Theoret. Chim. Acta (Berl.) 62, 443–460 (1983)

THEORETICA CHIMICA ACTA

Σ-Factorization Method: A New Development of Molecular-Orbital Theories Based on One-Centre Approximation of Atomic and Molecular Densities

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A new approach to one-centre approximation methods initiated by Mulliken and Ruedenberg in their earlier works has been developed in this paper. Despite the similarity of underlying ideas, the proposal to factorize the s-function product instead of the total density factorization along with a new technical background of the method provide more flexible and practical scheme since large orbital quantum numbers do present no longer the crucial point for extending the approach for compounds with heavy atoms. Both minimal and extended schemes are equally within the scope of the method. The technical links with the nuclear shell model formalism are discussed briefly.

Key words: Two-centre atomic densities – One-centre approximation – Angular momentum theory.

1. Introduction

Many approximate and semiempirical MO LCAO SCF methods are based on one-centre approximation of two-centre atomic and molecular density distributions. For the atomic distribution $\varphi(\boldsymbol{r}_{1a})\psi(\boldsymbol{r}_{1b})$, the general form of this approximation is:

$$\varphi(\boldsymbol{r}_{1a})\psi(\boldsymbol{r}_{1b}) \approx \sum_i C_i f_i(\boldsymbol{r}_{1a}) + \sum_j D_j \chi_j(\boldsymbol{r}_{1b}) \tag{1}$$

Since molecular density $\rho(\boldsymbol{r})$ is a linear combination of atomic distributions, its expansion has the similar structure

$$\rho(\boldsymbol{r}_1) = \sum_{a,i} C_{a,i} f_i(\boldsymbol{r}_{1a}), \tag{2}$$

where $\boldsymbol{r}_{1a} = \boldsymbol{r}_1 - \boldsymbol{R}_a$; $\boldsymbol{r}_1$ and $\boldsymbol{R}_a$ are the electron and nuclear coordinates, respectively.

A specific feature of Eqs. (1) and (2) is "additive factorization" of their right-hand sides with respect to $\boldsymbol{r}_{1a}$, $\boldsymbol{r}_{1b}, \ldots$ whereas the left-hand sides are characterized by "multiplicative factorization" with respect to these variables. In other words, the LCAO form is suggested not only for molecular orbitals, but also for their bilinear products (figuratively, we deal with "double" LCAO approximation in this approach). It is indeed a strong and far-reaching assumption. The most important merit of this approximation is the additive decomposition of multicentre two-electron integrals into Coulomb two-centre integrals. This remarkable simplification has been exploited in various approaches based on one-centre approximation: from "naive" semiquantitative approaches involving the least possible number of terms (usually two) in Eq. (1) (we call them *minimal* approximations) [1–5] up to more sophisticated methods involving sufficiently large number of terms to imitate *ab initio* calculations with satisfactory, for many purposes, accuracy. These latters will be referred to as *extended* approximations [6–9].

In some remote sense, it is possible to consider a limiting extension of the basis in the right-hand side of Eq. (1) which results in a complete set of functions (Ruedenberg's approximations [10]). This implies a transition from approximation by finite sums to an exact infinite expansion equivalent to some *ab initio* calculation scheme. One should bear in mind that such an interpretation is of purely speculative nature since the construction of effective two-centre basis[1] has so far not been considered, let alone the convergence of the corresponding expansions. In the following we always imply by "expansion" approximation of the densities by the finite number of factorized terms. This procedure will be referred to as a "*factorization* method".

Certain specific difficulties [5, 11–15] are encountered both in the minimal as well as in the extended schemes. Unsatisfactory approximation of atomic densities containing basis functions with non-zero orbital moments l is the main demerit of the minimal factorization methods. On the other hand, the extended factorization methods involve rather cumbersome expansions. As a result, the determining of the coefficients in Eq. (1) with the help of the least square method (LSM) becomes more and more tedious as the number of terms in the expansion increases [7–9].

There is a simple recipe to avoid these and other difficulties. Indeed, let us apply the expansion (1), not to the total atomic density, but to the product of s-functions which always enter implicitely into the total density notwithstanding whatever large l might be involved in it. By analogy with the traditional spectroscopic Σ,

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[1] It is supposed in the Ref. [10] that some complete orthonormalized sets of functions are centred on each of the nuclei a and b. Combining these sets together provides an overcomplete set. "Expansion" of a function over such a set is not unique. The criteria of closeness (Parceval's formula) and of completeness (Riesz–Fischer theorem) also seem to fail for such a set.

Π, Δ-classification, evidently, the distribution described by the two-centre product of s-functions will possess Σ-symmetry in the rotated coordinate system K_{rot} with the polar axis directed along $\boldsymbol{R}_{ba}$. The corresponding procedure is therefore called Σ-factorization. The idea underlying the method, which is exposed in [16], has been motivated by the observation that though Σ-factorization does not result in complete additive decomposition of atomic densities, the remaining non-additive contributions turn to be homogeneous polynomials of the Cartesian coordinates of electron and nuclear radius-vectors. Fortunately, two-centre products of these polynomials can be reduced to the desired one-centre form with the help of the *exact* addition theorems without taking recourse to the LSM procedure. To have an illustrative example, suppose

$$\varphi(\boldsymbol{r}_{1a}) = z_{1a} \exp(-\alpha r_{1a}), \qquad \psi(\boldsymbol{r}_{1b}) = z_{1b} \exp(-\beta r_{1b}) \tag{3}$$

in Eq. (1). Applying the additive decomposition procedure to the product of s-functions, we get

$$\exp(-\alpha r_{1a}) \exp(-\beta r_{1b}) \approx f(\boldsymbol{r}_{1a}) + \chi(\boldsymbol{r}_{1b}), \tag{4}$$

where f and χ denote one-centre expressions analogous to those in the right-hand side of Eq. (1). Though the total density

$$\varphi(\boldsymbol{r}_{1a})\psi(\boldsymbol{r}_{1b}) \approx z_{1a}z_{1b}f(\boldsymbol{r}_{1a}) + z_{1a}z_{1b}\chi(\boldsymbol{r}_{1b}) \tag{5}$$

takes but a partially factorized form, the interfering two-centre contribution $z_{1a}z_{1b}$ can be easily transformed[2] to the necessary one-centre form, applying $z_{1a}z_{1b} = z_{1a}^2 + Z_{ab}z_{1a}$ and $z_{1a}z_{1b} = z_{1b}^2 - Z_{ab}z_{1b}$ in the first and in the second term on the right-hand side of Eq. (5), respectively. Evidently, this leads to the desired one-centre form for the total density.

In comparison with this simple example, the general case do present, however, much more severe technical difficulties. Therefore, dispite the simplicity of underlying idea, the approach would be ineffective without the use of fundamental theorems of the angular momentum theory. Only a systematic use of these theorems provides a universal algorithm, allows the application of standard kinematical constants and permits compact consideration of basis functions with arbitrarily large orbital momenta.

