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Vibrational and rotational transitions in low-energy electron–diatomic-molecule collisions.*
I. Close-coupling theory in the moving body-fixed frame

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We present a vibrational-rotational close-coupling formulation of electron–diatomic-molecule scattering in a body-fixed frame, with the target molecular axis chosen to be the z axis. The resulting coupled differential equation is solved in the moving body-fixed frame throughout the entire region of space. The coupled differential equation and asymptotic boundary conditions are given in terms of definite parity, which are necessary for reducing the number of coupled channels. Procedures for evaluating cross sections employing this body-fixed formulation are outlined, thus rendering the present formulation directly applicable to numerical calculations. We discuss the advantages of the body-fixed formulation over a space-fixed formulation for introducing approximation schemes, for studying resonance scattering of vibrational transition, and for electron–heavy-molecule collisions. Aside from the formal equivalence between the two formulations, conditions are also discussed for obtaining identical results from them when a (finite) truncated basic set is used.

I. INTRODUCTION

The electron impact vibrational and rotational excitations of diatomic molecules are basic processes occurring in many gas discharge lasers providing the pumping mechanism directly and indirectly.[1] The vibrational and rotational transitions (excitation and deexcitation) in electron–diatomic-molecule collisions have also received much more attention in both atmospheric[2] physics and astrophysics.[3] Laboratory experimental data on electron-molecule collision cross sections are rather extensive[4,5] and much more developed than its theoretical counterpart.

Among the various theoretical approaches[5] that have been applied in the past are the classical binary encounter theory of Gryzinski,[6] plane-wave Born approximation (PWBA),[7] Glauber theory,[8] distorted-wave Born approximation (DWBA),[9] close-coupling theory,[10-12] fixed-[13] and adiabatic-nuclei theory,[14] and hybrid theory.[15] For resonance scattering, a Boomerang model[16] derived from the R matrix approach and the Feshbach approach[17] were suggested. At low energies, however, the classical theory and the Glauber theory are not appropriate. Only at very low energies close to threshold, PWBA is accurate because the scattering depends on the quadrupole moment interaction potential.[7] It is also extremely difficult to obtain rigorous solutions of R matrix and Feshbach approaches. Therefore, they must be considered more or less phenomenological approaches for the interpretation of experimental measurements.

The most general approach, from *ab initio* point of view, for studying the vibrational-rotational transitions of low-energy electron–diatomic-molecule collisions is the close-coupling theory which couples dynamically both the vibrational and the rotational state of the target molecule. Conventionally, this vibrational-rotational close-coupling theory is formulated in the space-fixed frame and is a natural extension of the well-known formulation of Arthurs and Dalgarno[10] for rotational close-coupling only.

In the space-fixed frame approach, one must include a large number of target state channels in the coupled differential equation when several vibrational states are considered. This situation becomes even worse for heavy target molecules due to the large number of rotational states in each vibrational manifold. Thus, most calculations performed on the electron-molecule collision cross sections with close-coupling approach, in the space-fixed frame, were limited to pure rotational transitions of light molecules.[5] Developments of reasonable approximation schemes within close-coupling theory which reduces the number of target state channels to a manageable level are both necessary and desirable.

The vibrational-rotational close-coupling theory can also be formulated in the moving body-fixed coordinate system, where the internuclear axis of the target molecule is chosen to be the z axis, and there appears several distinct advantages in such a formulation. First, while it is formally equivalent to that in the space-fixed coordinate system, the body-fixed formulation is more tractable than space-fixed formulation for introducing approximation schemes within the close-coupling theory.[18,19] Second, in the body-fixed formulation, the projections of incident electronic angular momentum onto the internuclear axis of target molecule are used instead of the rotational quantum numbers, and they are useful for describing the resonance electron-molecule scattering of vibrational transitions. Moreover, the body-fixed formulation has an advantage over that of space-fixed frame for electron–heavy-diatomic-molecule scattering as will be discussed later.

In this paper, we present a detailed vibrational-rotational (V-R) close-coupling formulation of electron–diatomic-molecule scattering in which the resulting coupled differential equation is solved in the body-fixed frame throughout the whole region. The coupled differential equation and asymptotic boundary conditions in the body-fixed frame are given for each parity. Considerations of parity are necessary for reducing the number of close-coupling channels. Procedures for the evaluation of V-R transition cross sections from the body-fixed transition and reactance matrix elements are also outlined, making this formulation directly amenable to numerical calculations. Since space-fixed and body-fixed formulation of close-coupling theory have their own merits depending on various circumstances, the conditions of obtaining identical results from both formulations when a finite truncated basis set is used are also discussed.

In the subsequent paper, the relation between the vibrational-rotational close-coupling theory and the hybrid theory of Chandra and Temkin will be studied. Within the framework of the body-fixed formulation developed in this paper, an improved approximation scheme is derived.

The arrangement of this paper is as follows. For clarity of explanation, we briefly review the V-R close-coupling theory of electron-molecule scattering in the space-fixed frame in Sec. II A. The V-R close-coupling formulation in the body-fixed frame is presented in Sec. II B. The discussions are given in Sec. III. Finally, a summary is made in Sec. IV.

II. FORMULATION

A. Review of V-R close-coupling theory in space-fixed frame

The total wave function and the Hamiltonian of the scattering system, i.e., the incident electron plus the target molecular system, are given by

$$\Psi_{Tvjm_j} = \Phi(\vec{r}_i', R)\Psi^{(+)}_{vjm_j}(\vec{r}, \vec{R}) , \tag{1}$$

$$H_T = H_0(\vec{r}_i', R) - \frac{\hbar^2}{2\mu_e}\nabla_r^2 - \frac{\hbar^2}{(M_A+M_B)}\sum_{i=1}^{n}\nabla_{r_i}\cdot\nabla_r - \frac{\hbar^2}{2\mu_N}\nabla_R^2 + V_T , \tag{2}$$

after the center-of-mass coordinates of the whole system have been separated out. Here, vjm_j are the initial vibrational-rotational quantum numbers and the projection of rotational quantum number, respectively, $\vec{r}, \vec{r}_i$ are the position vectors of the incident and the target electrons measured from the center of mass of the target nuclei. $\vec{R}$ is the internuclear vector and the prime denotes the coordinates with respect to a coordinate system in which the internuclear axis is chosen to be the z axis. μ_e and μ_N are the appropriate reduced masses:

$$\mu_e = \frac{m(M_A+M_B)}{M_A+M_B+m} \simeq m, \quad \mu_N = \frac{M_A M_B}{M_A+M_B} . \tag{3}$$

