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Theory of Electron-Molecule Collisions by Frame Transformations*

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Laboratory-frame and body-frame treatments are combined using the l-uncoupling transformation which had served to interpret the absorption spectrum of H_2. Application of a phase-amplitude procedure converts the Schrödinger equation to a Volterra-type integral form, which reduces to a Born-like approximation when the long-range interactions are weak. Attention is directed to features of low-energy collisions that must be considered by a realistic theory. This paper develops a formalism that can take advantage of different simplifying factors in different ranges of the electron-molecule distance. Detailed developments and applications are deferred.

I. INTRODUCTION

The scattering of low-energy electrons of molecules has traditionally been formulated either in a laboratory frame of coordinates or in a molecular frame (called "fixed-nuclei" or "body" frame). Even though both approaches have been utilized extensively, their connection does not seem to have been understood widely, as emphasized in recent reviews.[1] Actually the two approaches utilize alternative expansions of the electron-molecule wave function. This fact, pointed out by Bottcher,[2] permits the development of a comprehensive theory.

The alternative expansions are related by a quantum-mechanical frame transformation, which was developed in the context of photoabsorption by molecular hydrogen.[3] This H_2 work, to be called FH, pointed out that the final-state interaction in the ionized $e+H_2^+$ system is treated appropriately in the molecular or in the laboratory frame depending on whether the $e-H_2^+$ distance is short or long. This final-state interaction is the same as occurs in $e+H_2^+$ collisions. The relevance of these remarks to the general problem of electron-molecule collisions has been mentioned in preliminary notes.[4] The present paper lays a basis for their systematic exploitation.

We start by emphasizing that the interaction between an electron and a molecule exhibits qualitatively different features when their distance lies in different ranges. At large distances the interaction is weak and nearly central and permits the angular momenta of electron and molecule to remain uncoupled. At intermediate distances the interaction is sufficiently strong and noncentral to couple their angular momenta, whereby the electron effectively partakes of the molecular rotation; in this range the interaction is still represented adequately by a potential-energy function. At short distances the electron penetrates the molecule and is effectively incorporated in it to form a negative-ion "complex" (unless its energy is much higher than that of molecular electrons); this complex must be treated as a many-electron system.

In view of the complications of the problem as a whole, it seems essential to take advantage of any simplifying feature that may be available in each range of electron-molecule distances. To this end we shall not seek any single representation of the eigenfunctions of the complete system, because a representation which is realistic and suitable in one range becomes unsuitable in another range. Instead we shall consider separate representations appropriate to different ranges and connect them with one another at appropriate transition points between each range and the next one. In this paper we seek formulations of the Schrödinger equation appropriate to different ranges, quantitative criteria for identifying the ranges and their boundaries, and formulas for connecting the eigenfunctions obtained in adjacent ranges.

From this statement of our point of view we proceed now to survey how existing approaches fit within it. The concluding part of this introductory section will then outline the content, scope, and limitations of the present paper.

The laboratory-frame approach utilizes a set of base channels labeled by the rotational quantum number j of the molecule and by the orbital and spin quantum numbers (l, s) of the electron. The total angular momentum $\vec{J}=\vec{j}+\vec{l}+\vec{s}$ is a collision constant, of course. Introduction of the electron-molecule interaction couples different channels with the same J value. The formulation by Arthurs and Dalgarno[5] represents the interaction by a potential function $V(r,\vartheta')$, where r is the electron's radial distance and ϑ' its angle with the molecular axis; they then derive a system of coupled equations in the radial wave functions of the electron for the various channels. These equations are similar to the close-coupling equations for electron-atom scattering; their solution yields the rotational-excitation cross sections. In principle, the only approximation in this approach should lie in the formulation of the interaction potential; in practice one is forced to truncate the system because of its large size. The effects of truncation are not severe for large r where the potential V is weak and nearly central. Indeed the laboratory-frame approach is appropriate to this range where l and j are approximately good quantum numbers; it is not appropriate at shorter ranges where many base states with different (l,j) quantum numbers are required for a realistic description of the system.

The body-frame approach bypasses this difficulty by solving the scattering problem initially without reference to molecular rotation, in accordance with the Born-Oppenheimer approximation. In the case of a diatomic molecule, to which we direct our main attention, a constant of the motion is the angular momentum component along the internuclear axis $|\vec{J}\cdot\hat{R}|$ represented by a quantum number Λ or Ω. The existence of this constant simplifies the treatment. The effect of the collision upon molecular rotation is treated in a second step of calculation, as a by-product of the collisions[6]; we shall describe this step in detail. The assumption necessary here is that the electron moves much faster than the nuclei; this is the usual Born-Oppenheimer approximation of molecular theory, but is often called an adiabatic approximation (or "adiabatic-nuclei" approximation) in the context of electron collisions.

The relation of the electron's velocity to the nuclear motion is a matter we wish to stress. When the electron is close to the molecule, within its strongly attractive field, its velocity is high and approximately independent of nuclear motion. However, at large distances r, the phase of the electron's wave function depends on the *integral* of its velocity up to r (as illustrated, e.g., by a WKB procedure). This phase is thus sensitive to the partition of the total energy between the electron and the molecular vibration and rotation, unless the electron is very fast. As an index of the importance of this partition we consider the phase $k_{jv}r$ of a free-electron's wave function, when the electron is at the distance r from a molecule with rotational and vibrational quantum numbers j and v. Since variation of j or v affects the wave number k_{jv} expressed in atomic units by a small amount, the dependence of $k_{jv}r$ upon j and v remains small until r is fairly large, again in atomic units. One can and should use a body-frame formulation, that is, in essence, a Born-Oppenheimer approximation, while the dependence of the wave function on $k_{jv}r$ and that of $k_{jv}r$ on j and v remain negligible; at larger r one can no longer afford to do so and switching to a laboratory-frame description is called for.

The range of r values where a body-frame formulation is appropriate was called region A in FH, while region B indicated the range where the dependence of the wave function on j is essential (Fig. 1). Wave functions constructed separately for the two regions belong to representations characterized by the quantum number Λ in region A and j in region B. (The quantum number j is often replaced by N when coupling with electron spins is disregarded.) The quantum-mechanical frame transformation that connects these representations constitutes the l-uncoupling transition from the Hund-coupling case b to case d and is described in Sec. II below.

Note that region A does not extend outward quite as far for collisions between an electron and a neutral molecule as it does for electron-ion collisions. The reason is that the electron wave function does not depend sensitively on k_{jv} wherever the electron-molecule interaction V is much larger than $\frac{1}{2}k_{jv}^2$; when V includes a Coulomb potential $1/r$, region A extends automatically at least as far as $r\sim k_{jv}^{-2}$ a.u. In the absence of the Coulomb interaction, which is strong and amenable to analytic treatment, a study of the extension of region A requires some detailed analysis. In this paper we only note for purposes of orientation that region A extends roughly over $r\lesssim 10$ a.u. in the field of neutral molecules, because at $r\sim 10$ a.u. the quadrupole and polarization potentials are of the order

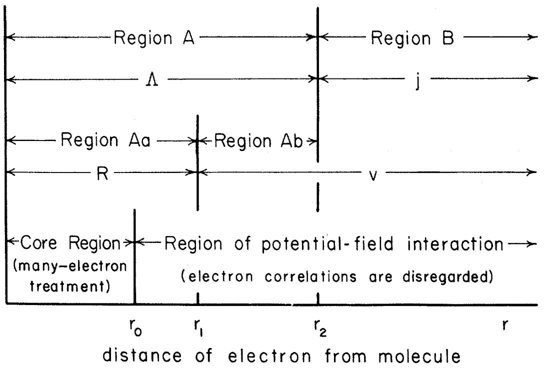

FIG. 1. Diagram showing quantum numbers relevant to different ranges of electron-molecule distance r. The abscissas are not drawn to scale.

of 10^{-3} a.u. (~100 cm^{-1}), which lies between rotational and vibrational energies.

In this paper, Sec. II reviews the relevant symmetries and the l-uncoupling transformation. Section III formulates the Schrödinger equations appropriate to regions A and B for an electron in the field of a neutral diatomic molecule; here, as in FH, we disregard the nuclear vibrations. Section IV extends the formulation to include the influence of vibrations. A procedure for the numerical solution of the Schrödinger equations, through regions A and B, in the presence of multipole and polarization potentials is developed in Sec. V. However applications are practical tests of this procedure are left for other works.[7] Sections VI and VII show how to obtain a scattering matrix and thence integral and differential cross sections from wave functions constructed by the procedure of Sec. V. Emphasis will be laid here, as in FH, on the simplifications that result when the long-range interactions are negligible, in which case the solution of the Schrödinger equations in regions A and B is trivial. The immediate result of this treatment amounts only to a rederivation of the adiabatic approximation results[6] in the context of frame transformations. Its real purpose is to provide a point of departure for calculations that evaluate and take into account the actual effects of long-range interactions. The analytical development of this paper refers for simplicity to an electron collision with a neutral molecule in a $^1\Sigma^+$ state. A partial extension to molecules in other states is outlined in the Appendix.

This paper does not consider explicitly the electron-molecule interaction at short ranges, i.e., in the "core" region where the electron penetrates the molecule. Instead, it represents the effects of this interaction through the values of a set of eigenfunctions over a sphere of radius r_0 surrounding the molecule. These values serve as initial boundary conditions for the outward integration of the region-A Schrödinger equation at $r > r_0$. In principle the values at r_0 should be obtained theoretically by a separate solution of the Schrödinger equation in the core region, but in FH and in other analogous situations[8] they have been obtained from analysis of photoabsorption experiments. The radius r_0 should be so chosen that the electron-molecule interaction is fairly represented by a potential $V(\vec{r})$ for $r \geqslant r_0$; in other words, *correlations* between the incident electron and the molecular electron—due to antisymmetrization or to Coulomb forces—should be negligible for $r \geqslant r_0$.

