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One-range addition theorems for combined Coulomb and Yukawa like central and noncentral interaction potentials and their derivatives

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In this work we present the combined one-range addition theorems for arbitrary Coulomb and Yukawa like central and noncentral interaction potentials and their first and second derivatives occurring in the Hartree–Fock–Roothaan approximation and explicitly correlated methods, and also in the study of electric field and its gradient induced by electrons at the nuclei of a molecule. The relationships obtained for addition theorems are valid for the arbitrary parameters of potentials.

KEY WORDS: addition theorems, Coulomb potential, Yukawa potential, Slater-type orbitals, Hartree–Fock–Roothaan approximation, correlated methods

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1. Introduction

It is well known that the series of electronic structure and electron–nuclei interaction properties of a molecule are very sensitive to the minor errors in the wave functions and their derivatives with respect to coordinates of the nuclei [1–3]. These computational problems, which have to be overcome, depend strongly on the basis functions being used. Therefore, the Slater-type orbitals (STOs), which are able to describe correctly the asymptotic behavior of exact solutions of atomic and molecular Schrödinger equation both in the vicinity of the nuclei [4] or at large distances away from the nuclei [5], nowadays play a negligible role in *ab initio* calculations. It should be noted that, if one tries to study, in particular, the electron–nuclei interactions in molecules with the help of Gaussian type orbitals, the slow convergence of which may lead to serious computational problems. The inherent limitations of Gaussian basis functions necessitate to use the addition theorems for interaction potentials and orbitals for the calculation of matrix elements in the MO LCAO theory with STOs. In our previous papers [6, 7], the one-range addition theorems were established for Coulomb and Yukawa interaction potentials and their derivatives.

The aim of this report is to obtain the combined one-range addition theorems for the Coulomb- and Yukawa-like central and noncentral interaction (CI and NCI) potentials and their derivatives. These addition theorems are especially useful for the calculation of multicenter electronic attraction, electric field and electric field gradient integrals occurring in the study of interaction between electrons and nuclei of a molecule when Hartree–Fock–Roothaan and explicitly correlated approaches are employed.

2. Addition theorems for potentials

The Coulomb–Yukawa-like CI and NCI potentials used in this work are defined as

$$f_{\mu\nu\sigma}(\zeta,\vec{r}) = f_{\mu}(\zeta,r)\left(\frac{4\pi}{2\nu+1}\right)^{1/2} S_{\nu\sigma}(\theta,\varphi), \tag{1}$$

where $\mu \geqslant 0$, $\zeta \geqslant o$ and $S_{\nu\sigma}(\theta,\varphi)$ are the complex (for $S_{\nu\sigma} \equiv Y_{\nu\sigma}$) or real spherical harmonics. Here, $f_{\mu}(\zeta,r)$ are the Coulomb ($\zeta = 0$) or Yukawa ($\zeta \neq 0$) like CI potentials determined by

$$f_{\mu}(\zeta,r) = f_{\mu 00}(\zeta,r) = r^{\mu-1}e^{-\zeta r}. \tag{2}$$

In order to derive the addition theorems for potentials (1) we shall use the following formulae for the translation of STOs [8]:

$$\chi_{\mu\nu\sigma}(\zeta,\vec{r}_{a1}) = \lim_{N\to\infty}\sum_{n=1}^{N}\sum_{l=0}^{n-1}\sum_{m=-l}^{l} V^{\alpha N}_{\mu\nu\sigma,nlm}(\zeta,\eta;\vec{R}_{ab})\chi_{nlm}(\eta,\vec{r}_{b1}), \tag{3}$$

where $\eta > 0$ and

$$\chi_{\mu\nu\sigma}(\zeta,\vec{r}) = (2\zeta)^{\mu+1/2}[(2\mu)!]^{-1/2}r^{\mu-1}e^{-\zeta r}S_{\nu\sigma}(\theta,\varphi) \tag{4}$$

$$V^{\alpha N}_{\mu\nu\sigma,nlm}(\zeta,\eta;\vec{R}_{ab}) = \sum_{n'=l+1}^{N}\Omega^{\alpha l}_{nn'}(N)S_{\mu\nu\sigma,n'-\alpha lm}(\zeta,\eta;\vec{R}_{ab}). \tag{5}$$

