

Radiative interactions in diatomic molecules

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Abstract. Radiative interactions which give rise to allowed and forbidden radiative transitions in diatomic molecules are presented as tensor operators. A translational expansion of these interaction operators from the centre of mass of the molecule to the atomic centres is discussed. It is found that the expansion of the magnetic dipole interaction operator generates an extra gradient operator which may contribute significantly towards the transition probability. The expansion of atomic orbitals from one centre to the other is also discussed and analytical expressions of the two-centre integrals which one may encounter in radiative processes are presented.

Keywords. Tensor operators; translational expansion; gradient operator; two-centre integrals.

1. Introduction

The interaction of diatomic molecules with an electromagnetic field involves clear understanding of the molecular wavefunctions and angular momenta. Since the angular momenta of the molecule obey reverse commutation rules with respect to molecule-fixed axes (Van Vleck 1951), care has to be taken in studying the molecule-field interaction problems. By virtue of the multipole expansion of the radiation field, the interaction operators refer to the space-fixed axis whose origin lies at the centre of mass of the molecule. The molecular angular momenta and wavefunctions, on the other hand, are given with respect to the molecule-fixed co-ordinate system. Hence, for calculation, a transformation of the operators from the space-fixed system to the molecule-fixed system or vice versa becomes necessary. Besides, if the electronic wavefunctions are presented in terms of atomic orbitals at nuclear sites and the operators refer to the centre of mass of the molecule, the electronic transition moment involves multi-centre integrals. To calculate them correctly, a translational expansion of the operators and orbitals from one centre to the other becomes essential. In this paper, we discuss transition in diatomic molecules by radiative interactions. Though the advent of fast computers have made the evaluation of matrix elements simpler even with complicated many-term wavefunctions, analytical expressions will always be welcome for wavefunctions and matrix elements. We shall try to achieve such analytical expressions wherever possible.

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2. The Born-Oppenheimer separation

For simplicity, we discuss this separation for a Hund's case (b) diatomic molecule (Herzberg 1950) where spin-internuclear axis interaction is relatively weak. $\Psi(x_\rho, y_\rho, z_\rho, R, \beta, \alpha, s_\rho)$ is taken as the total wavefunction for a Hund's case (b) molecule, $\rho = 1, 2, \dots, n$. (x_j, y_j, z_j) and (ξ_j, η_j, ζ_j) will be used as positional co-ordinates of the j th electron with respect to the space-fixed system (XYZ) and the molecule-fixed co-ordinate system $(\xi\eta\zeta)$, respectively. We let the centre of mass of the nuclei be at rest at the origin of the co-ordinate systems (XYZ) and $(\xi\eta\zeta)$ which is the rotated frame work of (XYZ) by virtue of the right-handed rotations through Euler angles $(\alpha\beta\gamma)$ (Rose 1961). The ζ -axis coincides with the molecular axis. Only two rotations (α, β) are sufficient to explain the orientation of a diatomic molecule (rigid-rotor type) in space. We may also introduce spin co-ordinates for electrons: s_j when they are related to the individual spin-axis and σ_j when the ζ -axis is chosen as the reference axis.

The exact Hamiltonian operator may be written as

$$H = -\frac{\hbar^2}{2\mu R^2} \left[\frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) + \frac{1}{\sin \beta} \frac{\partial}{\partial \beta} \left(\sin \beta \frac{\partial}{\partial \beta} \right) + \frac{1}{\sin^2 \beta} \frac{\partial^2}{\partial \alpha^2} \right] - \frac{\hbar^2}{2m} \sum_j \nabla^2(x_j, y_j, z_j) + V_{nn}(R) + V_{ee.en}(x_\rho, y_\rho, z_\rho; R, \beta, \alpha) + W(s_\rho), \quad (1)$$

where the first and second terms represent the kinetic energies of the nuclei and electrons, respectively. $V_{nn}(R)$ is the potential energy arising from nuclear interaction and $V_{ee.en}$ comprises of ordinary electron-electron and electron-nuclear Coulomb potentials. Here m is the electronic mass, μ the reduced mass and R is the internuclear distance. We have added the spin-dependent interaction term $W(s_\rho)$ in the Hamiltonian.

