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Addition theorem and matrix elements of radiative multipole operators

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The addition theorem for radiative multipole operators, i.e., electric-dipole, electric-quadropole or magnetic-dipole, etc., is derived through a translational transformation. The addition theorem of the μth component of the angular momentum operator, $L_\mu(\mathrm{r})$, is also derived as a simple expression that represents a general translation of the angular momentum operator along an arbitrary orientation of a displacement vector and when this displacement is along the Z-axis. The addition theorem of the multipole operators is then used to analytically evaluate the matrix elements of the electric and magnetic multipole operators over the basis functions, the spherical Laguerre Gaussian-type function (LGTF), $L_n^{l+(1/2)}(\alpha r^2) r^l Y_{lm}(\hat{\mathbf{r}}) \mathrm{e}^{-\alpha r^2}$. The explicit and simple formulas obtained for the matrix elements of these operators are in terms of vector-coupling coefficients and LGTFs of the internuclear coordinates. The matrix element of the magnetic multipole operator is shown to be a linear combination of the matrix element of the electric multipole operator.

KEY WORDS: Addition Theorem, radiative multipole operator, Theoretical chemistry

1. Introduction

To study the lifetime and decay mechanism of excited molecules via radiative transitions [1], one must calculate the radiative transition probability per unit time from an initially excited state Ψ_i to final states Ψ_f. The total transition probability is in terms of transition matrix elements of radiative operators, i.e., electric-dipole, electric-quadrupole or magnetic-dipole etc., over

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the electronic wave functions of the initial and final states [2,3]. These electronic wave functions are expanded as linear combinations of atomic orbitals and are therefore, multicentered. The atomic orbitals refer to various nuclear centers and the radiative operators are centered at the center of mass of the molecule [2]. Consequently, the transition matrix elements of the radiative operators for a molecule are multicentered.

In this work we will develop a technique to analytically evaluate these multicenter transition matrix elements of the radiative operators for a homonuclear diatomic molecule (the results derived here are also applicable to polyatomic molecules), by expanding the radiative operators from the center of mass to nuclear centers. The translational expansion is essentially an addition theorem for these operators.

Although the addition theorems as three-dimensional Taylor expansions for various *functions* are well known [4], we have not encountered many examples of translational expansion of *operators* (especially differential operators, such as the angular momentum operator) in the literature. Chiu [2] was able to expand the spherical components of magnetic-dipole operators, $L_m (m = 0, \pm 1)$, from the center of mass of a molecule to atomic centers in a right-handed coordinate system along the z-axis, also taken to be the internuclear axis. In this work, however, we will derive the addition theorem for the magnetic multipole operator which contains the angular momentum operator. To carry out this expansion, the angular momentum operators will be expanded along an arbitrary direction which reduces to Chiu's result along the z-axis.

In section 2, we will review multipole radiation [5,8] and present the general form for electric and magnetic multipole operators, as well as the addition theorem for these operators.

In section 3, we will apply the addition theorem to analytically evaluate the radiative transition matrix elements of these operators over spherical Laguerre Gaussian Type Function (LGTF) [4,6,7],$L_n^{l+(1/2)}(\alpha r^2) r^l Y_{lm}(\hat{\mathbf{r}}) \mathrm{e}^{-\alpha r^2}$, where $L_n^{l+(1/2)}(\alpha r^2)$ is a generalized Laguerre polynomial and $Y_{lm}(\hat{\mathrm{r}})$is the well-known spherical harmonic.

2. The addition theorem for multipole operators

The interaction Hamiltonian for the electron j of spin **S**, momentum **P,** and position **r** moving in an electromagnetic field with vector potential **A** is given as follows [3,8,9]:

$$H_q(\mathbf{r}_j) = -\left(\frac{e_j}{2m_j c}\right)\left\{g_l[\mathbf{A}_q(\mathbf{r}_j)\cdot\mathbf{P}_j + \mathbf{P}_j\cdot\mathbf{A}_q(\mathbf{r}_j)] + g_s\hbar\mathbf{S}_j\cdot\nabla\mathbf{x}\mathbf{A}_q(\mathbf{r}_j)\right\}. \quad (2.1)$$

In the above equations, e_j and m_j refer to the charge and the mass of the electron j, respectively. Furthermore, c is the velocity of light in vacuum, g_l

and g_s are the orbital and the spin g-factors, respectively, and q refers to the polarization of light. The first term describes the interaction between the electromagnetic field of light and the orbital motion of electron j, while the second term refers to the interaction between the light and the spin of electron j. We choose the space-fixed Z-axis to be the direction of light propagation so that $\mathbf{A}_q(\mathbf{r}_j) = \hat{\mathbf{e}}_\mathbf{q} e^{ikz_j}$, $k = 2\pi\nu/c$, and $\hat{\mathbf{e}}_\mathbf{q}$ is the unit vector of the polarization and is defined as follows:

$$\hat{\mathbf{e}}_{\pm 1} = \mp\left(\frac{1}{\sqrt{2}}\right)(\hat{\mathbf{x}} \pm i\hat{\mathbf{y}}), \qquad \hat{\mathbf{e}}_0 = \hat{\mathbf{e}}_z. \tag{2.2}$$

Here $\hat{\mathbf{e}}_{+1}$ and $\hat{\mathbf{e}}_{-1}$ represent right and left circular polarization, respectively, and $\hat{\mathbf{e}}_0$ represents the linear polarization along the Z-axis.

Expanding $\mathbf{A}_q(\mathbf{r}_j)$ in terms of vector spherical harmonics, for circularly polarized light propagating along the Z-axis with wavelength long compared with molecular dimension, we obtain the following multipole expansion of the interaction Hamiltonian:

$$H_q(r_j) = -\sum_l \frac{(i)^l (k)^l}{(2l-1)!!}\sqrt{\frac{l+1}{2l}}\left\{(E_{lm} + E'_{lm}) - iq(M_{lm} + M'_{lm})\right\}. \tag{2.3}$$

E_{lm} and E'_{lm}, respectively, are the charge and spin contribution to the electric mutipole radiation with parity of (-)^l. Similarly,M_{lm} and M'_{lm}, respectively, are the orbital and spin contributions to the magnetic radiation having the parity of (-)$^{l+1}$. The explicit form of these multipole operators, in the long-wavelength approximation [5] ($kr \ll 1$) with $\beta = e\hbar/2mc$, is given as follows [5,9]:

$$E_{lm}(\mathbf{r}_j) = -\sqrt{\frac{4\pi}{2l+1}}\frac{\beta_j}{k} g_l\left[\nabla\mathscr{Y}_{lm}(\mathbf{r}_j)\cdot\nabla + \nabla\cdot\nabla\mathscr{Y}_{lm}(\mathbf{r}_j)\right] \cong \sqrt{\frac{4\pi}{2l+1}}\mathrm{e}_j g_l \mathscr{Y}_{lm}(\mathbf{r}_j) \tag{2.4a}$$

$$\begin{aligned} M_{lm}(\mathbf{r}_j) &= \sqrt{\frac{4\pi}{2l+1}}\left(\frac{2\beta_j g_l}{l+1}\right)\nabla\mathscr{Y}_{lm}(\mathbf{r}_j)\cdot\mathbf{L} \\ &= \frac{2\beta_j g_l\,(4\pi l)^{1/2}}{l+1}\sum_\mu C(l-1,1,l;m-\mu,\mu)\mathscr{Y}_{l-1,m-\mu}(\mathbf{r}_j)L_\mu(\mathbf{r}_j) \end{aligned} \tag{2.4b}$$

