Theor Chem Acc (2000) 105:123–131
DOI 10.1007/s002140000189

Theoretical
Chemistry Accounts

Regular article

The Born closure approximation for the scattering amplitude of an electron-molecule collision

Yukikazu Itikawa

Institute of Space and Astronautical Science, Yoshinodai, Sagamihara 229-8510, Japan
e-mail: itikawa@pub.isas.ac.jp; Tel.: +81-42759-8205; Fax: +81-42759-8209

Received: 12 June 2000 / Accepted: 6 July 2000 / Published online: 24 October 2000

Abstract. When the fixed-nuclei (FN) approximation is applied to the calculation of electron scattering from a polar molecule, the resulting cross section diverges in the forward direction of scattering. This is due to the long-range nature of the interaction between the electron and the molecular dipole. To avoid this difficulty, a hybrid method is proposed for the calculation of the scattering amplitude. This method is based on the FN approximation for a close collision and the Born approximation for a distant collision. The present paper describes the detailed formulation of the method for practical applications. Furthermore the present approach is extended to other long-range interactions (due to quadrupole moment and/or polarization effect) and to a dipole-allowed vibrational excitation. In these cases, while no divergence occurs, it is often difficult to confirm the convergence of the partial-wave expansion. With the employment of the present approach, it is much easier to confirm the convergence and hence to obtain reliable cross sections. The formulas are given for diatomic molecules as well as for polyatomic ones.

Key words: Electron-molecule collision – Rotational transition – Vibrational excitation – Fixed-nuclei approximation – Polar molecule

Introduction

One of the specific features of electron-molecule scattering, in contrast to an electron scattering by an atom in its S state, is the presence of electric multipole moments of the molecule. The electric moment exerts a long-range, anisotropic force on the incident electron. Long-range forces are very important in low-energy collisions. In particular an electric dipole moment leads to a very large cross section for an electron scattering from a polar molecule. Electron-polar molecule collisions are of great practical importance and have been extensively studied both experimentally and theoretically [1, 2].

Another feature of electron-molecule collisions is the role of the nuclear degrees of freedom of the molecule. The nuclear motion increases the number of channels to be considered. To make the calculation more tractable, use is often made of the fixed nuclei (FN) approximation, in which the nuclear coordinates are held fixed during the collision [3]. Since the nuclear motion (i.e., molecular rotation and vibration) is relatively slow compared with the speed of the colliding electron, this approximation normally holds, unless the collision energy is extremely low or the collision time is particularly long due to long-range forces.

Most of the theoretical studies of electron-molecule collisions, particularly for polyatomic molecules, have employed the FN approximation. When we apply the FN approximation to the scattering of electrons from a polar molecule, however, the differential cross section (DCS) diverges in the forward scattering direction. This is due to the fact that the electron-dipole interaction decays very slowly with increasing distance. Because of this divergence, we cannot calculate the integral cross section for an electron-polar molecule collision in the FN approximation.

To avoid this divergence problem but still take advantage of the simplicity of the FN approximation, several hybrid approaches have been proposed. They usually divide the partial wave expansion into two parts. For lower partial waves, the main contribution comes from the electron interactions at distances close to the target. There the nuclear motion of the molecule is less effective in determining the electron motion, so that the FN approximation can be applied safely. On the other hand the higher partial waves are mainly determined by the interactions at distances far from the target. In this case, we have to take into account the nuclear motion correctly. The interaction at a large distance from the target is normally so weak that the first order perturbation (the Born) approximation can be used. Thus combining the Born formula for a distant collision with the FN approximation for a close one, we can derive an approximate formula for the cross section calculation of polar molecules without encountering any divergence problem.

On the basis of this philosophy Norcross and Padial developed an approximate method called MEAN [4]. In a similar manner Rescigno and others [5] proposed another approach that is based on the direct evaluation of the squared modulus of the scattering amplitude, for which the hybrid procedure is taken. Recently the present author derived a compact form of the cross section formula along the latter approach [6, 7]. It is more useful for practical applications and can be extended to various problems. The present paper gives the details of the method and shows its advantages over the others.

The present Born-closure method can easily be extended to long-range interactions other than the electron interaction with a permanent dipole. For instance, an electron interaction with a molecular quadrupole moment or with an induced dipole in the target also has long range. These interactions do not cause divergence of the cross section, but the convergence of the partial wave expansion is sometimes so slow that it is difficult to confirm. Another case is dipole-allowed vibrational transition. Since the vibrational motion is not necessarily slow compared with the electron speed, use is often made of the fixed-nuclear-orientation (FNO) approximation. In this approximation, the orientation of the molecule is fixed during the collision, but the vibrational motion is considered correctly. In the case of a dipole-allowed transition, the interaction responsible for the transition decays slowly with the electron-molecule distance. In this case the present Born-closure approach is also useful to obtain converged cross sections.

In the main part of the present paper, an electron collision with a diatomic molecule is considered. First a general outline of the formulation is described for rotational transitions. A DCS formula for rotational transitions is then derived on the basis of a direct evaluation of the squared scattering amplitude. The Born closure method is applied to the scattering amplitude. The formulation here is then applied to the quadrupole and/or induced-dipole interaction. Finally, vibrational transitions are considered followed by concluding remarks. The Born scattering amplitude and related quantities are presented in Appendix A. The formulas in the present paper can be extended to electron scattering from a polyatomic molecule. For the readers' convenience, formulas for a polyatomic molecule are presented in Appendix B.

Rotational cross section in the FN approximation

Here we apply the FN approximation to the problem of an electron scattering from a (polar) diatomic molecule. Furthermore only the rotational motion is considered for the nuclear degrees of freedom of the molecule. (Vibrational motion is considered later.) Atomic units are used throughout the present paper.

First we solve the scattering equation in the body-fixed frame (BF) of the coordinates. In this frame, the z axis is taken along the molecular axis, or more precisely along the direction of the molecular dipole. The scattering amplitude obtained in the FN approximation is given by [8]

$$f^{\mathrm{FN(BF)}} = \sum_{\ell}\sum_{\ell'}\sum_{\Lambda} \frac{2\pi}{k} i^{\ell-\ell'+1} T^{\Lambda}_{\ell\ell'} Y_{\ell'\Lambda}\left(\hat{k}'_{\mathrm{out}}\right) Y^{*}_{\ell\Lambda}\left(\hat{k}'_{\mathrm{in}}\right) \; . \tag{1}$$

Here ℓ (ℓ') is the initial (final) orbital angular momentum quantum number of the electron and k is the wave number of the colliding electron. In the FN approximation, the rotational energy is ignored with respect to the electron kinetic energy. Since the molecule is symmetric about the z axis, the z-component of the angular momentum (i.e., Λ) is conserved during the collision. The quantities $\hat{k}'_{\mathrm{in}}$ and $\hat{k}'_{\mathrm{out}}$ denote the directions of the incident and outgoing electrons in the BF, respectively. The transition matrix element $T^{\Lambda}_{\ell\ell'}$ is defined through the relation

$$S = 1 - T \; , \tag{2}$$

where S is the scattering matrix obtained in the BF scheme.

