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ORIGINAL PAPER

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Addition and expansion theorems for complete orthonormal sets of exponential-type orbitals in coordinate and momentum representations

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Abstract Analytical properties of new complete orthonormal sets of Ψ^α exponential-type orbitals (Ψ^α-ETOs where α=1, 0, −1, −2, ...), introduced by the author as finite linear combinations of Slater-type orbitals (STOs), are studied. Addition and expansion theorems for Ψ^α-ETOs are obtained in both coordinate and momentum representations. Using expressions of Ψ^α-ETOs in terms of STOs, the new methods are suggested to calculate multicenter multielectron integrals over STOs.

Keywords Exponential-type orbitals · Slater-type orbitals · Multicenter integrals · Fourier transform method

Introduction

It is well known that multicenter molecular integrals, which appear in the mathematical expressions of physical and chemical properties of molecules, are evaluated by the use of two types of orbitals: Gaussian-type orbitals (GTOs) and exponential-type orbitals (ETOs). As emphasized in [1], GTOs do not allow an adequate representation of important properties of the electronic wavefunction, such as the cusps at the nuclei [2] and the exponential decay at large distances. [3] For problems in which the long part of the wavefunction or its behavior in the neighborhood of the nuclei is important, it is desirable to use ETOs, which describe the physical situation more accurately than GTOs. Therefore, GTOs are inferior to ETOs in the study of molecular properties. However, difficulties in the calculation of multicenter molecular integrals have restricted the use of ETOs in quantum chemistry. As shown in the literature, there is now renewed interest in developing efficient methods for calculating molecular integrals by employing ETOs as basis sets (see e.g. [4, 5, 6, 7, 8, 9, 10] and the bibliography quoted in these papers). Thus, a thorough investigation of the analytical properties of ETOs is an urgent problem relevant to both the theory and practice of calculations dealing with atoms, molecules, and solids.

Computations of matrix elements in the molecular orbital (MO) linear combination of atomic orbitals (LCAO) theory for ETOs, in both coordinate and momentum representations, involve some difficulties, so one has to look for the most expedient analytical methods. On the other hand, the elaboration of algorithms for the calculation of matrix elements in the MO LCAO theory with Slater-type orbitals (STOs), which are a special case of the ETOs, necessitates progress in the development of methods to calculate multicenter integrals over ETOs.

The aim of this work is to present proofs for the relevant addition and expansion theorems of Ψ^α-ETOs, in both the coordinate and momentum spaces, and to yield methods for calculation of multicenter multielectron integrals, which appear in MO LCAO theory in the Ψ^α-ETOs basis.

Expansion theorems for products of ETOs

Coordinate representation

The Ψ^α-ETOs in the coordinate representation are defined by [11]

$$\Psi^\alpha_{nlm}(\zeta,\vec{r}) = R^\alpha_{nl}(\zeta,r)S_{lm}(\theta,\varphi) \tag{1}$$

$$R^\alpha_{nl}(\zeta,\vec{r}) = (-1)^\alpha\left[\frac{(2\zeta)^3(n-l-1)!}{(2n)^\alpha[(n+l+1-\alpha)!]^3}\right]^{1/2} \cdot (2\zeta r)^l e^{-\zeta r} L^{2l+2-\alpha}_{n+/+l-\alpha}(2\zeta r) \tag{2}$$

where α=1, 0, −1, −2, ..., ζ is the screening parameter $(0<\zeta<\infty)$ and L^p_q is the generalized Laguerre polynomial. [12] The spherical harmonics $S_{lm}(\theta,\phi)$ in Eq. (1) are determined by relation

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$$S_{lm}(\theta,\phi) = P_{l|m|}(\cos\theta)\Phi_m(\phi) \tag{3}$$

where $P_{l|m|}$ are normalized associated Legendre functions [12] and for complex spherical harmonics ($S_{lm} \equiv Y_{lm}$)

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi} \tag{4}$$

for real spherical harmonics

$$\Phi_m(\phi) = \frac{1}{\sqrt{\pi(1+\delta_{m0})}} \begin{cases} \cos|m|\phi \text{for} & m \geq 0 \\ \sin|m|\phi \text{for} & m < 0 \end{cases} \tag{5}$$

We notice that the definition of phases in this work for the complex spherical harmonics $\left(Y^*_{lm} = Y_{l-m}\right)$ differ from the Condon–Shortley phases [13] by the sign factor $(-1)^m$.

The Ψ^α are transformed into the STOs by [11]

$$\Psi^\alpha_{nlm}(\zeta,\vec{r}) = \sum_{n'=l+1}^{n} \omega^{\alpha l}_{nn'} \chi_{n'lm}(\zeta,\vec{r}) \tag{6}$$

$$R^\alpha_{nl}(\zeta,\vec{r}) = \sum_{n'=l+1}^{n} \omega^{\alpha l}_{nn'} R_{n'}(\zeta,\vec{r}) \tag{7}$$

where

$$\omega^{\alpha l}_{nn'} = (-1)^{n'-l-1}\left[\frac{(n'+l+1)!}{(2n)^\alpha(n'+l+1-\alpha)!} F_{n'+l+1-\alpha}(n+l+1 -\alpha) F_{n'-l-1}(n-l-1) \times F_{n'-l-1}(2n')\right]^{1/2} \tag{8}$$

$$\chi_{nlm}(\zeta,\vec{r}) = R^n(\zeta,r) S_{lm}(\theta,\varphi) \tag{9}$$

$$R_n(\zeta,r) = (2\zeta)^{n+1/2}[(2n)!]^{-1/2} r^{n-1} e^{-\zeta r} \tag{10}$$

Here $\chi_{nlm}(\zeta,\vec{r})$ are the normalized STOs and $F_s(n) = n!/[s!(n-s)!]$ is the binomial coefficient.

