

THE EVALUATION OF ELECTRONIC EXTRACULE AND INTRACULE DENSITIES AND RELATED PROBABILITY FUNCTIONS IN TERMS OF GAUSSIAN BASIS FUNCTIONS

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Abstract

The evaluation of the basic two-electron integrals involved in the calculation of extracule and intracule densities is described. Expressions are given for the evaluation of the related spherically averaged, longitudinal, and transverse probability functions from wave functions constructed from Gaussian basis sets. All results are expressed in closed analytical forms which are suited to efficient coding. Given that certain pair densities can be related to experimental scattering cross sections, the formulae reported herein will facilitate further comparison between experiment and theory and lead to a more comprehensive understanding of the electronic structures of molecules.

1. Introduction

The electron pair model by Lewis [1] and the valence-shell electron pair repulsion model by Gillespie and Nyholm [2] have ensured that the concept of electron pairs is one of the central models of chemistry. It is therefore remarkable that there have been very few studies of pair densities in molecules [3-12] relative to the extensive literature on one-electron densities [13]. We report here formulae required for the calculation of extracule and intracule densities from wave functions constructed from Gaussian basis sets. These formulae are suitable for calculations of pair densities in molecules and are given in a form suitable to interface with standard *ab initio* molecular orbital programs which employ Gaussian basis sets.

2. Extracular and intracular coordinates

The natural choice of coordinates to study pair densities without losing the genuine two-electron character of the electron pair density

$$\Gamma(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{2} \langle \Psi | \delta(\mathbf{r}_1 - \mathbf{r}'_1) \delta(\mathbf{r}_2 - \mathbf{r}'_2) | \Psi \rangle$$

is to introduce the extracular $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ and the intracular $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ coordinates [14]. The extracule and the intracule densities are then defined by

$$E(\mathbf{R}) = \langle \Psi | \sum_{i>j} \delta\left(\mathbf{R} - \frac{\mathbf{r}_i + \mathbf{r}_j}{2}\right) | \Psi \rangle \quad (1)$$

and

$$I(\mathbf{r}) = \langle \Psi | \sum_{i>j} \delta(\mathbf{r} - \mathbf{r}_i + \mathbf{r}_j) | \Psi \rangle, \quad (2)$$

respectively. One can then use the Slater–Condon rules for matrix elements between Slater determinants and write eqs. (1) and (2) in terms of the spin orbitals. Then, by introducing the usual definition of the elements of the density matrix in the Roothaan–Hall self-consistent field method for a closed shell, the extracule and intracule densities can be written in terms of the basis functions as

$$E(\mathbf{R}) = \sum_{\mu\nu\sigma\lambda} J_{\mu\nu\sigma\lambda}^{(e)} \left(\frac{1}{2} P_{\nu\mu} P_{\lambda\sigma} - \frac{1}{4} P_{\lambda\mu} P_{\nu\sigma} \right) \quad (3)$$

and

$$I(\mathbf{r}) = \sum_{\mu\nu\sigma\lambda} J_{\mu\nu\sigma\lambda}^{(i)} \left(\frac{1}{2} P_{\nu\mu} P_{\lambda\sigma} - \frac{1}{4} P_{\lambda\mu} P_{\nu\sigma} \right). \quad (4)$$

For an open shell, the corresponding expressions are

$$E(\mathbf{R}) = \sum_{\mu\nu\sigma\lambda} J_{\mu\nu\sigma\lambda}^{(e)} \left(P_{\nu\mu}^T P_{\lambda\sigma}^T - P_{\nu\sigma}^\alpha P_{\lambda\mu}^\alpha - P_{\nu\sigma}^\beta P_{\lambda\mu}^\beta \right), \quad (5)$$

$$I(\mathbf{r}) = \sum_{\mu\nu\sigma\lambda} J_{\mu\nu\sigma\lambda}^{(i)} \left(P_{\nu\mu}^T P_{\lambda\sigma}^T - P_{\nu\sigma}^\alpha P_{\lambda\mu}^\alpha - P_{\nu\sigma}^\beta P_{\lambda\mu}^\beta \right). \quad (6)$$

In eqs. (3)–(6), we have used the notation of Szabo and Ostlund [15]. The evaluation of eqs. (3)–(6) requires values for the basic two-electron extracule integral

$$J_{\mu\nu\sigma\lambda}^{(e)}(\mathbf{R}) = (\mu\nu \left| \delta \left(\mathbf{R} - \frac{\mathbf{r}_1 + \mathbf{r}_2}{2} \right) \right| \sigma\lambda) \quad (7)$$

and the basic two-electron intracule integral

$$J_{\mu\nu\sigma\lambda}^{(i)}(\mathbf{r}) = (\mu\nu \left| \delta(\mathbf{r} - \mathbf{r}_1 + \mathbf{r}_2) \right| \sigma\lambda). \quad (8)$$

In the next section, we shall describe the evaluation of these basic two-electron integrals in terms of Gaussian-type orbitals.

