Analytical Evaluation of the Two-Center Correlated Hybrid Integral over Slater-type Orbitals

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Abstract

The analytical evaluation of the two-center hybrid integral containing the electron correlation multiplier r_{12}^k, with the all values of k(even and odd) over Slater –type orbitals have been obtained .So that the combination of their analytical equations in the same expression leads to using a single algorithm, and this able decrease in the size of the program and to a simplification of quantum mechanical calculations for molecules .

Keywords: two-center hybrid ; Slater –type orbitals; electron correlation multiplier.

INTRODUCTION

As well known, the values of total energy of molecules can be obtained more exactly using wave function with inter electronic distance . However the total energy of molecules can be expressed by the two-center integrals with correlation multiplier $r_{12}^k \left(k \geq -1 \right)$ and containing Slater –type orbitals [1-5]. These integrals are evaluated by the use of two types of orbitals, Gaussian –type orbitals and Slater –type orbitals. Gaussian –type orbitals do not allow sufficiently representing important properties of the electronic wave function ,namely the cusps at the nuclei and exponential decay at large distances .For problems in which the long part of the wave function or its behavior in the neighborhood of the nuclei is important ,it is desirable to use Slater –type orbitals, which describe the physical situation more accurately than Gaussian –type orbitals .On the other hand a comparison of Slater –type orbitals and Gaussian –type orbitals bases of various size showed that a Gaussian –type orbitals basis needs about twice the size of a Slater –type orbitals basis to obtain comparable accuracy [5-9] Basic equations

The atomic correlation integral examined in this paper have the following form in which the orbitals are taken to be real:

$$I_H^k = \int \chi_{a_1}(1) \chi_{a_1'}(1) r_{12}^k \ \chi_{a_2''}(2) \ \chi_{b_2}(2) dv_1 dv_2$$

(1)

Where $\chi_i = \left(n_i \ell_i m_i \right)$ and $\chi_i' = \left(n_i' \ell_i' m_i' \right)$ are four different Slater atomic orbitals centered on nuclei $i = a,b$.

$$\chi_{nlm}(\zeta, r\theta\varphi) = \frac{(2\zeta)^{n+\frac{1}{2}}}{\sqrt{(2n)!}} \cdot e^{-\zeta r} \cdot r^{n-1} S_{lm}(\theta, \varphi)$$

(2)

$$S_{lm}(\theta,\varphi) = \frac{1}{\sqrt{\pi(1+\delta_{m0})}} \cdot P_l^{|m|}(\cos \theta) \cdot \begin{cases} \cos|m|\varphi \ for \quad m \geq 0 \\ \sin|m|\varphi \ for \quad m < 0 \end{cases}$$

(3)

Is an associated Legendre polynomial, $P_l^{|m|}(\cos\theta)$ and r_{12}^k is written as Perkins [10]:

$$r_{12}^k = 4\pi \sum_{\ell=0}^{\ell_1} \sum_{s=0}^{\ell_2} \sum_{m=-i}^{\ell} a_{k\ell s} r_1^{\ell+2s} r_2^{k-\ell-2s} S_{\ell m}\left(\theta_1,\phi_1\right) S_{\ell m}\left(\theta_2,\phi_2\right) \ , k \geq -1$$

(4)

With $\ell_1 = \dfrac{k}{2}, \ell_2 = \dfrac{k}{2}-\ell$ for even k, and $\ell_1 = \infty, \ell_2 = \dfrac{k+1}{2}$ for odd k and

$$a_{k\ell s} = \frac{(-4)^\ell (k+1)! \left(\dfrac{k}{2}-s\right)!(s+\ell)!}{s! \left(\dfrac{k}{2}-s-\ell\right)!(k-2s+1)!(2\ell+2s+1)!}$$

(5)

We can write the integral I_H^k in the following formula:

$$I_H^k = \int p_a(2) \chi_{a_2''}(2) \ \chi_{b_2}(2) dv_2$$

(6)

Where

$$p_a(2) = \int \chi_{a_1}(1)\chi_{a_1'}(1) r_{12}^k \ dv_1$$

(7)