$$\begin{aligned} E'_{lm}(\mathbf{r}_j,\mathbf{S}_j) &= -\left[\frac{4\pi}{2l+1}\right]^{1/2}\mathbf{L}\mathscr{Y}_{lm}(\mathbf{r}_j)\cdot\mathbf{S}_j \\ &= -\sqrt{\frac{4\pi l}{(l+1)(2l+1)}}k\beta_j g_s\sum_\mu C(l,1,l;m-\mu,\mu)\mathscr{Y}_{l,m-\mu}(\mathbf{r}_j)S_\mu \end{aligned} \tag{2.4c}$$

$$M'_{lm}(\mathbf{r}_j, \mathbf{S}_j) = \sqrt{\frac{4\pi}{2l+1}} \beta_j g_s \nabla \mathscr{Y}_{lm}(\mathbf{r}_j) \cdot \mathbf{S}_j = \sqrt{4\pi l} \beta_j g \times \sum_{\mu} C(l-1, 1, l; m-\mu, \mu) \mathscr{Y}_{l-1,m-\mu}(\mathbf{r}_j) S_\mu. \quad (2.4\text{d})$$

In the above equations, $\mathscr{Y}_{lm}(\mathbf{r}_j) = r_j^l Y_{lm}(\hat{\mathbf{r}}_j)$, is the solid harmonics referred to the space-fixed coordinate system, and L_μ $(\mathbf{r})$ is the μth ($\mu = 0, \pm 1$) spherical component of the angular momentum operator given by:

$$L_{\pm 1} = \mp \frac{1}{\sqrt{2}}(L_x + iL_y), \quad L_0 = L_z. \quad (2.5)$$

In this work, we will focus our attention on the matrix elements of the radiative operators $E_{lm}(\mathbf{r}_j)$ and $M_{lm}(\mathbf{r}_j)$, i.e. $\left\langle \psi(\mathbf{r_A}) \middle| \hat{O}(\mathbf{r}) \middle| \psi(\mathbf{r_B}) \right\rangle$. Here $\psi(\mathbf{r_A})$ and $\psi(\mathbf{r_B})$are LGTF atomic orbitals referring to nuclear centers **A** and **B**, respectively, and$\hat{O}(\mathrm{r})$is the electric or magnetic radiative operator in equations. (2.4a) and (2.4b), referred to the center of mass of the molecule. In order to evaluate the matrix elements, we will expand the radiative operators from the center of mass to the atomic centers using the addition theorems for these operators.

The translation of the radiative multipole operator, $\hat{O}(\mathbf{r})$,by $\boldsymbol{R}$ can be written as [10]

$$\hat{O}\,(\mathbf{r} + \mathbf{R}) = \mathrm{e}^{\mathbf{R}\cdot\nabla} \hat{O}(\mathbf{r}) \mathrm{e}^{-\mathbf{R}\cdot\nabla}, \quad (2.6)$$

which is basically a unitary transformation of the operator $\hat{O}(\mathbf{r})$ by the translation operator $\mathrm{e}^{\mathbf{R}\cdot\nabla}$.

This follows from the fact that the exponential operator, $\mathrm{e}^{\mathbf{R}\cdot\nabla} = \mathrm{e}^{i\mathbf{R}\cdot\frac{\nabla}{i}}$, is unitary since the operator $\mathbf{R}\cdot\frac{\nabla}{i}$ is Hermitian [11]. Equation (2.6) can be expressed in terms of commutator brackets, as follows [12]:

$$\hat{O}\,(\mathbf{r} + \mathbf{R}) = \mathrm{e}^{\mathbf{R}\cdot\nabla} \hat{O}(\mathbf{r}) \mathrm{e}^{-\mathbf{R}\cdot\nabla} = \hat{O}(\mathbf{r}) + \left[\mathbf{R}\cdot\nabla, \hat{O}(\mathbf{r})\right] + \frac{1}{2}\left[\mathbf{R}\cdot\nabla, \left[\mathbf{R}\cdot\nabla, \hat{O}(\mathrm{r})\right]\right] + \cdots \quad (2.7)$$

In the case of the electric multipole operator given in equation (2.4a), the addition theorem can be written as [4] (see Appendix A)

$$\mathscr{Y}_{lm}(\mathbf{r} + \mathbf{R}) = \mathrm{e}^{\mathbf{R}\cdot\nabla} \mathscr{Y}_{lm}(\mathbf{r}) \mathrm{e}^{-\mathbf{R}\cdot\nabla} = 4\pi \sum_{l_1=0}^{l} \sum_{m_1} \left(\frac{(l_1)!(l-l_1)!(2l+1)!}{(l)!(2l_1+1)!(2l-2l_1+1)!} \right) \times Z(l_, l_1, l-l_1; m_, m_1) \mathscr{Y}^*_{l_1 m_1}(\mathbf{R}) \mathscr{Y}_{l_2 - l_1, m_+ m_1}(\mathbf{r}), \quad (2.8)$$

where the Gaunt coefficient, denoted by Z in the above equation, is used in the coupling rule for spherical harmonics and is given in terms of the Clebsch–Gordan coefficients [4,6] by the following expression:

$$Z(l_1l_2l_3; m_1m_2m_3) = \left[\frac{(2l_1+1)(2l_2+1)}{4\pi(2l_3+1)}\right]^{1/2} C(l_1l_2l_3; m_1m_2m_3)C(l_1l_2l_3; 000). \tag{2.9}$$

The addition theorem for the magnetic multipole operator, as given in equation (2.4b), is given by (see Appendix A)

$$M_{lm}(\mathbf{r}+\mathbf{R}) = 4\pi B_l \sum_{\mu}\sum_{l'=0}^{l-1}\sum_{m'} \alpha^{lm}_{l'm'\mu} \mathcal{Y}^*_{l'm'}(\mathbf{R})\mathcal{Y}_{l-l'-1,m-\mu+m'}(\mathbf{r})\{L_\mu(\mathbf{r}) + \left(\frac{4\pi}{3}\right)\sqrt{2} \times \sum_{\nu}(-1)^{\nu+\mu}C(111; \nu-\mu, \mu)\mathcal{Y}_{1\nu}(\mathbf{R})Y_{1,\mu-\nu}(\nabla)\}, \tag{2.10}$$

where $\alpha^{lm}_{l'm'\mu}$is given in equation (A.15).

The quantity inside the curly bracket in equation (2.10), represents the translational expansion of the μth component of the angular momentum operator, $L_\mu(\mathbf{r})$.