The importance of electron-electron correlations at $r < r_0$ can be estimated from the following considerations. The problem of constructing theoretically the relevant eigenfunctions at $r=r_0$, and in particular their logarithmic derivatives, is essentially equivalent to the problem of evaluating discrete levels of the electron-molecule complex, that is, of evaluating the electron affinity of the molecule. General experience with quantum chemistry indicates that it is seldom realistic to approach such calculations by a single-electron model. Accordingly we feel that a realistic study of electron-molecule interactions within the core region requires taking into account correlations as one does in theoretical spectroscopy. (The term "theoretical spectroscopy" means, in this paper, the calculation of discrete spectral levels. The substantial equivalence between calculations of short-range scattering functions and of discrete spectral levels is implied by quantum-defect procedures though it remains to be demonstrated in detail.)

Yet another aspect of electron-molecule collisions which awaits detailed development is the treatment of the resonances due to virtual excitations of the rotational and vibrational motion. Here we shall only address ourselves to direct rotational and vibrational excitations, even though it should be straightforward to combine the approach of this paper with the treatment of rotational autoionization in FH.

II. SYMMETRIES AND TRANSFORMATION

Constants of an electron-molecule interaction are represented by the total angular momentum quantum numbers J and M; also constant are the parity I under inversion of all electron and nuclear coordinates and—for homonuclear diatomic molecules—the parities under inversion of electrons only (g or u) and under permutation of nuclei (s or a). We shall also regard as constant the spin quantum number S, which equals $\frac{1}{2}$ when the target molecule is in a singlet states, and the quantum number $K(\vec{K}=\vec{l}+\vec{j})$. In fact, we shall, for simplicity, disregard the electron spin altogether and identify K with J and also Λ with Ω. The orbital quantum number l of the incident electron is a good quantum number only at large radial distances r. Restricting ourselves to collisions with diatomic molecules, we shall use an additional parity quantum number $\eta = \pm 1$ which combines with J to yield the inversion parity in the form $I = \eta(-1)^J$. The quantum number η relates, as we shall see, to the transformation of the molecular wave function under reflection through a plane containing the internuclear axis $\hat{R} \equiv (\theta, \phi)$.

We are particularly interested in pairs of mutually incompatible quantum numbers which correspond to pairs of noncommuting operators. One such pair consists of j and Λ which correspond, respectively, to the angular momentum of the target molecule, and the component of $\vec{K}$ along $\hat{R}$—or, which is the same, to the component of the orbital momentum

$\vec{l} \cdot \hat{R}$. Another pair of incompatible variables, the vibrational quantum number v and the internuclear distance R, will be considered in Sec. IV. (For a homonuclear molecule in a Σ_g electronic state, only even values of j occur in s states of nuclear permutation and only odd values in a states.)

The eigenfunctions of total angular momentum to be used in our problem depend on the direction of the molecular axis, $\hat{R} \equiv (\theta, \phi)$, and on that of the colliding electron, $\hat{r} \equiv (\vartheta, \varphi) \equiv (\vartheta', \varphi')$, where the unprimed coordinates pertain to the laboratory frame and the primed ones to the body frame. As in FH we consider two types of rotational wave functions. One type, classified by the quantum number j, is defined by

$$\Phi_{JM}^{(lj)}(\hat{r}, \hat{R}) = \sum_m Y_{lm}(\vartheta, \varphi) Y_{j\, M-m}(\theta, \phi) \times (l\, m, j\, M-m \,|\, l\, j\, JM), \tag{1}$$

where the Y are ordinary spherical harmonics and $(\cdots|\cdots)$ is a Wigner coefficient. This wave function is the same as was used by Arthurs and Dalgarno[5]; its parity under inversion of all coordinates is

$$I \Phi_{JM}^{(lj)} = (-1)^{l+j} \Phi_{JM}^{(lj)}, \tag{2}$$

assuming that the target molecule is in a ${}^1\Sigma^+$ state. The other type is classified by the quantum number Λ, represents $\hat{r}$ in the body frame, and is defined by

$$X_{JM}^{(l\Lambda\eta)}(\hat{r}, \hat{R}) = [Y_{l\Lambda}(\vartheta', \varphi') D_{\Lambda M}^{(J)}(\theta, \phi) + \eta\, Y_{l\,-\Lambda}(\vartheta', \varphi') D_{-\Lambda M}^{(J)}(\theta, \phi)] \left(\frac{2J+1}{8\pi(1+\delta_{\Lambda 0})}\right)^{1/2}, \tag{3}$$

where the $D_{\Lambda M}^{(J)}$ are symmetric top wave functions. (The D functions, and hence $X_{JM}^{(l\Lambda\eta)}$, are defined only for $J \geqslant \Lambda$; note also that $X^{(l\Lambda\eta)}$ vanishes for $\Lambda = 0$ and $\eta = -1$, and it reduces to a single term for $\Lambda = 0$ and $\eta = +1$.) To determine the effect of coordinate inversion on the wave function X consider that this operation (i) changes the electron body-frame coordinates (ϑ', φ') into $(\vartheta', -\varphi')$, i.e., applied to $Y_{l\Lambda}$ the reflection σ_v at the body-frame coordinate plane $(x'z')$,

$$\sigma_v(x'z') Y_{l\Lambda}(\vartheta', \varphi') = (-1)^\Lambda Y_{l\,-\Lambda}(\vartheta', \varphi'),$$

and (ii) changes the set of Euler angles $(\psi = 0, \theta, \phi)$ connecting the laboratory and body frames into $(\pi - \psi = \pi,\ \pi - \theta,\ \phi + \pi)$, i.e., replaces $D_{\Lambda M}^{(J)}(\theta, \phi)$ by $(-1)^{J+\Lambda} D_{-\Lambda M}(\theta, \phi)$. Inversion thus interchanges the two terms of (3), to within the factor $\eta(-1)^J$, showing that X is an eigenvector of I,

$$I X_{JM}^{(l\Lambda\eta)} = \eta(-1)^J X_{JM}^{(l\Lambda\eta)}. \tag{4}$$

The sets of functions Φ and X are connected by an orthogonal transformation U discussed in FH, namely,

$$X_{JM}^{(l\Lambda\eta)} = \sum_j \Phi_{JM}^{(lJ)} U_{j\Lambda}^{(lJ\eta)}, \tag{5}$$

$$\Phi_{JM}^{(lj)} = \sum_\Lambda X_{JM}^{(l\Lambda\eta)} \tilde{U}_{\Lambda j}^{(lJ\eta)}, \tag{6}$$

where the tilde denotes the transpose. The matrix elements of U are given by

$$U_{j\Lambda}^{(lJ\eta)} = (-1)^{J+\Lambda-j} (l\, J\, j\, 0 \,|\, l\, -\Lambda, J\Lambda) \frac{1+\eta(-1)^{J-j-l}}{[2(1+\delta_{\Lambda 0})]^{1/2}}, \tag{7}$$

$$U_{j\Lambda}^{(lJ\eta)} = \left(\frac{2j+1}{2J+1}\right)^{1/2} (l\, \Lambda, j\, 0 \,|\, l\, j\, J\Lambda) \frac{1+\eta(-1)^{J-j-l}}{[2(1+\delta_{\Lambda 0})]^{1/2}}. \tag{7a}$$

This formula is a generalization of the one derived in Appendix A of FH (where η was taken to be $+1$, and j and l were taken to be odd), and may be derived in a similar manner. (An alternative derivation can be extracted from the Appendix of the present paper by setting $\Lambda = 0$ and $\eta = +1$.) The dimensions of the matrix U depend on the values of η and of the number $\mathcal{L} = \min(l, J)$. We have

$$\left.\begin{array}{l} j = |J-l|,\ |J-l|+2, \cdots, J+l \\ \Lambda = 0,\ 1, \cdots, \mathcal{L} \end{array}\right\} \text{ for } \eta = +1, \tag{8a}$$

$$\left.\begin{array}{l} j = |J-l|+1,\ |J-l|+3, \cdots, J+l-1 \\ \Lambda = 1,\ 2, \cdots, \mathcal{L} \end{array}\right\} \text{ for } \eta = -1. \tag{8b}$$

Therefore the matrix U is $(\mathcal{L}+1) \times (\mathcal{L}+1)$ for $\eta = 1$ and $\mathcal{L} \times \mathcal{L}$ for $\eta = -1$. The factor $1 + \eta(-1)^{J-j-l}$ of (7) vanishes unless the parity eigenvalues in (2) and (4) coincide; this property verified that the transformation U commutes with the inversion I. The orthogonality of U can be derived from the orthogonality of the matrices $(l\, J\, j\, 0 \,|\, l\, -\Lambda, J\Lambda)$ taking into account that

$$(-1)^{J-j-l}(l\, J\, j\, 0 \,|\, l\, -\Lambda, J\Lambda) = (l\, J\, j\, 0 \,|\, l\, \Lambda, J-\Lambda).$$

III. LABORATORY- AND BODY-FRAME EQUATIONS

In accordance with the discussion in Sec. I, we represent the interaction between an electron and a diatomic molecule by a potential energy $V(r, \vartheta')$, for $r \geqslant r_0$, i.e., outside the core, as though the molecule were a rigid axially symmetric body. We do not represent explicitly the position coordinates of the electrons in the molecule, or the doublet spin state of the combined electron and molecule, or the antisymmetrization of all electron coordinates. All these elements could be added to the treatment of this paper without affecting its results.

