ANALYTICAL EVALUATION OF MULTICENTER INTEGRALS WITH EXPONENTIAL FACTOR IN THE THEORY OF MOLECULES

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The convenient formulas are derived for the matrix elements with exponential factor arising in calculation of the different parameters of molecules. These matrix elements are expressed in terms of overlap integrals over Slater-type orbitals. The formulas of this paper can be used also in evaluation of multicenter matrix elements of Hartree-Fock-Roothaan equations.

It is well known, that the quantum mechanical methods are applied for theoretical research of molecules. The matrix elements arising in the calculation of the different molecule's parameters are expressed by one- and two-center integrals containing the following exponential factor:

$$f_{\mu\nu\sigma}(\alpha,\vec{r}) = r^{\mu-1} e^{-\alpha r}(\theta,\varphi) \qquad (1)$$

where $\mu \geq -(\nu+1)$, $\alpha \geq 0$ and $S_{\nu\sigma}$ - real spherical functions.

In this paper the molecular one- and two-electron integrals are as follows:

$$\overline{U}_{abc} = \int \overline{\chi}_{n_1 l_1 m_1}(\xi_1,\vec{r}_{a_1}) f_{\mu\nu\sigma}(\alpha,\vec{r}_{b_1}) \overline{\chi}_{n_2 l_2 m_2}(\xi_1',\vec{r}_{c_1}) dv_1 \qquad (2)$$

$$\overline{I}_{acdb} = \int \overline{\chi}_{n_1 l_1 m_1}(\xi_1,\vec{r}_{a_1}) \overline{\chi}_{n_2 l_2 m_2}(\xi_1',\vec{r}_{c_1}) f_{\mu\nu\sigma}(\alpha,\vec{r}_{21}) \times \overline{\chi}_{n_3 l_3 m_3}(\xi_2,\vec{r}_{d_2}) \overline{\chi}_{n_4 l_4 m_4}(\xi_2',\vec{r}_{b_2}) dv_1 dv_2 \qquad (3)$$

where
$\vec{r}_{kj} = \vec{r}_{aj} - \vec{r}_{ak}$; $\vec{r}_{21} = \vec{r}_{a_2} - \vec{r}_{b_2}$ ($j=1,2$ and $k=b,c,d$).
These integrals are expressed by the overlap ones with the Slater-type orbitals $\overline{\alpha}_{nlm}$ ($\overline{\alpha}_{nlm}$-real unnormalized Slater-type orbitals):

$$\overline{\chi}_{nlm}(\xi,\vec{r}) = (2\xi)^{n+1/2} r^{n-1} e^{-\xi r} S_{lm}(\theta,\varphi) \qquad (4)$$

Using the expansion of the electron density distribution [1] we can express the matrix elements (2) and (3) by the following two-center integrals:

$$\overline{U}_{nlm,\mu\nu\sigma}(\xi,\alpha;\vec{R}_{ab}) = \int \overline{\chi}_{nlm}(\xi,\vec{r}_a) f_{\mu\nu\sigma}(\alpha,\vec{r}_{b_1}) dv_1 \qquad (5)$$

$$\overline{I}_{nlm,\mu\nu\sigma,n_1 l_1 m_1, n_2 l_2 m_2}(\xi,\alpha;\xi_1,\xi_2';\vec{R}_{ab}) = \int \overline{U}_{nlm,\mu\nu\sigma}(\xi,\alpha,\vec{r}_{a_2}) \overline{\chi}_{n_1 l_1 m_1}(\xi_1,\vec{r}_{b_2}) \overline{\chi}_{n_2 l_2 m_2}(\xi_2',\vec{r}_{b_2}) dv_2 \qquad (6)$$

These integrals can be calculated with the aid of obtained one-center expansion of the function $f_{\mu\nu\sigma}(\alpha,\vec{r})$ of the atomic Slater-type orbitals:

$$f_{\mu\nu\sigma}(\alpha,\vec{r}) = \lim_{N\to\infty} \sum_{\mu'+\nu'+1}^{N} \overline{F}^{N}_{\mu\nu,\mu'\nu'}(\xi,t) \overline{\chi}_{\mu'\nu'\sigma}(\xi,\vec{r}) \quad , (7)$$

where $t=(\xi-x)/(\xi+x)$. Note that in the case of $\mu \leq 0$ the expansion series (7) is true under condition $x<0$. In (7) the following notations are given as:

$$\overline{F}^{N}_{\mu\nu,\mu'\nu'}(\xi,t) = \sum_{\mu'+\nu'+1}^{N} \Omega^{l}_{\mu'\mu'}(N) \alpha_{\mu'\mu}(\xi,t) \qquad (8)$$

