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The Two-center Correlated Exchange Integral over Slater-type Orbitals

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Abstract

The two-center **exchange** integral containing the electron correlation multiplier r_{12}^{k}, over Slater –type orbitals have been obtained when k is even and when k is odd . The combination of their analytical equations in the same expression have been established . leads to using a single algorithm, which simplifying the calculation of quantum mechanical for molecules .

Keywords: two-center **exchange integral** , Slater –type orbitals; electron correlation multiplier.

INTRODUCTION

The total energy of molecules can be expressed by the two-center integrals with correlation multiplier $r_{12}^{k}\left(k\geq -1\right)$ over Slater –type orbitals [1-5] **and over**

Gaussian –type orbitals**.** But the comparison of Slater –type orbitals and Gaussian –type orbital bases of various size showed that a Gaussian –type orbital basis needs about twice the size of a Slater –type orbitals basis to obtain comparable accuracy [6-10].

The exchange correlated integral have the following form in which the orbitals are taken to be real:

$$I_{EX}^{k}=\int \chi_{a_1}\left(1\right)\chi_{b_2}\left(2\right)r_{12}^{k}\;\chi_{a_1'}\left(1\right)\;\chi_{b_2'}\left(2\right)dv_1dv_2 \qquad (1)$$

Where

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

$S_{l\,m}(\theta,\varphi)$ is real spherical harmonics [11] and r_{12}^{k} is written as Perkins [12]

$$r_{12}^{k}=4\pi\sum_{\ell=0}^{\ell_1}\sum_{s=0}^{\ell_2}\sum_{m=-i}^{\ell}a_{k\ell s}r_1^{\ell+2s}r_2^{k-\ell-2s}S_{\ell m}\left(\theta_1,\phi_1\right)S_{\ell m}\left(\theta_2,\phi_2\right)\;,k\geq -1 \qquad (3)$$

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

To calculate the integral I_{EX}^{k} when k is even, equation (3) has been used into equation (1) with the elliptical coordinates. Hence ,the following formula has been obtained :

$$\begin{aligned}I_{EX}^{k}&=N_{n_{a_1}n_{b_1}}\left(1,t\right)N_{n_a''n_b'}\left(1,t'\right)\cdot\left(\xi_a+\xi_b\right)^{n_a+n_b+1}\cdot\left(\xi_a'+\xi_b'\right)^{n_a'+n_b'+1}\\&\cdot\sum_{s\ell m}\sum_{L_aM_a}\sum_{L_a'M_a'}\sqrt{\left(2L_a+1\right)\left(2L_a'+1\right)}\cdot a_{k\ell s}\cdot A_{\sigma_a\sigma_a'}^{m}A_{m\sigma_a'}^{\sigma_b}\cdot C^{\ell|m|}\left(\ell_a\sigma_a,\ell_a'\sigma_a'\right)\\&\cdot\int r_{a_1}^{n_a+\ell+2s-1}r_{b_1}^{n_b-1}e^{-\xi_a r_{a_1}-\xi_b\xi_{b_1}}S_{L_aM_a}\left(\theta_{a_1},\phi_{a_1}\right)S_{L_b'M_a'}\left(\theta_{b_1},\phi_{b_1}\right)dv_1\\&\cdot\int r_{a_2}^{n_a'+\ell-2s-1}r_{b_2}^{n_b'-1}e^{-\xi_a'r_{a_2}-\xi_b'\xi_{b_2}}S_{L_a'M_a'}\left(\theta_{a_2},\phi_{a_2}\right)S_{L_b'M_a'}\left(\theta_{b_2},\phi_{b_2}\right)dv_2\end{aligned} \qquad (4)$$

Using the elliptical coordinates in the right part side of the formula (4) ,and integrating over azimuthal angle ,finally obtained the following analytical expression for the correlated exchange integral:

$$\begin{aligned}I_{EX}^{k}&=\left(\frac{R}{2}\right)^{k}N_{n_an_b}\left(p,t\right)N_{n_a''n_b}\left(p',t'\right)\sum_{\ell sm}\sum_{L_aL_a'}\sqrt{\left(2L_a+1\right)\left(2L_a'+1\right)}\\&\cdot a_{k\ell s}A_{\sigma_am}^{\sigma_b}A_{m\sigma_a'}^{\sigma_b'}\;C^{L_a|\sigma_a|}\left(\ell m,\ell_a'\sigma_a'\right)\cdot\sum_{\alpha\beta q}g_{\alpha\beta}^{q}\left(L\left|\sigma_b\right|,\ell_b\left|\sigma_b\right|,\left|\sigma_b\right|\right)\\&\cdot\sum_{\alpha'\beta'q'}g_{\alpha'\beta'}^{q'}\left(L_a'\left|\sigma_b'\right|,\ell_b'\left|\sigma_b'\right|,\left|\sigma_b'\right|\right)\cdot\sum_{\sigma=n_6}^{n_{11}}F_{\gamma}\left(n_{12},n_b-\beta\right)A_{n_{13}}\left(p_a\right)\beta_{q+\gamma}\left(p\;t\right)\\&\sum_{\gamma=0}^{n_{14}}F_{\gamma}\left(n_{15},n_b'-\beta'\right)A_{n_{16}}\left(p_a\right)\beta_{q'+\gamma'}\left(p't'\right)\end{aligned} \qquad (5)$$

