Theor Chem Acc (1997) 96:135–139

Theoretical
Chemistry Accounts

Analogy between real irreducible tensor operator and molecular two-particle operator

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Received: 3 September 1996 / Accepted: 19 December 1996

Abstract. Molecular matrix elements of a physical operator are expanded in terms of polycentric matrix elements in the atomic basis by multiplying each by a geometrical factor. The number of terms in the expansion can be minimized by using molecular symmetry. We have shown that irreducible tensor operators can be used to imitate the actual physical operators. The matrix elements of irreducible tensor operators are easily computed by choosing rational irreducible tensor operators and irreducible bases. A set of geometrical factors generated from the expansion of the matrix elements of irreducible tensor operator can be transferred to the expansion of the matrix elements of the physical operator to compute the molecular matrix elements of the physical operator. Two scalar product operators are employed to simulate molecular two-particle operators. Thus two equivalent approaches to generating the geometrical factors are provided, where real irreducible tensor sets with real bases are used.

Key words: Irreducible tensor operator – Matrix element – Real basis – Symmetry

1 Introduction

A physical operator can be regarded as an irreducible tensor operator, and the calculation of its matrix elements can be simplified using irreducible tensor methods [1–9]. The application of the irreducible tensor methods to atomic problems or monocentric systems, such as atomic spectroscopy [1–3, 10], magnetic circular dichroism [11], and the theory of ligand fields [12–14], has been very successful. Regarding molecular problems, however, difficulties arise due to the polycentric nature of such problems, requiring application of the theory of polycentric invariants. Fieck [15–18] constructed a theory referred to as "polycentric tensor algebra", by which the processing of the physical quantities is still intricate. Zhang [19] provided a simple "group overlap" method, by which the matrix elements of one-particle operators can be easily reduced. In fact, a more common scheme to present Fieck's [15] and Zhang's [19] treatments is that be described below.

In general, a molecular matrix element $M(i)$ of a physical operator, which usually is expressed in the molecular basis constructed from linear combination of atomic orbitals, can be expanded in terms of a set of physical factors $\{A(j)\}$ and geometrical factors $\{C(i,j)\}$ by

$$M(i) = \sum_j Z(j) \cdot C(i,j) \cdot A(j) \ , \tag{1}$$

where $Z(j)$ is the numbers of matrix elements of jth set of symmetry equivalent matrix elements. Here we use i and j as the sets of indices for clarity. The geometrical factors $\{C(i,j)\}$ only depend on the molecular geometrical skeleton and symmetry. The physical factors $\{A(j)\}$ usually are the matrix elements in the real atomic basis. The simplification of calculation of the molecular matrix elements $\{M(i)\}$ thus depends upon how to classify and compute the geometrical factors and the physical factors. In this paper, we treat only the generation of the geometrical factors.

One can find a real irreducible tensor operator to imitate the actual physical operator, and expand its molecular matrix element, which is expressed in terms of irreducible bases belonging to the symmetry species of actual orbitals, as

$$L(i) = \sum_j Z(j) \cdot C(i,j) \cdot R(j) \ , \tag{2}$$

where the geometrical factors $\{C(i,j)\}$ are the same as those in Eq. (1). By choosing rational irreducible tensor operator and irreducible bases, the matrix elements $L(i)$ and $R(j)$ can be easily computed. The geometrical factors $\{C(i,j)\}$ thus are generated by Eq. (2), and can be transferred into Eq. (1). Then, the molecular matrix elements in Eq. (1) can be computed by using the geometrical factors, if the corresponding physical factors have been computed.

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This scheme can be used to simplify calculations in many cases. For example, the molecular matrix element of a two-particle operator must be expanded in terms of four-center integrals in the atomic basis. The processing of a lot of four-center integrals is a serious difficulty encountered in quantum chemical calculations. Although many symmetry techniques [20–35] have been employed to simplify the calculation of the matrix elements, few incorporate the irreducible tensor methods. In the present paper, we employ real irreducible tensor operators to imitate molecular two-particle operators, by working along the routine described above. Two equivalent treatments are provided.

