

# Coupled Body-Frame Scattering Equations for Electron-Molecule Scattering

Hao Feng\*

*College of Physics, Sichuan University,  
Chengdu, Sichuan, 610065, P.R.China*

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## Abstract

This note is modified from Prof. Michael A. Morrison's note in April 1977. The author derived all equations and augmented some proofs and corrected some errors.

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\*Electronic address: [ddsteed@163.com](mailto:ddsteed@163.com)

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## I. EQUATION FOR THE SCATTERING FUNCTION

The general (N-electron) molecule wavefunction cannot be separated as the H<sub>2</sub> can, so we write the electronic wavefunction as

$$\Phi_{(n\Lambda)_\gamma}(\tau; R_\alpha) = \frac{1}{\sqrt{N!}} \sum_{\alpha\beta\cdots\pi} \epsilon_{\alpha\beta\cdots\pi} \bar{\phi}_\alpha(1) \bar{\phi}_\beta(2) \cdots \bar{\phi}_\pi(N) \quad (1)$$

where  $\tau$  denotes the collection of target molecular electrons,  $\bar{\phi}_\alpha(i)$  is the  $\alpha^{th}$  single-particle spin orbital for particle  $i$ , and  $\epsilon_{\alpha\beta\cdots\pi}$  is the Levi-Civita density[2]

$$\epsilon_{\alpha\beta\cdots\pi} = \begin{cases} 0 & \text{if any 2 indices are equal} \\ +1 & \text{even permutations} \\ -1 & \text{odd permutations} \end{cases}$$

We use  $R_\alpha$  to denote the nuclear coordinates (collectively). Since we are in the Body-Fixed reference frame,  $(n\Lambda)_\gamma$  denote the electronic state eigenfunction and its spin, respectively, for the  $\gamma^{th}$  state of the target molecule. Thus  $n$  collectively denotes symmetry ( $\pm$ )  $g$  or  $u$ ; and  $\Lambda$ , the projection of the total orbital angular momentum (of the molecule) along  $\hat{z} = \hat{R}$  ( $\Sigma, \Pi, \Delta$  for  $\Lambda = 0, 1, 2$ , etc.). Now since we neglect rotation, the “remaining” molecular wavefunction can be written as (Born-Oppenheimer)

$$\mathbf{X}_{(n\Lambda v)_\gamma}(\tau; R_\alpha) = \Phi_{(n\Lambda)_\gamma}(\tau; R_\alpha) \chi_{(n\Lambda v)_\gamma}^{vib}(R_\alpha) \quad (2)$$

with  $\chi_{(n\Lambda v)_\gamma}^{vib}$  the vibrational wavefunction. Note that  $\Phi_{(n\Lambda)_\gamma}$  here depends on the spin coordinates of the target electrons,  $\sigma_1, \dots, \sigma_N$ . When we mean the  $\alpha^{th}$  spin orbital, we write  $\bar{\phi}_\alpha(i)$ ; the corresponding spatial orbital is  $\phi_\alpha(\vec{r}_i)$ . Thus

$$\bar{\phi}_\alpha(i) = \phi_\alpha(\vec{r}_i) \chi_{m_s}^\alpha(\sigma_i) \quad (3)$$

The full molecular wavefunction of Eq. (2) satisfies the Schrödinger Equation

$$\hat{\mathcal{H}}_{mol} \mathbf{X}_{(n\Lambda v)_\gamma}(\tau; R_\alpha) = E_{(n\Lambda v)_\gamma} \mathbf{X}_{(n\Lambda v)_\gamma}(\tau; R_\alpha) \quad (4)$$

where  $\hat{\mathcal{H}}_{mol}$  is the full non-relativistic molecular Hamiltonian, written in general as

$$\hat{\mathcal{H}}_{mol} = \hat{\mathbf{T}} + \sum_{\alpha\beta} \frac{Z_\alpha Z_\beta}{|\vec{R}_\alpha - \vec{R}_\beta|} - \sum_{\alpha i} \frac{Z_\alpha}{|\vec{R}_\alpha - \vec{r}_i|} + \sum_{ij} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

Now, the wavefunction for the system of electron + molecule is expanded as

$$\psi_\gamma(\tau, \vec{r}, \sigma; R_\alpha) = \frac{1}{\sqrt{N+1}} \sum_{\gamma'} \sum_{i=1}^{N+1} (-1)^{N+1-i} \mathbf{X}_{\gamma'}(1, 2, \dots, i-1, i+1, \dots, N+1; R_\alpha) \bar{F}_\gamma^\gamma(i) \quad (5)$$

where  $\bar{F}_\gamma^\gamma(i)$  is the scattering function including the spin dependence

$$\bar{F}_\gamma^\gamma(i) = F_{\gamma'}^{(\gamma)}(\vec{r}_i) \chi_{m_s}^\gamma(\sigma_i) \quad (6)$$

and the factor of  $(N+1)^{-1/2}$  ensure consistent normalization with Eq. (1). This function is anti-symmetric. For convenience, we shall denote the target wavefunction as

$$\mathbf{X}_{\gamma'}(1, 2, \dots, i-1, i+1, \dots, N+1; R_\alpha) = \mathbf{X}_{\gamma'}(\bar{i}; R_\alpha) \quad (7)$$

where  $\bar{i}$  denotes not including the  $i^{th}$  electron.

Thus

$$\psi_\gamma(\tau, \vec{r}, \sigma; R_\alpha) = \frac{1}{\sqrt{N+1}} \sum_{\gamma'} \sum_{i=1}^{N+1} (-1)^{N+1-i} \mathbf{X}_{\gamma'}(\vec{i}; R_\alpha) \bar{F}_{\gamma'}^\gamma(i) \quad (8)$$

NOTE that for each  $\gamma'$  we carry out the indicated  $\sum_i$  — this summation is for purposes of antisymmetrizing and must be treated carefully! Here  $\gamma$  also labels the initial spin of the scattering  $e^-$ .

Our object is to determine an equation for the scattering function  $F_{\gamma'}^{(\gamma)}(\vec{r}_i)$  such that  $\psi_\gamma(\tau, \vec{r}, \sigma; R_\alpha)$  satisfies the SE

$$(\hat{\mathcal{H}} - E)\psi_\gamma(\tau, \vec{r}, \sigma; R_\alpha) = 0 \quad (9)$$

where  $E$ , the total energy of the system, is related to the target energy (for state  $\gamma$ ) by

$$E = \frac{1}{2}k_\gamma^2 + E_{(n\Lambda v)_\gamma} \quad (10)$$

The full Hamiltonian is

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_{mol}(\tau; R_\alpha) + \hat{\mathbf{T}}_e(\vec{r}) + V_{int}(\vec{r}_i, \vec{r}; R_\alpha) \quad (11)$$

where  $\vec{r}_i$  denotes all the spatial target electron coordinates, i.e.,  $\tau \equiv (\vec{r}_i, \sigma_i)$ . In general, the electron-molecule interaction potential energy is (atomic units)

$$V_{int} = - \sum_{\alpha} \frac{Z_\alpha}{|\vec{r} - \vec{R}_\alpha|} + \sum_i \frac{1}{|\vec{r} - \vec{r}_i|} \quad (12)$$

We shall eventually make the usual single-center expansion of the (spatial) scattering function  $F_{\gamma'}^{(\gamma)}(\vec{r}_i)$ , i.e.,

$$F_{\gamma'}^{(\gamma)}(\vec{r}_i) = \frac{1}{r} \sum_{\ell_{\gamma'} m_{\gamma'}} \mathcal{Y}_{\gamma'}^{(\gamma)}(r) Y_{\ell_{\gamma'}}^{m_{\gamma'}}(\hat{r}) \quad (13)$$

where the sum is over  $\ell_{\gamma'}$  and  $m_{\gamma'}$ , of course.

Alright, the SE for the system becomes (from Eq. (8) and Eq. (9))

$$(\hat{\mathcal{H}} - E) \frac{1}{\sqrt{N+1}} \sum_{\gamma'} \sum_i (-1)^{N+1-i} \mathbf{X}_{\gamma'}(\vec{i}; R_\alpha) \bar{F}_{\gamma'}^\gamma(i) \quad (14)$$

We now  $\otimes$

$$\left[ \mathbf{X}_{\gamma''}(\overline{N+1}; R_\alpha) \chi_{m_s}^{\gamma''}(\sigma_{N+1}) \right]^*$$

and integrate over  $d\tau \equiv d1 \cdots dN$  (includes sums over the spin coordinates) and sum over  $\sigma_{N+1}$ [3]. We also integrate over  $dR_\alpha$  (the vibrational coordinates), we get

$$I = \langle \mathbf{X}_{\gamma''}(\overline{N+1}; R_\alpha) \chi_{m_s}^{\gamma''}(\sigma_{N+1}) \mid \hat{\mathcal{H}} - E \mid \sum_{\gamma'} \sum_i (-1)^{N+1-i} \mathbf{X}_{\gamma'}(\bar{i}; R_\alpha) \bar{F}_{\gamma'}^\gamma(i) \rangle = 0 \quad (15)$$

Before we begin churning way on the algebra for this, let's summarizing the orthogonality relations we have to help us out:

1. We'll assure that the target wavefunctions, which satisfy Eq. (4) have been normalized,

$$\langle \mathbf{X}_{(n\Lambda v)_\gamma} \mid \mathbf{X}_{(n\Lambda v)_{\gamma'}} \rangle = \delta_{n_\gamma n_{\gamma'}} \delta_{\Lambda_\gamma \Lambda_{\gamma'}} \delta_{v_\gamma v_{\gamma'}} \quad (16)$$

2. For closed-shell targets, the PEP (Pauli Exclusive Principle) forbids the incident electron occupying a target orbital of the same symmetry, viz., for any scattering orbital, we have

$$\langle \bar{\phi}_\alpha(i) \mid \bar{F}_{\gamma'}^\gamma(i) \rangle = 0, \quad \forall \alpha \in \gamma' \quad (17)$$

It is easy (and useful!) to show the equivalence of Eq. (17) to a more general result, consider

$$I_t \equiv \langle \Phi_{(n\Lambda)_{\gamma'}}(\bar{i}; R_\alpha) \mid \bar{F}_{\gamma'}^\gamma(j) \rangle_j, \quad [\text{except } i = j = N + 1] \quad (18)$$

Using Eq. (1) for  $\Phi$ , this integral becomes

$$\begin{aligned} I_t &= \frac{1}{\sqrt{N!}} \sum_{\alpha\beta\cdots\pi} \epsilon_{\alpha\beta\cdots\pi} \langle \bar{\phi}_\alpha(1) \bar{\phi}_\beta(2) \cdots \bar{\phi}_\pi(N) \mid \bar{F}_{\gamma'}^\gamma(j) \rangle_j \\ &= \frac{1}{\sqrt{N!}} \sum_{\alpha\beta\cdots\pi} \epsilon_{\alpha\beta\cdots\pi} \bar{\phi}_\alpha(1) \bar{\phi}_\beta(2) \cdots \bar{\phi}_{\gamma-1}(j-1) \bar{\phi}_{\gamma+1}(j+1) \cdots \bar{\phi}_\pi(N) \langle \bar{\phi}_\gamma(j) \mid \bar{F}_{\gamma'}^\gamma(j) \rangle_j \end{aligned}$$

where  $\bar{\phi}_\gamma(j)$  is the spin-orbital corresponding to coordinates  $j$  in each term in the summation.

But by Eq. (17),  $I_t = 0$ , so we have for any  $i$  (except  $i = j = N + 1$ )

$$\langle \mathbf{X}_{(n\Lambda v)_{\gamma'}}(\bar{i}; R_\alpha) \mid \bar{F}_{\gamma'}^\gamma(j) \rangle_j = 0, \quad 1 \leq j \leq N + 1 \quad (19)$$

where we have combined  $I_t = 0$  with Eq. (17). Notice that many possibilities are covered by Eq. (19).

(From here on, we'll specialize to the case where no electronic excitation is allowed. The treatment of orthogonality becomes somewhat confusing if we allow for electronic excitation. And note that once we use Eq. (19), we are restricted to closed shell targets.)

Pulling the summation (now over  $v_{\gamma'}$  only) outside of Eq. (15), we have the integral

$$I \equiv \sum_{v_{\gamma'}} \langle \mathbf{X}_{\gamma''}(\overline{N+1}; R_\alpha) \chi_{m_s}^{\gamma''}(\sigma_{N+1}) \mid \hat{\mathcal{H}} - E \mid \sum_i (-1)^{N+1-i} \mathbf{X}_{\gamma'}(\bar{i}; R_\alpha) \bar{F}_{\gamma'}^\gamma(i) \rangle = 0 \quad (20)$$

This must be reduced to coupled integro-differential equations for  $F_{\gamma'}^{(\gamma)}(\vec{r}_i)$ . The best way to do this is to isolate types of terms which obtain  $\hat{\mathcal{H}}$  of Eq. (11) into Eq. (20). The  $\gamma'^{th}$  term here is

$$I_1^{(\gamma')} = \langle \mathbf{X}_{\gamma''}(\overline{N+1}; R_\alpha) \chi_{m_s}^{\gamma''}(\sigma_{N+1}) \mid \hat{\mathcal{H}}_{mol} \mid \sum_i (-1)^{N+1-i} \mathbf{X}_{\gamma'}(\bar{i}; R_\alpha) \bar{F}_{\gamma'}^\gamma(i) \rangle \quad (21a)$$

$$I_2^{(\gamma')} = \langle \mathbf{X}_{\gamma''}(\overline{N+1}; R_\alpha) \chi_{m_s}^{\gamma''}(\sigma_{N+1}) \mid \hat{\mathbf{T}}_e \mid \sum_i (-1)^{N+1-i} \mathbf{X}_{\gamma'}(\bar{i}; R_\alpha) \bar{F}_{\gamma'}^\gamma(i) \rangle \quad (21b)$$

$$I_3^{(\gamma')} = \langle \mathbf{X}_{\gamma''}(\overline{N+1}; R_\alpha) \chi_{m_s}^{\gamma''}(\sigma_{N+1}) \mid V_{int} \mid \sum_i (-1)^{N+1-i} \mathbf{X}_{\gamma'}(\bar{i}; R_\alpha) \bar{F}_{\gamma'}^\gamma(i) \rangle \quad (21c)$$

$$I_4^{(\gamma')} = \langle \mathbf{X}_{\gamma''}(\overline{N+1}; R_\alpha) \chi_{m_s}^{\gamma''}(\sigma_{N+1}) \mid \sum_i (-1)^{N+1-i} \mathbf{X}_{\gamma'}(\bar{i}; R_\alpha) \bar{F}_{\gamma'}^\gamma(i) \rangle \quad (21d)$$

and

$$I^{(\gamma')} = \sum_{i=1}^3 I_i^{(\gamma')} - E I_4^{(\gamma')}$$

$$I = \sum_{v_{\gamma'}} I^{(\gamma')}$$

We'll do each integral in turn:

1.  $I_1^{(\gamma')}$

$$I_1^{(\gamma')} = \langle \mathbf{X}_{\gamma''}(\overline{N+1}; R_\alpha) \chi_{m_s}^{\gamma''}(\sigma_{N+1}) \mid \hat{\mathcal{H}}_{mol} \mid \sum_{i=1}^{N+1} (-1)^{N+1-i} \mathbf{X}_{\gamma'}(\bar{i}; R_\alpha) \bar{F}_{\gamma'}^\gamma(i) \rangle$$

where

$$\hat{\mathcal{H}}_{mol} = \hat{\mathcal{H}}_{mol}(1, 2, \dots, N)$$

and

$$\mathbf{X}_{\gamma'}(\bar{i}; R_\alpha) = \mathbf{X}_{\gamma'}(1, 2, \dots, i-1, i+1, \dots, N+1; R_\alpha)$$

Thus

$$I_1^{(\gamma')} = \sum_i^N (-1)^{N+1-i} \langle \mathbf{X}_{\gamma''}(\overline{N+1}; R_\alpha) \chi_{m_s}^{\gamma''}(\sigma_{N+1}) \mid \hat{\mathcal{H}}_{mol} \mid \mathbf{X}_{\gamma'}(\bar{i}; R_\alpha) \bar{F}_{\gamma'}^\gamma(i) \rangle$$

$$+ \langle \mathbf{X}_{\gamma''}(\overline{N+1}; R_\alpha) \chi_{m_s}^{\gamma''}(\sigma_{N+1}) \mid \hat{\mathcal{H}}_{mol} \mid \mathbf{X}_{\gamma'}(\overline{N+1}; R_\alpha) \bar{F}_{\gamma'}^\gamma(N+1) \rangle$$

From Eq. (4) and Eq. (6), we get

$$\begin{aligned} I_1^{(\gamma')} &= \sum_{i=1}^N (-1)^{N+1-i} E_{\gamma''} \langle \mathbf{X}_{\gamma''}(\overline{N+1}; R_\alpha) \chi_{m_s}^{\gamma''}(\sigma_{N+1}) \mid \mathbf{X}_{\gamma'}(\bar{i}; R_\alpha) \bar{F}_{\gamma'}^\gamma(i) \rangle \\ &\quad + E_{\gamma''} \delta_{\gamma'\gamma''} F_{\gamma'}^{(\gamma)}(\vec{r}_{N+1}) \end{aligned}$$

From Eq. (19), the first term is 0. So,

$$I_1^{(\gamma')} = E_{\gamma'} \delta_{\gamma'\gamma''} F_{\gamma'}^{(\gamma)}(\vec{r}_{N+1}) \quad (22)$$

2.  $I_2^{(\gamma')}$

$$\begin{aligned} I_2^{(\gamma')} &= \langle \mathbf{X}_{\gamma''}(1, 2, \dots, N; R_\alpha) \chi_{m_s}^{\gamma''}(\sigma_{N+1}) \mid \\ &\quad \hat{\mathbf{T}}_e(N+1) \\ &\quad \mid \sum_{i=1}^{N+1} (-1)^{N+1-i} \mathbf{X}_{\gamma'}(1, 2, \dots, i-1, i+1, \dots, N+1; R_\alpha) \bar{F}_{\gamma'}^\gamma(i) \rangle \end{aligned}$$

so,

$$\begin{aligned} I_2^{(\gamma')} &= \sum_{i=1}^N (-1)^{N+1-i} \langle \mathbf{X}_{\gamma''}(1, 2, \dots, N; R_\alpha) \chi_{m_s}^{\gamma''}(\sigma_{N+1}) \mid \\ &\quad \hat{\mathbf{T}}_e(N+1) \\ &\quad \mid \mathbf{X}_{\gamma'}(1, 2, \dots, i-1, i+1, \dots, N+1; R_\alpha) \bar{F}_{\gamma'}^\gamma(i) \rangle \\ &\quad + \langle \mathbf{X}_{\gamma''}(1, 2, \dots, N; R_\alpha) \chi_{m_s}^{\gamma''}(\sigma_{N+1}) \mid \\ &\quad \hat{\mathbf{T}}_e(N+1) \\ &\quad \mid \mathbf{X}_{\gamma'}(1, 2, \dots, N; R_\alpha) \bar{F}_{\gamma'}^\gamma(N+1) \rangle \end{aligned} \quad (23)$$

The first term in Eq. (23) — the  $\sum_i$  — is zero by orthogonality [Eq. (19)] (Since  $i = N+1$  is excluded from the sum and  $\hat{\mathbf{T}}_e$  operates only on  $\vec{r}_{N+1}$ ). The second term is simply

$$I_2^{(\gamma')} = -\frac{1}{2} \nabla_{N+1}^2 F_{\gamma'}^{(\gamma)}(\vec{r}_{N+1}) \delta_{\gamma'\gamma''} \quad (24)$$

3.  $I_3^{(\gamma')}$  (the tough one!)

$$I_3^{(\gamma')} = \langle \mathbf{X}_{\gamma''}(\overline{N+1}; R_\alpha) \chi_{m_s}^{\gamma''}(\sigma_{N+1}) \mid V_{int} \mid \sum_{i=1}^{N+1} (-1)^{N+1-i} \mathbf{X}_{\gamma'}(\bar{i}; R_\alpha) \bar{F}_{\gamma'}^\gamma(i) \rangle \quad (25)$$

where

$$V_{int} = - \sum_{\alpha} \frac{Z_{\alpha}}{r_{\alpha,N+1}} + \sum_j \frac{1}{r_{j,N+1}} \quad (26)$$

We have defined in Eq. (26) the equations

$$r_{\alpha,N+1} = |\vec{R}_{\alpha} - \vec{r}_{N+1}| \quad (27a)$$

$$r_{j,N+1} = |\vec{r}_j - \vec{r}_{N+1}| \quad (27b)$$

The first term in Eq. (25) — which comes from the electron-nucleus part of Eq. (26) — is identical to  $I_2^{(\gamma')}$  in form except for the  $\int d\tau_{\alpha}$ . Thus we get from this term

$$\langle \chi_{v_{\gamma''}}(R_{\alpha}) | - \sum_{\alpha} \frac{Z_{\alpha}}{|\vec{r}_{N+1} - \vec{R}_{\alpha}|} | \chi_{v_{\gamma'}}(R_{\alpha}) \rangle \int_{dR_{\alpha}} F_{\gamma'}^{(\gamma)}(\vec{r}_{N+1}) \quad (28)$$

where  $\chi_{v_{\gamma'}}(R_{\alpha})$  is the nuclear vibrational wavefunction.

We are left with the “two-electron” integral(s), call them  $I_{3b}$ :

$$I_{3b} \equiv \sum_{j=1}^N \langle \mathbf{X}_{\gamma''}(\overline{N+1}; R_{\alpha}) \chi_{m_s}^{\gamma''}(\sigma_{N+1}) | \frac{1}{r_{j,N+1}} | \sum_{i=1}^{N+1} (-1)^{N+1-i} \mathbf{X}_{\gamma'}(\bar{i}; R_{\alpha}) \bar{F}_{\gamma'}^{\gamma}(i) \rangle \quad (29)$$

So,

$$\begin{aligned} I_{3b} = & \sum_{j=1}^N \langle \mathbf{X}_{\gamma''}(\overline{N+1}; R_{\alpha}) \chi_{m_s}^{\gamma''}(\sigma_{N+1}) | \frac{1}{r_{j,N+1}} | \sum_{i=1}^N (-1)^{N+1-i} \mathbf{X}_{\gamma'}(\bar{i}; R_{\alpha}) \bar{F}_{\gamma'}^{\gamma}(i) \rangle \\ & + \sum_{j=1}^N \langle \mathbf{X}_{\gamma''}(\overline{N+1}; R_{\alpha}) \chi_{m_s}^{\gamma''}(\sigma_{N+1}) | \frac{1}{r_{j,N+1}} | \mathbf{X}_{\gamma'}(\overline{N+1}; R_{\alpha}) \bar{F}_{\gamma'}^{\gamma}(N+1) \rangle \end{aligned} \quad (30)$$

The second term in Eq. (30) is (doing the spin integration) by referring to Eq. (2) and Eq. (6)

$$\begin{aligned} & \sum_{j=1}^N \langle \mathbf{X}_{\gamma''}(\overline{N+1}; R_{\alpha}) | \frac{1}{r_{j,N+1}} | \mathbf{X}_{\gamma'}(\overline{N+1}; R_{\alpha}) \rangle F_{\gamma'}^{(\gamma)}(\vec{r}_{N+1}) \\ = & \int \chi_{v_{\gamma''}}^*(R_{\alpha}) \langle \Phi_{(n\Lambda)_{\gamma''}}(\tau; R_{\alpha}) | \sum_j \frac{1}{r_{j,N+1}} | \Phi_{(n\Lambda)_{\gamma'}}(\tau; R_{\alpha}) \rangle \int_{\tau} \chi_{v_{\gamma'}}(R_{\alpha}) dR_{\alpha} F_{\gamma'}^{(\gamma)}(\vec{r}_{N+1}) \end{aligned} \quad (31)$$

So, the second term in Eq. (30) is

$$V_{\gamma''\gamma'}^{el,st}(\vec{r}_{N+1}) F_{\gamma'}^{(\gamma)}(\vec{r}_{N+1}) \quad (32a)$$



where

$$V_{\gamma''\gamma'}^{el,st}(\vec{r}_{N+1}) = \int \chi_{v_{\gamma''}}^*(R_\alpha) \langle \Phi_{(n\Lambda)_{\gamma''}}(\tau; R_\alpha) | \sum_j^N \frac{1}{r_{j,N+1}} | \Phi_{(n\Lambda)_{\gamma'}}(\tau; R_\alpha) \rangle_{\tau} \chi_{v_{\gamma'}}(R_\alpha) dR_\alpha \quad (32b)$$

The remaining term in Eq. (30), call it  $I'_{3b}$ , is

$$I'_{3b} \equiv \sum_{j=1}^N \sum_{i=1}^N (-1)^{N+1-i} \langle \mathbf{X}_{\gamma''}(1, 2, \dots, N; R_\alpha) \chi_{m_s}^{\gamma''}(\sigma_{N+1}) | \frac{1}{r_{j,N+1}} | \mathbf{X}_{\gamma'}(1, 2, \dots, i-1, i+1, \dots, N+1; R_\alpha) \bar{F}_{\gamma'}^\gamma(i) \rangle \quad (33)$$

It is clear from the outset that this is the exchange contribution. All the terms except  $j = i$  are zero by orthogonality of Eq. (19). We have remaining

$$I'_{3b} = \sum_{j=1}^N (-1)^{N+1-j} \langle \mathbf{X}_{\gamma''}(1, 2, \dots, N; R_\alpha) \chi_{m_s}^{\gamma''}(\sigma_{N+1}) | \frac{1}{r_{j,N+1}} | \mathbf{X}_{\gamma'}(1, 2, \dots, j-1, j+1, \dots, N+1; R_\alpha) \bar{F}_{\gamma'}^\gamma(j) \rangle \quad (34)$$

Let's define

$$\langle j \rangle \equiv \langle \mathbf{X}_{\gamma''}(1, 2, \dots, N; R_\alpha) \chi_{m_s}^{\gamma''}(\sigma_{N+1}) | \frac{1}{r_{j,N+1}} | \mathbf{X}_{\gamma'}(1, 2, \dots, j-1, j+1, \dots, N+1; R_\alpha) \bar{F}_{\gamma'}^\gamma(j) \rangle$$

So,

$$I'_{3b} = \sum_{j=1}^N (-1)^{N+1-j} \langle j \rangle$$

Now, from the symmetry properties of  $\mathbf{X}_{\gamma'}(1, 2, \dots, N; R_\alpha)$  under  $P_{ij}$  and the fact that the integral in  $\langle j \rangle$  sums for  $d1 \cdots dN$ , we see that for any  $j = 2, 3, \dots, N, [4]$

$$\langle j \rangle = \pm \langle 1 \rangle \quad \text{with} \quad \begin{cases} +, & \text{for } j \text{ is odd} \\ -, & \text{for } j \text{ is even} \end{cases} \quad (35)$$

For clarification, we take two examples:  $j = 2$  and 3

(a)  $j = 2$

$$\begin{aligned}
\langle 2 \rangle &= \langle \mathbf{X}_{\gamma''}(1, 2, \dots, N; R_\alpha) \chi_{m_s}^{\gamma''}(\sigma_{N+1}) \mid \frac{1}{r_{2,N+1}} \mid \mathbf{X}_{\gamma'}(1, 3, \dots, N+1; R_\alpha) \bar{F}_{\gamma'}^\gamma(2) \rangle \\
&= \langle \mathbf{X}_{\gamma''}(2, 1, \dots, N; R_\alpha) \chi_{m_s}^{\gamma''}(\sigma_{N+1}) \mid \frac{1}{r_{1,N+1}} \mid \mathbf{X}_{\gamma'}(2, 3, \dots, N+1; R_\alpha) \bar{F}_{\gamma'}^\gamma(1) \rangle \\
&= \langle -\mathbf{X}_{\gamma''}(1, 2, \dots, N; R_\alpha) \chi_{m_s}^{\gamma''}(\sigma_{N+1}) \mid \frac{1}{r_{1,N+1}} \mid \mathbf{X}_{\gamma'}(2, 3, \dots, N+1; R_\alpha) \bar{F}_{\gamma'}^\gamma(1) \rangle \\
&= -\langle 1 \rangle
\end{aligned}$$