The axial symmetry is manifest in the body frame; hence V depends on the primed coordinate ϑ' but not on φ'. In this section we disregard the dependence of V on the internuclear distance R, as well as the vibrational part of the molecular Hamiltonian. The Hamiltonian of the system is then represented, in atomic units, by

$$\mathcal{H}=\mathcal{H}_{\text{rot}}-\tfrac{1}{2}\nabla_{\vec{r}}^{2}+V(r,\vartheta')\,, \qquad (9)$$

where $\mathcal{H}_{\text{rot}}$ is the rotational part of the molecular Hamiltonian; the eigenvalues of $\mathcal{H}_{\text{rot}}$ are $Bj(j+1)$ if one disregards rotational stretching.

Following Arthurs and Dalgarno[5] the laboratory-frame treatment represents an eigenfunction of $\mathcal{H}$, $|\vec{J}|^2$, J_z and parity by the superposition

$$\Psi_{JM}^{(\eta)}(r,\hat{r},\hat{R})=\sum_{lj} r^{-1}F_{lj}^{(J\eta)}(r)\,\Phi_{JM}^{(lj)}(\hat{r},\hat{R})\,. \qquad (10)$$

[The index η serves, even in the laboratory frame, to characterize the parity $I=\eta(-1)^J$.] Substitution of this expansion reduces the Schrödinger equation with the Hamiltonian (9) and energy eigenvalue E to the system of coupled equation in the radial eigenfunctions F:

$$\left(-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l(l+1)}{2r^2}+Bj(j+1)-E\right)F_{lj}^{(J\eta)}(r)$$

$$+\sum_{l'j'}\left(\Phi_{JM}^{(lj)}\middle|V\middle|\Phi_{JM}^{(l'j')}\right)F_{l'j'}^{(J\eta)}(r)=0\,. \qquad (11)$$

The matrix element

$$\left(\Phi_{JM}^{(lj)}\middle|V\middle|\Phi_{JM}^{(l'j')}\right)\delta_{\eta\eta'}\,\delta_{JJ'}\,\delta_{MM'}$$

$$=\int d\hat{r}\int d\hat{R}\,\Phi_{JM}^{(lj)*}(\hat{r},\hat{R})\,V(r,\vartheta')\,\Phi_{J'M'}^{(l'j')}(\hat{r},\hat{R}) \qquad (12)$$

is a function of r, diagonal in J and M and independent of M owing to invariance of V under rotation of all coordinates, which leaves ϑ' unchanged. The potential V is also invariant under the inversion I of all coordinates. Accordingly the matrix element (12) vanishes unless $(l+j)-(l'+j')$ is even, whereby the system (11) interlinks only functions $F_{lj}^{(J\eta)}$ with the same J and with $l+j$ values of the same parity, $I=(-1)^{l+j}=\eta(-1)^J$. For homonuclear molecules in Σ^+ states, the parity of j is fixed by the nuclear permutation symmetry (s or a); therefore the system (11) interlinks only functions $F_{lj}^{(J\eta)}$ with l values of the same parity.

A body-frame treatment represents the eigenfunctions of (9) by the expansion

$$\Psi_{JM}^{(\eta)}(r,\hat{r},\hat{R})=\sum_{l\Lambda} r^{-1}G_{l\Lambda}^{(J\eta)}(r)\,X_{JM}^{(l\Lambda\eta)}(\hat{r},\hat{R}). \qquad (13)$$

This expansion reduces the Schrödinger equation to a system of radial equations alternative to (11), namely,

$$\left(-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l(l+1)}{2r^2}-E\right)G_{l\Lambda}^{(J\eta)}(r)$$

$$+\sum_{\Lambda'}\left(X_{JM}^{(l\Lambda\eta)}\middle|\mathcal{H}_{\text{rot}}\middle|X_{JM}^{(l\Lambda'\eta)}\right)G_{l\Lambda'}^{(J\eta)}(r)$$

$$+\sum_{l'}\left(X_{JM}^{(l\Lambda\eta)}\middle|V\middle|X_{JM}^{(l'\Lambda\eta)}\right)G_{l'\Lambda}^{(J\eta)}(r)=0\,. \qquad (14)$$

Here it is important that the equations are interlinked in Λ and in l by separate terms. The matrix elements of $\mathcal{H}_{\text{rot}}$,

$$\left(X_{JM}^{(l\Lambda\eta)}\middle|\mathcal{H}_{\text{rot}}\middle|X_{JM}^{(l\Lambda'\eta)}\right)=B\sum\nolimits_j \tilde{U}_{\Lambda j}^{(lJ\eta)}\,j(j+1)\,U_{j\Lambda'}^{(lJ\eta)}, \qquad (15)$$

are diagonal in l, η, J, and M and independent of r and M. The interaction matrix elements

$$\left(X_{JM}^{(l\Lambda\eta)}\middle|V(r,\vartheta')\middle|X_{JM}^{(l'\Lambda\eta)}\right)$$

$$=\int d\hat{r}'\,Y_{l\Lambda}^{*}(\vartheta',\varphi')\,V(r,\vartheta')\,Y_{l'\Lambda}(\vartheta',\varphi')\,\delta_{\Lambda\Lambda'}$$

$$=(l\Lambda|\,V\,|l'\Lambda)\,\delta_{\Lambda\Lambda'} \qquad (16)$$

are diagonal in Λ, η, J, and M owing to invariance of V under the relevant operations; moreover they are independent not only of η and M but also of J. For homonuclear molecules the potential V is an even function of $\cos\vartheta'$; hence the matrix elements (16) vanish also for odd values of $l-l'$.

The wave-function expansions (10) and (13) are related by the transformations (5) and (6) which connect the Φ and X functions. The same transformations connect the radial functions F and G,

$$F_{lj}^{(J\eta)}(r)=\sum\nolimits_\Lambda G_{l\Lambda}^{(J\eta)}(r)\,\tilde{U}_{\Lambda j}^{(lJ\eta)}, \qquad (17)$$

$$G_{l\Lambda}^{(J\eta)}(r)=\sum\nolimits_j F_{lj}^{(J\eta)}(r)\,U_{j\Lambda}^{(lJ\eta)}. \qquad (18)$$

The systems of Eqs. (11) and (14) are thus formally equivalent. Their respective appropriateness for integration in region B and in region A emerges from the properties of the matrix elements of $\mathcal{H}_R$ and V in the two regions.

In region A, the matrix elements of $\mathcal{H}_{\text{rot}}$ are negligible as compared with those of V, since the rotational constant B is of the order of 10^{-4} a.u. at most. Disregarding $\mathcal{H}_{\text{rot}}$ in this region splits the system (14) into separate systems for different values of Λ, each system being independent of J and η in accordance with the Born-Oppenheimer approximation. In region B, the cumulative effect of $\mathcal{H}_{\text{rot}}$ on the integration up to large r becomes non-negligible, as discussed in Sec. I. However V tends to become negligible here, except for very low electron energies, whereby the system (11) splits into separate equations. The separation actually hinges only on the interaction V becoming effectively central at large r. In fact, our approach should prove practical insofar as the *commutator of* $\mathcal{H}_{\text{rot}}$ *and* V *is small at all* r even though the two operators do not commute and are not separately negligible. When this commutator is altogether negligible our results reduce to those of the adiabatic theory.

The conditions under which $\mathcal{H}_{\text{rot}}$ should not be disregarded can be characterized with reference to Eq. (11) and in the light of the preliminary discussion of Sec. I. The operator in the brackets of (11) has free-particle eigenfunctions $j_l(k_j r)$ and $y_l(k_j r)$, where k_j is defined by $\frac{1}{2}k_j^2 = E - B\, j(j+1)$. Since B is a small number, $k_{j+2} - k_j$ is also small and the differences between the values of $j_l(k_j r)$ [or of $y_l(k_j r)$] for the different relevant values of j will remain negligible up to some rather large value of r. This value will be called r_2 and is indicated in Fig. 1 as the boundary between region A, where $\mathcal{H}_{\text{rot}}$ is disregarded, and region B.

The adiabatic theory of electron-molecule collisions[6] disregards the rotational Hamiltonian altogether in the calculation of cross sections. Thereby it assumes that the scattering matrix is determined adequately by solving a Schrödinger equation independent of J and η in region A only. This approximation tends to become poor for slow electron collisions, since the contribution of region B to the scattering matrix becomes very important once the electron wavelength exceeds the size of region A. The laboratory-frame treatment, on the other hand, fails to take advantage of the approximate commutability of $\mathcal{H}_{\text{rot}}$ and V; this treatment is adequate by itself, with reasonable truncation, only at very low energies, such that electrons with $l > 0$ fail to penetrate even as close as region A. Under these circumstances solution of (11) by Born approximation may be simple and adequate.[9]

A clarification of the connection between the approaches has thus been achieved. It will be complemented in Sec. V by a method of integration of the systems (14) and (11) which permits one to take advantage of the smallness of interlinkage terms without striking them off at the outset.

IV. COUPLING WITH VIBRATIONS

Thus far we have treated the target diatomic molecule as a rigid body, with fixed internuclear distance R. The variations of R will now be treated in a manner altogether parallel to that used for the variations of the orientation $\hat{R}$.

