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Vibrational and rotational transitions in low-energy electron–diatomic-molecule collisions.*
II. Hybrid theory and close-coupling theory:
An $l_{z'}$-conserving close-coupling approximation

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The hybrid theory for low-energy electron–diatomic-molecule scattering, proposed by Chandra and Temkin, is systematically reformulated. It is shown that the hybrid theory can be equivalently derived from the vibrational-rotational (V-R) close-coupling theory when the dependences on the rotational quantum numbers are neglected in both the energy levels and the radial parts of V-R wave functions of target molecule. The expressions of scattering amplitude, differential, integral, and momentum-transfer cross sections of hybrid theory for the simultaneous V-R transition of target molecules obtained in our formulation are thus in the same form as those of V-R close-coupling theory. Distorted-wave Born approximation expressions for the cross sections of hybrid theory are also presented. It is pointed out that the neglect of rotational quantum number dependence in the radial part of wave functions is required to obtain fixed-nuclei approximation or hybrid theory, where the internuclear axis components of incident electron angular momentum $l_{z'}$ are conserved. An $l_{z'}$-conserving close-coupling approximation is proposed which is derived from the V-R close-coupling formulation in the moving body-fixed frame. This approach has a nature and simplicity similar to the original hybrid theory in that the $l_{z'}$ conservation is satisfied, but the rotational motions of target molecule are partly taken into account.

I. INTRODUCTION

In the preceding paper (hereafter referred to as I), we have reviewed the vibrational-rotational (V – R) close-coupling theory for low-energy electron-diatomic-molecule collisions in space-fixed frame and presented a new formulation in a moving body-fixed frame.[1] The vibrational-rotational close-coupling theory, whether in space or body-fixed frame, are the most general and realistic approach in the sense that they can, in principle, produce accurate V – R transition cross sections when sufficiently large number of basis states are included. However, even with the capability of present-day computers, calculations become difficult if many vibrational states (say ~ 10) are considered, due to the large number of rotational states within each vibrational manifold. Therefore, it is both desirable and necessary to develop other approaches to keep the computational efforts within manageable level. On the other hand, the *ab initio* approach of the vibrational-rotational close-coupling theory must serve as a basic standard to which other approaches should be compared.[2-10]

Among the more efficient approaches, from the practical computational point of view, is the hybrid theory recently proposed by Chandra and Temkin.[9] Based on physical arguments, they suggested that the vibrational states of the target molecule be coupled dynamically through close-coupling theory while the rotational state transitions, because of their long time scale, are treated with adiabatic-nuclei approximation.[5] The internuclear axis component of the incident electronic angular momentum $l_{z'}$ is conserved in the fixed-nuclei approximation[4]; the Hamiltonian of the system is invariant under rotation of the incident electron around this axis. Because of the $l_{z'}$ conservation, the coupled differential equation, the asymptotic boundary condition, and the number of the coupled channels are considerably reduced. However, because of the way the hybrid theory was derived, its relationship and connection with the vibrational-rotational close-coupling theory was not at all transparent.

In this paper, we present a reformulation of the hybrid theory of Chandra and Temkin[9] and obtain the expression of scattering amplitude and formula of differential, integral, and momentum transfer cross sections for the simultaneous V – R transitions of hybrid theory in the same forms as those of V – R close-coupling theory. Distorted-wave Born approximation (DWBA) expressions of cross sections of hybrid theory are also presented. We show that the hybrid theory can be derived from V – R close-coupling theory in body-fixed and space-fixed frame when the dependence on the rotational quantum numbers are neglected in both energy levels and the radial parts of V – R wave functions of target molecule. That is, our approximation is entirely equivalent to the synthesis of fixed and adiabatic-nuclei approaches as proposed by Chandra and Temkin.

Based on the relation between the hybrid and the close-coupling theory, an improvement scheme, the $l_{z'}$-conserving close-coupling approximation derived from body-fixed formulation of I, is proposed. This approach has a similar nature and simplicity as the hybrid theory in that the internuclear axis components of incident electronic angular momentum, $l_{z'}$, are conserved, but the rotational motion of the target molecule is partly taken into account, that is, the fixed-nuclei assumption is relaxed to a certain extent.

In Sec. II A, the hybrid theory is reformulated; and relations between close-coupling and hybrid theory are treated in Sec. II B. Distorted-wave Born approximation (DWBA) expression of hybrid theory is given in Sec. II C. The $l_{z'}$-conserving close-coupling approximation is described in Sec. II D. Brief summary of the present work and discussions are made in Sec. III. In this paper, notations the same as I will be used throughout and Eq. (I-n) denotes Eq. (n) of I.

II. HYBRID AND CLOSE-COUPLING THEORY

A. Reformulation of hybrid theory for V-R transitions

In this section we present a reformulation of the hybrid theory which was first proposed by Chandra and Temkin.[9] Our reformulation follows the same physical argument as given by those authors but differs in the sequence of the derivation. Further, our derivation is formulated in the total J representation, with the resulting expressions different from those given by Chandra and Temkin but directly amenable to comparison with the V – R close-coupling theory result of I.

In hybrid theory proposed by Chandra and Temkin, the V – R transition cross sections are obtained from a synthesis of close-coupling theory for vibrational states with fixed-nuclei approximation,[4] and adiabatic-nuclei theory[5] for rotational states. The rotational angular momentum of target molecule is neglected in H, that is,

$$\begin{aligned} -\frac{\hbar^2}{2\mu_N}\nabla_R^2 &= -\frac{\hbar^2}{2\mu_N}\frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right) \\ &\quad -\frac{\hbar^2}{2\mu_N R^2}(\vec{R}\times\nabla_R)^2 \\ &\simeq -\frac{\hbar^2}{2\mu_N}\frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right). \end{aligned} \tag{1}$$

The radial wave function and energy level, $\phi_v(R)$ and ϵ_v, are obtained from

$$\left[-\frac{\hbar^2}{2\mu_N}\frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right)+\epsilon_0(R)\right]\phi_v(R)=\epsilon_v\phi_v(R)\,. \tag{2}$$