We transform the coordinate system into the laboratory-fixed frame (LF), where the z axis is taken along the direction of the incident electron. The scattering amplitude (Eq. 1) is transformed into

$$\begin{aligned} f^{\mathrm{FN(LF)}} = {} & \sum_{j}\sum_{\mu}\sum_{\ell}\sum_{\ell'}\sum_{\Lambda} \frac{2\pi}{k} i^{\ell-\ell'+1} T^{\Lambda}_{\ell\ell'} \\ & \times (-1)^{\Lambda}[(2j+1)(2l+1)]^{\frac{1}{2}} \\ & \times \begin{pmatrix} \ell' & \ell & j \\ \mu & 0 & -\mu \end{pmatrix} \\ & \times \begin{pmatrix} \ell' & \ell & j \\ \Lambda & -\Lambda & 0 \end{pmatrix} Y_{\ell'\mu}\left(\hat{k}_{\mathrm{out}}\right) Y_{j,-\mu}\left(\hat{R}\right) \; . \end{aligned} \tag{3}$$

Here the directions of the outgoing electron and the molecular axis in the LF are denoted by $\hat{k}_{\mathrm{out}}$ and $\hat{R}$, respectively, and $\begin{pmatrix} \ell' & \ell & j \\ \mu & 0 & -\mu \end{pmatrix}$ etc. are the 3-j symbols. The 3-j symbols are defined elsewhere [9]. For the sake of clarity, we rewrite the scattering amplitude (Eq. 3) in the form

$$f^{\mathrm{FN(LF)}} = \sum_{\ell}\sum_{\ell'} f^{\mathrm{FN}}_{\ell\ell'} \tag{4}$$

with

$$f^{\mathrm{FN}}_{\ell\ell'} = \sum_{j}\sum_{\mu} a_{j\mu}(\ell\ell') \tilde{T}^{j}_{\ell\ell'} Y_{j,-\mu}(\hat{R}) \; . \tag{5}$$

In Eq. (5) we have introduced two quantities, $a_{j\mu}$ and $\tilde{T}^{j}_{\ell\ell'}$. They are defined by

$$\begin{aligned} a_{j\mu} = {} & \frac{2\pi}{k} i^{\ell-\ell'+1} [(2j+1)(2\ell+1)]^{\frac{1}{2}} \\ & \times \begin{pmatrix} \ell' & \ell & j \\ \mu & 0 & -\mu \end{pmatrix} Y_{\ell'\mu}\left(\hat{k}_{\mathrm{out}}\right) \end{aligned} \tag{6}$$

and

$$\tilde{T}^{j}_{\ell\ell'} = \sum_{\Lambda} (-1)^{\Lambda} \begin{pmatrix} \ell' & \ell & j \\ \Lambda & -\Lambda & 0 \end{pmatrix} T^{\Lambda}_{\ell\ell'} \ . \tag{7}$$

The quantity j represents the angular momentum transfer during the collision.

In the FN approximation, the scattering amplitude for the rotational transition is evaluated with the formula [3]

$$f^{\mathrm{FN,rot}}(j_0 m_{j0} \to j_1 m_{j1}) = \int \mathrm{d}\hat{R}\, Y^{*}_{j_1 m_{j1}}(\hat{R}) f^{\mathrm{FN(LF)}} \times (\hat{R})\, Y_{j_0 m_{j0}}(\hat{R}) \ , \tag{8}$$

where j_0 (j_1) is the rotational quantum number of the initial (final) state and m_{j0} (m_{j1}) denotes the respective sublevel. The DCS for the rotational transition is now obtained by

$$q^{\mathrm{FN}}(j_0 \to j_1) = \frac{1}{2j_0+1} \sum_{m_{j0}} \sum_{m_{j1}} \left| f^{\mathrm{FN,rot}}(j_0 m_{j0} \to j_1 m_{j1}) \right|^2 \ . \tag{9}$$

With the use of Eqs. (8) and (3), and taking an integration over the molecular orientation, we have the cross section in the form

$$q^{\mathrm{FN}}(j_0 \to j_1) = \sum_{j} (2j_1+1) \begin{pmatrix} j_0 & j_1 & j \\ 0 & 0 & 0 \end{pmatrix}^2 \tilde{q}(j) \tag{10}$$

with

$$\tilde{q}(j) = \sum_{\lambda} \tilde{A}_{\lambda}(j) P_{\lambda}(\cos\theta) \ . \tag{11}$$

In this equation, P_{λ} is a Legendre polynomial, θ is the scattering angle in the LF frame, and the coefficient $\tilde{A}_{\lambda}(j)$ is given by

$$\begin{aligned} \tilde{A}_{\lambda}(j) = {} & \frac{1}{4k^2} (2j+1)(2\lambda+1) \sum_{\ell\ell'} \sum_{\bar{\ell}\bar{\ell}'} i^{\ell-\ell'-\bar{\ell}+\bar{\ell}'} \\ & \times (-1)^{\lambda+j} \tilde{T}^{j}_{\ell\ell'} \left(\tilde{T}^{j}_{\bar{\ell}\bar{\ell}'}\right)^{*} \\ & \times \left[(2\ell+1)(2\ell'+1)(2\bar{\ell}+1)(2\bar{\ell}'+1)\right]^{\frac{1}{2}} \\ & \times \begin{pmatrix} \ell & \bar{\ell} & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell' & \bar{\ell}' & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} \ell & \ell' & j \\ \bar{\ell}' & \bar{\ell} & \lambda \end{Bmatrix} \ . \end{aligned} \tag{12}$$

Here $\begin{Bmatrix} \ell & \ell' & j \\ \bar{\ell}' & \bar{\ell} & \lambda \end{Bmatrix}$ is the 6-j symbol, which is defined elsewhere [9].

When we define the vibrationally elastic cross section by

$$q^{\mathrm{FN}}_{\mathrm{elas}}(j_0) = \sum_{j_1} q^{\mathrm{FN}}(j_0 \to j_1) \ , \tag{13}$$

it is simply obtained from Eq. (10) as

$$q^{\mathrm{FN}}_{\mathrm{elas}}(j_0) = \sum_{j} \tilde{q}(j) \ . \tag{14}$$

It should be noted that the cross section for the vibrationally elastic process, therefore, does not depend on the initial state (j_0) of the molecular rotation. This is one of the specific features of the FN approximation.

Now we consider the convergence of the partial wave expansion. In principle, the summation over ℓ (and $\bar{\ell}$) in Eq. (12) should be taken to infinity. (Note that once ℓ and λ are fixed the summation over ℓ' is limited to a finite range.) If the interaction between the electron and the molecule is not so long-ranged as the dipole one, the convergence over ℓ is reasonably rapid. In such a case, we can safely truncate the sum at a finite value of ℓ (say, $\ell = \ell_{\mathrm{max}}$). Then the summation over λ in Eq. (11) needs to be taken only over the range $\lambda \leq 2\ell_{\mathrm{max}}$. It is well known, however, that, in the FN approximation, the partial wave expansion does not converge for a dipole interaction [1, 2]. To solve this problem, several methods have been proposed.