(b)  $j = 3$

$$\begin{aligned}
\langle 3 \rangle &= \langle \mathbf{X}_{\gamma''}(1, 2, \dots, N; R_\alpha) \chi_{m_s}^{\gamma''}(\sigma_{N+1}) \mid \frac{1}{r_{3,N+1}} \mid \mathbf{X}_{\gamma'}(1, 2, 4, \dots, N+1; R_\alpha) \bar{F}_{\gamma'}^\gamma(3) \rangle \\
&= \langle \mathbf{X}_{\gamma''}(3, 2, 1, \dots, N; R_\alpha) \chi_{m_s}^{\gamma''}(\sigma_{N+1}) \mid \frac{1}{r_{1,N+1}} \mid \mathbf{X}_{\gamma'}(3, 2, 4, \dots, N+1; R_\alpha) \bar{F}_{\gamma'}^\gamma(1) \rangle \\
&= \langle -\mathbf{X}_{\gamma''}(1, 2, 3, \dots, N; R_\alpha) \chi_{m_s}^{\gamma''}(\sigma_{N+1}) \mid \frac{1}{r_{1,N+1}} \mid -\mathbf{X}_{\gamma'}(2, 3, 4, \dots, N+1; R_\alpha) \bar{F}_{\gamma'}^\gamma(1) \rangle \\
&= \langle 1 \rangle
\end{aligned}$$

Further, since for closed-shell target,  $N$  is even,

$$\begin{aligned}
(-1)^{N+1-j} \langle j \rangle &= (-1)^{N+1-j} \langle 1 \rangle (\pm 1) \\
&= +\langle 1 \rangle \quad [j = 1, 2, 3, \dots, N]
\end{aligned}$$

where

$$I'_{3b} = +N \langle 1 \rangle$$

or

$$I'_{3b} = +N \langle \mathbf{X}_{\gamma''}(1, 2, \dots, N; R_\alpha) \chi_{m_s}^{\gamma''}(\sigma_{N+1}) \mid \frac{1}{r_{1,N+1}} \mid \mathbf{X}_{\gamma'}(2, 3, \dots, N+1; R_\alpha) \bar{F}_{\gamma'}^\gamma(1) \rangle \quad (36)$$

Putting all this together — Eq. (28), Eq. (32a), and Eq. (36), we get

$$\begin{aligned}
I_3^{(\gamma')} &= \langle \chi_{v_{\gamma''}}(R_\alpha) \mid - \sum_{\alpha} \frac{Z_\alpha}{|\vec{r}_{N+1} - \vec{R}_\alpha|} \mid \chi_{v_{\gamma'}}(R_\alpha) \rangle F_{\gamma'}^{(\gamma)}(\vec{r}_{N+1}) \\
&\quad + V_{\gamma''\gamma'}^{el,st}(\vec{r}_{N+1}) F_{\gamma'}^{(\gamma)}(\vec{r}_{N+1}) \\
&\quad + N \langle \mathbf{X}_{\gamma''}(\overline{N+1}; R_\alpha) \chi_{m_s}^{\gamma''}(\sigma_{N+1}) \mid \frac{1}{r_{1,N+1}} \mid \mathbf{X}_{\gamma'}(\bar{1}; R_\alpha) \bar{F}_{\gamma'}^\gamma(1) \rangle
\end{aligned} \quad (37)$$

#### 4. $I_4^{(\gamma')}$

This obtains trivially from the algebra used to evaluate  $I_1^{(\gamma')}$ , to wit:

$$I_4^{(\gamma')} = \langle \mathbf{X}_{\gamma''}(\overline{N+1}; R_\alpha) \chi_{m_s}^{\gamma''}(\sigma_{N+1}) \mid \sum_{i=1}^{N+1} (-1)^{N+1-i} \mathbf{X}_{\gamma'}(\bar{i}; R_\alpha) \bar{F}_{\gamma'}^\gamma(i) \rangle$$

so,

$$I_4^{(\gamma')} = \delta_{\gamma'\gamma''} F_{\gamma'}^{(\gamma)}(\vec{r}_{N+1}) \quad (38)$$

Finally, we can assemble the coupled equations from Eq. (22), Eq. (24), Eq. (37), and Eq. (38), and sum over  $\gamma''$  we get (interchange  $\gamma'$  and  $\gamma''$ ,  $\gamma' \leftrightarrow \gamma''$ )

$$\begin{aligned} 0 = & \left[ -\frac{1}{2} \nabla_{N+1}^2 + (E_{\gamma'} - E) \right] F_{\gamma'}^{(\gamma)}(\vec{r}_{N+1}) + \sum_{v_{\gamma''}} V_{\gamma'\gamma''}^{st} F_{\gamma''}^{(\gamma)}(\vec{r}_{N+1}) \\ & + N \sum_{v_{\gamma''}} \langle \mathbf{X}_{\gamma'}(\overline{N+1}; R_\alpha) \chi_{m_s}^{\gamma'}(\sigma_{N+1}) \mid \frac{1}{r_{1,N+1}} \mid \mathbf{X}_{\gamma''}(\bar{1}; R_\alpha) \bar{F}_{\gamma''}^\gamma(1) \rangle \end{aligned} \quad (39)$$

where  $V_{\gamma'\gamma''}^{st}(\vec{r}_{N+1})$  is the sum of the nuclear + electron terms, viz.,

$$\begin{aligned} V_{\gamma'\gamma''}^{st}(\vec{r}_{N+1}) = & \langle \chi_{v_{\gamma'}}(R_\alpha) \mid - \sum_{\alpha} \frac{Z_\alpha}{|\vec{r}_{N+1} - \vec{R}_\alpha|} \mid \chi_{v_{\gamma''}}(R_\alpha) \rangle_{R_\alpha} \\ & + \int \chi_{v_{\gamma'}}^*(R_\alpha) \langle \Phi_{(n\Lambda)_{\gamma'}}(\tau; R_\alpha) \mid \sum_j^N \frac{1}{r_{j,N+1}} \mid \Phi_{(n\Lambda)_{\gamma''}}(\tau; R_\alpha) \rangle_{\tau} \chi_{v_{\gamma''}}(R_\alpha) dR_\alpha \\ = & V_{\gamma'\gamma''}^{st,nuc} + V_{\gamma'\gamma''}^{st,el} \end{aligned} \quad (40)$$

#### A. Comments on the Scattering Equation

Before we go on to the next useful formula, we'll have to stop for a little while here to make some comments on the scattering equation of Eq. (39).

- Eq. (39) is restricted to closed shell, as well as no electronic and rotation excitation are included, i.e., we only consider molecular vibrational motion. (See page 3 and page 5.)
- the superscript  $\gamma$  denotes the state of electron + molecule, i.e., it is only a symbol that reminds us that some specific state is considered here. (See page 3.)
- the subscripts  $\gamma'$  and  $\gamma''$  denote the state of the molecule and the state of the corresponding scattered electron. (See page 3 and page 5.)

- the sum index  $v_{\gamma''}$  is over target vibrational states.
- the static attraction term is integrated over  $dR_\alpha$
- the static repulsion term is integrated over  $d1 d2 \cdots dN \times dR_\alpha$ , i.e., for every  $R_\alpha$ , integrated over  $d1 d2 \cdots dN$ , then over  $dR_\alpha$
- the exchange term is integrated over  $d1 d2 \cdots dN$  and summed over  $\sigma_{N+1}$
- $d1 d2 \cdots dN = d\vec{r}_1 d\vec{r}_2 \cdots d\vec{r}_N \sum \sigma_1 \sum \sigma_2 \cdots \sum \sigma_N$ , i.e., it includes integration over the spatial coordinates and sums over the spin coordinates.

## B. Special Case: Elastic Scattering

If we do not allow vibrational excitation, then  $v_{\gamma'} = v_{\gamma''}$ . In fact, if we treat the system as a rigid rotor, then the Eq. (39) reduces to the more familiar form (ELASTIC)

$$0 = \left[ -\frac{1}{2} \nabla_{N+1}^2 + V_{st}(\vec{r}_{N+1}) - \frac{1}{2} k^2 \right] F^{(\gamma)}(\vec{r}_{N+1}) \\ + N \langle \Phi_{(n\Lambda)_\gamma}(\overline{N+1}; R_\alpha) \chi_{m_s}^\gamma(\sigma_{N+1}) \mid \frac{1}{r_{1,N+1}} \mid \Phi_{(n\Lambda)_\gamma}(\bar{1}; R_\alpha) \bar{F}^{(\gamma)}(1) \rangle \quad (41)$$

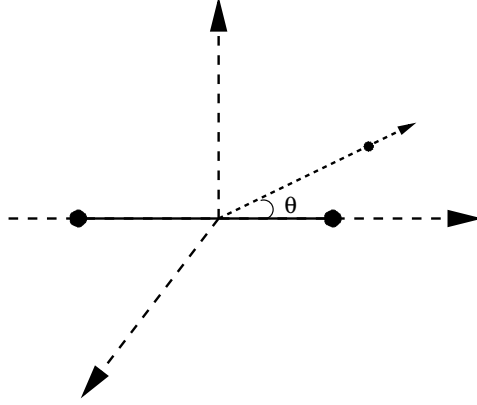
where the integration in the exchange matrix element is over  $d1 \cdots dN \sum \sigma_{N+1}$  and where  $k^2$  is the scattering energy in Rydberg. Recall that  $\Phi_{(n\Lambda)_\gamma}$  is the antisymmetrical target electronic wavefunction. The static potential is just

$$V_{st}(\vec{r}_{N+1}) = \langle \Phi_{(n\Lambda)_\gamma}(\tau) \mid V_{int}(\tau; \vec{r}_{N+1}) \mid \Phi_{(n\Lambda)_\gamma}(\tau) \rangle_\tau \quad (42)$$

with  $V_{int}(\tau; \vec{r}_{N+1})$  given by Eq. (12). Here  $\gamma$  denotes the electronic state of the target (ground).

## II. SINGLE-CENTER EXPANSIONS: REDUCTION TO RADIAL EQUATIONS

our approach to the solution of Eq. (41) is based on the use of a single-center coordiante system, as



Everything is referred to the origin of coordinate chosed as the center of mass. Thus, for example, we expand the static potential energy Eq. (42) as

$$V_{st}(\vec{r}_{N+1}) = \sum_{\lambda=0}^{\infty} v_{\lambda}^{st}(r_{N+1}) P_{\lambda}(\cos \theta_{N+1}) \quad (43)$$

where for  $D_{\infty h}$  targets only  $\lambda = \text{even}$  appear.

### A. The Static Potential

We've discussed the evaluation of  $v_{\lambda}^{st}$  in considerable detail in the PhD thesis for a  $D_{\infty h}$  molecule — in particular, for  $\text{CO}_2$  [5]. Summarizing, we choose to work from the charge density  $\rho_{\gamma}(\vec{r})$  of the target, which is defined for state  $\gamma$  as

$$\rho_{\gamma}(\vec{r}) = \int \Phi_{\gamma}^*(1, 2, \dots, N) \Phi_{\gamma}(1, 2, \dots, N) d1 \cdots d(N-1) \sum \sigma_N \quad (44)$$

Note that  $\rho(\vec{r}) = \rho(\vec{r}, R_{\alpha})$  since  $\Phi_{\gamma}$  depends parametrically on the nuclear geometry. In terms of the spatial orbitals  $\phi_{\alpha}(\vec{r})$  of Eq. (1) and Eq. (3), we get

$$\rho(\vec{r}) = \sum_{j=1}^{N_{occ}} N_j |\phi_j(\vec{r})|^2 \quad (45)$$

where  $N_j$  = occupation number of  $j^{th}$  occupied spatial orbital. Clearly, this makes sense only for a single configuration wavefunction of the form of Eq. (1).  $N_{occ}$  = number of occupied spatial orbitals.

We expand  $\rho(\vec{r}) = \rho(r, \theta)$  in Legendre polynomials, obtaining

$$\rho(r, \theta) = \sum_{\lambda=0}^{\infty} a_{\lambda}(r) P_{\lambda}(\cos \theta) \quad (46)$$

where

$$a_\lambda(r) = \frac{2\lambda + 1}{2} \int_0^\pi \rho(r, \theta) P_\lambda(\cos \theta) \sin \theta d\theta \quad (47)$$

Again, only even- $\lambda$  coefficients contribute for  $D_{\infty h}$  systems in Eq. (46).

Each  $v_\lambda^{st}$  can be written

$$v_\lambda^{st}(r) = v_\lambda^{nuc}(r) + v_\lambda^{el}(r) \quad (48)$$

where  $v_\lambda^{nuc}(r)$  arises from the  $e$ -nuclear interaction terms in  $V_{int}$  and  $v_\lambda^{el}$  from the  $e$ - $e$  term.

The nuclear term is easily evaluated. For example, for a homonuclear diatomic target, we get

$$v_\lambda^{nuc}(r) = -2Z_\alpha \frac{\rho_{<}^\lambda}{\rho_{>}^{\lambda+1}} \quad (49)$$

where  $Z_\alpha$  is the nuclear charge on one of the centers and

$$\rho_{>} = \min_{\max} \left\{ r, \frac{1}{2}R \right\} \quad (50)$$

with  $R$  the internuclear separation. For a triatomic  $D_{\infty h}$  molecule with charge  $Z_\beta$  at the origin, we get instead

$$v_\lambda^{nuc}(r) = -\frac{Z_\beta}{r} \delta_{\lambda 0} - 2Z_\alpha \frac{\rho_{<}^\lambda}{\rho_{>}^{\lambda+1}} \quad (51)$$

The evaluation of the electronic term is more arduous, but left to the similar expansion

$$v_\lambda^{el}(r) = \frac{4\pi}{2\lambda + 1} \int_0^\infty a_\lambda(r') \frac{r_{<}^\lambda}{r_{>}^{\lambda+1}} r'^2 dr' \quad (52)$$

where

$$r_{>} = \min_{\max} \{ r, r' \} \quad (53)$$

and  $a_\lambda(r)$  comes from the expansion of Eq. (46) and Eq. (47).