3. The Laguerre Gaussian-type function (LGTF) and the matrix elements of the radiative mltipole operators

A. *The Laguerre Gaussian-type Function (LGTF)*

The spherical LGTF, $\psi^a_{n_al_am_a}(\mathbf{r}_\mathrm{A})$, used here as the basis function in the matrix elements of the radiative operators, is defined as follows [4,6,7]:

$$\psi^a_{n_al_am_a}(\mathbf{r}_\mathbf{A}) = C^a_{n_al_a} L^{l_a+(1/2)}_{n_a}(ar_A^2)\mathrm{e}^{-ar_A^2}\mathcal{Y}_{l_am_a}(\mathbf{r}_\mathbf{A}), \tag{3.1}$$

where the constant $C^a_{n_al_a}$ is given by

$$C^a_{n_al_a} = (-1)^{n_a}2^{2n_a+l_a}(n_a!)(a)^{n_a+l_a} \tag{3.2}$$

and the generalized Laguerre polynomial, $L^{l_a+(1/2)}_{n_a}(ar_A^2)$, is defined as

$$L^{l_a+(1/2)}_{n_a}(ar_A^2) = \sum_{t=0}^{n_a}\binom{n_a+l_a+1/2}{n_a-t}\frac{(-ar_A^2)^t}{t!}, \tag{3.3}$$

and

$$\mathcal{Y}_{l_am_a}(\mathbf{r}_\mathbf{A}) = r_A^{l_a}Y_{l_am_a}(\hat{\mathbf{r}}_\mathbf{A}) \tag{3.4}$$

is the solid harmonics. The coordinate of an electron referred to nuclear center $\mathbf{A}$ is $\mathbf{r_A} = \mathbf{r} - \mathbf{A}$.

The spherical LGTF in equation (3.1) can be generated by operating a generalized gradient operator on a Gaussian exponential function as follows [6,13,14]:

$$\mathcal{Y}_{nlm}(\nabla_{\mathrm{A}})\mathrm{e}^{-ar_A^2} = (-1)^l \mathcal{Y}_{nlm}(\nabla_{\mathrm{r_A}})\mathrm{e}^{-ar_A^2} = \psi^a_{nlm}(\mathbf{r_A}), \tag{3.5}$$

where the generalized spherical gradient operator,

$$\mathcal{Y}_{nlm}(\nabla) = \nabla^{2n}\mathcal{Y}_{lm}(\nabla) \tag{3.6}$$

is defined by replacing the components of the variable $\mathbf{r}$, i.e., x, y, and z in the homogeneous solid harmonics, $\mathcal{Y}_{nlm}(\mathbf{r}) = r^{2n}\mathcal{Y}_{lm}(\mathbf{r})$, with the components of the corresponding gradient operator, i.e., $\partial/\partial x$, $\partial/\partial y$, $\partial/\partial z$. The differential operators with respect to the Cartesian coordinates of the nuclear center $\mathbf{A}=(A_x, A_y, A_z)$ and the electronic coordinate $\mathbf{r_A}=(x_A, y_A, z_A)$ are $\nabla_{\mathbf{A}}$ and $\nabla_{\mathbf{r_A}}$, respectively. As irreducible tensor operators on the same kinematic space, the spherical gradient operators, follow the coupling rule for solid harmonics [6,11], viz.,

$$\mathcal{Y}_{n_1l_1m_1}(\nabla)\mathcal{Y}_{n_2l_2m_2}(\nabla) = \sum_l Z(l_1l_2l;\, m_1m_2)\mathcal{Y}_{nl,m_1+m_2}(\nabla), \tag{3.7}$$

where

$$2n + l = 2n_1 + 2n_2 + l_1 + l_2, \tag{3.8}$$

and the Z coefficient, the coupling coefficient of two spherical harmonics, is given in equation (2.9).

Combining equations (3.5) and (3.7), we have

$$\mathcal{Y}_{n_1l_1m_1}(\nabla)\psi^a_{n_2l_2m_2}(\mathbf{r}) = (-1)^{l_2}\sum_l Z(l_1l_2l;\, m_1m_2)\psi^a_{nl,m_1+m_2}(\mathbf{r}), \tag{3.9}$$

where n is given by equation (3.8).

In order to evaluate the matrix elements, we will make use of the well-known Gaussian product theorem [15] which states that the product of two s-type Gaussians having different centers $\mathbf{A}$ and $\mathbf{B}$ is itself a Gaussian (apart from a constant factor) with a center $\mathbf{P}$, located somewhere on the line connecting center $\mathbf{A}$ to center $\mathbf{B}$, i.e., $\mathbf{R_{AB}}$. Specifically,

$$\mathrm{e}^{-a\,r_{\mathrm{A}}^2}\mathrm{e}^{-b\,r_{\mathrm{B}}^2} = \mathrm{e}^{-\sigma_{ab}\,R_{\mathrm{AB}}^2}\mathrm{e}^{-p\,r_P^2}, \tag{3.10}$$

where

$$\sigma_{ab} = \frac{ab}{a+b}, \quad p = (a+b), \quad \mathbf{R_{AB}} = \mathbf{B} - \mathbf{A} \text{ and } \mathbf{r_P} = \mathbf{r} - \mathbf{P}. \tag{3.11}$$

Center **P** is the weighted mean point of **A** and **B** and is given as [6]

$$\mathbf{P} = \alpha\mathbf{A} + \beta\mathbf{B}, \tag{3.12}$$

where $\alpha = a/(a+b)$ and $\beta = b/(a+b)$.

The Gaussian product theorem in equation (3.10) can be verified by making use of Equations (3.11) and (3.12), and replacing $\mathbf{r}_\mathrm{A}$ with $\mathbf{r_A} = \mathbf{r_P} + \mathbf{R_{AP}}$ and $\mathbf{r_B}$ with $\mathbf{r_B} = \mathbf{r_P} + \mathbf{R_{BP}}$, where $\mathbf{r_P} = \mathbf{r} - \mathbf{P} = \alpha\mathbf{r_A} + \beta\mathbf{r_B}$, $\mathbf{R_{AP}} = \mathbf{P} - \mathbf{A}$, and $\mathbf{R_{BP}} = \mathbf{P} - \mathbf{B}$. $\mathbf{R_{AP}}$ and $\mathbf{R_{BP}}$ are position vectors pointing from centers **A** and **B** to center **P**, respectively.

From equations (3.5) and (3.10), the product of two electronic LGTFs, centered at **A** and **B** may be factored into a nuclear part and an electronic part as follows: [6,13,14]

$$\begin{aligned}
\psi^{a*}_{n_a l_a m_a}(\mathbf{r_A})\psi^{b}_{n_b l_b m_b}(\mathbf{r_B})
&= [\mathscr{Y}_{n_a l_a m_a^*}(\nabla_\mathbf{A})\mathscr{Y}_{n_b l_b m_b}(\nabla_\mathbf{B})\mathrm{e}^{-\sigma_{ab} R^2_{\mathrm{AB}}}]\mathrm{e}^{-p\,\mathbf{r}_P^2}. \\
&= \left[(-1)^{l_b+m_a}\sum_{l_{ab}} Z(l_a l_b l_{ab};\, -m_a m_b)\mathscr{Y}_{n_a l_a,-m_a+m_b}(\nabla_\mathbf{A})\mathrm{e}^{-\sigma_{ab} R^2_{\mathbf{AB}}}\right]\mathrm{e}^{-p\,\mathbf{r}_P^2} \\
&= \left[(-1)^{l_b+m_a}\sum_{l_{ab}} Z(l_a l_b l_{ab};\, -m_a m_b)\psi^{\sigma_{ab}}_{n_{ab} l_{ab},m_{ab}}(\mathbf{R_{AB}})\right]\mathrm{e}^{-p\,r_P^2},
\end{aligned} \tag{3.13}$$

where $m_{ab} = m_b - m_a$ and $2n_{ab} = 2n_a + 2n_b + l_a + l_b - l_{ab}$.