3. The two-electron integrals

The basic two-electron integrals, eqs. (8) and (9), will be evaluated using Cartesian Gaussian basis functions, defined in the usual manner:

$$\phi_{\mu}(\alpha_{\mu}, \mathbf{R}_{\mu}, l, m, n; \mathbf{r}) = (x - X_{\mu})^l (y - Y_{\mu})^m (z - Z_{\mu})^n e^{-\alpha_{\mu}|\mathbf{r} - \mathbf{R}_{\mu}|^2}.$$

The Gaussian functions contraction theorem [16] allows us to write

$$\begin{aligned} & \phi_{\mu}(\alpha_{\mu}, \mathbf{R}_{\mu}, l_1, m_1, n_1; \mathbf{r}_1) \phi_{\nu}(\alpha_{\nu}, \mathbf{R}_{\nu}, l_2, m_2, n_2; \mathbf{r}_1) \\ & \times \phi_{\sigma}(\alpha_{\sigma}, \mathbf{R}_{\sigma}, l_3, m_3, n_3; \mathbf{r}_2) \phi_{\lambda}(\alpha_{\lambda}, \mathbf{R}_{\lambda}, l_4, m_4, n_4; \mathbf{r}_2) \\ & = K \sum_{l=0}^{l_1+l_2} \sum_{l'=0}^{l_3+l_4} \sum_{m=0}^{m_1+m_2} \sum_{m'=0}^{m_3+m_4} \sum_{n=0}^{n_1+n_2} \sum_{n'=0}^{n_3+n_4} f_l f_{l'} f_m f_{m'} f_n f_{n'} (x_1 - X_P)^l (x_2 - X_Q)^{l'} \\ & \times (y_1 - Y_P)^m (y_2 - Y_Q)^{m'} \times (z_1 - Z_P)^n (z_2 - Z_Q)^{n'} \exp(-\gamma_1 |\mathbf{r}_1 - \mathbf{R}_P|^2 - \gamma_2 |\mathbf{r}_2 - \mathbf{R}_Q|^2), \end{aligned}$$

where:

$$\mathbf{R}_P = (\alpha_{\mu} \mathbf{R}_{\mu} + \alpha_{\nu} \mathbf{R}_{\nu}) / \gamma_1,$$

$$\mathbf{R}_Q = (\alpha_{\sigma} \mathbf{R}_{\sigma} + \alpha_{\lambda} \mathbf{R}_{\lambda}) / \gamma_2,$$

$$\gamma_1 = \alpha_{\mu} + \alpha_{\nu},$$

$$\gamma_2 = \alpha_{\sigma} + \alpha_{\lambda},$$

$$K = \exp(-\alpha_{\mu} \alpha_{\nu} |\mathbf{R}_{\mu} - \mathbf{R}_{\nu}|^2 / \gamma_1 - \alpha_{\sigma} \alpha_{\lambda} |\mathbf{R}_{\sigma} - \mathbf{R}_{\lambda}|^2 / \gamma_2).$$

Then, using the Fourier transform of the delta function,

$$\delta(\mathbf{r} - \mathbf{A}) = \left(\frac{1}{2\pi}\right)^3 \int d\mathbf{k} e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{A})},$$

the two-electron integrals $J_{\mu\nu\sigma\lambda}^{(e)}(\mathbf{R})$ and $J_{\mu\nu\sigma\lambda}^{(i)}(\mathbf{r})$ can be factorized, respectively, as:

$$\begin{aligned} & J_{\mu\nu\sigma\lambda}^{(e)}(\mathbf{R}) \\ &= \left(\frac{1}{2\pi}\right)^3 K \sum_{l=0}^{l_1+l_2} \sum_{l'=0}^{l_3+l_4} \sum_{m=0}^{m_1+m_2} \sum_{m'=0}^{m_3+m_4} \sum_{n=0}^{n_1+n_2} \sum_{n'=0}^{n_3+n_4} f_l f_{l'} f_m f_{m'} f_n f_{n'} \int d\mathbf{k} e^{i\mathbf{k} \cdot \left(\mathbf{R} - \frac{\mathbf{R}_P + \mathbf{R}_Q}{2}\right)} \\ &\times I_l^-(k_x/2, \gamma_1) I_{l'}^-(k_x/2, \gamma_2) I_m^-(k_y/2, \gamma_1) I_{m'}^-(k_y/2, \gamma_2) I_n^-(k_z/2, \gamma_1) I_{n'}^-(k_z/2, \gamma_2) \end{aligned} \quad (9)$$

and

$$\begin{aligned} & J_{\mu\nu\sigma\lambda}^{(i)}(\mathbf{r}) \\ &= \left(\frac{1}{2\pi}\right)^3 K \sum_{l=0}^{l_1+l_2} \sum_{l'=0}^{l_3+l_4} \sum_{m=0}^{m_1+m_2} \sum_{m'=0}^{m_3+m_4} \sum_{n=0}^{n_1+n_2} \sum_{n'=0}^{n_3+n_4} f_l f_{l'} f_m f_{m'} f_n f_{n'} \int d\mathbf{k} e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{R}_P + \mathbf{R}_Q)} \\ &\times I_l^+(k_x, \gamma_1) I_{l'}^-(k_x, \gamma_2) I_m^+(k_y, \gamma_1) I_{m'}^-(k_y, \gamma_2) I_n^+(k_z, \gamma_1) I_{n'}^-(k_z, \gamma_2), \end{aligned} \quad (10)$$

where the integral

$$I_j^\pm(k, \gamma) = \int_{-\infty}^{\infty} dx x^j e^{\pm i k x - \gamma x^2} \quad (11)$$

is related to the Hermite polynomials $H_n(x)$ by [17]

$$I_j^\pm(k, \gamma) = i^j \left(\frac{\pi}{\gamma}\right)^{1/2} \left(\frac{1}{2\sqrt{\gamma}}\right)^j e^{-k^2/4\gamma} H_j(\pm k/2\sqrt{\gamma}). \quad (12)$$

Substitution of eq. (12) into (9) and (10) gives

$$\begin{aligned}
 J_{\mu\nu\sigma\lambda}^{(e)}(\mathbf{R}) &= \left(\frac{1}{2\pi}\right)^3 K \sum_{l=0}^{l_1+l_2} \sum_{l'=0}^{l_3+l_4} \sum_{m=0}^{m_1+m_2} \sum_{m'=0}^{m_3+m_4} \sum_{n=0}^{n_1+n_2} \sum_{n'=0}^{n_3+n_4} \\
 &\times f_l f_{l'} f_m f_{m'} f_n f_{n'} \frac{\pi^3 \left(\frac{i}{2}\right)^{l+m+n+l'+m'+n'}}{(\sqrt{\gamma_1})^{l+m+n+3} (\sqrt{\gamma_2})^{l'+m'+n'+3}} \\
 &\times J_{l,l'}^- \left[\left(X - \frac{X_P + X_Q}{2} \right), 16 \right] J_{m,m'}^- \left[\left(Y - \frac{Y_P + Y_Q}{2} \right), 16 \right] J_{n,n'}^- \left[\left(Z - \frac{Z_P + Z_Q}{2} \right), 16 \right]
 \end{aligned} \tag{13}$$

and

$$\begin{aligned}
 J_{\mu\nu\sigma\lambda}^{(i)}(\mathbf{r}) &= \left(\frac{1}{2\pi}\right)^3 K \sum_{l=0}^{l_1+l_2} \sum_{l'=0}^{l_3+l_4} \sum_{m=0}^{m_1+m_2} \sum_{m'=0}^{m_3+m_4} \sum_{n=0}^{n_1+n_2} \sum_{n'=0}^{n_3+n_4} \\
 &\times f_l f_{l'} f_m f_{m'} f_n f_{n'} \frac{\pi^3 \left(\frac{i}{2}\right)^{l+m+n+l'+m'+n'}}{(\sqrt{\gamma_1})^{l+m+n+3} (\sqrt{\gamma_2})^{l'+m'+n'+3}} \\
 &\times J_{l,l'}^+ [(x - X_P + X_Q), 4] J_{m,m'}^+ [(y - Y_P + Y_Q), 4] J_{n,n'}^+ [(z - Z_P + Z_Q), 4],
 \end{aligned} \tag{14}$$