2. Reduced Atomic Densities

We shall write the Slater function $\psi(\boldsymbol{r})$ as a product of the nonnormalized radial part $e(r)$ and the spherical function $Y(\boldsymbol{r})$ with the Condon–Shortley phase [17a, 18a, 19a]:

$$\psi_{\alpha,n,l,m}(\boldsymbol{r}) = e_{\alpha,n}(r)\, Y_{l,m}(\boldsymbol{r}), \tag{6}$$

$$e_{\alpha,n}(r) = r^n \exp(-\alpha r) \equiv \sqrt{4\pi}\,\psi_{\alpha,n,0,0}(\boldsymbol{r}), \tag{7}$$

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[2] The possibility of such transformation, in this simplest form, has been indicated in private communication, independently but posterior to author's observation, by V. G. Vochmin (*A.W.N.*)

where $\boldsymbol{r}$ in $Y(\boldsymbol{r})$ denotes the set of *angular* coordinates θ, φ of the vector $\boldsymbol{r}$. The second part of Eq. (7) follows from the relationship $Y_{0,0}(\boldsymbol{r}) = 1/\sqrt{4\pi}$. We take, as usually, that the function (6) describes some $|n+1, l\rangle$-state (or $s, p, d, \ldots$-states, if $l = 0, 1, 2, \ldots$) and the function (7) describes the $|n+1, 0\rangle$-state (or s-state, since $l = 0$).

For brevity, let

$$[i] \equiv [\alpha_i, n_i, l_i, m_i] \equiv [(i), m_i], \qquad (i) \equiv (\alpha_i, n_i, l_i) \tag{8}$$

then we can write the Slater function centered at the point $\boldsymbol{R}_a$ as

$$\psi^a_{[i]}(\boldsymbol{r}_1) = \psi_{[i]}(\boldsymbol{r}_{1a}) = \psi_{(i)m_i}(\boldsymbol{r}_{1a}), \qquad \boldsymbol{r}_{1a} = \boldsymbol{r}_1 - \boldsymbol{R}_a. \tag{9}$$

Consequently, the two-centre atomic density can be written using any of the following notations:

$$\Pi^{a,b}_{[i,j]}(\boldsymbol{r}_1) = \Pi_{(i,j)m_i,m_j}(\boldsymbol{r}_{1a}, \boldsymbol{r}_{1b}) = \psi^a_{[i]}(\boldsymbol{r}_1)\psi^b_{[j]}(\boldsymbol{r}_1). \tag{10}$$

From the viewpoint of transformation properties, the atomic density Π differs from the basis function ψ in that, under rotation, the former do not satisfy the same simple transformation law as the latter. Indeed, let $\Omega(\alpha, \beta, \gamma)$ be some Euler rotation (through α about the z-axis, through β about a new position of the y-axis, and through γ about a new z-axis) which converts the coordinate system of basis unit vectors K into a new system $K_{\text{rot}} \equiv K'$ (Fig. 1 shows a particular rotation $\alpha = \varphi_{\boldsymbol{R}}$, $\beta = \theta_{\boldsymbol{R}}$, $\gamma = 0$). Let a vector $\boldsymbol{r}$ in K be transformed into $\boldsymbol{r}'$ in K' (θ', φ' in terms of polar coordinates, see Fig. 1). Symbolically, the resulting coordinate transformation can be expressed as $\boldsymbol{r}' = \Omega\boldsymbol{r}$. The function Y, and consequently ψ, are transformed by irreducible representation of the rotation group. In other words:

$$\psi_{(i)m_i}(\boldsymbol{r}'_{1a}) = \psi_{(i)m_i}(\Omega\boldsymbol{r}_{1a}) = \sum_{m_i'=-l_i}^{l_i} D^{l_i}_{m_i',m_i}(\Omega)\psi_{(i)m_i'}(\boldsymbol{r}_{1a}), \tag{11}$$

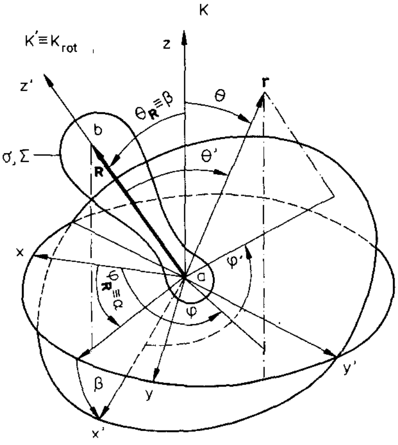

Fig. 1. Coordinate system K and $K' \equiv K_{\text{rot}}$ (for explanation see Sect. 2 and 4)

where $D(\Omega)$ is the Wigner matrix [17b, 18b, 19b]. Any quantity satisfying Eq. (11) is called an *irreducible spherical tensor* (IST). The atomic density Π is expressed as a *direct tensor product* (DTP) of two IST, and is not therefore a component of some IST but satisfies a transformation law more complicated than Eq. (11).

To simplify the transformation properties of atomic density relative to rotations[3] we shall use, in place of the direct product (10), an *irreducible tensor product* (ITP) [17c, 18c, 19c]:

$$\begin{aligned}\pi^{a,b}_{(i,j)l,m}(\boldsymbol{r}_1) &= \pi_{(i,j)l,m}(\boldsymbol{r}_{1a}, \boldsymbol{r}_{1b}) = \{\psi_{(i)}(\boldsymbol{r}_{1a}) \otimes \psi_{(j)}(\boldsymbol{r}_{1b})\}_{l,m} \\ &= \sum_{\substack{m_i, m_j \\ (m_i+m_j=m)}} \langle l_i m_i l_j m_j | lm \rangle \psi_{(i)m_i}(\boldsymbol{r}_{1a}) \psi_{(j)m_j}(\boldsymbol{r}_{1b}),\end{aligned} \tag{12}$$

where $\langle a\alpha b\beta | c\gamma \rangle$ are the Clebsch–Gordan coefficients [17d, 18d, 19d]. Note that the ITP (12) satisfies the triangle condition $|l_i - l_j| \leq l \leq l_i + l_j$, where the quantity $l_i + l_j - l$ may assume any integer value. We call the quantity π *reduced* (or irreducible) *atomic density*. Since the transformation Eq. (12) is unitary [17e, 18e] the initial atomic density can be expressed through reduced densities as follows:

$$\Pi_{(i,j)m_i,m_j}(\boldsymbol{r}_{1a}, \boldsymbol{r}_{1b}) = \sum_{\substack{l=|l_i-l_j| \\ (m=m_i+m_j)}}^{l_i+l_j} \langle l_i m_i l_j m_j | lm \rangle \{\psi_{(i)}(\boldsymbol{r}_{1a}) \otimes \psi_{(j)}(\boldsymbol{r}_{1b})\}_{l,m} \tag{13}$$

Reduced atomic densities in Eq. (12) satisfy the same simple transformation law. Eq. (11) as the basis functions.

3. Preliminary Multiplicative Factorization

The usual extended factorization scheme is based on the expansion

$$\Pi^{a,b}_{[i,j]}(\boldsymbol{r}_1) = \sum_{[q,r]} C_{a[i,j,q,r]}(\boldsymbol{R}) \Pi^{a,a}_{[q,r]}(\boldsymbol{r}_1) + \sum_{[q,r]} C_{b[i,j,q,r]}(\boldsymbol{R}) \Pi^{b,b}_{[q,r]}(\boldsymbol{r}_1) \tag{14}$$

where the one-centre densities $\Pi^{a,a}$ and $\Pi^{b,b}$ are constructed, as a rule, from the functions present in the basis (additional functions can, in principle, be introduced) and the coefficients C are found by the LSM [7–9], imposing some additional conditions [9, 5], if necessary, to improve the approximation.

The analytical properties (transformation properties, in particular) of the basis functions are not altogether taken into account in the Eq. (14). If the basis set contains functions of complicate geometry (large l-values), the number of terms necessary for a satisfactory accuracy may be quite great. Even for small orbital numbers, inversion of matrices of large dimensions in the usual LSM [9] is rather tedious, and certain complications arise due to nearly degenerate matrices.