To this end, the Hamiltonian (9) will be complemented by a vibrational term $\mathcal{H}_v$ with eigenfunctions $\chi_v(R)$; the eigenvalues of $\mathcal{H}_v$ equal $(v+\frac{1}{2})\omega$ in the harmonic approximation. Moreover the potential V is now regarded as a function of R also, whereby it does not commute with $\mathcal{H}_v$ as it does not commune with $\mathcal{H}_{\text{rot}}$. Equation (9) is thus replaced by

$$\mathcal{H} = \mathcal{H}_{\text{rot}} + \mathcal{H}_v - \tfrac{1}{2}\nabla_{\vec{r}}^2 + V(r, \vartheta', R). \tag{19}$$

The expansion (10) and the radial system (11) take now the forms

$$\Psi_{JM}^{(\eta)}(r, \hat{r}; R, \hat{R}) = \sum_{ljv} r^{-1} F_{ljv}^{(J\eta)}(r)\, \chi_v(R)\, \Phi_{JM}^{(lj)}(\hat{r}, \hat{R}) \tag{20}$$

and[10]

$$\left(-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + Bj(j+1) + \omega(v+\tfrac{1}{2}) - E\right) F_{ljv}^{(J\eta)}(r) + \sum_{l'j'v'} \left(\Phi_{JM}^{(lj)}\chi_v \middle| V(r, \vartheta', R) \middle| \Phi_{JM}^{(l'j')}\chi_{v'}\right) F_{l'j'v'}^{(J\eta)}(r) = 0\,. \tag{21}$$

Similarly, the expansion (13) and the system (14) become

$$\Psi_{JM}^{(\eta)}(r, \hat{r}; R, \hat{R}) = \sum_{l\Lambda v} r^{-1} G_{l\Lambda v}^{(J\eta)}(r)\, \chi_v(R)\, X_{JM}^{(l\Lambda\eta)}(\hat{r}, \hat{R}) \tag{22}$$

and

$$\left(-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + \omega(v+\tfrac{1}{2}) - E\right) G_{l\Lambda v}^{(J\eta)}(r) + B\sum_{\Lambda'}\Big[\sum_j \tilde{U}_{\Lambda j}^{(lJ\eta)}\, j(j+1)\, U_{j\Lambda'}^{(lJ\eta)}\Big] G_{l\Lambda' v}^{(J\eta)}(r) + \sum_{l'v'} (\Lambda l v | V(r, \vartheta', R) | \Lambda l' v')\, G_{l'\Lambda v'}^{(J\eta)}(r) = 0. \tag{23}$$

The extension thus achieved increases the size of the system of equations and thus tends to make its practical solution much more difficult. However, this difficulty might not be great because the potential V does not seem to depend strongly on R for values of r which are fairly large and are indicated in Fig. 1 as region Ab.[11] Matrix elements of V off-diagonal in (v, v') might accordingly be negligible, in which case the equations reduce to those of Sec. III, or should become at least sufficiently small to allow the couplings in v to be unraveled by perturbation methods. The actual situation should be explored quantitatively.

At any rate, since the interaction V increases in strength rapidly with decreasing r, the matrix elements off-diagonal in (v, v') should become important at low r. Furthermore, as the interaction V increases, the separation between the different eigenvalues of $\mathcal{H}_v$ becomes less and less relevant and it may well be disregarded. This is done by applying yet another transformation to a fully Born-Oppenheimer frame in which the interaction is diagonal in the internuclear distance R.

The transformation and its inverse are analogous to the pair (17) and (18), but here the elements of the orthogonal matrices consist of the (real) vibrational eigenfunctions χ_v. Thus we define a new set of radial wave functions

$$H_{l\Lambda}^{(J\eta)}(r, R) = \textstyle\sum_v G_{l\Lambda v}^{(J\eta)}(r)\, \chi_v(R) \tag{24}$$

in terms of which the G are given by the inverse transformation

$$G_{l\Lambda v}^{(J\eta)}(r) = \int_0^\infty dR\, \chi_v(R)\, H_{l\Lambda}^{(J\eta)}(r, R)\ . \tag{25}$$

Substitution of (25) reduces the system (23) to the form

$$\left(-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l(l+1)}{2r^2}-E\right)H_{l\Lambda}^{(J\eta)}(r,R)+B\sum_{\Lambda'}\Big[\sum_{j}\tilde{U}_{\Lambda j}^{(lJ\eta)}\,j(j+1)U_{j\Lambda'}^{(lJ\eta)}\Big]H_{l\Lambda'}^{(J\eta)}(r,R)$$
$$+\omega\int_0^\infty dR'\Big[\sum_v\chi_v(R)\,(v+\tfrac{1}{2})\,\chi_v(R')\Big]H_{l\Lambda}^{(J\eta)}(r,R')+\sum_{l'}(l\Lambda|\,V(r,\vartheta',R)\,|l'\Lambda)H_{l'\Lambda}^{(J\eta)}(r,R)=0\;. \tag{26}$$

Here again the system simplifies greatly, splitting into portions diagonal in Λ and R, if the rotational parameter B and the vibrational parameter ω are both negligible.

The range of r where this simplification is appropriate is indicated in Fig. 1 as region Aa, the name Ab being applied to the range where $\mathcal{H}_R$ is negligible but $\mathcal{H}_v$ is not. Equation (23) is the form of the Schrödinger equation appropriate to region Ab. The boundary between regions Aa and Ab is called r_1 in Fig. 1. The value of r_1 can be estimated as was done for r_2 in Sec. III and in accordance with the qualitative discussion in Sec. I. We set

$$\tfrac{1}{2}k_{jv}^2=E-Bj(j+1)-\omega(v+\tfrac{1}{2}) \tag{27}$$

and consider the dependence of the wave functions $H_{l\Lambda}^{(J\eta)}(r,R)$ on the parameter $k_{jv}r$, more properly on the differences between the values of these parameters for different v and j. This dependence should be negligible throughout region Aa, that is, for $r\leqslant r_1$.

V. INTEGRATION BY PHASE-AMPLITUDE METHOD

The Schrödinger equation for the radial motion of the coliding electron has been given alternative forms in Secs. III and IV with the intent of minimizing and unraveling the influences of the electron-molecule interaction at long ranges and of the rotational and vibrational Hamiltonians at shorter ranges. Yet these influences cannot be disregarded nor has it been shown that they can be treated by perturbation methods. Accordingly we recast the equations once more, into a form that is solved by quadratures and is very suitable for a perturbation treatment whenever appropriate.

Such a transformation is provided by application of the multichannel-phase-amplitude-method.[12] In essence, one represents the solutions of a system of radial equations, e.g., of (21), as superpositions of two independent solutions of the main diagonal part of each equation; the coefficients of the superpositions would then be constant except for the influence of the interlinkages and of other minor terms of the system of equations. Thus we express the dependent variable of (21) in the form

$$F_{ljv}^{(J\eta)}(r)=f_{ljv}^{(J\eta)}(r)\,u_l(k_{jv}r)-\bar{f}_{ljv}^{(J\eta)}(r)\,\bar{u}_l(k_{jv}r)\;, \tag{28}$$

where

$$u_l(k_{jv}r)=k_{jv}^{1/2}\,r\,j_l(k_{jv}r)\;,$$

$$\bar{u}_l(k_{jv}r)=k_{jv}^{1/2}\,r\,y_l(k_{jv}r). \tag{29}$$

Here k_{jv} is given by (27), while j_l and y_l are the usual spherical Bessel functions[13]; note that $u_l\to k_{jv}^{-1/2}\sin(k_{jv}r-l\tfrac{1}{2}\pi)$ and $\bar{u}_l\to -k_{jv}^{-1/2}\cos(k_{jv}r-l\tfrac{1}{2}\pi)$ as $r\to\infty$ and that their Wronskian

$$u_l\frac{d\bar{u}_l}{dr}-\bar{u}_l\frac{du_l}{dr}=1\;.$$

The two coefficients f and $\bar{f}$ constitute new dependent variables which replace $F_{ljv}^{(Jv)}(r)$; these coefficients are not independent but are given in terms of a single new variable β by

$$\frac{df_{ljv}^{(J\eta)}}{dr}=\bar{u}_l(k_{jv}r)\,\beta_{ljv}^{(J\eta)}(r)\;,\quad \frac{d\bar{f}_{ljv}^{(J\eta)}}{dr}=u_l(kj_vr)\,\beta_{ljv}^{(J\eta)}(r)\;. \tag{30}$$

With these substitutions, the system (21) reduces to

$$\beta_{ljv}^{(J\eta)}(r)=-2\sum_{l'j'v'}(\phi_{lj}^{(J\eta)}\chi_v|\,V\,|\phi_{l'j'}^{(J\eta)}\chi_{v'})$$
$$\times\big[f_{l'j'v'}^{(J\eta)}(r)\,u_{l'}(k_{j'v'}r)-\bar{f}_{l'j'v'}^{(J\eta)}(r)\,\bar{u}_{l'}(k_{j'v'}r)\big]\;, \tag{31}$$

where the function in the square brackets is $F_{ljv}^{(J\eta)}(r)$ itself. This expression permits one to obtain the values of f and $\bar{f}$ at any point $r>r_2$ by succesive steps of numerical integration from a knowledge of the matrix elements of V and of initial values of f and $\bar{f}$ at the boundary $r=r_2$ of region B. Thus we have

$$f_{ljv}^{(J\eta)}(r)=f_{ljv}^{(J\eta)}(r_2)$$
$$-2\sum_{l'j'v'}\int_{r_2}^{r}dr'\,\bar{u}_l(k_{jv}r')\,(\phi_{lj}^{(J\eta)}\chi_v|\,V\,|\phi_{l'j'}^{(J\eta)}\chi_{v'})$$
$$\times\big[f_{l'j'v'}^{(J\eta)}(r')\,u_{l'}(k_{j'v'}r')-\bar{f}_{l'j'v'}^{(J\eta)}(r')\,\bar{u}_{l'}(k_{j'v'}r')\big]\;. \tag{32}$$

When f and $\bar{f}$ vary but little over the range of integration, their values at r' in the integral of (32) may be replaced by their values at r_2. This replacement constitutes a Born approximation inasmuch as it gives the variation of f as a linear function of integrals over the interaction $V(r,\vartheta',R)$; however this approximation is more readily tested and probably more accurate than the plane-wave Born approximation considered in Ref. 9 and in the other references cited therein.

