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Analytical evaluation of Coulomb potential generated by multielectron molecule at arbitrary positions in space using one-range addition theorems of Slater type orbitals

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Abstract By the use of unsymmetrical one-range addition theorems for Slater type orbitals (STO) and Coulomb potential introduced by the author, the analytical formulae in terms of two- and three-center nuclear attraction integrals, and linear combination coefficients of molecular orbitals are derived for the potential produced by the charges of molecule. These formulae can be useful for the study of interaction between atomic-molecular systems containing any number of closed and open shells when the STO are used in the combined Hartree-Fock-Roothaan (HFR) theory suggested by the author. It should be noted that the symmetry of the potential obtained is the same as the symmetry of the molecule. As an example of application, the calculations have been performed for the potential produced by the ground state of BH_3 molecule $\left((1a_1)^2 (2a_1)^2 (1e_x)^2 (1e_y)^2, {}^1A_1 \right)$.

Keywords Electron-molecule interaction potential · Multicenter nuclear attraction integrals · One-range addition theorems · Slater type orbitals

Introduction

In the electronic structure calculations of atoms and molecules, a natural choice of reliable basis function set is the exponential type orbitals (ETO) as the behavior of ETO is close to the exact atomic orbitals. During the past few years, the Gaussian type orbitals (GTO) are used on a large scale in calculations. This is motivated by the practical requirement for easy and rapid evaluation of multicenter integrals. Unfortunately, the GTO basis functions fail to satisfy two mathematical conditions for atomic electronic distributions, namely, the cusp condition at the origin [1] and exponential decay at long range [2]. ETO would be desirable for basis sets because they satisfy these conditions. In a previous paper [3], the series of expansion formulae has been derived for the potential of electric field produced by the charges of molecule using complete orthonormal sets of ψ^a-ETO introduced in [4]. The aim of this work, which presents the development of our previous papers (see Ref. [3] and references quoted therein), is to establish the new formulae for the electron-molecule Coulomb interaction potential using STO basis functions.

Theory

The operator of Coulomb potential for electric field of N-electron molecule is defined in atomic units by (see Fig.1):

$$\widehat{\varphi}(\vec{r}_g) = \widehat{\varphi}_N(\vec{r}_g) + \widehat{\varphi}_E(\vec{r}_g), \tag{1}$$

where N and E stand for nuclear and electronic parts, respectively,

$$\widehat{\varphi}_N(\vec{r}_g) = \sum_a \frac{Z_a}{r_{ag}} \tag{2}$$

$$\widehat{\varphi}_E(\vec{r}_g) = -\sum_{i=1}^{N} \frac{1}{r_{ig}}. \tag{3}$$

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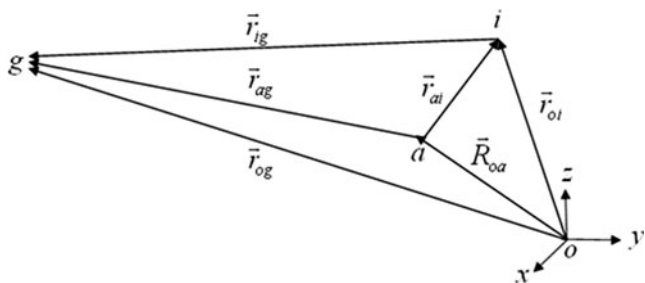Çanakkale, Turkey
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Fig. 1 The position of charges of molecule and point g

Here, Z_a is the charge of nucleus a ($a \equiv b, c, ...$); $\vec{r}_g$ is the radius-vector of the point g with respect to the origin of the molecular coordinate system.

