \left(\frac{\pi}{k_i}\right)^2 g \frac{1}{2J_i + 1} \sum_{M_i} \sum_{J_f} \sum_{M_f} \sum_{\Lambda_{Tf}} |T_{fi}|^2$$

$$= \left(\frac{\pi}{k_i}\right)^2 \frac{1}{2J_i + 1} \sum_{M_i J_f M_f} \sum_{\Lambda_{Tf}} \left| \int d\hat{R} J(\hat{R}) Y_{J_f M_f}{}^{*}(\hat{R}) Y_{J_i M_i}(R) \right|^2 . \tag{27}$$

As in Sec. II, no sum over Λ_{Ti} is taken (the positive value is assumed as already mentioned) to avoid mere duplication of terms. g is an electron-spin weight factor (singlet, triplet, etc.), to the extent that is not implicit in the V's.

The sum over J_f is introduced with the valid assumption (with present experimental techniques) that the final rotation states that contribute to the sum are unresolvable and have small $\Delta J = J_f - J_i$. The terms with J_f greatly different from J_i are expected with the already discussed assumptions of these formulas to be negligible and therefore do not contribute to the sum over J_f. The form of Eq. (27) allows us to use the closure of final state rule and the Unsold theorem in the form given in (B4), i.e.,

$$\sum_{M_i} \sum_{J_f} \sum_{M_f} \left| \int d\hat{R} J(\hat{R}) Y_{J_f M_f}{}^{*} Y_{J_i M_i} \right|^2 = \frac{2 J_i + 1}{4\pi} \int d\hat{R}\, |J(\hat{R})| \,. \tag{B4}$$

This reduces the expression to

$$\sigma_{fi}(\Omega) = \frac{\pi}{4k_i^2} g \sum_{\Lambda_{Tf}} \int d\hat{R} |J(\hat{R})|^2 \tag{27'}$$

The simplification which removed the Y_{J_f} and Y_{J_i} factors from (27) is the usual orientation average procedure that naturally accompanies an electron scattering process that is completed in a time so short that the molecule has no time to reorient. To make (27) explicit, the expression (25) which defines $J(\hat{R})$ should be substituted, giving

$$\sigma_{fi}(\Omega) = \frac{4\pi^3}{R_{i^2}} g \sum_{\Lambda_{Tf}} \sum_{\Lambda_r} \sum_{\Lambda_r'} \sum_{L_i} \sum_{L_i'} \sum_{L_f} \sum_{L_f'} (\chi V g V \chi)_{fi}$$

$$\times (\chi V g V \chi)_{f'i'}{}^{*} \int d\hat{R}\, Y_{L_f \mu_{fr}}{}^{*}(\hat{k}_f) Y_{L_f' \mu'_{fr}}(\hat{k}_f) Y_{L_i \mu_{ir}}(\hat{k}_i) Y_{L'_i \mu'_{ir}}{}^{*}(\hat{k}_i) \,.$$

The limits of summation for the L's are given in (25). The Λ's are summed over $\pm\Lambda$ (if they are non-zero). Now the last integral over the four spherical harmonics is evaluated in Appendix C and given by (C.5) in terms of $P_l(\cos\theta_{if})$. The $(\chi V g V \chi)$ factors may be written more explicitly in terms of the expansion form of g_{F_R}. If further we make the Franck-Condon approximation (a simplifying but not necessary assumption) and remove the V's from these integrals as relatively slowly-varying factors, the remaining vibrational factors $(\chi g \chi)_{fi}$ are independent of all the indices of summation and constitute an overall vibrational-resonant factor. Thus the differential cross section for vibrational excitation finally becomes

$$\sigma_{fi}(\Omega) = \frac{\pi^2}{k_i^2} g \text{ (vibrational-resonant factor) } \sum_{\Lambda_{T_f}} \sum_{\Lambda_r, \Lambda_r'} \sum_{L_i, L_i'} \sum_{L_f, L_f'} V_{L_f |\mu_{fr}|}^{*} V_{L_f' |\mu_{fr}'|}$$

$$\times V_{L_i|\mu_{ir}|} V^*_{L_i'|\mu_{ir}'|}[(2L_i+1)(2L_i'+1)(2L_f+1)(2Lf'+1)]^{1/2}(-1)^{\mu_{fr'}+\mu_{ir'}}$$

$$\times \textstyle\sum_l (2l+1)^{-1} C(L_i, L_i', l; \mu_{ir'}, -\mu_{ir}')C(L_f, L_f', l; \mu_{fr'}, -\mu_{fr}')C(L_i, L_i', l; 00)C(L_f, L_f', l; 00)P_l(\cos\theta_{if}), \quad (28)$$

where

$$\text{(vibrational-resonant factor)} = \text{(vrf)} = |(\chi g \chi)_{fi}|^2$$

$$= \left| \sum_v \frac{C_{v_i v}{}^* C_{v v_f}}{E - [E_r(R_0) + E_{vJ_i}] + \frac{1}{2} i \Gamma^v} + \int dE_k \exp[-\rho_{J_i}(E_k)] \frac{C_{v_i k}{}^* C_{k v_f}}{E - E_k} \right|^2 \quad (29)$$

and the C_{ij}'s are Franck-Condon overlap integrals between the $\chi_{vi\,(vf)}$ and the resonant state χ's. The Clebsch-Gordan coefficients restrict the sum over l by the triangle inequality between l and the pair L_i, L_i', or L_f, L_f' and to only even (or odd) terms.