Here $\alpha = 1, 0, -1, -2, \ldots$ and $S_{\mu\nu\sigma,n'-\alpha lm}(\zeta,\eta;\vec{R}_{ab})$ are the overlap integrals with the different screening constants:

$$S_{\mu\nu\sigma,n'-\alpha lm}(\zeta,\eta;\vec{R}_{ab}) = \int \chi^{*}_{\mu\nu\sigma}(\zeta,\vec{r}_{a1})\chi_{n'-\alpha lm}(\eta,\vec{r}_{b1})\mathrm{d}V. \tag{6}$$

See ref. [8] for the exact definition of coefficients $\Omega^{\alpha l}_{nn'}(N)$.

Now we take in equation (5) into account equation (21) of ref. [8] for the one-center expansion of $\chi_{\mu\nu\sigma}(\zeta,\vec{r}_{a1})$ and equation (61) of ref. [9] for the overlap integrals with the same screening constants. Then, the coefficients $V^{\alpha N}$, equation (5), become

$$V^{\alpha N}_{\mu\nu\sigma,nlm}(\zeta,\eta;\vec{R}_{ab}) = \sum_{n'=l+1}^{N} \Omega^{\alpha l}_{nn'}(N) \lim_{N'\to\infty} \sum_{\mu'=\nu+1}^{N'} V^{\alpha N'}_{\mu\nu,\mu'\nu}(t) S_{\mu'\nu\sigma,n'-\alpha lm}(\eta,\eta;\vec{R}_{ab}), \quad (7)$$

where $t = \dfrac{\zeta-\eta}{\zeta+\eta}$ and

$$V^{\alpha N'}_{\mu\nu,\mu'\nu}(t) = \sum_{\mu''=\nu+1}^{N'} \frac{(\mu+\mu''-\alpha)!}{\{(2\mu)![2(\mu''-\alpha)]!\}^{1/2}} \Omega^{\alpha\nu}_{\mu'\mu''}(N')(1+t)^{\mu+1/2}(1-t)^{\mu''-\alpha+1/2} \quad (8)$$

$$S_{\mu'\nu\sigma,n'-\alpha lm}(\eta,\eta;\vec{R}_{ab}) = \frac{1}{\eta^{3/2}} \sum_{u=1}^{\mu'+n'-\alpha+1} \sum_{\upsilon=0}^{u-1} \sum_{s=-\upsilon}^{\upsilon} g^{\alpha u\upsilon s}_{\mu'\nu\sigma,n'-\alpha lm} \chi^{*}_{u\upsilon s}(\eta,\vec{R}_{ab}). \quad (9)$$

See ref. [6] for the exact definition of the coefficients $g^{\alpha u\upsilon s}$.

Using equation (7) and (9) in (3) it is easy to establish for STO, the following addition theorems:

$$\chi_{\mu\nu\sigma}(\zeta,\vec{r}_{a1}) = \frac{1}{\eta^{3/2}} \lim_{\substack{N\to\infty \\ N'\to\infty}} \sum_{n=1}^{N}\sum_{l=0}^{n-1}\sum_{m=-l}^{l} \times\left[\sum_{u=1}^{N+N'-\alpha+1}\sum_{\upsilon=0}^{u-1}\sum_{s=-\upsilon}^{\upsilon} D^{\alpha u\upsilon s}_{\mu\nu\sigma,nlm}(N,N';t)\chi^{*}_{u\upsilon s}(\eta,\vec{R}_{ab})\right]\chi_{nlm}(\eta,\vec{r}_{b1}), \quad (10)$$

where

$$D^{\alpha u\upsilon s}_{\mu\nu\sigma,nlm}(N,N';t) = \sum_{n'=l+1}^{N} \Omega^{\alpha l}_{nn'}(N) \sum_{\mu'=\nu+1}^{N'} g^{\alpha u\upsilon s}_{\mu'\nu\sigma,n'-\alpha lm} \sum_{\mu''=\nu+1}^{N'} \frac{(\mu+\mu''-\alpha)!}{\{(2\mu)![2(\mu''-\alpha)]!\}^{1/2}} \times\Omega^{\alpha\nu}_{\mu'\mu''}(N')(1+t)^{\mu+1/2}(1-t)^{\mu''-\alpha+1/2}. \quad (11)$$

Here, $t = \dfrac{\zeta-\eta}{\zeta+\eta}$ and $g^{\alpha u\upsilon s}_{\mu'\nu\sigma,n'-\alpha lm} \equiv 0$ for $u > \mu'+n'-\alpha+1$.