M_A, M_B, and m are the masses of nuclei A and B and the electron, respectively. V_T is given by

$$V_T = \sum_{i=1}^{n}\frac{e^2}{|\vec{r}-\vec{r}_i|} - \frac{Z_A e^2}{|\vec{r}-[M_B/(M_A+M_B)]\vec{R}|} - \frac{Z_B e^2}{|\vec{r}+[M_A/(M_A+M_B)]\vec{R}|} . \tag{4}$$

n is the number of electrons in the target molecule, and $Z_A e, Z_B e$ are the nuclear charges of nuclei A and B (cf. Fig. 1). $H_0(\vec{r}_i', R)$ is the Hamiltonian of the target molecule with the nuclei fixed at a distance R apart, and $\Phi(\vec{r}_i', R)$ is the MO-LCAO solution,[20] that is,

$$H_0(\vec{r}_i', R)\Phi(\vec{r}_i', R) \simeq \epsilon_0(R)\Phi(\vec{r}_i', R) , \tag{5}$$

with

$$H_0(\vec{r}_i', R) = -\frac{\hbar^2}{2\mu_e}\sum_{i=1}^{n}\nabla_{r_i}^2 - \frac{\hbar^2}{2(M_A+M_B)}\sum_{i\neq j}^{n}\nabla_{r_i}\circ\nabla_{r_j} + V_0(\vec{r}_i', R) , \tag{5'}$$

of the ground electronic state of the target molecule.[21]

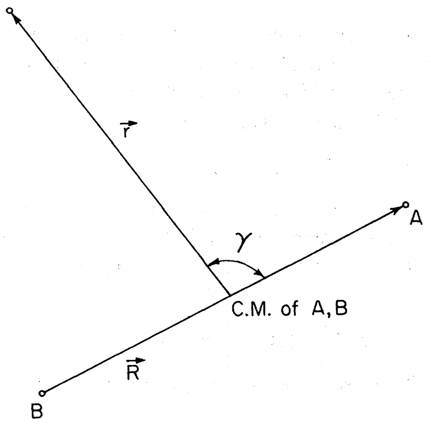

FIG. 1. Geometry of the scattering between an electron and a diatomic molecule.

[In the present paper, we confine ourselves to ${}^1\Sigma$ state of the target molecule. The cross ∇ terms in Eqs. (2) and (5′) are usually neglected.] Ψ_{Tvjm_j} satisfies the Schrödinger equation,

$$H_T\Psi_{Tvjm_j}=E\Psi_{Tvjm_j}\,; \tag{6}$$

E is the total energy of the system. Multiplying the above equation by $\Phi^*(\vec{r}_i',R)$ on the left and integrating over target electronic coordinates $\vec{r}_i'$, we have

$$H\Psi^{(+)}_{vjm_j}(\vec{r},\vec{R})=E\Psi^{(+)}_{vjm_j}(\vec{r},\vec{R}) \tag{7}$$

using the Born-Oppenheimer approximation,

$$-\frac{\hbar^2}{2\mu_N}[\nabla_R^2\Phi(\vec{r}_i',R)]\Psi^{(+)}_{vjm_j}(\vec{r},\vec{R})\simeq 0\,,$$

$$-\frac{\hbar^2}{\mu_N}\nabla_R\Phi(\vec{r}_i',R)\circ\nabla_R\Psi^{(+)}_{vjm_j}(\vec{r},\vec{R})\simeq 0\,.$$

Here,

$$H=-\frac{\hbar^2}{2\mu_e}\nabla_r^2-\frac{\hbar^2}{2\mu_N}\nabla_R^2+V(r,R,\gamma)+\epsilon_0(R) \tag{8}$$

and

$$V(r,R,\gamma)=(\Phi|V_T|\Phi)_{r_i}\,. \tag{9}$$

The subscript r_i indicates the integration over $\vec{r}_i'$, and $\cos\gamma=\vec{r}\cdot\vec{R}/rR$.

We would like to mention about our notation of electronic wave function $\Phi(\vec{r}_i',R)$ of target molecule. If one defines the wave function $\tilde{\Phi}(\vec{r}_i,\vec{R})$ in the space-fixed coordinate system from $\Phi(\vec{r}_i',R)=\tilde{\Phi}(\vec{r}_i,\vec{R})$, then the meaning of $\nabla_R\tilde{\Phi}(\vec{r}_i,\vec{R})$ is clear. But in a specific primed coordinate system defined by Euler angles $(\phi_R,\theta_R,0)$,

$$\nabla_R\Phi(\vec{r}_i',R)=\left(\frac{1}{R}\vec{R}\,\frac{\partial}{\partial R}+\frac{i}{\hbar}\,\frac{1}{R^2}\vec{R}\times\vec{L}^{(e)}\right)\Phi(\vec{r}_i',R)$$

for Σ state $(L^{(e)}_{z'}=0)$. This is not trivial. Here $\vec{L}^{(e)}$ is the total electronic angular momentum of target molecule and thus, for example,

$$L^{(e)}_{x'}=\frac{\hbar}{i}\sum_{i=1}^{n}\left(y_i'\,\frac{\partial}{\partial z_i'}-z_i'\,\frac{\partial}{\partial y_i'}\right),$$

$$L^{(e)}_{z'}=\frac{\hbar}{i}\sum_{i=1}^{n}\left(x_i'\,\frac{\partial}{\partial y_i'}-y_i'\,\frac{\partial}{\partial x_i'}\right).$$

$(\theta_R,\phi_R)\equiv(\hat{R})$ are the polar angles of $\vec{R}$ in the space-fixed coordinate system. The reason why we use the present notation of wave functions is that MO-LCAO wave functions are essentially given in the primed coordinate system.

So far we have neglected the antisymmetry of the incident and the target electrons, i.e., the coordinates $\vec{r}$ and $\vec{r}_i$ in Ψ_{Tvjm_j}. In practice, one takes into account of this exchange effect by including an appropriate local exchange potential in $V(r,R,\gamma)$. One also includes an additional polarization potential due to induced polarizabilities in $V(r,R,\gamma)$.

The close-coupling formulation is concerned with solving Eq. (7), where $\Psi^{(+)}_{vjm_j}(\vec{r},\vec{R})$ is given by[11]

$$\Psi^{(+)}_{vjm_j}(\vec{r},\vec{R})=\frac{4\pi}{k_{vj}r}\sum_{\substack{v'j'l'l\\JM}}g^J_{v'j'l',vjl}(r)\phi_{v'j'}(R)\,Y^{l'j'}_{JM}(\hat{r},\hat{R})\langle lM-m_j\,jm_j|JM\rangle Y^*_{lM-m_j}(\hat{k}_{vj})$$

$$\underset{r\to\infty}{\sim}e^{i\vec{k}_{vj}\cdot\vec{r}}\phi_{vj}(R)Y_{jm_j}(\hat{R})+\sum_{v'j'm_j'}\frac{1}{r}e^{ik_{v'j'}r}\phi_{v'j'}(R)Y_{j'm_j'}(\hat{R})f_{v'j'm_j',vjm_j}(\hat{r})\,. \tag{10}$$