In deriving equation (3.13) we have used the transformation $\mathscr{Y}_{n_b l_b m_b}(\nabla_\mathbf{B}) = (-1)^{l_B}\mathscr{Y}_{n_b l_b m_b}(\nabla_\mathbf{A})$, and subsequently we have coupled the two nuclear gradient operators of the same argument using equation (3.17). The final result containing $\psi^{\sigma_{ab}}_{n_{ab} l_{ab},m_{ab}}(\mathbf{R_{AB}})$ is obtained by using equation (3.5)

B. *Matrix element of the electric multipole operator*

Using equation (2.4a), we can write the matrix element of the electric multipole operator as

$$\left\langle\psi^{a}_{n_a l_a m_a}(\mathbf{r_A})\left|E_{lm}(\mathbf{r_C})\right|\psi^{b}_{n_b l_b m_b}(\mathbf{r_B})\right\rangle = A_l\int\psi^{a*}_{n_a l_a m_a}(\mathbf{r_A})\mathscr{Y}_{lm}(\mathbf{r_C})\psi^{b}_{n_b l_b m_b}(\mathbf{r_B})\mathrm{d}\tau, \tag{3.14}$$

where

$$A_l = \sqrt{\frac{4\pi}{2l+1}}eg_l \quad . \tag{3.15}$$

The coordinate of an electron referred to nuclear center **B** is $\mathbf{r_B} = \mathbf{r} - \mathbf{B}$ and $\mathbf{r_C} = \mathbf{r} - \mathbf{C}$ is the coordinate of the same electron with respect to the center of mass **C** (which can be taken as the center of nuclei **A** and **B** by a very good approximation). The coordinates at centers **A**, **B** and **C** are mutually parallel and also parallel to a frame of reference which may be arbitrary or space-fixed. These coordinate systems are all right-handed. The atomic center **A** is displaced from center **B** through a vector $\mathbf{R_{AB}}$ and the center of mass **C** is separated from the weighted center **P** through vector $\mathbf{R_{CP}}$, as follows:

$$\mathbf{R_{AB}} = \mathbf{B} - \mathbf{A} = \mathbf{r_A} - \mathbf{r_B} \text{ and } \mathbf{R_{CP}} = \mathbf{P} - \mathbf{C} = \mathbf{r_C} - \mathbf{r_P}. \tag{3.16}$$

Here $\mathbf{R_{AB}}$ is the vector from **A** to **B**, and $\mathbf{R_{CP}}$ is the vector pointing from center **C** to center **P**.

The integral on the right-hand side of equation (3.14) is a three-center integral. To evaluate this integral, first we expand the solid harmonics, $\mathcal{Y}_{lm}(\mathbf{r_C})$, referring to the center of mass of the molecule, to the weighted center **P** by using the vector identity in equations (3.16) and (A.4) (see Appendix A),

$$\begin{aligned}\mathcal{Y}_{lm}(\mathbf{r_C}) = \mathcal{Y}_{lm}(\mathbf{R_{CP}} + \mathbf{r_P}) &= \mathrm{e}^{\mathbf{R}_{\mathrm{CP}}\cdot\nabla_{\mathrm{r_P}}}\mathcal{Y}_{lm}(\mathbf{r_P}) \\ &= 4\pi \sum_{l_1=0}^{l}\sum_{m_1}\left[\frac{(l_1)!(l-l_1)!(2l+1)!}{(l)!(2l_1+1)!(2l-2l_1+1)!}\right] \\ &\quad\times Z(l, l_1, l-l_1; m, m_1)\mathcal{Y}^*_{l_1m_1}(\mathbf{R_{CP}})\mathcal{Y}_{l-l_1,m+m_1}(\mathbf{r_P}).\end{aligned} \tag{3.17}$$

The three-center integral on the right-hand side of equation (3.15) becomes

$$\begin{aligned}&\int \psi^{a*}_{n_al_am_a}(\mathbf{r}_A)\mathcal{Y}_{lm}(\mathbf{r_C})\psi^{b}_{n_bl_bm_b}(\mathbf{r_B})\mathrm{d}\tau \\ &= 4\pi \sum_{l_1=0}^{l}\sum_{m_1}\left[\frac{(l_1)!(l-l_1)!(2l+1)!}{(l)!(2l_1+1)!(2l-2l_1+1)!}\right] Z(l, l_1, l-l_1; m, m_1) \\ &\quad\times\mathcal{Y}^*_{l_1m_1}(\mathbf{R_{CP}})\int \psi^{a*}_{n_al_am_a}(\mathbf{r_A})\mathcal{Y}_{l-l_1,m+m_1}(\mathbf{r_P})\psi^{b}_{n_bl_bm_b}(\mathbf{r_B})\mathrm{d}\tau.\end{aligned} \tag{3.18}$$

Applying equation (3.13) for the product of LGTFs and the transformation $\mathcal{Y}_{n_bl_bm_b}(\nabla_\mathrm{B}) = (-1)^{l_B}\mathcal{Y}_{n_bl_bm_b}(\nabla_\mathrm{A})$[6], and subsequently making use of the coupling rule in equation (3.7) for $\mathcal{Y}_{n_al_am_a}(\nabla_\mathrm{A})$ and $Y_{n_bl_bm_b}(\nabla_\mathrm{A})$, we find that the integral on the right-hand side of equation (3.18) becomes

$$\begin{aligned}&\int \psi^{a*}_{n_al_am_a}(\mathbf{r}_\mathrm{A})\mathcal{Y}_{l-l_1,m+m_1}(\mathbf{r_P})\psi^{b}_{n_bl_bm_b}(\mathbf{r_B})\mathrm{d}\tau \\ &= (-1)^{l_b+m_a}\frac{\pi}{2(a+b)^{3/2}}\sum_{l_{ab}} Z(l_al_bl_{ab}; -m_am_b)\psi^{\sigma_{ab}}_{n_{ab}l_{ab},m_{ab}}(\mathrm{R_{AB}}) \times \delta_{l_1,l}\delta_{m_1,-m}.\end{aligned} \tag{3.19}$$

Making use of equations (3.18) and (3.19), we express the matrix element of the electric multipole operator in equation (3.14) as

$$\left\langle \psi^{a}_{n_a l_a m_a}(\mathbf{r_A}) \left| E_{lm}(\mathbf{r_C}) \right| \psi^{b}_{n_b l_b m_b}(\mathbf{r_B}) \right\rangle = A_l \; I^{l_a l l_b}_{m_a m m_b}(\mathbf{R_{AB}}, \mathbf{R_{CP}}), \tag{3.20}$$

where A_l is given in equation (3.15) and

$$\begin{aligned} I^{l_a l l_b}_{m_a m m_b}(\mathbf{R_{AB}}, \mathbf{R_{CP}}) &= \int \psi^{a*}_{n_a l_a m_a}(\mathbf{r_A}) \mathcal{Y}_{lm}(\mathbf{r_C}) \psi^{b}_{n_b l_b m_b}(\mathbf{r_B}) \mathrm{d}\tau \\ &= (-1)^{l_b+m_a+m} \left(\frac{\pi}{a+b}\right)^{3/2} \sum_{l_{ab}} Z(l_a l_b l_{ab}; -m_a m_b) \\ &\quad \times \mathcal{Y}_{lm}(\mathbf{R_{CP}}) \psi^{\sigma_{ab}}_{n_{ab} l_{ab} m_{ab}}(\mathbf{R_{AB}}) \end{aligned} \tag{3.21}$$

is a three-center matrix element of the electric multipole operator, $\mathcal{Y}_{lm}(\mathbf{r_C})$.