Now we can move on to the derivation of addition theorems for potentials. For this purpose we take into account the relations $1+t = 2\zeta/(\zeta+\eta)$, $1-t = 2\eta/(\zeta+\eta)$ and utilize the equations (1), (4), (10) and (11). Then, it is easy to obtain the desired one-range addition theorems for the combined Coulomb–Yukawa-like CI and NCI potentials in the following form:

$$f_{\mu\nu\sigma}(\zeta,\vec{r}_{a1}) = \frac{2^{3/2}}{(2\eta)^{\mu+2}} \lim_{\substack{N\to\infty \\ N'\to\infty}} \sum_{n=1}^{N}\sum_{l=0}^{n-1}\sum_{m=-l}^{l} \times\left[\sum_{u=1}^{N+N'-\alpha+1}\sum_{\upsilon=0}^{u-1}\sum_{s=-\upsilon}^{\upsilon} A^{\alpha\,u\upsilon s}_{\mu\nu\sigma,nlm}(N,N';\zeta,\eta)\chi^{*}_{u\upsilon s}(\eta,\vec{R}_{ab})\right]\chi_{nlm}(\eta,\vec{r}_{b1}), \tag{12}$$

where $\zeta \geqslant 0$ and

$$A^{\alpha u\upsilon s}_{\mu\nu\sigma,nlm}(N,N';\zeta,\eta) = \left(\frac{4\pi}{2\nu+1}\right)^{1/2} \sum_{n'=l+1}^{N} \Omega^{\alpha l}_{nn'}(N) \sum_{\mu'=\nu+1}^{N'} g^{\alpha\,u\upsilon s}_{\mu'\nu\sigma,n'-\alpha lm} \times \sum_{\mu''=\nu+1}^{N'} \frac{(\mu+\mu''-\alpha)!}{\{[2(\mu''-\alpha)]!\}^{1/2}} \times \Omega^{\alpha\nu}_{\mu'\mu''}(N')\left(\frac{2\eta}{\zeta+\eta}\right)^{\mu+\mu''-\alpha+1}. \tag{13}$$

Taking into account equation (12) for $a \to 2, b \to a, \vec{R}_{ab} \to \vec{r}_{2a} = \vec{r}_{21} - \vec{r}_{a1}$ and the relation $\chi_{u\upsilon s}(\eta,\vec{r}_{2a}) = (-1)^{\upsilon}\chi_{u\upsilon s}(\eta,\vec{r}_{a2})$ we rewrite the addition theorems for potentials in the following form:

$$f_{\mu\nu\sigma}(\zeta,\vec{r}_{21}) = \frac{2^{3/2}}{(2\eta)^{\mu+2}} \lim_{\substack{N\to\infty \\ N'\to\infty}} \sum_{n=1}^{N}\sum_{l=0}^{n-1}\sum_{m=-l}^{l} \times\left[\sum_{u=1}^{N+N'-\alpha+1}\sum_{\upsilon=0}^{u-1}\sum_{s=-\upsilon}^{\upsilon} B^{\alpha\,u\upsilon s}_{\mu\nu\sigma,nlm}(N,N';\zeta,\eta)\chi^{*}_{u\upsilon s}(\eta,\vec{r}_{2})\right]\chi_{nlm}(\eta,\vec{r}_{1}), \tag{14}$$

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

$$B^{\alpha\,u\upsilon s}_{\mu\nu\sigma,nlm}(N,N';\zeta,\eta) = (-1)^{\upsilon} A^{\alpha\,u\upsilon s}_{\mu\nu\sigma,nlm}(N,N';\zeta,\eta). \tag{15}$$

equation (14) is the desired one-range addition theorems for Coulomb–Yukawa-like CI ($\nu = \sigma = 0$) and NCI ($\nu \neq 0$) potentials: any potential having the difference of the radius vectors, $\vec{r}_{21} = \vec{r}_{a1} - \vec{r}_{a2}$, as its argument, can be expanded into a series over products of STOs depending on $\vec{r}_{a1}$ and $\vec{r}_{a2}$, separately.