Here, $\vec{k}_{vj}$ is the incident electron momentum and

$$k^2_{v'j'}=\frac{2\mu_e}{\hbar^2}(E-\epsilon_{v'j'})\,. \tag{11}$$

$\phi_{v'j'}(R)$ and $\epsilon_{v'j'}$ are the radial part of V-R wave function $[\phi_{v'j'}(R)Y_{j'm_j'}(\hat{R})]$ and V-R energy level of the target molecule, respectively. l' is the incident electronic angular momentum relative to the center of mass of the target molecule and J is that of the (total) electron plus target molecule, and

$$Y^{l'j'}_{JM}(\hat{r},\hat{R})=\sum_{m_1m_2}\langle l'm_1j'm_2|JM\rangle Y_{l'm_1}(\hat{r})Y_{j'm_2}(\hat{R})\,. \tag{12}$$

$\langle l'm_1j'm_2|JM\rangle$ is the Clebsch-Gordan coefficient.[22]

Substituting the first part of Eq. (10) into Eq. (7) projected onto appropriate target molecular basis and from the last part of Eq. (10), we have

$$\left(\frac{d^2}{dr^2}-\frac{l'(l'+1)}{r^2}+k^2_{v'j'}\right)g^J_{v'j'l',vjl}(r)=\frac{2\mu_e}{\hbar^2}\sum_{v''j''l''}V^J_{v'j'l',v''j''l''}(r)g^J_{v''j''l'',vjl}(r) \tag{13}$$

and

$$g^J_{v'j'l',vjl}(r)\underset{r\to\infty}{\sim}i^{l'}\left(\frac{k_{vj}}{k_{v'j'}}\right)^{1/2}[\delta_{v'v}\,\delta_{j'j}\delta_{l'l}F_{v'j'l'}(r)+T^J_{v'j'l',vjl}(G_{v'j'l'}(r)+iF_{v'j'l'}(r))]\,. \tag{14}$$

Here,

$$V^{J}_{v'j'l',v''j''l''}(r) = \int R^2 dR\, \phi_{v'j'}(R)\phi_{v''j''}(R) \int d\hat{R}\, d\hat{r}\, Y^{l'j'*}_{JM}(\hat{r},\hat{R})V(r,R,\gamma)Y^{l''j''}_{JM}(\hat{r},\hat{R})$$

$$= (-1)^{j'+j''+J}[(2l'+1)(2l''+1)(2j'+1)(2j''+1)]^{1/2}$$

$$\times \sum_{\lambda} \frac{1}{2\lambda+1} \langle j'oj''o|\lambda o\rangle \langle l'ol''o|\lambda o\rangle \begin{Bmatrix} l' & j' & J \\ j'' & l'' & \lambda \end{Bmatrix} V^{\lambda}_{v'j',v''j''}(r)\,. \tag{15}$$

$$\begin{Bmatrix} l' & j' & J \\ j'' & l'' & \lambda \end{Bmatrix}$$

is the 6-j symbol[22] and

$$V^{\lambda}_{v'j',v''j''}(r) = \int R^2 dR\, \phi_{v'j'}(R)V_{\lambda}(r,R)\phi_{v''j''}(R)\,. \tag{16}$$

$V_{\lambda}(r,R)$ is the λth harmonic component of $V(r,R,\gamma)$, i.e.,

$$V(r,R,\gamma) = \sum_{\lambda} V_{\lambda}(r,R)P_{\lambda}(\cos\gamma) \tag{17}$$

and

$$F_{v'j'l'}(r) = k_{v'j'}rj_{l'}(k_{v'j'}r)\,,$$
$$G_{v'j'l'}(r) = -k_{v'j'}rn_{l'}(k_{v'j'}r)\,, \tag{18}$$

with $j_{l'}$ and $n_{l'}$ being the spherical Bessel and Neumann functions, respectively.

$T^{J}_{v'j'l',vjl}$ is the transition matrix element in the total angular momentum representation. One would employ (real) reactance matrix boundary condition and obtain transition matrix from reactance matrix [see Sec. IIB]. $f_{v'j'm'_j,vjm_j}(\hat{r})$ is the scattering amplitude when $\vec{k}_{vj}$ is chosen to be the z axis and one substitutes the scattering angles θ, ϕ for $\hat{r}$. Then,

$$f_{v'j'm'_j,vjm_j}(\theta,\phi) = \left(\frac{4\pi}{k_{vj}k_{v'j'}}\right)^{1/2} \sum_{Jl'l} (2l+1)^{1/2} \langle l'm_j - m'_j j'm'_j | Jm_j\rangle \times \langle lojm_j | Jm_j\rangle T^{J}_{v'j'l',vjl} \times Y_{l'm_j-m'_j}(\theta,\phi)\,. \tag{19}$$

The differential, integral, and momentum transfer cross sections for the transition $vj \rightarrow v'j'$ are given by

$$\frac{d\sigma_{vj\rightarrow v'j'}}{d\Omega}(\theta) = \frac{k_{v'j'}}{k_{vj}} \frac{1}{2j+1} \sum_{m_j m'_j} |f_{v'j'm'_j,vjm_j}(\theta,\phi)|^2\,, \tag{20}$$

$$\sigma_{vj\rightarrow v'j'} = \int d\Omega\, \frac{d\sigma_{vj\rightarrow v'j'}}{d\Omega}(\theta) = \frac{4\pi}{k^2_{vj}} \frac{1}{2j+1} \sum_{Jl'l} (2J+1)|T^{J}_{v'j'l',vjl}|^2\,, \tag{21}$$

$$\sigma^{(M)}_{vj\rightarrow v'j'} = \int d\Omega (1-\cos\theta) \frac{d\sigma_{vj\rightarrow v'j'}}{d\Omega}(\theta)\,. \tag{22}$$

It is known that the parity $(-1)^{J+l+j}$ is conserved, i.e., $(-1)^{J+l+j} = (-1)^{J+l'+j'} = (-1)^{J+l''+j''}$ in Eqs. (14) and (15) and that, from the symmetry of reactance matrix, we obtain[11] $T^{J}_{v'j'l',vjl} = (-1)^{l'+l} \times T^{J}_{vjl,v'j'l'}$. Therefore, the principle of detailed balance

$$(2j+1)\,k^2_{vj}\sigma_{vj\rightarrow v'j'} = (2j'+1)\,k^2_{v'j'}\sigma_{v'j'\rightarrow vj} \tag{23}$$

is satisfied in the above formulation.

This is an extension of the Arthurs-Dalgarno formulation,[10] who first proposed a similar formulation as above for pure rotational transitions of atom-diatom scattering with the assumption that the target molecule is a rigid rotator. The above formulation, in principle, gives convergent cross sections for V-R transitions when one includes a sufficiently large number of V-R basis states. The number of channels in the coupled differential equations [Eq. (13)] for a given J is large in that case.

B. V-R close-coupling theory in body-fixed frame

In this section, we present the formulation of the V-R close-coupling theory in the body-fixed coordinate system directly amenable to numerical calculations.