Use of a large basis in Eq. (14) is essential largely to represent the geometric relief of Π-distribution due to the angular factors Y. Since the structure of

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[3] This leads, simultaneously, to significant simplification of translational properties of the polynomial parts of the densities to be introduced in the Sec. 5.

angular parts does not change from one compound to another or when the Slater parameters are varied, it is desirable to separate and treat them in an explicit form with some exact procedure, while using the LSM only for approximating the contribution due to the exponential factors. It is convenient to separate the angular parts together with the power multipliers: thus we easily obtain polynomial structures, and the analytical transformations are considerably simplified. Now consider the function

$$\mathscr{Y}^{k}_{l,m}(\boldsymbol{r}) = r^{l+2k} Y_{l,m}(\boldsymbol{r}) = r^{2k} \mathscr{Y}^{0}_{l,m}(\boldsymbol{r}) \tag{15}$$

implicitly contained in the Eq. (6). If k is a non-negative integer (the case considered henceforth), the IST (15) is a uniform tensor polynomial of the Cartesian coordinates x, y, z of the vector $\boldsymbol{r}$. If $k = 0$ then the expression (15) satisfies the Laplace equation, i.e. is a uniform harmonic polynomial. Now write Eq. (6) as

$$\psi_{\alpha,n,l,m}(\boldsymbol{r}) = e_{\alpha,\nu}(r) \mathscr{Y}^{k}_{l,m}(\boldsymbol{r}), \qquad \nu = n - l - 2k \tag{16}$$

Separation of the s-function e in Eq. (16) is not unique. Let $n = 2J(n) + j(n)$, where $J(n)$ is the integral part of $n/2$. For the function e to represent some $|\nu + 1, s\rangle$-state (we also admit $|0, s\rangle$-states described by the Helmholtz function), besides $k \geq 0$, it is also necessary that $\nu = n - l - 2k \geq -1$. Then, we obtain

$$0 \leq k \leq J(n - l + 1). \tag{17}$$

In particular, if $k = 0$, then

$$\psi_{\alpha,n,l,m}(\boldsymbol{r}) = e_{\alpha,n-l}(r) \mathscr{Y}^{0}_{l,m}(\boldsymbol{r}). \tag{18}$$

The other two particular cases

$$\psi_{\alpha,n,l,m}(\boldsymbol{r}) = e_{\alpha,j(n-l)}(r) \mathscr{Y}^{J(n-l)}_{l,m}(\boldsymbol{r}), \tag{19}$$

$$\psi_{\alpha,n,l,m}(\boldsymbol{r}) = e_{\alpha,-j(n-l)}(r) \mathscr{Y}^{J(n-l+1)}_{l,m}(\boldsymbol{r}) \tag{20}$$

correspond to minimum possible principal quantum numbers of the s-state e. For even $n - l$, both the functions $e_{\alpha,j(n-l)} = e_{\alpha,-j(n-l)} = e_{\alpha,0}$ are related to $|1, s\rangle$ type. For odd $n - l$, the functions $e_{\alpha,j(n-l)} = e_{\alpha,1}$ and $e_{\alpha,-j(n-l)} = e_{\alpha,-1}$ are related to $|2, s\rangle$ and $|0, s\rangle$ types, respectively. The quantity k can be chosen arbitrarily in constructing different approximate calculation schemes.

For brevity, denoting

$$\nu_{i(j)} = n_{i(j)} - l_{i(j)} - 2k_{i(j)}, \tag{21}$$

$$\langle i \rangle \equiv \langle \alpha_i, \nu_i \rangle, \qquad \langle i, j \rangle \equiv \langle \alpha_i, \nu_i, \alpha_j, \nu_j \rangle, \tag{22}$$

we write the reduced atomic density as

$$\pi_{\langle i,j \rangle l,m}(\boldsymbol{r}_{1a}, \boldsymbol{r}_{1b}) = \sigma_{\langle i,j \rangle}(r_{1a}, r_{1b}) \{\mathscr{Y}^{k_i}_{l_i}(\boldsymbol{r}_{1a}) \otimes \mathscr{Y}^{k_j}_{l_j}(\boldsymbol{r}_{1b})\}_{l,m}, \tag{23}$$

$$\sigma_{\langle i,j \rangle}(r_{1a}, r_{1b}) = e_{\alpha_i,\nu_i}(r_{1a}) e_{\alpha_j,\nu_j}(r_{1b}). \tag{24}$$

In accordance with the foregoing remark, we apply additive decomposition Eq. (14), not to the total density (23), but to the function σ, i.e. to the product of s-states e.

4. Σ-Factorization in terms of Basis Functions of Correct Symmetry

Since the function σ in any system K' with a polar axis along $\boldsymbol{R}_{ba}$ is Σ-symmetric, it is desirable to use Σ-symmetric functions in auxiliary expansion, too. A simple Euler rotation under which the z-axis assumes the direction $\boldsymbol{R}_{ba}$ is $\Omega = (\varphi_{\boldsymbol{R}}, \theta_{\boldsymbol{R}}, 0)$ (see Fig. 1). Let $D(\boldsymbol{R})$ denote the matrix corresponding to this rotation, and Σ denote the same static relief in the system K' as the function σ in the system K, i.e. $\Sigma(\boldsymbol{r}') = \sigma(\boldsymbol{r})$. To approximate the axisymmetric distribution Σ in the system K', we should use functions with zero momentum projections onto the z'-axis. Thus, the Σ-factorization approximation should have the form:

$$\Sigma(\boldsymbol{r}'_1) = \sum_{(q)} C_{a'(q)}(R)\psi^{a'}_{(q)0}(\boldsymbol{r}'_1) + \sum_{(q)} C_{b'(q)}(R)\psi^{b'}_{(q)0}(\boldsymbol{r}'_1). \tag{25}$$

By virtue of Eq. (11), we obtain

$$\psi_{(q)0}(\boldsymbol{r}'_1) = \sum_{m_q=-l_q}^{l_q} D^{l_q}_{m_q,0}(\boldsymbol{R})\psi_{(q)m_q}(\boldsymbol{r}_1). \tag{26}$$

A particular form of D-function in Eq. (26) with zero momentum projection can be expressed in spherical functions [17f, 18a]

$$D^{l_q}_{m_q,0}(\boldsymbol{R}) \equiv D^{l_q}_{m_q,0}(\varphi_{\boldsymbol{R}}, \theta_{\boldsymbol{R}}, 0) = \sqrt{\frac{4\pi}{2l_q+1}}\, Y_{l_q,m_q}(\boldsymbol{R}). \tag{27}$$

From the definition of the scalar product of two IST of the same rank [17g, 19e]

$$(f_l \cdot \varphi_l) = \sum_m f_{lm}\overset{*}{\varphi}_{lm} \tag{28}$$

after substituting Eq. (27) into Eq. (26), we obtain[4]

$$\psi_{(q)_0}(\boldsymbol{r}'_1) = \sqrt{\frac{4\pi}{2l_q+1}}\,(Y_{l_q}(\boldsymbol{R}) \cdot \psi_{(q)}(\boldsymbol{r}_1)). \tag{29}$$