Now we can obtain the expansion theorem for the product of two Ψ^α-ETOs by representing it as a finite sum of Ψ^α-ETO terms:

$$\Psi^{\alpha*}{}_{nlm}(\zeta,\vec{r})\Psi^\alpha_{n'l'm'}(\zeta',\vec{r}) = (2z)^{3/2} \sum_{N=1}^{n+n'+1} \sum_{L=0}^{N-1} \sum_{M=-1}^{L} B^{\alpha NLM}_{nlm,n'l'm'}(\zeta,\zeta',z) \Psi^{\alpha*}_{NLM}(z,\vec{r}) \tag{11}$$

where $z = \zeta + \zeta'$ and

$$B^{\alpha NLM}_{nlm,n'l'm'}(\zeta,\zeta',z) = \frac{1}{(2z)^{3/2}} \int \Psi^{\alpha*}{}_{n'l'm'}(\zeta,\vec{r}) \cdot \Psi^\alpha{}_{n'l'm'}(\zeta',\vec{r}) \overline{\Psi}^\alpha_{NLM}(z,\vec{r}) d^3\vec{r} \tag{12}$$

$$\overline{\Psi}^\alpha_{nlm}(\zeta,\vec{r}) = \left(\frac{n}{\zeta r}\right)^\alpha \Psi^\alpha_{nlm}(\zeta,\vec{r}) = \overline{R}^\alpha_{nl}(\zeta,r) S_{lm}(\theta,\varphi) \tag{13}$$

$$\overline{R}^\alpha_{nl}(\zeta,r) = \left(\frac{n}{\zeta r}\right)^\alpha R^\alpha_{nl}(\zeta,r) \tag{14}$$

Here we have taken into account the orthonormality relation of Ψ^α_{nlm}–ETOswith$\overline{\Psi}^\alpha_{nlm}$–ETOs functions (see Eq. (4) of [11]):

$$\int \Psi^{\alpha*}_{nlm}(\zeta,\vec{r}) \overline{\Psi}^\alpha_{n'l'm'}(\zeta,\vec{r}) d^3\vec{r} = \int \Psi^{\alpha*}_{nlm}(\zeta,\vec{r}) \left(\frac{n'}{\zeta r}\right)^\alpha \Psi^\alpha_{n'l'm'}(\zeta,\vec{r}) d^3\vec{r} = \delta_{nn'}\delta_{ll'}\delta_{mm'} \tag{15}$$

Thus, the coefficients $B^{\alpha NLM}_{nlm,n'l'm'}$ are obtained by multiplying Eq. (11) by $\overline{\Psi}^\alpha_{N'L'M'}(z,\vec{r})$ and taking into account the fact that the functions $\Psi^\alpha_{NLM}(z,\vec{r})$ are orthogonal with the weight $(N/zr)^\alpha$.

It is easy to show that the $\overline{\Psi}^\alpha_{nlm}$–ETOs are also represented as finite linear combinations of STOs:

$$\overline{\Psi}^\alpha_{nlm}(\zeta,\vec{r}) = (2n)^\alpha \sum_{n'=l+1}^{n} \omega^{\alpha l}_{nn'} \left[\frac{(2(n'-\alpha))!}{(2n')!}\right]^{1/2} \cdot \chi_{n'-\alpha\, lm}(\zeta,\vec{r}) \tag{16}$$

Note that the scale parameter of the function $\Psi^\alpha_{NLM}(z,\vec{r})$ in Eq. (11) must be $z = \zeta + \zeta$, because of addition of the exponents of the functions (2).

Now using Eqs. (6), (7), (16) and the result [14]

$$S^*_{lm}(\theta,\varphi) S_{l'm'}(\theta,\varphi) = \sum_{L=|l-l'|}^{l+l'} \sum_{M=-l}^{L} \left(\frac{2L+1}{4\pi}\right)^{1/2} \cdot C^{L|M|}(lm,l'm') A^M_{mm'} S^*_{LM}(\theta,\varphi) \tag{17}$$

we get from Eq. (12)

$$B^{\alpha NLM}_{nlm,n'l'm'}(\zeta,\zeta',z) = \left(\frac{2L+1}{4\pi}\right)^{1/2} C^{L|M|}(lm,l'm') A^M_{mm'} \times (2N)^\alpha \sum_{k=l+1}^{n} \sum_{k'=l'+1}^{n'} \sum_{K=L+1}^{N} \omega^{\alpha l}_{nk} \omega^{\alpha l'}_{n'k'} \omega^{\alpha l}_{NK} \cdot \frac{(k+k'+K-\alpha-1)!}{[(2k)!(2k')!(2K)!]^{1/2}} \left(\frac{\zeta}{z}\right)^{k+1/2} \left(\frac{\zeta'}{z}\right)^{k'+1/2} \tag{18}$$

where

$$A^M_{mm'} = \begin{cases} \delta_{M,m-m'} & \text{for complex } S_{lm} \\ \frac{1}{\sqrt{2}}\left(2 - \left|\eta^{m-m'}_{mm'}\right|\right)^{1/2} \delta_{M,\varepsilon|m-m'|} + \frac{1}{\sqrt{2}} \eta^{m+m'}_{mm'} \delta_{M,\varepsilon|m-m'|} & \text{for real } S_{lm}. \end{cases} \tag{19}$$

Here the symbol $\varepsilon \equiv \varepsilon_{mm'}$ may have the values ±1 the sign of which is determined by the product of the signs m and m' (the sign of zero is regarded as positive). The symbol $\eta^{m\pm m'}_{mm'}$ may be have the values ±1 and 0: if among the indices m, m' and $m \pm m'$ there occurs a value equal to zero, then $\eta_{mm'}^{m\pm m'}$ is also zero; if all the indices differ from zero, $\eta_{mm'}^{m\pm m'} = \pm 1$ and the sign is determined by the product of the signs of m, $\acute{m}$ and $m\pm\acute{m}$. Thus the coefficients $A_{mm'}^{M}$ differ from zero only with the values $M=m'-m'$, $m+m'$. Therefore, in the case of real spherical harmonics in Eq. (17), we have two kinds of coefficients $C^{L|m-m'|}$ and $C^{L|m+m'|}$ determined by

$$C^{L|M|}(lm,l'm') = \begin{cases} C^{L}(lm,l'm') & \text{for}|M| = |m-m'| \\ C^{L}(lm,l'-m') & \text{for}|M| = |m+m'| \end{cases} \tag{20}$$

where $C^{L}(lm,l'm')$ is the known Gaunt coefficient.