Equation (28) is the desired expression for the differential cross section. The form of Eq. (28) points out that the resonant structure in the differential cross section as a function of energy should mirror the vibrational spacings of the resonance.[7] Well defined peaks should be seen if the widths are not much greater than the vibrational spacings. The continuum region of the resonant nuclear motion gives rise to a smooth cross section. The varied possible cross section patterns given by the discrete part of Eq. (28) when the widths are large compared with the vibrational spacings has been studied by Mies.[8] Equation (28) says that in general the angular dependence is given by an infinite sum of terms; each term denoted by the eight indices L_f, L_f', L_i, L_i', Λ_{Tf}, Λ_r, Λ_r', and the implicit Λ_{Ti}. Since the $V_{L|\mu|}$ are energy dependent they can be viewed as energy dependent electronic weighting factors for the angular factors in in each term. The angular dependence is therefore *usually a function of energy* even in the pure resonant region. However, as in Sec. II, the formulas simplify when we make the one-center approximation for the incident (and final) free electron; an approximation which is frequently very good. In this case the L's are not summed over, and so the energy dependent V's are merely an overall factor so that the cross section is separable into an energy dependent factor and an *energy independent* angular factor. Under these latter conditions the normalized angular dependence should be similar all through the resonant region even as the energy changes. This factor can be used to recognize the existence of a resonance even when the vibration factor does not show peaks and structure.[3]

We now specialize to the lowest L (one-center) approximation in Eq. (28). These values, L_{i0} and L_{f0}, come from the lowest (in absolute value) μ's, i.e. μ_{ir0} and μ_{fr0}, respectively. Since the μ's are determined by the values of Λ_r and Λ_{Tf} through Eq. (23) (given $\Lambda_{Ti} = +|\Lambda_{Ti}|$), this choice also restricts the sums over the Λ's. If the Λ's were all different from zero, then only a single term from each sum would contribute to μ_{i0} (or μ_{f0}) and all summations could simply be dropped. However, when only Λ_r is nonvanishing, then $\mu_i = \mu_f = \pm|\Lambda_r|$ and the sum over Λ_r cannot be dropped, but simply produces a factor of 2. Likewise when Λ_{Tf} but not Λ_r is nonvanishing the sum over Λ_{Tf} produces a factor of 2. The reader may verify that all combinations of vanishing and nonvanishing Λ's are correctly accounted for if we set $\Lambda_r' = +|\Lambda_r'|$ and $\Lambda_{Tf} = +|\Lambda_{Ti}|$, retain the sum over Λ_r in order to cover the special case $\Lambda_{Ti} = \Lambda_{Tf} = 0$, and multiply by an over-all factor $\Delta(\Lambda)$, where

$$\begin{aligned}\Delta(\Lambda) &= 1 (\text{if } \Lambda_r = \Lambda_{Tf} = 0;\ \text{or if } \Lambda_r \text{ and } \Lambda_{Ti} \text{ are both non-zero}) \\ &= 2\ (\text{otherwise})\ . \end{aligned} \quad (30)$$

The differential cross section then takes the relatively simple form

$$\sigma_{fi}(\Omega) = \frac{\pi^2}{k_i^2}\ \text{(vibrational factor)} \left| V_{L_{f0}|\mu f_{r0}|} \right|^2 \left| V_{L_{i0}|\mu f_{r0}|} \right|^2 \Delta(\Lambda) \sum_{l=0}^{2L_0} \frac{(2L_{i0}+1)(2L_{f0}+1)}{2l+1}$$

$$\times P_l(\cos\theta_{if}) C(L_{i0} L_{i0} l; 00) C(L_{f0} L_{f0} l; 00) \textstyle\sum'_{\Lambda_r} (-1)^{\mu_{fr0} + \mu_{ir0}}$$

$$\times C(L_{i0} L_{i0} l; \Lambda_r - |\Lambda_{T_i}|, |\Lambda_{T_i}| - |\Lambda_r|) C(L_{f0} L_{f0} l; \Lambda_r - |\Lambda_{Tf0}|, |\Lambda_{Tf0}| - |\Lambda_r|), \quad (31)$$

where L_0 is the smaller of L_{i0} and L_{f0}, and the primed sum over Λ_r indicates that the sum need be taken only if Λ_r alone is nonvanishing. Otherwise only $+|\Lambda_r|$ contributes. The useful approximation Eq. (31) exhibits the properties already mentioned, i.e., separate vibrational factor independent of angle, and the angular factor independent of energy. Perhaps the most useful is the fact that, as with DA in Sec. II, the angular dependence in this approximate formula follows entirely from the symmetries of the initial, final and resonant electronic states, and so requires no calculation.

Equations (28) and (31) contain the main results of this section, the full expression and the one center expression for the angular dependence of resonant vibrational excitation in the "slow rotation" approximation.