For vibrational transitions, the angular parts of V – R wave functions of the target molecule are not considered in hybrid theory and thus the scattering wave function $\Psi_v^{(+)}(\vec{r},\vec{R})$ is given as

$$\Psi_v^{(+)}(\vec{r},\vec{R})=\frac{4\pi}{k_v r}\sum_{\substack{ll'v'\\ mm'}} g_{l'v',lv}^{(m')}(r)\phi_{v'}(R)Y_{l'm'}(\hat{r}')D_{mm'}^{l*}(\hat{R})Y_{lm}^{*}(\hat{k}_v)\underset{r\to\infty}{\simeq} e^{i\vec{k}_v\cdot\vec{r}}\phi_v(R)+\sum_{v'}\frac{e^{ik_{v'}r}}{r}f_{v',v}(\hat{R},\hat{r})\phi_{v'}(R)\,. \tag{3}$$

Here, $k_v^2=(2\mu_e/\hbar^2)(E-\epsilon_v)$ and $\hat{r}'$ denotes the polar angles of $\hat{r}$ with respect to a coordinate system in which the internuclear axis $\vec{R}$ is chosen to be the z axis. $D_{mm'}^{l}(\hat{R})=D_{mm'}^{l}(\phi_R,\theta_R,0)$ is the rotation matrix element.[11] $\hat{R}$ is treated as parameters in the fixed-nuclei approximation or hybrid theory. From Eqs. (I-7), (1), (2), and (3), we have

$$\left(\frac{d^2}{dr^2}-\frac{l'(l'+1)}{r^2}+k_{v'}^2\right)g_{l'v',lv}^{(m')}(r)=\frac{2\mu_e}{\hbar^2}\sum_{l''v''}V_{l'v',l''v''}^{(m')}(r)g_{l''v'',lv}^{(m')}(r)\quad(l,l',l''\geqslant|m'|) \tag{4}$$

and

$$g_{l'v',lv}^{(m')}(r)\underset{r\to\infty}{\simeq} i^{l'}\left(\frac{k_v}{k_{v'}}\right)^{1/2}\left[\delta_{l'l}\delta_{v'v}F_{l'v'}(r)+T_{l'v',lv}^{(m')}(G_{l'v'}(r)+iF_{l'v'}(r))\right]. \tag{5}$$

Here,

$$\begin{aligned} V_{l'v',l''v''}^{(m')}(r) &= (-1)^{m'}\sum_{\lambda}\frac{1}{2\lambda+1}\left[(2l'+1)(2l''+1)\right]^{1/2}\langle l'ol''o|\lambda o\rangle\langle l'm'l''-m'|\lambda o\rangle V_{v'v''}^{\lambda}(r)\,, \\ V_{v'v''}^{\lambda}(r) &= \int R^2\,dR\,\phi_{v'}(R)V_\lambda(r,R)\phi_{v''}(R)\,, \\ F_{l'v'}(r) &= k_{v'}rj_{l'}(k_{v'}r)\,, \\ G_{l'v'}(r) &= -k_{v'}rn_{l'}(k_{v'}r). \end{aligned} \tag{6}$$

It is seen that m', the internuclear axis component of the incident electronic angular momentum (which is also that component of the total electronic angular momentum of electron plus target molecular compound system), is conserved in hybrid theory or in fixed-nuclei approximation. Thus the coupled differential equation is solved separately for each m' and it is sufficient to consider non-negative m', since

$$\begin{aligned} V^{(m')}_{l'v',l''v''}(r) &= V^{(-m')}_{l'v',l''v''}(r), \\ g^{(m')}_{l'v',lv}(r) &= g^{(-m')}_{l'v',lv}(r), \\ T^{(m')}_{l'v',lv} &= T^{(-m')}_{l'v',lv}. \end{aligned} \tag{7}$$

$T^{(m')}_{l'v',lv}$ is the vibrational transition matrix element of hybrid theory. Following the same procedures as in obtaining Eq. (I-19), we have scattering amplitude

$$\begin{aligned} f_{v',v}(\hat{R},\theta,\phi) &= \left(\frac{4\pi}{k_v k_{v'}}\right)^{1/2} \sum_{l'lm'm} (2l+1)^{1/2} T^{(m')}_{l'v',lv} \\ &\quad \times D^{l'}_{mm'}(\hat{R}) D^{l*}_{om'}(\hat{R}) Y_{l'm}(\theta,\phi). \end{aligned} \tag{8}$$

The differential, integral, and momentum transfer cross sections of the vibrational transitions in the hybrid theory are then given by

$$\begin{aligned} \frac{d\sigma_{v\to v'}}{d\Omega}(\theta) &= \frac{k_{v'}}{k_v}\frac{1}{4\pi}\int d\hat{R}\,|f_{v',v}(\hat{R},\theta,\phi)|^2 \\ &= \frac{4\pi}{k_v^2}\sum_{\lambda\mu}\frac{1}{2\lambda+1}\left|\sum_{l'lm'}(-1)^{m'}(2l+1)^{1/2}\langle l'\mu lo|\lambda\mu\rangle\langle l'm'l-m'|\lambda o\rangle T^{(m')}_{l'v',lv}Y_{l'\mu}(\theta,\phi)\right|^2 \\ &= \frac{1}{k_v^2}\sum_{\lambda}B_\lambda(v\to v')P_\lambda(\cos\theta), \end{aligned} \tag{9}$$

$$\sigma_{v\to v'} = \int d\Omega\,\frac{d\sigma_{v\to v'}}{d\Omega}(\theta) = \frac{4\pi}{k_v^2}B_o(v\to v') = \frac{4\pi}{k_v^2}\sum_{l'lm'}|T^{(m')}_{l'v',lv}|^2, \tag{10}$$

$$\sigma^{(M)}_{v\to v'} = \int d\Omega\,(1-\cos\theta)\frac{d\sigma_{v\to v'}}{d\Omega}(\theta) = \frac{4\pi}{k_v^2}[B_o(v\to v') - \tfrac{1}{3}B_1(v\to v')]. \tag{11}$$