To express both H and Ψ relative to the moving figure axis (Judd 1975; Chiu 1964), we transform the positional co-ordinates as follows:

$$\begin{pmatrix} \xi_j \\ \eta_j \\ \zeta_j \end{pmatrix} = \begin{pmatrix} \cos \alpha \cos \beta & \sin \alpha \cos \beta & -\sin \beta \\ -\sin \alpha & \cos \alpha & 0 \\ \cos \alpha \sin \beta & \sin \alpha \sin \beta & \cos \beta \end{pmatrix} \begin{pmatrix} x_j \\ y_j \\ z_j \end{pmatrix}, \quad (2)$$

and the differential operators in the two co-ordinate systems are now related as

$$\begin{aligned} (\partial/\partial\beta)_{\text{space}} &= (\partial/\partial\beta)_{\text{mol}} - iL_\eta, \\ (\partial/\partial\alpha)_{\text{space}} &= (\partial/\partial\alpha)_{\text{mol}} + iL_\xi \sin \beta - iL_\zeta \cos \beta, \end{aligned} \quad (3)$$

where L_ξ, L_η, L_ζ represent the components of the angular momentum of the electron in the moving co-ordinate system $(\xi\eta\zeta)$ in units of \hbar . With these transformations, the Schrodinger equation becomes,

$$\begin{aligned}
& \left\{ H_e(\xi_\rho, \eta_\rho, \zeta_\rho, R, s_\rho) - B \left[\frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) \right. \right. \\
& + \frac{1}{\sin \beta} \left(\frac{\partial}{\partial \beta} - iL_\eta \right) \sin \beta \left(\frac{\partial}{\partial \beta} - iL_\eta \right) \\
& \left. \left. + \frac{1}{\sin^2 \beta} \left(\frac{\partial}{\partial \alpha} + iL_\xi \sin \beta - iL_\zeta \cos \beta \right)^2 \right] \right. \\
& \left. + V_{nn}(R) - E \right\} \Psi(\xi_\rho, \eta_\rho, \zeta_\rho, R, \beta, \alpha, s_\rho) = 0, \quad (4)
\end{aligned}$$

where

$$H_e = -\frac{\hbar^2}{2m} \sum_j \nabla^2(\xi_j, \eta_j, \zeta_j) + V_{ee.en}(\xi_\rho, \eta_\rho, \zeta_\rho, R) + W(s_\rho), \quad (5)$$

and $B = \hbar^2/2\mu R^2$.

In the Born-Oppenheimer separation, we assume that the electronic problem with the fixed nuclei is solved. And, with the omission of a few interaction terms, the total molecular wavefunction Ψ can be separated into electronic ϕ^e , rotational $\Theta(\alpha, \beta)$ and radial $P(R)$ wavefunctions, which are solutions of the following differential equations:

$$\begin{aligned}
& [H_e(\xi_\rho, \eta_\rho, \zeta_\rho, R, s_\rho) - E_e(R)] \phi^e(\xi_\rho, \eta_\rho, \zeta_\rho, R, s_\rho) = 0, \\
& B \left[\cot \beta \frac{\partial}{\partial \beta} + \frac{\partial^2}{\partial \beta^2} + \frac{1}{\sin^2 \beta} \left(\frac{\partial}{\partial \alpha} - i\Lambda \cos \beta \right)^2 \right] \Theta(\alpha, \beta) + E_{\text{rot}} \Theta(\alpha, \beta) = 0, \\
& \left[B \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) - E_e(R) - V_{nn}(R) - E_{\text{rot}} - \bar{U}(R) + E \right] P(R) = 0. \quad (6)
\end{aligned}$$