Let u_i denote the molecular orbitals of the molecule in its ground state. The average expectation value of potential defined by Eq. 1 for multideterminantal single electron configuration states with any number of closed and open shells of molecule is then given by (see Refs. [3] and [5]):

$$\varphi\left(\vec{r}_g\right) = \sum_a \frac{Z_a}{r_{ag}} - 2\sum_{i=1}^{\kappa} f_i I_i^g, \qquad (4)$$

Where $\kappa = \kappa_c + \kappa_0$ is the number of occupied orbitals of closed (κ_c) and open (κ_0) shells, f_i is the fractional occupancy of shell i and

$$I_i^g = \int u_i^*(\vec{r}_1) u_i(\vec{r}_1) \frac{1}{r_{g1}} dv_1. \qquad (5)$$

Now we use in Eq. 5 the formula

$$u_i = \sum_p \chi_p C_{pi} \qquad (6)$$

for the molecular orbitals in terms of χ – STO determined by

$$\chi_{nlm}(\zeta, \vec{r}) = R_n(\zeta, r) S_{lm}(\theta, \phi) \qquad (7a)$$

$$R_n(\zeta, r) = [(2n)!]^{-1/2}(2\zeta)^{n+1/2} r^{n-1} e^{-\zeta r}, \qquad (7b)$$

where $S_{lm}(\theta, \phi)$ are the complex (for $S_{lm} \equiv Y_{lm}$) or real spherical harmonics and $\zeta > 0$ is the orbital exponent. Then, we obtain

$$I_i^g = \sum_{p_1 p_1'} C_{p_1 i}^* C_{p_1' i} I_{p_1 p_1'}^{ac,g}\left(\zeta_1, \zeta_1'\right). \qquad (8)$$

Here, $p_1 \equiv n_1 l_1 m_1$, $p_1' \equiv n_1' l_1' m_1'$ and

$$I_{p_1 p_1'}^{ac,g}\left(\zeta_1, \zeta_1'\right) = \int \chi_{p_1}^*(\zeta_1, \vec{r}_{a1}) \chi_{p_1'}\left(\zeta_1', \vec{r}_{c1}\right) \frac{1}{r_{g1}} dv_1. \qquad (9)$$

With the evaluation of multicenter nuclear attraction integrals 9 we use the following relation for the unsym-

metrical one-range addition theorems established in a previous paper [6] for the charge density of STO:for one-center case

$$\chi_{p_1}^*\left(\zeta_1, \vec{r}_{a1}\right) \chi_{p_1'}\left(\zeta_1', \vec{r}_{a1}\right)$$

$$= \frac{1}{\sqrt{4\pi}} \sum_{l=|l_1-l_1'|}^{l_1+l_1'} \sum_{m=-l}^{l} W_{p_1 p_1' p}\left(\zeta_1, \zeta_1', z\right) \chi_p^*(z, \vec{r}_{a1}), \qquad (10)$$

for two-center case

$$\chi_{p_1}^*\left(\zeta_1, \vec{r}_{a1}\right) \chi_{p_1'}\left(\zeta_1', \vec{r}_{c1}\right)$$

$$= \frac{1}{\sqrt{4\pi}} \lim_{N\to\infty} \sum_{n=1}^{N} \sum_{l=0}^{n-1} \sum_{m=-l}^{l} W_{p_1 p_1' p}^{\alpha N}\left(\zeta_1, \zeta_1', z; \vec{R}_{ca}, 0\right) \chi_p^*(z, \vec{r}_{a1}), \qquad (11)$$

where $p \equiv nlm$, $n = n_1 + n_1' - 1$, $z = \zeta_1 + \zeta_1'$ and $\alpha = 1, 0, -1, -2, ...$; the indices N is a positive integer number. Taking into account Eqs. 10 and 11 in 9 we obtain:

$$I_{p_1 p_1'}^{aa,g}\left(\zeta_1, \zeta_1'\right)$$

$$= \sum_{l=|l_1-l_1'|}^{l_1+l_1'} \sum_{m=-l}^{l} W_{p_1 p_1' p}\left(\zeta_1, \zeta_1', z\right) J_p\left(z, \vec{r}_{ag}\right) \qquad (12)$$

$$I_{p_1 p_1'}^{ac,g}\left(\zeta_1, \zeta_1'\right)$$

$$= \lim_{N\to\infty} \sum_{n=1}^{N} \sum_{l=0}^{n-1} \sum_{m=-l}^{l} W_{p_1 p_1' p}^{\alpha N}\left(\zeta_1, \zeta_1', z; \vec{R}_{ca}, 0\right) J_p\left(z, \vec{r}_{ag}\right), \qquad (13)$$

where $J_p\left(z, \vec{r}_{ag}\right)$ is the two-center basic nuclear-attraction integral defined as

$$J_p\left(z, \vec{r}_{ag}\right) = \frac{1}{\sqrt{4\pi}} \int \chi_p^*(z, \vec{r}_{a1}) \frac{1}{r_{g1}} dv_1. \qquad (14)$$