Here,

$$\begin{aligned} B_\lambda(v\to v') &= \sum_{\substack{ll'm' \\ \bar{l}\bar{l}'\bar{m}'}}\frac{1}{2\lambda+1}[(2l'+1)(2\bar{l}'+1)(2l+1)(2\bar{l}+1)]^{1/2}\langle l'o\bar{l}'o|\lambda o\rangle\langle lo\bar{l}o|\lambda o\rangle \\ &\quad \times\langle l'm'\bar{l}'-\bar{m}'|\lambda m'-\bar{m}'\rangle\langle lm'\bar{l}-\bar{m}'|\lambda m'-\bar{m}'\rangle T^{(m')}_{l'v',lv}T^{(\bar{m}')*}_{\bar{l}'v',\bar{l}v}. \end{aligned} \tag{12}$$

In deriving the last part of Eq. (9), we have used the well-known relations,

$$\begin{aligned} &\sum_{m_2}\langle j_1m_1j_2m_2|j_5m_1+m_2\rangle\langle j_5m_1+m_2j_4m-m_2|j_3m_1+m\rangle\langle j_2m_2j_4m-m_2|j_6m\rangle \\ &\qquad = (-1)^{j_1+j_2+j_3+j_4}[(2j_5+1)(2j_6+1)]^{1/2}\langle j_1m_1j_6m|j_3m_1+m\rangle\begin{Bmatrix} j_1 & j_2 & j_5 \\ j_4 & j_3 & j_6 \end{Bmatrix} \end{aligned} \tag{13}$$

and

$$\begin{aligned} &\sum_{j_6}[(2j_5+1)(2j_6+1)]^{1/2}\begin{Bmatrix} j_1 & j_2 & j_5 \\ j_4 & j_3 & j_6 \end{Bmatrix}\langle j_2m_2j_4m_4|j_6m_2+m_4\rangle\langle j_1m_1j_6m_2+m_4|j_3m_3\rangle \\ &\qquad = (-1)^{j_1+j_2+j_3+j_4}\langle j_1m_1j_2m_2|j_5m_1+m_2\rangle\langle j_5m_1+m_2j_4m_4|j_3m_3\rangle. \end{aligned} \tag{14}$$

When solving the coupled differential equation [Eq. (4)], the real (rather than complex) wave functions $f^{(m')}_{l'v',lv}(r)$, with following real boundary condition

$$f^{(m')}_{l'v',lv}(r)\underset{r\to\infty}{\sim}\left(\frac{k_v}{k_{v'}}\right)^{1/2}[\delta_{l'l}\delta_{v'v}F_{l'v'}(r) + K^{(m')}_{l'v',lv}G_{l'v'}(r)], \tag{15}$$

are more convenient to use.

Introducing square matrices $g^{(m')}(r)$, $f^{(m')}(r)$, $T^{(m')}$, $K^{(m')}$, I, and Λ as

$$\begin{aligned} g^{(m')}(r) &= (g^{(m')}_{l'v',lv}(r)), \\ f^{(m')}(r) &= (f^{(m')}_{l'v',lv}(r)), \\ T^{(m')} &= (T^{(m')}_{l'v',lv}), \\ K^{(m')} &= (K^{(m')}_{l'v',lv}), \\ I &= (i^{l'}\delta_{l'l}\delta_{v'v}), \\ \Lambda &= (k_{v'}^{1/2}\delta_{l'l}\delta_{v'v}), \end{aligned} \tag{16}$$

we obtain

$$g^{(m')}(r) = f^{(m')}(r)D^{(m')}, \tag{17}$$

$$T^{(m')} = I^{\dagger}\frac{K^{(m')}}{1 - iK^{(m')}}I, \tag{18}$$

with

$$D^{(m')} = I\Lambda^{-1}(1 + iT^{(m')})\Lambda. \tag{19}$$

$K^{(m')}$ is the reactance matrix and it is real, symmetric, i.e., $K^{(m')}_{l'v',lv} = K^{(m')}_{lv,l'v'}$. Thus $T^{(m')}_{l'v',lv} = (-1)^{l'+l}T^{(m')}_{lv,l'v'}$ and the principle of detailed balance

$$k_v^2\sigma_{v\to v'} = k_{v'}^2\sigma_{v'\to v} \tag{20}$$

is satisfied.
The (partial) cross section

$$\sigma^{(m')}_{v\to v'} = \frac{4\pi}{k_v^2}\sum_{l'l}|T^{(m')}_{l'v',lv}|^2 \tag{21}$$

is used for studying the resonance scattering cross sections.

In hybrid theory, the scattering amplitude $f_{v'j'm'_j,vjm_j}(\theta,\phi)$ for the simultaneous V – R transition $(vjm_j)\to(v'j'm'_j)$ is obtained from close-coupling scattering amplitude of vibrational transition, $f_{v',v}(\hat{R},\theta,\phi)$, given by Eq. (8) as follows:

$$f_{v'j'm'_j,vjm_j}(\theta,\phi) = \int d\hat{R}\, Y^*_{j'm'_j}(\hat{R}) \times f_{v',v}(\hat{R},\theta,\phi)Y_{jm_j}(\hat{R}). \tag{22}$$

This is the adiabatic-nuclei approach.[5] Carrying out the integration over $\hat{R}$, we have

$$\begin{aligned} f_{v'j'm'_j,vjm_j}(\theta,\phi) &= \left(\frac{4\pi}{k_v k_{v'}}\right)^{1/2}\sum_{Jl'l}(2l+1)^{1/2}\langle l'm_j - m'_j j'm'_j|Jm_j\rangle \\ &\quad\times\langle lojm_j|Jm_j\rangle\tilde{T}^J_{v'j'l',vjl} \\ &\quad\times Y_{l'm_j-m'_j}(\theta,\phi) \end{aligned} \tag{23}$$

with

$$\tilde{T}^J_{v'j'l',vjl} = \frac{[(2j'+1)(2j+1)]^{1/2}}{2J+1} \times\sum_{m'}\langle l'm'j'o|Jm'\rangle T^{(m')}_{l'v',lv}\langle lm'jo|Jm'\rangle. \tag{24}$$