In deriving the above equations, the conditions,

$$L_\xi \phi^e = \Lambda \phi^e,$$

$$\text{and } \langle \phi^e | L_\xi | \phi^e \rangle = \langle \phi^e | L_\eta | \phi^e \rangle = 0, \quad (7)$$

have been imposed. Λ , the electronic angular momentum along the internuclear axis is measured in units of \hbar . $\bar{U}(R)$ appearing in the radial equation is defined as:

$$\bar{U}(R) = B \left\langle \phi^e \left| L_\xi^2 + L_\eta^2 - \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) - \frac{2R^2}{P} \frac{\partial}{\partial R} P \frac{\partial}{\partial R} \right| \phi^e \right\rangle. \quad (8)$$

The total wavefunction for a Hund's case (b) symmetric top diatomic molecule at a particular rotational level N may be expressed as:

$$\Psi_{Nm\Lambda vs m_s} = P_v(R) \Psi_{Nm\Lambda}(\xi_\rho, \eta_\rho, \zeta_\rho, R, \alpha, \beta, \gamma) \chi_{s, m_s}(s_\rho), \quad (9)$$

where $\Psi_{Nm\Lambda}$ is the electronic-rotational wavefunction, which may again be expressed as (Bhattacharyya and Chiu 1977)

$$\Psi_{Nm\Lambda}^\pm = \left[\frac{2N+1}{16\pi^2} \right]^{1/2} [\mathcal{D}_{m\Lambda}^{N*}(\alpha\beta\gamma) \phi_\Lambda^e \pm (-1)^N \mathcal{D}_{m, -\Lambda}^{N*}(\alpha\beta\gamma) \phi_{-\Lambda}^e] \quad (10)$$

where $\mathcal{D}_{m\Lambda}^N$ is the rotation matrix element (Brink and Satchler 1962). The quantum numbers m and Λ are components of the angular momentum $N\hbar$ along the fixed

Z-axis and the moving figure-axis respectively. The \pm sign refers to the eigenvalue ± 1 under inversion operation. States $+\Lambda$ and $-\Lambda$ are degenerate and are called Λ -doublets.

3. Radiative interaction operators

The operators causing radiative interactions may be expressed as tensor operators (Brink and Satchler 1962) so that the matrix elements of these operators may be evaluated by using the Racah algebra. We consider absorption or emission of a single photon of energy $\hbar c k_\lambda$ and after separating the photon part, the Hamiltonian $H(\mathbf{r}, \lambda)$ which operates on the molecular system only is given by a sum of the spin-independent part of the interaction:

$$H_r(\mathbf{r}, \lambda) = -\left(\frac{e}{2mc}\right) \sum_i [\mathbf{A}_\lambda^*(\mathbf{r}_i) \cdot \mathbf{p}_i + \mathbf{p}_i \cdot \mathbf{A}_\lambda^*(\mathbf{r}_i)], \quad (11)$$

and the spin-dependent part of the interaction:

$$H_s(\mathbf{r}, \lambda) = -\left(\frac{e}{2mc}\right) \sum_i 2\hbar \mathbf{s}_i \cdot \nabla \times \mathbf{A}_\lambda^*(\mathbf{r}_i). \quad (12)$$

Here e and m are respectively electronic charge and mass, c is the velocity of light, \mathbf{p}_i and \mathbf{s}_i are the linear momentum and spin of the electron i respectively. $\mathbf{A}_\lambda(\mathbf{r}_i)$ is the vector potential of the transverse electromagnetic field that interacts with the charged particle.