## B. The Coupled Equation for Elastic Scattering

We shall expand the scattering function  $F^{(\gamma)}(\vec{r}_{N+1})$  in single-center partial waves as

$$F^{(\gamma)}(\vec{r}_{N+1}) = \frac{1}{r_{N+1}} \sum_{\ell'=0}^\infty \sum_{m'} \mathcal{Y}_{\ell'm'}^{(\gamma)}(r_{N+1}) Y_{\ell'}^{m'}(\hat{r}_{N+1}) \quad (54)$$

The approach is the usual one — shove Eq. (54) into Eq. (41), multiplied by  $Y_{\ell'}^{m'}(\hat{r}_{N+1})$  and  $\int d\hat{r}_{N+1}$ , viz.,

$$\begin{aligned} & \left[ -\frac{1}{2} \nabla_{N+1}^2 + V_{st}(\vec{r}_{N+1}) - \frac{1}{2} k^2 \right] \frac{1}{r_{N+1}} \sum_{\ell'm'} \mathcal{Y}_{\ell'm'}^{(\gamma)}(r_{N+1}) Y_{\ell'}^{m'}(\hat{r}_{N+1}) \\ &= -N \langle \Phi_\gamma(\overline{N+1}; R_\alpha) \chi_{m_s}^\gamma(\sigma_{N+1}) \mid \frac{1}{r_{1,N+1}} \mid \Phi_\gamma(\overline{1}; R_\alpha) \sum_{\ell'm'} \frac{1}{r_1} \mathcal{Y}_{\ell'm'}^{(\gamma)}(r_1) Y_{\ell'}^{m'}(\hat{r}_1) \chi_{m_s}^\gamma(\sigma_1) \rangle \end{aligned} \quad (55)$$

This can be written as

$$\begin{aligned} & [\nabla_{N+1}^2 + k^2] F^{(\gamma)}(\vec{r}_{N+1}) - 2V_{st}(\vec{r}_{N+1})F^{(\gamma)}(\vec{r}_{N+1}) \\ & = 2N \langle \Phi_\gamma(\overline{N+1}; R_\alpha) \chi_{m_s}^\gamma(\sigma_{N+1}) \mid \frac{1}{r_{1,N+1}} \mid \Phi_\gamma(\bar{1}; R_\alpha) \bar{F}^{(\gamma)}(1) \rangle \end{aligned} \quad (56)$$

If the exchange term were zero, we know what comes out of this, viz.,

$$\left[ \frac{d^2}{dr_{N+1}^2} - \frac{\ell'(\ell'+1)}{r_{N+1}^2} + k^2 \right] \mathcal{Y}_{\ell'm'}^{(\gamma)}(r_{N+1}) = 2 \sum_{\ell''} V_{\ell'\ell''}^{(m')}(r_{N+1}) \mathcal{Y}_{\ell''m'}^{(\gamma)}(r_{N+1}) \quad (57)$$

with

$$V_{\ell'\ell''}^{(m')}(r) = (-1)^{m'} \sqrt{(2\ell'+1)(2\ell''+1)} \sum_{\lambda} \frac{1}{2\lambda+1} v_{\lambda}^{st}(r) C(\ell'\ell''\lambda; 00) C(\ell'\ell''\lambda; -m', m') \quad (58)$$

with  $\lambda = \text{even}$  for  $D_{\infty h}$ . Alas, the exchange term is NOT zero!

Using what we know, we can reduce Eq. (55) [after  $\otimes \int Y_{\ell''}^{m'*}(\hat{r}_{N+1}) d\hat{r}_{N+1}$  and interchange  $\ell'$  and  $\ell''$ ] to

$$\begin{aligned} & \left[ -\frac{1}{2} \frac{d^2}{dr_{N+1}^2} + \frac{\ell'(\ell'+1)}{2r_{N+1}^2} - \frac{1}{2} k^2 \right] \mathcal{Y}_{\ell'm'}^{(\gamma)}(r_{N+1}) + \sum_{\ell''} V_{\ell'\ell''}^{(m')}(r_{N+1}) \mathcal{Y}_{\ell''m'}^{(\gamma)}(r_{N+1}) \\ & = -r_{N+1} N \sum_{\ell''} \int Y_{\ell''}^{m'*}(\hat{r}_{N+1}) \\ & \quad \langle \Phi_\gamma(\overline{N+1}; R_\alpha) \chi_{m_s}^\gamma(\sigma_{N+1}) \mid \frac{1}{r_{1,N+1}} \mid \Phi_\gamma(\bar{1}; R_\alpha) \left[ \frac{1}{r_1} \mathcal{Y}_{\ell''m'}^{(\gamma)}(r_1) Y_{\ell''}^{m'}(\hat{r}_1) \chi_{m_s}^\gamma(\sigma_1) \right] \rangle d\hat{r}_{N+1} \end{aligned} \quad (59)$$

and we must do something with the right side of Eq. (59). [Note that the integration is over  $d1 \cdots dN d\hat{r}_{N+1} \sum \sigma_{N+1}$ .]

We must resort to our formula Eq. (1) for the molecular target electronic wavefunctions,

$$\Phi_{(n\Lambda)_\gamma}(\tau; R_\alpha) = \frac{1}{\sqrt{N!}} \sum_{\alpha_i \beta_i \cdots \pi_i} \epsilon_{\alpha_i \beta_i \cdots \pi_i} \bar{\phi}_{\alpha_i}(1) \bar{\phi}_{\beta_i}(2) \cdots \bar{\phi}_{\pi_i}(N) \quad (60)$$

where we've added a subscript  $i$ , which we'll need later.

### C. Structure of the Exchange Kernel: Reduction to $e\text{-H}_2$

Before proceeding for this, se should note that we can write Eq. (59) as

$$\begin{aligned} & \left[ -\frac{1}{2} \frac{d^2}{dr_{N+1}^2} + \frac{\ell'(\ell'+1)}{2r_{N+1}^2} - \frac{1}{2} k^2 \right] \mathcal{Y}_{\ell'm'}^{(\gamma)}(r_{N+1}) + \sum_{\ell''} V_{\ell'\ell''}^{(m')}(r_{N+1}) \mathcal{Y}_{\ell''m'}^{(\gamma)}(r_{N+1}) \\ & = \sum_{\ell''} \int_0^\infty K^{(m')}(\ell'\ell''|r_1 r_{N+1}) \mathcal{Y}_{\ell''m'}^{(\gamma)}(r_1) dr_1 \end{aligned} \quad (61)$$

where

$$\begin{aligned} K^{(m')}(\ell' \ell'' | r_1 r_{N+1}) = & -N \frac{r_{N+1}}{r_1} \int Y_{\ell'}^{m'*}(\hat{r}_{N+1}) \Phi_{\gamma}^*(\overline{N+1}; R_{\alpha}) \chi_{m_s}^{\gamma*}(\sigma_{N+1}) \frac{1}{r_{1,N+1}} \Phi_{\gamma}(\bar{1}; R_{\alpha}) \\ & Y_{\ell''}^{m'}(\hat{r}_1) \chi_{m_s}^{\gamma}(\sigma_1) d\hat{r}_1 \sum \sigma_1 d2 \cdots dN d\hat{r}_{N+1} \sum \sigma_{N+1} \end{aligned} \quad (62)$$

is the exchange kernel. For  $H_2$  target, this reduces to

$$\begin{aligned} K^{(m')}(\ell' \ell'' | r_1 r_3) = & -2 \frac{r_3}{r_1} \int Y_{\ell'}^{m'*}(\hat{r}_3) \Phi_{\gamma}^*(1, 2; R) \chi_{m_s}^{\gamma*}(\sigma_3) \frac{1}{r_{1,3}} \Phi_{\gamma}(2, 3; R) \\ & Y_{\ell''}^{m'}(\hat{r}_1) \chi_{m_s}^{\gamma}(\sigma_1) d\hat{r}_1 \sum \sigma_1 d2 d\hat{r}_3 \sum \sigma_3 \end{aligned} \quad (63)$$

where

$$\Phi_{\gamma}(2, 3; R) \equiv \Phi(\vec{r}_1, \vec{r}_2; R) \bar{\delta}(\sigma_1 \sigma_2) \quad (64)$$

For the  $^1\Sigma_g^+$  of  $H_2$ , the spin function is

$$\bar{\delta}(\sigma_1 \sigma_2) = \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad (65)$$

Here  $\Phi(\vec{r}_1, \vec{r}_2; R)$  is the spatial molecular target function. Hence we have

$$\begin{aligned} K^{(m')}(\ell' \ell'' | r_1 r_3) = & -2 \frac{r_3}{r_1} \int Y_{\ell'}^{m'*}(\hat{r}_3) \Phi_{\gamma}^*(\vec{r}_1, \vec{r}_2; R) \frac{1}{r_{1,3}} \Phi_{\gamma}(\vec{r}_2, \vec{r}_3; R) \\ & Y_{\ell''}^{m'}(\hat{r}_1) d\hat{r}_1 d\vec{r}_2 d\hat{r}_3 \langle \bar{\delta}(\sigma_1 \sigma_2 \sigma_3) | \bar{\delta}(\sigma_2 \sigma_3 \sigma_1) \rangle \end{aligned} \quad (66)$$

where the system spin function (3-electrons) is

$$\bar{\delta}(\sigma_i \sigma_j \sigma_k) \equiv \frac{1}{\sqrt{2}} [\alpha(i)\beta(j) - \beta(i)\alpha(j)] \chi_{m_s}(k) \quad (67)$$

and  $\chi_{m_s}(k)$  is either  $\alpha(k)$  or  $\beta(k)$ .

The matrix element

$$\begin{aligned} \langle \bar{\delta}(\sigma_1 \sigma_2 \sigma_3) | \bar{\delta}(\sigma_2 \sigma_3 \sigma_1) \rangle = & \sum_{1,2,3} \frac{1}{\sqrt{2}} [\alpha^*(1)\beta^*(2) - \beta^*(1)\alpha^*(2)] \chi^*(3) \\ & \times \frac{1}{\sqrt{2}} [\alpha(2)\beta(3) - \beta(2)\alpha(3)] \chi(1) \\ = & \frac{1}{2} \sum_{1,3} \alpha^*(1)\beta(3) \chi^*(3) \chi(1) \sum_2 \beta^*(2)\alpha(2) \\ & - \frac{1}{2} \sum_{1,3} \beta^*(1)\beta(3) \chi^*(3) \chi(1) \sum_2 \alpha^*(2)\alpha(2) \\ & - \frac{1}{2} \sum_{1,3} \alpha^*(1)\alpha(3) \chi^*(3) \chi(1) \sum_2 \beta^*(2)\beta(2) \\ & + \frac{1}{2} \sum_{1,3} \beta^*(1)\alpha(3) \chi^*(3) \chi(1) \sum_2 \alpha^*(2)\beta(2) \end{aligned}$$



And we have

$$\begin{aligned}\sum_i \alpha^*(i) \alpha(i) &= 1 \\ \sum_i \beta^*(i) \beta(i) &= 1 \\ \sum_i \alpha^*(i) \beta(i) &= 0 \\ \sum_i \beta^*(i) \alpha(i) &= 0\end{aligned}$$

So,

$$\begin{aligned}\langle \bar{\delta}(\sigma_1 \sigma_2 \sigma_3) | \bar{\delta}(\sigma_2 \sigma_3 \sigma_1) \rangle &= -\frac{1}{2} \sum_{1,3} \beta^*(1) \beta(3) \chi^*(3) \chi(1) \\ &\quad - \frac{1}{2} \sum_{1,3} \alpha^*(1) \alpha(3) \chi^*(3) \chi(1)\end{aligned}$$

Whether  $\chi$  is  $\alpha$  or  $\beta$ , we have

$$\langle \bar{\delta}(\sigma_1 \sigma_2 \sigma_3) | \bar{\delta}(\sigma_2 \sigma_3 \sigma_1) \rangle = -\frac{1}{2} \quad (68)$$

for doublet composite state + singlet ground state, our current example. We therefore see that our SE equations reduce to the results we obtained earlier for elastic  $e$ -H<sub>2</sub>, viz., we have

$$\begin{aligned}&\left[ -\frac{d^2}{dr_3^2} + \frac{\ell'(\ell' + 1)}{r_3^2} - k^2 \right] \mathcal{Y}_{\ell' \ell_0}^{(m')}(r_3) + 2 \sum_{\ell''} V_{\ell' \ell''}^{(m')}(r_3) \mathcal{Y}_{\ell'' \ell_0}^{(m')}(r_3) \\ &= 2 \sum_{\ell''} \int_0^\infty K^{(m')}(\ell' \ell'' | r_1 r_3) \mathcal{Y}_{\ell'' \ell_0}^{(m')}(r_1) dr_1\end{aligned} \quad (69)$$

where

$$K^{(m')}(\ell' \ell'' | r_1 r_3) = \frac{r_3}{r_1} \int Y_{\ell'}^{m'*}(\hat{r}_3) \Phi_\gamma^*(\vec{r}_1, \vec{r}_2; R) \frac{1}{r_{1,3}} \Phi_\gamma(\vec{r}_2, \vec{r}_3; R) Y_{\ell''}^{m'}(\hat{r}_1) d\hat{r}_1 d\vec{r}_2 d\hat{r}_3 \quad (70)$$

and  $\ell_0$  denotes initial channel.

#### D. General Exchange Kernel

Now, let's call the exchange term [Right side of Eq. (59)]  $-I$ , viz.,

$$\begin{aligned}-I &\equiv r_{N+1} N \sum_{\ell''} \int Y_{\ell'}^{m'*}(\hat{r}_{N+1}) \\ &\quad \langle \Phi_\gamma(\overline{N+1}; R_\alpha) \chi_{m_s}^\gamma(\sigma_{N+1}) | \frac{1}{r_{1,N+1}} | \Phi_\gamma(\bar{1}; R_\alpha) \left[ \frac{1}{r_1} \mathcal{Y}_{\ell''}^{(m')}(r_1) Y_{\ell''}^{m'}(\hat{r}_1) \chi_{m_s}^\gamma(\sigma_1) \right] \rangle d\hat{r}_{N+1}\end{aligned} \quad (71)$$

Note: drop  $(\gamma)$  from  $\mathcal{Y}_{\ell''m'}^{(\gamma)}(r_1)$  here.