As can be seen from Eqs. (7) and (24),

$$(-1)^{j'+l'+J} = (-1)^{j+l+J}. \tag{25}$$

In deriving Eq. (23), we have expressed $Y^*_{j'm'_j}(\hat{R}), Y_{jm_j}(\hat{R})$ in terms of rotation matrix elements. Next, the Clebsch-Gordan series for each pair $D^{l'}, D^{j'}$ and D^l, D^j, and the orthogonalities of the rotation matrix elements have been used. It is instructive to compare Eq. (23) with Eq. (I-19). Then, it is seen that $\tilde{T}^J_{v'j'l',vjl}$ of hybrid theory corresponds to $T^J_{v'j'l',vjl}$, the transition matrix element, in total angular momentum representation, of the close-coupling theory described in Sec. II A of I. Furthermore, the parity $(-1)^{j'+l'+J}$ is known to be conserved in that theory. Therefore, the above correspondence provides us with a detailed comparison between V – R close-coupling and hybrid theory, not only cross sections but also transition matrix elements, for electron–diatomic-molecule scattering. The differential cross section of V – R transition $vj\to v'j'$ in the hybrid theory is then given by

$$\begin{aligned} \frac{d\sigma_{vj\to v'j'}}{d\Omega}(\theta) &= \frac{k_{v'}}{k_v}\frac{1}{2j+1}\sum_{m_jm'_j}|f_{v'j'm'_j,vjm_j}(\theta,\phi)|^2 \\ &= \frac{1}{k_v^2(2j+1)}\sum_{\lambda}B_\lambda(vj\to v'j')P_\lambda(\cos\theta) \end{aligned} \tag{26}$$

with

$$\begin{aligned} B_\lambda(vj\to v'j') &= (-1)^{j'+j}\sum_{\substack{ll'J\\ \bar{l}\bar{l}'\bar{J}}}(2J+1)(2\bar{J}+1)[(2l'+1)(2\bar{l}'+1)(2l+1)(2\bar{l}+1)]^{1/2} \\ &\quad\times\langle l'o\bar{l}'o|\lambda o\rangle\langle lo\bar{l}o|\lambda o\rangle\begin{Bmatrix}\lambda & \bar{J} & J\\ j' & l' & \bar{l}'\end{Bmatrix}\begin{Bmatrix}\lambda & \bar{J} & J\\ j & l & \bar{l}\end{Bmatrix}\tilde{T}^J_{v'j'l',vjl}\tilde{T}^{\bar{J}*}_{v'j'\bar{l}',vj\bar{l}}. \end{aligned} \tag{27}$$

Here, we have used Eqs. (13) and (25). The integral and momentum transfer cross sections for the transition, $vj\to v'j'$, in the hybrid theory are given by

$$\sigma_{vj\to v'j'}=\int d\Omega\,\frac{d\sigma_{vj\to v'j'}}{d\Omega}(\theta)$$
$$=\frac{4\pi}{k_v^2(2j+1)}B_o(vj\to v'j')$$
$$=\frac{4\pi}{k_v^2(2j+1)}\sum_{ll'J}(2J+1)\left|\tilde{T}^J_{v'j'l',vjl}\right|^2 \qquad (28)$$

and

$$\sigma^{(M)}_{vj\to v'j'}=\int d\Omega\,(1-\cos\theta)\,\frac{d\sigma_{vj\to v'j'}}{d\Omega}(\theta)$$
$$=\frac{4\pi}{k_v^2(2j+1)}\Big[B_o(vj\to v'j')$$
$$-\tfrac{1}{3}B_1(vj\to v'j')\Big]. \qquad (29)$$

The principle of detailed balance

$$k_v^2(2j+1)\sigma_{vj\to v'j'}=k_{v'}^2(2j'+1)\sigma_{v'j'\to vj} \qquad (30)$$

is satisfied, since $\tilde{T}^J_{v'j'l',vjl}=(-1)^{l'+l}\tilde{T}^J_{vjl,v'j'l'}$. From Eqs. (9)–(11), (26), (28), and (29), it is seen that

$$\frac{d\sigma_{v\to v'}}{d\Omega}(\theta)=\sum_{j'}\frac{d\sigma_{vj\to v'j'}}{d\Omega}(\theta)\,, \qquad (31)$$

$$\sigma_{v\to v'}=\sum_{j'}\sigma_{vj\to v'j'}\,, \qquad (32)$$

$$\sigma^{(M)}_{v\to v'}=\sum_{j'}\sigma^{(M)}_{vj\to v'j'}\,, \qquad (33)$$

by applying the closure property of spherical harmonics to Eq. (22). In fact, one can show that

$$B_\lambda(v\to v')=\frac{1}{2j+1}\sum_{j'}B_\lambda(vj\to v'j') \qquad (34)$$

using Eq. (14).

The right-hand sides of Eqs. (31)–(33) are independent of the initial rotational quantum number j. This is a property of hybrid theory. It is not so in (accurate) V – R close-coupling theory of Sec. II A in I. It should also be noted that, comparing Eq. (I-19) with Eq. (23), the differential cross section of V – R transitions of close-coupling theory in that section of I [Eq. (I-20)] will have the same harmonic expansion as above [Eq. (27)] with $\tilde{T}^J_{v'j'l',vjl}$ replaced by $T^J_{v'j'l',vjl}$. So far, we have derived the formulas for differential, integral, and momentum transfer cross sections of hybrid theory for the simultaneous V – R transitions, which have different forms from the original expressions given by Chandra and Temkin. Since the underlying physical concepts are the same in the present and their treatment of hybrid theory, both (present and their) formulas will give identical results for V – R transition cross sections. But the correspondence between the hybrid and V – R close-coupling theory is transparent in the present formula while not so in theirs, because they did not use the total angular momentum ($\vec{J}=\vec{l}+\vec{j}$) representation.

B. Relationship between the V-R close-coupling theory and hybrid theory

In this section we discuss the derivation of hybrid theory as a direct approximation of the V – R close-coupling theory given in I. The formal derivation is obtained in the body-fixed frame formulation as it is much simpler than in the space-fixed frame. The relationship between these two theories is of course the same in the space-fixed frame.