where the integral

$$J_{j,j'}^{\pm}(x, a) = \int_{-\infty}^{\infty} dk e^{ikx - k^2(\gamma_1 + \gamma_2)/a} \gamma_1 \gamma_2 H_j(-k/\sqrt{a\gamma_1}) H_{j'}(\pm k/\sqrt{a\gamma_2}) \tag{15}$$

can be expressed as a linear combination of $I_j^{\pm}(k, \gamma)$ -like integrals. After evaluating the integral in eq. (15) and substituting the results into eqs. (13) and (14), some tedious algebra leads to

$$\begin{aligned}
 J_{\mu\nu\sigma\lambda}^{(e)}(\mathbf{R}) &= K \left(\frac{4\pi}{\gamma_1 + \gamma_2} \right)^{3/2} e^{-4\Delta^2 |R - \frac{R_P + R_Q}{2}|^2} T_{l_1, l_2, l_3, l_4}^+ (2X - X_P - X_Q) \\
 &\times T_{m_1, m_2, m_3, m_4}^+ (2Y - Y_P - Y_Q) \times T_{n_1, n_2, n_3, n_4}^+ (2Z - Z_P - Z_Q),
 \end{aligned} \tag{16}$$

$$\begin{aligned}
 J_{\mu\nu\sigma\lambda}^{(i)}(\mathbf{r}) &= K \left(\frac{\pi}{\gamma_1 + \gamma_2} \right)^{3/2} e^{-\Delta^2 |r - R_P + R_Q|^2} T_{l_1, l_2, l_3, l_4}^- (x - X_P + X_Q) \\
 &\times T_{m_1, m_2, m_3, m_4}^- (y - Y_P + Y_Q) \times T_{n_1, n_2, n_3, n_4}^- (z - Z_P + Z_Q),
 \end{aligned} \tag{17}$$

where $\Delta^2 = \gamma_1 \gamma_2 / (\gamma_1 + \gamma_2)$ and $T^\pm(x)$ is the angular factor introduced by Thakkar et al. [10,18]

$$T_{j_1 j_2 j_3 j_4}^\pm(x) = \sum_{\tilde{j}} W^\pm(\tilde{j}_i) H_{\tilde{j}_i}(\Delta x), \quad (18)$$

where

$$\sum_{\tilde{j}_i} \equiv \sum_{j=0}^{j_1+j_2} \sum_{j'=0}^{j_3+j_4} \sum_{i=0}^{[j/2]} \sum_{i'=0}^{[j'/2]}, \quad (19)$$

$$\tilde{j}_i = j + j' - 2(i + i'),$$

$$W^\pm(\tilde{j}_i) = \frac{(\pm 1)^{j'} f_j f_{j'} j! j'! \gamma_1^{i-j} \gamma_2^{i'-j'} \Delta^{\tilde{j}_i}}{2^{j+j'} i! i'! (j-2i)! (j'-2i')!}. \quad (20)$$

Equations (16) and (17), respectively, are operationally equivalent to the computational procedures of Thakkar and Moore [18], and Thakkar et al. [10]. Note that eqs. (16)–(20) allow us to check for the normalization of both the extracule and intracule densities, i.e.:

$$\int d\mathbf{R} E(\mathbf{R}) = \int dr I(r) = \binom{N}{2}. \quad (21)$$

4. The spherically averaged two-electron integrals

It has long been known that for an incident X-ray frequency far removed from the characteristic electronic absorption bands of the target atom or molecule, it is possible to interpret the total X-ray scattered intensity in terms of the radial intracule density function [6]. The evaluation of the spherically averaged and radial extracule and intracule density functions requires values for the following basic two-electron integrals:

$$J_{\mu\nu\sigma\lambda}^{(e)}(\mathbf{R}) = K \left(\frac{4\pi}{\gamma_1 + \gamma_2} \right)^{3/2} R^2 e^{-\Delta^2(4R^2 + A^2)} S_{l,m,n}^+(2R, A), \quad (22)$$

$$J_{\mu\nu\sigma\lambda}^{(i)}(r) = K \left(\frac{\pi}{\gamma_1 + \gamma_2} \right)^{3/2} r^2 e^{-\Delta^2(r^2 + B^2)} S_{l,m,n}^-(r, B), \quad (23)$$

where

$$A = |\overline{\mathbf{R}}_P + \overline{\mathbf{R}}_Q|, \quad B = |\overline{\mathbf{R}}_P - \overline{\mathbf{R}}_Q|, \quad j = (j_1 j_2 j_3 j_4)$$