We define the body fixed $(x'y'z')$ coordinate system moving with electron–diatomic-molecular plane as follows[23]:

$$\hat{z}' = \vec{R}/R\,,\quad \hat{y}' = (\vec{R}\times\vec{r})/|\vec{R}\times\vec{r}|\,,\quad \hat{x}' = \hat{y}'\times\hat{z}'\,. \tag{24}$$

We note that this coordinate system is different from the "body-fixed" coordinate system customarily used in the study of atom-diatom scattering where $\hat{z}' = \vec{r}/r$. Thus the coupled differential equation and the asymptotic boundary conditions of the present formulation are different, again, from those of atom-molecule scattering.[24,25]

The formulation of V-R close-coupling theory in the body-fixed frame is obtained from that of the space-fixed frame by changing the angular basis functions $Y_{JM}^{lj}(\hat{r},\hat{R})$ of Sec. II A to

$$D_{JM}^{lm}(\theta_R,\phi_R,\gamma,\chi)=\left(\frac{2J+1}{4\pi}\right)^{1/2}\times D_{Mm}^{J*}(\phi_R,\theta_R,\chi)Y_{lm}(\gamma,0)\,. \tag{25}$$

$D_{Mm}^{J}(\phi_R,\theta_R,\chi)$ is the rotation matrix element[26] and ϕ_R,θ_R,χ are the Euler angles of rotation from space-fixed frame to body-fixed frame ($\cos\gamma=\vec{R}\cdot\vec{r}/Rr$). From the following property of the rotation matrix,

$$Y_{JM}^{lj}(\hat{r},\hat{R})=\sum_m D_{Mm}^{J*}(\phi_R,\theta_R,\chi)Y_{Jm}^{lj}(\hat{r}',\hat{R}')\,, \tag{26}$$

we have

$$Y_{JM}^{lj}(\hat{r},\hat{R})=\sum_m U_{jm}^{Jl}D_{JM}^{lm}(\theta_R,\phi_R,\gamma,\chi) \tag{27}$$

with

$$U_{jm}^{Jl}=\left(\frac{2j+1}{2J+1}\right)^{1/2}\langle lmj0|Jm\rangle\,. \tag{28}$$

Here, primes indicate the polar angles with respect to the body-fixed frame. It is seen that

$$\begin{aligned}&\sum_m U_{j'm}^{Jl}U_{jm}^{Jl}=\delta_{j'j}\,,\\&\sum_j U_{jm'}^{Jl}U_{jm}^{Jl}=\delta_{m'm}\,.\end{aligned} \tag{29}$$

The angular basis functions of space-fixed and body-fixed frame are the eigenfunctions of $\vec{j}^{\,2}$ and $\vec{R}\cdot\vec{l}/R=\vec{R}\cdot\vec{J}/R$, respectively, in addition to $\vec{l}^{\,2}$, $\vec{J}^{\,2}$, and J_z. j' and m' are incompatible quantum numbers, since $[\vec{j}^{\,2},\vec{R}\cdot\vec{l}/R]\neq 0$. Notice that $\vec{j}=(\hbar/i)\vec{R}\times\nabla_R$, $\vec{l}=(\hbar/i)\vec{r}\times\nabla_r$ and $\vec{J}=\vec{l}+\vec{j}$. Using Eqs. (27)–(29), $\Psi_{vjm_j}^{(+)}$ in Eq. (10) can now be rewritten as

$$\Psi_{vjm_j}^{(+)}=\frac{4\pi}{k_{vj}r}\sum_{\substack{v'l'lJM\\m'm''m}}\bar{g}_{v'l'm',vlm}^{J}(r)\bar{\phi}_{v'l'm',m''}^{J}(R)\times D_{JM}^{l'm''}(\theta_R,\phi_R,\gamma,\chi)\,Y_{ljm_j}^{JMm}(\hat{k}_{vj})\,. \tag{30}$$

Here,

$$\bar{g}_{v'l'm',vlm}^{J}(r)=\sum_{j'j}U_{j'm'}^{Jl'}g_{v'j'l',vjl}^{J}(r)\,U_{jm}^{Jl}\,, \tag{31}$$

$$\bar{\phi}_{v'l'm',m''}^{J}(R)=\sum_{j'}U_{j'm'}^{Jl'}\phi_{v'j'}(R)\,U_{j'm''}^{Jl'}\,, \tag{32}$$

$$Y_{ljm_j}^{JMm}(\hat{k}_{vj})=U_{jm}^{Jl}\langle lM-m_j\,jm_j|JM\rangle\,Y_{lM-m_j}^{*}(\hat{k}_{vj})\,. \tag{33}$$

Substituting Eq. (30) into the Schrödinger equation [Eq. (7)] and projecting onto appropriate basis functions, we have

$$\left(\frac{d^2}{dr^2}-\frac{l'(l'+1)}{r^2}\right)\bar{g}_{v'l'm',vlm}^{J}(r)=\frac{2\mu_e}{\hbar^2}\sum_{v''l''m''}[\bar{V}_{v'l'm',v''l''m''}^{J}(r)-\delta_{v'v''}\delta_{l'l''}\times\bar{\epsilon}_{v'l'm',m''}^{J}]\bar{g}_{v''l''m'',vlm}^{J}(r)\,, \tag{34}$$

with

$$\bar{V}_{v'l'm',v''l''m''}^{J}(r)=\sum_{j'j''}U_{j'm'}^{Jl'}V_{v'j'l',v''j''l''}^{J}(r)\,U_{j''m''}^{Jl''}\,, \tag{35}$$

$$\frac{2\mu_e}{\hbar^2}\bar{\epsilon}_{v'l'm',m''}^{J}=\sum_{j'}U_{j'm'}^{Jl'}\,k_{v'j'}^2U_{j'm''}^{Jl'}\,, \tag{36}$$

$$(|m'|\leq l',|m''|\leq l'',|m|\leq l,|m'|,|m''|,|m|\leq J)\,.$$

In deriving Eq. (34), we have used the following relations:

$$\left[-\frac{\hbar^2}{2\mu_N}\frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right)+\frac{j'(j'+1)\hbar^2}{2\mu_NR^2}+\epsilon_0(R)\right]\times\phi_{v'j'}(R)=\epsilon_{v'j'}\phi_{v'j'}(R)\,, \tag{37}$$

$$\int R^2dR\,\phi_{v'j'}(R)\phi_{v''j'}(R)=\delta_{v'v''}\,, \tag{38}$$

$$\int\sin\theta_R\sin\gamma\,d\theta_R\,d\gamma\,d\phi_R\,d\chi\times D_{JM}^{lm*}(\theta_R,\phi_R,\gamma,\chi)\,\vec{j}^{\,2}D_{JM}^{lm'}(\theta_R,\phi_R,\gamma,\chi)=\sum_j j(j+1)U_{jm}^{Jl}U_{jm'}^{Jl}\,. \tag{39}$$

The right-hand side of Eq. (39) is known to vanish unless $m-m'=0,\pm 1$ and it should be noted that $\bar{V}_{v'l'm',v''l''m''}^{J}(r)$ is not diagonal with respect to m indices due to the j dependences in $\phi_{vj}(R)$.[27,28]