2 Two-particle interaction operator

In order to utilize molecular symmetry, we will express the matrix elements of a operator in the symmetry orbital (SO) basis. Each SO, denoted by $|\Gamma\gamma(nlm)\rangle$, belonging the symmetry species ($\Gamma\gamma$) of the point group can be constructed [19] from the linear combination of atomic orbitals (AOs), i.e.

$$|\Gamma\gamma(nlm)\rangle = \frac{1}{g}\sum_{p\lambda}|\boldsymbol{p}\, nlm\lambda\rangle\langle\boldsymbol{p}\, nlm\lambda|\Gamma\gamma(nlm)\rangle \ , \tag{3}$$

where $\boldsymbol{p}$ indicates the p^{th} atom and l and m are the quantum numbers characteristic of the angular dependence (Y_m^l) of the atomic basis function. The third quantum number, n, represents a different function on each atom of a given l, m. For the sake of clarity, we will not write out the third quantum number n again. Here we mean that each sum over l, m also run over n. $\lambda = c$ (or s) indicates that the angular part of the AO behaves like a cosine (or a sine) function. The normalization factor g may be chosen to be unity for some cases such as the ligand group-orbitals of coordination molecules.

The matrix elements of a two-particle operator are expressed in terms of two-particle functions which can be constructed as the coupling function [5, 37] of the one-particle functions in Eq. (3), i.e.

$$|[\Gamma_1,\Gamma_2]_{\ \beta}\Gamma\gamma\rangle = \sum_{\gamma_1\gamma_2}(\Gamma_1\Gamma_2\gamma_1\gamma_2|\Gamma\gamma)_\beta\cdot|\Gamma_1\gamma_1\rangle|\Gamma_2\gamma_2\rangle \ , \tag{4}$$

where β denotes the multiplicity index of the irreducible representation Γ that occurs at all direct products $\Gamma_i\times\Gamma_j$ that includes Γ. When the matrix elements possess the symmetry of interchanging its bra and ket, β denotes the multiplicity index of Γ that occurs at all symmetrized product $[\Gamma_i\times\Gamma_j]$.

Similar to Eq. (1), the matrix element of a two-particle operator $\mathbf{Q}(1,2)$ can be written in the symmetry coupling basis as [35]

$$\begin{aligned} M(\Gamma\alpha\beta) &\equiv \left\langle \left[\Gamma_1',\Gamma_2'\right]_{\ \alpha}\Gamma\gamma|\mathbf{Q}(1,2)|[\Gamma_1,\Gamma_2]_\beta\Gamma\gamma\right\rangle \\ &= \sum_{\square}\frac{Z(\square)}{K_\Gamma}C_{\square}^{\Gamma\alpha\beta}A(\square) \ , \end{aligned} \tag{5}$$

where K_Γ is the dimension of the irreducible representation Γ, and $Z(\square)$ is the size of a set of equivalent standard four-center integrals, each set being labelled by the symbol "$\square$", which is a collection of indices, i.e.

$$\square = \left(\boldsymbol{p}_1 n_1' l_1' m_1' \lambda_1', \boldsymbol{p}_2 n_2' l_2' m_2' \lambda_2'; \boldsymbol{q}_1 n_1 l_1 m_1 \lambda_1, \boldsymbol{q}_2 n_2 l_2 m_2 \lambda_2\right). \tag{6}$$

The physical factor $A(\square)$, referred to as the "standard four-center integral" [19, 35], is the matrix element of the operator $\mathbf{Q}(1,2)$ in the real atomic basis, i.e.

$$A(\square) \equiv \langle \boldsymbol{p}_1 l_1' m_1' \lambda_1', \boldsymbol{p}_2 l_2' m_2' \lambda_2'|\mathbf{Q}(1,2)|\boldsymbol{q}_1 l_1 m_1 \lambda_1, \boldsymbol{q}_2 l_2 m_2 \lambda_2\rangle^0. \tag{7}$$

The geometrical factor is defined as:

$$\begin{aligned} C_{\square}^{\Gamma\alpha\beta} \equiv \sum_\gamma &\left\langle \left[\Gamma_1',\Gamma_2'\right]_{\ \alpha}\Gamma\gamma|\boldsymbol{p}_1 l_1' m_1' \lambda_1' \ \boldsymbol{p}_2 l_2' m_2' \lambda_2'\right\rangle^0 \\ &\cdot\left\langle \boldsymbol{q}_1 l_1 m_1 \lambda_1 \ \boldsymbol{q}_2 l_2 m_2 \lambda_2|[\Gamma_1,\Gamma_2]_{\ \beta}\Gamma\gamma\right\rangle^0. \end{aligned} \tag{8}$$

In Eq. (5), the sum only runs over the equivalent sets $\{\square\}$, or over the symmetry non-redundant integrals rather than over all integrals. It is obvious that the calculation of the two-particle integrals and the transformation of the integrals from AO basis to SO basis, are simultaneously reduced by Eq. (5). In the next section, we use the irreducible tensor method to derive the relation to calculate the geometrical factors.