With the evaluation of integral 14 we use the following relation established in a previous paper [7]:

$$J_p\left(z, \vec{r}_{ag}\right) = \sqrt{4\pi} J_{nl}\left(z, r_{ag}\right) S_{lm}^*\left(\theta_{ag}, \phi_{ag}\right), \qquad (15)$$

where

$$J_{nl}\left(z, r_{ag}\right) = \frac{2^n (2/F_n(2n)z)^{1/2} F_n(n+l+1)(l+1)!}{(2l+1)(zr_{ag})^{l+1}}$$

$$\times \left[1 - e^{-zr_{ag}} \sum_{k=0}^{n+l} \gamma_k(n,l) \frac{(zr_{ag})^k}{k!}\right]. \qquad (16)$$

Using Eqs. 8, 12, 13 and 15 in 4, we obtain finally for the potential the following relation:

$$
\varphi\left(\vec{r}_{og}\right) = \sum_{a} \frac{Z_a}{r_{ag}} - 2\sum_{i=1}^{\kappa} f_i \sum_{p_1 p_1'} C_{p_1 i}^* C_{p_1' i}
$$

$$
\times \left\{ \begin{array}{ll} \displaystyle\sum_{l=|l_1-l_1'|}^{l_1+l_1'} \sum_{m=-l}^{l} W_{p_1 p_1' p}\left(\zeta_1, \zeta_1', z\right) & \text{for } c \equiv a \\[6pt] \displaystyle\lim_{N\to\infty} \sum_{l=0}^{N-1} \sum_{m=-l}^{l} \sum_{n=l+1}^{N} W_{p_1 p_1' p}^{\alpha N}\left(\zeta_1, \zeta_1', z; \vec{R}_{ca}, 0\right) & \text{for } c \neq a \end{array} \right\} J_p\left(z, \vec{r}_{ag}\right).
$$

(17)

See Eqs. 4, 13, 14, and 19 of Ref. [6] for the exact definition of charge density expansion coefficients $W_{p_1 p_1' p}\left(\zeta_1, \zeta_1', z\right)$ and $W_{p_1 p_1' p}^{\alpha N}\left(\zeta_1, \zeta_1', z; \vec{R}_{ca}, 0\right)$ occurring in these equations. The Coulomb interaction potential 17 can also be expanded in multipole potentials:

$$
\varphi\left(\vec{r}_{og}\right) = \sum_{L=0}^{\infty} \sum_{M=-L}^{L} \varphi_{LM}^{\alpha *}\left(r_{og}\right) S_{LM}\left(\theta_{og}, \phi_{og}\right),
$$

(18)

where

$$
\varphi_{LM}^{\alpha}\left(r_{og}\right) = \int \varphi^*\left(\vec{r}_{og}\right) S_{LM}\left(\theta_{og}, \phi_{og}\right) d\Omega_{og}.
$$

(19)

The evaluation of integral 19 for the radial part of multipole potentials can be performed using the one-range addition theorems of STO and Coulomb potential of nuclei (see Ref [8]). For the multipole expansions of basic nuclear attraction integrals and Coulomb potential of nuclei occurring in Eqs. 17 and 19 we find:

$$
J_p\left(z, \vec{r}_{ag}\right) = \sqrt{4\pi} \sum_{L=0}^{\infty} \sum_{M=-L}^{L} \lim_{K\to\infty}
$$

$$
\times \sum_{N=L+1}^{K} V_{nlm,NLM}^{\alpha}\left(z, z; \vec{R}_{ao}\right) J_{NL}\left(z, r_{og}\right) S_{LM}^*\left(\theta_{og}, \phi_{og}\right)
$$