We notice that in the case of addition theorems for Coulomb-like CI and NCI potentials ($\zeta = 0$) the coefficients $A^{\alpha\,u\upsilon s}$ and $B^{\alpha\,u\upsilon s}$ determined by the relations (13) and (15) do not depend on the parameter η, i.e. $A^{\alpha\,u\upsilon s}_{\mu\nu\sigma,nlm}(N,N';0,\eta) = A^{\alpha\,u\upsilon s}_{\mu\nu\sigma,nlm}(N,N')$ and $B^{\alpha\,u\upsilon s}_{\mu\nu\sigma,nlm}(N,N';0,\eta) = B^{\alpha\,u\upsilon s}_{\mu\nu\sigma,nlm}(N,N')$.

3. Addition theorems for derivatives of potentials

As can be seen from equation (14) and ref. [10], the derivatives of potentials with respect to Cartesian coordinates of second electron can be expressed through the STOs by the following relations:

$$f^{i}_{\mu\nu\sigma}(\zeta,\vec{r}_{21}) = \frac{\partial}{\partial x_2^i} f_{\mu\nu\sigma}(\zeta,\vec{r}_{21}) = \frac{2^{3/2}}{(2\eta)^{\mu+2}} \lim_{\substack{N\to\infty \\ N'\to\infty}} \sum_{n=1}^{N}\sum_{l=0}^{n-1}\sum_{m=-l}^{l} \times\left[\sum_{u=1}^{N+N'-\alpha+1}\sum_{\upsilon=0}^{u-1}\sum_{s=-\upsilon}^{\upsilon} B^{\alpha\, u\upsilon s}_{\mu\nu\sigma,nlm}(N,N';\zeta,\eta)\chi^{i*}_{u\upsilon s}(\eta,\vec{r}_2)\right]\chi_{nlm}(\eta,\vec{r}_1), \tag{16}$$

$$f^{ij}_{\mu\nu\sigma}(\zeta,\vec{r}_{21}) = \frac{\partial^2}{\partial x_2^i \partial x_2^j} f_{\mu\nu\sigma}(\zeta,\vec{r}_{21}) = \frac{2^{3/2}}{(2\eta)^{\mu+2}} \lim_{\substack{N\to\infty \\ N'\to\infty}} \sum_{n=1}^{N}\sum_{l=0}^{n-1}\sum_{m=-l}^{l} \times\left[\sum_{u=1}^{N+N'-\alpha+1}\sum_{\upsilon=0}^{u-1}\sum_{s=-\upsilon}^{\upsilon} B^{\alpha\, u\upsilon s}_{\mu\nu\sigma,nlm}(N,N';\zeta,\eta)\chi^{ij*}_{u\upsilon s}(\eta,\vec{r}_2)\right]\chi_{nlm}(\eta,\vec{r}_1). \tag{17}$$

Here, $i,\ j = 1,-1,0,\ x_2^1 = x_2,\ x_2^{-1} = y_2,\ x_2^0 = z_2$ and

$$\chi^{i}_{u\upsilon s}(\eta,\vec{r}) = \frac{\partial}{\partial x^i}\chi_{u\upsilon s}(\eta,\vec{r}) = 2\eta\left\{\beta^{11}_{u\upsilon}\sum_{s'=-(\upsilon-1)}^{\upsilon-1} a^{i}_{\upsilon s,s'}\chi_{u-1\upsilon-1s'}(\eta,\vec{r}) + \frac{x^i}{r}\left[(u-\upsilon-1)\beta^{10}_{u\upsilon}\chi_{u-1\upsilon s}(\eta,\vec{r}) - \frac{1}{2}\chi_{u\upsilon s}(\eta,\vec{r})\right]\right\} \tag{18}$$