3 Scalar product operator

According to the scheme described in Sect. 1, in order to calculate the geometrical factors in the polycentric expansion of the molecular matrix element, we can choose fictitious operators and bases to replace the actual operators included in the molecular Hamiltonian and the actual bases, respectively. Because all terms that appear in the molecular Hamiltonian are scalar operators, the two-particle operator thus can be simulated by the following scalar product of the irreducible real tensor operator:

$$T^k(1)\cdot T^k(2) = \sum_{m\lambda}T_{m\lambda}^k(1)T_{m\lambda}^k(2) \ , \tag{9}$$

where the irreducible real tensor operator is

$$T_{m\lambda}^k = \sqrt{\frac{4\pi}{2k+1}}Y_{m\lambda}^k \ , \tag{10}$$

where, in turn, the real spherical harmonics $Y_{m\lambda}^k$ is constructed from the complex spherical harmonics in Fano and Racah's (F-R) phase convention [2] or in Condon and Shortley's (C-S) phase convention [3] by a unitary transformation [19, 36, 37]:

$$\begin{aligned} Y_{m\lambda}^k &= \eta\cdot 2^{-\frac{1}{2}(\delta_{m0}+1)}\left[(-1)^m Y_m^k + (-1)^\lambda Y_{\bar{m}}^k\right] \\ \eta &= \begin{cases}(-i)^{k+\lambda} & \text{for F-R conv.}\\ (-i)^\lambda & \text{for C-S conv.}\end{cases}; \quad \lambda = \begin{cases}C=0\\ S=1\end{cases}. \end{aligned} \tag{11}$$

Similar to Eq. (3), we can construct the symmetry-adapted functions of the molecular polyhedron as the following linear combination

$$Y^j_{\Gamma\gamma} = \frac{1}{g^j_\Gamma(m)} \sum_{p\lambda} Y^j_{m\lambda}(\boldsymbol{p}) \langle \boldsymbol{p} lm\lambda | \Gamma\gamma(lm) \rangle \ , \tag{12}$$

where $g^j_\Gamma(m)$ is the normalization factor called "group-overlap" [19]. The coefficient $\langle \boldsymbol{p} lm\lambda | \Gamma\gamma(lm) \rangle$ is same as the coefficient in Eq. (3). The symmetry coupling function corresponding to the left-hand side of Eq. (4) can be constructed as

$$\begin{aligned} \left| \left[Y^{j_1}_{\Gamma_1}, Y^{j_2}_{\Gamma_2} \right] \alpha\Gamma\gamma \right\rangle = & \frac{1}{g^{j_1}_{\Gamma_1}(m_1) g^{j_2}_{\Gamma_2}(m_2)} \\ & \cdot \sum_{p_1\lambda_1} \sum_{p_2\lambda_2} \left| Y^{j_1}_{m_1\lambda_1}(\boldsymbol{p}_1) Y^{j_2}_{m_2\lambda_2}(\boldsymbol{p}_2) \right\rangle \\ & \cdot \langle \boldsymbol{p}_1 l_1 m_1 \lambda_1 \boldsymbol{p}_2 l_2 m_2 \lambda_2 | [\Gamma_1, \Gamma_2] \alpha\Gamma\gamma \rangle \ . \end{aligned} \tag{13}$$

The matrix element of the scalar product operator in the symmetry coupling basis can be expressed as

$$L(\Gamma\alpha\beta) = \left\langle \left[Y^{j'_1}_{\Gamma'_1}, Y^{j'_2}_{\Gamma'_2} \right]_\alpha \Gamma\gamma \middle| T^k(1) \cdot T^k(2) \middle| \left[Y^{j_1}_{\Gamma_1}, Y^{j_2}_{\Gamma_2} \right]_\beta \Gamma\gamma \right\rangle, \tag{14}$$

which here is referred to as the "left matrix element". By the same procedure of deriving Eq. (5), we obtain a formula to show the symmetry reduction of the "left matrix element" as follows:

$$L(\Gamma\alpha\beta) = \frac{1}{G} \sum_\square \frac{Z(\square)}{K_\Gamma} C^{\Gamma\alpha\beta}_\square \cdot R(\square). \tag{15}$$