In the above equation,

$$m_{ab} = m_b - m_a \text{ and } 2n_{ab} = 2n_a + 2n_b + l_a + l_b - l_{ab}.$$

C. *Matrix element of the magnetic multipole operator*

The matrix element of the magnetic multipole operator is written as

$$\left\langle \psi^{a}_{n_a l_a m_a}(\mathbf{r_A}) \left| M_{lm}(\mathbf{r_C}) \right| \psi^{b}_{n_b l_b m_b}(\mathbf{r_B}) \right\rangle = \int \psi^{a*}_{n_a l_a m_a}(\mathbf{r_A}) M_{lm}(\mathbf{r_C}) \psi^{b}_{n_b l_b m_b}(\mathbf{r_B}) \, \mathrm{d}\tau, \tag{3.22}$$

where the magnetic operator M_{lm} is defined in equation (2.4b) and is referred to the center of mass **C**. The coordinate of electron referred to center **C** is $\mathbf{r_C} = \mathbf{r} - \mathbf{C}$. The LGTFs $\psi^{a}_{n_a l_a m_a}(\mathbf{r_A})$ and $\psi^{b}_{n_b l_b m_b}(\mathbf{r_B})$ are defined by equation (3.1). Using equation (2.10) for the addition theorem of the magnetic operator and the vector identity $\mathbf{r_C} = \mathrm{R}_{\mathbf{CB}} + \mathbf{r_B}$, we expand the magnetic multipole operator M_{lm} in equation (3.22) at center **B** as

$$\begin{aligned} &\left\langle \psi^{a}_{n_a l_a m_a}(\mathbf{r_A}) \left| M_{lm}(\mathbf{r_C}) \right| \psi^{b}_{n_b l_b m_b}(\mathbf{r_B}) \right\rangle \\ &= 4\pi \, B_l \sum_{\mu} \sum_{l'=0}^{l-1} \sum_{m'} \alpha^{lm}_{l'm'\mu} \, \mathcal{Y}^{*}_{l'm'}(\mathrm{R}_{\mathbf{CB}}) \\ &\quad \times \left\{ \int \psi^{a*}_{n_a l_a m_a}(\mathbf{r}_{\mathrm{A}}) \mathcal{Y}_{l-l'-1, m-\mu+m'}(\mathbf{r_B}) L_{\mu}(\mathbf{r_B}) \psi^{b}_{n_b l_b m_b}(\mathbf{r_B}) \, \mathrm{d}\tau \right. \\ &\quad + \sqrt{\frac{32}{9}} \pi \sum_{\nu} (-1)^{\nu+\mu} C(111; \; \nu-\mu, \mu) \mathcal{Y}_{1\nu}(\mathrm{R}_{\mathbf{CB}}) \\ &\quad \left. \times \int \psi^{a*}_{n_a l_a m_a}(\mathbf{r_A}) \mathcal{Y}_{l-l'-1, m-\mu+m'}(\mathbf{r_B}) \mathcal{Y}_{1,\,\mu-\nu}(\nabla_{\mathbf{r_B}}) \psi^{b}_{n_b l_b m_b}(\mathbf{r_B}) \; \mathrm{d}\tau \right\}. \end{aligned} \tag{3.23}$$

Using equation (3.1) and the well-known result of operating the angular momentum operator $L_\mu(\mathbf{r})$ on the spherical harmonic $Y_{lm}(\hat{\mathbf{r}})$ [5,11],

$$L_\mu(\mathbf{r_B})\,\psi^b_{n_b l_b m_b}(\mathbf{r_B}) = (-1)^\mu\,[l_b(l_b+1)]^{1/2} \times C(l_b 1 l_b;\, m_b+\mu, -\mu)\,\psi^b_{n_b l_b m_b+\mu}(\mathbf{r_B}), \tag{3.24}$$

we see that the first integral containing the angular momentum operator $L_\mu(\mathbf{r_B})$ in equation (3.23) becomes

$$\int \psi^{a*}_{n_a l_a m_a}(\mathbf{r}_\mathrm{A})\mathscr{Y}_{l-l'-1,m-\mu+m'}(\mathbf{r_B})\psi^b_{n_b l_b m_b}(\mathbf{r_B})\mathrm{d}\tau = (-1)^\mu[l_b(l_b+1)]^{1/2}C(l_b 1 l_b;\, m_b+\mu, -\mu),\, \times I_{m_a,m-\mu+m',m_b+\mu}(\mathbf{R_{AB}}, \mathbf{R_{BP}}). \tag{3.25}$$

In the above equation,

$$\begin{aligned} I^{l,l-l'-1,l_b}_{m_a,m-\mu+m',m_b+\mu}(\mathbf{R_{AB}}, \mathbf{R_{BP}}) &= \int \psi^{a*}_{n_a l_a m_a}(\mathbf{r_A})\mathscr{Y}_{l-l'-1,m-\mu+m'}(\mathbf{r_B})\,\psi^b_{n_b l_b m_b}(\mathbf{r_B})\,\mathrm{d}\tau \\ &= (-1)^{l_b+m_a+m-\mu+m'}\left(\frac{\pi}{a+b}\right)^{3/2} \\ &\quad \times \sum_{l_{ab}} Z(l_a l_b l_{ab};\, -m_a m_b+\mu) \\ &\quad \times \mathscr{Y}_{l-l'-1,\,m-\mu+m'}(\mathbf{R_{BP}})\,\psi^{\sigma_{ab}}_{n_{ab} l_{ab} m_{ab}}(\mathbf{R_{AB}}), \end{aligned} \tag{3.26}$$

where $m_{ab} = m_b+\mu-m_a$ and $2n_{ab} = 2n_a+2n_b+l_a+l_b-l_{ab}$, is a two-center electric multipole integral which can be easily derived from the three-center electric multipole integral given in equation (3.21) by replacing center **C** with **B**, l with $l - l' - 1$, and m with $m - \mu + m'$.

Making use of equation (3.9) for the gradient operator $\mathscr{Y}_{1,\,\mu-\nu}(\nabla_{\mathbf{r_B}})$ operating on the LGTF $\psi^b_{n_b l_b m_b}(\mathbf{r_B})$,

$$\mathscr{Y}_{1,\,\mu-\nu}(\nabla_{\mathbf{r_B}})\,\psi^b_{n_b l_b m_b}(\mathbf{r_B}) = (-1)^{l_b}\sum_j Z(1 l_b j;\, \mu-\nu, m_b)\psi^b_{n\,j,m_b+\mu-\nu}(\mathbf{r_B}) \tag{3.27}$$

where $2n+j = 2n_b+l_b+1$, we see that the second integral containing the gradient operator $\mathscr{Y}_{1,\,\mu-\nu}(\nabla_{\mathbf{r_B}})$ in equation (3.23) becomes

$$\int \psi^{a*}_{n_a l_a m_a}(\mathbf{r_A})\mathscr{Y}_{l-l'-1,m-\mu+m'}(\mathbf{r_B})\mathscr{Y}_{1,\,\mu-\nu}(\nabla_{\mathbf{r_B}})\,\psi^b_{n_b l_b m_b}(\mathbf{r_B})\,\mathrm{d}\tau = (-1)^{l_b}\sum_j Z(1 l_b j;\, \mu-\nu, m_b)\ \times I^{l_a,l-l'-1,j}_{m_a,m-\mu+m',m_b+\mu-\nu}(\mathbf{R_{AB}}, \mathbf{R_{BP}}). \tag{3.28}$$