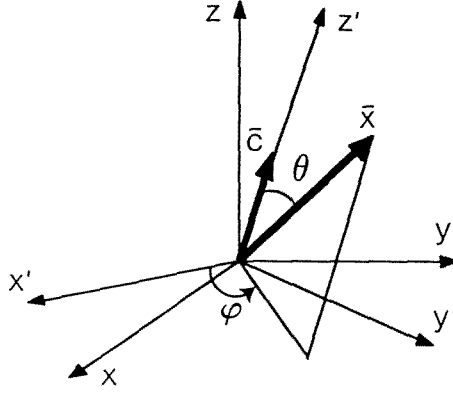


Fig. 1. The coordinate system used.

and

$$S_{\tilde{l},m,n}^{\pm}(x, c) = \int_0^{\infty} d\theta \sin \theta e^{2\Delta^2 cx \cos \theta} \times \int_0^{2\pi} T_{l_1 l_2 l_3 l_4}^{\pm}(v_1) T_{m_1 m_2 m_3 m_4}^{\pm}(v_2) T_{n_1 n_2 n_3 n_4}^{\pm}(v_3) d\varphi, \quad (24)$$

where

$$v = \begin{pmatrix} v_1 \\ v_2 \\ v_3 \end{pmatrix} = \mathbf{u} \begin{pmatrix} |\bar{x}| \sin \theta \cos \varphi \\ |\bar{x}| \sin \theta \sin \varphi \\ |\bar{x}| \cos \theta - c \end{pmatrix} \quad (25)$$

and the transformation matrix \mathbf{u} changes the coordinates to a new system where the vector c lies in the z -direction (see fig. 1). Bearing in mind the expression for $T^{\pm}(x)$ (see eq. (18)), the integral over φ in eq. (24) can be written as a linear combination of beta functions, $B(x, y)$ [19]. Then, the integral over θ is solved to obtain

$$S_{\tilde{l},m,n}^{\pm}(x, c) = 2 \sum_{\tilde{l}_i} W^{\pm}(\tilde{l}_i) \sum_P C(p, \tilde{l}_i) \Delta^p K(p, 1) \sum_{\tilde{m}_j} W^{\pm}(\tilde{m}_j) \times \sum_q C(q, \tilde{m}_j) \Delta^q K(q, 2) \sum_{\tilde{n}_k} W^{\pm}(\tilde{n}_k) \sum_r C(r, \tilde{n}_k) \Delta^r K(r, 3) \times x^{i_1+i_3} c^{i-i_1-i_3} B\left(\frac{i_2+1}{2}, \frac{i_1-i_2+1}{2}\right) I(i_1; 2\Delta^2 cx), \quad (26)$$

where $C(i, j)$ is the i th coefficient of the j th order Hermite polynomial,

$$K(a, i) = \sum_{a_1=0}^a \binom{a}{a_1} \sum_{a_2=0}^{a_1} \binom{a_1}{a_2} u_{i_1}^{a_2} u_{i_2}^{a_1-a_2} \sum_{a_3=0}^{a-a_1} \binom{a-a_1}{a_3} (-1)^{a-a_1-a_3} u_{i_3}^{a-a_1} \quad (27)$$

and

$$I(a, y) = \sum_{t=0}^{a/2} \binom{a/2}{t} (-1)^t \frac{d^{a-2t}}{dy^{a-2t}} \left\{ \frac{\sinh(y)}{y} \right\}, \quad (28)$$

$$i = p + q + r, \quad i_1 = p_1 + q_1 + r_1, \quad i_2 = p_2 + q_2 + r_2, \quad i_3 = p_3 + q_3 + r_3.$$

For s -type Gaussian basis functions, $S_{l,m,n}^{\pm}(x, c)$ reduces to

$$S_{l,m,n}^{\pm}(x, c) = \frac{4\pi}{2\Delta^2 c x} \sinh(2\Delta^2 c x). \quad (29)$$

Substitution of eq. (29) into eq. (23) gives the spherically averaged basic intracule integral for spherical Gaussians which was reported recently [12]. It should be stressed that the fomulae given in this section are not restricted to linear molecules.