The first step will be to write I in terms of spin orbital using Eq. (60), as threatened earlier, we have for the  $\ell'''$  term in I,

$$\begin{aligned} I^{(\ell'')} = r_{N+1} \frac{N}{N!} \int Y_{\ell'}^{m'*}(\hat{r}_{N+1}) & \left[ \sum_i \epsilon_i \bar{\phi}_{\alpha_i}^*(1) \cdots \bar{\phi}_{\pi_i}^*(N) \right] \chi_{m_s}^*(\sigma_{N+1}) \frac{1}{r_{1,N+1}} \\ & \left[ \sum_j \epsilon_j \bar{\phi}_{\alpha_j}(N+1) \bar{\phi}_{\beta_j}(2) \cdots \bar{\phi}_{\pi_j}(N) \right] \\ & \frac{1}{r_1} \mathcal{Y}_{\ell''}^{(m')}(r_1) Y_{\ell'}^{m'}(\hat{r}_1) \chi_{m_s}^\gamma(\sigma_1) d1 \cdots dN d\hat{r}_{N+1} \sum \sigma_{N+1} \end{aligned} \quad (72)$$

where  $\epsilon_i \equiv \epsilon_{\alpha_i \beta_i \cdots \pi_i}$  and  $\sum_i = \sum_{\alpha_i \beta_i \cdots \pi_i}$ .

Clearly,

$$I = (-1)^N \sum_{\ell''} I^{(\ell'')} \quad (73)$$

since we have used

$$\begin{aligned} \Phi(2, 3, 4, \dots, N, N+1; R_\alpha) &= -\Phi(N+1, 3, 4, \dots, N, 2; R_\alpha) \\ &= +\Phi(N+1, 2, 4, \dots, N, 3; R_\alpha) \\ &= -\Phi(N+1, 2, 3, \dots, N, 4; R_\alpha) \\ &= (-1)^{i+1} \Phi(N+1, 2, 4, \dots, N, i; R_\alpha) \\ &= (-1)^{N-1+1} \Phi(N+1, 2, 4, \dots, N, N-1; R_\alpha) \\ &= (-1)^{N+1} \Phi(N+1, 2, 4, \dots, N-1, N; R_\alpha) \end{aligned}$$

Therefore Eq. (72) is “simply”

$$\begin{aligned} I^{(\ell'')} = r_{N+1} \frac{N}{N!} \sum_i \sum_j \epsilon_i \epsilon_j \int Y_{\ell'}^{m'*}(\hat{r}_{N+1}) \chi_{m_s}^*(\sigma_{N+1}) \bar{\phi}_{\alpha_j}(N+1) \sum \sigma_{N+1} \\ \otimes \int \bar{\phi}_{\beta_i}^*(2) \bar{\phi}_{\beta_j}^*(2) d2 \cdots \int \bar{\phi}_{\pi_i}^*(N) \bar{\phi}_{\pi_j}(N) dN \\ \otimes \int \bar{\phi}_{\alpha_i}^*(1) \frac{1}{r_{1,N+1}} \left[ \frac{1}{r_1} \mathcal{Y}_{\ell''}^{(m')}(r_1) Y_{\ell'}^{m'}(\hat{r}_1) \chi_{m_s}^\gamma(\sigma_1) \right] d1 d\hat{r}_{N+1} \end{aligned} \quad (74)$$

Let' not worry about the orthonormality integral on the second line at present. Instead, we'll work on

$$\begin{aligned} \bar{J}_{ij}^{(\ell'')} &\equiv \int Y_{\ell'}^{m'*}(\hat{r}_{N+1}) \chi_{m_s}^*(\sigma_{N+1}) \bar{\phi}_{\alpha_j}(N+1) \\ &\times \int \bar{\phi}_{\alpha_i}^*(1) \frac{1}{r_{1,N+1}} \left[ \frac{1}{r_1} \mathcal{Y}_{\ell''}^{(m')}(r_1) Y_{\ell'}^{m'}(\hat{r}_1) \right] \chi_{m_s}^\gamma(\sigma_1) d1 d\hat{r}_{N+1} \sum \sigma_{N+1} \end{aligned} \quad (75)$$

From Eq. (3) and the orthogonality of the spin wavefunction, the spin integrations give  $\delta_{m_s}(\alpha_j, N+1)\delta_{m_s}(\alpha_i, N+1)$  and the remaining radial  $\int$  is

$$J_{ij}^{(\ell'')} = \int Y_{\ell'}^{m'*}(\hat{r}_{N+1})\phi_{\alpha_j}(\vec{r}_{N+1})\phi_{\alpha_i}^*(\vec{r}_1)\frac{1}{r_{1,N+1}}\left[\frac{1}{r_1}\mathcal{Y}_{\ell''}^{(m')}(r_1)Y_{\ell''}^{m'}(\hat{r}_1)\right]d\vec{r}_1d\hat{r}_{N+1} \quad (76)$$

Now, as usual we expand

$$\frac{1}{r_{1,N+1}} = \sum_{\lambda=0}^{\infty} \frac{r_{<}^{\lambda}}{r_{>}^{\lambda+1}} P_{\lambda}(\cos \angle(\vec{r}_{N+1}, \vec{r}_1)) \quad (77)$$

where

$$r_{<} = \min_{\max}\{r_1, r_{N+1}\} \quad (78)$$

or (from (4.28) in [1])

$$\frac{1}{r_{1,N+1}} = \sum_{\lambda=0}^{\infty} \left(\frac{4\pi}{2\lambda+1}\right) \frac{r_{<}^{\lambda}}{r_{>}^{\lambda+1}} \sum_{\mu=-\lambda}^{+\lambda} Y_{\lambda}^{\mu}(\hat{r}_{N+1})Y_{\lambda}^{\mu*}(\hat{r}_1) \quad (79)$$

by the addition theorem of spherical harmonics. Therefore we have for Eq. (76)

$$J_{ij}^{(\ell'')} = \sum_{\lambda\mu} \left(\frac{4\pi}{2\lambda+1}\right) \int Y_{\ell'}^{m'*}(\hat{r}_{N+1})\phi_{\alpha_j}(\vec{r}_{N+1})\phi_{\alpha_i}^*(\vec{r}_1)\frac{r_{<}^{\lambda}}{r_{>}^{\lambda+1}} Y_{\lambda}^{\mu}(\hat{r}_{N+1})Y_{\lambda}^{\mu*}(\hat{r}_1) \\ \otimes \left[\frac{1}{r_1}\mathcal{Y}_{\ell''}^{(m')}(r_1)Y_{\ell''}^{m'}(\hat{r}_1)\right]d\vec{r}_1d\hat{r}_{N+1} \quad (80)$$

To proceed further in the reduction of  $J_{ij}^{(\ell'')}$ , we must expand the molecular orbitals in single-center radial functions as

$$\phi_{\alpha}(\vec{r}) = \frac{1}{r} \sum_{\ell} u_{\ell}^{\alpha}(r) Y_{\ell}^{m_{\alpha}}(\hat{r}) \quad (81)$$

and we note again axial symmetry, hence no  $\sum_{m_{\alpha}}$  in Eq. (81)

We'll re-introduce the sum over  $\ell''$  from Eq. (71) and consider the integral  $J_{ij} = \sum_{\ell''} J_{ij}^{(\ell'')}$ , i.e.,

$$J_{ij} \equiv \sum_{\ell''} \sum_{\lambda\mu} \left(\frac{4\pi}{2\lambda+1}\right) \int Y_{\ell'}^{m'*}(\hat{r}_{N+1})\phi_{\alpha_j}(\vec{r}_{N+1})\phi_{\alpha_i}^*(\vec{r}_1)\frac{r_{<}^{\lambda}}{r_{>}^{\lambda+1}} Y_{\lambda}^{\mu}(\hat{r}_{N+1})Y_{\lambda}^{\mu*}(\hat{r}_1) \\ \otimes \left[\frac{1}{r_1}\mathcal{Y}_{\ell''}^{(m')}(r_1)Y_{\ell''}^{m'}(\hat{r}_1)\right]d\vec{r}_1d\hat{r}_{N+1} \quad (82)$$

Before we begin, the integral we're trying to evaluate, Eq. (71), is

$$I' = (-1)^N r_{N+1} \frac{N}{N!} \sum_{ij} \epsilon_i \epsilon_j J_{ij} \delta_{m_s}(\alpha_j, N+1) \delta_{m_s}(\alpha_i, N+1) \quad (83)$$

$\otimes$ (orthogonal integral), where orthogonal integral is

$$\int \bar{\phi}_{\beta_i}^*(2) \bar{\phi}_{\beta_j}^*(2) d2 \cdots \int \bar{\phi}_{\pi_i}^*(N) \bar{\phi}_{\pi_j}(N) dN$$

Now, substituting Eq. (81) into Eq. (82), we get

$$\begin{aligned} J_{ij} = & \sum_{\ell''} \sum_{\lambda\mu} \left( \frac{4\pi}{2\lambda+1} \right) \int Y_{\ell''}^{m'*}(\hat{r}_{N+1}) \left[ \frac{1}{r_{N+1}} \sum_{\bar{\ell}} u_{\bar{\ell}}^{\alpha_j}(r_{N+1}) Y_{\bar{\ell}}^{m_{\alpha_j}}(\hat{r}_{N+1}) \right] \\ & \otimes \left[ \frac{1}{r_1} \sum_{\bar{\ell}'} u_{\bar{\ell}'}^{\alpha_i}(r_1) Y_{\bar{\ell}'}^{m_{\alpha_i}*}(\hat{r}_1) \right] \frac{r_{<}^{\lambda}}{r_{>}^{\lambda+1}} Y_{\lambda}^{\mu}(\hat{r}_{N+1}) Y_{\lambda}^{\mu*}(\hat{r}_1) \\ & \otimes \left[ \frac{1}{r_1} \mathcal{Y}_{\ell''}^{(m')}(r_1) Y_{\ell''}^{m'}(\hat{r}_1) \right] d\vec{r}_1 d\hat{r}_{N+1} \end{aligned} \quad (84)$$

Rearranging the spherical functions and note that  $d\vec{r} = r^2 dr d\hat{r}$ , we have

$$\begin{aligned} J_{ij} = & \sum_{\ell''} \sum_{\bar{\ell}\bar{\ell}'} \sum_{\lambda\mu} \left( \frac{4\pi}{2\lambda+1} \right) \frac{1}{r_{N+1}} u_{\bar{\ell}}^{\alpha_j}(r_{N+1}) \\ & \otimes \int r_1^2 dr_1 \frac{1}{r_1^2} u_{\bar{\ell}'}^{\alpha_i}(r_1) \mathcal{Y}_{\ell''}^{(m')}(r_1) \frac{r_{<}^{\lambda}}{r_{>}^{\lambda+1}} \\ & \otimes \int d\hat{r}_{N+1} Y_{\ell''}^{m'*}(\hat{r}_{N+1}) Y_{\bar{\ell}}^{m_{\alpha_j}}(\hat{r}_{N+1}) Y_{\lambda}^{\mu}(\hat{r}_{N+1}) \\ & \otimes \int d\hat{r}_1 Y_{\ell''}^{m'}(\hat{r}_1) Y_{\bar{\ell}'}^{m_{\alpha_i}*}(\hat{r}_1) Y_{\lambda}^{\mu*}(\hat{r}_1) \end{aligned} \quad (85)$$

The angular integrals are easily evaluated from the ever-popular Rose's formula (4.34) and (4.31) [1]

$$\int d\Omega Y_{\ell_3}^{m_3*} Y_{\ell_2}^{m_2} Y_{\ell_1}^{m_1} = \sqrt{\frac{(2\ell_1+1)(2\ell_2+1)}{4\pi(2\ell_3+1)}} C(\ell_1\ell_2\ell_3; m_1m_2m_3) C(\ell_1\ell_2\ell_3; 000) \quad (86)$$

and

$$Y_{\ell}^{m*} = (-1)^m Y_{\ell}^{-m} \quad (87)$$

We have in Eq. (85) two integrals of this type, i.e.,

$$\begin{aligned} \int d\Omega Y_{\ell'}^{m'*} Y_{\bar{\ell}}^{m_{\alpha_j}} Y_{\lambda}^{\mu} &= (-1)^{m'+m_{\alpha_j}} \int d\Omega Y_{\bar{\ell}}^{-m_{\alpha_j}*} Y_{\lambda}^{\mu} Y_{\ell'}^{-m'} \\ &= (-1)^{m'+m_{\alpha_j}} \sqrt{\frac{(2\ell'+1)(2\lambda+1)}{4\pi(2\bar{\ell}+1)}} C(\ell'\lambda\bar{\ell}; -m', \mu, -m_{\alpha_j}) C(\ell'\lambda\bar{\ell}; 000) \end{aligned} \quad (88)$$

and

$$\begin{aligned} \int d\Omega Y_{\ell''}^{m'} Y_{\bar{\ell}'}^{m_{\alpha_i}} Y_{\lambda}^{\mu*} &= (-1)^{\mu} \int d\Omega Y_{\bar{\ell}}^{m_{\alpha_i}} Y_{\lambda}^{-\mu} Y_{\ell''}^{m'} \\ &= (-1)^{\mu} \sqrt{\frac{(2\ell''+1)(2\lambda+1)}{4\pi(2\bar{\ell}'+1)}} C(\ell''\lambda\bar{\ell}'; m', -\mu, m_{\alpha_i}) C(\ell''\lambda\bar{\ell}'; 000) \end{aligned} \quad (89)$$