The total scattering cross section is gotten immediately from (28) by integrating over the scattering angle. This leaves only the $l=0$ term which in turn makes only the "diagonal" Clebsch-Gordan coefficients nonvanishing, i.e., those with $L_{i'}=L_i$, $\mu_{i'}=\mu_i$, etc. Substituting the numerical values for these coefficients, one obtains finally

$$\sigma_{fi}(\text{tot})=\frac{4\pi^3}{k_i^2}g\ (\text{vibrational factor})\sum_{\Lambda_{Tf}}\sum_{\Lambda_r}\sum_{L_i=|\mu_{ir}|}^{\infty}\sum_{L_f=|\mu_{fr}|}^{\infty}|V_{L_f|\mu_{fr}|}(k_f,R_e)|^2|V_{L_i|\mu_{ir}|}(k_i,R_e)|^2 \tag{32}$$

If the initial and final states are Σ states, then $|\mu|=|\Lambda_r|$ for all μ, and the formula (32) reduces to one similar to that derived by Chen[7]

$$\sigma_{i\to f}^{\text{tot}}=4\pi^3k_ig\sum_{L_f=|\Lambda_r|}\sum_{L_f=|\Lambda_r|}|V_{L_f|\Lambda_r|}(k_f,R_e)|^2|V_{L_i\Lambda_r}(k_i,R_e)|^2(\text{vrf})(2-\delta_{0,\Lambda_r}) .$$

In the formulas of this section are the basis for the treatment of many other problems. For example (24) holds the basis for the treatment of the resonance effects when initial and final rotational states can be resolved but slow rotation is still present. In this latter problem (27) would have to be modified by the removal of the sum over J_f. The simplifications of orientation averaging disappear and except for inserting the Clebsch–Gordan expressions for the integrals of the spherical harmonics little major simplification can be made. For pure rotational excitation the sums over L_i and L_f are usually limited at some multiple depending on the physics of the situation. Unfortunately in this latter problem potential scattering is very important and is by far the more difficult part to treat. The reader conversant with this section should be able to specialize these formulas to elastic scattering, inelastic electronic and vibrational excitation; pure vibrational, pure rotational, etc. The possibilities are simply too numerous to give detailed considerations. Various combinations of simplification will depend on the problem and the properties of the state treated. Other directions for extension not discussed here are the cases of two or more molecular resonances in the same energy range. This has been treated partly by Mies,[8] and more generally by Feshbach.[9]

IV. DISCUSSION

Given the formulas derived in Sec. II and III for the angular dependence of DA and of inelastic electron scattering, the most direct application of them would be to use the more exact Eqs. (13) and (28) in connection with an *ab initio* calculation of the matrix elements $V_{L|\mu|}(R)$, following from a determination of the resonant state ϕ_r (and of ϕ_{ad}). Although accurate calculations of the resonant potential energy curves have been made for H_2^-,[10] the same is not true of matrix elements V_a or more specifically $V_{L|\mu|}$. It might be pointed out here, that the evaluation of V_a is much easier than was previously believed. It is stressed in a future paper by one of us,[11] that, as was first shown by Miller,[12] "the stabilization method"[11-14] for computing resonances not only gives the shifted resonance energy but allows the evaluation of the $V_{\overline{a}}$ to be done by merely evaluating a straightforward integral. Good *ab initio* calculations of the $V_{L|\mu|}$ (and of Γ_a as a consequence) can therefore be expected in the near future for simple systems.

The second, and most immediate application of the results of this paper lies in the direct use of the approximate equations (14) and (31) to predict angular distributions without the need of any calculation. These approximate formulae are valid, as mentioned, to the extent that the lowest angular momentum (or one-center) approximation can be made for the slow incoming (or outgoing) electron. Combining this with the basic approximation (slow rotation) of this paper and other previous approximations, the various assumptions underlying these equations may be listed as follows.

(1) The single L value approximation for the $V_{\overline{a}}(\vec{R})$ can be made for either or both of the reasons (a) that ϕ_r can be expanded in a convergent one-center expansion; or (*b*) that the energy ranges, the partial wave index, and the range of force of the target are such that the lower spherical terms of the plane wave have greater amplitude.

(2) At least one of the slow rotation assumption (i) or (ii) of Sec. II holds.

(3) The Born–Oppenheimer approximation is accurate.

(4) The process is a pure resonant process.

(5) The scattering "structure" is due to one resonance state.

Let us consider dissociative attachment first in the approximation (14). To illustrate the angular dependence of the cross section (14) and the way it follows from the quantum numbers of the initial molecular state and the final resonant negative ion state, several known transitions in H_2 and O_2 are analyzed in Table I, using the simple approximate expression (14). The first two rows of the table are for DA from the ground state of H_2 to the two lowest resonant states of H_2^-,[4] corresponding to

TABLE I. Predicted approximate angular dependence for DA.

Initial	Final	Electronic parity	$\lvert\mu\rvert$	L_0	Angular dependence Eq. (14)
$H_2\ {}^1\Sigma_g{}^+$	$H_2^-\ {}^2\Sigma_u{}^+$	−1	0	1	$\cos^2\theta$
$H_2\ {}^1\Sigma_g{}^+$	$H_2^-\ {}^2\Sigma_g{}^+$	+1	0	0	const
$0_2\ {}^3\Sigma_g{}^-$	$0_2^-\ {}^2\Pi_u$	−1	1	1	$\sin^2\theta$
$0_2\ {}^1\Sigma_g{}^+$	$0_2^-\ {}^2\Pi_u$	−1	1	1	$\sin^2\theta$
$0_2 A\ {}^3\Sigma_u{}^+$	$0_2^-\ {}^2\Pi_u$	+1	1	2	$\sin^2(2\theta)$

the peaks observed at 3.7 and 11 eV. Here $\cos^2\theta$ and constant distributions follow from (14). The third row is for normal DA in O_2, where it appears that the final resonant state is the ${}^2\Pi_u$,[16] and a $\sin^2\theta$ distribution is found. The last two rows are for DA from two excited electronic states of O_2 to the same final state. They are included here mainly as exercises in applying the rules to derive the electron quantum numbers and hence the angular dependence of (14) from the initial and final states. It should be noted that the angular distribution given by (14) and (13) and illustrated in Table I are all consistent with the selection rules which Dunn[17] derived at $\theta = 0°$ and $90°$ for a class of reactions including DA.