By Taylor's expansion of $\mathbf{A}_\lambda^*(\mathbf{r}_i)$, we can obtain the multipole expansion of $H(\mathbf{r}, \lambda)$ (Brink and Satchler 1962; Chiu 1966):

$$H(\mathbf{r}, \lambda) = -\sum_{lm} \frac{i^l k_\lambda^l}{(2l-1)!!} \left(\frac{l+1}{2l}\right)^{1/2} \mathcal{D}_{mq}^l(\hat{R}) \{(\varepsilon_{lm} + \varepsilon'_{lm}) - iq(M_{lm} + M'_{lm})\}, \quad (13)$$

where $q = \pm 1$ are the transverse polarisations, ε_{lm} and ε'_{lm} are the electric multipole operators of parity $(-1)^l$ contributed by electronic charge and electron spin respectively. Similarly M_{lm} and M'_{lm} are the magnetic multipole operators of parity $(-1)^{l+1}$ contributed respectively by electronic charge and electron spin. The leading terms in the spin-independent interaction $H_r(\mathbf{r}, \lambda)$ and $Hq(E 1)$, the electric-dipole interaction, $Hq(M 1)$, the magnetic-dipole interaction with even parity and $Hq(E 2)$, the electric-quadruple interaction with even parity. They are expressed as tensor operators in the following way:

$$\begin{aligned} Hq(E 1) &= -ik_\lambda e \sum_{jm} \mathcal{D}_{mq}^1(\hat{R}) r_j c_m^1(\hat{r}_j), \\ Hq(E 2) &= (ek_\lambda^2/2\sqrt{3}) \sum_{jm} \mathcal{D}_{mq}^2(\hat{R}) r_j^2 c_m^2(\hat{r}_j), \\ Hq(M 1) &= -k_\lambda q\mu_\beta \sum_{jm} \mathcal{D}_{mq}^1(\hat{R}) L_m^1(\hat{r}_j). \end{aligned} \quad (14)$$

In the above equations, $\mu_\beta = e\hbar/2mc$ is the Bohr magneton, $C_m^l(\hat{r}_j) = [4\pi/(2l+1)]^{1/2} Y_{lm}(\hat{r}_j)$ is the modified spherical harmonics, $\hat{r}_j = (\theta_j, \phi_j)$ and \mathbf{r}_j are

referred to the centre of mass of the molecule in a space-fixed coordinate system. $\mathcal{D}_{mq}^l(\hat{R})$ is the rotation matrix element where $\hat{R} = (\alpha, \beta, \gamma)$ are the Euler angles which take the space-fixed quantisation axis into the direction of the propagation vector \mathbf{K}_λ , and

$$L_{\pm 1}^1(\mathbf{r}_j) = \mp \frac{1}{(2)^{1/2}} (L_{xj} \pm iL_{yj}), \quad L_0^1(\mathbf{r}_j) = L_{zj} \quad (15)$$

are the angular momentum operators expressed as tensors.

The spin-dependent Hamiltonian $H_s(\mathbf{r}, \lambda)$ comprises primarily of spin-dependent electric-dipole interaction $H_q(SE\ 1)$ and spin-dependent magnetic-quadrupole interaction $H_q(SM\ 2)$ which can be expressed as:

$$\begin{aligned} H_q(SE\ 1) &= 2^{1/2} ik_\lambda^2 \mu_\beta \sum_{jmv} \mathcal{D}_{mq}^1(\hat{R}) c(111; m-\nu\ \nu\ m) r_j c_{m-\nu}^1(\hat{r}_j) s_\nu(j), \\ H_q(SM\ 2) &= -2^{1/2} iqk_\lambda^2 \mu_\beta \sum_{jmv} \mathcal{D}_{mq}^2(\hat{R}) c(112; m-\nu\ \nu\ m) r_j c_{m-\nu}^1(\hat{r}_j) s_\nu(j). \end{aligned} \quad (16)$$

These are interactions with odd parity and can induce forbidden singlet-triplet transition (Mizushima 1964). $C(\dots)$ in the above is the Clebsch-Gordan coefficient (Rose 1961).