The initial values $f_{ljv}^{(J\eta)}(r_2)$ and $\bar{f}_{ljv}^{(J\eta)}(r_2)$ to be entered in (32)—and in the analogous formula for $\bar{f}$—should be provided by integration of the radial equation for region A, more specifically of the Eq.

(23) for region *Ab*. Here we set, in analogy to (28), (30), and (31),

$$G_{l\Lambda v}^{(J\eta)}(r)=g_{l\Lambda v}^{(J\eta)}(r)\,u_l(k_v r)-\bar{g}_{l\Lambda v}^{(J\eta)}(r)\,\bar{u}_l(k_v r)\;, \tag{33}$$

$$\frac{dg_{l\Lambda v}^{(J\eta)}}{dr}=\bar{u}_l(k_v r)\,\gamma_{l\Lambda v}^{(J\eta)}(r)\;,\qquad \frac{d\bar{g}_{l\Lambda v}^{(J\eta)}}{dr}=u_l(k_v r)\,\gamma_{l\Lambda v}^{(J\eta)}(r)\;, \tag{34}$$

$$\gamma_{l\Lambda v}^{(J\eta)}(r)=-2B\sum_{\Lambda'}\Big[\sum_{j}U_{\Lambda j}^{(lJ\eta)}\,j(j+1)\,U_{j\Lambda'}^{(lJ\eta)}\Big]G_{j\Lambda' v}^{(J\eta)}(r)$$
$$-2\sum_{l'v'}(\Lambda l v|V|\Lambda l' v')\,G_{l'\Lambda v'}^{(J\eta)}(r)\;. \tag{35}$$

Note that in accordance with the qualitative discussion in Sec. III the argument of u_l and $\bar{u}_l$ is now $k_v r$, with

$$\tfrac{1}{2}k_v^2=E-\omega(v+\tfrac{1}{2})\;. \tag{36}$$

Also, the term proportional to B in (35) should be negligible and the boundary r_2 between region A and region B is defined so that

$$u_l(k_{jv}r_2)\sim u_l(k_v r_2)\;,\quad \bar{u}_l(k_{jv}r_2)\sim\bar{u}_l(k_v r_2)\;. \tag{37}$$

It follows that the wave functions are joined at the boundary r_2 by formulas analogous to (18),

$$f_{ljv}^{(J\eta)}(r_2)=\textstyle\sum_\Lambda g_{l\Lambda j}^{(J\eta)}(r_2)\,\tilde{U}_{\Lambda j}^{(lJ\eta)}\;,$$
$$\bar{f}_{ljv}^{(J\eta)}(r_2)=\textstyle\sum_\Lambda \bar{g}_{l\Lambda v}^{(J\eta)}(r_2)\,\tilde{U}_{\Lambda j}\;. \tag{38}$$

Also, $g_{l\Lambda v}^{(J\eta)}(r_2)$ and $\bar{g}_{l\Lambda v}^{(J\eta)}(r_2)$ are obtained by integration formulas analogous to (32) and based on (35), starting from initial values of the same functions at the boundary r_1 between regions *Ab* and *Aa*.

This procedure is to be followed again for the integration in region *Aa*, which relates values of g and $\bar{g}$ at the boundary r_1 to initial values of analogous functions $h_{l\Lambda}^{(J\eta)}(r,R)$ and $\bar{h}_{l\Lambda}^{(J\eta)}(r,R)$ at the core boundary $r=r_0$. The formulas for this purpose are quite analogous to those given above and will not be written out here. The wave number relevant to region *Aa* is independent of j and v and is given by $\frac{1}{2}k^2=E$.

The values of wave functions at the core boundary are the essential parameters of our theory. They will be formulated from the point of view of FH, somewhat extended, which is also the point of view of Zemach's formulation of the multichannel-phase-amplitude method.[12] This formulation introduces a set eigenstates of the electron-molecule interaction within the core. In each of these eigenstates the electron's wave function emerges from the core at $r=r_0$ with a definite eigen-phase-shift δ. Since the core interaction can be evaluated within the Born-Oppenheimer approximation, within which the internuclear distance R and the quantum number Λ are fixed, each eigenstate corresponds to a definite R and Λ; an additional label α is appended to distinguish different eigenstates with the same Λ. The electron wave function for an eigenstate can be expanded in spherical harmonics in the body frame and is represented for $r\sim r_0$ by

$$\textstyle\sum_l Y_{l\Lambda}(\vartheta',\varphi')\big[u_l(kr)\cos\delta_{\alpha\Lambda}(R)$$
$$-\bar{u}_l(kr)\sin\delta_{\alpha\Lambda}(R)\big]\,C_{l\alpha}^{(\Lambda)}\;. \tag{39}$$

The expansion coefficients $C_{l\alpha}^{(\Lambda)}$ constitute an orthogonal matrix, such that

$$\textstyle\sum_\alpha C_{l\alpha}^{(\Lambda)}\tilde{C}_{\alpha l'}^{(\Lambda)}=\delta_{ll'},\quad \sum_l \tilde{C}_{\alpha l}^{(\Lambda)}C_{l\alpha'}^{(\Lambda)}=\delta_{\alpha\alpha'}\;. \tag{40}$$

The wave functions introduced in FH, e.g., in Eq. (13) of FH, had an analgous form, with the following main differences: (a) The Coulomb wave functions f and g were used instead of the free-electron wave functions u and $\bar{u}$; (b) the label α was omitted as a single eigenstate was relevant for each value of Λ; and (c) there was a single nonzero coefficient $C_{l\alpha}^{(\Lambda)}$ equal to 1, because only one value of l was relevant.

This paper no longer restricts l to a single value, introducing the coefficients $C_{l\alpha}^{(\Lambda)}$ which represent the admixture of different l in the same eigenstate α. Yet the generalization has only a weak effect for low-energy collisions, owing to the centrigual barrier that keeps slow electrons from approaching the core. The barrier effect limits the number of eigenstates α with non-negligible phase shifts and makes the matrix $C_{l\alpha}$ nearly diagonal; the assumption of FH was more drastic, implying that $C_{l\alpha}$ is exactly diagonal and thus breaks up into 1×1 diagonal blocks. Analytically the centrigual effect can be analyzed and evaluated with reference to the fact that the irregular solution $\bar{u}_l(kr)$ takes large values where kr is sufficiently small (e.g., for $kr \lesssim 2$) and l is sufficiently large (e.g., $l \gtrsim 2$). Large values of this function in the expansion (39) should be counterbalanced by small values of its coefficient $\sin\delta_{\alpha\Lambda}C_{l\alpha}^{(\Lambda)}$. Small values of this coefficient can be achieved under either of the following circumstances: (i) The phase shift $\delta_{\alpha\Lambda}$ is small, implying a weak interaction between electron and molecular core; we call such a state $|\alpha\Lambda)$ a *nonpenetrating orbit*; (ii) alternatively the coefficient $C_{l\alpha}^{(\Lambda)}$ is small for all large l in the *penetrating orbits*, whose $\delta_{\alpha\Lambda}$ is not small. An example of a penetrating orbit in a homonuclear molecule containing light atoms would be a σ state with primarily s character and with a small admixture of d and hardly any of g; an example of nonpenetrating orbit would be mostly d with a small admixture of s.[14]

We return now to the characterization of initial data for the integration of radial equations at $r>r_0$. Note that we had been considering wave functions for collision states with definite values of J and η, whereas the eigenstates $|\alpha\Lambda)$ pertain to the body frame only and have no such quantum numbers. Accordingly, our integration must start outward from r_0 with initial values corresponding to a superposition of eigenfunctions (39). Thus we set

$$h_{l\Lambda}^{(J\eta)}(r_0,R)=\sum_{\alpha} C_{l\alpha}^{(\Lambda)}\,[\cos\delta_{\alpha\Lambda}(R)]\,A_{\alpha\Lambda R}^{(J\eta)},$$
$$\bar{h}_{l\Lambda}^{(J\eta)}(r_0,R)=\sum_{\alpha} C_{l\alpha}^{(\Lambda)}[\sin\delta_{\alpha\Lambda}(R)]\,A_{\alpha\Lambda R}^{(J\eta)}. \tag{41}$$

The coefficients $A_{\alpha\Lambda R}^{(J\eta)}$ remain to be determined at the end of the integration process from the conditions which identify collision states of interest among all those that have the same energy and the same J and η.