From (3.5) in [1], notice that Eq. (88)

$$-m' + \mu = -m_{\alpha_j}$$

and

$$m' - \mu = m_{\alpha_i}$$

or

$$m' - \mu = m_{\alpha_j}$$

$$m' - \mu = m_{\alpha_i}$$

where we see that  $m_{\alpha_j} = m_{\alpha_i}$ . This important result simplifies the exchange term by limiting the number of MO's that appear in any given  $i^{th}$  term. We can further use this to carry out  $\sum_{\mu}$  in Eq. (85). Doing so with

$$\mu = m' - m_{\alpha_i} \quad (90)$$

we have

$$\begin{aligned} J_{ij} &= \sum_{\ell''} \sum_{\bar{\ell}'} \sum_{\lambda} \left( \frac{4\pi}{2\lambda+1} \right) \frac{1}{r_{N+1}} u_{\bar{\ell}}^{\alpha_j}(r_{N+1}) \\ &\quad \otimes \int dr_1 u_{\bar{\ell}'}^{\alpha_i}(r_1) \mathcal{Y}_{\ell''}^{(m')}(r_1) \frac{r_{<}^{\lambda}}{r_{>}^{\lambda+1}} \delta_{m_{\alpha}}(i, j) \\ &\quad \otimes (-1)^{m'+m_{\alpha_i}} \sqrt{\frac{(2\ell'+1)(2\lambda+1)}{4\pi(2\bar{\ell}'+1)}} C(\ell'\lambda\bar{\ell}; -m', m' - m_{\alpha_i}) C(\ell'\lambda\bar{\ell}; 00) \\ &\quad \otimes (-1)^{m'-m_{\alpha_i}} \sqrt{\frac{(2\ell''+1)(2\lambda+1)}{4\pi(2\bar{\ell}'+1)}} C(\ell''\lambda\bar{\ell}'; m', m_{\alpha_i} - m') C(\ell''\lambda\bar{\ell}'; 00) \end{aligned} \quad (91)$$

or

$$\begin{aligned} J_{ij} &= \sum_{\ell''} \sum_{\bar{\ell}} \sum_{\bar{\ell}'} \sum_{\lambda} \frac{1}{r_{N+1}} u_{\bar{\ell}}^{\alpha_j}(r_{N+1}) \delta_{m_{\alpha}}(i, j) \int dr_1 u_{\bar{\ell}'}^{\alpha_i}(r_1) \mathcal{Y}_{\ell''}^{(m')}(r_1) \frac{r_{<}^{\lambda}}{r_{>}^{\lambda+1}} \\ &\quad \otimes \sqrt{\frac{(2\ell'+1)(2\ell''+1)}{(2\bar{\ell}'+1)(2\ell'+1)}} C(\ell'\lambda\bar{\ell}; -m', m' - m_{\alpha_i}) C(\ell''\lambda\bar{\ell}'; m', m_{\alpha_i} - m') \\ &\quad \otimes C(\ell'\lambda\bar{\ell}; 00) C(\ell''\lambda\bar{\ell}'; 00) \end{aligned} \quad (92)$$

Let's define a constant

$$g_\lambda(\ell' \ell'' \bar{\ell} \bar{\ell}'; m', m_{\alpha_i}) \equiv \sqrt{\frac{(2\ell' + 1)(2\ell'' + 1)}{(2\bar{\ell} + 1)(2\bar{\ell}' + 1)}} C(\ell' \lambda \bar{\ell}; -m', m' - m_{\alpha_i}) \quad (93)$$

$$\otimes C(\ell'' \lambda \bar{\ell}'; m', m_{\alpha_i} - m') C(\ell' \lambda \bar{\ell}; 00) C(\ell'' \lambda \bar{\ell}'; 00)$$

so that

$$J_{ij} = \sum_{\bar{\ell} \bar{\ell}' \ell''} \sum_{\lambda} \frac{1}{r_{N+1}} u_{\bar{\ell}}^{\alpha_j}(r_{N+1}) \delta_{m_\alpha}(i, j) \int dr_1 u_{\bar{\ell}'}^{\alpha_i}(r_1) \mathcal{Y}_{\ell''}^{(m')}(r_1) \frac{r_{<}^\lambda}{r_{>}^{\lambda+1}} g_\lambda(\ell' \ell'' \bar{\ell} \bar{\ell}'; m', m_{\alpha_i}) \quad (94)$$

Therefore the final desired integral of Eq. (71) is,

$$I = (-1)^N r_{N+1} \frac{N}{N!} \sum_{ij} \epsilon_i \epsilon_j J_{ij} \delta_{m_s}(\alpha_j, N+1) \delta_{m_s}(\alpha_i, N+1) \quad (95)$$

$$\otimes \int \bar{\phi}_{\beta_i}^*(2) \bar{\phi}_{\beta_j}(2) d2 \cdots \int \bar{\phi}_{\pi_i}^*(N) \bar{\phi}_{\pi_j}(N) dN$$

Because of the  $\delta$ -function conditions in Eq. (94) and Eq. (95), together with  $N$  is even for closed-shell molecule,  $I$  becomes

$$I = r_{N+1} \frac{N}{N!} \sum_i \epsilon_i J_{ii} \delta_{m_s}(\alpha_i, N+1) \int \bar{\phi}_{\beta_i}^*(2) \bar{\phi}_{\beta_i}(2) d2 \cdots \int \bar{\phi}_{\pi_i}^*(N) \bar{\phi}_{\pi_i}(N) dN \quad (96)$$

$$= r_{N+1} \frac{N}{N!} (N-1)! \sum_{i=1}^N J_{ii} \delta_{m_s}(\alpha_i, N+1)$$

Notice that the last sum index  $i$  means summing from the first electron orbital over the  $N^{th}$  electron orbital.

Substituting Eq. (94) into Eq. (96), we get

$$I = \sum_i^N \sum_{\bar{\ell} \bar{\ell}' \ell'' \lambda} u_{\bar{\ell}}^{\alpha_i}(r_{N+1}) \delta_{m_s}(\alpha_i, N+1) g_\lambda(\ell' \ell'' \bar{\ell} \bar{\ell}'; m', m_{\alpha_i}) \int dr_1 u_{\bar{\ell}'}^{\alpha_i}(r_1) \mathcal{Y}_{\ell''}^{(m')}(r_1) \frac{r_{<}^\lambda}{r_{>}^{\lambda+1}} \quad (97)$$

Thus the coupled equations Eq. (59) become [we'll drop the  $\alpha$  stuff — call it  $i$ ]

$$\left[ -\frac{1}{2} \frac{d^2}{dr_{N+1}^2} + \frac{\ell'(\ell' + 1)}{2r_{N+1}^2} - \frac{1}{2} k^2 \right] \mathcal{Y}_{\ell' \ell_0}^{(m')}(r_{N+1}) + \sum_{\ell''} V_{\ell' \ell''}^{(m')}(r_{N+1}) \mathcal{Y}_{\ell'' \ell_0}^{(m')}(r_{N+1}) \quad (98)$$

$$= \sum_{i=1}^N \sum_{\bar{\ell} \bar{\ell}' \ell'' \lambda} u_{\bar{\ell}}^{(i)}(r_{N+1}) \delta_{m_s}(i, N+1) g_\lambda(\ell' \ell'' \bar{\ell} \bar{\ell}'; m', m_i) \int dr_1 u_{\bar{\ell}'}^{(i)}(r_1) \mathcal{Y}_{\ell'' \ell_0}^{(m')}(r_1) \frac{r_{<}^\lambda}{r_{>}^{\lambda+1}}$$

Notice that we only get an exchange term from electrons with the same spin as the scattering electron — because of  $\delta_{m_s}(i, N+1)$ . This is certainly reasonable (remember Hartree-Fock).

It is useful to modify our notation still further to clean up Eq. (98). Let  $\ell_0$  denote the initial angular momentum. Alas, of course, for closed-shell molecules, each spatial MO will contain one electron with the same spin as that of the  $(N + 1)^{th}$  electron (we'll treat  $\pi_g(x)$  and  $\pi_g(y)$  as different orbitals). Thus we have

$$\begin{aligned} & \left[ \frac{d^2}{dr_{N+1}^2} - \frac{\ell(\ell+1)}{r_{N+1}^2} + k^2 \right] \mathcal{Y}_{\ell\ell_0}^{(m)}(r_{N+1}) \\ &= 2 \sum_{\ell'} \left[ V_{\ell\ell'}^{(m)}(r_{N+1}) \mathcal{Y}_{\ell'\ell_0}^{(m)}(r_{N+1}) - \int dr_1 K^{(m)}(\ell\ell'|r_1 r_{N+1}) \mathcal{Y}_{\ell'\ell_0}^{(m)}(r_1) \right] \end{aligned} \quad (99)$$

where (notice the sum index  $i$  means summing from the lowest spatial orbital to the highest occupied spatial orbital)

$$K^{(m)}(\ell\ell'|r_1 r_{N+1}) = \sum_{i=1}^{N_{occ}} \sum_{\ell''\ell'''\lambda} u_{\ell''}^{(i)}(r_{N+1}) u_{\ell'''}^{(i)}(r_1) g_\lambda(\ell\ell'\ell''\ell'''; m, m_i) \frac{r_{<}^\lambda}{r_{>}^{\lambda+1}} \quad (100)$$

with

$$\begin{aligned} g_\lambda(\ell\ell'\ell''\ell'''; m, m_i) &= \sqrt{\frac{(2\ell+1)(2\ell'+1)}{(2\ell''+1)(2\ell''' + 1)}} C(\ell\lambda\ell''; -m, m - m_i) C(\ell\lambda\ell''; 00) \\ &\otimes C(\ell'\lambda\ell'''; m, m_i - m) C(\ell'\lambda\ell'''; 00) \end{aligned} \quad (101)$$

and

$$r_{>}^{\leq} = \min_{\max} \{r_1, r_{N+1}\} \quad (102)$$

Notice that for  $N_2$ , for instance, with configuration  $X^1\Sigma_g^+$ :

$$1\sigma_g^2 2\sigma_g^2 3\sigma_g^2 1\sigma_u^2 1\sigma_u^2 1\pi_u(x)^2 1\pi_u(y)^2$$

we have  $N_{occ} = 7$ .

There are some restrictions placed on the summations in the exchange kernel, i.e.,  $g_\lambda$  does it:

$$\ell + \lambda + \ell'' = \text{even} \quad (\lambda \geq 0) \quad (103a)$$

$$\ell' + \lambda + \ell''' = \text{even} \quad (103b)$$

$$|\ell - \ell''| \leq \lambda \leq \ell + \ell'' \quad [\Delta(\ell\lambda\ell'')] \quad (103c)$$

$$|\ell' - \ell'''| \leq \lambda \leq \ell' + \ell''' \quad [\Delta(\ell'\lambda\ell''')] \quad (103d)$$

but this would help much! Recall that, e.g.,  $u_{\ell''}^{(i)}(r)$  is the expansion coefficient of the  $i^{th}$  molecular orbital corresponding to  $P_{\ell''}(\cos\theta)$  — i.e., the  $\ell''^{th}$  partial wave. Note also that

we can write the exchange kernel as

$$K^{(m)}(\ell\ell'|r_1 r_{N+1}) = \sum_{i=1}^{N_{occ}} \sum_{\ell''\ell'''} u_{\ell''}^{(i)}(r_{N+1}) u_{\ell'''}^{(i)}(r_1) \sum_{\lambda} g_{\lambda}(\ell\ell'\ell''\ell'''; m, m_i) \frac{r_{<}^{\lambda}}{r_{>}^{\lambda+1}} \quad (104)$$

It is certainly not hard to see from Eq. (100) why the number of exchange kernel rapidly gets out of hand. For a given  $\ell$  (e.g.,  $\ell = 0 \sim$  “s-in”) we couple, say, one partial wave  $\ell'$  on the right hand side in the exchange term (we already know from painful experience how many  $\ell'$  are usually need in the static coupling term!). Then we get a huge number of exchange term arising from the  $\ell''\ell'''$  and  $\lambda$ , say, in  $K^{(m)}$ .

Of course, the static coupling matrix element in Eq. (58),

$$V_{\ell\ell'}^{(m)}(r_{N+1}) = (-1)^m \sqrt{(2\ell+1)(2\ell'+1)} \sum_{\lambda} \frac{1}{2\lambda+1} v_{\lambda}^{st}(r_{N+1}) C(\ell\ell'\lambda; 00) C(\ell\ell'\lambda; -m, m) \quad (105)$$

Parenthetically, we note that using the properties of the Clebesh-Gordon coefficients ([1]-(3.17c)), we get

$$C(\ell\ell'\lambda; -m, m) = (-1)^{\ell'+m} \sqrt{\frac{2\lambda+1}{2\ell+1}} C(\ell'\lambda\ell; -m, 0) \quad (106a)$$

$$C(\ell\ell'\lambda; 00) = (-1)^{\ell'} \sqrt{\frac{2\lambda+1}{2\ell+1}} C(\ell'\lambda\ell; 00) \quad (106b)$$

where

$$V_{\ell\ell'}^{(m)}(r_{N+1}) = \sqrt{\frac{2\ell'+1}{2\ell+1}} \sum_{\lambda} v_{\lambda}^{st}(r_{N+1}) C(\ell'\lambda\ell; -m, 0) C(\ell'\lambda\ell; 00) \quad (107)$$

or, using [1]-(3.16a),

$$V_{\ell\ell'}^{(m)}(r_{N+1}) = \sqrt{\frac{2\ell'+1}{2\ell+1}} \sum_{\lambda} v_{\lambda}^{st}(r_{N+1}) C(\ell'\lambda\ell; m, 0) C(\ell'\lambda\ell; 00) \quad (108)$$

For  $D_{\infty h}$  targets, only  $\lambda = \text{even}$  contribute to  $\sum_{\lambda}$  in Eq. (108).

### E. Example: $e\text{-H}_2$

We have

$$\begin{aligned} & \left[ \frac{d^2}{dr_3^2} - \frac{\ell(\ell+1)}{r_3^2} + k^2 \right] \mathcal{Y}_{\ell\ell_0}^{(m)}(r_3) \\ &= 2 \sum_{\ell'} \left[ V_{\ell\ell'}^{(m)}(r_3) \mathcal{Y}_{\ell'\ell_0}^{(m)}(r_3) - \int dr_1 K^{(m)}(\ell\ell'|r_1 r_3) \mathcal{Y}_{\ell'\ell_0}^{(m)}(r_1) \right] \end{aligned} \quad (109)$$



where

$$K^{(m)}(\ell\ell'|r_1r_3) = \sum_{\ell''\ell'''\lambda} u_{\ell''}^{(\sigma_g)}(r_3)u_{\ell'''}^{(\sigma_g)}(r_1)g_\lambda(\ell\ell'\ell''\ell''';m,0)\frac{r_{<}^\lambda}{r_{>}^{\lambda+1}} \quad (110)$$

where we note that for  $H_2$  there is only one spatial orbital —  $\sigma_g$ , so the  $\sum_i$  vanishes; also, of course,  $m(\sigma_g) = 0$ .