Hence, from the relation between tensor scalar product and irreducible product [17h, 19f]

$$(Y_l(\boldsymbol{a}) \cdot Y_l(\boldsymbol{b})) = (-l)^l\sqrt{2l+1}\{Y_l(\boldsymbol{a}) \otimes Y_l(\boldsymbol{b})\}_{0,0} \tag{30}$$

we obtain

$$\psi_{(q)_0}(\boldsymbol{r}'_1) = (-1)^{l_q}\sqrt{4\pi}\{Y_{l_q}(\boldsymbol{R}) \otimes \psi_{(q)}(\boldsymbol{r}_1)\}_{0,0}. \tag{31}$$

Formula (31) gives an expression for the basis functions of proper symmetry. By virtue of the relation between Σ and σ, after including the constants into C_a, C_b, we obtain the Σ-factorization equation in the form:

$$\begin{aligned}\sigma_{\langle i,j\rangle}(r_{1a}, r_{1b}) = {} & \sum_{(q)} C^{\langle i,j\rangle}_{a(q)}(R)\{Y_{l_q}(\boldsymbol{R}) \otimes \psi_{(q)}(\boldsymbol{r}_{1a})\}_{0,0} \\ & + \sum_{(q)} C^{\langle i,j\rangle}_{b(q)}(R)\{Y_{l_q}(\boldsymbol{R}) \otimes \psi_{(q)}(\boldsymbol{r}_{1b})\}_{0,0}.\end{aligned} \tag{32}$$

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[4] Analogous statement for usual vectors is trivial, because $(\boldsymbol{R} \cdot \boldsymbol{r}_1)$ is invariant under rotations about an axis parallel to $\boldsymbol{R}$.

The coefficients C, just like in the conventional scheme Eq. (14), can be found, using some variational method. Let us note the difference between the expansion Eq. (32) and conventional scheme Eq. (14). First, Eq. (32) is linear in ψ, while Eq. (14) is bilinear. The inclusion of the double products of atomic orbitals in the Eq. (14) is a forced measure needed to enrich the set of functions of complicate relief geometry. Otherwise, it is impossible to describe reasonably even the qualitative behaviour of atomic density[5]. Possibility to limit the expansion only to terms linear in ψ (pure LCAO form) is the obvious advantage. Second, an auxiliary basis of smaller length, than that in Eq. (14), can be used, because the product of s-functions which is the only function approximated has the simplest geometric structure amongst the atomic densities. Third, the coefficients C in Eq. (32) depend only on the scalar parameter R but not on the vector argument $\boldsymbol{R}$ as in Eq. (14). This is an advantage in calculations involving variation of bond angles. The possibility of the *a priori* construction of auxiliary functions of correct symmetry, and no need for the use of "polarization" functions should also be numbered amongst the merits of the approach.

Substituting Eq. (32) into Eq. (23), and by virtue of the simple property of tensor products [17i, 18f]

$$f_{00}\varphi_{lm} = \{f_0 \otimes \varphi_l\}_{l,m} \tag{33}$$

we obtain

$$\pi_{(i,j)l,m}(\boldsymbol{r}_{1a}, \boldsymbol{r}_{1b}) = \sum_{c=a}^{b} \sum_{(q)} C_{c(q)}^{(i,j)}(R)\rho_{c(q)l,m}^{i,j}(\boldsymbol{r}_{1a}, \boldsymbol{r}_{1b}), \tag{34}$$

$$\rho_{c(q)l,m}^{i,j}(\boldsymbol{r}_{1a}, \boldsymbol{r}_{1b}) = \{\{Y_{l_q}(\boldsymbol{R}) \otimes \psi_{(q)}(\boldsymbol{r}_{1c})\}_0 \otimes \{\mathscr{Y}_{l_i}^{k_i}(\boldsymbol{r}_{1a}) \otimes \mathscr{Y}_{l_j}^{k_j}(\boldsymbol{r}_{1b})\}_l\}_{lm}. \tag{35}$$

Equation (34) for the time being gives a partially decomposed expression for the reduced density. Note that the expression in Eq. (35) depends on four IST exclusively through ITP, i.e. is of purely tensor nature.

5. Addition Theorem for the Polynomials $\mathscr{Y}$

To secure final factorization of the expression (34), a tensor form of the Taylor series should be used for the function $\mathscr{Y}(\boldsymbol{r}_{1c} - \boldsymbol{R})$ in the Eq. (35). Though the result can also be obtained as a particular case of a general expansion [20] valid for any k, we give an independent proof of the theorem for integral k. This case is worth special treatment because the functions $\mathscr{Y}$ have certain properties which are not revealed in the framework of the general formalism. Herewith, there is no need to take recourse to generalized functions [20]. On the other hand, our approach gives a simple generating function for the typical structures involved in the Σ-factorization method and permits us to introduce certain important concepts and relationships.

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[5] In the case of diatomics with minimal (s, p) basis for each atom, the product $p\sigma_a \times p\pi_b$ is orthogonal to all the basis functions. The product $p_a \times p_a = s_a + d_a$ (Clebsch–Gordon series) contains a term d_a, on which the projection of $p\sigma_a \times p\pi_b$ is non-zero.

A fundamental property of the polynomials $\mathcal{Y}$ is that the plane wave is a bilinear generating function for these polynomials. Expanding a plane wave (modified case) as [17j, 21]

$$\exp[2\boldsymbol{ab}] = \sum_{l=0}^{\infty} \left(\frac{\pi}{ab}\right)^{1/2} (l+\tfrac{1}{2}) I_{l+\frac{1}{2}}(2ab) P_l[\cos(\boldsymbol{a}, \boldsymbol{b})], \tag{36}$$

where I_ν is the modified Bessel function and P_l is the Legendre polynomial, and representing $I_{l+\frac{1}{2}}$ as a power series, expressing P_l in a tensor form

$$P_l[\cos(\boldsymbol{a}, \boldsymbol{b})] = (-1)^l 4\pi (2l+1)^{-1/2} \{Y_l(\boldsymbol{a}) \otimes Y_l(\boldsymbol{b})\}_{0,0}, \tag{37}$$

which is equivalent to the addition theorem for spherical functions [17k, 18g] and putting the scalar factors inside the tensor product, we obtain:

$$\exp[2\boldsymbol{ab}] = \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} a(k, l) \{\mathcal{Y}_l^k(\boldsymbol{a}) \otimes \mathcal{Y}_l^k(\boldsymbol{b})\}_{0,0}, \tag{38}$$

$$a(k, l) = (-1)^l 2\pi^{3/2} (2l+1)^{1/2} / [k!\,\Gamma(k+l+3/2)] \tag{39}$$

which proves our assertion.