5. Longitudinal and transverse two-electron integrals

Standard cylindrical coordinate representations of intracule (b, z, ϕ) and extracule (B, Z, Φ) densities are appropriate for discussion of the two-electron properties [9] of linear molecules. The basic two-electron integrals which should be solved in order to evaluate the longitudinal and transverse intracule and extracule probability functions are:

$$L_{\mu\nu\sigma\lambda}^{(e)}(Z) = \frac{\pi}{2} K \left(\frac{4\pi}{\gamma_1 + \gamma_2} \right)^{3/2} e^{-\Delta^2(2Z-Z_P-Z_Q)^2} T_{n_1 n_2 n_3 n_4}^+ (2Z - Z_P - Z_Q) \\ \times T_{m_1 m_2 m_3 m_4}^+(0) t_{l_1 l_2 l_3 l_4}^+(1, 0), \quad (30)$$

$$L_{\mu\nu\sigma\lambda}^{(i)}(z) = 2\pi K \left(\frac{\pi}{\gamma_1 + \gamma_2} \right)^{3/2} e^{-\Delta^2(z-Z_P+Z_Q)^2} T_{n_1 n_2 n_3 n_4}^- (z - Z_P + Z_Q) \\ \times T_{m_1 m_2 m_3 m_4}^-(0) t_{l_1 l_2 l_3 l_4}^-(1, 0), \quad (31)$$

$$T_{\mu\nu\sigma\lambda}^{(e)}(B) = \pi K \left(\frac{4\pi}{\gamma_1 + \gamma_2} \right)^{3/2} B e^{-4\Delta^2 B^2} T_{n_1 n_2 n_3 n_4}^+ (2B) \times T_{m_1 m_2 m_3 m_4}^+(0) t_{l_1 l_2 l_3 l_4}^+(0, -\infty), \tag{32}$$

$$T_{\mu\nu\sigma\lambda}^{(i)}(b) = 2\pi K \left(\frac{\pi}{\gamma_1 + \gamma_2} \right)^{3/2} b e^{-\Delta^2 b^2} T_{n_1 n_2 n_3 n_4}^-(b) \times T_{m_1 m_2 m_3 m_4}^-(0) t_{l_1 l_2 l_3 l_4}^-(0, -\infty), \tag{33}$$

where

$$t_{j_1 j_2 j_3 j_4}^\pm(j, x) = \int_x^\infty e^{-\Delta^2 y^2} T_{j_1 j_2 j_3 j_4}^\pm(y) y^j dy. \tag{34}$$

The integral of eq. (34) can be done analytically and the result is:

$$t_{j_1 j_2 j_3 j_4}^\pm(1, 0) = \frac{1}{2\Delta^2} \sum_{\tilde{j}_i} W^\pm(\tilde{j}_i) G_{\tilde{j}_i}^\mp, \tag{35}$$

$$t_{j_1 j_2 j_3 j_4}^\pm(0, -\infty) = \frac{\sqrt{\pi}}{2\Delta} \sum_{\substack{j=0 \\ (\text{even})}}^{j_1+j_2} \sum_{\substack{j'=0 \\ (\text{even})}}^{j_3+j_4} \frac{f_j f_{j'} j! j'!}{2^{j+j'} \gamma_1^{j/2} \gamma_2^{j'/2} \left(\frac{j}{2}\right)! \left(\frac{j'}{2}\right)!}, \tag{36}$$

where the function G_n is defined by

$$G_n = n! \sum_{i=0}^{\lfloor n/2 \rfloor} \frac{(-1)^i \Gamma\left(\frac{n}{2} + 1 - i\right)}{i! (n - 2i)!} 2^{n-2i} \tag{37}$$

and is closely related to the ultraspheric polynomials C_n^α [19] by

$$G_n = \frac{n!}{\Gamma\left(1 - \frac{n}{2}\right)} C_n^{(1-n/2)}(1)$$

for $n \leq 3$.