$$\begin{aligned}\chi^{ij}_{u\upsilon s}(\eta,\vec{r}) = \frac{\partial^2}{\partial x^i\partial x^j}\chi_{u\upsilon s}(\eta,\vec{r}) &= (2\eta)^2\left\{\beta^{22}_{u\upsilon}\sum_{s'=-(\upsilon-2)}^{\upsilon-2} a^{ij}_{\upsilon s,s'}\chi_{u-2\upsilon-2s'}(\eta,\vec{r})\right.\\
&+\sum_{s'=-(\upsilon-1)}^{\upsilon-1}\left[a^{i}_{\upsilon s,s'}\left(\frac{x^j}{r}\right) + a^{j}_{\upsilon s,s'}\left(\frac{x^i}{r}\right)\right]\left[(u-\upsilon-1)\beta^{21}_{u\upsilon}\chi_{u-2\upsilon-1s'}(\eta,\vec{r})\right.\\
&\left.-\frac{1}{2}\beta^{11}_{u\upsilon}\chi_{u-1\upsilon-1s'}(\eta,\vec{r})\right] + \left(\frac{x^i}{r}\right)\left(\frac{x^j}{r}\right)\left[(u-\upsilon-1)\right.\\
&\times(u-\upsilon-3)\beta^{20}_{u\upsilon}\chi_{u-2\upsilon s}(\eta,\vec{r}) - \frac{1}{2}(2u-2\upsilon-3)\beta^{10}_{u\upsilon}\chi_{u-1\upsilon s}(\eta,\vec{r})\\
&\left.\left.+\frac{1}{4}\chi_{u\upsilon s}(\eta,\vec{r})\right] + \delta_{ij}\left[(u-\upsilon-1)\beta^{20}_{u\upsilon}\chi_{u-2\upsilon s}(\eta,\vec{r}) - \frac{1}{2}\beta^{10}_{u\upsilon}\chi_{u-1\upsilon s}(\eta,\vec{r})\right]\right\},\end{aligned} \tag{19}$$

where $\vec{r} = \vec{r}_2$ and $x^i = x_2^i$. See refs. [10] and [11] for the exact definition of coefficients $\beta^{kk'}_{u\upsilon}$, $a^{i}_{\upsilon s,s'}$ and $a^{ij}_{\upsilon s,s'}$.

As can be seen from the formulae presented in this work, all the one-range addition theorems for combined Coulomb–Yukawa-like CI and NCI potentials and their derivatives are expressed through the STOs. In refs. [6] and [7], the convergence and numerical stability of series occurring in this paper have been tested separately in the cases of Coulomb-and Yukawa-like potentials. The addition theorems obtained in this study would be a valuable addition to the evaluation of multicenter integrals that arise in molecular orbital calculations over Slater functions.

References

[1] C.A. Weatherford and H.W. Jones, *International Conference on ETO Multicenter Integrals* (Reidel, Dordrecht, 1982).
[2] I.N. Levine, *Quantum Chemistry*, 5th ed. (Prentice Hall, New Jersey, 2000).
[3] J.N. Latosinska, Int. J. Quantum Chem. 91 (2003) 284.
[4] T. Kato, Commun. Pure Appl. Math. 10 (1957) 151.
[5] S. Agmon, *Lectures on Exponential Decay of Solutions of Second-Order Elliptic Equations: Bounds on Eigenfunctions of N-Body Schrödinger Operators* (Princeton University Press, Princeton, NJ, 1982).
[6] I.I. Guseinov, Chem. Phys. 309 (2005) 209.
[7] I.I.Guseinov, Bull. Chem. Soc. Jpn. 78 (2005) 611.
[8] I.I. Guseinov, Int. J. Quantum Chem. 90 (2002) 114.
[9] I.I. Guseinov, J. Mol. Model. 9 (2003) 135.
[10] I.I. Guseinov, J. Mol. Model. 10 (2004) 212.
[11] I.I. Guseinov, J. Phys. A. Math. Gen. 37 (2004) 957.