As can be seen from Eqs. (11) and (18), the resulting expansion of the product of Ψ^{α}-ETOs is a finite sum of Ψ^{α}-ETOs terms, that is the expansion theorem for complete orthonormal sets Ψ^{α}-ETOs in the coordinate representation.

Momentum representation

The Ψ^{α}-ETOs and $\overline{\Psi}^{\alpha}-$ETOs in the momentum representation are defined as the Fourier transforms of the functions (6) and (13), respectively:

$$\Phi_{nlm}^{\alpha}\left(\zeta,\vec{k}\right) = (2\pi)^{-3/2}\int e^{-i\vec{k}\vec{r}}\Psi_{nlm}^{\alpha}(\zeta,\vec{r})d^{3}\vec{r} \tag{21}$$

$$\overline{\Phi}_{nlm}^{\alpha}\left(\zeta,\vec{k}\right) = (2\pi)^{-3/2}\int e^{-i\vec{k}\vec{r}}\overline{\Psi}_{nlm}^{\alpha}(\zeta,\vec{r})d^{3}\vec{r} \tag{22}$$

Taking into account Eqs. (6) and (16) in Eqs. (21) and (22) we obtain:

$$\Phi_{nlm}^{\alpha}\left(\zeta,\vec{k}\right) = \sum_{n'=l+1}^{n}\omega_{nn'}^{\alpha l}U_{n'lm}\left(\zeta,\vec{k}\right) \tag{23}$$

$$\overline{\Phi}_{nlm}^{\alpha}\left(\zeta,\vec{k}\right) = (2n)^{\alpha}\sum_{n'=l+1}^{n}\omega_{nn'}^{\alpha\, l}\left[\frac{(2(n'-\alpha))!}{(2n')!}\right]^{1/2}\cdot \cdot U_{n'-\alpha lm}\left(\zeta,\vec{k}\right) \tag{24}$$

where $U_{nlm}\left(\zeta,\vec{k}\right)$ is the Fourier transform of the STOs:

$$U_{nlm}\left(\zeta,\vec{k}\right) = (2\pi)^{-3/2}\int e^{-i\vec{k}\vec{r}}\chi_{nlm}(\zeta,\vec{r})d^{3}\vec{r} \tag{25}$$

It should be noted that the Fourier transformations convert the functions

$\Phi_{nlm}^{\alpha}\left(\zeta,\vec{k}\right)$, $\overline{\Phi}_{nlm}^{\alpha}\left(\zeta,\vec{k}\right)$ and $U_{nlm}\left(\zeta,\vec{k}\right)$

into the functions

$\Phi_{nlm}^{\alpha}(\zeta,\vec{r}), \overline{\Phi}_{nlm}^{\alpha}(\zeta,\vec{r})$ and $\chi_{nlm}(\zeta,\vec{r})$:

$$\Psi_{nlm}^{\alpha}(\zeta,\vec{r}) = (2\pi)^{-3/2}\int e^{i\vec{k}\vec{r}}\Phi_{nlm}^{\alpha}\left(\zeta,\vec{k}\right)d^{3}\vec{k} \tag{26}$$

$$\Psi_{nlm}^{\alpha}(\zeta,\vec{r}) = (2\pi)^{-3/2}\int e^{i\vec{k}\vec{r}}\overline{\Phi}_{nlm}^{\alpha}\left(\zeta,\vec{k}\right)d^{3}\vec{k} \tag{27}$$

$$\chi_{nlm}(\zeta,\vec{r}) = (2\pi)^{-3/2}\int e^{i\vec{k}\vec{r}}U_{nlm}\left(\zeta,\vec{k}\right)d^{3}\vec{k} \tag{28}$$

In order to calculate $U_{nlm}\left(\zeta,\vec{k}\right)$, we use the known expansion of $e^{i\vec{k}\vec{r}}$ into a series over the spherical harmonics:

$$e^{i\vec{k}\vec{r}} = 4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l}j_{l}(kr)S_{lm}(\vec{r}/r)\tilde{S}^{*}{}_{lm}\left(\vec{k}/k\right) \tag{29}$$

where $\tilde{S}_{lm}\left(\vec{k}/k\right) = (-i)^{l}S_{lm}\left(\vec{k}/k\right)$ is a modified spherical harmonic in momentum space, $j_l(kr)$ is the spherical Bessel function. The functions $j_l(kr)$ can be expressed in terms of Bessel functions of the first kind in the form [15]:

$$j_{l}(kr) = \left(\frac{\pi}{2kr}\right)^{1/2}J_{l+1/2}(kr) \tag{30}$$

With the calculation of integral (25) we also take into account the result [12]

$$\int_{0}^{\infty} e^{-\zeta r}J_{l+1/2}(kr)r^{n+1/2}dr = \frac{1}{\sqrt{\pi}}l!(n-l)!(2k)^{l+1/2}\left(\frac{x}{\zeta}\right)^{n+l+2}C_{n-l}^{l+1}(x) \tag{31}$$

where $x = \zeta/\sqrt{\zeta^{2}+k^{2}}$ and $C_{n}^{\beta}(x)$ is the Gegenbauer polynomial defined by [12]