Equation (34) is the coupled differential equation in the body-fixed frame and $\bar{g}_{v'l'm',vlm}^{J}(r)$ has the following asymptotic behavior:

$$\bar{g}_{v'l'm',vlm}^{J}(r)\underset{r\to\infty}{\sim}i^{l'}\sum_{m_1m_2}\Lambda_{v'l'm',m_1}^{-J}\Big\{\delta_{v'v}\,\delta_{l'l}\,\bar{F}_{v'l'm_1,m_2}^{J}(r)+\sum_{m_3}[\,\bar{G}_{v'l'm_1,m_3}^{J}(r)+i\bar{F}_{v'l'm_1,m_3}^{J}(r)]\,\bar{T}_{v'l'm_3,vlm_2}^{J}\Big\}\Lambda_{vlm_2,m}^{+J}\,, \tag{40}$$

or

$$\bar{g}'^{J}_{v'l'm',vlm}(r)=\sum_{m''}\bar{g}^{J}_{v'l'm',vlm''}(r)\,\Lambda^{-J}_{vlm'',m}$$

$$\underset{r\to\infty}{\sim}\; i^{l'}\sum_{m_1}\Lambda^{-J}_{v'l'm',m_1}\Big\{\delta_{v'v}\,\delta_{l'l}\,\bar{F}^{J}_{v'l'm_1,m}(r)+\sum_{m_3}\big[\bar{G}^{J}_{v'l'm_1,m_3}(r)+i\bar{F}^{J}_{v'l'm_1,m_3}(r)\big]\,\bar{T}^{J}_{v'l'm_3,vlm}\Big\}. \tag{41}$$

Here,

$$\Lambda^{\pm J}_{v'l'm',m''}=\sum_{j'}U^{Jl'}_{j'm'}\,k^{\pm 1/2}_{v'j'}\,U^{Jl'}_{j'm''}\,, \tag{42}$$

$$\begin{pmatrix}\bar{F}^{J}_{v'l'm',m''}(r)\\ \bar{G}^{J}_{v'l'm',m''}(r)\end{pmatrix}=\sum_{j'}U^{Jl'}_{j'm'}\begin{pmatrix}F_{v'j'l'}(r)\\ G_{v'j'l'}(r)\end{pmatrix}U^{Jl'}_{j'm''}\,, \tag{43}$$

$$\bar{T}^{J}_{v'l'm',vlm}=\sum_{j'j}U^{Jl'}_{j'm'}\,T^{J}_{v'j'l',vjl}\,U^{Jl}_{jm}\,. \tag{44}$$

$\bar{g}'^{J}_{v'l'm',vlm}(r)$ is seen to be a solution of the coupled differential equation [Eq. (34)] again.

$\bar{T}^{J}_{v'l'm',vlm}$ is considered as the transition matrix element in the body-fixed frame and $\bar{T}^{J}_{v'l'm',vlm}=(-1)^{l'+l}\,\bar{T}^{J}_{vlm,v'l'm'}$. Since the parity $(-1)^{J+l'+j'}$ is conserved in the space-fixed close-coupling theory, we have

$$\begin{aligned}\bar{V}^{J}_{v'l'm',vlm}(r)&=\bar{V}^{J}_{v'l'-m',vl-m}(r)\,,\\ \bar{g}^{J}_{v'l'm',vlm}(r)&=\bar{g}^{J}_{v'l'-m',vl-m}(r)\,,\\ \bar{T}^{J}_{v'l'm',vlm}&=\bar{T}^{J}_{v'l'-m',vl-m}\,,\end{aligned} \tag{45}$$

from Eqs. (35), (31), and (44).

Even without parity considerations, we obtain

$$\begin{aligned}\bar{\epsilon}^{J}_{v'l'm',m''}&=\bar{\epsilon}^{J}_{v'l'-m',-m''}\,,\\ \Lambda^{\pm J}_{v'l'm',m''}&=\Lambda^{\pm J}_{v'l'-m',-m''}\,,\\ \bar{F}^{J}_{v'l'm',m''}(r)&=\bar{F}^{J}_{v'l'-m',-m''}(r)\,,\\ \bar{G}^{J}_{v'l'm',m''}(r)&=\bar{G}^{J}_{v'l'-m',-m''}(r)\,.\end{aligned} \tag{46}$$

We now define the parity wave function, $\bar{g}'^{J(\pm)}_{v'l'm',vlm}(r)$, and other related quantities as follows

$$\begin{aligned}\bar{g}'^{J(\pm)}_{v'l'm',vlm}(r)&=\tfrac{1}{2}\{\bar{g}'^{J}_{v'l'm',vlm}(r)\pm\bar{g}'^{J}_{v'l'-m',vlm}(r)\}\,,\\ \bar{T}^{J(\pm)}_{v'l'm',vlm}&=\tfrac{1}{2}\{\bar{T}^{J}_{v'l'm',vlm}\pm\bar{T}^{J}_{v'l'-m',vlm}\}\,,\\ \bar{V}^{J(\pm)}_{v'l'm',v''l''m''}(r)&=\tfrac{1}{2}\{\bar{V}^{J}_{v'l'm',v''l''m''}(r)\\ &\qquad\pm\bar{V}^{J}_{v'l'-m',v''l''m''}(r)\}\,,\\ \bar{\epsilon}^{J(\pm)}_{v'l'm',m''}&=\tfrac{1}{2}\{\bar{\epsilon}^{J}_{v'l'm',m''}\pm\bar{\epsilon}^{J}_{v'l'-m',m''}\}\,,\\ \Lambda^{-J(\pm)}_{v'l'm',m''}&=\tfrac{1}{2}\{\Lambda^{-J}_{v'l'm',m''}\pm\Lambda^{-J}_{v'l'-m',m''}\}\,,\\ \bar{F}^{J(\pm)}_{v'l'm',m''}(r)&=\tfrac{1}{2}\{\bar{F}^{J}_{v'l'm',m''}(r)\pm\bar{F}^{J}_{v'l'-m',m''}(r)\}\,,\\ \bar{G}^{J(\pm)}_{v'l'm',m''}(r)&=\tfrac{1}{2}\{\bar{G}^{J}_{v'l'm',m''}(r)\pm\bar{G}^{J}_{v'l'-m',m''}(r)\}\,.\end{aligned} \tag{47}$$