$$\Omega^{l}_{nn'}(N) = \sum_{n''=\max(n,n')}^{N} \varpi^{l}_{n''n} \varpi^{l}_{n''n'} \qquad (9)$$

$$\varpi^{l}_{nn'} = (-1)^{n'+l+1} \left[F_{n'+l+1}(n+l+1,0) F_{n'-l-1}(n-l-1,0 \right. \qquad (10)$$

$$F_m(N,0) = \frac{N!}{m!\,(N-m)!} \qquad (11)$$

$$\alpha_{nn'}(\xi,t) = \frac{(n+n')!\,(1+t)^{n+n'+1}}{(2\xi)^{n+n'+1/2}} \qquad (12)$$

One can easily show that under the conditions $\xi=\alpha$ $(t=0)$ and $\mu \leq \nu+1$ the expansion coefficients $\overline{F}^{N}_{\mu\nu\mu'\nu'}(\xi,t)$ lead to Kranecker symbols:

$$\overline{F}^{N}_{\mu\nu,\mu'\nu'}(\alpha,0) = \frac{\delta_{\mu\mu'}}{(2\alpha)^{\mu+1/2}} \quad \text{for } \mu \geq \nu+1 \qquad (13)$$

Substituting (7) into (5) and (6) we have

$$\overline{U}_{nlm,\mu\nu\sigma}(\xi,\alpha;\vec{R}_{ab}) = \lim_{N\to\infty} \sum_{\mu'+\nu'+1}^{N} \overline{F}^{N}_{\mu\nu,\mu'\nu'}(\xi,t) \overline{S}_{nlm,\mu'\nu\sigma}(\xi,\xi;\vec{R}_{ab}) \qquad (14)$$

$$\overline{I}_{nlm,\mu'\nu'\sigma',n_1l_1m_1,n_2'l_2'm_2'}(\xi,\alpha;\xi_1,\xi_{12}';\vec{R}_{ab}) = \lim_{N\to\infty}\sum_{\mu'=\nu+1}^{N}\overline{F}^{N}_{\mu\nu,\mu'\nu'}(\xi,t)\overline{J}_{nlm,\mu'\nu'\sigma',n_1l_1m_1,n_2'l_2'm_2'}(\xi,\xi;\xi_1,\xi_{12}';\vec{R}_{ab}) \quad (15)$$

As it is seen from (14)-(15) the terms $\overline{I}$ in the right-hand part of formula (15) depends on the overlap integrals $\overline{S}_{nlm,\mu'\nu'\sigma'}$ with the same screening parameters. To calculate the values $\overline{I}$ we have found the following formula by means of which these overlap integrals are expressed by the Slater-type orbitals: (ref.[2])

$$\overline{S}_{nlm,\mu'l'm'}(\vec{P}) = \sum_{N=1}^{n+\mu'+1}\sum_{L=0}^{N-1}\sum_{M=-L}^{L}\overline{g}_{nlm,\mu'l'm'}\overline{\chi}_{NLM}(1,\vec{P}) \quad (16)$$

Substituting (16) into (15) we obtain for $\overline{I}$

$$\overline{J}_{nlm,\mu'\nu'\sigma',n_1l_1m_1,n_2'l_2'm_2'}(\xi,\xi;\xi_1,\xi_{12}';\vec{R}_{ab}) = \xi^{-3/2}\sum_{k=1}^{n+\mu'+1}\sum_{S=0}^{k-1}\sum_{\tau=-S}^{S}\overline{g}^{kS\tau}_{nlm,\mu'\nu'\sigma'}\overline{G}_{kS\tau,n_1l_1m_1,n_2'l_2'm_2'}(\xi,\xi_1,\xi_{12}';\vec{R}_{ab}) \quad (17)$$

where

$$\overline{G}_{kS\tau,n_1l_1m_1,n_2'l_2'm_2'}(\xi,\xi_1,\xi_{12}';\vec{R}_{ab}) = \int\overline{\chi}_{kS\tau}(\xi,\vec{r}_{a_2})\overline{\chi}_{n_1l_1m_1}(\xi_1,\vec{r}_{1_2})\overline{\chi}_{n_2'l_2'm_2'}(\xi_{12}',\vec{r}_{b_2})\,dv_2 \quad (18)$$