$$C_{n}^{\beta}(x) = \sum_{s=0}^{E(n/2)}(-1)^{s}d_{NS}^{\beta}(2x)^{n-2s} \tag{32}$$

where

$$E(n/2) = \frac{1}{2}\left[n-\frac{1}{2}(1-(-1)^{n}\right]$$

and

$$d_{ns}^{\beta} = F_{\beta-1}(\beta-1+n-s)F_{s}(n-s) \tag{33}$$

Substituting Eq. (29) into the integral in Eq. (25) and using Eq. (31) one gets:

$$U_{nlm}\left(\zeta,\vec{k}\right) = Q_{nl}(\zeta,k)S_{lm}\left(\frac{\vec{k}}{k}\right) \tag{34}$$

where $Q_{nl}(\zeta,k)$ is the radial part of STOs in the momentum representation determined by

$$Q_{nl}(\zeta,k) = \frac{2^{n+l+1}l!(n-l)!}{\zeta^{3/2}\sqrt{\pi(2n)!}}x^{n+2}\left(1-x^{2}\right)^{1/2}C_{n-l}^{l+1}(x) \tag{35}$$

As can be seen from Eqs. (34) and (35), the radial part of STOs in the momentum representation is determined by the Gegenbauer polynomials.

Thus the resulting formulae for the Ψ^{α}–ETOs and $\overline{\Psi}^{\alpha}$–ETOs in the momentum representation are

$$\Phi^{\alpha}_{nlm}\left(\zeta,\vec{k}\right)=\Pi^{\alpha}{}_{nl}(\zeta,k)S_{lm}\left(\frac{\vec{k}}{k}\right) \tag{36}$$

$$\overline{\Phi}^{\alpha}_{nlm}\left(\zeta,\vec{k}\right)=\left(\frac{n}{\zeta k}\right)^{\alpha}\Phi^{\alpha}_{nlm}\left(\zeta,\vec{k}\right)=\overline{\Pi}^{\alpha}{}_{nl}(\zeta,k)S_{lm}\left(\frac{\vec{k}}{k}\right) \tag{37}$$

where

$$\Pi^{\alpha}_{nl}(\zeta,k)=\sum_{n'=l+1}^{n}\omega^{\alpha l}_{nn'}Q_{n'l}(\zeta,k) \tag{38}$$

$$\overline{\Pi}^{\alpha}_{nlm}(\zeta,k)=(2\pi)^{\alpha}\sum_{n'=l+1}^{n}\omega^{\alpha l}_{nn'}\left[\frac{(2(n'-\alpha))!}{(2n')!}\right]^{1/2}Q_{n'-\alpha l}(\zeta,k) \tag{39}$$

It should be noted that the functions $\Phi^{\alpha}_{nlm}\left(\zeta,\vec{k}\right)$ obtained from the Fourier transformation of Ψ^{α}-ETOs are orthonormal with the weight $(n/\zeta k)^{\alpha}$ where α=1, 0, −1, −2, ... :

$$\int\Phi^{\alpha*}_{nlm}\left(\zeta,\vec{k}\right)\left(\frac{n'}{\zeta k}\right)^{\alpha}\Phi^{\alpha}_{n'l'm'}\left(\zeta,\vec{k}\right)\mathrm{d}^3\vec{k}=\int\Phi^{\alpha*}_{nlm}\left(\zeta,\vec{k}\right)\overline{\Phi}^{\alpha}_{n'l'm'}\left(\zeta,\vec{k}\right)\mathrm{d}^3\vec{k}=\delta_{nn'}\delta_{ll'}\delta_{mm'} \tag{40}$$

Thus, the Fourier transforms of Ψ^{α}-ETOs in the momentum representation are also complete orthonormal sets of functions and are expressed in terms of Fourier transforms of STOs by the finite linear combinations (see Eqs. (23) and (24)).

Now we are able to obtain the expansion theorem for the product of Ψ^{α}-ETOs in the momentum representation. Using the orthonormality relation (40) one gets the following infinite series:

$$\Phi^{\alpha*}_{nlm}\left(\zeta,\vec{k}\right)\Phi^{\alpha}_{n'l'm'}\left(\zeta,\vec{k}\right)=\left(\overline{\zeta}\right)^{-3/2}\sum_{N=l}^{\infty}\sum_{L=0}^{N-1}\sum_{M=-L}^{L}D^{\alpha NLM}_{nlm,n'l'm'}\left(\zeta,\zeta',\overline{\zeta}\right)\Phi^{\alpha*}_{NLM}\left(\overline{\zeta},\vec{k}\right) \tag{41}$$

where

$\overline{\zeta}=(\zeta+\zeta')/2$and

$$D^{\alpha NLM}_{nlm,n'l'm'}\left(\zeta,\zeta',\overline{\zeta}\right)=\frac{1}{2\pi}(2L+1)^{1/2}C^{L|M|}(lm,l'm')A^{M}_{mm'}\times(2N)^{\alpha}\sum_{s=l+1}^{n}\sum_{s'=l'+1}^{n'}\sum_{S=L+1}^{N}\omega^{\alpha l}_{ns}\omega^{\alpha l'}_{n's'}\omega^{\alpha L}_{NS}\cdot\frac{[(2(S-\alpha))!]^{1/2}}{[(2S)!]^{1/2}}Q^{S-\alpha L}_{sl,s'l'}\left(\zeta,\zeta',\overline{\zeta}\right) \tag{42}$$

Here the coefficients $Q^{NL}_{nl,n'l'}\left(\zeta,\zeta',\overline{\zeta}\right)$ are determined by means of radial parts of STOs in the momentum representation:

$$Q^{NL}_{nl,n'l'}\left(\zeta,\zeta',\overline{\zeta}\right)=\sqrt{2\pi}\left(\overline{\zeta}\right)^{3/2}\int_0^{\infty}Q_{nl}(\zeta,k)Q_{n'l'}(\zeta',k)Q_{NL}\left(\overline{\zeta},k\right)k^2\mathrm{d}k \tag{43}$$