If we calculate the rotational cross section without resorting to the FN approximation, the cross section can be expressed in the form [3]

$$q(j_0 \to j_1) = \sum_{\lambda}^{\infty} A_{\lambda}(j_0 \to j_1) P_{\lambda}(\cos\theta) \ . \tag{15}$$

Here the coefficient A_{λ} is a quantity similar to $\bar{A}_{\lambda}$ in Eq. (11), but evaluated without the FN approximation. Now we apply the Born approximation to the same collision problem, but take into account only the long-range part of the interaction. Since the distant collision is governed by the electric multipole moment of the molecule, we actually apply the Born approximation to the interaction between the electron and the multipoles of the molecule. (Hereafter we call that the Born-multipole approximation.) Then we have

$$q^{\mathrm{B(M)}}(j_0 \to j_1) = \sum_{\lambda}^{\infty} A^{\mathrm{B(M)}}_{\lambda}(j_0 \to j_1) P_{\lambda}(\cos\theta) \ , \tag{16}$$

where the index B(M) indicates the quantity evaluated in the Born-multipole approximation. With the use of Eqs. (15) and (16), we have an identity

$$\begin{aligned} q(j_0 \to j_1) = {} & q^{\mathrm{B(M)}}(j_0 \to j_1) \\ & + \sum_{\lambda}^{\infty} \left[A_{\lambda}(j_0 \to j_1) - A^{\mathrm{B(M)}}_{\lambda}(j_0 \to j_1) \right] \\ & \times P_{\lambda}(\cos\theta) \ . \end{aligned} \tag{17}$$

When λ is large, the contribution of higher partial waves dominates. For the higher partial waves, the scattering is mainly determined by the long-range part of the interaction and the Born-multipole approximation can be used. Thus, as the λ increases, the coefficient A_{λ} becomes closer to the Born multipole value $A^{\mathrm{B(M)}}_{\lambda}$. Accordingly the summation over λ in Eq. (17) can be truncated at a finite value of λ (say, $\lambda = \lambda_{\mathrm{max}}$). Furthermore, since only the short-range part of the interaction contributes to the difference $A_{\lambda} - A^{\mathrm{B(M)}}_{\lambda}$, it can be calculated in the FN approximation. Then we have an approximate formula to evaluate the rotational cross section without any divergence problem:

$$q^{\mathrm{MEAN}}(j_0 \to j_1) = q^{\mathrm{B(M)}}(j_0 - j_1) + \sum_{\lambda}^{\lambda_{\max}} \Big[A_\lambda^{\mathrm{FN}}(j_0 \to j_1) - A_\lambda^{\mathrm{B(M),FN}}(j_0 \to j_1) \Big] P_\lambda(\cos\theta) \ . \quad (18)$$

This has been proposed by Norcross and Padial [4] and called the MEAN (Multipole Extracted Adiabatic Nuclei) method. The coefficient A_λ^{FN} is now obtained with $\tilde{A}_\lambda$ in Eq. (12) in such a way that

$$A_\lambda^{\mathrm{FN}}(j_0 \to j_1) = \sum_j (2j_1 + 1) \begin{pmatrix} j_0 & j_1 & j \\ 0 & 0 & 0 \end{pmatrix}^2 \tilde{A}_\lambda(j) \ . \quad (19)$$

The coefficient $A_\lambda^{\mathrm{B(M),FN}}$ in Eq. (18) is calculated with the same formula as Eq. (19), but by replacing the transition matrix T with the corresponding quantity in the Born-multipole approximation.

For a polar molecule, the dipole moment is dominant in the long-range part of the interaction. Usually we consider only the dipole interaction in the Born-multipole approximation. In that case the rotational cross section in the Born approximation is given by [1]

$$q^{\mathrm{B(dipole)}}(j_0 \to j_1 | \theta) = \frac{4}{3} \mu_{\mathrm{D}}^2 \frac{j_>}{2j_0 + 1} \frac{k_1}{k_0} \frac{1}{k_0^2 + k_1^2 - 2k_0 k_1 \cos\theta} \delta_{j_1, j_0 \pm 1} \ . \quad (20)$$

Here μ_{D} is the dipole moment, k_0 (k_1) is the wave number of the electron before (after) the collision, and $j_>$ is the larger of (j_0, j_1). From the selection rule of the first-order perturbation theory, only the transition $j_0 \to j_1 = j_0 \pm 1$ is allowed in the Born-dipole approximation.

As is described above, the scattering at a high partial wave (say, for $\ell \geq \ell_{\mathrm{B}}$) can be treated by the Born-multipole approximation. That is, we have a relation

$$\tilde{T}^j_{\ell\ell'} = \left(\tilde{T}^j_{\ell\ell'}\right)^{\mathrm{B(M)}} \quad \text{for} \quad \ell \geq \ell_{\mathrm{B}} \ . \quad (21)$$

The quantity on the right side of Eq. (21) is the reduced T matrix element evaluated in the Born-multipole approximation (see Appendix A).

As can be seen in Eq. (12), A_λ is a quadratic form of the transition matrix. Each A_λ has a contribution of an interference term between $\tilde{T}$ with large ℓ and those with small ℓ. The term with large ℓ can be replaced with the Born value, but those with small ℓ cannot. Thus the interference terms in A_λ cannot simply be canceled with the corresponding terms in $A_\lambda^{\mathrm{B(M)}}$. As the λ increases, the contribution of the interference terms relatively decreases and hence A_λ should become gradually closer to the corresponding Born value. However, if the summation over λ is truncated too early, the resulting cross section has a nonphysical undulation in the angular distribution and sometimes even a negative value. Thus great care should be taken about where we truncate the summation over λ in Eq. (18).

The Born closure method for the scattering amplitude

There is another formula of the DCS for the rotational transition in the electron-molecule collision. It is based on the direct evaluation of the square modulus of the scattering amplitude. As is shown in Eqs. (4) and (5), the scattering amplitude in the FN approximation is of the form

$$f^{\mathrm{FN}} = \sum_\ell \sum_{\ell'} \sum_j \sum_\mu a_{j\mu}(\ell\ell') \tilde{T}^j_{\ell\ell'} Y_{j,-\mu}(\hat{R}) \ . \quad (22)$$

Substituting this into Eq. (8) and integrating it over the molecular orientation, we have the scattering amplitude for the rotational transition

$$\begin{aligned} f^{\mathrm{FN,rot}}(j_0 m_{j0} \to j_1 m_{j1}) &= (-1)^{m_{j1}} \left[\frac{(2j_0 + 1)(2j_1 + 1)}{4\pi} \right]^{\frac{1}{2}} \\ &\times \sum_j \sum_\mu \sum_\ell \sum_{\ell'} a_{j\mu}(\ell\ell') \tilde{T}^j_{\ell\ell'} (2j + 1)^{\frac{1}{2}} \\ &\times \begin{pmatrix} j_1 & j & j_0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j_1 & j & j_0 \\ -m_{j1} & -\mu & m_{j0} \end{pmatrix} \ . \end{aligned} \quad (23)$$

Inserting this into Eq. (9) and taking the summation over the rotational sublevels, we obtain the DCS in the form

$$q^{\mathrm{FN}}(j_0 \to j_1) = \sum_j (2j_1 + 1) \begin{pmatrix} j_0 & j_1 & j \\ 0 & 0 & 0 \end{pmatrix}^2 \tilde{q}(j) \quad (24)$$

with

$$\tilde{q}(j) = \frac{1}{4\pi} \sum_{\mu=-j}^{j} \left| \sum_\ell \sum_{\ell'} a_{j\mu}(\ell\ell') \tilde{T}^j_{\ell\ell'} \right|^2 \ . \quad (25)$$

It is not difficult to show that Eq. (11) can be derived from Eq. (25) or vice versa.

