

Evaluation of potential of electric field produced by molecule using symmetrical one-range addition theorems for Coulomb-Yukawa like correlated interaction potentials of integer and noninteger indices

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Abstract Using symmetrical one-range addition theorems the series expansion formulae in terms of multicenter charge density expansion coefficients for noninteger n Slater type orbitals (STO), parameters of Coulomb-Yukawa like correlated interaction potentials (CIP) of noninteger indices and linear combination coefficients of molecular orbitals are established for the potential of electrostatic field produced by the charges of molecule. The final results are useful for the study of interaction between atomic-molecular systems containing any number of closed and open shells when the Hartree-Fock-Roothaan (HFR) approximation and the explicitly correlated methods based upon the use of STO as basis functions and Coulomb-Yukawa like CIP are employed. As an example of application, the calculations have been performed for the Coulomb interaction potential produced by the ground state of CH_2 molecule ($1a_1^2 2a_1^2 1b_1^2 3a_1^1 1b_1^1, ^3B_1$).

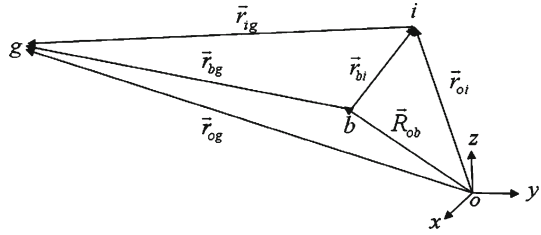
Keywords Coulomb-Yukawa like interaction potentials · Addition theorems · Hartree-Fock-Roothaan approximation · Slater type orbitals

1 Introduction

It is well known that the Gaussian type orbitals (GTO) is widely used in electronic structure calculations of molecules [1]. The STO are viable alternative to GTO because they belong to class of orbitals that possess the same asymptotic behavior as the true solutions of the Schrödinger equation [2,3]. Unfortunately, the STO functions are not orthogonal with respect to the principal quantum numbers that creates some difficulties in molecular electronic structure calculations. Thus, the necessity for using

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Fig. 1 The position of charges of molecule and point *g*



the complete orthonormal sets of $\psi^\alpha - ETO(\alpha = 1, 0, -1, -2, \dots)$ as basis functions arises [4]. In previous paper [5], with the help of $\psi^\alpha - ETO$ a large number of different sets of expansion formulae for multicenter integer and noninteger *n* STO charge densities has been established. These different sets have the further advantages that the multicenter charge density expansion formulae presented in Ref. [5] can be chosen properly according to the nature of the problems under consideration. This is rather important because the choice of series expansion relations will determine the rate of convergence of series expansions arising in molecular electronic structure calculations.

In this study, the series of expansion formulae are derived for the potential produced by molecule when the STO and the Coulomb–Yukawa like CIP approximation in HFR theory are employed. The results presented are especially useful for the investigation of interaction between molecules, electron scattering from molecules and their photoionization and photoluminescence.

2 Potential of electric field produced by molecule

The operator of noninteger μ^* potential examined in this work has the following form (see Fig. 1):

$$\hat{\phi}^{\mu^* \nu \sigma}(\xi, \vec{r}_{og}) = \sum_b Z_b h^{\mu^* \nu \sigma}(\xi, \vec{r}_{bg}) - \sum_{i=1}^N h^{\mu^* \nu \sigma}(\xi, \vec{r}_{ig}). \tag{1}$$

Here, \vec{r}_{og} and \vec{r}_{bg} are radius-vectors of the point *g* with respect to the origin of the molecular coordinate system and to the nuclei of *N* electron molecule, respectively ($b \equiv a, c, \dots$), Z_b is the charge of nucleus *b*, r_{ig} is the distance to the *i*th electron of molecule and $0 \leq \xi < \infty$. The Coulomb (for $\xi = 0$) and Yukawa (for $\xi \neq 0$) like CIP operators occurring in Eq. 1 are defined as [6]

$$h^{\mu^* \nu \sigma}(\xi, \vec{r}) = \left(\frac{4\pi}{2\nu + 1} \right)^{\frac{1}{2}} r^{\mu^* - 1} e^{-\xi r} S_{\nu \sigma}(\theta, \varphi), \tag{2}$$

where $S_{\nu \sigma}(\theta, \varphi)$ are the complex ($S_{\nu \sigma} \equiv Y_{\nu \sigma}$) or real spherical harmonics.