The factor G in Eq. (15) is the product of four group-overlap integrals, i.e.

$$G = g^{j'_1}_{\Gamma'_1}(m'_1) \cdot g^{j'_2}_{\Gamma'_2}(m'_2) \cdot g^{j_1}_{\Gamma_1}(m_1) \cdot g^{j_2}_{\Gamma_2}(m_2) \ . \tag{16}$$

The matrix element on the right-hand side of Eq. (15), referred to as the "right matrix element", is

$$R(\square) = \left\langle Y^{j'_1}_{m'_1\lambda'_1}(\boldsymbol{p}_1) Y^{j'_2}_{m'_2\lambda'_2}(\boldsymbol{p}_2) \middle| T^k(1) \cdot T^k(2) \middle| Y^{j_1}_{m_1\lambda_1}(\boldsymbol{q}_1) Y^{j_2}_{m_2\lambda_2}(\boldsymbol{q}_2) \right\rangle^0. \tag{17}$$

It should be noted that these spherical harmonics are defined at local coordinate systems with a common origin. Each local coordinate system has same orientations as the corresponding atomic local coordinate system at which the actual atomic orbitals are defined. Because the geometrical factors only depend on the angular part of the basis functions (or the orientations of the local coordinate systems), the geometrical factors in Eq. (15), referred to as the C coefficients [19, 35], are the same as those in Eq. (5). Equation (15) indeed involves a set of equations. All geometrical factors in Eq. (15) form a matrix which can be generated by resolving the set of equations, as long as the values of the "left matrix elements" in Eq. (14) and the "right matrix elements" in Eq. (17) are obtained. In the subsequent paragraphs, we give two ways to calculate the two kinds of matrix elements.

3.1 Procedure one

Employing the scalar product operator defined in Eq. (9), we first calculate the "left matrix elements". The coupling function of the molecular symmetry group H can be expressed in the coupling basis of the three-dimensional rotation group SO_3 by [14, 38]

$$\begin{aligned} \left| \left[Y^{j_1}_{\Gamma_1}, Y^{j_2}_{\Gamma_2} \right] \alpha\Gamma\gamma \right\rangle = & \sum_{jc} \sqrt{\frac{2j+1}{K_\Gamma}} \begin{pmatrix} j_1 & j_2 & j \\ \Gamma_1 & \Gamma_2 & c\Gamma \end{pmatrix} \cdot \Big| \\ & \left[Y^{j_1}, Y^{j_2} \right] jc\Gamma\gamma \rangle \ . \end{aligned} \tag{18}$$

On the right-hand side of Eq. (18), the second factor is the 3-jm factor [38], or the normal coupling coefficient [14] for the group chain $SO_3 \supset H$. Here, it is necessary to emphasize that the 3-jm factors are identical for both the real bases and the complex bases [14, 37]. Substituting Eq. (18) into Eq. (14), we obtain a formula to calculate the "left matrix element", i.e.

$$\begin{aligned} L(\Gamma\alpha\beta) = & \sum_{jc} \frac{2j+1}{K_\Gamma} \begin{pmatrix} j'_1 & j'_2 & j \\ \Gamma'_1 & \Gamma'_2 & c\Gamma \end{pmatrix}^* \cdot \begin{pmatrix} j_1 & j_2 & j \\ \Gamma_1 & \Gamma_2 & c\Gamma \end{pmatrix} \\ & \cdot \left\langle (j'_1, j'_2) jc\Gamma\gamma \middle| T^k(1) \cdot T^k(2) \middle| (j_1, j_2) jc\Gamma\gamma \right\rangle \ , \end{aligned} \tag{19}$$

where the matrix element of the scalar product operator can be computed by the following formula (cf. Eq. (37) of Ref. [36]):

$$\begin{aligned} & \left\langle (j'_1, j'_2) jc\Gamma\gamma \middle| T^k(1) \cdot T^k(2) \middle| (j_1, j_2) jc\Gamma\gamma \right\rangle \\ & \quad = (-1)^{j'_2 + j_1 + j + k} \begin{Bmatrix} j'_1 & k & j_1 \\ j_2 & j & j'_2 \end{Bmatrix} \\ & \quad \cdot \left\langle j'_1 \middle\| T^k(1) \middle\| j_1 \right\rangle \left\langle j'_2 \middle\| T^k(2) \middle\| j_2 \right\rangle \ , \end{aligned} \tag{20}$$

where the second factor is the 6-j symbol of the group SO_3 [39]. The reduced matrix element of the irreducible real tensor operator is same as the reduced matrix element of the irreducible complex spherical tensor operator in the F-R phase convention [36, 37].