An addition theorem for the polynomials $\mathcal{Y}$ follows directly from the obvious addition theorem for the generating function Eq. (38)

$$\exp[2\boldsymbol{a}(\boldsymbol{b}-\boldsymbol{c})] = \exp[2\boldsymbol{ab}] \exp[-2\boldsymbol{ac}]. \tag{40}$$

Indeed, using Eq. (38) for all the three exponents in (40), by virtue of Eq. (33), we obtain

$$\begin{aligned} &\sum_{k,l} a(k, l) \{\mathcal{Y}_l^k(\boldsymbol{a}) \otimes \mathcal{Y}_l^k(\boldsymbol{b}-\boldsymbol{c})\}_{0,0} \\ &\quad = \sum_{k_1 l_1 k_2 l_2} a(k_1, l_1) a(k_2, l_2) \{\{\mathcal{Y}_{l_1}^{k_1}(\boldsymbol{a}) \otimes \mathcal{Y}_{l_1}^{k_1}(\boldsymbol{b})\}_0 \otimes \{\mathcal{Y}_{l_2}^{k_2}(\boldsymbol{a}) \otimes \mathcal{Y}_{l_2}^{k_2}(-\boldsymbol{c})\}_0\}_{0,0}. \end{aligned} \tag{41}$$

Reassociating the factors in the irreducible product of four commuting IST (definition of 9*j*-symbols [17l, 18h, 19g]), we obtain

$$\begin{aligned} \{\{P_a \otimes Q_b\}_c \otimes \{R_d \otimes S_e\}_f\}_{k,m} &= \sum_{l,\lambda} \pi_{cfl\lambda} \begin{Bmatrix} a & b & c \\ d & e & f \\ l & \lambda & k \end{Bmatrix} \\ &\quad \times \{\{P_a \otimes R_d\}_l \otimes \{Q_b \otimes S_e\}_\lambda\}_{k,m}, \end{aligned} \tag{42}$$

where $\pi_{cf\ldots} = [(2c+1)(2f+1)\ldots]^{1/2}$. A specific type of Fano's coefficients resulting from the reassociation of the Eq. (41) leads to the selection rule $\lambda = l$, whence [18i, 19h]

$$\begin{Bmatrix} l_1 & l_1 & 0 \\ l_2 & l_2 & 0 \\ l & l & 0 \end{Bmatrix} = \pi^{-1}_{ll_1l_2}. \tag{43}$$

Using the standard addition theorem for spherical functions Y [17m, 18j], we can express the tensor product of the polynomials $\mathcal{Y}$ of the same argument as follows:

$$\{\mathcal{Y}_{l_1}^{k_1}(\boldsymbol{a}) \otimes \mathcal{Y}_{l_2}^{k_2}(\boldsymbol{a})\}_{l,m} = H(l_1, l_2, l)\mathcal{Y}_{l,m}^{k_1+k_2+(l_1+l_2-l)/2}(\boldsymbol{a}), \tag{44}$$

$$H(a, b, c) = (4\pi)^{-1/2}\pi_{ab}\langle a0b0|c0\rangle/\pi_c. \tag{45}$$

By virtue of the selection rule for the Clebsch–Gordon coefficients with zero momentum projections the quantity $l_1 + l_2 - l$ in the Eq. (44) should assume only even integer values.

Introducing the new variable $k = k_1 + k_2 + (l_1 + l_2 - l)/2$, we find that the right-hand side of Eq. (41) can be written in the same form as the left hand side with the exception that, in place of $\mathcal{Y}_l^k(\boldsymbol{b} - \boldsymbol{c})$, there appears some expression with contributions factorized with respect to $\boldsymbol{b}$ and $\boldsymbol{c}$. Since the functions $\mathcal{Y}_{lm}^k$ are linearly independent, the corresponding expressions can be equated to each other. Thus, we obtain the addition theorem for the polynomials $\mathcal{Y}$ (Taylor series in a tensor form):

$$\mathcal{Y}_{lm}^k(\boldsymbol{b} - \boldsymbol{c}) = \sum_{[l_1 k_1 l_2 k_2 | lk]} \mathcal{K}(lk, l_1 k_1, l_2 k_2)\{\mathcal{Y}_{l_1}^{k_1}(\boldsymbol{b}) \otimes \mathcal{Y}_{l_2}^{k_2}(\boldsymbol{c})\}_{l,m}, \tag{46}$$

$$\mathcal{K}(lk, l_1 k_1, l_2 k_2) = (-1)^{l_2} \frac{a(k_1, l_1)a(k_2, l_2)}{a(k, l)} \frac{\pi_l}{\pi_{l_1}\pi_{l_2}} H(l_1, l_2, l). \tag{47}$$

The symbol $[l_1 k_1 l_2 k_2 | lk]$ denotes the conditions imposed on summation variables[6] [22]:

$$l_1, k_1, l_2, k_2 \geq 0, \tag{48a}$$

$$\boldsymbol{l}_1 + \boldsymbol{l}_2 = \boldsymbol{l}, \tag{48b}$$

$$l_1 + 2k_1 + l_2 + 2k_2 = l + 2k. \tag{48c}$$

By virtue of Eq. (48), the right-hand side of Eq. (46) is a triple sum over a finite number of terms. If $k = 0$, by virtue of Eq. (48), we obtain $k_1 = k_2 = 0$, $l_1 + l_2 = l$, i.e. the triple sum in Eq. (46) occurs to be simple. In this case, the formula (46) is reduced to the well known Moshinsky expansion [23].

6. Summation Diagrams

The final factorization of the Eq. (35) is carried out in two steps. First, using the addition theorem (46), we express the product $\{\mathcal{Y}(\boldsymbol{r}_{1a}) \otimes \mathcal{Y}(\boldsymbol{r}_{1b})\}$ as a linear combination of the products $\{\mathcal{Y}(\boldsymbol{R}) \otimes \mathcal{Y}(\boldsymbol{r}_{1c})\}$ with some coefficients S (see Eq. (54)), where $\boldsymbol{r}_{1c} = \boldsymbol{r}_{1a}$ or $\boldsymbol{r}_{1c} = \boldsymbol{r}_{1b}$, depending on the argument of $\psi_{(q)}$ in the Eq. (35). Second, using Eq. (42) and applying the theorem Eq. (44) twice, we express the resulting quadruple IST product with pairwise coinciding arguments as a linear combination of double ITP.

Consider the case $c = a$ in Eq. (35). Writing $\mathcal{Y}(\boldsymbol{r}_{1b})$ as $\mathcal{Y}(\boldsymbol{r}_{1a} - \boldsymbol{R})$, where $\boldsymbol{R} = \boldsymbol{R}_{ba}$, and using the addition theorem Eq. (46), we can express the ITP $\{\mathcal{Y}(\boldsymbol{r}_{1a}) \otimes \mathcal{Y}(\boldsymbol{r}_{1b})\}$

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[6] Formula (6) in [22] is incorrect: its right-hand side should be multiplied by $(-1)^b(4\pi)^{1/2}$.

as a superposition of triple ITP in which two IST have the same argument, $\boldsymbol{r}_{1a}$. Using the relationship (see the definition of 6*j*-symbol [17n, 18k, 19i]):

$$\{\{P_a \otimes Q_b\}_c \otimes R_d\}_{lm} = (-1)^{a+b+c+d} \sum_{\lambda'} \pi_{\lambda' c} \begin{Bmatrix} a & b & c \\ d & l & \lambda' \end{Bmatrix} \{P_a \otimes \{Q_b \times R_d\}_{\lambda'}\}_{lm}, \tag{49}$$

the triple ITP can be reassociated so that the IST of the same argument would be coupled. Using the permutation rule [17o, 18l, 19j]:

$$\{f_l \otimes \varphi_\lambda\}_{\mathrm{LM}} = (-1)^{l+\lambda-L}\{\varphi_\lambda \otimes f_l\}_{\mathrm{LM}} \tag{50}$$

and since the sum of the momenta in $H(l_1, l_2, l)$ is always even, and applying the addition theorem (44), we can express the triple ITP as a linear combination of double ITP. Thus, we obtain