4. Translational expansion of interaction operators and atomic orbitals

In the evaluation of electronic transition moments (after separating the rotational and vibrational parts) of a diatomic molecules, one generally encounters single-electron two-centre integrals of the following type:

$$\langle g(\mathbf{r}_a) | M(\mathbf{r}) | h(\mathbf{r}_b) \rangle \quad \text{and} \quad \langle g(\mathbf{r}_a) | M(\mathbf{r}) | h(\mathbf{r}_a) \rangle, \quad (17)$$

and also other integrals by interchanging a and b . Here $g(\mathbf{r}_a)$ and $h(\mathbf{r}_b)$ are atomic orbitals centred at nuclei a and b respectively, and $M(\mathbf{r})$ is the radiative operator at the centre of mass. The integrals will have to be evaluated at a particular nuclear site or at the centre of mass. We, therefore, have to make a translational expansion of the operators, originally at the centre of mass, at nuclear sites a and b . Similarly, the atomic orbitals at a and b may also be expanded at other sites.

For this expansion, we may choose a coordinate system for centre a , centre b and the centre of mass (figure 1) so that

$$x_a = x_b = x, \quad y_a = y_b = y, \quad z_a = z + R/2 \quad \text{and} \quad z_b = z - R/2, \quad (18)$$

where R is the internuclear distance. Making use of these relations, the electric-dipole and electric-quadrupole operators can be expanded from the centre of mass of the molecule to the atomic centres a and b . Thus,

$$r^l c_m^l(\hat{r}) = \sum_{\sigma=|m|}^l \xi_\alpha^{-\sigma} \frac{(R/2)^{l-\sigma}}{(l-\sigma)!} \left[\frac{4\pi(l-m)!(l+m)!}{(2\sigma+1)(\sigma-m)!(\sigma+m)!} \right]^{1/2} r_\alpha^\sigma Y_{\sigma m}(\hat{r}_\alpha), \quad (19)$$

where α refers to either centre a or centre b . Here $\xi_a = -1$ and $\xi_b = 1$. Setting

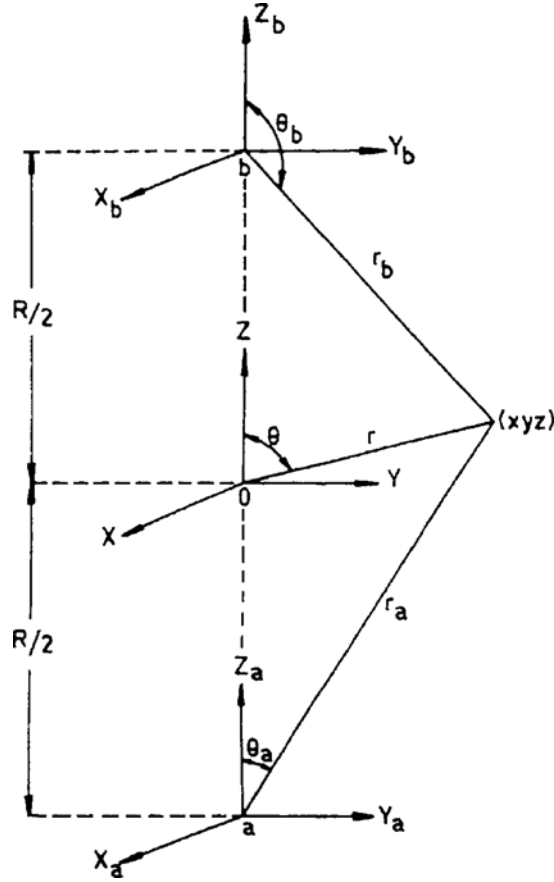


Figure 1. The coordinate systems for centre a , centre b and the centre of mass are all right-handed.

$l = 1$ and $l = 2$ in the above equation, we get in terms of tensors the expansion of electric-dipole and electric-quadrupole operators and so on. This expansion is quite in agreement with that derived from Hobson's formula (Hobson 1931; Chiu 1977).