In the calculation of the correlated potential function in equation (7) when k is even we must using the expansion of the product of two real spherical harmonics both with different centers and the elliptical coordinates [13], we obtain

$$p_a(2) = N_{n_a n_a'}(1,t_a) \sum_{\ell s m}\left[4\pi(2\ell+1)^{\frac{1}{2}}\right] \cdot a_{k\ell s} \ \cdot C^{\ell|m|}\left(\ell_a m_a, \ell_a' m_a'\right) A_{m_a m_a'}^{M_a} \cdot \frac{(n_a + n_a' + \ell)!}{\left(2\bar{\xi}_a\right)^{\ell+2s}} \cdot$$
$$S_{L_a M_a}\left(\theta_{a_2},\phi_{a_2}\right)$$

(8)

Also, when k is odd the correlated potential function have the following formula:

$$p_a(2) = N_{n_a n_a'}(1,t_a) \cdot \frac{(4\pi)^{\frac{1}{2}}}{\left(2\bar{\xi}_a\right)^k} \sum_{s=0}^{\frac{k+1}{2}} \sum_{\ell=0}^{s} \sum_{i=0}^{s} \sum_{L_a M_a L} b_{S\ell i}^K \ C^{L_a|M_a|}\left(\ell_a m_a, \ell_a' m_a'\right) A_{m_a m_a'}^{M_a} \cdot \frac{(n_1+1)!}{\left(2\bar{\xi}_a r_{a_2}\right)^{n_2}}$$
$$\cdot S_{L_a M_a}\left(\theta_{a_2},\phi_{a_2}\right) \cdot \left[1 - e^{-2\bar{\xi}_a r_{a_2}} \sum_{\sigma=0}^{n_1} \left(2\bar{\xi}_a r_{a_2}\right)^\sigma \gamma_\sigma^L (n_1 - L)\right]$$

(9)

Where

$$n_1 = n_a + n_a' + k + L - s - i \quad , \quad n_2 = L - s - i + 1$$

(10)

$$N_{nn'}(1,t) = \frac{(1+t)^{n+\frac{1}{2}}(1-t)^{n'+\frac{1}{2}}}{\sqrt{(2n)!(2n')!}}$$

(11)

$$\gamma_s^L(N) = \frac{1}{s!} - \frac{(N-k)!}{(N+1+k)!(s-2k-1)!}$$

(12)

and

$$b_{s\ell i}^k = \frac{(-1)^{s+i}\left(\frac{k+1}{2}\right)!\sqrt{(2\ell+1)}}{i!\left(\frac{1}{2}(k+1)-s\right)!\left(\frac{s-i-\ell}{2}\right)!}$$

(13)

to calculate the integral I_H^k when k is even ,equation(8) has been used into equation(6) with the elliptical coordinates ,and integrating over azimuthal angle ϕ .Then using the expansion of the product of two normalized associated Legendre functions, which have been obtained by Guseinov and yassen[13-14],finally, obtain for the hybrid integrals with correlation multiplier r_{12}^k ,the following analytical expression :

$$I_H^k = \left(\frac{R}{2}\right)^k N_{n_a n_a'}(1,t_a) N_{n_a'' n_b'}(p,t) \sum_{\ell sm}\sum_L \sqrt{(2\ell+1)(2L+1)} \cdot a_{k\ell s} \cdot A_{\sigma_a \sigma_a'}^m A_{m\sigma_a'}^{\sigma_b} \frac{(n_a+n_a'+\ell+2s)!}{p_a^{\ell+2s}} \cdot$$

$$C^{\ell|m|}(\ell_a\sigma_a,\ell_a'\sigma_a') \sum_{\alpha\beta q} g_{\alpha\beta}^q(L|\sigma_b|,\ell_b|\sigma_b|,|\sigma_b|) \cdot \sum_{\alpha\beta q} g_{\alpha\beta}^q(L|\sigma_b|,\ell_b|\sigma_b|,|\sigma_b|) \cdot \sum_{\gamma=0}^{n_3} F_\gamma(n_4,n_b-\beta)\cdot$$