Using the expansion formulas of the two Slater-type functions product with the equal centers [2] we can express the terms from (18) by the overlap integrals for $i=-$ and $i=+$. For the one- and two-center Coulomb integrals we have:

$$\overline{G}_{kS\tau,n_1l_1m_1,n_2'l_2'm_2'}(\xi,\xi_-,\xi_{12}';\vec{R}_{ab}) = \frac{\eta_-^{3/2}}{2^{N_-+3/2}}\beta_{n_-n_2'}(t_-)\sum_{LM}\sqrt{\frac{2L+1}{4\pi}}\times \quad \text{for } R_{ab}\geq 0 \quad (19)$$

$$\times C^{l|M|}(l_-m_-,l_2'm_2')\,A^{M}_{m_-m_2'}\overline{S}_{kS\tau,N_-LM}(\xi,\xi_-;\vec{R}_{ab})$$

For two-center hybrid integrals we find:

$$\overline{G}_{kS\tau,n_1l_1m_+,n_2'l_2'm_2'}(\xi,\xi_+,\xi_{12}';\vec{R}_{ab}) = \frac{\eta_+^{3/2}}{2^{N_++3/2}}\beta_{kn_+}(t_+)\sum_{LM}\sqrt{\frac{2L+1}{4\pi}}\times \quad \text{for } R_{ab}\geq 0 \quad (20)$$

$$\times C^{l|M|}(S\tau,l_+m_+)\,A^{M}_{m_+}\overline{S}_{N_+LM,n_2'l_2'm_2'}(\xi_+,\xi_{12}';\vec{R}_{ab})$$

where

$$\eta_- = \xi_- + \xi_{12}' \quad , \quad N_- = n_- + n_2' - 1 \quad , \quad t_- = \frac{\xi_- - \xi'}{\xi_- + \xi'}$$

$$\eta_+ = \xi + \xi_+ \quad , \quad N_+ = k + n_+ - 1 \quad , \quad t_+ = \frac{\xi - \xi_+}{\xi + \xi_+}$$

$$\beta_{nn'}(t) = (1+t)^{n+1/2}(1-t)^{n'+1/2}$$

Thus, the one- and two-electron multicenter matrix elements $f_{\mu\nu\sigma}(\alpha,\vec{r})$ are expressed by the overlap integrals for calculation of which the general analytical formulas are obtained in ref.[3]. The formulas obtained in the present paper are true in the case of $\mu=\nu=0$ and $\alpha=0$ $(t=1)$, what allows with the aid of them to calculate the multicenter integrals of the Hatree-Fock-Roothaan equations. It is necessary to point out that if the screening parameter α is equal to zero, then the divergences, arising not only in the multicenter integrals of the Hatree-Fock-Roothaan equations but also in the calculations of the molecular properties, are disappearing.

As it is seen from (13)-(15), if the screening parameters of the overlap integrals between the atomic orbitals and the functions $f_{\mu\nu\sigma}(\alpha,\vec{r})$ centered on the nucleuses a and b respectively, are equal to each other $(t=0)$, then we obtain the finite sums for the integrals $\overline{U}$ and $\overline{I}$ only under the condition $\mu \geq \nu+1$. If the screening parameters are different $(t\neq 0)$ and $\mu \geq \nu+1$, then the expressions for the two-center integrals and one- and two electron ones become the infinite expansion series. The calculation of these integrals on the ECM shows that the expansion series converges rapidly at the small values of the parameter t and therefore that is enough to take the few number of terms in (14) and (15).

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MOLEKULLAR NƏZƏRİYYƏSİNDƏ EKSPONENSİAL VURUQLU ÇOXMƏRKƏZLİ İNTEGRALLARIN ANALİTİK HESABLANMASI

Molekulların müxtəlif parametrlərinin hesablanması zamanı meydana çıxan eksponensial vuruqlu matris elementləri üçün analitik düsturlar alınmışdır. Bu matris elementləri Sleyter atom orbitalı örtmə integralları ilə ifadə olunmuşdur. İşdə alınan düsturlardan həmçinin Xartri-Fok-Rutan tənliklərinə daxil olan çoxmərkəzli matris elementlərin hesablanmasında da istifadə etmək olar.

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АНАЛИТИЧЕСКОЕ ВЫЧИСЛЕНИЕ МНОГОЦЕНТРОВЫХ ИНТЕГРАЛОВ С ЭКСПОНЕНЦИАЛЬНЫМ МНОЖИТЕЛЕМ В ТЕОРИИ МОЛЕКУЛ

Получены аналитические формулы для матричных элементов с экспоненциальным множителем, которые возникают при расчете различных параметров молекул. Эти матричные элементы выражены через интегралы перекрывания с орбиталями слейтеровского типа. Полученные в работе формулы также могут быть использованы в расчете многоцентровых матричных элементов уравнений Хартри-Фока-Рутана.

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