In the treatment of potential of the field produced by all the charges of molecule it is necessary to transform the operator (1), which depends upon the coordinates of three

points, in such a way that the coordinates of these points appear in a computationally more convenient form. This requires a separation of integration variables from those related to the geometry of the molecule. For this purpose we use the symmetrical one-range addition theorems established in a previous paper [7]. Then, we obtain for Coulomb–Yukawa like CIP the relations:

$$h^{\alpha\mu^*v\sigma}(\xi, \vec{r}_{ig}) = \lim_{M \rightarrow \infty} \sum_{\mu=v+1}^M Q_{\mu^*v, \mu v}^{\alpha M}(\xi, \eta) h^{\alpha\mu\nu\sigma}(\eta, \vec{r}_{ig}) \quad (3)$$

$$h^{\alpha\mu\nu\sigma}(\eta, \vec{r}_{ig}) = \sqrt{4\pi} \lim_{K, U \rightarrow \infty} \sum_{n=1}^K \sum_{l=0}^{n-1} \sum_{m=-l}^l V_{\mu\nu\sigma, nlm}^{\alpha KU^*}(\eta, \vec{r}_{og}) \chi_{nlm}(\eta, \vec{r}_{oi}), \quad (4)$$

where $\eta > 0$, $\alpha = 1, 0, -1, -2, \dots$ and

$$V_{\mu\nu\sigma, nlm}^{\alpha KU}(\eta, \vec{r}_{og}) = \sqrt{4\pi} \sum_{u=1}^{K+U-\alpha+1} \sum_{v=0}^{u-1} \sum_{s=-v}^v a_{\mu\nu\sigma, nlm}^{\alpha uvs}(K, U) \chi_{uvs}^*(\eta, \vec{r}_{og}) \quad (5)$$

$$a_{\mu\nu\sigma, nlm}^{\alpha uvs}(K, U) = \frac{(-1)^{v+v} 2^{3/2}}{(4\pi)(2\eta)^{\mu+2}} A_{\mu\nu\sigma, nlm}^{\alpha uvs}(K, U). \quad (6)$$

See Ref. [7] for the exact definition of coefficients occurring in these equations. We notice that the quantities $V_{\mu\nu\sigma, nlm}^{\alpha KU}(\eta, \vec{r}_{og})$ in Eq 5 are related to the radius vector of point where the potential of electric field produced by molecule is finding.

Substituting (3) and (4) into Eq. 1, we get for the separated form of potential operator the following formulae:

$$\hat{\varphi}^{\alpha\mu^*v\sigma}(\xi, \vec{r}_{og}) = \lim_{M \rightarrow \infty} \sum_{\mu=v+1}^M Q_{\mu^*v, \mu v}^{\alpha M}(\xi, \eta) \hat{\varphi}^{\alpha\mu\nu\sigma}(\eta, \vec{r}_{og}) \quad (7)$$

$$\begin{aligned} \hat{\varphi}^{\alpha\mu\nu\sigma}(\eta, \vec{r}_{og}) &= \lim_{K, U \rightarrow \infty} \sum_{n=1}^K \sum_{l=0}^{n-1} \sum_{m=-l}^l V_{\mu\nu\sigma, nlm}^{\alpha KU^*}(\eta, \vec{r}_{og}) \sqrt{4\pi} \\ &\times \left\{ \sum_b Z_b \chi_{nlm}(\eta, \vec{R}_{ob}) - \sum_{i=1}^N \chi_{nlm}(\eta, \vec{r}_{oi}) \right\}. \quad (8) \end{aligned}$$