The normalization chosen (see eq. (21)) for $I(r)$ and $E(R)$ ensures that

$$\int dZ L_{\mu\nu\sigma\lambda}^{(e)}(Z) = \int dz L_{\mu\nu\sigma\lambda}^{(i)}(z) = \int dB T_{\mu\nu\sigma\lambda}^{(e)}(B) = \int db T_{\mu\nu\sigma\lambda}^{(i)}(b) = \binom{N}{2}.$$

6. Discussion

Expressions for the intracule density were first given by Lester and Krauss [3], and for the extracule density by Thakkar and Moore [18]. Thakkar et al. [10] pointed out that the formulae of Lester and Krauss contain many errors and are not suited to efficient computation. Consequently, Thakkar et al. [10] published formulae that are more suited to efficient computation. They chose to calculate the spherical average of the intracule density by numerical integration of the intracule density with respect to the angles, taking advantage of the high symmetry of diatomic molecules. The formulae reported herein are, however, analytical and are easily extended to the analytical evaluation of the associated probability functions and their corresponding moments. They are also extendable to properties associated with the densities, such as gradients and Laplacians. The latter have proven useful for the analysis of the first-order electron density. In fact, a parallel analysis can be carried out for the second-order electron densities provided analytical representations of the intracule and extracule densities are available. The formulae reported in this paper make such an analysis possible.

7. Summary

Starting from the definitions of the extracule and the intracule densities (eqs. (2) and (3)) and using generalized Cartesian Gaussian-type basis set functions, we have evaluated all the basic two-electron integrals involved in the calculation of the two-electron densities and their related spherically averaged, longitudinal and transverse probability functions. This should facilitate the extraction of information from N -electron wave functions and lead to detailed descriptions of molecular structures comparable to those available for a few atomic states [20]. In the long term, information on two-electron distributions should complement the insight gained from the properties of the charge density in molecules. It must be noted, however, that whereas the effect of electron correlation on one-electron density distributions is relatively small [21,22], correlation effects cannot be ignored in the case of pair densities. Fortunately, the formulae reported here can be used to evaluate pair densities from configuration interaction (CI) wave functions, as demonstrated by our recent study of the intracule densities and electron correlation in the hydrogen molecule [12].

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References

- [1] G.N. Lewis, *J. Amer. Chem. Soc.* 38(1916)762.
- [2] R.J. Gillespie and R.S. Nyholm, *Q. Rev. Chem. Soc.* 11(1957)239.

- [3] W.A. Lester, Jr. and M. Krauss, *J. Chem. Phys.* 44(1966)207.
- [4] Y. Tal and J. Katriel, *J. Phys.* B7(1974)2113.
- [5] E.A. Colbourn, *J. Phys.* B8(1975)1926.
- [6] R.F. Stewart, *Irs. J. Chem.* 16(1977)111.
- [7] K.E. Banyard and C.E. Reed, *J. Phys.* B14(1981)441.
- [8] J.W. Moskowitz and M.H. Kalos, *Int. J. Quant. Chem.* 20(1981)1107.
- [9] B.S. Sharma and A.J. Thakkar, *J. Phys.* B17(1984)3405.
- [10] A.J. Thakkar, A.N. Tripathi and V.H. Smith, Jr., *Int. J. Quant. Chem.* 26(1984)157.
- [11] A.J. Thakkar, in: *Density Matrices and Density Functionals*, ed. R. Erdahl and V.H. Smith, Jr. (Reidel, Dordrecht, 1987).
- [12] R.J. Boyd, C. Sarasola and J.M. Ugalde, *J. Phys.* B21(1988)2555;
C. Sarasola, J.M. Ugalde and R.J. Boyd, *ibid.* 23(1990)1095.
- [13] R.F.W. Bader, *Acc. Chem. Res.* 18(1985)9.
- [14] A.J. Coleman, *Int. J. Quant. Chem. Symp.* 1(1967)457.
- [15] A. Szabo and N.S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory* (McMillan, New York, 1982).
- [16] V.R. Saunders, in: *Computational Techniques in Quantum Chemistry and Molecular Physics* (Reidel, Dordrecht, 1975).
- [17] N.N. Lebedev, *Special Functions and their Applications* (Dover, New York, 1972).
- [18] A.J. Thakkar and N.J. Moore, *Int. J. Quant. Chem. Symp.* 15(1981)393.
- [19] M. Abramowitz and I.A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1970).
- [20] J.M. Ugalde, R.J. Boyd and J.S. Perkyns, *J. Chem. Phys.* 87(1987)1216.
- [21] L.-C. Wang and R.J. Boyd, *J. Chem. Phys.* 90(1989)1083.
- [22] R.J. Boyd and L.-C. Wang, *J. Comput. Chem.* 10(1989)367.