(20)

$$
\frac{1}{r_{ag}} = \sqrt{4\pi} \sum_{L=0}^{\infty} \sum_{M=-L}^{L} \lim_{K\to\infty}
$$

$$
\times \sum_{N=L+1}^{K} W_{000,NLM}^{\alpha K}\left(0, z; \vec{R}_{ao}\right) R_N\left(z, r_{og}\right) S_{LM}^*\left(\theta_{og}, \phi_{og}\right).
$$

(21)

Taking into account Eqs. 18–21 in 17 we obtain for the multipole expansion of Coulomb potential the following relation:

Table 1 The orbital energies and linear combination coefficients of molecular orbitals for the ground state of $BH_3((1a_1)^2(2a_1)^2(1e_x)^2(1e_y)^2, {}^1A_1)$

ε_i	$\varepsilon_1 = \varepsilon_{1a_1}$	$\varepsilon_2 = \varepsilon_{2a_1}$	$\varepsilon_3 = \varepsilon_{1e_x}$	$\varepsilon_4 = \varepsilon_{1e_y}$
χ_p	−7.75364476	−0.73431275	−0.52420721	−0.52420700
χ_1 (ζ=1.18600)	0.00370169	−0.24290487	0.00000000	0.44504937
χ_2 (ζ=1.18600)	0.00370169	−0.24290487	0.38544838	−0.22252468
χ_3 (ζ=1.18600)	0.00370169	−0.24290487	−0.38544838	−0.22252468
χ_4 (ζ=4.67939)	0.00370169	0.18782755	0.00000000	0.00000000
χ_5 (ζ=1.28808)	−0.01919680	−0.59633593	0.00000000	0.00000000
χ_6 (ζ=1.21066)	0.00000000	0.00000000	−0.56646430	0.00000000
χ_7 (ζ=1.21066)	0.00000000	0.00000000	0.00000000	0.56649612
χ_1 (ζ=1.21066)	0.00000000	0.00000000	0.00000000	0.00000000
This work		Ref.[11]		
Total energy: -26.322082		−26.3377		

Table 2 The values of Coulomb potential of electric field produced by molecule BH_3

r / ϕ	3	4	5	6	7	8	9	10
30	1.09905	0.84182	0.67618	0.56310	0.48193	0.42109	0.37388	0.33619
150	1.09905	0.84182	0.67618	0.56310	0.48193	0.42109	0.37388	0.33619
270	1.09905	0.84182	0.67618	0.56310	0.48193	0.42109	0.37388	0.33619
90	1.80365	0.97708	0.70653	0.57076	0.48486	0.42273	0.37494	0.33691
210	1.80365	0.97708	0.70653	0.57076	0.48486	0.42273	0.37494	0.33691
330	1.80365	0.97708	0.70653	0.57076	0.48486	0.42273	0.37494	0.33691

$$
\varphi\left(\vec{r}_{og}\right) = \sqrt{4\pi} \sum_{L=0}^{\infty} \sum_{M=-L}^{L} \left\{ \sum_{a} Z_a \lim_{K\to\infty} \sum_{N=L+1}^{K} W_{000,NLM}^{\alpha K}\left(0,z;\vec{R}_{ao}\right) R_N\left(z,r_{og}\right) - 2 \sum_{i=1}^{\kappa} f_i \sum_{p_1 p_1'} C_{p_1 i}^{*} C_{p_1' i} \right.
$$

$$
\times \left[\begin{array}{ll} \sum_{l=|l_1-l_1'|}^{l_1+l_1'} \sum_{m=-l}^{l} W_{p_1 p_1' p}\left(\zeta_1, \zeta_1', z\right) & \text{for } c \equiv a \\ \lim_{N\to\infty} \sum_{l=0}^{N-1} \sum_{m=-l}^{l} \sum_{n=l+1}^{N} W_{p_1 p_1' p}^{\alpha N}\left(\zeta_1, \zeta_1', z; \vec{R}_{ca}, 0\right) & \text{for } c \not\equiv a \end{array} \right] \times \left. \lim_{K\to\infty} \sum_{N=L+1}^{K} V_{nlm,NLM}^{\alpha}\left(z,z;\vec{R}_{ao}\right) J_{NL}\left(z,r_{og}\right) \right\} S_{LM}^{*}\left(\theta_{og}, \phi_{og}\right).
$$

$$\tag{22}$$

Thus, we have established a large number of different $(\alpha = 1,0,-1,-2,\ldots)$ sets of formulae for the Coulomb potential produced by a molecule containing any number of closed and open shells in terms of two-center basic nuclear attraction integrals and linear combination coefficients for molecular orbitals.