Since the approximate angular distribution (14) like Dunn's 0° and 90° selection rules follows entirely from the symmetries of the initial and final states, this expression may be regarded as a natural generalization of Dunn's result to all angles.

Note that the symmetry of the O_2^- resonant state (${}^2\Pi_u$) was not directly established by the semi-empirical calculation of Ref. 16 and is merely a natural assumption from the potential curves. A measurement of the angular distribution would therefore be very desirable in order to confirm or disprove this assignment of quantum numbers. The same is even more true of other systems (CO^-, NO^-, etc.) where nothing at all is presently known of the resonant states responsible for DA, and a determination of their quantum numbers could be of great value.

While conditions (4) and (5) are not restrictive for dissociative attachment, they are quite restrictive for electron scattering. One process that probably fits conditions (4) and (5) is vibrational excitation of the ground state of small diatomics in the low energy region. Since the electron is so light and has such low energy, momentum transfer arguments favor the resonant part of the process. Also in the region of several volts above the ground state the resonant states are single particle and the large orbital for the resonant electron favors assumption (1a). The convergence of the expansion of $V_{\bar{a}}(\vec{R})$ due to expanding ϕ_r, whether it be for a single-particle resonance or not, is further enhanced by the assumption (1b). These considerations allow us to use Eq. (31), which implies that one should see a similar normalized angular dependence all through the resonant region. It should be the same no matter what point in the resonant structure one takes and no matter what final vibration state the target is left in. Three cases which appear likely to fit our requirements are the vibrational excitation of N_2, CO and H_2 measured in Ref. 3. In Ref. 3 qualitative arguments were used for these simple cases (in the above sense) to predict the qualitative features of the angular distributions. In N_2, since the first available orbit is Πg one expects an orientation averaged $d\Pi$ dependence. For CO the single particle orbital is Π (no g or u for heteronuclear) and one expects a $p\Pi$ dependence. H_2 has σ_u as its low single particle orbital and gives a $p\sigma$ dependence. Moreover in all cases if one uses the low energy expansions for the radial amplitude (Bessel functions) of the expansion of the plane wave in spherical harmonics, one finds in this energy region ($\approx 2-5$ eV), using effective molecular radii estimated from density graphs of excited and ground states of the target, that the amplitudes drop radically. As mentioned above, this causes the electron to sample mainly the lowest allowed moment of ϕ_r.

In Table II, the symmetries of the initial and resonant negative ion states are listed for the three experimentally studied molecules H_2, CO and N_2. Note that μ_{ir0} and L_{i0} follow directly from the difference in Λ and the relative parity. These happen to be all cases of $\Lambda_i = \Lambda_f = 0$ (the least simple case), so that both signs of μ contribute to (31). The last column gives the angular dependence predicted by Eq. (31), which as was mentioned is expected to be a good first approximation for these cases to the more exact result (28). These angular dependences may be compared directly with the corresponding experimental results of Ref. 3 where the angular distributions were measured for each molecule over a wide range of energies and for several states of final vibrational excitation. Only the appropriate mutual normalization is needed.

The experiments of Ref. 3 are found first to be in complete qualitative agreement with Table II as expected for all 3 molecules, with H_2 and CO being P wave dominated, while N_2 is D wave dominated. Also as hoped the angular dependence is very nearly identical all through the resonant region as well as for different levels of vibrational excitation. Further, as pointed out in Ref. 3, this constancy of angular dependence as a function of energy disappears in the elastic channel where non-resonant or potential scattering plays a role

TABLE II. Predicted approximate angular dependence for vibrational excitation.

Initial and final state	Resonance	μ_{ir_0}	L_{i_0}	Angular dependence
$H_2(^1\Sigma_g^+)$	$H_2^-(^2\Sigma_u^+)$	0	1	$1+2\cos^2\theta$
$CO(^1\Sigma^+)$	$CO^-(^2\Pi)$	±1	1	$1+7\cos^2\theta$
$N_2(^1\Sigma_g^+)$	$N_2^-(^2\Pi_g)$	±1	2	$1-3\cos^2\theta+14\cos^4\theta/3$

equally as important as resonant scattering and assumption 4 is violated.

For the case of N_2 the agreement of the simple theory with experiment is even better than expected, being exact to within the small experimental error. This is especially gratifying in view of the rather complicated $(1-3\cos^2\theta+14\cos^4\theta/3)$ angular dependence which is predicted.