Now, let us consider the "right matrix elements," i.e. Eq. (17). Because the real spherical harmonics are defined in different local coordinate systems, the right matrix elements cannot be calculated directly. However, these local coordinate systems have a common origin. Hence, they can be rotated, by Euler angles $R_p = (\phi_p, \theta_p, \omega_{pq})$, into a common coordinate system such as the molecular coordinate system, while the real spherical harmonics transform in accordance with

$$\begin{aligned} \mathbf{P}\left(R_p^{-1}\right) Y^j_{m\lambda}(\boldsymbol{p}^0) &= \sum_{\tilde{m}\tilde{\lambda}} D^j_{\tilde{m}\tilde{\lambda}, m\lambda} \left(R_p^{-1}\right)_{\text{axes}} \cdot Y^j_{\tilde{m}\tilde{\lambda}}(\mathbf{o}) \\ &= \sum_{\tilde{m}\tilde{\lambda}} D^j_{m\lambda, \tilde{m}\tilde{\lambda}} \left(\phi_p, \theta_p, \omega_{pq}\right)_{\text{axes}} \cdot Y^j_{\tilde{m}\tilde{\lambda}}(\mathbf{o}), \end{aligned} \tag{21}$$

where the matrix elements of the rotation related to the real basis can be calculated by using the matrix elements of the rotation related to the complex basis by some relations [19, 37]. The value of the "right matrix element" in Eq. (17) is not affected by the rotations.

By using Eq. (21), the "right matrix element" can be calculated by

$$R(\square) = \sum_{\tilde{m}'_1\tilde{\lambda}'_1}\sum_{\tilde{m}'_2\tilde{\lambda}'_2}\sum_{\tilde{m}_1\tilde{\lambda}_1}\sum_{\tilde{m}_2\tilde{\lambda}_2} \left\langle Y^{j'_1}_{\tilde{m}'_1\tilde{\lambda}'_1} Y^{j_1}_{\tilde{m}_1\tilde{\lambda}_1} \middle| T^k(1)\cdot T^k(2) \middle| Y^{j'_2}_{\tilde{m}'_2\tilde{\lambda}'_2} Y^{j_2}_{\tilde{m}_2\tilde{\lambda}_2} \right\rangle \cdot D^{j'_1}_{m'_1\lambda'_1,\tilde{m}'_1\tilde{\lambda}'_1}(\boldsymbol{p}_1^0) D^{j'_2\,*}_{m'_2\lambda'_2,\tilde{m}'_2\tilde{\lambda}'_2}(\boldsymbol{p}_2^0) D^{j_1}_{m_1\lambda_1,\tilde{m}_1\tilde{\lambda}_1}(\boldsymbol{q}_1^0) \cdot D^{j_2}_{m_2\lambda_2,\tilde{m}_2\tilde{\lambda}_2}(\boldsymbol{q}_2^0) \ , \quad (22)$$

where the matrix element of the scalar product operator is

$$\left\langle Y^{j'_1}_{\tilde{m}'_1\tilde{\lambda}'_1} Y^{j'_2}_{\tilde{m}'_2\tilde{\lambda}'_2} \middle| T^k(1)\cdot T^k(2) \middle| Y^{j_1}_{\tilde{m}_1\tilde{\lambda}_1} Y^{j_2}_{\tilde{m}_2\tilde{\lambda}_2} \right\rangle = \sum_{m\lambda} \left\langle Y^{j'_1}_{\tilde{m}'_1\tilde{\lambda}'_1} \middle| T^k_{m\lambda}(1) \middle| Y^{j_1}_{\tilde{m}_1\tilde{\lambda}_1} \right\rangle \left\langle Y^{j'_2}_{\tilde{m}'_2\tilde{\lambda}'_2} \middle| T^k_{m\lambda}(2) \middle| Y^{j_2}_{\tilde{m}_2\tilde{\lambda}_2} \right\rangle . \quad (23)$$

On the right-hand side of Eq. (23), the two matrix elements of the one-particle real irreducible spherical tensor operator in the real spherical harmonics basis can be computed by using the real version of the Wigner-Eckart theorem [36, 37] which requires the real 3-1 symbols [37] derived from the 3-j symbols [39].