In the case where both the functions $\Phi^{\alpha}_{nlm}\left(\zeta,\vec{k}\right)$ and $\Phi^{\alpha}_{n'l'm'}\left(\zeta,\vec{k}\right)$ depend on the same parameter ζ=ζ', the infinite series (41) is reduced to the finite sum:

$$\Phi^{\alpha*}_{nlm}\left(\zeta,\vec{k}\right)\Phi^{\alpha}_{n'l'm'}\left(\zeta,\vec{k}\right)=(\zeta)^{-3/2}\sum_{N=1}^{n+n'+1}\sum_{L=0}^{N-1}\sum_{M=-l}^{L}D^{\alpha NLM}_{nlm,n'l'm'}\Phi^{\alpha*}_{NLM}\left(\zeta,\vec{k}\right) \tag{44}$$

It should be noted that for ζ=ζ', the coefficients $D^{\alpha NLM}_{nlm,n'l'm'}\left(\zeta,\zeta',\overline{\zeta}\right)$ and $Q^{NL}_{nl,n'l'}\left(\zeta,\zeta',\overline{\zeta}\right)$ determined by the relations (42) and (43) do not depend on the parameters ζ, i.e.

$D^{\alpha NLM}_{nlm,n'l'm'}=D^{\alpha NLM}_{nlm,n'l'm'}(\zeta,\zeta,\zeta)$ and $Q^{NL}_{nl,n'l'}=Q^{NL}_{nl,n'l'}(\zeta,\zeta,\zeta)$

The relationships for $Q^{NL}_{nl,n'l'}$ are obtained in the Appendix. The difficulty in the problem of the finite sum expansion of the Φ^{α} product in the case where they depend on different parameters $\zeta$and ζ', lies completely in the fact that the function $\Phi^{\alpha}_{NLM}\left(\overline{\zeta},\vec{k}\right)$ on the right-hand side of Eq. (41) is represented by the parameter $\overline{\zeta}\neq\zeta+\zeta'$.

Addition theorems for Ψ^{α} and Φ^{α} functions

In order to obtain the addition theorems for Ψ^{α}-ETOs in coordinate and momentum spaces, we use the following expansions of $\mathrm{e}^{-\mathrm{i}\vec{k}\vec{r}}$ and $\mathrm{e}^{\mathrm{i}\vec{k}\vec{r}}$ into series over the orbitals $\Psi^{\alpha}_{nlm}(\zeta,\vec{r})$ and $\Phi^{\alpha}_{nlm}\left(\zeta,\vec{k}\right)$, respectively:

$$\mathrm{e}^{-\mathrm{i}\vec{k}\vec{r}}=(2\pi)^{3/2}\sum_{NLM}\overline{\Phi}^{\alpha}_{NLM}\left(\zeta,\vec{k}\right)\Psi^{\alpha*}_{NLM}(\zeta,\vec{r}) \tag{45}$$

$$\mathrm{e}^{\mathrm{i}\vec{k}\vec{r}}=(2\pi)^{3/2}\sum_{NLM}\overline{\Psi}^{\alpha}_{NLM}(\zeta,\vec{r})\Phi^{\alpha*}_{NLM}\left(\zeta,\vec{k}\right) \tag{46}$$

Equations (45) and (46) can easily be derived by means of the orthonormality relations (15) and (40), and the Fourier transformations (21), (22), (26) and (27).

Coordinate representation

Let us consider the Fourier transform of the function $\Psi^{\alpha}_{nlm}\left(\zeta,\vec{r}-\vec{R}\right)$,

$$\Psi^{\alpha}_{nlm}\left(\zeta,\vec{r}-\vec{R}\right) = (2\pi)^{-3/2}\int e^{i\vec{k}\left(\vec{r}-\vec{R}\right)}\,\Phi^{\alpha}_{nlm}\left(\zeta,\vec{k}\right)d^{3}\vec{k} \tag{47}$$

Substituting the expansion (46) into the integral in (47), one obtains:

$$\Psi^{\alpha}_{nlm}\left(\zeta,\vec{r}-\vec{R}\right) = \sum_{n'l'm'}\overline{\Psi}^{\alpha}_{n'l'm'}(\zeta',\vec{r})\int e^{-i\vec{k}\vec{R}}\cdot \cdot\Phi^{\alpha}_{nlm}\left(\zeta,\vec{k}\right)\Phi^{\alpha*}_{n'l'm'}\left(\zeta',\vec{k}\right)d^{3}\vec{k} \tag{48}$$

Next we use the expansion (41) and Eq. (26) to give

$$\Psi^{\alpha}_{nlm}\left(\zeta,\vec{r}-\vec{R}\right) = \left(\frac{2\pi}{\zeta}\right)^{3/2}\sum_{n'=1}^{\infty}\sum_{l'=0}^{n'-1}\sum_{m'=-l'}^{l'}\cdot \cdot\left(\sum_{N=1}^{\infty}\sum_{L=0}^{N-1}\sum_{M=-L}^{L}D^{\alpha NLM}_{nlm,n'l'm'}\left(\zeta,\zeta',\overline{\zeta}\right)\Psi^{\alpha*}_{NLM}\left(\overline{\zeta},\vec{R}\right)\right)\cdot \cdot\overline{P}si^{\alpha}_{n'l'm'}(\zeta',\vec{r}) \tag{49}$$

The expansion (49) enables one to formulate a theorem on the representation of Ψ^{α}-ETOs, depending on the parameter ζ, in terms of the functions depending on another parameter $\overline{\zeta}$. This representation may be useful in applications.