$$\begin{aligned} \{\mathscr{Y}_{l_i}^{k_i}(\boldsymbol{r}_{1a}) \otimes \mathscr{Y}_{l_j}^{k_j}(\boldsymbol{r}_{1b})\}_{lm} = &\sum_{l'_j k'_j l''_j k''_j} \mathscr{K}(l_j k_j, l'_j k'_j, l''_j k''_j) \\ &\times \sum_{\lambda'} \pi_{\lambda' l_j} \begin{Bmatrix} l''_j & l'_j & l_j \\ l_i & l & \lambda' \end{Bmatrix} H(l'_j, l_i, \lambda') \\ &\times \{\mathscr{Y}_{l''_j}^{k''_j}(\boldsymbol{R}) \otimes \mathscr{Y}_{\lambda'}^{k'_j+k_i+(l'_j+l_i-\lambda')/2}(\boldsymbol{r}_{1a})\}_{lm}, \end{aligned} \tag{51}$$

where $[l'_j k'_j l''_j k''_j | l_j k_j]$ (see Eq. (48)), and summation over λ' is taken over all values consistent with the triangle conditions (conservation of momenta) that are implicitly contained in the Racah coefficients in Eq. (51). Thus, summation in Eq. (51) is not simple. The situation is complicated by one more factor. To obtain the coefficients in Eq. (51) in an explicit form, it is necessary to introduce a new variable

$$\nu' = k'_j + k_i + (l'_j + l_i - \lambda')/2 \tag{52}$$

and to change the summation order so that $l''_j, k''_j, \lambda', \nu'$ become the outer summation variables.

Intricate summations and change of summation order are the typical difficulties encountered when one applies the Racah algebra to molecular [22, 24] and nuclear [25] problems. We give here a simple and convenient procedure for these transformations. The conditions imposed on all the indices in Eq. (51) (both outer variables and summation variables) can be represented by the diagram in Fig. 2a. Each simple vertex contains some orbital moment, while a double vertex contains an orbital moment and an "energy" variable (of the type k in Eq. (48). Simple triangle corresponds to the triangle condition imposed on momenta by the Racah coefficients (as well as by the quantities $\mathscr{K}$ and H). Altogether, there are four conditions for the conservation of momentum. Double triangle means that for variables at the double vertex, besides the "orbital" condition the "energy" condition Eq. (48c) is also fulfilled (solid line means that the corresponding energy combinations of the type $l+2k$ are contained on the same side of the equation and have the same sign). Outer vertices correspond to outer (fixed) indices, while inner ones-to inner (summation) variables.

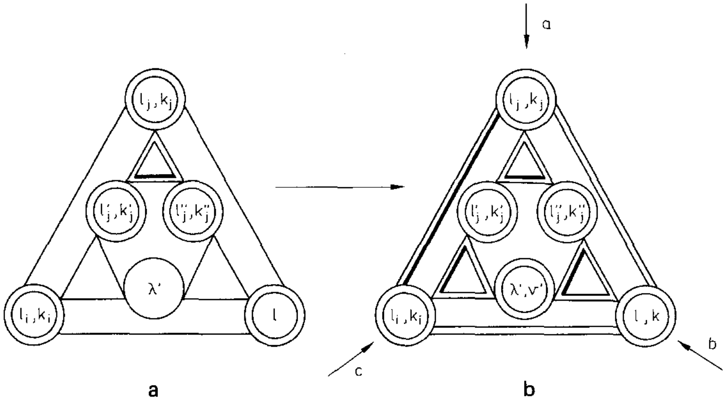

Fig. 2. Summation diagram for coefficients S (54), (55) (for explanation see Sect. 6 and 7)

Obviously, a double triangle corresponds to the total set of the conditions Eq. (48).

Such a diagram can be symmetrized, if all simple vertices and triangles are transformed into double ones, by introducing additional "energy" variables for simple vertices and imposing a condition of the type (48c) on each new triplet. Analytically, this procedure is unique for any simple triangle with two double vertices, say, for the triangle on the bottom to the left in Fig. 2a. By induction, this, in turn, gives a unique procedure for the triangle on the right as well. As a result we obtain a symmetric diagram (Fig. 2b) in which six double sets of indices are related by the following four sets of similar conditions

$$[l_ik_il_jk_j|lk],\ [l'_jk'_jl''_jk''_j|l_jk_j],\ [l'_jk'_jl_ik_i|\lambda'\nu'],\ [l''_jk''_j\lambda'\nu'|lk]. \tag{53}$$

It is easy to show that the "energy" equality corresponding to any of these four sets follows from the other three conditions.

7. Final Decomposition of Reduced Density

Due to the symmetry of the diagram (Fig. 2b), we can choose either the summation route b or the route c, in place of the initial path a. Analytically, this means the sets in Eq. (53) can be permuted without violating the conditions contained in them. Therefore, any set of primed indices in one of the three sets in Eq. (53) (except the first) can be taken as the outer summation variables. Choosing the summation route b (Fig. 2b), we obtain

$$\{\mathscr{Y}^{k_i}_{l_i}(\boldsymbol{r}_{1a})\otimes\mathscr{Y}^{k_j}_{l_j}(\boldsymbol{r}_{1b})\}_{lm}=\sum_{\substack{\text{all}\\ \text{primes}}} S^{l_ik_il_jk_j}_{l''_jk''_j\lambda'\nu'}(l,a)\{\mathscr{Y}^{k''_j}_{l''_j}(\boldsymbol{R})\otimes\mathscr{Y}^{\nu'}_{\lambda'}(\boldsymbol{r}_{1a})\}_{lm} \tag{54}$$

$$S^{l_ik_il_jk_j}_{l''_jk''_j\lambda'\nu'}(l,a)=\pi_{\lambda'l_j}\sum_{l'_jk'_j}\mathscr{K}(l_ik_j,l'_jk'_j,l''_jk''_j)H(l'_j,l_i,\lambda')\begin{Bmatrix} l''_j & l'_j & l_j\\ l_i & l & \lambda'\end{Bmatrix} \tag{55}$$

where[7]

$$[l_j''k_j''\lambda'\nu'|lk],\ [l_j'k_j'l_j''k_j''|l_jk_j],\ [l_j'k_j'l_ik_i|\lambda'\nu'] \tag{56}$$

and

$$[l_ik_il_jk_j|lk]. \tag{57}$$

In calculating the coefficients S, note that summation in Eq. (55) is, in fact, simple, since by virtue of Eq. (52), the index k_j' can be expressed through outer, with respect to k_j', parameters. Nevertheless, the expressions in Eqs. (55)–(57) are more convenient in further consideration.

For $c = b$, in Eq. (54), we should put $\boldsymbol{r}_{1a} = \boldsymbol{r}_{1b} + \boldsymbol{R}$. Because of Eq. (50) and due to the equality [17p, 18m]

$$\mathcal{Y}^{k}_{lm}(-\boldsymbol{R}) = (-1)^{l}\mathcal{Y}^{k}_{lm}(\boldsymbol{R}) \tag{58}$$

we can readily show that factorization of the left-hand side of Eq. (54) over $\boldsymbol{R}$, $\boldsymbol{r}_{1b}$ is given by a similar expression, with the exception that

$$S^{l_ik_il_jk_j}_{l_j''k_j''\lambda'\nu'}(l, b) = (-1)^{l_i+l_j+l_j''+l} S^{l_jk_jl_ik_i}_{l_j''k_j''\lambda'\nu'}(l, a). \tag{59}$$

The coefficients $S(l, a)$, $S(l, b)$ are particular cases of the general coefficients $S(l, \delta)$, which represent a specially parametrized form of the Smirnov coefficients [22] and depend on continuous parameter $\delta(-1 \leq \delta \leq 1)$. Accurate to a phase factor, $\delta = 1$ for $S(l, a)$ and $\delta = -1$ for $S(l, b)$. For the particular coefficient $S(l, \pm 1)$, we obtain a simplification not inherent in the general case.