(14)

$$A_{n_5}(p)\cdot\beta_{q+\gamma}(pt)$$

Where

$$n_3 = n_a''+n_b+k-\alpha-\beta-\ell-2s \quad,$$
$$n_4 = n_a''+k-\alpha-\ell-2s$$

(15)

$$n_5 = n_3-\gamma+q \qquad ,p_a = R\bar{\xi}_a \qquad ,\bar{\xi}_a = \frac{1}{2}\left(\xi_a+\xi_a'\right)$$

(16)

$$p = \frac{R}{2}\left(\xi_a''+\xi_b\right) \quad, \qquad t_a = \frac{\xi_a-\xi_a'}{\xi_a+\xi_a'} \quad, \qquad t = \frac{\xi_a''-\xi_b'}{\xi_a''+\xi_b'}$$

(17)

Here R- is the inter nuclear distance, $C^{\ell|M|}(\ell m,\ell'm')$ is defined by using Gaunt coefficients [10] and $F_m(N,N'), g_{\alpha\beta}^q(L|\sigma_b|,\ell_b|\sigma_b|,|\sigma_b|), N_{nn'}(1,t), A_{mm'}^m$ are defined by references [11-14].

To evaluate the integral I_H^k when k is odd , equation(9) has been used into equation (6) with the elliptical coordinates ,and integrating over azimuthal angle ϕ. Finally, obtain for the hybrid integrals with correlation multiplier r_{12}^k, the following analytical expression:

$$
I_H^k = \left(\frac{R}{2}\right)^k N_{n_a n_a'}(1,t_a) N_{n_a'' n_b}(p,t) \sum_{\ell s i} \sum_{L_a M_a} \sum_{L L_1} \sqrt{(2L_1+1)} \cdot A_{\sigma_a \sigma_a'}^{M_a} A_{M_a \sigma_a'}^{\sigma_b} \, b_{s\ell i}^k \, \frac{(n_1+1)!}{p_a^{k+n_2}} C^{L_a|M_a|}(\ell_a \sigma_a, \ell_a' \sigma_a') \cdot
$$

$$
\begin{bmatrix}
\sum_{\alpha=-|\sigma_b|}^{L_1} \sum_{\beta=|\sigma_b|}^{\ell_b} \sum_{q'=\alpha+|\sigma_b|}^{\alpha+\beta} G_{-(n_6,n_b-\beta)}^{-q'}(p,t,p_a) - g_{\alpha\beta}^{q'}(L_1|\sigma_b|,\ell_b|\sigma_b|,|\sigma_b|) \\
-\sum_{\alpha\beta q} g_{\alpha\beta}^q(L|\sigma_b|,\ell_b|\sigma_b|,|\sigma_b|)
\end{bmatrix} \cdot
$$

$$
\sum_{\sigma=n_6}^{n_7} \sum_{\gamma=0}^{n_8} p_a^\sigma \gamma_\sigma^L(n_7) F_\gamma(n_9,n_b-\beta) A_{n_{10}}(p_a) \beta_{q+\gamma}(p_{ab} t_{ab})
$$

(18)

Where

$$
n_6 = L + \alpha + 1 - n_a'' - s - i \quad ,
$$
$$
n_7 = n_a + n_a' - s - i + k
$$

(19)

$$
n_8 = n_a'' + n_b + \sigma + s + i - L - \alpha - \beta - 1
$$

(20)

$$
n_9 = n_a'' + n_b + s + i + L - \alpha + \gamma
$$

(21)

$$
n_{10} = n_8 + q - \gamma \quad , \quad t_{ab} = \frac{\xi_a + \xi_a' + \xi_a'' - \xi_b'}{\xi_a + \xi_a' + \xi_a'' + \xi_b'}
$$

(22)

The combination of the analytical equations (14) and (18) in the same expression might make it possible to carry out calculations of the hybrid integrals with correlation multiplier r_{12}^k ,on a computer using single algorithm ,and this would lead to an appreciable decrease in the size of the program and to a simplification of quantum mechanical calculations for molecules .To obtain a combined expression for the analytical expressions in equations (14) and equation(18)we using the following definitions :