We have seen that the internuclear axis ($\vec{R}$) component of incident electronic angular momentum m' is conserved in fixed-nuclei approximation or hybrid theory but it is not so in close-coupling theory of body-fixed frame in I. The difference between the equations of motion of incident electron in fixed nuclear frame and moving body-fixed frame is clear in the classical picture. In body-fixed frame, we have effective forces exerted on the electron which includes "Coriolis force," in addition to the (external) force due to the interaction between electron and target molecule. Thus the off-diagonal elements in $\bar{\epsilon}^J_{v'l'm',m''}$ (i.e., $\bar{\epsilon}^J_{v'l'm',m''}$ with $m'\neq m''$) may be called "Coriolis m-coupling energy." The off-diagonal elements of $\bar{V}^J_{v'l'm',v''l''m''}(r)$ for m indices also originate from the inertial nature of interaction potential viewed from moving frame. If we first neglect j' dependence in $\phi_{v'j'}(R)$, in other words, if we replace $\phi_{v'j'}(R)$ by $\phi_{v'}(R)$ in the body-fixed formulation of I, then we obtain

$$\bar{V}^J_{v'l'm',v''l''m''}(r)=\int R^2\,dR\,\phi_{v'}(R)\phi_{v''}(R)$$
$$\times\int\sin\theta_R\sin\gamma\,d\theta_R\,d\gamma\,d\phi_R\,d\chi$$
$$\times D^{l'm'\,*}_{JM}(\theta_R,\phi_R,\gamma,\chi)V(r,R,\gamma)D^{l''m''}_{JM}(\theta_R,\phi_R,\gamma,\chi)$$
$$=\delta_{m'm''}V^{(m')}_{l'v',l''v''}(r) \qquad (35)$$

from Eqs. (I-15) and (I-35).

Next, if we neglect j' dependence in $k_{v'j'}$ (or $\epsilon_{v'j'}$), that is, if the replacement $k_{v'j'}\to k_{v'}$ is made in that formulation of I, then

$$\frac{2\mu_e}{\hbar^2}\bar{\epsilon}^{J}_{v'l'm',m''}=\delta_{m'm''}k^2_{v'},$$

$$\Lambda^{\pm J}_{v'l'm',m''}=\delta_{m'm''}k^{\pm 1/2}_{v'}, \tag{36}$$

$$\begin{pmatrix}\bar{F}^{J}_{v'l'm',m''}(r)\\ \bar{G}^{J}_{v'l'm',m''}(r)\end{pmatrix}=\delta_{m'm''}\begin{pmatrix}F_{l'v'}(r)\\ G_{l'v'}(r)\end{pmatrix},$$

from Eqs. (I-36), (I-42), and (I-43). In deriving Eqs. (35)–(36), we have also used Eqs. (I-27)–(I-29). It is seen that m' is conserved in the body-fixed coupled differential equation [Eq. (I-34)] in this case. Moreover, the solution of that equation is independent of total angular momentum J. Thus from the asymptotic boundary condition [Eq. (I-40)], we obtain

$$\begin{aligned}\bar{T}^{J}_{v'l'm',vlm}&=\delta_{m'm}T^{(m')}_{l'v',lv},\\ \bar{g}^{J}_{v'l'm',vlm}(r)&=\delta_{m'm}g^{(m')}_{l'v',lv}(r).\end{aligned} \tag{37}$$

Equations (I-34), (I-40), and (I-53) are then reduced to Eqs. (4), (5), and (24) of hybrid theory of Sec. II A, respectively [cf. Eq. (I-28)], and thus the scattering amplitude and all cross sections for the V – R transitions of body-fixed close-coupling formulation are given by Eqs. (23) and (26)–(29) of that section. By the same arguments as above,

$$\begin{aligned}\bar{K}^{J}_{v'l'm',vlm}&=\delta_{m'm}K^{(m')}_{l'v',lv},\\ \bar{f}^{J}_{v'l'm',vlm}(r)&=\delta_{m'm}f^{(m')}_{l'v',lv}(r),\end{aligned} \tag{38}$$

when the substitutions $\phi_{v'j'}(R)\to\phi_{v'}(R)$, $\epsilon_{v'j'}\to\epsilon_{v'}$ are made in the body-fixed formulation of I. Equations (I-61) and (I-66) are then reduced to the Eqs. (15) and (18), respectively. From the above discussions, we have seen that the hybrid theory is entirely equivalent to the V – R close-coupling theory in the body-fixed frame when j dependences in $\phi_{vj}(R)$ and k_{vj} (or ϵ_{vj}) are neglected in the latter. Thus one derives, alternatively, all the formulas of cross sections and equations of hybrid theory simply by replacing $\phi_{vj}(R)$ and k_{vj} by $\phi_v(R)$ and k_v in the V – R close-coupling formulation of body-fixed frame, without using the synthesis of fixed and adiabatic-nuclei approach [Eq. (22)] originally proposed by Chandra and Temkin.

The V – R close-coupling formulation of the body-fixed frame is equivalent to that of the space-fixed frame. One-to-one correspondence exists between the quantities defined in the body-fixed and space-fixed frames. Thus we have found a very interesting fact: The hybrid theory is also equivalent to the V – R close-coupling formulation of the space-fixed frame of Sec. II A in I when the replacements $\phi_{v'j'}(R)Y_{j'm'_j}(\hat{R})\to\phi_{v'}(R)Y_{j'm'_j}(\hat{R})$, $k_{v'j'}\to k_{v'}$ (or $\epsilon_{v'j'}\to\epsilon_{v'}$) are made there. More specifically, if one substitutes $\phi_{v'}(R)$ and $k_{v'}$ for $\phi_{v'j'}(R)$ and $k_{v'j'}$, respectively, in the space-fixed coupled differential equation [Eq. (I-13)], asymptotic boundary condition [Eq. (I-14)] and other equations defining potential coupling terms, and computes all the cross sections from space-fixed transition matrix element, $T^J_{v'j'l',vjl}$, by solving the above coupled differential equation, one will get the same cross sections as obtained from hybrid theory. Even more explicitly, when the above substitutions are made into V – R close-coupling formulation of space-fixed frame, one will get the same formula of all cross sections of hybrid theory. The proof of this statement entirely relies on the equivalence relation between space-fixed and body-fixed frame [Eq. (I-29)]. The j' dependence is significant not only in $\epsilon_{v'j'}$, but also in $\phi_{v'j'}(R)$ for sufficiently large j', although it may not be so for low j'.[12] Therefore, if one neglects j' dependence in $\epsilon_{v'j'}$ only (in the close-coupling theory), as in a work of Bottcher[13] for pure rotational transitions, one will not get Eqs. (35), (37), and (38), and thus neither fixed-nuclei approximation nor hybrid theory can be obtained. The reason is that, as mentioned earlier, hybrid theory (or adiabatic-nuclei procedure [Eq. (22)] is based on the fixed-nuclei approximation where m' is conserved. (In the fixed-nuclei approximation, the rotational motion of target molecule is completely ignored and the Hamiltonian is invariant under the rotation of incident electron around internuclear axis. Thus the internuclear axis component of incident electronic angular momentum should be conserved.) Similar coupled differential equation and transition matrix elements obtained by him are those of neither (moving) body-fixed formulation of I nor fixed-nuclei approximation, but they are intermediate forms between the two of above, because they are independent of J, while m' is not conserved in them.