Thus, we have proven the desired addition theorem for Ψ^{α}-ETOs in coordinate space: any Ψ^{α}-ETOs with the difference of the radius vectors, $\vec{r}-\vec{R}$, as its argument is expanded into a series over products of Ψ^{α}-ETOs depending on $\vec{r}$ and $\vec{R}$, separately.

Momentum representation

In order to obtain the addition theorem for Ψ^{α}-ETOs in momentum space, we consider the Fourier transform of ETOs,

$$\Phi^{\alpha}_{nlm}\left(\zeta,\vec{k}-\vec{p}\right) = (2\pi)^{-3/2}\int e^{i\vec{k}(\vec{r}-\vec{p})\vec{r}}\Psi^{\alpha}_{nlm}(\zeta,\vec{r})d^{3}\vec{r} \tag{50}$$

Applying expansion (45) to the exponential, one has

$$\Phi^{\alpha}_{nlm}\left(\zeta,\vec{k}-\vec{p}\right) = \sum_{n'l'm'}\overline{\Phi}^{\alpha}_{n'l'm'}\left(\zeta',\vec{k}\right)\int e^{i\vec{p}\vec{r}}\cdot \cdot\Psi^{\alpha}_{nlm}(\zeta,\vec{r})\Psi^{*\alpha}_{n'l'm'}(\zeta',\vec{r})d^{3}\vec{r} \tag{51}$$

Now we take into account expansion (11) and Eq. (21). Then, finally, we obtain:

$$\Phi^{\alpha}_{nlm}\left(\zeta,\vec{k}-\vec{p}\right) = (4\pi z)^{3/2}\sum_{n'=1}^{\infty}\sum_{l'=0}^{n'-1}\sum_{m'=-l'}^{l'}\cdot \cdot\left(\sum_{N=1}^{n+n'+1}\sum_{L=0}^{N-1}\sum_{M=-L}^{L}B^{\alpha NLM}_{nlm,n'l'm'}(\zeta,\zeta',z)\Phi^{\alpha*}_{NLM}(z,\vec{p})\right)\cdot \cdot\overline{\Phi}^{\alpha}_{n'l'm'}\left(\zeta',\vec{k}\right) \tag{52}$$

Here the coefficients $B^{\alpha NLM}_{nlm,n'l'm'}(\zeta,\zeta',z)$ for $\zeta=\zeta'$ do not depend on the parameter ζ, i.e. $B^{\alpha NLM}_{nlm,n'l'm'} \equiv B^{\alpha NLM}_{nlm,n'l'm'}(\zeta,\zeta,2\zeta)$.

We notice that the function $\Phi^{\alpha}_{nlm}\left(\zeta,\ \vec{k}-\vec{p}\right)$ is factorized in the Φ^{α} functions depending on $\vec{k}$ and $\vec{p}$, separately, and on the parameters ζ and z =ζ+ ζ, respectively. The parameter ζ is arbitrary and may be chosen appropriately for any particular calculation in the theory of molecules.

Thus, we have considered the addition and expansion theorems for Ψ^{α}-ETOs, in both coordinate and momentum spaces, and have found a relationship between them.

Arbitrary multicenter multielectron integrals of Ψ^{α}-ETOs

We are now able to consider the multicenter multielectron integrals of Ψ^{α}-ETOs appearing in the MO LCAO method of the quantum theory of molecules. Since the Ψ^{α}-ETOs are expressed in terms of STOs, according to Eq. (6), these integrals can be reduced to multicenter multielectron integrals over STOs. Using the translation formulae of STOs obtained in [11] with the help of Ψ^{α}-ETOs, one can derive the series expansion formulae for the multicenter molecular integrals with an arbitrary *s*-electron operator (*s*=1, 2, 3, …) in terms of overlap integrals with the same screening parameter of STOs.

Our next subject is the overlap integrals over STOs with the same screening parameter, which occur in the multicenter multielectron integrals of Ψ^{α}-ETOs. The integral under consideration has the form

$$S_{nlm,n'l'm'}\left(\zeta,\vec{R}\right) = \int \chi^{*}_{nlm}(\zeta,\vec{r})\chi_{n'l'm'}\left(\zeta,\vec{r}-\vec{R}\right)d^{3}\vec{r} \tag{53}$$

For the evaluation of integral (53), we use Eq. (28) for Fourier transform of STOs. Then we obtain:

$$S_{nlm,n'l'm'}\left(\zeta,\vec{R}\right) = \int e^{-i\vec{k}\vec{R}}U^{*}_{nlm}\left(\zeta,\vec{k}\right)\cdot \cdot U_{n'l'm'}\left(\zeta,\vec{k}\right)d^{3}\vec{k} \tag{54}$$

where $U_{nlm}\left(\zeta,\vec{k}\right)$ is determined by Eqs. (34) and (35).

Now we expand the product of two functions on the right-hand side of Eq. (54) in terms of the Ψ^{α}-ETOs in the momentum representation:

$$U^{*}{}_{nlm}\left(\zeta,\vec{k}\right)U_{n'l'm'}\left(\zeta,\vec{k}\right) = (2\pi\zeta)^{-3/2}\sum_{N=1}^{n+n'+1}\sum_{L=0}^{N-1}\sum_{M=-l}^{L}M^{\alpha NLM}_{nlm,n'l'm'}\Phi^{\alpha*}_{NLM}\left(\zeta,\vec{k}\right) \tag{55}$$

where α=1, 0, −1, −2, … and

$$M^{\alpha NLM}_{nlm,n'l'm'} = \int U^{*}_{nlm}\left(\zeta,\vec{k}\right)U_{n'l'm'}\left(\zeta,\vec{k}\right)\cdot \cdot\overline{\Phi}^{\alpha}_{NLM}\left(\zeta,\vec{k}\right)d^{3}\vec{k} \tag{56}$$

Here we have taken into account the orthonormality relation (40).