To avoid the direct evaluation of the infinite sum over the partial waves in Eq. (25), we introduce the Born closure method. As in the previous section, we apply the Born approximation to the electron-multipole interaction and have the scattering amplitude in the form

$$f^{\mathrm{B(M),FN}} = \sum_\ell \sum_{\ell'} f^{\mathrm{B(M),FN}}_{\ell\ell'} \ . \quad (26)$$

Then we introduce an identity relation

$$f^{\mathrm{FN}} = f^{\mathrm{B(M),FN}} + \sum_\ell \sum_{\ell'} \left[f^{\mathrm{FN}}_{\ell\ell'} - f^{\mathrm{B(M),FN}}_{\ell\ell'} \right] \ . \quad (27)$$

With the use of the relation at Eq. (5) and the corresponding formula in the Born approximation (see Appendix A), this can be written in the form

$$f^{\mathrm{FN}} = \sum_j \sum_{\mu=-j}^{j} \left\{ B_j^{-\mu}(\boldsymbol{K}) + \sum_\ell \sum_{\ell'} a_{j\mu}(\ell\ell') \left[\tilde{T}^j_{\ell\ell'} - \left(\tilde{T}^j_{\ell\ell'}\right)^{\mathrm{B(M)}} \right] \right\} Y_{j,-\mu}(\hat{R}) \ . \quad (28)$$

The term B on the right-hand side of Eq. (28) is given by

$$B_j^{-\mu}(\boldsymbol{K}) = -\frac{8\pi}{2j+1} i^j v^j(K) Y^*_{j,-\mu}(\hat{K}) \ , \tag{29}$$

where $v^j(K)$ is an integral defined by Eq. (A.4) in Appendix A.

In exactly the same way as in the derivation of Eq. (25) from Eq. (22), the following formula is derived from Eq. (28):

$$\tilde{q}(j) = \frac{1}{4\pi}\sum_{\mu=-j}^{j}\left| B_j^{-\mu}(\boldsymbol{K}) + \sum_{\ell}\sum_{\ell'} a_{j\mu}(\ell\ell')\left[\tilde{T}^j_{\ell\ell'} - \left(\tilde{T}^j_{\ell\ell'}\right)^{\mathrm{B(M)}}\right]\right|^2 . \tag{30}$$

With the use of the relation at Eq. (21), we can safely truncate the summation over ℓ at $\ell = \ell_{\mathrm{B}}$. That is, we have an approximate formula of the DCS in the form

$$\tilde{q}^{\mathrm{app}}(j) = \frac{1}{4\pi}\sum_{\mu=-j}^{j}\left| B_j^{-\mu}(\boldsymbol{K}) + \sum_{\ell}^{\ell_{\mathrm{B}}}\sum_{\ell'} a_{j\mu}(\ell\ell')\left[\tilde{T}^j_{\ell\ell'} - \left(\tilde{T}^j_{\ell\ell'}\right)^{\mathrm{B(M)}}\right]\right|^2 . \tag{31}$$

When we put Eq. (31) into Eq. (24), we obtain an approximate formula of the cross section for the rotational transition. This formula has only one parameter ℓ_{B}. It can be clearly determined from the relation at Eq. (21). The formula at Eq. (31) is in contrast to the MEAN formula (Eq. 18), in which it is not a simple matter to determine the parameter $\lambda_{\max}$. In this sense, the present formula (Eq. 31) is more reliable to calculate the DCS. The idea of using the Born closure for the scattering amplitude, instead of the MEAN method, was first proposed by Fliflet and McKoy [5] in their calculation of the (dipole allowed) electronic transition of a hydrogen molecule in the collision with electrons. Later Rescigno and his colleagues [5] showed clearly its advantage over the MEAN method. In their treatment, however, the integration over the molecular orientation was taken numerically and hence no analytic form of the cross section with the Born closure was presented explicitly. They stated in their paper that the numerical integration procedure is preferred because it is easier to extend to polyatomic molecules. This is not the case actually. It is not difficult to extend the present formula to any polyatomic molecule (see Appendix B).

As in the case of MEAN, the formula at Eq. (31) can be applied to any (long-ranged) interaction between the electron and the molecule. In the following, the Born closure method is applied to the dipole interaction. (Other long-range interactions are considered in the next section.) In the Born approximation, the dipole moment contributes only to the term with $j = 1$ (see Appendix A). We adopt, therefore, the term with $j = 1$ from the approximate formula at Eq. (31) and others from the correct formula (Eq. 25). For the latter, the summation over ℓ can be truncated at a finite value. In the multipole expansion of the interaction potential (see Eq. A.2), the dipole term of the interaction has the form

$$V_1^{\mathrm{dipole}} = -\frac{\mu_{\mathrm{D}}}{r^2} \ . \tag{32}$$

The Born amplitude (Eq. 29) with $j = 1$ becomes

$$B_1^{-\mu} = \frac{8\pi}{3} i\mu_{\mathrm{D}} \frac{1}{K} Y^*_{1,-\mu}(\hat{K}) \ . \tag{33}$$

A spherical harmonic function can be separated into two parts in such a way that

$$Y_{\ell m}(\theta,\phi) = C_{\ell m}(\theta)\exp(im\phi) \ . \tag{34}$$

With the use of this, the terms B and a in Eq. (31) are rewritten as

$$B_1^{-\mu} = \frac{8\pi}{3} i\mu_{\mathrm{D}} \frac{1}{K} C_{1,-\mu}(\theta_K)\exp(i\mu\phi_K) \tag{35}$$

and

$$a_{1\mu} = \frac{2\pi}{k} i^{\ell-\ell'+1}[3(2\ell+1)]^{\frac{1}{2}} \times \begin{pmatrix} \ell' & \ell & 1 \\ \mu & 0 & -\mu \end{pmatrix} C_{\ell'\mu}(\theta)\exp(i\mu\phi) \ . \tag{36}$$