Using the method set out in Ref. [8] it is easy to show that the average expectation value of potential defined by Eq. 8 for multideterminantal single electron configuration states with any number of closed and open shells of molecule is given by the formula

$$\varphi^{\alpha\mu\nu\sigma}(\eta, \vec{r}_{og}) = \lim_{K,U \rightarrow \infty} \sum_{n=1}^K \sum_{l=0}^{n-1} \sum_{m=-l}^l V_{\mu\nu\sigma,nlm}^{\alpha KU*}(\eta, \vec{r}_{og}) \left\{ \sqrt{4\pi} \sum_b Z_b \chi_{nlm}(\eta, \vec{R}_{ob}) - 2 \sum_{i=1}^{\kappa} f_i I_{nlm,i}^*(\eta) \right\}. \tag{9}$$

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

$$I_{nlm,i}(\eta) = \sqrt{4\pi} \int \chi_{nlm}^*(\eta, \vec{r}_{o1}) u_i(\vec{r}_1) u_i^*(\vec{r}_1) dv_1. \tag{10}$$

Here, u_i are the molecular orbitals defined from the following linear combination of integer and noninteger n STO:

$$u_i = \sum_{p^*} \chi_{p^*} C_{p^*i}, \tag{11}$$

where $p^* \equiv n^*lm$. The normalized STO with nonintegral values of the principal quantum number n^* are defined by

$$\chi_{p^*}(\zeta, \vec{r}) \equiv \chi_{n^*lm}(\zeta, \vec{r}) \equiv (2\zeta)^{n^*+1/2} [\Gamma(2n^* + 1)]^{-1/2} r^{n^*-1} e^{-\zeta r} S_{lm}(\theta, \varphi). \tag{12}$$

Here, ζ ($0 < \zeta < \infty$) is the screening constant and $\Gamma(x)$ is the gamma function [9]. The normalized integer n STO can be obtained from Eq. 12 for $n^* = n$, where n is an integer:

$$\chi_p \equiv \chi_{nlm}(\zeta, \vec{r}) \equiv (2\zeta)^{n+1/2} [(2n)!]^{-1/2} r^{n-1} e^{-\zeta r} S_{lm}(\theta, \varphi). \tag{13}$$

The linear combination coefficients C_{p^*i} can be determined by solving the combined HFR equations for molecule (see Ref. [8]).

Now we use in Eq. 10 the expression (11) for the molecular orbitals:

$$I_{nlm,i}(\eta) \equiv I_{nlm,i}^{oac}(\eta) = \sum_{p^*} \sum_{p'^*} C_{p^*i} C_{p'^*i}^* S_{pp^*p'^*}^{oac}(\eta, \zeta, \zeta'), \tag{14}$$

where $p \equiv nlm$ and S^{oac} is the three-center overlap integral defined by

$$S_{pp^*p'^*}^{oac}(\eta, \zeta, \zeta') = \sqrt{4\pi} \int \chi_p^*(\eta, \vec{r}_{o1}) \chi_{p^*}(\zeta, \vec{r}_{a1}) \chi_{p'^*}(\zeta', \vec{r}_{c1}) dv_1. \tag{15}$$

In order to evaluate the integral (15) we use Eq. 10 of previous paper [5] for the series expansion of the two-center charge densities in terms of integer n STO. Then, we obtain:

$$S_{pp^*p^*}^{\alpha oac}(\eta, \zeta, \zeta') = \lim_{N \rightarrow \infty} \sum_{\mu=1}^N \sum_{\nu=0}^{\mu-1} \sum_{\sigma=-\nu}^{\nu} W_{p^*p^*q}^{\alpha N}(\zeta, \zeta', z; \vec{R}_{ca}, 0) S_{pq}(\eta, z; \vec{R}_{oa}), \quad (16)$$

where $z = \zeta + \zeta'$, $q \equiv \mu\nu\sigma$ and

$$S_{pq}(\eta, z; \vec{R}_{oa}) = \int \chi_p^*(\eta, \vec{r}_{o1}) \chi_q(z, \vec{r}_{a1}) dV_1. \quad (17)$$