The integration process described in this section determines eventually the asymptotic values at $r=\infty$ of the coefficients f and $\bar{f}$ in (28), as linear functions of the initial values (41). We do not carry out the numerical calculation but indicate its result in the form

$$f_{ljv}^{(J\eta)}(\infty)=\sum_{l'\Lambda}\int_0^\infty dR\sum_{\alpha}[M_{ljv,l'\Lambda R}\cos\delta_{\alpha\Lambda}(R)$$
$$+N_{ljv,l'\Lambda R}\sin\delta_{\alpha\Lambda}(R)]\,C_{l'\alpha}^{(\Lambda)}\,A_{\alpha\Lambda R}^{(J\eta)},$$
$$\bar{f}_{ljv}^{(J\eta)}(\infty)=\sum_{l'\Lambda}\int_0^\infty dR\sum_{\alpha}[\bar{N}_{ljv,l'\Lambda R}\cos\delta_{\alpha\Lambda}(R)$$
$$+\bar{M}_{ljv,l'\Lambda R}\sin\delta_{\alpha\Lambda}(R)]\,C_{l'\alpha}^{(\Lambda)}\,A_{\alpha\Lambda R}^{(J\eta)} \tag{42}$$

In the limit of vanishing long-range interactions, to which we shall restrict part of our considerations as was done in FH, the integrals in (32) and in analgous equations vanish. In this event the matrices N and $\bar{N}$ in (42) vanish and the matrices M and $\bar{M}$ reduce to frame transformation coefficients:

$$\left.\begin{array}{l} M_{ljv,l'\Lambda R}\sim\bar{M}_{ljv,l'\Lambda R}\sim\delta_{ll'}\,U_{j\Lambda}^{(lJ\eta)}\chi_v(R) \\ N_{ljv,l'\Lambda R}\sim\bar{N}_{ljv,l'\Lambda R}\sim 0 \end{array}\right\}\text{ for } V\sim 0. \tag{43}$$

VI. SCATTERING MATRIX

Cross sections for electron-molecule collisions can be obtained conveniently in terms of the scattering matrix. This matrix resolves into a set of invariant submatrices which are diagonal in the quantum numbers J, M, and η. Each of these submatrices can be extracted from the large-r form of the wave function $\Psi_{JM}^{(\eta)}$ which satisfies suitable boundary conditions at $r=\infty$. To obtain the scattering matrix, we then write $\Psi_{JM}^{(\eta)}$, as given by (20), as a superposition of incoming and outgoing spherical waves using the form (28) of $F^{(J\eta)}$ and the limiting values (42) of the coefficients $f^{(J\eta)}$ anf $\bar{f}^{(J\eta)}$. This wave function is

$$\Psi_{JM}^{(\eta)}(r,\hat{r};R,\hat{R})\to\sum_{ljv}\chi_v(R)\,\Phi_{JM}^{(lj)}(\hat{r},\hat{R})$$
$$\times k_{jv}^{-1/2}\left\{\frac{e^{ik_{jv}r}}{r}\left[\frac{f_{ljv}^{(J\eta)}(\infty)+i\bar{f}_{ljv}^{(J\eta)}(\infty)}{2i}\,i^{-l}\right]\right.$$
$$\left.+\frac{e^{-ik_{jv}r}}{r}\left[\frac{f_{ljv}^{(J\eta)}(\infty)-i\bar{f}_{ljv}^{(J\eta)}(\infty)}{-2i}\,i^{l}\right]\right\}\quad\text{as } r\to\infty. \tag{44}$$

The two terms in the braces of this formula would be complex conjugate if the coefficients $A_{\alpha\Lambda R}^{(J\eta)}$ were real. In our application these coefficients are not real. However we take advantage of the partial symmetry of (44) in ± by rewriting the coefficient of the outgoing wave in the form

$$\frac{f_{ljv}^{(J\eta)}(\infty)+i\bar{f}_{ljv}^{(J\eta)}(\infty)}{2i}\,i^{-l}=\sum_{\alpha\Lambda}\int_0^\infty dR\,B_{ljv,\alpha VR}^{(J\eta)}A_{\alpha\Lambda R}^{(J\eta)}. \tag{45}$$

Comparison with (42) shows that the matrix $B^{(J\eta)}$ is

$$B_{ljv,\alpha\Lambda R}^{(J\eta)}=\tfrac{1}{2}\,i^{-l-1}\sum_{l'}[(M_{ljv,l'\Lambda R}+i\bar{N}_{ljv,l'\Lambda R})\cos\delta_{\alpha\Lambda}(R)$$
$$+(N_{ljv,l'\Lambda R}+i\bar{M}_{ljv,l'\Lambda R})\sin\delta_{\alpha\Lambda}(R)]\,C_{l'\alpha}^{(\Lambda)}. \tag{46}$$

Substitution of (45) reduces (44) to the form

$$\Psi_{JM}^{(\eta)}\to\sum_{ljv}\chi_v\,\Phi_{JM}^{(jl)}\,k_{jv}^{-1/2}\left(\frac{e^{ik_{jv}r}}{r}\sum_{\alpha\Lambda}\int_0^\infty dR\,B_{ljv,\alpha\Lambda R}^{(J\eta)}\right.$$
$$\left.+\text{c.c.}\right)A_{\alpha\Lambda R}^{(J\eta)}\quad\text{as } r\to\infty. \tag{47}$$

The spherical waves are normalized here in accordance to the prescription of the collision treatment by Blatt and Weisskopf, that is, each term represents one unit of electron flux entering or outgoing through a large-r spherical surface.[15] As in this reference, we consider a complete set of states characterized by the so-called "outgoing-wave boundary condition" and often indicated by a symbol +. Each of these states has a wave function (47) that contains a *single incoming wave* with quantum numbers (l_0, j_0, v_0) and with amplitude $(-1)^{-l_0}$. The coefficients $A^{(J\eta)}$ for this state will be labeled by the index + and by the quantum numbers (l_0, j_0, v_0). They are identified as the roots of the system of linear inhomogeneous equations

$$\sum_{\alpha\Lambda}\int_0^\infty dR\,\left(B_{ljv,\alpha\Lambda R}^{(J\eta)}\right)^* A_{\alpha\Lambda R,l_0j_0v_0}^{(J\eta+)}$$
$$=\delta_{ll_0}\,\delta_{jj_0}\,\delta_{vv_0}(-1)^{l_0} \tag{48}$$

as one verifies by inspection of (47). This equation can be cast in matrix form by regarding the various sets of coefficients $A_{ljv}^{(J\eta+)}$ as constituting a matrix,

$$[(B^{(J\eta)})^*A^{(J\eta+)}]_{ljv,l_0j_0v_0}=\delta_{ll_0}\,\delta_{jj_0}\,\delta_{vv_0}(-1)^{l_0}. \tag{48a}$$

The formal solution of this equation is represented by

$$A_{\alpha\Lambda R,l_0j_0v_0}^{(J\eta+)}=(-1)^{l_0}[(B^{(J\eta)})^*]^{-1}_{\alpha\Lambda R,l_0j_0v_0}. \tag{49}$$

Given the set of wave functions (47) identified by the coefficients (49), the coefficient of each outgoing spherical wave represents one element of the desired scattering matrix.[15] Thus we write

$$(ljv|\,S^{(J\eta)}\,|\,l_0 j_0 v_0) = \sum_{\alpha\Lambda} \int_0^\infty dR\, B^{(J\eta)}_{ljv,\alpha\Lambda R}\, A^{(J\eta+)}_{\alpha\Lambda R, l_0 j_0 v_0}\,, \tag{50}$$

$$= (-1)^{l_0} (ljv|\, B^{(J\eta)}[(B^{(J\eta)})^*]^{-1}\,|\,l_0 j_0 v_0)\ . \tag{50a}$$

(The M quantum number need not be entered in the matrix representation of $S^{(J\eta)}$ because this matrix is diagonal in M and independent of M.) The structure of (50a) verifies that the reciprocal of the scattering matrix is its Hermitian conjugate, i.e., that $S^{(J\eta)}$ is unitary. The elements of the matrix $B^{(J\eta)}$ have the character of Jost functions.[16]

Numerical calculation of the matrix $B^{(J\eta)}$ using its definition (46) and the results of the integration procedure of Sec. V should be straightforward though laborious in a general case. The inversion of this matrix, required by (49), is further complicated in principle by its infinite dimensionality. In practice, only a finite portion of the matrix should be relevant and its inversion should prove feasible. We do not pursue this investigation in the present paper. Recall, however, that our treatment is designed to take advantage of the weakness of long-range interaction. The construction and inversion of $B^{(J\eta)}$ are trivial in the limit of weak interaction; they should be feasible near this limit. Indeed we obtain in the limit, substituting (43) into (46), (49), and (50),

$$B^{(J\eta)}_{ljv,\alpha\Lambda R} = \tfrac{1}{2} i^{-l-1}\, U^{(lJ\eta)}_{j\Lambda}\, \chi_v(R)\, C^{(\Lambda)}_{l\alpha}\, e^{i\,\delta_{\alpha\Lambda}(R)}, \tag{51}$$

$$A^{(J\eta+)}_{\alpha\Lambda R, l_0 j_0 v_0} = 2 i^{l_0 - 1}\, e^{i\,\delta_{\alpha\Lambda}(R)}\, \tilde{C}^{(\Lambda)}_{\alpha l_0}\, \chi_{v_0}(R)\, \tilde{U}^{(l_0 J\eta)}_{\Lambda j_0}\,, \tag{52}$$

$$(ljv|\,S^{(J\eta)}\,|\,l_0 j_0 v_0) = -\,i^{\,l_0 - l} \sum_{\alpha\Lambda} U^{(lJ\eta)}_{j\Lambda} \times \int_0^\infty dR\, \chi_v(R)\, C^{(\Lambda)}_{l\alpha}\, e^{2i\,\delta_{\alpha\Lambda}(R)}\, \tilde{C}^{(\Lambda)}_{\alpha l_0}\, \chi_{v_0}(R)\, \tilde{U}^{(l_0 J\eta)}_{\Lambda j_0}\,. \tag{53}$$

Equation (53) represents the result of a full set of frame transformations in its basic form. Its content is equivalent to that of the adiabatic-approximation theory. In fact, (53) casts the results of the adiabatic approximation in a form that should be amenable to higher approximations as they may be required.