For CO the experiments show a small but finite deviation of the experimental curves from the predicted $(1+7\cos^2\theta)$ dependence, apparently of the order of 10%. This is illustrated in Fig. 2, where the experimental points are to be compared with the solid theoretical curve. Since both experiment and theoretical formula are unnormalized [the magnitude of the cross section is given in (31)], but it will take a major computational effort to evaluate it), the two were found to correspond most closely when they were normalized to one another near zero degrees. The dashed curve is the same theoretical curve, but normalized to experiment at the minimum (90°), as it was drawn in Ref. 3, for comparison. This is reproduced in order to show that the conclusion reached in Ref. 3, namely that the agreement for CO is more qualitative than quantitative, is largely the result of a non-optimal choice of the relative normalization.

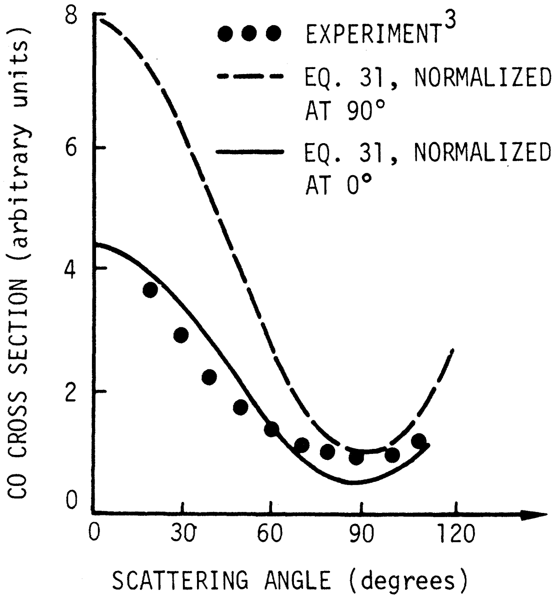

FIG. 2. Differential cross section for electron excitation of the $v=1$ state in CO. The electron energy is about 2.5 eV and the cross section normalization is arbitrary. The two theoretical curves (solid and dashed) differ only in the way they are normalized relative to the experimental points of Ref. 3.

It is interesting to investigate the origin of the small deviation of the experimental angular distribution curves in CO from the theoretical formula based on the approximate Eq. (31). Since (31) truncates the partial wave sums over L_i and L_f of (28) at the lowest term, the contribution of these higher terms ($L \geq 2$ in this case) is the obvious explanation for the deviation. This is borne out by the flattening and hint of additional structure in the experimental curve for the highest energy studied (3.0 eV). Wavelength arguments then indicate as discussed earlier that as the energy is lowered the amount of the higher partial waves should decrease fairly rapidly. This trend is also borne out by the experiments as the energy is first lowered from the highest value reproduced. However at the lowest energy studied (1.55 eV) the trend is reversed and the deviation is a little greater at this energy. This reversal cannot be attributed to the higher partial waves. It can be explained however by the presence of a small amount of direct or nonresonant excitation, so that assumption (4) above (pure resonant process) must be violated to some small degree. This diagnosis is directly confirmed by the total cross section measurements of Ref. 3, which show a small low-energy tail in the $v=1$ excitation which is clearly due to direct excitation. The same experiments show no direct excitation for $v \geq 2$.

For H_2 like CO the experimental curves of Ref. 3 agree qualitatively with the distribution $(1+2\cos^2\theta)$ of Table II, but again there is a quantitative deviation which is perhaps twice as large for H_2 as for CO. (For this case theory is best normalized to experiment somewhere in the neighborhood of 90°.) The deviation from Table II, which is marked by a strong forward peaking for H_2, seems to be due again largely to higher partial waves (here mainly the F wave). This is further confirmed by some additional structure at the very highest energy and an apparent trend toward a better fit as the energy decreases. Again there is probably some direct excitation in the $v=1$ channel, but it is difficult to assess how much since the resonance is so broad that it covers up any low energy tail in the total cross section.

There is one specific indication of direct excitation in H_2 to be found in the angular distributions of Ref. 3. For the homonuclear molecule H_2, the full equation (28) indicates that not only the leading term (P^2) but also all of the higher partial wave correction terms (PF, etc.) are completely symmetric about 90°. Therefore the small asymmetry which is evident in experiment must be attributed to interference between the resonant excitation (due to P and F waves) and direct excitation which presumably is S wave dominated.

The good agreement of Eq.(28) and even of (31) with experiments on vibrational excitation over a range of energies confirms the strong expectation that the slow rotation approximation is an extremely good one. This immediately implies the same for the dissociative attachment results of Sec. II in the same energy range, and especially for H_2 where the DA threshold is at 3.75 eV.

Needless to say, the formulas supplied here, and modified under various assumptions, can be used to parametrize many experiments.

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APPENDIX A. THE COMPLEX ENERGY-SHIFT OPERATOR F

The complex energy-shift operator F of I, which is used in Eq. (8) of this paper, is given in the first member of Eq. (I-4.10) as

$$F = \langle \phi_r QHPG_P PHQ\phi_r\rangle_e \, . \tag{A1}$$

The implied integral is over electronic but not nuclear coordinates. G_P is the Green's function for the operator $P(E-H)P$, whose basis states span the space of all electronic, vibrational and rotational wave functions with the constraint that the former are orthogonal to the function $\phi_r(R)$ for all R.