Then, they have the following properties:

$$\begin{aligned}\bar{g}'^{J(\pm)}_{v'l'm',vlm}(r)&=\pm\bar{g}'^{J(\pm)}_{v'l'-m',vlm}(r)=\pm\bar{g}'^{J(\pm)}_{v'l'm',vl-m}(r)\,,\\ \bar{T}^{J(\pm)}_{v'l'm',vlm}&=\pm\bar{T}^{J(\pm)}_{v'l'-m',vlm}=\pm\bar{T}^{J(\pm)}_{v'l'm',vl-m}\,,\\ \bar{V}^{J(\pm)}_{v'l'm',v''l''m''}(r)&=\pm\bar{V}^{J(\pm)}_{v'l'-m',v''l''m''}(r)\\ &=\pm\bar{V}^{J(\pm)}_{v'l'm',v''l''-m''}(r)\,,\\ \bar{\epsilon}^{J(\pm)}_{v'l'm',m''}&=\pm\bar{\epsilon}^{J(\pm)}_{v'l'-m',m''}=\pm\bar{\epsilon}^{J(\pm)}_{v'l'm',-m''}\,;\end{aligned} \tag{48}$$

and

$$\begin{aligned}\bar{g}'^{J}_{v'l'm',vlm}(r)&=\bar{g}'^{J(+)}_{v'l'm',vlm}(r)+\bar{g}'^{J(-)}_{v'l'm',vlm}(r)\,,\\ \bar{T}^{J}_{v'l'm',vlm}&=\bar{T}^{J(+)}_{v'l'm',vlm}+\bar{T}^{J(-)}_{v'l'm',vlm}\,,\\ \bar{V}^{J}_{v'l'm',v''l''m''}(r)&=\bar{V}^{J(+)}_{v'l'm',v''l''m''}(r)\\ &\qquad+\bar{V}^{J(-)}_{v'l'm',v''l''m''}(r)\,,\\ \bar{\epsilon}^{J}_{v'l'm',m''}&=\bar{\epsilon}^{J(+)}_{v'l'm',m''}+\bar{\epsilon}^{J(-)}_{v'l'm',m''}\,.\end{aligned} \tag{49}$$

The same relations hold for $\Lambda^{-J(\pm)}_{v'l'm',m''}$, $\bar{F}^{J(\pm)}_{v'l'm',m''}(r)$, and $\bar{G}^{J(\pm)}_{v'l'm',m''}(r)$ as $\bar{\epsilon}^{J(\pm)}_{v'l'm',m''}$ in Eqs. (48) and (49).

From Eqs. (31), (35), (36), (42), (43), and (44), one infers that (±), here, corresponds to the parity $(-1)^{J+l'+j'}=(\pm)$ of space-fixed close-coupling formulations of Sec. II A. The parity wave function, $\bar{g}'^{J(\pm)}_{v'l'm',vlm}(r)$, is again a solution of the coupled differential equation [Eq. (34)] as seen from Eqs. (45) and (46), but it is convenient to rewrite that equation as

$$\begin{aligned}\left(\frac{d^2}{dr^2}-\frac{l'(l'+1)}{r^2}\right)\bar{g}'^{J(\pm)}_{v'l'm',vlm}(r)&=\frac{2\mu_e}{\hbar^2}\sum_{v''l''m''}\big(\bar{V}^{J(\pm)}_{v'l'm',v''l''m''}(r)-\delta_{v'v''}\delta_{l'l''}\bar{\epsilon}^{J(\pm)}_{v'l'm',m''}\big)\bar{g}'^{J(\pm)}_{v''l''m'',vlm}(r)\\ &=\frac{2\mu_e}{\hbar^2}\sum_{v''l''m''}^{(\pm)}\big(\bar{V}^{J(\pm)}_{v'l'm',v''l''m''}(r)-\delta_{v'v''}\delta_{l'l''}\bar{\epsilon}^{J(\pm)}_{v'l'm',m''}\big)\bar{g}'^{J(\pm)}_{v''l''m'',vlm}(r)\,.\end{aligned} \tag{50}$$

Here,

$$\sum_{m''}^{(\pm)} A_{m''}^{(\pm)} B_{m''}^{(\pm)} = \begin{cases} A_0^{(+)} B_0^{(+)} + 2 \sum_{m''>0} A_{m''}^{(+)} B_{m''}^{(+)}, & \text{for } (+) \text{ parity} \\ 2 \sum_{m''>0} A_{m''}^{(-)} B_{m''}^{(-)}, & \text{for } (-) \text{ parity}. \end{cases} \tag{51}$$

The asymptotic boundary condition is proved to be

$$\begin{aligned} \bar{g}'^{J(\pm)}_{v'l'm',vlm}(r) &\underset{r\to\infty}{\sim} i^{l'} \sum_{m_1} \Lambda^{-J(\pm)}_{v'l'm',m_1} \left\{ \delta_{v'v}\, \delta_{l'l} \bar{F}^{J(\pm)}_{v'l'm_1,m}(r) + \sum_{m_3} [\bar{G}^{J(\pm)}_{v'l'm_1,m_3}(r) + i\bar{F}^{J(\pm)}_{v'l'm_1,m_3}(r)]\, \bar{T}^{J(\pm)}_{v'l'm_3,vlm} \right\} \\ &= i^{l'} \sum_{m_1}^{(\pm)} \Lambda^{-J(\pm)}_{v'l'm',m_1} \left\{ \delta_{v'v}\, \delta_{l'l} \bar{F}^{J(\pm)}_{v'l'm_1,m}(r) + \sum_{m_3}^{(\pm)} [\bar{G}^{J(\pm)}_{v'l'm_1,m_3}(r) + i\bar{F}^{J(\pm)}_{v'l'm_1,m_3}(r)]\, \bar{T}^{J(\pm)}_{v'l'm_3,vlm} \right\}. \end{aligned} \tag{52}$$

From Eqs. (48)–(52), it is sufficient to consider the non-negative and positive m' indices of rows and columns in the quantities defined above for (+) and (–) parity, respectively. Therefore, if one employs the parity wave function, $\bar{g}'^{J(\pm)}_{v'l'm',vlm}(r)$, the number of channels of the coupled differential equation is considerably reduced.

In the present body-fixed formulation, we solve the coupled differential equation of the body-fixed frame [Eq. (50)] up to the asymptotic region where the interaction potential between the incident electron and the target molecule is negligible and match the solution with the asymptotic boundary condition of Eq. (52) in that region, evaluating $\bar{T}^{J(\pm)}_{v'l'm',vlm}$ for $m', m \geq 0$ or $m', m > 0$ depending on (±) parity, by appropriate numerical procedures. We then find the body-fixed transition matrix elements, $\bar{T}^{J}_{v'l'm',vlm}$, from the second of Eq. (49). Since we have already obtained the expressions of all cross sections in terms of space-fixed transition matrix elements, $T^{J}_{v'j'l',vjl}$, it is simpler to evaluate the cross sections through these matrix elements without further analysis. They are obtained from the body-fixed transition matrix elements as follows:

$$T^{J}_{v'j'l',vjl} = \sum_{m'm} U^{Jl'}_{j'm'}\, \bar{T}^{J}_{v'l'm',vlm} U^{Jl}_{jm} \tag{53}$$

which is the inversion of Eq. (44). Since $T^{J}_{v'j'l',vjl} = 0$ when $(-1)^{J+j'+l'} \neq (-1)^{J+j+l}$, defining $T^{J(\pm)}_{v'j'l',vjl} = T^{J}_{v'j'l',vjl}$ with $(-1)^{J+j'+l'} = (-1)^{J+j+l} = (\pm)$, we obtain

$$\begin{aligned} T^{J(\pm)}_{v'j'l',vjl} &= \sum_{m'm} U^{Jl'(\pm)}_{j'm'}\, \bar{T}^{J(\pm)}_{v'l'm',vlm}\, U^{Jl(\pm)}_{jm} \\ &= \sum_{m'}^{(\pm)} \sum_{m}^{(\pm)} U^{Jl'(\pm)}_{j'm'}\, \bar{T}^{J(\pm)}_{v'l'm',vlm}\, U^{Jl(\pm)}_{jm}. \end{aligned} \tag{54}$$

Here, $U^{Jl'(\pm)}_{j'm'} = U^{Jl'}_{j'm'}$ with $(-1)^{J+l'+j'} = (\pm)$. The use of Eq. (54) is more convenient than that of Eq. (53). The scattering amplitude and all cross sections of V-R transitions by electron impact, then, are computed from Eqs. (19)–(22) of Sec. II A.