Using Eq. (54), the expression (35) for the density can be rewritten in a one-centre form:

$$\rho^{i,j}_{c(q)l,m} = \sum_{l_j''k_j''\lambda'\nu'} S^{l_ik_il_jk_j}_{l_j''k_j''\lambda'\nu'}(l, c)\{\{Y_{l_q}(\boldsymbol{R}) \otimes \psi_{(q)}(\boldsymbol{r}_{1c})\}_0 \otimes \{\mathcal{Y}^{k_j''}_{l_j''}(\boldsymbol{R}) \otimes \mathcal{Y}^{\nu'}_{\lambda'}(\boldsymbol{r}_{1c})\}_l\}_{lm} \tag{60}$$

where $c = a, b$.

To simplify this expression we should couple one-centre contributions. Taking the scalar factors $e_{\alpha_q,n_q}(r_{1c})$ outside the sign of ITP, expressing both spherical functions in the first ITP as $\mathcal{Y}^{-l_q/2}_{l_q,m_q}$, using the reassociation rule Eq. (42), and since [17q, 18n, 19k]

$$\begin{Bmatrix} l_q & l_q & 0 \\ l_j'' & \lambda' & l \\ l_1 & l_2 & l \end{Bmatrix} = (-1)^{l_1+\lambda'+l+l_q}\pi^{-1}_{l_ql}\begin{Bmatrix} l_2 & l & l \\ l_j'' & \lambda' & l_q \end{Bmatrix}, \tag{61}$$

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[7] The definition of k is contained in Eq. (57). Eq. (52) is contained in the third set of Eq. (56). The structure of summation over l_j'', k_j'', λ', ν' in Eq. (54) is described by the first set in Eq. (56). The range of summation over l_j', k_j' (l_j'', k_j'', λ', ν' being fixed) in Eq. (55) is described by the second and third sets in Eq. (56). The dependence of S in Eq. (55) on ν' is implicitly defined by the third set in Eq. (56).

after applying the addition theorem Eq. (44) twice, we obtain

$$\{\{Y_{l_q}(\boldsymbol{R}) \otimes \psi_{(q)}(\boldsymbol{r}_{1c})\}_0 \otimes \{\mathcal{Y}_{l''_j}^{k''_j}(\boldsymbol{R}) \otimes \mathcal{Y}_{\lambda'}^{\nu'}(\boldsymbol{r}_{1c})\}_l\}_{lm}$$

$$= \sum_{l_1,l_2} G_{l_q l_1 l_2 l}^{l''_j\lambda'}\{\mathcal{Y}_{l_1}^{k''_j+(l''_j-l_1)/2}(\boldsymbol{R}) \otimes \mathcal{Y}_{l_2}^{\nu'+(\lambda'-l_2)/2}(\boldsymbol{r}_{1c})\}_{lm} e_{\alpha_q,n_q}(r_{1c}), \tag{62}$$

$$G_{l_q l_1 l_2 l}^{l''_j\lambda'} = (-1)^{l_1+\lambda'+l+l_q} \pi_{l_1 l_2} \pi_{l_q}^{-1} H(l_q, l''_j, l_1) H(l_q, \lambda', l_2) \begin{Bmatrix} l_2 & l_1 & l \\ l''_j & \lambda' & l_q \end{Bmatrix}. \tag{63}$$

Substituting Eq. (62) into Eq. (60), introduce the following new summation variables:

$$n_1 = k''_j + (l''_j - l_1)/2, \qquad n_2 = \nu' + (\lambda' - l_2)/2. \tag{64}$$

To determine the new coefficients T, the indices l_1, n_1, l_2, n_2 should be given the meaning of outer summation variables. In terms of the summation diagrams, Eq. (62) is described by a six-vertex graph similar to that in Fig. 2b (the factors $Y_{l_q}(\boldsymbol{R})$ and $\psi_{(q)}(\boldsymbol{r}_{1c})$ can be represented by the same vertex with the indices l_q, $-l_q/2$).

Duplicating all the elements in the graph and combining it with the diagram in Fig. 2b and since both graphs have three common vertices, we obtain the diagram in Fig. 3 which describes the resulting summation. Allowing for the possibility of different routes, we obtain

$$\rho_{c(q)l,m}^{i,j} = \sum_{l_1 n_1 l_2 n_2} T_{l_1 n_1 l_2 n_2}^{i,j(q)}(l, c)\{\mathcal{Y}_{l_1}^{n_1}(\boldsymbol{R}) \otimes \mathcal{Y}_{l_2}^{n_2}(\boldsymbol{r}_{1c})\}_{l,m} e_{\alpha_q,n_q}(r_{1c}), \tag{65}$$

$$T_{l_1 n_1 l_2 n_2}^{i,j(q)}(l, c) = \sum_{l''_j k''_j \lambda' \nu'} S_{l''_j k''_j \lambda' \nu'}^{l_i k_i l_j k_j}(l, c) G_{l_q l_1 l_2 l}^{l''_j\lambda'}, \tag{66}$$

where

$$[l_1 n_1 l_2 n_2 | lk], [l_1 n_1 l_q - l_q/2 | l''_j k''_j], [l_2 n_2 l_q - l_q/2 | \lambda' \nu'], [l''_j k''_j \lambda' \nu' | lk]. \tag{67}$$

In calculating the coefficients T, one should take into account that not all the summation variables in Eq. (67) are linearly independent. These dependences can be easily found from Eq. (48) for each condition set in Eq. (67) (or from the summation diagram Fig. 3).

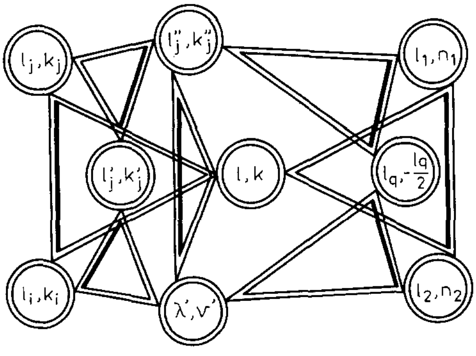

Fig. 3. Summation diagram for coefficients T (65), (66) (for explanation see Sect. 7)

8. Summary

To present a general outline of the Σ-factorization method we shall give here the most important equations which constitute the technical background of the method.