Considering the relation between the momentum transfer vector and the direction of the scattered electron, we can put ϕ_{K} to be equal to ϕ (see Appendix A). Then we have

$$\tilde{q}^{\mathrm{app}}(1) = \frac{1}{4\pi}\sum_{\mu=-1}^{1} \left| \frac{8\pi}{3}\mu_D \frac{1}{K} C_{1,-\mu}(\theta_K) + \sum_{\ell}^{\ell_{\mathrm{B}}}\sum_{\ell'} \frac{2\pi}{\mathrm{k}} i^{\ell-\ell'}[3(2\ell+1)]^{\frac{1}{2}} \times \begin{pmatrix} \ell' & \ell & 1 \\ \mu & 0 & -\mu \end{pmatrix} C_{\ell'\mu}(\theta)\left[\tilde{T}^1_{\ell\ell'} - \left(\tilde{T}^1_{\ell\ell'}\right)^{\mathrm{B}}\right]\right|^2 . \tag{37}$$

Now the cross section $\tilde{q}^{\mathrm{app}}$ depends only on the scattering angle θ (see Appendix A for the relation between θ and θ_K). The Born transition matrix element for the dipole interaction is given in Eq. (A.17), the letter M in the superfix being simply omitted here):

$$\left(\tilde{T}^1_{\ell\ell'}\right)^{\mathrm{B}} = -\frac{4}{3} i\mu_{\mathrm{D}} k[(2\ell+1)(2\ell'+1)]^{\frac{1}{2}} \begin{pmatrix} \ell' & \ell & 1 \\ 0 & 0 & 0 \end{pmatrix} I^1_{\ell\ell'}(kk) \tag{38}$$

with

$$I^1_{\ell\ell'}(kk) = \frac{\sin\left[\frac{\pi(\ell-\ell')}{2}\right]}{k(\ell-\ell')(\ell+\ell'+1)} \ . \tag{39}$$

Since the momentum transfer K vanishes at $\theta = 0$, the first term in the right-side of Eq. (37) diverges there. Similarly to the MEAN method, we can modify the formula at Eq. (37) by introducing the Born scattering amplitude for a rotating dipole. Usually the difference between the formulas of the fixed-dipole and the rotating-dipole appears only in the close vicinity of the forward direction. If we are not interested in the forward scattering, we can use the formula at Eq. (37) as it is. The DCS for the forward scattering can be evaluated with sufficient accuracy by using the Born formula for the rotating dipole (i.e., Eq. 20).

The Born closure formula for the quadrupole and/or induced-dipole interaction

Equation (31) in the previous section can be used for any kind of long-ranged interaction. Except for the dipole one, the resulting cross section converges with respect to the partial wave expansion. In some cases, however, the convergence may be very slow. In such cases, the Born closure approximation (Eq. 31) is helpful. For the convenience of practical applications, detailed formulas for the quadrupole and/or induced-dipole interaction are presented below.

The electron interaction with a quadrupole moment (denoted by Θ) of the molecule contributes to the term with $n=2$ in the multipole expansion (Eq. A.2). If we take into account the polarization of the target (i.e., the induced dipole), this provides a second contribution to the $n=2$ term of the potential. Adding both contributions, one obtains

$$V_2^{\text{quadrupole}} = -\frac{\Theta}{r^3} - \frac{\alpha'}{2r^4} \ , \tag{40}$$

where α' represents the anisotropic part of the molecular polarizability. From Eq. (31), an approximate form of the cross section term with $j = 2$ is given by

$$\tilde{q}^{\text{app}}(2) = \frac{1}{4\pi}\sum_{\mu=-2}^{2}\left| B_2^{-\mu}(\boldsymbol{K}) + \sum_{\ell}^{\ell_{\text{B}}}\sum_{\ell'} a_{2\mu}(\ell\ell')\left[\tilde{T}^2_{\ell\ell'} - \left(\tilde{T}^2_{\ell\ell'}\right)^{\text{B}}\right]\right|^2 \tag{41}$$

with

$$B_2^{-\mu}(\boldsymbol{K}) = \left(-\frac{8\pi}{15}\Theta - \frac{\pi^2}{20}\alpha' K\right) Y^*_{2,-\mu}(\hat{K}) \ . \tag{42}$$

The corresponding transition matrix elements in the Born approximation are obtained as (see Appendix A)

$$\begin{aligned}\left(\tilde{T}^2_{\ell\ell'}\right)^{\text{B}} = &-\frac{4}{5} i\Theta k[(2\ell+1)(2\ell'+1)]^{\frac{1}{2}}\begin{pmatrix} \ell' & \ell & 2 \\ 0 & 0 & 0\end{pmatrix} I^2_{\ell\ell'}(kk) \\ &-\frac{2}{5} i\alpha' k[(2\ell+1)(2\ell'+1)]^{\frac{1}{2}}\begin{pmatrix} \ell' & \ell & 2 \\ 0 & 0 & 0\end{pmatrix} I^3_{\ell\ell'}(kk) \ .\end{aligned} \tag{43}$$

The integrals $I^2_{\ell\ell'}(kk)$ and $I^3_{\ell\ell'}(kk)$ are evaluated analytically with the use of the formula at Eq. (A.15) in Appendix A.

The isotropic part of the polarization interaction contributes to the multipole term with $n = 0$:

$$V_0^{\text{pol}} = -\frac{\alpha}{2r^4} \ , \tag{44}$$

where α is the isotropic part of the polarizability. The corresponding cross section can be calculated by

$$\tilde{q}^{\text{app}}(0) = \frac{1}{4\pi}\left| B_0(\boldsymbol{K}) + \sum_{\ell}^{\ell_{\text{B}}}\sum_{\ell'} a_{00}(\ell\ell')\left[\tilde{T}^0_{\ell\ell'} - \left(\tilde{T}^0_{\ell\ell'}\right)^{\text{B}}\right]\right|^2 \tag{45}$$

with

$$B_0 = 2\sqrt{\pi}\alpha I_0^p(K) \ . \tag{46}$$

The transition matrix element in the Born approximation is given by

$$\left(\tilde{T}^0_{\ell\ell'}\right)^{\text{B}} = -2i\alpha k(2\ell+1)\begin{pmatrix} \ell & \ell & 0 \\ 0 & 0 & 0\end{pmatrix} I^p_{\ell\ell'}(k)\delta_{\ell\ell'} \ . \tag{47}$$

Here we have introduced the integrals

$$I_0^p(K) = \int_0^\infty \mathrm{d}r\, r^{-2} j_0(Kr) \tag{48}$$

and

$$I^p_{\ell\ell'}(k) = \int_0^\infty \mathrm{d}r\, r^{-2} j_\ell(kr) j_{\ell'}(kr) \ . \tag{49}$$

When we evaluate the integral at Eq. (48), the lower limit (i.e., $r = 0$) of the integral gives rise to a problem. However, since the integral at Eq. (49) with $\ell = \ell' = 0$ has exactly the same problem, taking the difference of the two terms in Eq. (45) solves the difficulty.