One can equivalently describe the present formulation in terms of the real wave functions. The real solution, $f^{J}_{v'j'l',vjl}(r)$, of the space-fixed coupled differential equation [Eq. (13)] satisfies the following asymptotic boundary condition:

$$\begin{aligned} f^{J}_{v'j'l',vjl}(r) \underset{r\to\infty}{\sim} \left(\frac{k_{vj}}{k_{v'j'}}\right)^{1/2} [&\delta_{v'v}\delta_{j'j}\delta_{l'l} F_{v'j'l'}(r) \\ &+ K^{J}_{v'j'l',vjl} G_{v'j'l'}(r)]. \end{aligned} \tag{55}$$

$K^{J}_{v'j'l',vjl}$ is the reactance matrix element of space-fixed frame and it is real, symmetric ($K^{J}_{v'j'l',vjl} = K^{J}_{vjl,v'j'l'}$). It is known that[11]

$$g^{J}_{v'j'l',vjl}(r) = \sum_{v''j''l''} f^{J}_{v'j'l',v''j''l''}(r) D^{J}_{v''j''l'',vjl}, \tag{56}$$

$$\begin{aligned} \sum_{v''j''l''} (\delta_{v'v''}\delta_{j'j''}\delta_{l'l''} - iK^{J}_{v'j'l',v''j''l''}) \\ \times i^{l''-l} T^{J}_{v''j''l'',vjl} = K^{J}_{v'j'l',vjl}, \end{aligned} \tag{57}$$

with

$$D^{J}_{v'j'l',vjl} = i^{l'} \left(\frac{k_{vj}}{k_{v'j'}}\right)^{1/2} (\delta_{v'v}\delta_{j'j}\delta_{l'l} + iT^{J}_{v'j'l',vjl}). \tag{58}$$

From Eqs. (27)–(29), one can show that the real functions, $\bar{f}^{J}_{v'l'm',vlm}(r)$ and $\bar{f}'^{J}_{v'l'm',vlm}(r)$, defined as

$$\bar{f}^{J}_{v'l'm',vlm}(r) = \sum_{j'j} U^{Jl'}_{j'm'} f^{J}_{v'j'l',vjl}(r) U^{Jl}_{jm}, \tag{59}$$

$$\bar{f}'^{J}_{v'l'm',vlm}(r) = \sum_{m''} \bar{f}^{J}_{v'l'm',vlm''}(r) \Lambda^{-J}_{vlm'',m}, \tag{60}$$

are the real solutions of body-fixed coupled differential equation [Eq. (34)] and

$$\begin{aligned} \bar{f}^{J}_{v'l'm',vlm}(r) & \\ \underset{r\to\infty}{\sim} \sum_{m_1 m_2} \Lambda^{-J}_{v'l'm',m_1} \Big(& \delta_{v'v}\delta_{l'l} \bar{F}^{J}_{v'l'm_1,m_2}(r) \\ &+ \sum_{m_3} \bar{G}^{J}_{v'l'm_1,m_3}(r) \bar{K}^{J}_{v'l'm_3,vlm_2} \Big) \Lambda^{+J}_{vlm_2,m}, \end{aligned} \tag{61}$$

$$\bar{f}'^{J}_{v'l'm',vlm}(r) \underset{r\to\infty}{\simeq} \sum_{m_1} \Lambda^{-J}_{v'l'm',m_1}\Big(\delta_{v'v}\delta_{l'l}\bar{F}^{J}_{v'l'm_1,m}(r) + \sum_{m_3} \bar{G}^{J}_{v'l'm_1,m_3}(r)\bar{K}^{J}_{v'l'm_3,vlm}\Big), \tag{62}$$

with

$$\bar{K}^{J}_{v'l'm',vlm} = \sum_{j'j} U^{Jl'}_{j'm'} K^{J}_{v'j'l',vjl} U^{Jl}_{jm} . \tag{63}$$

$\bar{K}^{J}_{v'l'm',vlm}$ is the reactance matrix element in the body-fixed frame and it is real, symmetric again $(\bar{K}^{J}_{v'l'm',vlm} = \bar{K}^{J}_{vlm,v'l'm'})$. From Eqs. (56)–(60), we obtain

$$\bar{g}^{J}_{v'l'm',vlm}(r) = \sum_{v''l''m''} \bar{f}^{J}_{v'l'm',v''l''m''}(r)\bar{D}^{J}_{v''l''m'',vlm} , \tag{64}$$

$$\bar{g}'^{J}_{v'l'm',vlm}(r) = \sum_{v''l''m''} \bar{f}'^{J}_{v'l'm',v''l''m''}(r)\bar{D}'^{J}_{v''l''m'',vlm} , \tag{65}$$

$$\sum_{v''l''m''} (\delta_{v'v''}\delta_{l'l''}\delta_{m'm''} - i\bar{K}^{J}_{v'l'm',v''l''m''}) \times i^{l''-l}\bar{T}^{J}_{v''l''m'',vlm} = \bar{K}^{J}_{v'l'm',vlm} . \tag{66}$$

The expressions for $\bar{D}^{J}_{v'l'm',vlm}$ and $\bar{D}'^{J}_{v'l'm',vlm}$ are easily understood. If one defines $\bar{f}'^{J(\pm)}_{v'l'm',vlm}(r)$ and $\bar{K}^{J(\pm)}_{v'l'm',vlm}$ from $\bar{f}'^{J}_{v'l'm',vlm}(r)$ and $\bar{K}^{J}_{v'l'm',vlm}$ in the same way as Eq. (47), then they have the properties expressed in Eqs. (48) and (49). Furthermore, $\bar{f}'^{J(\pm)}_{v'l'm',vlm}(r)$ is a solution of both Eqs. (34) and (50) and satisfies an asymptotic boundary condition which contains $\bar{K}^{J(\pm)}_{v'l'm',vlm}$. The detailed discussions of the calculational procedures will be deferred until the numerical results are reported. It is sufficient to note here that the following relation,

$$\begin{aligned} \sum_{v''l''m''} & (\delta_{v'v''}\delta_{l'l''}\delta^{(\pm)}_{m'm''} - i\bar{K}^{J(\pm)}_{v'l'm',v''l''m''}) \times i^{l''-l}\bar{T}^{J(\pm)}_{v''l''m'',vlm} \\ &= \sum_{v''l''m''}^{(\pm)} (\delta_{v'v''}\delta_{l'l''}\delta^{(\pm)}_{m',m''} - i\bar{K}^{J(\pm)}_{v'l'm',v''l''m''}) \times i^{l''-l}\bar{T}^{J(\pm)}_{v''l''m'',vlm} \\ &= \bar{K}^{J(\pm)}_{v'l'm',vlm} \end{aligned} \tag{67}$$

with $\delta^{(\pm)}_{m',m''} = \frac{1}{2}(\delta_{m',m''} \pm \delta_{-m',m''})$, is important.