At this point, we would like to discuss heteronuclear target molecule with strong permanent dipole moment (polar molecule). From Eqs. (I-4) and (I-9), the static interaction potential is given by

$$V^{\mathrm{stat}}(r,R,\gamma)=\sum_{\lambda}V^{\mathrm{stat}}_{\lambda}(r,R)P_{\lambda}(\cos\lambda) \tag{39}$$

with

$$\begin{aligned}V^{\mathrm{stat}}_{\lambda}(r,R)=e^2\biggl(2\pi\int r'^2\,dr'\sin\theta'\,d\theta'&\\ \times\rho(r'|,\theta',R)\frac{r^{\lambda}_{<}}{r^{\lambda+1}_{>}}P_{\lambda}(\cos\theta')&\\ -Z_A\frac{r^{\lambda}_{b<}}{r^{\lambda+1}_{b>}}-Z_B(-1)^{\lambda}\frac{r^{\lambda}_{a<}}{r^{\lambda+1}_{a>}}\biggr)&\end{aligned} \tag{40}$$

for close shell target molecule (and thus $^1\Sigma$ state). Here,

$$\rho(r',\theta',R)=\sum_{\alpha}\rho_{\alpha}(r',\theta',R)$$

$$=\sum_{\alpha}|\phi_{\alpha}(r',\theta',\phi',R)|^2,$$

$$\begin{bmatrix} r_{\gtrless} \\ r_{a\gtrless} \\ r_{b\gtrless} \end{bmatrix} = \begin{matrix}\text{the larger or}\\ \text{the smaller of}\end{matrix} \begin{bmatrix} (r,r') \\ (r,aR) \\ (r,bR) \end{bmatrix} \tag{41}$$

$$a=M_A/(M_A+M_B),\quad b=M_B/(M_A+M_B).$$

$\phi_{\alpha}(\vec{r}',R)=\phi_{\alpha}(r',\theta',\phi',R)$ is the single centered molecular orbital wave function and θ',ϕ' are polar angles of target electronic coordinate with respect to $\vec{R}$. Σ_{α} is the summation over all occupied orbitals. It is seen that

$$V^{\text{stat}}(r,R,\gamma)\underset{r\to\infty}{\simeq}-\frac{e\mu(R)}{r^2}\cos\gamma. \tag{42}$$

Here

$$\mu(R)\doteq-e\left[2\pi\int r'^2\,dr'\sin\theta'\,d\theta'\,\rho(r',\theta',R)\right.$$
$$\left.\times[r'\cos\theta']-\left(\frac{Z_AM_B-Z_BM_A}{M_A+M_B}\right)R\right] \tag{43}$$

is the permanent dipole moment of target molecule and thus

$$V^{(m')}_{l'v',l''v''}(r)\underset{r\to\infty}{\simeq}-\frac{\mu^{(m')}_{l'v',l''v''}}{r^2}. \tag{44}$$

The meaning of $\mu^{(m')}_{l'v',l''v''}$ is clear from Eq. (6) and $(l'l''1)$ satisfies the triangular relation. If the magnitude of $\mu(R)$ is significantly large, we have a somewhat ambiguous situation when defining asymptotic (scattering) boundary conditions because of $1/r^2$ dependence in Eq. (44) which is the same as in the centrifugal potential $l(l+1)/r^2$. A similar problem is encountered for close-coupling theory of space-fixed or moving body-fixed frame of I. For example, if one includes the above static potential in $V(r,R,\gamma)$,

$$V^{J}_{v'j'l',v''j''l''}(r)\underset{r\to\infty}{\simeq}-\frac{\mu^{J}_{v'j'l',v''j''l''}}{r^2}. \tag{45}$$

[The meaning of $\mu^{J}_{v'j'l',v''j''l''}$ can be inferred again from Eq. (I-15)]. However, careful calculation[14] and mathematical examination[15] show that the close-coupling cross sections of electron-polar molecule scattering are finite due to the finite energy separation between j states which are neglected in fixed-nuclei theory.

C. DWBA expression of hybrid theory

We briefly discuss the DWBA for electron–diatomic-molecule scattering, since the calculation of V – R transition cross sections with DWBA are much simpler to carry out than those of either hybrid theory or V – R close-coupling theory. Moreover, it is useful for rough, but quick estimation of collision cross sections considering the fact that the agreements on the pure rotational excitation cross sections for electron–diatomic-molecule scattering between DWBA and close-coupling theory are within 40% in many cases.[3] By direct calculations, it is seen that the scattering amplitude for V – R transitions employing DWBA is expressed by the form of Eq. (23) with $\tilde{T}^{J}_{v'j'l',vjl}$ replaced by $\bar{\bar{T}}^{J}_{v'j'l',vjl}$ given as follows:

$$\bar{\bar{T}}^{J}_{v'j'l',vjl}=-\frac{2\mu_e}{\hbar^2}(k_{v'j'}k_{vj})^{1/2}i^{l-l'}e^{i(\delta'_{l'}+\delta_l)}$$
$$\times\int r^2\,dr\,R_{l'}(k_{v'j'},r)$$
$$\times V^{J}_{v'j'l',vjl}(r)R_l(k_{vj},r). \tag{46}$$