Using Eq. (23) one can prove the following identity:

$$\sum_{N=1}^{n+n'+1}\sum_{L=0}^{N-1}\sum_{M=-l}^{L} M^{\alpha NLM}_{nlm,n'l'm'}\Phi^{\alpha *}_{NLM}\left(\zeta,\vec{k}\right)$$
$$=\sum_{N=1}^{n+n'+1}\sum_{L=0}^{N-1}\sum_{M=-l}^{L}\left(\sum_{N'=N}^{n+n'+1}\omega^{\alpha L}_{N'N}M^{\alpha N'LM}_{nlm,n'l'm'}\right)\cdot$$
$$\cdot\, U^{*}{}_{NLM}\left(\zeta,\vec{k}\right) \qquad (57)$$

Now we take into account Eq. (24) in Eqs. (56) and (57). Then we finally obtain for the expansion of the product of Fourier transforms in terms of their linear combinations the following relation:

$$U^{*}_{nlm}\left(\zeta,\vec{k}\right)U_{n'l'm'}\left(\zeta,\vec{k}\right)=(2\pi\zeta)^{-3/2}\sum_{N=1}^{n+n'+1}\sum_{L=0}^{N-1}\sum_{M=-L}^{L}\cdot$$
$$\cdot\left(\sum_{N'=L+1}^{n+n'+1}\Omega^{\alpha L}_{NN'}(n+n'+1)T^{N'LM}_{nlm,n'l'm'}\right)U^{\alpha *}_{NLM}\left(\zeta,\vec{k}\right) \qquad (58)$$

where

$$\Omega^{\alpha l}_{n\kappa}(N)=\left[\frac{[2(k-\alpha)]!}{(2\kappa)!}\right]^{1/2}\sum_{n'=\max(n,\kappa)}^{N}(2n')^{\alpha}\omega^{\alpha l}_{n'n}\omega^{\alpha l}_{n'\kappa} \qquad (59)$$

$$T^{NLM}_{nlm,n'l'm'}=(2\pi\zeta)^{\frac{3}{2}}\int U^{*}{}_{nlm}\left(\zeta,\vec{k}\right)U_{n'l'm'}\left(\zeta,\vec{k}\right)\cdot$$
$$\cdot\, U_{NLM}\left(\zeta,\vec{k}\right)\mathrm{d}^3\vec{k}=(-1)^{(l-l'-L)/2}(2\pi(2L$$
$$+1))^{1/2}C^{L|M|}(lm,l'm')A^{M}_{mm'}Q^{NL}_{nl,n'l'} \qquad (60)$$

where $Q^{NL}_{nl,n'l'}$ is determined by Eq. (69) of the Appendix.

Now we are able to calculate the overlap integrals of STOs with the same screening parameter. Substitute expansion (58) into the integral in (54) and use Eq. (28) and the result is

$$S_{nlm,n'l'm'}\left(\zeta,\vec{R}\right)$$
$$=\zeta^{-3/2}\sum_{N=1}^{n+n'+1}\sum_{L=0}^{N-1}\sum_{M=-l}^{L}g^{\alpha NLM}_{nlm,n'l'm'}\chi^{*}_{NLM}\left(\zeta,\vec{R}\right) \qquad (61)$$

where α=1,0,–1,–2,… and

$$g^{\alpha NLM}_{nlm,n'l'm'}=\sum_{N'=1}^{n+n'+1}\Omega^{\alpha l.}_{NN'}(n+n'+1)T^{N'LM}_{nlm,n'l'm'} \qquad (62)$$

Thus, the sets of formulae for overlap integrals with the same screening parameter are determined solely from the linear combination of STOs.

On the basis of the addition and expansion formulae obtained in this paper, we constructed a program for evaluating the multicenter electron-repulsion integrals with STOs:

$$I_{p_1p'_i;p_2p'_2}\left(\zeta_1,\zeta'_1,\zeta_2,\zeta'_2;\vec{R}_{ca},\vec{R}_{ba},\vec{R}_{da}\right)$$
$$=\int\chi^{*}_{p_i}(\zeta_1,\vec{r}_{a1})\chi_{p'_1}(\zeta'_1,\vec{r}_{c1})\cdot$$
$$\cdot\frac{1}{r_{21}}\chi_{p_2}(\zeta_2,\vec{r}_{b2})\chi^{*}_{p'_2}(\zeta'_2,\vec{r}_{d2})\mathrm{d}V_1\mathrm{d}V_2 \qquad (63)$$

where

$p_i\equiv n_il_im_i,\;\; p'_i\equiv n'_il'_im'_i,\;\; \vec{R}_{gh}=\vec{R}_h-\vec{R}_g,$

$\vec{r}_{gi}=\vec{r}_i-\vec{R}_g\;\; (i=1,2$ and $g=a,b,c,d);\; \vec{r}_i$ and $\vec{R}_g$ are the radius vectors of electron and nucleus relative to the molecule-fixed axes centered at a reference origin O.

The results of the calculation in atomic units for the two-center hybrid, two-center Coulomb, and two-center exchange electron-repulsion integrals obtained with a Pentium III 800 MHz computer (using the TURBO PASCAL 7.0 language) are shown in Tables 1 and 2. The comparative values obtained from the expansion of different Ψ^{α}-ETOs are shown in these tables. We see from the tables that the computation time and accuracy of the computer results for different expansion formulae obtained from Ψ^{0}-ETOs, Ψ^{1}-ETOs, and Ψ^{-1}-ETOs are satisfactory.