With the same relations as in (18), the individual components L_x, L_y, L_z can be translationally expanded from the centre of mass to atomic site α and the operators $L_{\pm 1}^1$ and L_0^1 appearing in magnetic-dipole interaction become

$$\begin{aligned} L_{\pm 1}^1(\mathbf{r}) &= L_{\pm 1}^1(\mathbf{r}_\alpha) \pm \xi_\alpha(R/2) \nabla_{\pm 1}^1(\mathbf{r}_\alpha), \\ L_0^1(\mathbf{r}) &= L_0^1(\mathbf{r}_\alpha), \end{aligned} \quad (20)$$

where $\nabla_{\pm 1}^1(\mathbf{r}_\alpha) = \mp (1/\sqrt{2})(\partial/\partial x_\alpha \pm i\partial/\partial y_\alpha)$ is the gradient operator (also a tensor operator) at atomic centre α . The above equation gives essentially a translational expansion of the magnetic-dipole interaction operator whereby an additional gradient operator $\nabla_{\pm 1}^1$ is generated. Applying the gradient formula (Rose 1961), we obtain the result of operating $L_{\pm 1}^1(\mathbf{r})$ on the atomic orbital of angular momentum l and centred at nucleus α :

$$\begin{aligned} L_{\pm 1}^1(\mathbf{r}) \phi(\mathbf{r}_\alpha) Y_{lm}(\hat{r}_\alpha) &= [l(l+1)]^{1/2} c(l1l; m \pm 1 m \pm 1) \phi(\mathbf{r}_\alpha) Y_{l, m \pm 1}(\hat{r}_\alpha) \\ &\pm (R/2) \xi_\alpha \left[\left(\frac{l+1}{2l+1} \right)^{1/2} \left(\frac{d\phi}{dr_\alpha} - \frac{l}{r_\alpha} \phi \right) c(l+1 1 l; m \pm 1 \mp 1 m) Y_{l+1, m \pm 1}(\hat{r}_\alpha) \right. \end{aligned}$$

$$-\left(\frac{l}{2l+1}\right)^{1/2} \left(\frac{d\phi}{dr_\alpha} + \frac{l+1}{r_\alpha} \phi\right) c(l-1 \ 1 \ l; m \pm 1 \mp 1 \ m) Y_{l-1, m \pm 1}(\hat{r}_\alpha) \Big], \quad (21)$$

where again $\xi_a = -1$ and $\xi_b = 1$. Atomic functions of angular momentum $l \pm 1$, in addition to that of l , are generated by this additional gradient operator and they may contribute significantly to the magnetic dipole transition moment.

The atomic orbitals centred at a and b may also be expanded from one atomic centre to the other separated by R . These orbitals are usually the normalised Slater orbitals containing radial functions like $r_\alpha^k e^{-\xi_\alpha r_\alpha}$ ($R = n - l - 1 = 0, 1, 2, \dots$). In our chosen coordinate frame work (figure 1), the exponential functions $e^{-\xi_b r_b}$ etc centred at b may be expanded into functions centred at a in accordance with the Barnett and Coulson expansion (Barnett and Coulson 1951). Thus

$$e^{-\xi_b r_b} = \sum_{l=0}^{\infty} (-1)^l [4\pi(2l+1)]^{1/2} Y_{l0}(\hat{r}_a) \times \{(\zeta_b r_<) i_{l+1}(\zeta_b r_<) k_l(\zeta_b r_>) + (\zeta_b r_>) i_l(\zeta_b r_<) k_{l-1}(\zeta_b r_>)\}. \quad (22)$$

In the above expansion, $r_>$ (or $r_<$) means the larger (or smaller) of r_a and R . $k_n(\zeta r)$ and $i_n(\zeta r)$ ($n = l, l \pm 1$) are Bessel functions (Watson 1944) which can be expressed in terms of finite series. For interchange of a and b , an extra factor of $(-1)^l$ should be introduced on the right hand side of the expansion (22). Exponential functions like $r_b e^{-\xi_b r_b}$, $r_b^2 e^{-\xi_b r_b}$ etc may be obtained by differentiating (22) with respect to r_b and using the proper recursion relations (Watson 1944).