III. DISCUSSIONS

In this section, we make some general comments and discuss the merits of the present body-fixed formulation.

The vibrational transition cross section is defined as

$$\sigma_{vj\to v'} = \sum_{j'} \sigma_{vj\to v'j'} . \tag{68}$$

From Eqs. (21), (29), and (53), we obtain

$$\sigma_{vj\to v'} = \sum_{m'} \sigma^{(m')}_{vj\to v'} \tag{69}$$

with

$$\sigma^{(m')}_{vj\to v'} = \frac{4\pi}{k^2_{vj}} \frac{1}{2j+1} \sum_{Jl'l} (2J+1) \left| \sum_{m} \bar{T}^{J}_{v'l'm',vlm} U^{Jl}_{jm} \right|^2 . \tag{70}$$

The internuclear axis component of scattered electronic angular momentum m' is also that component of the total electronic angular momentum of electron plus molecular compound system when the target molecule is in Σ state, and thus the partial cross sections $\sigma^{(m')}_{vj\to v'}$ may be used to study the resonance scattering. For comparison with experimental data on vibrational transitions, the following averaged cross section is frequently used.

$$\tilde{\sigma}_{v\to v'} = \sum_{j} \rho_{vj}\sigma_{vj\to v'} \Big/ \sum_{j} \rho_{vj} . \tag{71}$$

Here, ρ_{vj} is the equilibrium distribution of V-R states of target molecule.

In the present body-fixed close-coupling theory approach, the coupled differential equation are solved entirely in the body-fixed frame throughout the whole region, obtaining transition matrix in that frame; and one evaluates the cross sections as described above. Thus, it differs from the "frame transformation theory" of Chang and Fano[18] in which they considered the body-fixed and space-fixed frame in internal and external region, respectively. We want to emphasize that present close-coupling formulation of body-fixed frame is entirely equivalent to that of space-fixed frame in Sec. II A (more specifically for each J). The channel index $(v'l'j')$ of space-fixed frame corresponds to $(v'l'm')$ of body-fixed frame for given J.

However, one should consider the above equivalence with caution in practical situations where truncated basis are used. Let us assume that the number of vibrational states are the same for both space-fixed and body-fixed coupled differential equation. In space-fixed close-coupling theory, it is customary to truncate the rotational states up to $j'_{\max}(v')$ in each vibrational manifold.[5,10-12] In this case, one cannot guarantee that both space-fixed and body-fixed close-coupling theory would give identical results on the cross sections. In order that the results from both theory to be the same in actual computation, one should not put any definite upper limits in j' and m' values, except they are restricted as follows:

$$
\begin{aligned}
&|J-l'| \leqslant j' \leqslant J+l' \ \text{ with } (-1)^{J+l'+j'}=+1(+) \ \text{ or } (-1)^{J+l'+j'}=-1(-)\,, && \text{(for space-fixed theory)} \\
&J \geqslant m',\, l' \geqslant m' \ \text{ with } m' \geqslant 0(+) \ \text{ or } m'>0(-) && \text{(for body-fixed theory)}
\end{aligned}
\tag{72}
$$

for given J, l', but put the same upper limit $l'_{\max}$ on l' value. The number of channels of corresponding parity of both space-fixed and body-fixed coupled differential equation is equal to each other in that case.

However, there are many circumstances in which the truncations of j' values in space-fixed formulation or m' values in body-fixed formulation of close-coupling theory are inevitable in order to keep the number of channels in a manageable size. Then the results from both formulations may not be identical.

In the electron–diatomic-molecule scattering with heavy target (in particular, heteronuclear) molecule, many terms of harmonic components of potential are usually needed. The rotational levels are closely spaced in such target molecules and the contributions of rotational states up to $j'_{\max} \simeq 14$–16 to the cross sections are more or less equally significant. In body-fixed formulation, all rotational states are taken into account to a certain extent, however one may truncate the m' values. Rather than considering all those rotational states in the space-fixed close-coupling formulation which is practically difficult, it will be efficient to use body-fixed formulation with m' values truncated appropriately; and m' is a better quantum number in a heavier target molecule than in lighter one. Therefore, one is encouraged to use the present body-fixed formulation in this situation.

The internuclear axis ($\vec{R}$) component of incident electronic angular momentum, m', is not conserved in the present (moving) body-fixed formulation, while it is so in those of fixed-nuclei approximation or hybrid theory as will be discussed in the following paper. {Formulations of Secs. II A and B can be generalized to non-Σ electronic states of target molecule replacing $\Phi Y_{j m_j}$ by $[(2j+1/16\pi^2)]^{1/2}(\Phi_\Lambda D^{j\,*}_{m_j\Lambda} \pm \Phi_{-\Lambda} D^{j\,*}_{m_j-\Lambda})$, where $|\Lambda|$ corresponds to $\Sigma, \pi, \Delta, \ldots,$ states. $\vec{j}^{\,2}$ in ∇^2_R should also be modified accordingly.}

IV. SUMMARY REMARKS

We have presented in this paper a V-R close-coupling formulation in a moving body-fixed frame. The resulting coupled differential equation is solved throughout the entire region of interaction between incident electron and target molecule up to the asymptotic region. The coupled differential equation and asymptotic boundary conditions in the body-fixed frame were given in terms of definite parity which are needed for reducing the number of channels [the method of enumerating channels of body-fixed coupled differential equation for given J and parity is clear from Eq. (72)]. Procedures of evaluating cross sections from body-fixed transition and reactance matrix elements were outlined. Thus the present formulation is directly amenable to numerical calculation.

While there is formal equivalence between space-fixed and body-fixed close-coupling approach, conditions for obtaining identical results from them when (finite) truncated basis set is used are not easily satisfied. Thus when one uses body-fixed and space-fixed formulation of close-coupling theory in internal and external region, respectively, and truncates either j' or m' values, or both, in their respective region, the two solutions cannot be matched accurately on the boundary unless one introduces further approximations.

It should be emphasized that both body-fixed and space-fixed formulation have their own merits. For studying resonance scattering of vibrational transitions and electron–heavy-target-molecule scattering, the body-fixed formulation will be more efficient, and the study of such an application is presently being carried out. For electron–light-target-molecule scattering where rotational levels are widely separated, the space-fixed formulation seems to be more convenient. However, all present results indicate that body-fixed treatment will be advantageous even for the lightest molecule (H_2), except for very low energies close to threshold where PWBA is accurate (for rotational transition).[7] The body-fixed formulation is also a convenient framework to develop further approximation schemes. In the next paper, an $l_{z'}$-conserving close-coupling approximation is derived within the body-fixed formulation.

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