First, we introduce the reduced atomic density in accordance with Eq. (12) as follows

$$\pi_{(i,j)l,m}(\boldsymbol{r}_{1a}, \boldsymbol{r}_{1b}) = \{\psi_{(i)}(\boldsymbol{r}_{1a}) \otimes \psi_{(j)}(\boldsymbol{r}_{1b})\}_{l,m}. \tag{68}$$

The initial direct atomic product Π has the following simple expression in terms of the reduced densities

$$\Pi_{(i,j)m_i,m_j}(\boldsymbol{r}_{1a}, \boldsymbol{r}_{1b}) = \sum_{l} \langle l_i m_i l_j m_j | l, m_i + m_j \rangle \pi_{(i,j)l,m_i+m_j}(\boldsymbol{r}_{1a}, \boldsymbol{r}_{1b}), \tag{69}$$

Second, in agreement with Eq. (23) we separate the quantity π onto the exponential part σ possessing the simple Σ-symmetry and the polynomial part $\{\mathscr{Y} \otimes \mathscr{Y}\}$

$$\pi_{(i,j)l,m}(\boldsymbol{r}_{1a}, \boldsymbol{r}_{1b}) = \sigma_{\langle i,j \rangle}(r_{1a}, r_{1b}) \{\mathscr{Y}_{l_i}^{k_i}(\boldsymbol{r}_{1a}) \otimes \mathscr{Y}_{l_j}^{k_j}(\boldsymbol{r}_{1b})\}_{l,m}, \tag{70}$$

where

$$\sigma_{\langle i,j \rangle}(r_{1a}, r_{1b}) = e_{\alpha_i, n_i - l_i - 2k_i}(r_{1a}) e_{\alpha_j, n_j - l_j - 2k_j}(r_{1b}) \equiv e_{\alpha_i, \nu_i} e_{\alpha_j, \nu_j} \tag{71}$$

and

$$0 \le k_i \le J(n_i - l_i + 1), \qquad 0 \le k_j \le J(n_j - l_j + 1) \tag{72}$$

The application of the least square method procedure for the additive separation of the σ-part of the density π (Σ-factorization) with the polynomial part $\{\mathscr{Y} \otimes \mathscr{Y}\}$ left untouched at this stage leads to the partial additive factorization of the density π which in agreement with Eqs. (34), (35) takes the form

$$\pi_{(i,j)l,m}(\boldsymbol{r}_{1a}, \boldsymbol{r}_{1b}) = \sum_{c=a}^{b} \sum_{(q)} C_{c(q)}^{\langle i,j \rangle}(\boldsymbol{R}) \rho_{c(q)l,m}^{i,j}(\boldsymbol{r}_{1a}, \boldsymbol{r}_{1b}), \tag{73}$$

$$\rho_{c(q)l,m}^{i,j}(\boldsymbol{r}_{1a}, \boldsymbol{r}_{1b}) = \{\{Y_{l_q}(\boldsymbol{R}) \otimes \psi_{(q)}(\boldsymbol{r}_{1c})\}_0 \otimes \{\mathscr{Y}_{l_i}^{k_i}(\boldsymbol{r}_{1a}) \otimes \mathscr{Y}_{l_j}^{k_j}(\boldsymbol{r}_{1b})\}_l\}_{l,m} \tag{74}$$

With the help of the translation transformation (54) for the polynomials $\mathscr{Y}$ the quantity ρ in Eq. (74) can be expressed in one-centre form as in Eq. (60)

$$\rho_{c(q)l,m}^{i,j} = \sum_{l_j'' k_j'' \lambda' \nu'} S_{l_j'' k_j'' \lambda' \nu'}^{l_i k_i l_j k_j}(l, c) \{\{Y_{l_q}(\boldsymbol{R}) \otimes \psi_{(q)}(\boldsymbol{r}_{1c})\}_0 \otimes \{\mathscr{Y}_{l_j''}^{k_j''}(\boldsymbol{R}) \otimes \mathscr{Y}_{\lambda'}^{\nu'}(\boldsymbol{r}_{1c})\}_{l,m} \tag{75}$$

which, however, is not expedient for calculations since one-centre contributions enter into this equation in an uncoupled form. The reassociation of the quadruple tensor product in Eq. (75) according to Eqs. (62), (63), (64) leads to a new type of transformation coefficients T Eq. (66) and permits a compact one-centre representation of the density ρ

$$\rho^{i,j}_{c(q)l,m} = \sum_{l_1,n_1l_2n_2} T^{i,j(q)}_{l_1n_1l_2n_2}(l, c)\{\mathcal{Y}^{n_1}_{l_1}(\boldsymbol{R}) \otimes \mathcal{Y}^{n_2}_{l_2}(\boldsymbol{r}_{1c})\}_{lm} e_{\alpha_q,n_q}(r_{1c}). \tag{76}$$

All the necessary summations in Eqs. (75), (76) along with the conditions on the outer summation indices are represented by the diagrams in Figs. 2 and 3.

9. Concluding Remarks

Thus, using the Σ-factorization approach, we can reformulate the problem of additive factorization of electron density in the class of one-centre functions.

The concept of reduced atomic density Eq. (68) permits us to formulate the problem in terms of tensor products, to avoid the piling of the Clebsh–Gordon coefficients in the intermediate calculations, and facilitates the use of the Racah algebra. Such a formulation is not a "superfluous" artificial step which could be avoided with the help of some other technique. In fact, the tensor nature of the initial objects gives rise to, in some way, a transformation of the type (69), which is often masked by the introduction of unconventional auxiliary coefficients and functions.

Separation of the σ-part in Eq. (70) permits us to represent the two-center atomic density as the product of the exponential expression σ (71) which is analytically complicated yet possesses the simple Σ-symmetry and the polynomial expression $\{\mathcal{Y} \otimes \mathcal{Y}\}$ which is, *vice versa*, analytically simple yet possesses an intricate symmetry. Since the latter expression can be factorized exactly with the help of the addition theorems, this permits us to deal with the densities of any complicate geometry (large orbital numbers l) while applying the approximate Σ-factorization procedure only to the simplest exponential product σ. Evidently, this hints at the possible application of the Σ-factorization method to compounds with complex ions.

Various approximation schemes are possible as the representation of atomic density Eq. (70) in the form of a product of exponential and polynomial distributions is not unique. In the particular cases $k_i = J(n_i - l_i)$, $k_j = J(n_j - l_j)$ or $k_i = J(n_i - l_i + 1)$, $k_j = J(n_j - l_j + 1)$ in Eq. (70), approximate factorization with the help of LSM is applied to the product of states possessing not only minimum orbital, numbers l_i, l_j, but also minimum principal quantum numbers $\nu_i + 1$, $\nu_j + 1$ (see the note to Eqs. (19), (20)). Bounded number of approximated functions guarantees more uniform error for different states and better control over approximation. This is achieved through cumbersome translation formulas for non-harmonic polynomials in Eqs. (19) and (20) which leads to triple sum in Eq. (46). On the other hand, in the case of harmonic approximation Eq. (18), the corresponding sums are simple (see the note to Eq. (48)), consequently the formalism is simplified.

The heavy use of the Racah algebra is unavoidable to present the approximate LSM-decomposition of the σ-distribution, the exact translational factorization of the polynomial part and the subsequent reduction of quadruple ITP in Eq. (74) in a uniform and compact manner. This results in a new type of the transformation coefficient T in Eq. (76), whose calculation is the central point of the method as regards to the technical details. It is important that the coefficients T are directly related to the standard kinematical constants of the angular momentum theory. The summation diagram technique simplifies the analysis and determination of these coefficients.

Evidently, the use of the Mulliken approximation (or any other two-term approximation) to factorize the σ-component of density, while preserving the exact form of the angular part leads to a much simpler expression for the coefficients T. Since the Σ-factorization approach takes account of the exact behaviour of density due to the two-center product of spherical functions, the error in the minimal Σ-factorization method is due, exclusively, to the approximation of the s-function product and, therefore, is uniform for the basis functions with arbitrary orbital quantum numbers. Hencewith, it should not exceed the error in the Mulliken approximation for the s-functions. It is well known, the Mulliken approximation gives much better results for the s-functions than for any other functions [5, 11, 14, 26]. This indirectly suggests that even the minimal Σ-approximation might prove useful in describing the electron structure of compounds with heavy atoms.

Acknowledgment. The authors express their gratitude to N. M. Klimenko, O. P. Charkin and W. Kołos for useful discussion of the problems considered in this paper.

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Received September 23, 1981/July 5, 1982