Here, $R_l(k_{vj},r)$ and $R_{l'}(k_{v'j'},r)$ are the incident and scattered partial waves of the electron, distorted by the appropriate (central) potential between electron and molecule. They have the following asymptotic behaviors:

$$R_l(k_{vj},r)\underset{r\to\infty}{\simeq}\frac{\sin(k_{vj}r-\frac{1}{2}l\pi+\delta_l)}{k_{vj}r},$$
$$R_{l'}(k_{v'j'},r)\underset{r\to\infty}{\simeq}\frac{\sin(k_{v'j'}r-\frac{1}{2}l'\pi+\delta'_{l'})}{k_{v'j'}r}. \tag{47}$$

From Eqs. (I-15), (6), and (13), one can show that

$$\bar{\bar{T}}^{J}_{v'j'l',vjl}=\frac{[(2j'+1)(2j+1)]^{1/2}}{2J+1}$$
$$\times\sum_{m'}\langle l'm'j'o|Jm'\rangle\bar{\bar{T}}^{(m')}_{l'v',lv}\langle lm'jo|Jm'\rangle \tag{48}$$

with

$$\bar{\bar{T}}^{(m')}_{l'v',lv}=-\frac{2\mu_e}{\hbar^2}(k_vk_{v'})^{1/2}i^{l-l'}e^{i(\delta'_{l'}+\delta_l)}$$
$$\times\int r^2\,dr\,R_{l'}(k_{v'},r)V^{(m')}_{l'v',lv}(r)R_l(k_v,r). \tag{49}$$

Here, we have neglected again the j dependences in k_{vj} and $\phi_{vj}(R)$. Then $\bar{\bar{T}}^{(m')}_{l'v',lv}$ is the DWBA expression for vibrational transition matrix element of hybrid theory.

D. $l_{z'}$-conserving close-coupling formulation

For each $m'\geq 0$, the number of channels N needed to solve the coupled differential equation [Eq. (4)]

of hybrid theory is seen to be

$$N=(l'_{\max}-m'+1)\times(\text{number of vibrational states coupled}) \qquad (50)$$

for heteronuclear target molecule. For homonuclear target molecule, the number of channels is about half of the number given by the above equation [Eq. (50)] for each $\vec{r}$ parity $(-1)^{l'}$. These numbers are considerably smaller than those of V – R close-coupling theory in either space-fixed or body-fixed frame of I when many vibrational states are coupled. For example, the number of channels N' in the coupled differential equation of body-fixed frame [Eq. (I-50)], for given J and when m' values are not truncated, is given as

$$N'=[\text{number of }(l'm')\text{ with } l'_{\max}\geq l'\geq m'\geq 0 \text{ and } J\geq m'] \times(\text{number of vibrational states coupled}) \qquad (51)$$

for heteronuclear target molecule and (+) parity. In this section, we present a scheme which has a similar nature and simplicity as hybrid theory, that is, m' is conserved in that scheme, but the rotational motion of target molecule is also partly taken into account. We have seen that hybrid theory is equivalent to j independence in ϵ_{vj} and $\phi_{vj}(R)$. We now relax this condition, retaining j indices [in ϵ_{vj} and $\phi_{vj}(R)$], and follow the V – R close-coupling formulation of body-fixed frame in I. But we neglect off-diagonal elements of all quantities defined there. More specifically, we put

$$\begin{gathered}\bar{V}^{J}_{v'l'm',v''l''m''}(r)=0,\quad \bar{\epsilon}^{J}_{v'l'm',m''}=0,\Lambda^{\pm J}_{v'l'm',m''}=0\\ \bar{F}^{J}_{v'l'm',m''}(r)=0,\quad \bar{G}^{J}_{v'l'm',m''}(r)=0 \text{ for } m'\neq m''.\end{gathered} \qquad (52)$$

Then m' is conserved in the body-fixed coupled differential equation [Eq. (I-34)] and thus, from the asymptotic boundary condition [Eq. (I-40)], we obtain

$$\bar{T}^{J}_{v'l'm',vlm}=0,\quad \bar{g}^{J}_{v'l'm',vlm}(r)=0 \ \text{ when } m'\neq m. \qquad (53)$$

Equations (I-34) and (I-40) of close-coupling formulation of moving body-fixed frame are then reduced to

$$\left(\frac{d^2}{dr^2}-\frac{l'(l'+1)}{r^2}+\frac{2\mu_e}{\hbar^2}\bar{\epsilon}^{J}_{v'l'm',m'}\right)\bar{g}^{J}_{v'l'm',vlm'}(r) =\frac{2\mu_e}{\hbar^2}\sum_{v''l''}\bar{V}^{J}_{v'l'm',v''l''m'}(r)\bar{g}^{J}_{v''l''m',vlm'}(r) \qquad (l,l',l''\geqslant|m'|) \qquad (54)$$

and

$$\bar{g}^{J}_{v'l'm',vlm'}(r) \underset{r\to\infty}{\sim} i^{l'}\Lambda^{-J}_{v'l'm',m'}[\delta_{v'v}\delta_{l'l}\bar{F}^{J}_{v'l'm',m'}(r) +(\bar{G}^{J}_{v'l'm',m'}(r)+i\bar{F}^{J}_{v'l'm',m'}(r)) \times\bar{T}^{J}_{v'l'm',vlm'}]\Lambda^{+J}_{vlm',m'}, \qquad (55)$$

respectively, and above Eqs. (54) and (55) are of the similar forms as those of hybrid theory [Eqs. (4) and (5)], except they depend on both m' and J, the total angular momentum. Therefore, one has to solve the coupled differential equation for each m' and J with $J\geq m'\geq 0$, separately, but the number of channels is equal to that of hybrid theory given by Eq. (50) and the equation below. It is seen that the procedures of evaluating V – R transition cross sections are the same as those in hybrid theory, replacing $T^{(m')}_{l'v',lv}$ by $\bar{T}^{J}_{v'l'm',vlm'}$, after solutions of coupled differential equation are obtained. The vibrational transition cross section of the present scheme is