In evaluating G_P, a valuable simplification results from consistently using the adiabatic approximation in P space as made in Sec. 5 of I and used in the formulas in the body of the present paper. This approximation consists of neglecting in P space first the very small "direct" transitions, i.e., nonresonant transitions caused by deviations from the Born-Oppenheimer approximation, and secondly, of assuming that any additional resonant states are remote. (If there are additional resonances nearby, the entire problem is more complicated as indicated in Sec. 6 of I and requires special treatment.)

With this adiabatic assumption, the Green's function G_P may be formally expanded in the (uncoupled) electronic, vibrational, and rotational states which make up the spectrum of PHP:

$$G_P = \sum_n |\chi_n\rangle \frac{1}{(E+i\epsilon-E_n)} \langle\chi_n| \, . \tag{A2}$$

The summation index n runs independently over all possible states of PHP, electronic, vibrational, and rotational. In particular, it includes (a) all electronic states, their full energy, and angular momentum spectrum; (b) since these include continuum states, for these the angular momentum sum implies integration over all momentum orientations of the free (outgoing) electrons (this is of special interest for the present paper, which treats the dependence of the matrix elements on just these orientations), and finally (c) all vibrational and rotational states, with quantum numbers v, J, and M.

It follows from (A1) and (A2) that, as a function of the nuclear coordinates, F is in general complex, non-local, angular dependent and energy dependent. In using F in I – 5, the approximation was made, as had been done previously,[19] of a local and spherically symmetric F, i.e., $F = \Delta(R) - \frac{1}{2}i\Gamma_a(R)$. This is a good approximation in general, but the steps in arriving at it should be made explicit, especially to see *how* the locality and spherical symmetry are arrived at. This is the purpose of the present appendix.

In order to derive this local and spherically symmetric result, it is easiest to first single out the vibrational and rotational sum in (A2) by writing it

$$G_P = \sum_{v,J,M} |\chi_{v,J,M}\rangle\langle\chi_{v,J,M}| G_{\mathrm{el},v,J} \, . \tag{A2′}$$

The dependence of the electronic Green's function on v and J is through the conservation of total energy, which conditions the energy of the electronic states on the energy level v and J through the simple relation $E_{\mathrm{el}} = E_{\mathrm{tot}} - E_v - E_J$.

At this point the crucial and only approximation of this appendix is made. We treat both rotational and vibrational motion as *quasiclassical* in the sense that their energy levels are closely spaced by comparison with the electron's energy. This assumed smallness of nuclear motion frequencies as compared with electronic frequencies will be recognized as the underlying source of the adiabatic approximation referred to above (and in fact all adiabatic approximations), as well as the slow rotation approximation and indeed of apparently all approximations made in the text and in I.

Having assumed then that the v and J levels are closely spaced, it follows that the dependence of $G_{\mathrm{el},v,J}$ on these indices in (A2′) is negligible over a large number of states and may therefore be neglected. The $G_{\mathrm{el},v,J} \simeq G_{\mathrm{el}}$ may therefore be taken outside the summation in (A2′) over nuclear states. The sum then reduces by closure to unity,[20] leaving

$$G_P \simeq G_{\mathrm{el}} = \sum_n |\phi_n \langle (E+i\epsilon-E_n)^{-1}\rangle \phi_n| \, . \tag{A3}$$

The sum over n is now over electronic states only and is given by (a) and (b) above, i.e., over the energy, spin, and angular momentum spectrum of electronic states, with the latter implying integration over all momentum orientations for continuum states. Since all dependence on the nuclear wave function has now been eliminated as a result of the quasiclassical approximation for v and J, the nuclear coordinates no longer appear in G (now G_{el}) except parametrically in the electronic wave functions. This immediately implies locality. Note that if these approximations had not been made, the rotational terms in (A2) would be explicitly angle dependent as well as nonlocal in $\vec{\mathrm{R}}$. Substitution of (A3) and (A1) gives formally

$$F=\sum_n \langle \phi_r H_{\mathrm{el}} \phi_n \rangle \, (E+i\epsilon-E_n)^{-1} \langle \phi_n H_{\mathrm{el}} \phi_r \rangle$$

$$=\sum_n V_n(\vec{\mathrm{R}})(E+i\epsilon-E_n)^{-1} V_n{}^*(\vec{R}) \tag{A4}$$

Now each of the electronic matrix elements is of the form of $V_a(\vec{\mathrm{R}})$ in (2). It follows from the same analysis as in Sec. I that (for the continuum states only) these have the angular dependence on $\vec{\mathrm{R}}$ given by (5), only this time with the z axis being that of the *ejected* electron. Note that this angular dependence, like the R dependence, is parametric, as opposed to the quantum mechanical $\vec{\mathrm{R}}$ dependence eliminated by the approximation (A3). Performing the sum or integral over orientations, described in step (b) above, averages over these orientations, giving a result which is *spherically symmetric* as well as local

$$F=\Delta(R)-\tfrac{1}{2}\, i\, \Gamma_{a,\mathrm{av}}(R) \ . \tag{A5}$$

The imaginary part results as usual from the $i\epsilon$ term in (A4) which produces a delta function of energy. Both quantities $\Delta(R)$ and $\Gamma_{a,\mathrm{av}}(R)$, now symmetric as the result of (b), are summed or integrated over all electronic states in P space. $\Gamma_{a,\mathrm{av}}(R)$ becomes a sum of terms of the form of $\Gamma_{\bar{a}}$ following I-15′:

$$\Gamma_{a,\mathrm{av}}(R)=\sum_i \Gamma_{a,i,\mathrm{av}}(R)$$

$$=2\pi\sum_i\sum_\Lambda\sum_L |V_{L|\mu|}{}^{(i)}(R)|^2 \ . \tag{A6}$$

The sum over i is over all open electronic channels. In any simple model, there is only one such electronic channel, the incident channel, which has been denoted by an $\bar{a}$. However, (A6) is the general expression. The corresponding level shift Δ is similarly the principal part of the sum or integral (A4), carried over energy states and momentum directions.