Numerical results and discussion

As an application of formulae 17 for the potential, we have solved combined HFR equations for the ground state
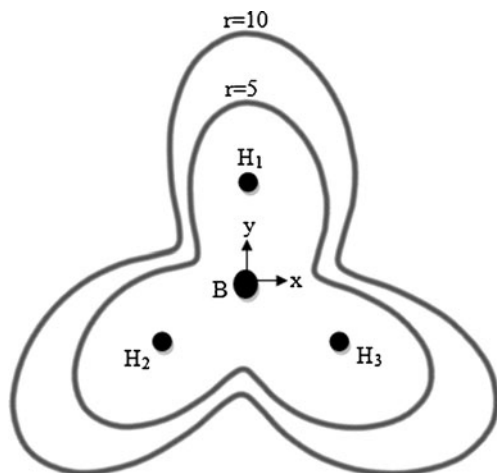

Fig. 2 Dependence of the potential $\varphi(\vec{r})$ produced by BH_3 on ϕ for $r=5$, $r=10$, $\theta=90^0$, $\alpha=0$ and $N=5$ (a.u.)

of $BH_3((1a_1)^2(2a_1)^2(1e_x)^2(1e_y)^2, {}^1A_1)$ using STO as a minimal basis set. All of the multicenter integrals over STO appearing in the combined HFR equations for BH_3 molecule have been evaluated with the help of computer programs presented in our previous paper [9]. For the atoms of BH_3, we have used the following coordinates:

	X	Y	Z
H_1	0	R	0
H_2	$-\frac{\sqrt{3}}{2}R$	$-\frac{R}{2}$	0
H_3	$\frac{\sqrt{3}}{2}R$	$-\frac{R}{2}$	0
B	0	0	0,

where $R = R_{BH} = 2.26014098$ a.u. The Slater orbitals χ_p are denoted as

The results of computer calculations for orbital and total energies, and linear combination coefficients of molecular orbitals are presented in Table 1. The data for the screening constants of STO were taken from Ref. [10]. The results obtained using minimal basis set of STO agree well with published data [11] which used $R_{BH} = 2.25$ au as the B-H distance in BH_3.

On the basis of formulae 17 for the potential we have also constructed the programs taking into account the values of

χ_{nlm}:	χ_{100} (H_1)	χ_{100} (H_2)	χ_{100} (H_3)	χ_{100} (B)	χ_{200} (B)	χ_{211} (B)	$\chi_{21\text{-}1}$ (B)	χ_{210} (B)
χ_p:	χ_1	χ_2	χ_3	χ_4	χ_5	χ_6	χ_7	χ_8.

linear combination coefficients given in Table 1. The results of calculations in atomic units for the potential $\varphi(\vec{r}_g)$ on xy-plane are presented in Table 2 and Fig. 2. As can be seen from Table 2 and Fig. 2 the potential is low between H-atoms of molecule as would be expected from classical electrostatics. With the help of Eq. 17, the potential of molecule can also be found in any point of space. Thus, we have demonstrated the applicability of Eq. 17 to the study of potential produced by molecule.

Conclusions

A general formula has been established for the Coulomb potential of electric field produced by an N-electron molecule at arbitrary positions in space. The purposed algorithm is especially useful for computation of potential generated by multielectron molecule containing any number of open shells. As an example of application, the general formula obtained has been utilized for the calculation of potential produced by the ground state of BH_3 molecule using minimal basis set of STO. Because BH_3 dimerizes rapidly to B_2H_6, for the R_{BH} distance in BH_3 we employed the corresponding distance (terminal) in diborane. We notice that the same results can also be obtained only by the use of extended basis set of GTO [12]. Therefore, the presented theory can be employed as a practicable alternative to the conventional Gaussian methodology. We are sure that all these features make the presented analytical model very useful for the study of interaction between molecules, electron scattering from molecules and their photoionization and photoluminescence which require *ab initio* electron-molecule potential.

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