The correlated interaction potential (9) can also be expanded in multipole potentials:

$$\varphi^{\alpha\mu\nu\sigma}(\eta, \vec{r}_{og}) = \sum_{L=0}^{\infty} \sum_{M=-L}^L \varphi_{LM}^{\alpha\mu\nu\sigma*}(\eta, r_{og}) S_{LM}(\theta_{og}, \phi_{og}), \quad (18)$$

where

$$\varphi_{LM}^{\alpha\mu\nu\sigma}(\eta, r_{og}) = \int \varphi^{\alpha\mu\nu\sigma*}(\eta, \vec{r}_{og}) S_{LM}(\theta_{og}, \phi_{og}) d\Omega_{og}. \quad (19)$$

In order to evaluate the integral (19) we use Eq. 9. Then, we obtain for the radial part of multipole potentials the following relation:

$$\varphi_{LM}^{\alpha\mu\nu\sigma}(\eta, r_{og}) = \sqrt{4\pi} \lim_{K, U \rightarrow \infty} \sum_{n=1}^K \sum_{l=0}^{n-1} \sum_{m=-l}^l \sum_{u=L+1}^{K+U-\alpha+1} a_{\mu\nu\sigma, nlm}^{\alpha u LM}(K, U) R_u(\eta, r_{og}) \times \left[\sqrt{4\pi} \sum_b Z_b \chi_{nlm}(\eta, \vec{R}_{ob}) - 2 \sum_{i=1}^k f_i I_{nlm, i}^{oac}(\eta) \right], \quad (20)$$

where $R_u(\eta, r_{og})$ is the radial part of $\chi - STO$.

As can be seen from Eqs. 9, 18 and 14–17, we have established a large number of different sets of series expansion relations ($\alpha = 1, 0, -1, -2, \dots$) for the potential produced by molecule in terms of multicenter charge density expansion coefficients, linear combination coefficients of molecular orbitals and two-center overlap integrals over integer n STO. For the calculation of two-center overlap integrals the efficient computer programs especially useful for large quantum numbers are available in our group [10]. Therefore by using the computer programs for the overlap integrals one can calculate the potential of the field produced by molecule.

3 Numerical results and discussion

On the basis of Eqs. 9, 14 and 16 we constructed the programs which were performed in the Turbo Pascal 7.0 language packages. Using integer n -STO as a minimal basis set we calculated the Coulomb interaction potential ($\mu = \nu = \sigma = \xi = 0$) produced by ground state of CH_2 molecule. All of the linear combination coefficients C_{pi} and

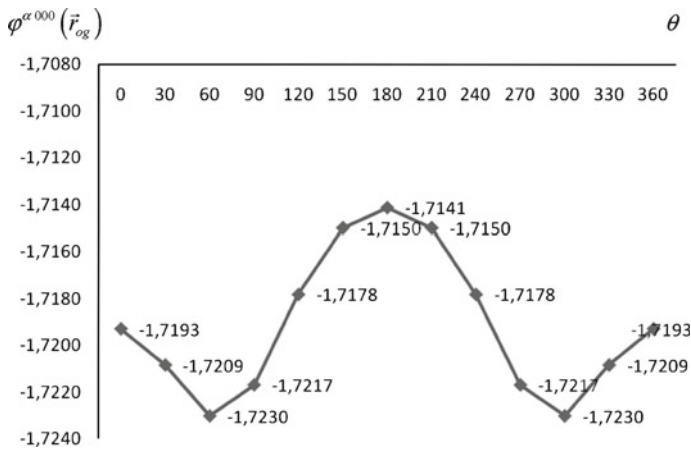


Fig. 2 Dependence of the potential $\varphi^{\alpha 000}(\vec{r}_{og})$ produced by CH_2 on θ for $r_{og} = 15$, $\phi = 90$, $\alpha = 1, 0, -1, \dots$ and $N = 8$

coordinates of atoms appearing in Eqs. 9, 14 and 16 have been taken from a previous paper [11]. The results of calculations in atomic units for the potential $\varphi^{\alpha 000}(\vec{r}_{og})$ are presented in Fig. 2. As can be seen from this figure that the molecule CH_2 , its dipole moment and calculated interaction potential lie on yz -plane. As would be expected from the classical electrostatics, the potential is highest at 180° . Unfortunately, there are no previous results found in the literature to compare. Thus, we have demonstrated the applicability of the symmetrical one-range addition theorems to the study of potential produced by molecule.

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