The Born closure formula for the vibrational transition in the FNO approximation

In this section, vibrational excitation of a diatomic molecule is considered. Here the rotational motion is treated in the sudden approximation, but the vibrational motion is considered correctly. In other words, use is made of the fixed-nuclear orientation (FNO) approximation [6]. In this sense, the following formulation is a simple extension of the (vibrationally) elastic case in the previous sections to the inelastic case.

In the FNO approximation, the scattering amplitude for the vibrational transition $n_0 \rightarrow n_1$ is given by

$$f^{\text{FNO}}(n_0 \rightarrow n_1) = \sum_{\ell}\sum_{\ell'} f^{\text{FNO}}_{\ell\ell'} \tag{50}$$

and

$$f^{\text{FNO}}_{\ell\ell'} = \sum_{j}\sum_{\mu} a_{j\mu}(\ell\ell'|k_0k_1)\tilde{T}^j_{n_0\ell,n_1\ell'} Y_{j,-\mu}(\hat{R}) \ . \tag{51}$$

Here we consider the vibrationally inelastic problem so that k_0 and k_1 are the electron wave numbers before and after the collision. Now the coefficient a and the reduced transition matrix element $\tilde{T}^j_{n_0\ell,n_1\ell'}$, respectively, have the forms

$$\begin{aligned} a_{j\mu}(\ell\ell'|k_0k_1) = &\frac{2\pi}{\sqrt{k_0k_1}} i^{\ell-\ell'+1}[(2j+1)(2\ell+1)]^{\frac{1}{2}} \\ &\times \begin{pmatrix} \ell' & \ell & j \\ \mu & 0 & -\mu\end{pmatrix} Y_{\ell'\mu}\left(\hat{k}_{\text{out}}\right)\end{aligned} \tag{52}$$

and

$$\tilde{T}^j_{n_0\ell,n_1\ell'} = \sum_{\Lambda}(-1)^{\Lambda}\begin{pmatrix} \ell' & \ell & j \\ \Lambda & -\Lambda & 0\end{pmatrix} T^{\Lambda}_{n_0\ell,n_1\ell'} \ . \tag{53}$$

The cross section for vibrational excitation is obtained as

$$q^{\mathrm{FNO}}(n_0 \to n_1) = \sum_j \tilde{q}(n_0 \to n_1|j) \tag{54}$$

and

$$\tilde{q}(n_0 \to n_1|j) = \frac{1}{4\pi}\sum_{\mu=-j}^{j}\left|\sum_{\ell}\sum_{\ell'} a_{j\mu}(\ell\ell'|k_0k_1)\tilde{T}^{j}_{n_0\ell,n_1\ell'}\right|^2 \ . \tag{55}$$

Here we have taken a sum over the final rotational states and an average over the initial rotational states.

In the vibrationally inelastic problem, the interaction matrix element with respect to the initial and the final vibrational states is the point of concern. If the matrix element decays slowly with the distance, the convergence of the partial wave expansion is very slow. In particular if the vibrational transition considered is dipole allowed, we may have a difficulty of slow convergence. (It should be noted that no divergence occurs in the inelastic process.) In such a case, the Born closure approximation is useful. The approximate formula for the vibrational transition caused by the dipole interaction is given in the form [6]

$$\begin{aligned}\tilde{q}^{\mathrm{app}}(n_0 \to n_1|1) = \frac{1}{4\pi}\sum_{\mu=-1}^{1}\Bigg| & B_1^{-\mu}(\boldsymbol{K}) \\ & + \sum_{\ell}^{\ell_{\mathrm{B}}}\sum_{\ell'} a_{1\mu}(\ell\ell'|k_0k_1) \\ & \times \left[\tilde{T}^1_{n_0\ell,n_1\ell'} - \left(\tilde{T}^1_{n_0\ell,n_1\ell'}\right)^{\mathrm{B}}\right]\Bigg|^2\end{aligned} \tag{56}$$

with

$$B_1^{-\mu} = \frac{8\pi}{3} i\langle n_1|\mu_{\mathrm{D}}|n_0\rangle \frac{1}{K} Y^*_{1,-\mu}(\hat{K}) \ . \tag{57}$$

In this equation, the matrix element of the dipole moment with respect to the initial and final vibrational states is denoted by $\langle n_1|\mu_{\mathrm{D}}|n_0\rangle$. It should be noted that the momentum transfer for the inelastic case is given by

$$K^2 = k_0^2 + k_1^2 - 2k_0k_1 \ \cos\theta \tag{58}$$

Considering the dipole interaction, the Born formula for the transition matrix element is of the form

$$\begin{aligned}\left(\tilde{T}^1_{n_0\ell,n_1\ell'}\right)^{\mathrm{B}} &= -\frac{4}{3} ik\langle n_1|\mu_{\mathrm{D}}|n_0\rangle[(2\ell+1)(2\ell'+1)]^{\frac{1}{2}} \\ &\times \begin{pmatrix} \ell' & \ell & 1 \\ 0 & 0 & 0 \end{pmatrix} I^1_{\ell\ell'}(k_0k_1) \ .\end{aligned} \tag{59}$$

The integral $I^1_{\ell\ell'}(k_0k_1)$ can be evaluated with the formula at Eq. (A.15) in Appendix A.

Conclusion

One of the specific features of electron-molecule collisions is the long-range nature of the interaction. Since the interaction decays slowly with the electron-molecule distance, the partial-wave expansion often converges very slowly. The electron-dipole interaction has the longest range so that the worst case is electron scattering from a polar molecule. In particular, if we apply the fixed-nuclei approximation to the electron-polar molecule collision, the resulting cross section diverges in the forward scattering direction. To remedy these difficulties and accelerate the convergence of the partial-wave expansion, a Born-closure method has been proposed for the calculation of scattering amplitude.

In the present paper, the Born-closure method for the scattering amplitude is described in detail. For the application to low-energy electron-molecule collisions, detailed formulations are given for the rotational or vibrational excitation of molecules. After a general formula is derived for any kind of long-range interaction, more detailed formulas are presented for the interactions between the electron and static dipole and quadrupole moments and also an induced-dipole moment.

Practical applications of the present formulas have been attempted so far in two cases: rotational excitation of HCl [7] and excitation of dipole-allowed mode of vibration of CO_2 [6]. The results are satisfactory in both cases.