5. Two-centre integrals

If the electronic wavefunction is given in terms of atomic orbitals, then with the help of this translational expansion of operators and orbitals, one should in principle be able to have analytical expressions for the electronic integrals. All the two-centre integrals encountered should be of the following form:

$$\int e^{-\xi_a r_a} r_a^n Y_{lm}(\hat{r}_a) r_b^m e^{-\xi_b r_b} Y_{l'm'}(\hat{r}_b) d\tau_a, \quad (23)$$

or similar expressions by interchanging a and b . This can be integrated analytically. First, we may want to express $r_b^m e^{-\xi_b r_b} Y_{l'm'}(\hat{r}_b)$ as a product of a solid spherical harmonics $r_b^{l'} Y_{l'm'}(\hat{r}_b)$ and another function like $r_b^{m-l'} e^{-\xi_b r_b}$. These two terms may be expanded into functions centred at a as discussed in the previous section. Next, integration over $d\Omega_a$ will truncate the infinite series of expansion (as obtained from the $r_b^k e^{-\xi_b r_b}$ expansion) in l [see (22)]. The final integration is over dr_a . By expressing $k_l(\zeta_b r)$ and $i_l(\zeta_b r)$ in terms of finite series, the remaining radial integral breaks into a linear combination of integrals which can be integrated analytically. Thus for $l \geq 0$ and $n \geq (l+1)$; we have

$$\int_R^\infty r^n k_l(\zeta_b r) e^{-\xi_a r} dr = (-1)^{l+1} \zeta_b^{-1} \sum_{p=0}^l \sum_{s=0}^d \frac{(l+p)! d! R^{d-s} e^{-(\xi_a + \xi_b) R}}{2^p p! (l-p)! \zeta_b^p (d-s)! (\xi_a + \xi_b)^{s+1}}, \quad (24)$$

where $d = n - 1 - p$ and

$$\int_0^R r^n i_l(\zeta_b r) e^{-\zeta_a r} dr = (2\zeta_b)^{-1} \sum_{p=0}^l \frac{(l+p)! d!}{2^p p! (l-p)! \zeta_b^p} \\ \times \left\{ \frac{(-1)^p}{(\zeta_a - \zeta_b)^{n-p}} + \frac{(-1)^{l+1}}{(\zeta_a + \zeta_b)^{n-p}} \right. \\ \left. + \sum_{s=0}^d \frac{R^{d-s}}{(d-s)!} \left[\frac{(-1)^{p+1} e^{-(\zeta_a - \zeta_b)R}}{(\zeta_a - \zeta_b)^{s+1}} + \frac{(-1)^l e^{-(\zeta_a + \zeta_b)R}}{(\zeta_a + \zeta_b)^{s+1}} \right] \right\}; \\ \zeta_a \neq \zeta_b. \quad (25)$$

For the case $\zeta_a = \zeta_b$, the curly bracket on the right hand side of (25) becomes

$$\left\{ \left(\frac{(-1)^p R^{n-p}}{d!(n-p)} + \frac{(-1)^{l+1}}{(\zeta_a + \zeta_b)^{n-p}} + \sum_{s=0}^d \frac{(-1)^l R^{d-s} e^{-(\zeta_a + \zeta_b)R}}{(d-s)! (\zeta_a + \zeta_b)^{s+1}} \right) \right\}. \quad (26)$$

Hopefully, these sort of analytical expressions may be achieved for radiative interactions. For non-radiative interactions in diatomic molecules, one may not be sure, since the form of the integrals will depend on the choice of the interaction operators. Search for analytical expressions of two-centre integrals is an old phenomenon (Joy and Parr 1958; Prosser and Blanchard 1962; Geller 1964). In some of the methods, the operator expansion is not even necessary. But in these methods one can treat coulombic type two-centre integrals only, and furthermore these cannot treat all cases with generality. The analytical expressions achieved through translational expansion of orbitals and operators seem to be quite general for radiative interactions.

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