In this equation, $I^{l_a,l-l'-1,j}_{m_a,m-\mu+m',m_b+\mu-\nu}(\mathbf{R_{AB}},\mathbf{R_{BP}})$ is a two-center electric multipole integral and is given by

$$\begin{aligned}
&I^{l_a,l-l'-1,j}_{m_a,m-\mu+m',m_b+\mu-\nu}(\mathbf{R_{AB}},\mathbf{R_{BP}})\\
&\quad=\int \psi^{a*}_{n_a l_a m_a}(\mathbf{r_A})\,\mathcal{Y}_{l-l'-1,m-\mu+m'}(\mathbf{r_B})\,\psi^{b}_{n\,j,m_b+\mu-\nu}(\mathbf{r_B})\,\mathrm{d}\tau\\
&\quad=(-1)^{j+m_a+m-\mu+m'}\left(\frac{\pi}{a+b}\right)^{3/2}\\
&\quad\times\sum_{l_{ab}} Z(l_a j l_{ab};-m_a m_b+\mu-\nu)\,\mathcal{Y}_{l-l'-1,\,m-\mu+m'}(\mathbf{R_{BP}})\,\psi^{\sigma_{ab}}_{n_{ab}l_{ab}m_{ab}}(\mathbf{R_{AB}}),
\end{aligned}\tag{3.29}$$

where $m_{ab}=m_b+\mu-\nu-m_a$ and $2n_{ab}=2n_a+2n+l_a+j-l_{ab}$.

Finally, the matrix element of the magnetic multipole operator in equation (3.23), after using equations (3.25) and (3.28), becomes

$$\begin{aligned}
&\left\langle\psi^{a}_{n_a l_a m_a}(\mathbf{r_A})\,|M_{lm}(\mathbf{r_C})|\,\psi^{b}_{n_b l_b m_b}(\mathbf{r_B})\right\rangle\\
&\quad=4\pi\,B_l\sum_{\mu}\sum_{l'=0}^{l-1}\sum_{m'}\alpha^{lm}_{l'm'\mu}\,\mathcal{Y}^{*}_{l'm'}(\mathbf{R_{CB}})\\
&\quad\times\{\,(-1)^{\mu}\,[l_b(l_b+1)]^{1/2}\,C(l_b 1 l_b;m_b+\mu,-\mu)\\
&\quad\times I^{l,l-l'-1,l_b}_{m_a,m-\mu+m',m_b+\mu}(\mathbf{R_{AB}},\mathbf{R_{BP}})\\
&\quad+\sqrt{\frac{32}{9}}\pi\sum_{\nu}(-1)^{\nu+\mu}C(111;\nu-\mu,\mu)\mathcal{Y}_{1\nu}(\mathbf{R_{CB}})(-1)^{l_b}\sum_{j}Z(1l_b j;\mu-\nu,m_b)\\
&\quad\times I^{l_a,l-l'-1,j}_{m_a,m-\mu+m',m_b+\mu-\nu}(\mathbf{R_{AB}},\mathbf{R_{BP}})\,\}\,,
\end{aligned}\tag{3.30}$$

whereB_l and $\alpha^{lm}_{l'm'\mu}$are given by equations (A.5) and (A.15), respectively.

The matrix element of the magnetic multipole operator becomes a linear combination of two-center electric multipole matrix elements, $I(\mathbf{R_{AB}},\mathbf{R_{BP}})$, as shown in equation (3.30).

4. Discussion

The three-dimensional translation operator, $\mathbf{T_R}=\mathrm{e}^{\mathbf{R}\cdot\nabla}=\mathrm{e}^{\frac{i}{\hbar}\mathbf{R}\cdot\mathbf{P}}$, where $\mathbf{P}$ is the linear momentum operator, is a linear operator whose effect is to shift the coordinates by a constant distance $\mathbf{R}$. The effect of this operator on a function $f(\mathbf{r})$, is to generate $f(\mathbf{r}+\mathbf{R})=\mathrm{e}^{\mathbf{R}\cdot\nabla}f(\mathbf{r})$ by doing a three-dimensional Taylor expansion of f around $\mathbf{r}$ [4]. However, in the case of an operator, or a function of an operator $\hat{\mathbf{O}}(\mathbf{r})$, the effect of the translation operator is to transform the operator into $\hat{\mathbf{O}}(\mathbf{r}+\mathbf{R})=\mathrm{e}^{\mathbf{R}\cdot\nabla}\hat{\mathbf{O}}(\mathbf{r})\,\mathrm{e}^{-\mathbf{R}\cdot\nabla}$, which is equivalent to a unitary transformation of the operator $\hat{\mathbf{O}}(\mathbf{r})$. In this work, the operator $\hat{\mathbf{O}}(\mathbf{r})$ represents the electric multipole operator, $\mathscr{Y}_{lm}(\mathbf{r})$, and the magnetic multipole operator which is the electric multipole operator coupled with the angular momentum operator, $\mathscr{Y}_{l,m}(\mathbf{r})L_{\mu}(\mathbf{r})$.

It is shown in the Appendix that the unitary transformations of these operators lead to translational expansions, also known as addition theorems for these operators are given by equations (A.4) and (A.15). These results are obtained by Taylor expansion of the exponential operators in $e^{\mathbf{R}\cdot\nabla}\hat{\mathbf{O}}(\mathbf{r})\,e^{-\mathbf{R}\cdot\nabla}$, leading to the commutation relationships in equation (A.1) [10,12]. These addition theorems are then used to analytically evaluate the matrix elements of the electric and magnetic operators, centered at the center of mass **C**, over the LGTFs, $\psi^{a*}_{n_a l_a m_a}(\mathbf{r_A})$ and $\psi^{b}_{n_b l_b m_b}(\mathbf{r_B})$, respectively.

To evaluate the matrix element of the electric multipole operator, which is a three-center integral, the operator, $\mathscr{Y}_{lm}(\mathbf{r_C})$, was expanded using equation (3.17), from the center of mass to a weighted mean point **P**, as defined by equation (3.12). This gives rise to the integral shown in equation (3.18). Making use of equation (3.13) reduces the expression for the matrix element to a linear combination of LGTF of internuclear coordinate $\mathbf{R_{AB}}$, $\psi^{\sigma_{ab}}_{n_{ab}l_{ab},m_{ab}}(\mathbf{R_{AB}})$, and a one-center electronic integral which is easily integrated. This one-center integral containing the electronic Gaussian exponential factor with respect to center **P**, i.e., $e^{-p\,r_P^2}$, and the electric multipole operator with respect to $\mathbf{r}_p$, $\mathscr{Y}_{lm}(\mathbf{r_P})$,when integrated, will truncate the summations which were generated in the first step by the expansion of the solid harmonic from center of mass **C** into center **P**. The final result for the electric multipole matrix element is quite simple and it only contains one finite summation over the LGTF of internuclear coordinate $\mathbf{R_{AB}}$, $\Psi^{\sigma_{ab}}_{n_{ab}l_{ab}m_{ab}}(\mathbf{R_{AB}})$, and the solid harmonic of internuclear distance $\mathbf{R_{CP}}$, $\mathscr{Y}_{lm}(\mathrm{R}_{\mathbf{CP}})$.