Appendix A. Scattering amplitude in the Born approximation

In the first-order perturbation theory, the scattering amplitude is evaluated with the formula

$$f^{\mathrm{B}} = -\frac{1}{2\pi}\int \mathrm{d}\boldsymbol{r}\ \exp(\boldsymbol{i}\boldsymbol{K}\cdot\boldsymbol{r})V \ , \tag{A.1}$$

where V is the interaction potential and $\boldsymbol{K}$ is the momentum transfer during the collision. Since the molecule is axi-symmetric, the interaction potential can be expanded as

$$V = \sum_n V_n(r)P_n(\hat{r}\cdot\hat{R}) \ . \tag{A.2}$$

With the use of this and the partial wave expansion of exp $(\boldsymbol{iK}\cdot\boldsymbol{r})$, the scattering amplitude (in the LF) can be calculated as

$$f^{\mathrm{B}} = \sum_n\sum_{m_n}\left(-\frac{8\pi}{2n+1}\right)i^n Y^*_{nm_n}(\hat{K})Y_{nm_n}(\hat{R})\upsilon^n(K) \ , \tag{A.3}$$

where

$$\upsilon^n(K) = \int_0^\infty \mathrm{d}r\ r^2 j_n(Kr)V_n(r) \ . \tag{A.4}$$

Here j_n is the spherical Bessel function. Denoting the momenta of the incident and the scattered electrons by $\boldsymbol{k}$ and $\boldsymbol{k}'$, respectively, we have the relation $\exp(\boldsymbol{iK}\cdot\boldsymbol{r}) = \exp(\boldsymbol{ik}\cdot\boldsymbol{r})\ \exp(\text{-}\boldsymbol{ik}'\cdot\boldsymbol{r})$. With the partial wave expansion of each of $\exp(\boldsymbol{ik}\cdot\boldsymbol{r})$ and $\exp(\text{-}\boldsymbol{ik}'\cdot\boldsymbol{r})$, another form of f^{B} is obtained in such a way that

$$
\begin{aligned}
f^{\mathrm{B}} = {} & \sum_{\ell}\sum_{\ell'}\sum_{n}\sum_{m_n} \frac{2\pi}{\sqrt{kk'}} i^{\ell-\ell'+1} [(2n+1)(2\ell+1)]^{\frac{1}{2}} \\
& \times \begin{pmatrix} \ell' & \ell & n \\ m_n & 0 & -m_n \end{pmatrix} Y_{\ell' m_n}\left(\hat{k}_{\mathrm{out}}\right) \theta \frac{4i\sqrt{kk'}}{2n+1} \\
& \times [(2\ell+1)(2\ell'+1)]^{\frac{1}{2}} \\
& \times \begin{pmatrix} \ell' & \ell & n \\ 0 & 0 & 0 \end{pmatrix} Y_{n,-m_n}\left(\hat{R}\right) \upsilon^{n}_{\ell\ell'}(kk') \ .
\end{aligned}
\tag{A.5}
$$

with

$$\upsilon^{n}_{\ell\ell'}(kk') = \int_0^\infty \mathrm{d}r\, r^2 j_\ell(kr) j_{\ell'}(k'r) V_n(r) \ . \tag{A.6}$$

The direction of the momentum transfer, denoted by $(\theta_K,\ \phi_K)$, is related to the directions of the scattered electron as

$$\cos\theta_K = \frac{k}{K} - \frac{k'}{K}\cos\theta \tag{A.7}$$

$$\sin\theta_K = -\frac{k'}{K}\sin\theta \tag{A.8}$$

$$\phi_K = \phi \tag{A.9}$$

and

$$K^2 = k^2 + k'^2 - 2kk' \ \cos\theta \ . \tag{A.10}$$

Now we apply the Born approximation to the interaction of the electron with the electric multipole moments of the molecule. The multipole term of the interaction potential has the form

$$V_n^{\mathrm{M}}(r) = -\frac{M_n}{r^{n+1}} \ , \tag{A.11}$$

where the constant M_n is related to the multipole moment of the molecule. The integrals over r in the Eqs. (A.4) and (A.6) can now be evaluated through the quantities

$$\upsilon^n(K) = -M_n I^n(K) \tag{A.12}$$

$$\upsilon^n_{\ell\ell'}(kk') = -M_n I^n_{\ell\ell'}(kk') \tag{A.13}$$

with

$$I^n(K) = \int_0^\infty \mathrm{d}r\, r^{1-n} j_n(Kr) \tag{A.14}$$

$$I^n_{\ell\ell'}(kk') = \int_0^\infty \mathrm{d}r\, r^{1-n} j_\ell(kr) j_{\ell'}(k'r) \ . \tag{A.15}$$

Furthermore, we employ the FN approximation. Then we have the same formulas as above, but with the relation $k = k'$ and $K^2 = 2k^2(1–\cos\theta)$. Thus the Born scattering amplitude for the electron-multipole interaction, evaluated in the FN approximation, is of the form

$$f^{\mathrm{B(M),FN}}_{\ell\ell'} = \sum_j \sum_\mu a_{j\mu}(\ell\ell') \left(\tilde{T}^j_{\ell\ell'}\right)^{\mathrm{B(M)}} Y_{j,-\mu}\left(\hat{R}\right) \ . \tag{A.16}$$

Here the coefficient $a_{j\mu}(\ell\ell')$ is the same as in Eq. (6) in the text and the corresponding transition matrix element is given by

$$
\begin{aligned}
\left(\tilde{T}^j_{\ell\ell'}\right)^{\mathrm{B(M)}} = {} & -M_j \frac{4ik}{2j+1} [(2\ell+1)(2\ell'+1)]^{\frac{1}{2}} \\
& \times \begin{pmatrix} \ell & \ell' & j \\ 0 & 0 & 0 \end{pmatrix} I^j_{\ell\ell'}(kk)
\end{aligned}
\tag{A.17}
$$

It should be noted that only the multipole moment M_j of the molecule contributes to the transition matrix element with the angular momentum transfer j.

Appendix B. The Born-closure formulas for polyatomic (polar) molecules

Here an electron collision with polyatomic molecules is considered in the fixed-nuclear orientation (FNO) approximation to give a cross section for vibrational excitation [10]. Cross sections for a vibrationally elastic process can be easily derived in the same manner as in this Appendix. First we solve the scattering equation in the BF scheme, where the z-axis is taken along the dipole moment of the molecule. When we ignore the rotational motion of the molecule, the total wave function of the (electron + molecule) system is expressed as

$$\Psi = \sum_{n'\ell'v'} r^{-1} u_{n'\ell'v'}(r) \chi_{n'}(\xi) X^{v'}_{\ell'}(\hat{r}') \ . \tag{B.1}$$

Here $\chi_{\mathrm{n}}(\xi)$ is the vibrational wave function, for which the normal coordinates and the vibrational quantum numbers are collectively denoted by ξ and n, respectively. The angular part of the electron motion is expressed in terms of a symmetry-adapted angular basis function

$$X^v_\ell(\hat{r}') = \sum_{\mu_\ell} b^v_{\ell\mu_\ell} Y_{\ell\mu_\ell}(\hat{r}') \ . \tag{B.2}$$

The radial part of the wave function of the colliding electron satisfies a set of coupled equations

$$
\begin{aligned}
& \left[\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{\ell'(\ell'+1)}{r^2} + k^2_{n'}\right] u_{n'\ell'v'}(r) \\
& \quad = 2 \sum_{n''\ell''v''} \langle n'\ell'v' | V | n''\ell''v'' \rangle u_{n''\ell''v''}(r) \ ,
\end{aligned}
\tag{B.3}
$$

where the interaction matrix elements are defined by

$$
\begin{aligned}
\langle n'\ell'v' | V | n''\ell''v'' \rangle = {} & \int \mathrm{d}\xi \int \mathrm{d}\hat{r}'\ \chi^*_{n'}(\xi) \left(X^{v'}_{\ell'}(\hat{r}')\right)^* \\
& \times V \chi_{n''}(\xi) X^{v''}_{\ell''}(\hat{r}') \ .
\end{aligned}
\tag{B.4}
$$

In Eq. (B.3), $k_{n'}$ is the wave number of the scattered electron in the channel $(n',\ \ell',\ v')$. From the solution of Eq. (B.3), we derive the scattering matrix (in the BF) in a standard manner.