I-when k is even

$$
S_{\gamma q}^{n\sigma L} = \sum_{\gamma=0}^{n_6} F_\gamma(n_4,n_b-\beta) \cdot A_{n_5}(p) \cdot B_{q+\gamma}(pt)
$$

(23)

$$
T_{ksi}^{n\ell m} = \sum_{s\ell m} \sum_L \sqrt{(2\ell+1)(2L+1)} \, a_{k\ell s} C^{L|m|}(\ell_a \sigma_a, \ell_a' \sigma_a') C^{L|\sigma_b|}(\ell m, \ell_a'' \sigma_a'') \cdot
$$

$$
A_{\sigma_a \sigma_a'}^m A_{m\sigma_a''}^{\sigma_b} \cdot \frac{(n_a + n_a' + 2s + \ell)!}{p_a^{\ell+2s}}
$$

(24)

$$R_{\alpha\beta}^{q} = \sum_{\alpha\beta q} g_{\alpha\beta}^{q} \left(L \left| \sigma_b \right|, \ell_b \left| \sigma_b \right|, \left| \sigma_b \right| \right)$$

(25)

II-when k is odd

$$S_{\gamma q}^{n\sigma L} = \sum_{\sigma=n_6}^{n_7} \sum_{\gamma=0}^{n_8} p_a^{\sigma} \gamma_{\sigma}^{L} \left(n_7 \right) F_{\gamma} \left(n_9, n_b - \beta \right) \cdot A_{n_{10}} \left(p_{ab} \right) \cdot B_{q+\gamma} \left(p_{ab} t_{ab} \right)$$

(26)

$$T_{ksi}^{n\ell m} = \sum_{s\ell i} \sum_{L_a M_a} \sum_{LL_1} \sqrt{(2L_1+1)} b_{s\ell i}^{k} \ C^{L_a|M_a|} \left(\ell_a \sigma_a, \ell_a' \sigma_a' \right) \cdot C^{L_1|\sigma_b|} \left(\ell_a'' \sigma'', L_a M_a \right) \cdot$$

$$A_{\sigma_a \sigma_a'}^{M_a} A_{M_a \sigma_a''}^{\sigma_b} \cdot \frac{(n_1+1)!}{p_a^{k+n_2}}$$

(27)

$$R_{\alpha\beta}^{q} = \sum_{\alpha=-|\sigma_b|}^{L_1} \sum_{\beta=|\sigma_b|}^{\ell_b} \sum_{q'=\alpha+|\sigma_b|}^{\alpha+\beta} g_{\alpha\beta}^{q'} \left(L_1 \left| \sigma_b \right|, \ell_b \left| \sigma_b \right|, \left| \sigma_b \right| \right) \cdot$$

$$\left[G_{-(n_6,n_b-\beta)}^{-q'} \left(p, t, p_a \right) - \sum_{\alpha\beta q} g_{\alpha\beta}^{q} \left(L \left| \sigma_b \right|, \ell_b \left| \sigma_b \right|, \left| \sigma_b \right| \right) \right]$$

(28)

The above equations[(23)- (28)] have been used and finally ,obtained for the two-center correlated hybrid integral the following combined analytical expression :

$$I_H^k = \left(\frac{R}{2} \right)^k N_{n_a n_a'} \left(1, t_a \right) N_{n_a'' n_b} \left(p, t \right) \cdot T_{ksi}^{n\ell m} \cdot S_{\gamma q}^{n\sigma L} \cdot R_{\alpha\beta}^{q}$$

(29)

for the all values of k(even and odd)

CONCLUSION

It is clear that ,for k=-1 formula (29) going to the formula (4) in the work by Guseinov and Yassen [12] for the two- center hybrid integral over Slater –type orbitals .

A large number of computer calculations of the two-center hybrid integral with the correlation multiplier r_{12}^{k} carried out by using the combined analytical equation (29)for the all values of k.

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