The final result (A5) of this appendix states that, under the stated assumptions of adiabaticity in P space and close-lying quasiclassical vibrational and rotational levels (as compared with electronic energy), the level shift and width operators Δ and $\Gamma_{a,\mathrm{av}}$ are *local and spherically symmetric* functions of R. It is interesting to note that it is not inconsistent to sum over vibrations in P space (using closure) and not in Q space [see Eq. (2)]. If one does not sum one gets more complicated but generally more valid expressions. In Q space our inability to ignore quantities of the magnitude of the widths prevents us from dropping ΔE_v. For very broad resonances one could still get a correct result by applying vibrational closure in Q space. In P space (this appendix) the relevant equation is (A2) as opposed to (20) for Q space. In the absence of any width Γ in this equation, the smallness of ΔE_v must be measured against the characteristic electron energy [as opposed to the width Γ_a in Eq. (20)]. Clearly the criteria are different and independent for the two cases. Some consequences of relaxing the adiabatic assumption were discussed in I-6. As for the quasiclassical approximation made in this appendix, it is clear that it is generally much better for rotational than for vibrational states, because of the relative magnitude of the level spacings. Therefore when DA is treated (as it always has been) by using Eq. (8) with local Δ and Γ, the consistency of treating the rotational states J quantum mechanically should always be questioned, since we have just seen that this locality results from treating vibration quasiclassically. [The practical criteria for treating rotation classically rather than quantally were discussed in the text under (i) and (ii) following Eq. (10).]

Finally, even with rotation consistently treated, there are some cases when only one vibrational level is energetically accessible following autoionization, as for example in thermal dissociative recombination.[21] In this case the vibrational states are far apart compared to electronic energy and the present local approximation for Γ_a and Δ should not be made.

Regarding the approximations leading to the result (A5) of this appendix, chief of which is that of slow or quasiclassical nuclear motion, it is not the purpose of the authors to demonstrate their accuracy (although it is believed that they are generally quite good). Rather we wish to make these approximations clear and explicit so that it will be evident just when the result (A5) is good and when it should be abandoned for the more exact (nonlocal) expression. Moreover, in taking Q to be defined by an already given $\phi_r(r,R)$, we continue as in paper I to leave the way open to any of the several basically different techniques for defining and constructing adiabatic quasistationary states ϕ_r.

APPENDIX B

In this appendix we evaluate the expression

$$S=\sum_{M_i=-J_i}^{J_i}\sum_{J_f}\sum_{M_f=-J_f}^{J_f}\left|\int d_x\, \tau(x) Y_{J_iM_i}(x) Y_{J_fM_f}(x)\right|^2 \ . \tag{B1}$$

First we write out the absolute square more explicitly:

$$S=\sum_{M_i}\sum_{J_f,M_f}\int dx\int dx'\tau(x)Y_{J_i}(x)\tau^*(x')Y_{J_i}{}^*(x')Y_{J_fM_f}(x)Y_{J_fM_f}{}^*(x') \ . \tag{B2}$$

Now if τ is independent of J_f and M_f or, as is argued in the text, is very insensitive to J_f over the range that contributes to the sum, then the sum over J_f and M_f can be taken inside the integral and the τ's.

The closure relation then gives

$$\sum_{J_f M_f} Y^*_{J_f M_f}(x) Y_{J_f M_f}(x') = \delta(x - x') \ . \tag{B3}$$

Using (B3) in (B2) and (B1), and integrating over x', reduces S to

$$S = \sum_{M_i} \sum_{J_f} \sum_{M_f} \left| \int dx\, \tau(x) Y_{J_i M_i}(x) Y_{J_f M_f}(x) \right|^2$$

$$= \sum_{M_i} \int dx\, |\tau(x)|^2 |Y_{J_i}(x)|^2 = \int dx\, |\tau(x)|^2 \sum_{M_i} |Y_{J_i}(x)|^2 = \frac{(2J_i + 1)}{4\pi} \int dx\, |\tau(x)|^2 \tag{B4}$$

Equation (B4) is the desired result. It holds, as mentioned, whenever the dependence of $\tau(x)$ on J_i can accurately be neglected (note that there is normally no dependence at all on the degenerate states M_i).