3.2 Procedure two

In an alternative procedure, we adopt a new scalar product operator rather than the operator in Eq. (9). The new operator is defined according to the irreducible basis of the point group, i.e.

$$T^{k\mathrm{P}}(1)\cdot T^{k\mathrm{P}}(2) = \sum_{\rho} T^{k\mathrm{P}}_{\rho}(1) T^{k\mathrm{P}}_{\rho}(2) \ , \quad (24)$$

where the superscript k denotes the irreducible representation of the group SO_3, and P the irreducible representation of the point group. The sum runs over the real components of P. Here, we neglect the multiplicity of the k-P branch for the sake of clarity. The irreducible tensor operator of the point group can be obtained from the irreducible spherical tensor operator of the group SO_3 by a unitary transformation, i.e. the symmetrization of spherical harmonics [37, 40–44]:

$$T^k_{\mathrm{P}\rho} = \sum_{m\lambda} S^k_{m\lambda,\mathrm{P}\rho}\cdot T^k_{m\lambda} \ , \quad (25)$$

where the real S coefficients can be calculated by some close formulae [37]. Although the new scalar product operator results in new "left matrix elements" and "right matrix elements" different from those in Eqs. (14) and (17), the same geometrical factors (the C coefficients) will be obtained.

Now, by using Eq. (4.50) of Ref. [14], the new "left matrix element" can be calculated by

$$L'(\Gamma\alpha\beta) = (-1)^{\Gamma_1+\Gamma'_2+\mathrm{P}+\Gamma}\ W\begin{pmatrix}\Gamma'_1 & \Gamma'_2 & \Gamma\\ \Gamma_2 & \Gamma_1 & \mathrm{P}\end{pmatrix} \cdot \langle j'_1\Gamma'_1 \| T^{k\mathrm{P}}(1) \| j_1\Gamma_1\rangle \langle j'_2\Gamma'_2 \| T^{k\mathrm{P}}(2) \| j_2\Gamma_2\rangle \ , \quad (26)$$

where the phase factor is caused by the exchanging of the columns of the V coefficients of the point group. The second factor in the W coefficient of the point group [5, 14] (or the 6-j symbol of the point group [38, 39]). The reduced matrix element of the operator in the real basis of the point group can be transferred to that of the group SO_3 as follows

$$\langle j'_1\Gamma'_1 \| T^{k\mathrm{P}} \| j_1\Gamma_1\rangle = \begin{pmatrix} j'_1 & j_1 & j\\ \Gamma'_1 & \Gamma_1 & \mathrm{P}\end{pmatrix} \cdot \langle j'_1 \| T^k \| j_1\rangle \ , \quad (27)$$

where the first factor is the normalized isoscalar factor [14, 38] for the group chain $SO_3 \supset H$.

The new "right matrix elements" can be calculated by

$$R'(\square) = \sum_{\tilde{m}'_1\tilde{\lambda}'_1}\sum_{\tilde{m}'_2\tilde{\lambda}'_2}\sum_{\tilde{m}_1\tilde{\lambda}_1}\sum_{\tilde{m}_2\tilde{\lambda}_2} \left\langle Y^{j'_1}_{\tilde{m}'_1\tilde{\lambda}'_1} Y^{j_1}_{\tilde{m}_1\tilde{\lambda}_1} \middle| T^{k\mathrm{P}}(1)\cdot T^{k\mathrm{P}}(2) \middle| Y^{j'_2}_{\tilde{m}'_2\tilde{\lambda}'_2} Y^{j_2}_{\tilde{m}_2\tilde{\lambda}_2} \right\rangle \cdot D^{j'_1}_{m'_1\lambda'_1,\tilde{m}'_1\tilde{\lambda}'_1}(\boldsymbol{p}_1^0) D^{j'_2}_{m'_2\lambda'_2,\tilde{m}'_2\tilde{\lambda}'_2}(\boldsymbol{p}_2^0) \cdot D^{j_1}_{m_1\lambda_1,\tilde{m}_1\tilde{\lambda}_1}(\boldsymbol{q}_1^0) D^{j_2}_{m_2\lambda_2,\tilde{m}_2\tilde{\lambda}_2}(\boldsymbol{q}_2^0) \ , \quad (28)$$