With the use of the scattering matrix, the scattering amplitude is obtained as

$$f^{\mathrm{FNO(BF)}} = \sum_{\ell\ell'} \sum_{vv`} \sum_{nn'} \frac{2\pi}{\sqrt{k_n k_{n'}}} i^{\ell-\ell'+1} T^{n\ell v}_{n'\ell' v`} X^{v`}_{\ell'}\left(\hat{k}'_{n'}\right) X^{v*}_{\ell}\left(\hat{k}'_{n}\right) , \tag{B.5}$$

where the transition matrix is defined by Eq. (2). Transforming the scattering amplitude in the BF into that in the LF, we finally have the form

$$f^{\mathrm{FNO}}(n_0 \to n_1) = \sum_{\ell} \sum_{\ell'} f^{\mathrm{FNO}}_{\ell\ell'} \tag{B.6}$$

with

$$f^{\mathrm{FNO}}_{\ell\ell'} = \sum_{j} \sum_{m} \sum_{\Lambda_j} A_{jm}(\ell\ell'|k_0 k_1) \tilde{T}^{j\Lambda_j}_{n_0\ell,n_1\ell'} D^{j*}_{-m,\Lambda_j}(\omega) , \tag{B.7}$$

where ω denotes the molecular orientation in the LF. Here the coefficient A and the reduced form of the transition matrix element are given by

$$A_{jm}(\ell\ell'|k_0 k_1) = \sqrt{\frac{\pi}{k_0 k_1}} i^{\ell-\ell'+1} (2\ell+1)^{\frac{1}{2}} (2j+1) \times \begin{pmatrix} \ell' & \ell & j \\ m & 0 & -m \end{pmatrix} Y_{\ell' m}\left(\hat{k}_1\right) \tag{B.8}$$

and

$$\tilde{T}^{j\Lambda_j}_{n_0\ell,n_1\ell'} = \sum_{\mu_\ell} \sum_{\mu_{\ell'}} (-1)^{\mu_\ell} \begin{pmatrix} \ell' & \ell & j \\ \mu_\ell & -\mu_{\ell'} & \Lambda_j \end{pmatrix} \times \left(\sum_{v} \sum_{v'} b^{v'}_{\ell'\mu_{\ell'}} T^{n_0 \ell v}_{n_1 \ell' v'} b^{v*}_{\ell\mu_\ell} \right) \tag{B.9}$$

The differential cross section for the vibrational transition is derived with the use of the formula

$$q^{\mathrm{FNO}}(n_0 \to n_1) = \frac{1}{8\pi^2} \int \mathrm{d}\omega \left| f^{\mathrm{FNO}}(n_0 \to n_1) \right|^2 \tag{B.10}$$

By using Eq. (B.7) and after the integration over the molecular orientation, the DCS is obtained in the form

$$q^{\mathrm{FNO}}(n_0 \to n_1) = \sum_{j} \sum_{m} \sum_{\Lambda_j} \frac{1}{2j+1} \times \left| \sum_{\ell} \sum_{\ell'} A_{jm}(\ell\ell'|k_0 k_1) \tilde{T}^{j\Lambda_j}_{n_0\ell,n_1\ell'} \right|^2 . \tag{B.11}$$

If the molecule is diatomic, the formula at Eq. (B.11) is easily shown to reduce to the corresponding one, Eq. (54) with Eq. (55). When we apply the Born closure method for the dipole interaction, we have an approximate formula of the form

$$\begin{aligned} q^{\mathrm{app}}(n_0 \to n_1) = {} & \sum_{m} \sum_{\Lambda_1} \frac{1}{3} \Bigg| \sqrt{\frac{3}{4\pi}} B_1^{-m}(\boldsymbol{K}) \delta_{\Lambda_1,0} \\ & + \sum_{\ell}^{\ell_{\mathrm{B}}} \sum_{\ell'} A_{1m}(\ell\ell'|k_0 k_1) \left[\tilde{T}^{1\Lambda_1}_{n_0\ell,n_1\ell'} - \left(\tilde{T}^{1\Lambda_1}_{n_0\ell,n_1\ell'} \right)^{\mathrm{B}} \right] \Bigg|^2 \\ & \times \sum_{j\neq 1} \sum_{m} \sum_{\Lambda_j} \frac{1}{2j+1} \left| \sum_{\ell} \sum_{\ell'} A_{jm}(\ell\ell'|k_0 k_1) \tilde{T}^{j\Lambda_j}_{n_0\ell,n_1\ell'} \right|^2 . \end{aligned} \tag{B.12}$$

Here B_1^{-m} is the quantity defined in Eq. (57) and the Born transition matrix element for the dipole interaction is given by

$$\left(\tilde{T}^{1\Lambda_1}_{n_0\ell,n_1\ell'} \right)^{\mathrm{B}} = -\frac{4}{3} ik \langle n_1 | \mu_D | n_0 \rangle [(2\ell+1)(2\ell'+1)]^{\frac{1}{2}} \times \begin{pmatrix} \ell' & \ell & 1 \\ 0 & 0 & 0 \end{pmatrix} I^{1}_{\ell\ell'}(k_0 k_1) \delta_{\Lambda_1,0} . \tag{B.13}$$

References

1. Itikawa Y (1978) Phys Rep 46: 117
2. Gianturco FA, Paioletti P (1998) In: Becker KH (ed) Novel aspects of electron-molecule collisions. World Scientific, Singapore, p 57
3. For a general theory of electron-molecule collisions see, for example, Lane NF (1980) Rev Mod Phys 52: 29
4. Norcross DW, Padial NT (1982) Phys Rev A 25: 226
5. Fliflet AW, McKoy V (1980) Phys Rev A 21: 1863; Rescigno TN, Schneider BI (1992) Phys Rev A 45: 2894; Rescigno TN, Lengsfield BH, McCurdy CW, Parken SD (1992) Phys Rev A 45: 7800
6. Takekawa M, Itikawa Y (1998) J Phys B 31: 3245
7. Shimoi M, Itikawa Y (1999) J Phys B 32: 65
8. Morrison MA, Sun W (1995) In: Huo W, Gianturco FA (eds) Computational methods for electron-molecule collisions. Plenum, New York, p 131
9. Zare RN (1988) Angular momentum. Wiley, New York
10. For a general theory of electron-impact vibrational excitation of polyatomic molecules, see Itikawa Y (1997) Int Rev Phys Chem 16: 155