VII. CROSS SECTIONS

The cross section $\sigma(jv \leftarrow j_0 v_0)$ for elastic or inelastic scattering integrated over the direction of the scattered electron is expressed in terms of the S matrix by the familiar type formula[15]

$$\sigma(jv \leftarrow j_0 v_0) = \frac{\pi}{k^2_{j_0 v_0}} \sum_{l l_0 J\eta} (2J+1)\,|\,(ljv|\,S^{(J\eta)} - 1\,|\,l_0 j_0 v_0)\,|^2\ . \tag{54}$$

The sum over η is purely formal since the value of η is fixed at $(-1)^{J - l_0 - j_0}$ by parity conservation, as discussed in Sec. II. The unit matrix is subtracted from the S matrix in (54), as usual, to eliminate the contribution of the unscattered wave.

The differential cross section for elastic or inelastic scattering in a specified direction can be established and formulated in various manners. It has often been found convenient, e.g., in Ref. 6, to express this cross section in terms of the angular momentum $\vec{j}_t = \vec{l}_0 - \vec{l} = \vec{j} - \vec{j}_0$ transferred by the incident electron to the molecular rotation. The range of the quantum number j_t, such that $|\vec{j} - \vec{j}_0|^2 = j_t(j_t+1)\hbar^2$, is often more narrowly limited than the range of the total angular momentum quantum number J. Moreover the differential cross section can be represented as a single sum of terms corresponding to various values of j_t, whereas a double sum over pairs of values (J, J') is otherwise required. Finally, j_t replaces J altogether when the interaction is restricted to the body frame. These matters and the development of the theory in terms of j_t have been discussed in a recent separate paper,[17] called here FD, whose results require only straightforward generalization for the present application.

A main feature of the method of FD consists of replacing the scattering matrix $S^{(J\eta)}$ by an equivalent matrix $\bar{S}(j_t)$ through the transformation formula

$$(ljv|\,\bar{S}(j_t)\,|\,l_0 j_0 v_0) = \sum_{J\eta} (-1)^{j_0 - l_0 - J} (2J+1) \begin{Bmatrix} l & j & J \\ j_0 & l_0 & j_t \end{Bmatrix} \times (ljv|\,S^{(J\eta)}\,|\,l_0 j_0 v_0)\ . \tag{55}$$

The angular distribution is represented by the superposition of a set of functions that depend only on angular momentum quantum numbers of the incident and scattered electron and not on the collision dynamics,

$$\Theta(j_t\,;\, l_0 l_0' l l'\,;\, \vartheta) = (-1)^{j_t} (2j_t+1)\, \frac{(2l+1)^{1/2}(2l'+1)^{1/2}}{4\pi} \sum_k \begin{Bmatrix} l_0' & l_0 & k \\ l & l' & j_t \end{Bmatrix} \times (l0,\ l'0\,|\,l\,l'\,k\,0)\, P_k(\cos\vartheta)\, (l\,l'\,k\,0\,|\,l_0 0,\ l_0' 0)\ . \tag{56}$$

The values of the $6j$ coefficient and of the Wigner coefficients in this formula are obtained from tables[18]; the range of values of k is limited by the triangular relations. Equation (56) differs from Eq. (15) of FD by allowing two distinct values $(l_0,\ l_0')$ for the incidence orbital quantum number in place of a single j_r and by restricting to zero the value of the incidence quantum number m_r.

The differential scattering cross section equals the product of the dimenional factor $\pi/k^2_{j_0 v_0}$ which appears in (54) and of an average of the functions Θ for all relevant values of the quantum numbers, weighted by elements of the scattering matrix (55). The formula, analogous to Eq. (14) of FD, is

$$\frac{d\sigma(jv \leftarrow j_0 v_0)}{d\omega} = \pi k_{j_0 v_0}^{-2} (2j_0+1)^{-1} \sum_{l_0 l_0' l l' j_t} (2l_0+1)^{1/2}$$

$$\times (2l_0'+1)^{1/2}\ (ljv\,|\,\bar{S}(j_t)\,|\,l_0 j_0 v_0)$$

$$\times (l_0' j_0 v_0\,|\,\bar{S}(j_t)\,|\,l' jv)\ \Theta(j_t\,;\,l_0 l_0',\,ll';\,\vartheta)\ . \qquad (57)$$

Note that the unit matrix has not been subtracted formally from the S matrix in Eq. (57); this is unnecessary for scattering at angles $\theta \neq 0$. However, this subtraction might be useful for the elastic channel, i.e., for $(jv) = (j_0 v_0)$, to sort out which terms of (57) contribute significantly to the multiple summation.

The transformation formula (55) may be combined with other features of our approach to carry out the summation over J and η analytically and thus to eliminate these quantum numbers altogether. This simplification is made possible, at least in principle, by the fact that the scattering matrix $S^{(J\eta)}$ depends on J primarily through the transformation matrix $U_{j\Lambda}^{(lJ\eta)}$. The application is straightforward in the limiting case where $S^{(J\eta)}$ has the simple form (53), a bilinear function of U and $\tilde{U}$. When (53) is substituted in (58), we can use an identity of Racah algebra[19] which gives

$$\sum_{J\eta} (-1)^{j_0 - l_0 - J}\ (2J+1) \begin{Bmatrix} l & j & J \\ j_0 & l_0 & j_t \end{Bmatrix}\ U_{j\Lambda}^{(lJ\eta)}\ \tilde{U}_{\Lambda j_0}^{(l_0 J\eta)}$$

$$= (-1)^{2j_0+j+l_0+\Lambda} (2j+1)^{1/2} (2j_0+1)^{1/2} \begin{pmatrix} j_0 & j & j_t \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l_0 & j_t \\ \Lambda & -\Lambda & 0 \end{pmatrix} \frac{2}{1+\delta_{\Lambda 0}}\ . \qquad (58)$$

Thus we find

$$(ljv\,|\bar{S}(j_t)\,|l_0 j_0 v_0) = -\,i^{l_0 - l} (-1)^{2j_0+j} (2j+1)^{1/2} (2j_0+1)^{1/2} \begin{pmatrix} j_0 & j & j_t \\ 0 & 0 & 0 \end{pmatrix}$$

$$\times \sum_{\Lambda} (-1)^{l_0+\Lambda} \frac{2}{1+\delta_{\Lambda 0}} \begin{pmatrix} l & l_0 & j_t \\ \Lambda & -\Lambda & 0 \end{pmatrix} \int_0^{\infty} dR\, \chi_v(R) \sum_{\alpha} (C_{l\alpha}^{(\Lambda)}\, e^{2i\delta_{\alpha\Lambda}(R)}\, \tilde{C}_{\alpha l_0}^{(\Lambda)})\, \chi_{v_0}(R)\ . \qquad (59)$$

Note how the dependence on the rotational quantum numbers j and j_0 is factored out in Eq. (59). The $\sum_\Lambda$ in this formula involves only parameters defined in the body frame. Note also that the factor $2/(1+\delta_{\Lambda 0})$ can be removed by extending the sum over Λ to negative values of this quantum number; this extension of the sum applies throughout the theory whenever the parity quantum number η is not introduced explicitly as, e.g., in Refs. 6, 17, and 20.

The factorization of $\bar{S}(j_t)$ into rotation-dependent and body-frame contributions can be readily extended when long-range forces are present but confined to region A. However the separability of body-frame and laboratory-frame effects breaks down when the interaction extends into region B. In this event the matrix $B^{(J\eta)}$ is still a linear function of $U^{(lJ\eta)}$ but the inversion formula (49) does not yield the matrix $A^{(J\eta+)}$ readily as a linear function of $\tilde{U}^{(l_0 J\eta)}$. The search for taking maximum advantage of the quasiseparability of the two frames is pressed no further in this paper.

APPENDIX: TARGET MOLECULES IN NON-Σ^+ STATES

We extend here the treatment of Sec. II to a target diatomic molecule with quantum numbers $\bar{J}$, $\bar{\Lambda} \geq 0$ and $\bar{\eta} = \pm 1$. Its electronic (and vibrational) wave function will be indicated by $w_{\bar{\Lambda}}$ and will still be restricted to singlet states. Reflection on the body-frame coordinate plane $(x'z')$, represented by the operator σ_v, changes $w_{\bar{\Lambda}}$ into $(-1)^{\bar{\Lambda}} w_{-\bar{\Lambda}}$. Recall that $w_{\bar{\Lambda}}$ and $w_{-\bar{\Lambda}}$ are different but degenerate for $\bar{\Lambda} \neq 0$. For $\bar{\Lambda} = 0$, we have only nondegenerate states of definite parity, $\sigma_v w_0 = \bar{\eta}\, w_0$; we shall represent this situation by the general formula $\sigma_v w_{\bar{\Lambda}} = (-1)^{\bar{\Lambda}} w_{-\bar{\Lambda}}$, complemented by the convention $w_{-0} = \bar{\eta}\, w_0$. The rotational wave function of the target molecule is thus represented by

$$(w_{\bar{\Lambda}} D_{\bar{\Lambda}\bar{M}}^{(\bar{J})} + \bar{\eta}\, w_{-\bar{\Lambda}} D_{-\bar{\Lambda}\bar{M}}^{(\bar{J})}) \left[\frac{(2J+1)}{8\pi(1+\delta_{\bar{\Lambda}0})}\right]^{1/2}\ ; \qquad (A1)$$

its parity is $I = \bar{\eta}(-1)^{J}$. (The quantum number $\bar{J}$ was called j elsewhere in this paper.)