which is similar to Eq. (22), but the matrix element of the new scalar product operator is

$$\left\langle Y^{j'_1}_{\tilde{m}'_1\tilde{\lambda}'_1} Y^{j'_2}_{\tilde{m}'_2\tilde{\lambda}'_2} \middle| T^{k\mathrm{P}}(1)\cdot T^{k\mathrm{P}}(2) \middle| Y^{j_1}_{\tilde{m}_1\tilde{\lambda}_1} Y^{j_2}_{\tilde{m}_2\tilde{\lambda}_2} \right\rangle = \sum_{\rho}\sum_{m_1\lambda_1}\sum_{m_2\lambda_2} S^k_{m_1\lambda_1,\mathrm{P}\rho}\cdot S^k_{m_2\lambda_2,\mathrm{P}\rho} \cdot \left\langle Y^{j'_1}_{\tilde{m}'_1\tilde{\lambda}'_1} \middle| T^k_{m_1\lambda_1} \middle| Y^{j_1}_{\tilde{m}_1\tilde{\lambda}_1} \right\rangle \left\langle Y^{j'_2}_{\tilde{m}'_2\tilde{\lambda}'_2} \middle| T^k_{m_2\lambda_2} \middle| Y^{j_2}_{\tilde{m}_2\tilde{\lambda}_2} \right\rangle \quad (29)$$

3.3 Equivalence of the two procedures

The scalar product operator in Eq. (9) is related to the new scalar product operator in Eq. (24) by

$$T^k(1)\cdot T^k(2) = \sum_{b\mathrm{P}} T^{kb\mathrm{P}}(1)\cdot T^{kb\mathrm{P}}(2) \ , \quad (30)$$

where b indicates the multiplicity of the k-P branch, k and P being the irreps of the group SO_3 and the point group respectively. Therefore, we have the relation between the two left matrix elements

$$L(\Gamma\alpha\beta) = \sum_{b\mathrm{P}} L'(\Gamma\alpha\beta) \ . \quad (31)$$

Substituting Eq. (30) into Eq. (14) and employing Eq. (26) and Eq. (27), we obtain a formula to calculate the left matrix element as follows:

$$L(\Gamma\alpha\beta) = \sum_{b\mathrm{P}} (-1)^{\Gamma_1+\Gamma'_2+\mathrm{P}+\Gamma} \cdot W\begin{pmatrix}\Gamma'_1 & \Gamma'_2 & \Gamma\\ \Gamma_2 & \Gamma_1 & \mathrm{P}\end{pmatrix} \begin{pmatrix} j'_1 & j_1 & j\\ \Gamma'_1 & \Gamma_1 & b\mathrm{P}\end{pmatrix} \begin{pmatrix} j'_2 & j_2 & j\\ \Gamma'_2 & \Gamma_2 & b\mathrm{P}\end{pmatrix} \cdot \left\langle j'_1 \| T^k(1) \| j_1\right\rangle \langle j'_2 \| T^k(2) \| j_2\rangle \ . \quad (32)$$

One can see that Eq. (32) is equivalent to Eq. (19).

We now show that Eq. (28) is equivalent to Eq. (22). This is just the equivalence of Eq. (29) and Eq. (23). Summing Eq. (29) over the multiplicity indices $\{b\}$ and the irreducible representations $\{\mathrm{P}\}$ and their components $\{\rho\}$ of the point group H, and using the orthonormality of the real S coefficients [37]

$$\sum_{b\mathrm{P}\rho} S^k_{m_1\lambda_1,b\mathrm{P}\rho} \cdot S^k_{m_2\lambda_2,b\mathrm{P}\rho} = \delta(m_1\lambda_1; m_2\lambda_2) \ , \tag{33}$$

we arrive at Eq. (23). This shows that the two procedures are equivalent.

4 Conclusion

The irreducible tensor method provides a useful tool for the calculation of the molecular physical quantities. The theory of the irreducible tensorial sets was extended to the irreducible real bases of the group SO_3 [36, 40–44] and the point groups [5, 37]. The present paper shows that the real irreducible tensorial sets can be utilized in the processing of the molecular quantum mechanics problems. The monocentric theory of the irreducible tensor method is extended to the polycentric form for polyatomic molecules. The symmetry of the molecule can be employed to reduce the calculation of the molecular matrix elements, as well as molecular physical quantities [45–47].

Acknowledgement This work was supported by the National Natural Science Foundation of China.

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