$$\sigma_{vj\to v'}=\sum_{j'}\sigma_{vj\to v'j'} =\frac{4\pi}{k^2_{vj}}\frac{1}{2j+1}\sum_{Jl'lm'}(2J+1) \times\left|U^{Jl}_{jm'}\bar{T}^{J}_{v'l'm',vlm'}\right|^2, \qquad (56)$$

which has slightly different form from that of hybrid theory [Eq. (10)] and depends on the initial rotational quantum number. If the reactance matrix boundary condition is used, we have

$$\bar{K}^{J}_{v'l'm',vlm}=0,\quad \bar{f}^{J}_{v'l'm',vlm}(r)=0 \ \text{ when } m'\neq m, \qquad (57)$$

by the same argument as above. $\bar{T}^{J}_{v'l'm',vlm}$ obtained from $\bar{K}^{J}_{v'l'm',vlm}$ through Eq. (I-66) have the property of Eq. (53). This scheme requires a little more work than the original hybrid theory, yet it is much simpler to perform close-coupling calculation in this approach than in the (exact) V – R close-coupling formulation of space-fixed and body-fixed frame. While the internuclear axis component of incident electronic angular momentum is conserved in the present approach, the rotational motions of target molecule are also partly taken into consideration as seen from $\vec{J}=\vec{l}+\vec{j}$ and $J\neq l'$, in general, obtaining $\vec{j}\neq 0$. We propose this $l_{z'}$-conserving close-coupling formulation for calculation of V – R transition cross sections by low-energy electron-molecule collisions. It should be pointed out that another method of including the j dependence of the radial part of the V – R wave function $\phi_{vj}(R)$ has been given by Temkin and Sullivan[16] derived from fixed-nuclei theory as a function of R. While the vibrational states are not dynamically coupled in their method, it is simpler than the present scheme proposed in this section.

III. SUMMARY AND DISCUSSIONS

We have presented a reformulation of hybrid theory for V – R transitions of electron–diatomic-molecule collisions, first proposed by Chandra and Temkin.[9] We obtained the expressions of scattering amplitude, differential, integral, and momentum transfer cross sections of hybrid theory for the simultaneous V – R transitions in corresponding forms as those of V – R close-coupling theory, except the transition matrix elements, $T^{J}_{v'j'l';vjl}$, of total angular momentum representation are replaced by $\tilde{T}^{J}_{v'j'l',vjl}$ given by Eq. (24). Thus the transition matrix elements of both V – R close-coupling and hybrid theory can be compared with each other in addition to corresponding cross sections. DWBA expression of vibrational transition matrix elements of hybrid theory has also been presented.

We have further shown that the V – R close-coupling theory is equivalent to the hybrid theory in both body-fixed and space-fixed frame when j dependences in $\phi_{vj}(R)$ and ϵ_{vj} are neglected. That is, results of hybrid theory can be obtained by simple substitutions $\phi_{vj}(R) \rightarrow \phi_{v}(R), \epsilon_{vj} \rightarrow \epsilon_{v}$ into the V – R close-coupling formulation of a body-fixed frame of I; these substitutions turn out to correspond to the synthesis of vibrational close-coupling theory with fixed-nuclei approximation and rotationally adiabatic-nuclei approach [Eq. (22)]. We point out that the neglect of j dependence in $\phi_{vj}(R)$ is also required to obtain fixed-nuclei approximation or hybrid theory, where the internuclear axis component of incident electronic angular momentum is conserved, from close-coupling theory.

We point out here also that, in the V – R close-coupling theory, if one neglects rotational quantum number dependences for the energy levels only, as in a work of Bottcher[13] for pure rotational transitions, one will get neither fixed-nuclei approximation nor hybrid theory where internuclear axis components of incident electronic angular momentum are conserved. The reason is that the effects of rotational quantum numbers are also appreciable in the radial parts of target molecular wave functions when those quantum numbers are sufficiently large.

In the expressions for the V – R transition cross section of hybrid theory given by Chandra and Temkin, the relations between hybrid and close-coupling theory in both space-fixed and body-fixed frame presented above are not transparent, because they did not use the total angular momentum representation in their formulation. It is now clear that the discrepancies between the result of the hybrid theory and the V – R close-coupling theory originate from the assumption of j independence in $\phi_{vj}(R)$ and ϵ_{vj}. It is known, however, that the effects of j indices are significant even in $V^{\lambda}_{vj,v'j'}(r)$ in Eq. (I-16) for $v \neq v'$ due to j dependence in $\phi_{vj}(R)$.[17]

An $l_{z'}$-conserving close-coupling formulation, derived from V – R close-coupling formulation in the moving body-fixed frame of I, has also been presented. This formulation has a similar nature and simplicity to hybrid theory in that m' is conserved, but the rotational motions of target molecule are also partly taken into consideration during the collision process. In other words, the fixed-nuclei assumption is relaxed to a certain extent. It is interesting to see the above formulation in the classical picture again. In the fixed-nuclei approach, the incident electron keeps precessing around the (space) fixed internuclear axis; but in our formulation, it keeps precessing around "moving" internuclear axis when the appropriate initial conditions are set up. In the (exact) V – R close-coupling formulation of either body-fixed or space-fixed frame, the electron will not keep precessing around the internuclear axis whatever the initial conditions may be. Therefore, one might call it "$l_{z'}$-conserving close-coupling approximation."

A final remark about hybrid theory and the present scheme will be added here. The m' (or $l_{z'}$) conservation plays a fundamental role for reducing the dimension (or the number of channels) of coupled differential equation in both the original hybrid theory and the present approximation scheme. In comparison with the original hybrid theory, the appearance of the total angular momentum J in our scheme does not increase the dimension of the coupled equation, while it does require solving the coupled differential equation more often. Thus when the exchange and polarization potentials are correctly included, the original hybrid approach becomes much simpler than the present one and it could be an enormous gain. We simply want to point out that the present scheme is also tractable in that case.

The approximation scheme proposed in Sec. II D is being tested by direct numerical calculations. The results of the calculation using our $l_{z'}$-conserving close-coupling approximation as well as the V – R close-coupling formulation in the body-fixed frame of I and that of the hybrid theory will be reported in a later publication.

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