Table 1 Comparison of methods of computing two-center electron-repulsion integrals over STOs obtained in the molecular coordinate system in a.u. for $N=N'=15$, $\theta_{ca}=120°$, $\phi_{ca}=180°$, $\theta_{db}=120°$, $\phi_{db}=180°$, $\theta_{ba}=30°$, $\phi_{ba}=90°$

n_1	l_1	m_1	ζ_1	n'_1	l'_1	m'_1	ζ'_1	n_2	l_2	m_2	ζ_2	n'_2	l'_2	m'_2	ζ'_2
2	1	0	6.5	2	1	0	4.4	2	1	0	4.6	2	1	0	3.1
2	1	1	5.6	2	1	1	2.4	2	1	0	8.4	2	1	0	5.3
2	1	1	8.5	2	1	1	6.2	2	1	1	7.8	2	1	1	6
3	2	1	4.8	3	2	1	2.6	3	1	1	3.7	2	1	1	1.6
2	1	0	6.4	2	1	0	4.2	2	1	0	5.3	2	0	0	3.1
2	1	1	8.6	2	1	1	5.4	2	1	1	7.5	2	1	1	5.3
3	2	0	10.6	3	2	0	7.5	2	1	1	9.7	2	1	1	8.5
3	2	1	8.1	3	2	1	5.7	2	1	1	6.9	2	1	1	4.8
2	1	0	5.8	2	1	0	6.3	2	1	0	5.8	2	1	0	6.3
2	1	0	7.5	1	0	0	4.6	2	1	0	7.5	1	0	0	4.6
2	1	1	8.7	2	1	0	6.4	2	1	1	8.7	2	1	0	6.4
2	1	1	5.8	2	1	1	2.6	2	1	1	5.8	2	1	1	2.6

Table 2 Comparison of methods of computing two-center electron-repulsion integrals over STOs obtained in the molecular coordinate system in a.u. for N=N'=15, θ_{ca}=120°, ϕ_{ca}=180°, θ_{db}=120°, ϕ_{db}=180°, θ_{ba}=30°, ϕ_{ba}=90°

R_{ca}	R_{db}	R_{ba}	Eq. (<equationcite>63</equationcite>), α=1	Eq. (<equationcite>63</equationcite>), α=0	Eq. (<equationcite>63</equationcite>), α=−1	CPU (ms)
0	0.4	0	9.5797637176E−1	9.5797637176E−3	9.5797637175E−3	27.1
0	2.8	0	−1.8679407277E−5	−1.8679407264E−5	−1.8679407258E−5	42.2
0	3.2	0	4.4165329011E−7	4.4165329113E−7	4.4165329314E−7	47.2
0	1.3	0	2.5574326839E−1	2.5574326815E−1	2.5574326827E−1	65.8
0	0	0.3	−1.3317612696E−1	−1.3317612694E−1	−1.3317612677E−1	23.4
0	0	3.3	2.4435258748E−1	2.4435258746E−1	2.4435258729E−1	29.0
0	0	4.3	2.0741168617E−1	2.0741168617E−1	2.0741168625E−1	45.3
0	0	7.6	1.0881681470E−1	1.0881681467E−1	1.0881681455E−1	53.8
0.8	0.8	0	1.3429866341E−2	1.3429866361E−2	1.3429866237E−2	65.5
2	2	0	2.2546218186E−5	2.2546218241E−5	2.2546218311E−5	57.4
2.5	2.5	0	4.5310176221E−5	4.5310176184E−5	4.5310176400E−5	68.7
1.4	1.4	0	5.2992746237E−2	5.2992746177E−2	5.2992745732E−2	82.6

Appendix

As can be seen from Eqs. (60), (61) and (62), the overlap integrals with the same screening parameter are expressed through the integral

$$Q^{NL}_{nl,nT} = \sqrt{\pi}\zeta^{3/2}\int_0^\infty Q_{nl}(\zeta,k)Q_{n'l'}(\zeta,k)Q_{NL}(\zeta,k)k^2\mathrm{d}k \tag{64}$$

where $Q_{nl}(\zeta,k)$ is determined by the Gegenbauer polynomials (Eq. (35)). Using Eqs. (32) and (33), we can easily establish for the products of Gegenbauer polynomials the following relations:

$$C^{\beta}_{n}(x)C^{\beta'}_{n'}(x) = \sum_{s=0}^{E(n/2)+E(n'/2)} (-1)^s d^{\beta\beta'}_{nn's}(2x)^{n+n'-2s} \tag{65}$$

$$C^{\beta}_{n}(x)C^{\beta'}_{n'}(x)C^{\beta''}_{n''}(x) = \sum_{s=0}^{E(n/2)+E(n'/2)+E(n''/2)} (-1)^s d^{\beta\beta'\beta''}_{nn'n''s}(2x)^{n+n'+n''-2s} \tag{66}$$

where

$$d^{\beta\beta'}_{nn's} = \sum_{m=0}^{E(n/2)} d^{\beta}_{nm}d^{\beta'}_{n's-m} \tag{67}$$

$$d^{\beta\beta'\beta''}_{nn'n''s} = \sum_{m=0}^{E(n/2)} d^{\beta}_{nm}d^{\beta'\beta''}_{n'n''s-m} \tag{68}$$

Now using Eq. (66) and the result [12]

$$\int_0^1 \frac{x^{2n}}{\sqrt{1-x^2}}\mathrm{d}x = \frac{(2n-1)!}{2^{2n}n!(n-1)!}\pi \tag{69}$$

we get from Eq. (64)

$$Q^{NL}_{nl,n'l'} = \left[F_1(n)F_{l'}(n')F_L(N)\sqrt{F_n(2n)F_{n'}(2n')F_N(2N)}\right]^{-1} \times \sum_{s=0}^{k}(-1)^s d^{l+1,l'+1,L+1}_{n-l,n'-l',n-L,s} b_{n+n'+N+1-g-s,g} \tag{70}$$

where

$$k = E\left(\frac{n-l}{2}\right) + E\left(\frac{n'-l'}{2}\right) + E\left(\frac{N-L}{2}\right)$$

and

$$b_{i,j} = \sum_{m=0}^{j+1}(-1)^m 2^{2j+1-2m}F_m(j+1)F_{i+m}(2(i+m)-1)$$

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