We know from experience that about 3 partial waves is sufficient — say  $s$ ,  $d$ ,  $g$  — to coverage the static problem. Consider  $\sigma$ -wave scattering ( $m = 0$ ), i.e.,  $\Sigma_g$  symmetry  $+\Sigma_u$

1.  $s$ -wave ( $\ell = 0$ )  $\Rightarrow$  always have  $\lambda = \ell''$  by Eq. (103c)  $[\Sigma_g]$

(a) Expand MO in 1 term (spherical only)  $\Rightarrow \ell'' = \ell''' = 0 \Rightarrow \lambda = 0$  (by Eq. (103c))  
 $\Rightarrow \ell' = 0$  (by Eq. (103d))

Exchange term in Eq. (109) becomes

$$-2 \int dr_1 K^{(0)}(00|r_1r_3)\mathcal{Y}_{0\ell_0}^{(0)}$$

with

$$K^{(0)}(00|r_1r_3) = u_0^{(\sigma_g)}(r_3)u_0^{(\sigma_g)}(r_1)g_0(0000;00)\frac{1}{r_1}$$

One exchange term only.

(b) Expand MO in 2 terms:  $\ell'' = 0, 2$ ;  $\ell''' = 0, 2$  allowed and  $\lambda = \ell''$  (by Eq. (103c))

Exchange kernel becomes ( $\sum' \Rightarrow$  even only),

$$K^{(0)}(0\ell'|r_1r_3) = \sum_{\ell''=0}^2 \sum_{\ell'''=0}^2 u_{\ell''}^{(\sigma_g)}(r_3)u_{\ell'''}^{(\sigma_g)}(r_1)g_{\ell''}(0\ell'\ell''\ell''';00)\frac{r_{<}^{\ell''}}{r_{>}^{\ell''+1}}$$

with  $|\ell' - \ell'''| \leq \ell'' \leq \ell' + \ell'''$

Exchange term becomes

$$-2 \int dr_1 \left[ K^{(0)}(00|r_1r_3)\mathcal{Y}_{0\ell_0}^{(0)}(r_1) + K^{(0)}(02|r_1r_3)\mathcal{Y}_{2\ell_0}^{(0)}(r_1) + K^{(0)}(04|r_1r_3)\mathcal{Y}_{4\ell_0}^{(0)}(r_1) \right]$$

2.  $p$ -wave ( $\ell = 1$ )  $\Rightarrow |1 - \ell''| \leq \lambda \leq 1 + \ell''$   $[\Sigma_u]$

(a) Expand MO in 1 term  $\Rightarrow \ell'' = \ell''' = 0 \Rightarrow \lambda = 1$  and  $\ell' = 1$

Again only

$$-2 \int dr_1 K^{(0)}(11|r_1r_3)\mathcal{Y}_{1\ell_0}^{(0)}(r_1)$$

with

$$K^{(0)}(11|r_1r_3) = u_0^{(\sigma_g)}(r_3)u_0^{(\sigma_g)}(r_1)g_1(1100;00)\frac{r_{<}}{r_{>}^2}$$

- (b) Expand MO in 2 terms:  $\ell'' = 0, 2$ ;  $\ell''' = 0, 2$  allowed and  $|1 - \ell''| \leq \lambda \leq 1 + \ell''$   
and  $|\ell' - \ell'''| \leq \lambda \leq \ell' + \ell'''$

Exchange term

$$-2 \int dr_1 \left[ K^{(0)}(11|r_1 r_3) \mathcal{Y}_{1\ell_0}^{(0)}(r_1) + K^{(0)}(13|r_1 r_3) \mathcal{Y}_{3\ell_0}^{(0)}(r_1) + K^{(0)}(15|r_1 r_3) \mathcal{Y}_{5\ell_0}^{(0)}(r_1) \right]$$

## F. The General Case: “Simplification” of the exchange term

Let’s return to the case of an  $N$  electron target with  $N_{occ}$  spatial orbitals. Suppose an molecule has  $\sigma$  and  $\pi$  molecular orbitals. We can write (no longer treating  $\pi_x$  separately from  $\pi_y$ )

$$\begin{aligned} K^{(m)}(\ell\ell'|r_1 r_{N+1}) &= \sum_{i=1}^{N_{occ}(\sigma)} \sum_{\ell''\ell'''\lambda} u_{\ell''}^{(\sigma_i)}(r_{N+1}) u_{\ell'''}^{(\sigma_i)}(r_1) g_\lambda(\ell\ell'\ell''\ell'''; m, 0) \frac{r_{<}^\lambda}{r_{>}^{\lambda+1}} \\ &+ \sum_{i=1}^{N_{occ}(\pi)} \sum_{\ell''\ell'''\lambda} u_{\ell''}^{(\pi_i)}(r_{N+1}) u_{\ell'''}^{(\pi_i)}(r_1) g_\lambda(\ell\ell'\ell''\ell'''; m, +1) \frac{r_{<}^\lambda}{r_{>}^{\lambda+1}} \\ &+ \sum_{i=1}^{N_{occ}(\pi)} \sum_{\ell''\ell'''\lambda} u_{\ell''}^{(\pi_i)}(r_{N+1}) u_{\ell'''}^{(\pi_i)}(r_1) g_\lambda(\ell\ell'\ell''\ell'''; m, -1) \frac{r_{<}^\lambda}{r_{>}^{\lambda+1}} \end{aligned} \quad (111)$$

For the  $\sigma$ -orbital, we call

$$g_\lambda(\ell\ell'\ell''\ell'''; m, 0) \equiv A(\ell\ell'\ell''\ell'''; 0, m) \quad (112)$$

and for the  $\pi$ -orbital, we call

$$g_\lambda(\ell\ell'\ell''\ell'''; m, +1) + g_\lambda(\ell\ell'\ell''\ell'''; m, -1) \equiv B(\ell\ell'\ell''\ell'''; 1, m) \quad (113)$$

Thus we get (in this notation)

$$\begin{aligned} K^{(m)}(\ell\ell'|r_1 r_{N+1}) &= \sum_{i=1}^{N_{occ}(\sigma)} \sum_{\ell''\ell'''\lambda} u_{\ell''}^{(\sigma_i)}(r_{N+1}) u_{\ell'''}^{(\sigma_i)}(r_1) \frac{r_{<}^\lambda}{r_{>}^{\lambda+1}} A(\ell\ell'\ell''\ell'''; 0, m) \\ &+ \sum_{i=1}^{N_{occ}(\pi)} \sum_{\ell''\ell'''\lambda} u_{\ell''}^{(\pi_i)}(r_{N+1}) u_{\ell'''}^{(\pi_i)}(r_1) \frac{r_{<}^\lambda}{r_{>}^{\lambda+1}} B(\ell\ell'\ell''\ell'''; 1, m) \end{aligned} \quad (114)$$

and the exchange term in the scattering equations becomes (call it I)

$$\begin{aligned}
I &\equiv -2 \sum_{\ell'} \int dr_1 K^{(m)}(\ell\ell'|r_1 r_{N+1}) \mathcal{Y}_{\ell'\ell_0}^{(m)}(r_1) \\
&= -2 \sum_{\ell'} \int dr_1 \left[ \sum_{i=1}^{N_{occ}(\sigma)} \sum_{\ell''\ell'''\lambda} u_{\ell''}^{(\sigma_i)}(r_{N+1}) u_{\ell'''}^{(\sigma_i)}(r_1) \frac{r_{<}^\lambda}{r_{>}^{\lambda+1}} A(\ell\ell'\ell''\ell'''; 0, m) \right. \\
&\quad \left. + \sum_{i=1}^{N_{occ}(\pi)} \sum_{\ell''\ell'''\lambda} u_{\ell''}^{(\pi_i)}(r_{N+1}) u_{\ell'''}^{(\pi_i)}(r_1) \frac{r_{<}^\lambda}{r_{>}^{\lambda+1}} B(\ell\ell'\ell''\ell'''; 1, m) \right] \mathcal{Y}_{\ell'\ell_0}^{(m)}(r_1) \\
&= -2 \sum_{\ell'} \left[ \sum_{i=1}^{N_{occ}(\sigma)} \sum_{\ell''\ell'''\lambda} u_{\ell''}^{(\sigma_i)}(r_{N+1}) A(\ell\ell'\ell''\ell'''; 0, m) \int_0^\infty dr_1 u_{\ell'''}^{(\sigma_i)}(r_1) \mathcal{Y}_{\ell'\ell_0}^{(m)}(r_1) \frac{r_{<}^\lambda}{r_{>}^{\lambda+1}} \right. \\
&\quad \left. + \sum_{i=1}^{N_{occ}(\pi)} \sum_{\ell''\ell'''\lambda} u_{\ell''}^{(\pi_i)}(r_{N+1}) B(\ell\ell'\ell''\ell'''; 1, m) \int_0^\infty dr_1 u_{\ell'''}^{(\pi_i)}(r_1) \mathcal{Y}_{\ell'\ell_0}^{(m)}(r_1) \frac{r_{<}^\lambda}{r_{>}^{\lambda+1}} \right]
\end{aligned} \tag{115}$$

If we define

$$Z_\lambda[f_1, f_2; r'] \equiv \int_0^\infty dr f_1(r) f_2(r) \frac{r_{<}^\lambda}{r_{>}^{\lambda+1}} \tag{116}$$

with

$$r_{>} = \min_{\max} \{r, r'\}$$

Expanding, we have

$$Z_\lambda[f_1, f_2; r'] = \frac{1}{r'^{\lambda+1}} \int_0^{r'} dr [r^\lambda f_1(r) f_2(r)] + r'^\lambda \int_{r'}^\infty dr \left[ \frac{1}{r^{\lambda+1}} f_1(r) f_2(r) \right] \tag{117}$$

Then the exchange term becomes

$$\begin{aligned}
I &= -2 \sum_{\ell'} \left\{ \sum_{i=1}^{N_{occ}(\sigma)} \sum_{\ell''\ell'''\lambda} u_{\ell''}^{(\sigma_i)}(r_{N+1}) A(\ell\ell'\ell''\ell'''; 0, m) Z_\lambda \left[ u_{\ell'''}^{(\sigma_i)}(r_1) \mathcal{Y}_{\ell'\ell_0}^{(m)}(r_1); r_{N+1} \right] \right. \\
&\quad \left. + \sum_{i=1}^{N_{occ}(\pi)} \sum_{\ell''\ell'''\lambda} u_{\ell''}^{(\pi_i)}(r_{N+1}) B(\ell\ell'\ell''\ell'''; 1, m) Z_\lambda \left[ u_{\ell'''}^{(\pi_i)}(r_1) \mathcal{Y}_{\ell'\ell_0}^{(m)}(r_1); r_{N+1} \right] \right\}
\end{aligned} \tag{118}$$

[For  $N_2$ ,  $N_{occ}(\sigma) = 5$ ,  $N_{occ}(\pi) = 1$ .]

Then the coupled equations Eq. (99) become

$$\begin{aligned}
& \left[ \frac{d^2}{dr_{N+1}^2} - \frac{\ell(\ell+1)}{r_{N+1}^2} + k^2 \right] \mathcal{Y}_{\ell\ell_0}^{(m)}(r_{N+1}) \\
&= 2 \sum_{\ell'} V_{\ell\ell'}^{(m)}(r_{N+1}) \mathcal{Y}_{\ell'\ell_0}^{(m)}(r_{N+1}) \\
&- 2 \sum_{i=1}^{N_{occ}(\sigma)} \sum_{\ell'\ell''\ell'''\lambda} A(\ell\ell'\ell''\ell'''; 0, m) u_{\ell'''}^{(\sigma_i)}(r_{N+1}) Z_\lambda \left[ u_{\ell'''}^{(\sigma_i)}(r_1) \mathcal{Y}_{\ell'\ell_0}^{(m)}(r_1); r_{N+1} \right] \\
&- 2 \sum_{i=1}^{N_{occ}(\pi)} \sum_{\ell'\ell''\ell'''\lambda} B(\ell\ell'\ell''\ell'''; 1, m) u_{\ell'''}^{(\pi_i)}(r_{N+1}) Z_\lambda \left[ u_{\ell'''}^{(\pi_i)}(r_1) \mathcal{Y}_{\ell'\ell_0}^{(m)}(r_1); r_{N+1} \right]
\end{aligned} \tag{119}$$

## G. Summary

In a truly heroic effort, we have derived the coupled scattering equations for electron-molecule scattering in the body-fixed frame of reference including exchange. We make the Born-Oppenheimer approximation on the target and do not allow for electronic excitation by electron impact. Restricting ourselves to closed-shell targets. We obtain the coupled equations of Eq. (39) for the scattering functions  $F_{\gamma'}^{(\gamma)}(\vec{r}_{N+1})$  for vibrational excitation.

The reduction to radial equations has been carried out for elastic scattering in a 1-center coordinate system. We find that an exchange term appears for each target electron which has the same spin as that of the  $(N+1)^{th}$  electron. We get Eq. (99)-Eq. (101) for the radial scattering function  $\mathcal{Y}_{\ell\ell_0}^{(m)}(r_{N+1})$ . The static matrix element is given by Eq. (58) or, equivalently, Eq. (105). The exchange kernel is given by Eq. (100) subject to the restrictions of Eq. (103a). The functions  $u_\ell^{(i)}$  appearing in Eq. (100) are the single-center expansion terms of the  $i^{th}$  spatial MO — see Eq. (81). Finally, we showed that the coupled equation can be written in the magically more useful form Eq. (119).

## III. THE COUPLED EQUATION FOR VIBRATIONALLY INELASTIC SCATTERING

Although we have derived the scattering equation Eq. (99), we have to keep in mind that Eq. (99) is derived from the original Eq. (41), which treats the system as a rigid rotor and does not allow vibrational excitation. So Eq. (99) is only available for elastic scattering.

If we want to consider the vibrational excitation, we'll go back to Eq. (39). From Eq. (2),

we notice that the difference between Eq. (99) and Eq. (39) is that we omit the nuclear vibrational function  $\chi_{(n\Lambda v)_\gamma}^{vib}(R_\alpha)$  and the sum index  $v_{\gamma''}$ . Checking carefully from Eq. (41) to Eq. (99), we can find that although we treated the target in fixed nuclei and derived the static coupling matrix element Eq. (107) and the exchange kernel Eq. (100), we can easily add the nuclear vibrational function and do not effect the exchange kernel.