With this target wave function and the orbital wave function $Y_{lm}(\vartheta, \varphi)$ of the incident electron, we construct a laboratory-frame wave function analogous to (1):

$$\Phi_{JM}^{(l\bar{J}\bar{\Lambda}\bar{\eta})}(\hat{r}, \hat{R}) = \sum_m Y_{lm}(\vartheta, \varphi)\,[w_{\bar{\Lambda}} D_{\bar{\Lambda}, M-m}^{(\bar{J})}(\theta, \phi)$$

$$+\ \bar{\eta}\, w_{-\bar{\Lambda}} D_{-\Lambda, M-m}^{(\bar{J})}(\theta, \phi)] \left[\frac{(2\bar{J}+1)}{8\pi(1+\delta_{\bar{\Lambda}0})}\right]^{1/2}$$

$$\times (lm, \bar{J}M-m\,|\,l\bar{J}JM)\ . \qquad (A2)$$

The parity of this wave function under coordinate inversion is $I=\bar\eta(-1)^{l+\bar J}$. To transform to the body frame, substitute in (A2) the transformation formula of the incident-electron's wave function

$$Y_{lm}(\vartheta,\varphi)=\textstyle\sum_\lambda Y_{l\lambda}(\vartheta',\varphi')\,D^{(l)}_{\lambda m}(0,\theta,\phi)\,. \tag{A3}$$

The resulting product of D functions is then expanded by the reduction formula[21]

$$D^{(l)}_{\lambda m}(0,\theta,\phi)\,D^{(\bar J)}_{\bar\Lambda M-m}(0,\theta,\phi)=\sum_{J'}(l\,\lambda,\bar J\,\bar\Lambda|l\bar J J'\,\lambda+\bar\Lambda)\,D^{(J')}_{\lambda+\bar\Lambda M}(0,\,\theta,\,\phi)\,(l\bar J J' M|l\,m,\bar J M-m)\,. \tag{A4}$$

Substitution into (A2) permits us to carry out analytically the $\sum_m$ over a product of Wigner coefficients, yielding the orthonormality result $\delta_{J'J}$. Thus we find a representation of Φ_{JM} in terms of body-frame coordinates

$$\Phi^{(l\bar J\bar\Lambda\bar\eta)}_{JM}(\hat r,\hat R)=\sum_\lambda Y_{l\lambda}(\vartheta',\varphi')\,[w_{\bar\Lambda}(l\,\lambda,\bar J\,\bar\Lambda|l\bar J J\,\lambda+\bar\Lambda)\,D^{(J)}_{\lambda+\bar\Lambda,M}(0,\theta,\phi)+\bar\eta\,w_{-\bar\Lambda}(l\,\lambda,\bar J-\bar\Lambda|l\bar J J\,\lambda-\bar\Lambda)\,D^{(J)}_{\lambda-\bar\Lambda,M}(0,\theta,\phi)]$$
$$\times\left[\frac{(2\bar J+1)}{8\pi(1+\delta_{\bar\Lambda 0})}\right]^{1/2}. \tag{A5}$$

The remaining task consists of casting this equation in a form analogous to (6). To this end one may replace the index λ by $-\lambda$ in the second term in the brackets of (A5) and then use the identity

$$(l-\lambda,\bar J-\bar\Lambda|l\bar J J-\lambda-\Lambda)$$
$$=(-1)^{J-l-\bar J}(l\,\lambda,\bar J\,\bar\Lambda|l\bar J J\,\lambda+\bar\Lambda)\,,$$

whereby (A5) becomes

$$\Phi^{(l\bar J\bar\Lambda\bar\eta)}_{JM}$$
$$=\sum_\lambda\,[Y_{l\lambda}w_{\bar\Lambda}D^{(J)}_{\lambda+\bar\Lambda,M}+\bar\eta(-1)^{J-l-\bar J}\,Y_{l\,-\lambda}\,w_{-\bar\Lambda}\,D^{(J)}_{-\lambda-\bar\Lambda,M}]$$
$$\times(l\,\lambda,\bar J\,\bar\Lambda|l\bar J J\,\lambda+\bar\Lambda)\left[\frac{(2\bar J+1)}{8\pi(1+\delta_{\lambda 0}\,\delta_{\bar\Lambda 0})}\right]^{1/2}\cdot \tag{A6}$$

The normalization factor of this formula has been adjusted because the two terms of the sum coincide now only for $\lambda=\bar\Lambda=0$. The expression in the brackets has the desired structure of a rotational X wave function, with electronic factors $Y_{l\lambda}w_{\bar\Lambda}$ and

$$Y_{l\,-\lambda}\,w_{-\bar\Lambda}=(-1)^{\lambda+\bar\Lambda}\,\sigma_v Y_{l\lambda}\,w_{\bar\Lambda}\,,$$

with quantum number $\eta=\bar\eta(-1)^{J-l-\bar J}$ and with parity $I=\eta(-1)^J$. The quantum number Λ of the X function would be identified with $\lambda+\bar\Lambda$, were it not that Λ should be non-negative while $\lambda+\bar\Lambda$ may become negative for $\lambda<0$ and $l>\bar\Lambda$. This circumstance brings out the fact that the $\sum_\lambda$ in (A6) does not reduce to a simple $\sum_\Lambda$. When $l>\bar\Lambda>0$, the sum actually contains pairs of terms with the same value of Λ and different λ, namely, $\Lambda=\lambda+\bar\Lambda=|-\lambda'+\bar\Lambda|$. (Recall that, e.g., an excited molecule with a rydberg d electron and a Π ionic core has two types of π states, constructed with $d\sigma$ and $d\delta$.) Accordingly we define X functions labeled by λ and $\bar\Lambda$ rather than by Λ and $\bar\Lambda$,

$$X^{(l\lambda\bar\Lambda\eta)}_{JM}=(Y_{l\lambda}w_{\bar\Lambda}D^{(J)}_{\lambda+\bar\Lambda,M}+\eta\;Y_{l\,-\lambda}\,w_{-\bar\Lambda}\,D^{(J)}_{-\lambda-\bar\Lambda,M})$$
$$\times\left[\frac{(2J+1)}{8\pi(1+\delta_{\lambda 0}\,\delta_{\bar\Lambda 0})}\right]^{1/2}. \tag{A7}$$

With this definition (A6) takes the form

$$\Phi^{(l\bar J\bar\Lambda\bar\eta)}_{JM}=\textstyle\sum_\lambda X^{(l\lambda\bar\Lambda\bar\eta)}_{JM}\,\tilde U^{(lJ\eta,\bar\Lambda\bar\eta)}_{\lambda+\bar\Lambda\bar J}\,, \tag{A8}$$

which is the analog of (6). Sorting out the coefficients of (A6) and (A7) we see that the transformation matrix is given by

$$\tilde U^{(lJ\eta,\bar\Lambda\bar\eta)}_{\lambda+\bar\Lambda\bar J}$$
$$=(l\,\lambda,\bar J\,\bar\Lambda|l\bar J J\,\lambda+\bar\Lambda)\;\frac{(2\bar J+1)^{1/2}}{(2J+1)^{1/2}}\,\frac{1+\eta\,\bar\eta(-1)^{J-l-\bar J}}{2}$$
$$=(-1)^{J+\lambda-\bar J}(l-\lambda,J\,\lambda+\bar\Lambda|lJ\bar J\,\bar\Lambda)\frac{1+\eta\,\bar\eta(-1)^{J-l-\bar J}}{2}. \tag{A9}$$

This formula is equivalent to (7) in the special case where $\bar\Lambda=0$.

The present treatment is exact in the sense that it considers the quantum number of $\bar\eta$ of the target molecule explicitly. In practice for non-Σ target states, the energy difference of a pair of states differing only in $\bar\eta$ (i.e., the Λ doubling) is usually negligible, being proportional to $B^2/[E(\Lambda)-E(\Lambda')]$, where B is the rotational constant and Λ and Λ' are two different relevant electronic states.[22] Therefore, when dealing with experiments that resolve the target rotational states though not the Λ doubling, one must sum over the final state value of $\bar\eta$ and average over its initial-state value.

In homonuclear molecules the two Λ-doubled states have opposite nuclear permutation symmetry (symmetric or antisymmetric). This symmetry character is invariant in the collision as is also the parity of l. The over-all parity of the electron-molecule system $I=\eta(-1)^J$ is invariant of course. It follows then from (A9) that the parity $\bar{I}=\bar{\eta}(-1)^{\bar{J}}$ of the molecule alone is a collision invariant for homonuclear molecules. This means that in electron scattering by non-Σ homonuclear molecules, the rotational transition $\Delta\bar{J}=$ odd integer is *allowed*, but *only* with a simultaneous change of the quantum number $\bar{\eta}$. The occurrence of the $\Delta\bar{J}=$ odd-integer transition has been emphasized by Temkin and Faisal.[20]

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Angular Momentum Transfer in the Theory of Angular Distributions[*]

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The angular distribution of collision products is expressed as a sum of incoherent contributions corresponding to different magnitudes of the angular momentum $\vec{j}_t$ transferred to an unpolarized target. For targets with a characteristic internal reference frame (e.g., molecules) the coefficients of this sum are interpreted as generalized 2^{j_t}-pole polarizabilities of the target in its internal reference frame, analogous to the scalar and quadrupole polarizabilities that determine the Raman effect. The theory is developed in the context of photoionization, but is applicable to more general collision processes as well. It is illustrated by use and extension of diagrammatic techniques.

Theoretical expressions of the angular distribution of radiations from single-collision (or decay) processes have repeatedly been given in terms of the angular momentum $\vec{j}_t$ transferred from one reactant to another.[1] In view of the increasing role of angular-distribution studies in atomic and mo-