Where

$$\begin{aligned}&n_{11}=n_a+n_b+2s-\alpha-\beta+\ell\quad,n_{12}=n_a+2s-\alpha+\ell\\&n_{13}=n_{11}-\gamma+q\quad,n_{14}=n_a'+n_b'-2s-\alpha'-\ell-\beta'\\&n_{15}=n_a'+k-2s-\alpha'-\ell,\;n_{16}=n_a'+n_b'-2s-\alpha'-\ell-\beta'+q'\\&p=\frac{R}{2}\left(\xi_a+\xi_b\right)\;,p'=\frac{R}{2}\left(\xi_a'+\xi_b'\right)\;,t=\frac{\xi_a-\xi_b}{\xi_a+\xi_b},t'=\frac{\xi_a'-\xi_b'}{\xi_a'+\xi_b'}\end{aligned} \qquad (6)$$

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Here R- is the inter nuclear distance, $C^{\ell|M|}(\ell m,\ell' m')$ is Gaunt coefficients [12] and
$F_m(N,N'), g^{q}_{\alpha\beta}(L|\sigma_b|,\ell_b|\sigma_b|,|\sigma_b|), N_{nn'}(1,t), A^{m}_{mm'}$
are determined by [13-19].

To evaluate the integral I^{k}_{EX} when k is odd , the correlation multiplier r^{k}_{12} ,which we can be written in the form $r^{k}_{12}=\frac{1}{r_{12}}r^{k+1}_{12}$,and the expansion of r^{k}_{12} in equation (3)have been used ,and finally it is easily obtained the following analytical expression :

$$I^{k}_{EX}=\sum_{\ell sm}\sum_{L_aM_a}\sum_{L'_aM'_a}\sqrt{\frac{(2L_a+1)(2L'_a+1)(2N'_a)!(2N_a)!}{(2n_a)!(2n'_a)}}$$
$$\cdot a_{k+1\ell s}A^{M_a}_{\sigma_a m}A^{M'_a}_{\sigma'_a m_a}\ C^{L_a|M_a|}(\ell_a\sigma_a,\ell m)$$
$$\cdot C^{L'_a|M'_a|}(\ell'_a\sigma'_a,\ell m)\left[(N_aL_aM_a)(N'_aL'_aM'_a)\left|\frac{1}{r_{12}}\right|(n_b\ell_bm_b)(n'_b\ell'_bm'_b)\right] \quad (7)$$

Where

$$N'_a=n'_a+k+1-\ell-2s\quad ,N_a=n_a+\ell+2s \quad (8)$$

And $\left[(N_aL_aM_a)(N'_aL'_aM'_a)\left|\frac{1}{r_{12}}\right|(n_b\ell_bm_b)(n'_b\ell'_bm'_b)\right]$ have been expressed by formula (5) in the work by Guseinov and Yassen [13].

Combination of the two-center exchange integrals with the correlation multiplier r^{k}_{12} , can be obtained in the following analytical expression :

$$I^{k}_{EX}=\left(\frac{R}{2}\right)^{k}N_{n_an_b}(p,t)N_{n''_an_b}(p',t')$$
$$\cdot\sum_{\ell sm}\sum_{L_aL'_a}\sqrt{(2L_a+1)(2L'_a+1)}\ I^{k\ell sL_am}_{\alpha\beta q\gamma}\partial_{w+} \quad (9)$$
$$+\sum_{\ell sm}\sum_{L_aM_a}\sum_{L'_aM'_a}\sqrt{\frac{(2L_a+1)(2L'_a+1)(2N'_a)!(2N_a)!}{(2n_a)!(2n'_a)}}I^{k\ell sm}_{L_aM_a}\partial_{w-}$$

Where

$$I^{k\ell sL_am}_{\alpha\beta q\gamma}=a_{k\ell s}A^{\sigma_b}_{\sigma_a m}A^{\sigma'_b}_{m\sigma'_a}\ C^{L_a|\sigma_a|}(\ell m,\ell'_a\sigma'_a)\cdot\sum_{\alpha\beta q}g^{q}_{\alpha\beta}(L|\sigma_b|,\ell_b|\sigma_b|,|\sigma_b|)$$
$$\cdot\sum_{\alpha'\beta'q'}g^{q'}_{\alpha'\beta'}(L'_a|\sigma'_b|,\ell'_b|\sigma'_b|,|\sigma'_b|)\cdot\sum_{\sigma=n_6}^{n_{11}}F_\gamma(n_{12},n_b-\beta)A_{n_{13}}(p_a)\beta_{q+\gamma}(p\ t)$$
$$\cdot\sum_{\gamma=0}^{n_{14}}F_\gamma(n_{15},n'_b-\beta')A_{n_{16}}(p_a)\beta_{q'+\gamma'}(p't') \quad (10)$$

For the even values of k ,and

$$I^{k\ell sm}_{L_aM_a}==a_{k+1\ell s}A^{M_a}_{\sigma_a m}A^{M'_a}_{\sigma'_a m_a}\ C^{L_a|M_a|}(\ell_a\sigma_a,\ell m)$$
$$\cdot C^{L'_a|M'_a|}(\ell'_a\sigma'_a,\ell m)\left[(N_aL_aM_a)(N'_aL'_aM'_a)\left|\frac{1}{r_{12}}\right|(n_b\ell_bm_b)(n'_b\ell'_bm'_b)\right] \quad (11)$$

For the odd values of k.

Here w= +,w= - for the even and odd values of k respectively .

It should be noted that ,for k=-1 ,formula (9) going to the formula (5) in the work by Guseinov and Yassen [13] for the two-center exchange integrals over Slater type orbitals .

CONCLUSION

In this paper ,the analytical evaluation of two-center exchange integral with correlation multiplier has been established for the following cases :

(i) when k is even [equation (5)].

(ii) when k is odd [equation (7)].

(iii) for the all values of k[equation (9)] .

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