So, we can write the coupled equation for vibrationally inelastic scattering as (replacing  $v_{\gamma'}$  to  $v'$  for simplicity)

$$\left[ \frac{d^2}{dr_{N+1}^2} - \frac{\ell(\ell+1)}{r_{N+1}^2} + k_v^2 \right] \mathcal{Y}_{v\ell, v_0\ell_0}^{(m)}(r_{N+1}) \\ = 2 \sum_{v'\ell'} \left[ V_{v\ell, v'\ell'}^{(m)}(r_{N+1}) \mathcal{Y}_{v'\ell', v_0\ell_0}^{(m)}(r_{N+1}) - \int dr_1 K_{vv'}^{(m)}(\ell\ell'|r_1 r_{N+1}) \mathcal{Y}_{v'\ell', v_0\ell_0}^{(m)}(r_1) \right] \quad (120)$$

with

$$V_{v\ell, v'\ell'}^{(m)}(r_{N+1}) = \int \chi_v^*(R_\alpha) V_{\ell\ell'}^{(m)}(r_{N+1}; R_\alpha) \chi_{v'}(R_\alpha) dR_\alpha \quad (121)$$

and

$$K_{vv'}^{(m)}(\ell\ell'|r_1 r_{N+1}) = \int \chi_v^*(R_\alpha) K^{(m)}(\ell\ell'|r_1 r_{N+1}; R_\alpha) \chi_{v'}(R_\alpha) dR_\alpha \quad (122)$$

### A. Polarization Potential

Recalling that we specialize to the case where no electronic excitation is allowed (in page 5). i.e., we have neglected all of the higher discrete and continuum electronic states. However, the presence of a charged scattering projectile will cause the target molecular system to distort. This distortion or “polarization” of the target density gives rise an additional contribution to the system. This additional contribution to the system energy is known as a *polarization potential*. This difference in the system energy when calculated with a distorting charge present and in its absence can be taken into account by adding a polarization term  $\hat{\mathcal{V}}_{pol}$ .

Unfortunately, the polarization term is a non-local one. So exact polarization term is hardly calculated. If we take a model potential, which is supposed to be only subject to the spatial coordinates of the scattering electron —  $V_{pol}(\vec{r}_{N+1})$ , and expand it in Legendre polynomials as Eq. (43), we have

$$V_{pol}(\vec{r}_{N+1}; R_\alpha) = \sum_{\lambda=0}^{\infty} v_\lambda^{pol}(r_{N+1}; R_\alpha) P_\lambda(\cos \theta_{N+1}) \quad (123)$$

So, we can define

$$v_{\lambda}^{st,pol}(r_{N+1}; R_{\alpha}) = v_{\lambda}^{st}(r_{N+1}; R_{\alpha}) + v_{\lambda}^{pol}(r_{N+1}; R_{\alpha}) \quad (124)$$

and Eq. (108) becomes

$$V_{\ell\ell'}^{(m)}(r_{N+1}; R_{\alpha}) = \sqrt{\frac{2\ell'+1}{2\ell+1}} \sum_{\lambda} v_{\lambda}^{st,pol}(r_{N+1}; R_{\alpha}) C(\ell'\lambda\ell; m, 0) C(\ell'\lambda\ell; 00) \quad (125)$$

Substituting Eq. (125) into Eq. (121), we get

$$\begin{aligned} V_{v\ell, v'\ell'}^{(m)}(r_{N+1}) &= \sum_{\lambda} \left[ \int \chi_v^*(R_{\alpha}) v_{\lambda}^{st,pol}(r_{N+1}; R_{\alpha}) \chi_{v'}(R_{\alpha}) dR_{\alpha} \right] \\ &\times \sqrt{\frac{2\ell'+1}{2\ell+1}} C(\ell'\lambda\ell; m, 0) C(\ell'\lambda\ell; 00) \end{aligned} \quad (126)$$

If we define

$$p_{\lambda}(\ell\ell'; m) = \sqrt{\frac{2\ell'+1}{2\ell+1}} C(\ell'\lambda\ell; m, 0) C(\ell'\lambda\ell; 00) \quad (127)$$

and

$$\omega_{v, v'}^{\lambda}(r_{N+1}) = \int \chi_v^*(R_{\alpha}) v_{\lambda}^{st,pol}(r_{N+1}; R_{\alpha}) \chi_{v'}(R_{\alpha}) dR_{\alpha} \quad (128)$$

Eq. (126) becomes

$$V_{v\ell, v'\ell'}^{(m)}(r_{N+1}) = \sum_{\lambda} p_{\lambda}(\ell\ell'; m) \omega_{v, v'}^{\lambda}(r_{N+1}) \quad (129)$$

## B. Arrangement of the Coupled Equation for Vibrationally Inelastic Scattering

In most references, the index  $m$  is usually replaced by  $\Lambda$  for electron scattering from diatomic molecules in body-fixed frame. So we rewrite all the coupled equations as

$$\begin{aligned} &\left[ \frac{d^2}{dr_{N+1}^2} - \frac{\ell(\ell+1)}{r_{N+1}^2} + k_v^2 \right] \mathcal{Y}_{v\ell, v_0\ell_0}^{(\Lambda)}(r_{N+1}) \\ &= 2 \sum_{v'\ell'} \left[ V_{v\ell, v'\ell'}^{(\Lambda)}(r_{N+1}) \mathcal{Y}_{v'\ell', v_0\ell_0}^{(\Lambda)}(r_{N+1}) - \int dr_1 K_{vv'}^{(\Lambda)}(\ell\ell'|r_1 r_{N+1}) \mathcal{Y}_{v'\ell', v_0\ell_0}^{(\Lambda)}(r_1) \right] \end{aligned} \quad (130)$$

where the coupled local potential is

$$\begin{aligned} V_{v\ell, v'\ell'}^{(\Lambda)}(r_{N+1}) &= \sum_{\lambda} \left[ \int \chi_v^*(R_{\alpha}) v_{\lambda}^{st,pol}(r_{N+1}; R_{\alpha}) \chi_{v'}(R_{\alpha}) dR_{\alpha} \right] \\ &\times \sqrt{\frac{2\ell'+1}{2\ell+1}} C(\ell'\lambda\ell; \Lambda, 0) C(\ell'\lambda\ell; 00) \end{aligned} \quad (131)$$

and the coupled exchange term is

$$K_{vv'}^{(\Lambda)}(\ell\ell'|r_1r_{N+1}) = \int \chi_v^*(R_\alpha) K^{(\Lambda)}(\ell\ell'|r_1r_{N+1}; R_\alpha) \chi_{v'}(R_\alpha) dR_\alpha \quad (132)$$

in which the exchange kernel is

$$K^{(\Lambda)}(\ell\ell'|r_1r_{N+1}; R_\alpha) = \sum_{i=1}^{N_{occ}} \sum_{\ell''\ell'''} u_{\ell''}^{(i)}(r_{N+1}; R_\alpha) u_{\ell'''}^{(i)}(r_1; R_\alpha) \sum_{\lambda} g_{\lambda}(\ell\ell'\ell''\ell'''; \Lambda, m_i) \frac{r_{<}^{\lambda}}{r_{>}^{\lambda+1}} \quad (133)$$

with

$$g_{\lambda}(\ell\ell'\ell''\ell'''; \Lambda, m_i) = \sqrt{\frac{(2\ell+1)(2\ell'+1)}{(2\ell''+1)(2\ell''' + 1)}} C(\ell\lambda\ell''; -\Lambda, \Lambda - m_i) C(\ell\lambda\ell'''; 00) \\ \otimes C(\ell'\lambda\ell'''; \Lambda, m_i - \Lambda) C(\ell'\lambda\ell''; 00) \quad (134)$$

If the isolated molecule only contains  $\sigma$  and  $\pi$  orbitals, both of which are fully occupied, we have (from Eq. (114)),

$$K^{(\Lambda)}(\ell\ell'|r_1r_{N+1}; R_\alpha) = \sum_{i=1}^{N_{occ}(\sigma)} \sum_{\ell''\ell'''\lambda} u_{\ell''}^{(\sigma_i)}(r_{N+1}; R_\alpha) u_{\ell'''}^{(\sigma_i)}(r_1; R_\alpha) \frac{r_{<}^{\lambda}}{r_{>}^{\lambda+1}} A(\ell\ell'\ell''\ell'''; 0, \Lambda) \\ + \sum_{i=1}^{N_{occ}(\pi)} \sum_{\ell''\ell'''\lambda} u_{\ell''}^{(\pi_i)}(r_{N+1}; R_\alpha) u_{\ell'''}^{(\pi_i)}(r_1; R_\alpha) \frac{r_{<}^{\lambda}}{r_{>}^{\lambda+1}} B(\ell\ell'\ell''\ell'''; 1, \Lambda) \quad (135)$$

where

$$A(\ell\ell'\ell''\ell'''; 0, \Lambda) = g_{\lambda}(\ell\ell'\ell''\ell'''; \Lambda, 0) \quad (136)$$

and

$$B(\ell\ell'\ell''\ell'''; 1, \Lambda) = g_{\lambda}(\ell\ell'\ell''\ell'''; \Lambda, +1) + g_{\lambda}(\ell\ell'\ell''\ell'''; \Lambda, -1) \quad (137)$$

We must note that in Eq. (135) *there is only one  $\pi$  orbital for  $N_2$  since  $\pi(x)$  and  $\pi(y)$  are summed up through Eq. (137).*

### C. Comments on the Vibrationally Inelastic Scattering Equationns

Using Eq. (130)-Eq. (137), we could calculate the scattering function numerically. Before doing that, we have to understand the physical meaning of every variable and function.

- $r_{N+1}$ : the radial coordinate of the scattering electron
- $\ell_0$  and  $\ell$ : the initial and highest orbital angular momentum number of the scattering electron

- $\Lambda$ : the eigenvalue of  $\ell_z$ , projection of  $\vec{\ell}$  along the  $\hat{e}_z$  (the internuclear axis for a diatomic molecule,  $\hat{e}_z = R$ ).

Since  $\hat{\mathcal{H}}_m^{(r)} = 0$  in the FNO (Fixed-Nuclear-Orientation) approximation,  $\hat{\ell}_z$ , the projection of the operator  $\hat{L}$  onto the internuclear axis  $R$  (denoted by the symbol  $\Lambda$ ) is a *constant-of-motion*. Thus scattering quantities such as the K-matrix and T-matrix are diagonal in  $\Lambda$ . This leads to considerable simplifications, so much so, that various values of  $\Lambda$  have been assigned specific names. For homonuclear diatomic molecule, the inversion symmetry  $g$  or  $u$  is specified. The first four symmetry designations are

$$\Sigma_g \quad \Lambda = 0 \quad \ell = 0, 2, 4, \dots \quad (138a)$$

$$\Sigma_u \quad \Lambda = 0 \quad \ell = 1, 3, 5, \dots \quad (138b)$$

$$\Pi_u \quad \Lambda = 1 \quad \ell = 1, 3, 5, \dots \quad (138c)$$

$$\Pi_g \quad \Lambda = 1 \quad \ell = 2, 4, 6, \dots \quad (138d)$$

From Eq. (130), we only get T-matrix  $T_{v\ell, v_0\ell_0}^\Lambda$ , through which the cross sections are calculated,

$$\sigma_{v_0 \rightarrow v}^\Lambda = \frac{\pi}{k_0} \sum_{\ell, \ell_0} |T_{v\ell, v_0\ell_0}^\Lambda|^2 \quad (139a)$$

$$\sigma_{v_0 \rightarrow v} = \sum_{\Lambda} \sigma_{v_0 \rightarrow v}^\Lambda \quad (139b)$$

- $k_v$ : energy of the scattering electron

$$k_v^2 = 2(E - \epsilon_v) \quad (140)$$

where  $\epsilon_v$  is the molecular energy at the  $v^{th}$  vibrational state and  $E$  is the total energy of the scattering system.

- $\ell'$ : summing index, the same meaning as  $\ell$

For each  $\Lambda$ , we should specify a maximum of  $\ell$  —  $\ell_{\max}$ . Thus  $\ell_0$ ,  $\ell$  and  $\ell'$  range from  $\ell_{\min}$  and  $\ell_{\max}$ . For example, if we specify  $\ell_{\max} = 9$  for  $\Pi_u$ ,  $\ell_0$ ,  $\ell$  and  $\ell'$  could be 1, 3, 5, 7 and 9.

- $v_0$  and  $v$ : the initial and final vibrational state of the target.



- $v'$ : summing index. More vibrational states are included to calculate the vibrational scattering. For example, for  $v_0 = 0 \Rightarrow v = 1$  of  $e\text{-N}_2$ , 15 vibrational states are needed. So the sum over  $v'$  is from 0 to 14.
- $\lambda$ : summing index.  $\lambda$  is the index of Legendre polynomials to expand  $1/r_{1,N+1}$ .  $\lambda$  is from 0 to  $\lambda_{\max}$ . However, from Eq. (103a),  $\ell + \lambda + \ell''$  should be even, the initial  $\lambda$  is  $\text{mod}(\ell + \ell'', 2)$  and the step is also 2 for homonuclear molecule.
- $i$ : summing index, the number of the molecular orbitals.
- $\ell''$  and  $\ell'''$ : summing index, the number of spherical harmonic functions to expand the molecular orbitals from Eq. (81) and Eq. (99).

$$\sigma_g \quad \ell''(\ell''') = 0, 2, 4, \dots \quad (141a)$$

$$\sigma_u \quad \ell''(\ell''') = 1, 3, 5, \dots \quad (141b)$$

$$\pi_u \quad \ell''(\ell''') = 1, 3, 5, \dots \quad (141c)$$

- $m_i$ : the parity of the molecular orbital.

$$\sigma \quad m_i = 0 \quad (142a)$$

$$\pi \quad m_i = 1 \quad (142b)$$

- 
- [1] M. E. Rose, *Elementary theory of angular momentum* (John Wiley & Sons, Inc., 1957).
- [2] We sum over all possible values of  $\alpha, \beta, \dots, \pi$ . So for  $\text{N}_2$  with 14 molecular (spin) orbital, we have  $\alpha, \beta, \gamma, \delta, \epsilon, \phi$  and each  $\sum$  runs, e.g.,  $\alpha = 1, 2, \dots, 14$ . Lots of them!
- [3] This is the most important step! Please learn this procedure.
- [4] would have been written with  $\langle N \rangle$  instead. Then  $\langle j \rangle = \pm \langle N \rangle$  with  $+$ ,  $j$  is even and  $-$ ,  $j$  is odd
- [5] see Michael A. Morrison's thesis