It should also be mentioned that expanding the operators from the center of mass **C** into either nuclear centers **A** or **B**, or vice versa, did not generate simple expressions and also the intermediate integrals were tedious. One obvious reason for this difficulty is due to the fact that when this expansion (from **C** to either **A** or **B**) is carried out, the solid harmonic of the electronic coordinate of the new center, $\mathscr{Y}_{lm}(\mathbf{r_A})$ or $\mathscr{Y}_{lm}(\mathbf{r_B})$, generated through the addition theorem in Eq. (A4), will be coupled with the LGTF of center **A** or **B** to generate a function that is *not* a LGTF.

In the case of the matrix element of the magnetic multipole operator, the magnetic operator was expanded from the center of mass to atomic center **B** by using the addition theorem of this operator as given by equation (A.15) in Appendix A. The expansion generated a linear combination of intermediate integrals which were finally reduced to the two-center electric multipole matrix elements. These two-center integrals were easily evaluated using the three-center matrix elements of electric operators evaluated in section 3B. The final results are in terms of finite summation over vector-coupling coefficients and functions of internuclear coordinates.

Appendix A: Addition theorems for electric and magnetic multipole operators

For any two non-commuting operators **X** and **Y**, we have [12]

$$\mathrm{e}^{\mathbf{X}}\,\mathbf{Y}\,\mathrm{e}^{-\mathbf{X}} = \mathbf{Y} + [\mathbf{X},\,\mathbf{Y}] + \frac{1}{2}\,[\mathbf{X},\,[\mathbf{X},\,\mathbf{Y}]] + \cdots \tag{A.1}$$

where $\mathrm{e}^{\mathbf{X}} = 1+\mathbf{X}+\frac{\mathbf{X}^2}{2!}+\cdots$, is the exponential operator and $[\mathbf{X},\,\mathbf{Y}] = \mathbf{XY}-\mathbf{YX}$ is the commutator of operators **X** and **Y**. Equations (A.1) can be verified by the Taylor expansion of $\mathrm{e}^{\mathbf{X}}$ and $\mathrm{e}^{-\mathbf{X}}$. Writing equation (A.1) in a compact form, we have [16]

$$\mathrm{e}^{\mathbf{X}}\mathbf{Y}\mathrm{e}^{-\mathbf{X}} = \sum_n \frac{\mathscr{X}^n}{n!}\mathbf{Y} = \mathrm{e}^{\mathscr{X}}\mathbf{Y}, \tag{A.2}$$

in which $\mathscr{X}^n\mathbf{Y}$ denotes the commutator nested to the nth degree,

$$\mathscr{X}^n\mathbf{Y} = [\mathbf{X},[\mathbf{X},[\mathbf{X},\ldots[\mathbf{X},\mathbf{Y}]\ldots]]].$$

When **X** is a differential operator, as it is in our case, (i.e., $\mathbf{X} = \mathbf{R}\cdot\nabla$), equation (A.2) becomes

$$\mathrm{e}^{\mathbf{X}}\mathbf{Y}\mathrm{e}^{-\mathbf{X}} = \sum_n \frac{\mathbf{X}^n}{n!}\mathbf{Y} = \mathrm{e}^{\mathbf{X}}\mathbf{Y}, \tag{A.3}$$

a result that is valid only because operator **X** possesses the derivation property [17]. It may be easily verified by induction for $n = 0, 1, 2, \ldots$ in equation (A.2). For example,

$$\mathscr{X}^0\mathbf{Y} = \mathbf{Y}, \quad \mathscr{X}\mathbf{Y} = [\mathbf{X},\mathbf{Y}] = \mathbf{XY}, \quad \mathscr{X}^2\mathbf{Y} = [\mathbf{X},[\mathbf{X},\mathbf{Y}]] = \mathbf{X}^2\mathbf{Y}, \text{ etc.}$$

Making use of equation (A.3) for the electric multipole operator, which is effectively a solid harmonics operator, we have the well-known result for the addition theorem of solid harmonics [4,6],

$$\begin{aligned}\mathscr{Y}_{lm}(\mathrm{r}+\mathbf{R}) &= \mathrm{e}^{\mathbf{R}\cdot\nabla}\mathscr{Y}_{lm}(\mathbf{r})\\ &= 4\pi\sum_{l_1=0}^{l}\sum_{m_1}\left(\frac{(l_1)!(l-l_1)!(2l+1)!}{(l_)!(2l_1+1)!(2l\_2l_1+1)!}\right)\\ &\quad\times Z(l,l_1,l\_l_1;m,m_1)\mathscr{Y}^*_{l_1m_1}(\mathbf{R})\mathscr{Y}_{l-l_1,m+m_1}(\mathbf{r}),\end{aligned} \tag{A.4}$$

where the Z coefficient is given by equation (2.9).

To derive the addition theorem for magnetic multipole operator, $M_{lm}(\mathbf{r})$, in equation (2.4b), we note that the translation operator $e^{\mathbf{R}\cdot\nabla}$ transforms the operator $M_{lm}(\mathbf{r})$into $e^{\mathbf{R}\cdot\nabla}M_{lm}(\mathbf{r})e^{-\mathbf{R}\cdot\nabla}$ [5,10–12],

$$\begin{aligned} M_{lm}(\mathbf{r}+\mathbf{R}) &= e^{\mathbf{R}\cdot\nabla}M_{lm}(\mathbf{r})e^{-\mathbf{R}\cdot\nabla} \\ &= B_l\sum_{\mu} C(l-1,1,l;m-\mu,\mu)e^{\mathbf{R}\cdot\nabla}\mathscr{Y}_{l-1,m-\mu}(\mathbf{r})L_\mu(\mathbf{r})e^{-\mathbf{R}\cdot\nabla}, \end{aligned} \tag{A.5}$$

where $B_l = \dfrac{2\beta_j g_l\,(4\pi l)^{1/2}}{l+1}$.

We also note that

$$\begin{aligned} e^{\mathbf{R}\cdot\nabla}\mathscr{Y}_{l-1,m-\mu}(\mathbf{r})L_\mu(\mathbf{r})e^{-\mathbf{R}\cdot\nabla} &= e^{\mathbf{R}\cdot\nabla}\mathscr{Y}_{l-1,m-\mu}(\mathbf{r})e^{-\mathbf{R}\cdot\nabla}e^{\mathbf{R}\cdot\nabla}L_\mu(\mathbf{r})e^{-\mathbf{R}\cdot\nabla} \\ &= \mathscr{Y}_{l-1,m-\mu}(\mathbf{r}+\mathbf{R})L_\mu(\mathbf{r}+\mathbf{R}), \end{aligned} \tag{A.6}$$

so that

$$M_{lm}(\mathbf{r}+\mathbf{R}) = B_l\sum_{\mu} C(l-1,1,l;m-\mu,\mu)\mathscr{Y}_{l-1,m-\mu}(\mathbf{r}+\mathbf{R})L_\mu(\mathbf{r}+\mathbf{R}). \tag{A.7}$$

To complete the addition theorem for this operator, we now need to derive an expression for $L_\mu(\mathbf{r}+\mathbf{R})$, the μth spherical component of the angular momentum operator given in equation (2.5). Replacing $\mathbf{X}$ with $\mathrm{R}\cdot\nabla$ and $\mathbf{Y}$ with $L_\mu(\mathbf{r})$ in equation (A.1), we have

$$\begin{aligned} L_\mu(\mathbf{r}+\mathbf{R}) &= e^{\mathbf{R}\cdot\nabla}L_\mu(\mathbf{r})e^{-\mathbf{R}\cdot\nabla} \\ &= L_\mu(\mathbf{r}) + [\mathbf{R}\cdot\nabla, L_\mu] + \frac{1}{2}[\mathbf{R}\cdot\nabla,[\mathbf{R}\cdot\nabla, L_\mu]] + \cdots \end{aligned} \tag{A.8}$$