APPENDIX C

We wish to evaluate the integral

$$I = \int d\hat{R}\, Y_{L_f, \mu_{fr}}{}^*(\hat{k}_f)_R Y_{L'_f, \mu'_{fr}}(\hat{k}_f)_R Y_{L_i, \mu_{ir}}(\hat{k}_i)_R Y_{L_f{}', \mu'_{ir}}{}^*(\hat{k}_i)_R \ , \tag{C1}$$

where the integral is over all orientations $\hat{R}$ of the molecular axis and the subscripts R indicate that the k vectors are measured relative to the R axis. This is an integral of four spherical harmonics with two different arguments, $\hat{k}_i$ and $\hat{k}_f$. To simplify (C1) we first combine the first and second pair of Y's using the Clebsch-Gordan series:

$$Y_{L,M}{}^*(\hat{k}) Y_{L',M'}(\hat{k}) = (-1)^{M'} \sum_l \left(\frac{(2L+1)(2L'+1)}{4\pi(2l+1)} \right)^{1/2} C(L, L', l; -M, M') C(L, L', l; 00) Y_{l, M-M'}{}^*(\hat{k}).$$

The l's are restricted by the triangle relation and parity as usual to the values $|L - L'|, |L - L'| + 2, \ldots, |L + L'|$. This reduces (C1) to the form

$$I = (-1)^{\mu_{fr}{}' + \mu_{ir}{}'} \sum_{l, l'} \frac{1}{4\pi} \left(\frac{(2L_f + 1)(2L_f{}' + 1)(2L_i + 1)(2L_i{}' + 1)}{(2l+1)(2l'+1)} \right)^{1/2}$$

$$\times C(L_f, L_f{}', l; \mu_{fr}, -\mu_{fr}{}') C(L_i, L_i{}', l'; \mu_{ir}, -\mu_{ir}{}') C(L_f, L_f{}', l; 00) C(L_i, L_i{}', l'; 00) J \ , \tag{C2}$$

where $J = \int dR\, Y_{l, \mu_{fr} - \mu_{fr}{}'}{}^*(\hat{k}_f)_R Y_{l', \mu_{ir} - \mu_{ir}{}'}(\hat{k}_i)_R \ .$ (C3)

Now if the arguments in (C3) were the same it would simply be the orthonormality integral. As it is we must consider the vector $(\vec{k}_f)_R$ to be related to the vector $(\vec{k}_f)_i$ by the rotation operator $D(i \rightarrow R)$ so that, using the rotation matrices of Ref. 2 in the form

$$Y_{L,M}{}^*(\hat{k}_f)_R = \sum_{M''} Y_{L,M''}{}^*(\hat{k}_f)_i [D_{M,M''}{}^L(\hat{k}_i)_R]^*,$$

we have for an integral of the type (C2)

$$J = \int d\hat{R}\, Y_{L,M}{}^*(\hat{k}_f)_R Y_{L',M'}(\hat{k}_i)_R = \int d\hat{R} \sum_{M''} Y_{L,M''}{}^*(\hat{k}_f)_i [D_{M,M''}{}^L(\hat{k}_i)_R]^* Y_{L',M'}(\hat{k}_i)_R$$

$$= [(2L'+1)/4\pi]^{1/2} \sum_{M''} Y_{L,M''}{}^*(\hat{k}_f)_i \int d\hat{R} [D_{M,M''}{}^L(\hat{k}_i)_R]^* D_{M',0}{}^{L'}(\hat{k}_i)_R,$$

where $Y_{L',M'}$ has been expressed as the corresponding D matrix element. To complete the integral, which is over $\hat{R}$, the counterpart of Eq. (12) which relates the functions of the inverse angles $\hat{i}_R$ and $\hat{R}_i$ is used (in this case it is the unitarity property of the matrix) to give

$$J = [(2L'+1)/4\pi]^{1/2} \sum_{M''} Y_{L,M''}{}^*(\hat{k}_f)_i \int d\hat{R}\, D_{M'',M}{}^L(\hat{R})_i [D_{0,M'}{}^{L'}(\hat{R})_i]^* = P_L(\cos\theta_{fi}) \delta_{L,L'} \delta_{M,M'} \tag{C4}$$

using the orthogonality relations of the D's. Therefore, putting together (C4) and (C2) into (C1) we have finally the desired result:

$$\int d\hat{R}\, Y_{L_f,\mu_{fr}}{}^*(\hat{k}_f) Y_{L_f',\mu_{fr}'}(\hat{k}_f) Y_{L_i,\mu_{ir}}(\hat{k}_i) Y_{L_i',\mu_{ir}'}{}^*(k_i)$$

$$= (1/4\pi)(-1)^{\mu_{fr}'+\mu_{ir}'}[(2L_f+1)(2L_f'+1)(2L_i+1)(2L_i'+1)]^{1/2}\sum_l (2l+1)^{-1}$$

$$\times C(L_f,L_f',l;\mu_{fr},-\mu_{fr}')C(L_i,L_i',l;\mu_{ir},-\mu_{ir}')C(L_f,L_f',l;00)C(L_i,L_i',l;00)P_l(\cos\theta_{fi}). \qquad \text{(C5)}$$

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[20] To avoid any possible confusion over the fact that the closure relation in (A2′) results in unity while in Eq. (10) closure resulted in the delta function, the respective relations are $\sum_n |\psi_n\rangle\ \langle\psi_n = 1$, while $\sum_n \psi_n{}^*(x) \times \psi_n(x') = \delta(x-x')$. Putting aside differences in abstractness, the first relation is simply the integral of the second over x'.

[21] *Footnote added in Proof.* In this connection see J. N. Bardsley, J. Phys. B (Proc. Phys. Soc.) 1, 349 (1968), where the appropriate non-local form of F for this case is employed.