Using the expansion of $\mathbf{R}\cdot\nabla$ in terms of its spherical components [11],

$$\mathbf{R}\cdot\nabla = \sum_\nu R_\nu\nabla_{-\nu} = \left(\frac{4\pi}{3}\right)\sum_\nu(-1)^\nu\mathscr{Y}_{1\nu}(\mathbf{R})\mathscr{Y}_{1,-\nu}(\nabla), \tag{A.9}$$

where we have used $\nabla_{-\nu} = \sqrt{\frac{4\pi}{3}}\mathscr{Y}_{1,-\nu}(\nabla)$ and R_ν is defined similarly, the commutator $[\mathbf{R}\cdot\nabla, L_\mu(\mathbf{r})]$ can be expressed as

$$\left[\mathbf{R}\cdot\nabla, L_\mu(\mathbf{r})\right] = \left(\frac{4\pi}{3}\right)\sum_\nu(-1)^\nu\mathscr{Y}_{1\nu}(\mathbf{R})\left[\mathscr{Y}_{1,-\nu}(\nabla), L_\mu(\mathbf{r})\right]. \tag{A.10}$$

$\mathscr{Y}_{1,-\nu}(\nabla)$ is the spherical gradient operator [6,13,14], which is obtained by replacing the Cartesian component of the variable $\mathbf{r}$ in the solid harmonic $\mathscr{Y}_{1,-\nu}(\mathbf{r})$ with the corresponding components of the gradient operator ∇, for example,

$$\mathscr{Y}_{1,\pm1}(\nabla) = \mp\sqrt{\frac{3}{8\pi}}\left(\frac{\partial}{\partial x}\pm i\frac{\partial}{\partial y}\right)\ \text{and}\ \mathscr{Y}_{10}(\nabla) = \sqrt{\frac{3}{4\pi}}\frac{\partial}{\partial z}.$$

Making use of Racah's definition of irreducible tensor operators [5,11],

$$\left[\mathscr{Y}_{1,-\nu}(\nabla), L_\mu(\mathbf{r})\right] = \sqrt{2}(-1)^\mu C(111; \nu-\mu, \mu)\mathscr{Y}_{1,\mu-\nu}(\nabla), \tag{A.11}$$

one finds that the basic commutator $[\mathbf{R}\cdot\nabla, L_\mu(\mathbf{r})]$ in equation (A.10) becomes

$$\left[\mathbf{R}\cdot\nabla, L_\mu(\mathbf{r})\right] = \sqrt{2}\left(\frac{4\pi}{3}\right)\sum_\nu (-1)^{\nu+\mu} C(111; \nu-\mu, \mu) \times\mathscr{Y}_{1\nu}(\mathbf{R})\mathscr{Y}_{1,\mu-\nu}(\nabla). \tag{A.12}$$

By using equations (A.9) and (A.12), it can easily be seen that the operator $\mathbf{R}\cdot\nabla$ commutes with the commutator $[\mathbf{R}\cdot\nabla, L_\mu]$, so that the doubly nested commutator $[\mathbf{R}\cdot\nabla, [\mathbf{R}\cdot\nabla, L_\mu]]$, as well as all nested commutators of higher degree in equation (A.8), vanish. The substitution of these results into equation (A.8) reduces the addition theorem for the μth component of the angular momentum operator to the more simple form,

$$\begin{aligned} L_\mu(\mathbf{r}+\mathbf{R}) &= \mathrm{e}^{\mathbf{R}\cdot\nabla} L_\mu(\mathbf{r})\mathrm{e}^{-\mathbf{R}\cdot\nabla} = L_\mu(\mathbf{r}) + [\mathbf{R}\cdot\nabla, L_\mu] \\ &= L_\mu(\mathbf{r}) + \left(\frac{4\pi}{3}\right)\sqrt{2}\sum_\nu (-1)^{\nu+\mu} C(111; \nu-\mu, \mu) \\ &\quad \times\mathscr{Y}_{1\nu}(\mathbf{R})\mathscr{Y}_{1,\mu-\nu}(\nabla). \end{aligned} \tag{A.13}$$

The importance of this rather simple result is that it represents a general translation of the angular momentum operator along an arbitrary orientation of position vector $\mathbf{R}$. It is interesting to note that when $\mathbf{R}$ is along the Z-axis, $\mathscr{Y}_{1\nu}(\mathbf{R}) = \sqrt{3/4\pi}\, R\delta_{\nu,0}$, and equation (A.13) now becomes

$$L_\mu(\mathbf{r}+\mathbf{R}) = L_\mu(\mathbf{r}) + \sqrt{2}(-1)^\mu C(111; -\mu, \mu) R\nabla_\mu, \tag{A.14}$$

where we have used, $\mathscr{Y}_{1\mu}(\nabla) = \sqrt{3/4\pi}\,\nabla_\mu$. Equation (A.14) represents the translation of the μth component of the angular momentum operator along the Z-axis, which is in agreement with Chiu's result [2].

Upon substituting equations (A.4) and (A.13) in equation (A.7), the addition theorem for the magnetic multipole operator may now be written as

$$\begin{aligned} M_{lm}(\mathbf{r}+\mathbf{R}) = 4\pi B_l \sum_\mu \sum_{l'=0}^{l-1} \sum_{m'} &\alpha^{lm}_{l'm'\mu} \mathscr{Y}^*_{l'm'}(\mathbf{R}) \mathscr{Y}_{l-l'-1,m-\mu+m'}(\mathbf{r})\{L_\mu(\mathbf{r}) \\ &+\sqrt{\frac{32}{9}}\pi \sum_\nu (-1)^{\nu+\mu} C(111; \nu-\mu, \mu) \\ &\times\mathscr{Y}_{1\nu}(\mathbf{R})\mathscr{Y}_{1,\mu-\nu}(\nabla)\}, \end{aligned} \tag{A.15}$$

where

$$\alpha^{lm}_{l'm'\mu} = \frac{(l')!(2l-1)!(l-l'-1)!}{(l-1)!(2l'+1)!(2l-2l'-1)!} C(l-1,1,l;m-\mu,\mu) \times Z(l-1,l',l-l'-1;m-\mu,m').$$

For translation along the Z-axis, equation (A.15) is simplified, since $\mathscr{Y}^*_{l'm'}(\mathbf{R}) = (-1)^{m'}\sqrt{3/4\pi}\,R^{l'}\delta_{m',0}$ and $\mathscr{Y}_{1\nu}(\mathbf{R}) = \sqrt{3/4\pi}\,R\delta_{\nu,0}$. By using these expressions for the solid harmonics of argument $\mathbf{R}$, the addition theorem of the magnetic multipole operator as given in equation (A.15), can be expressed as

$$M_{lm}(\mathbf{r}+\mathbf{R}) = \sqrt{12\pi}\,B_l \sum_{\mu}\sum_{l'=0}^{l-1} \alpha^{lm}_{l'0\mu} R^{l'} \mathscr{Y}_{l-l'-1,m-\mu}(\mathbf{r}) \times \{L_\mu(\mathbf{r}) + \sqrt{2}(-1)^\mu C(111;-\mu,\mu)R\nabla_\mu\}. \quad \text{(A.16)}$$

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