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Convergence of the Laplace and the alternative multipole expansion approximation series for the Coulomb potential

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Multipole expansion is a powerful technique used in many-body physics to solve dynamical problems involving correlated interactions between constituent particles. The Laplace multipole expansion series of the Coulomb potential is well established in literature. We compare its convergence with our recently developed perturbative and analytical alternative multipole expansion series of the Coulomb potential. In our working, we confirm that the Laplace and the alternative analytical multipole expansion series are equivalent as expected. In terms of performance, the perturbative alternative multipole expansion series underapproximate the expected results to some extent while the Laplace and the analytical alternative multipole expansion series yield results which are relatively accurate but oscillatory in nature even with a higher number of angular momentum terms employed. As a practical example, we have evaluated the Slater double integrals for two-electron systems using the multipole expansion techniques and a mean field approximation. The estimated results show that only spherical interactions are dominant while the higher-order interactions are negligible. Our findings are likely to be useful in the treatment of the Coulomb potential in electronic structure calculations as well as in celestial mechanics.

I. INTRODUCTION

The Laplace multipole expansion series is established in the works of Laplace and Legendre in their search for solutions to the problem of attractions. The historical developments that led to the derivation of the expansion series and the introduction of the Legendre polynomials, for the first time, as the coefficients used in the Laplace expansion are captured in Laden's thesis[1]. The Laplace multipole expansion has become conventional knowledge in physics textbooks[2] and it is quite useful in solving the many-body physics problems in celestial mechanics, quantum physics and chemistry, nuclear physics, and condensed matter physics.

Naturally, the multipole expansion becomes convenient to use in solving physical problems in $3D$ if expressed in the spherical polar coordinates. This decomposes the problem as a product of both radial and angular parts. The radial part can be treated as a $1D$ case while the well defined angular algebra[3] can be used to simplify the angular parts. Several studies have employed multipole expansion techniques in the recent past in solving physical problems of interest[4–9].

In our alternative multipole expansion of the Coulomb potential[10,11], we stated that the Laplace multipole expansion series of the Coulomb repulsion term is incomplete, and therefore inaccurate. Vaman clarified that both the Laplace and the alternative multipole expansion are in deed equivalent[12]. Since the Laplace expansion series is a single-index summation while the alternative method is a double-index summation series, it becomes necessary to test the conditions for convergence of the two methods. We also compare the accuracy of the Laplace expansion method, relative to our perturbative and analytical alternative multipole expansion methods, in estimating the expected results. We have seen in literature that such a comparison, not exactly similar to the current study, is reported in ref.[13,14]. Comparison of different methods allows characterization of relative accuracy and capabilities, which is quite instrumental in guiding application[13]. This is particularly important given the fact that the alternative multipole expansion has already been successfully employed in determining the electronic structure for neutral atoms[15,16].

II. THEORY

The Coulomb repulsion potential term can be expressed as

$$\frac{1}{|\vec{r}_i - \vec{r}_j|} = \frac{1}{r_>}\left(1 - 2x\tilde{t} + \tilde{t}^2\right)^{-\frac{1}{2}} \tag{1}$$

which reduces to the Laplace multipole expansion series,

$$\frac{1}{|\vec{r}_i - \vec{r}_j|} = \frac{1}{r_>}\sum_{l=0}^{\infty} \tilde{t}^l P_l(x), \tag{2}$$

where $\tilde{t} = r_</r_>$, $r_> = \max\{r_i, r_j\}$, $r_< = \min\{r_i, r_j\}$, $x = \cos\theta$, with θ being the relative angle between the position vectors $\vec{r}_i$ and $\vec{r}_j$, l are non-negative integers, and $P_l(x)$ are the l^{th} order Laplace coefficients of $\tilde{t}^l$, also known as the Legendre polynomials. It is important to note that the form given by Eq. (1) is considered as the generating function for the Legendre polynomials[2,17].

In the alternative approach[10,11], the multipole expansion of the Coulomb potential

$$\frac{1}{|\vec{r}_i - \vec{r}_j|} = \frac{1}{r_>}\sum_{l=0}^{\infty} h_l(\tilde{t})\, P_l(x) \tag{3}$$

can also be expressed in the basis of Legendre polynomials, where the coefficients

$$h_l(\tilde{t}) = \frac{(2l+1)}{\sqrt{1+\tilde{t}^2}}\tilde{j}_l(\tilde{t}), \tag{4}$$

are a function of the spherical Bessel-like functions, $\tilde{j}_l(\tilde{t})$, which can be expanded in the perturbative polynomial form as[10,11]

$$j_0(\tilde{t}) \;= 1+\textstyle\sum_{k=1}^{\infty} \frac{(4k-1)!!}{(2k)!!(2k+1)!!}\left(\frac{\tilde{t}}{1+\tilde{t}^2}\right)^{2k} \tag{5}$$

$$j_{l>0}(\tilde{t}) \;= \textstyle\sum_{k=0}^{\infty} \frac{(2l+4k-1)!!}{(2k)!!(2l+2k+1)!!}\left(\frac{\tilde{t}}{1+\tilde{t}^2}\right)^{l+2k} \tag{6}$$

or analytically as a differential equation[11]

$$\tilde{j}_l(t) = (-1)^l \frac{t^l}{(2l+1)!!}\left[\frac{1}{t}\frac{\mathrm{d}}{\mathrm{dt}}\right]^l \left\{\frac{1}{2t}\left[(1+2t)^{l+\frac{1}{2}}-(1-2t)^{l+\frac{1}{2}}\right]\right\}, \tag{7}$$

with

$$t = \frac{r_i r_j}{r_i^2+r_j^2} = \frac{\tilde{t}}{1+\tilde{t}^2} \tag{8}$$

defined in terms of $\tilde{t}$ in this case.

The equivalence of Eqs. (2) and (3) shows that

$$\tilde{t}^l = \frac{(2l+1)}{\sqrt{1+\tilde{t}^2}}\sum_{k=0}^{k_{max}\to\infty}\frac{(2l+4k-1)!!}{(2k)!!(2l+2k+1)!!}\left(\frac{\tilde{t}}{1+\tilde{t}^2}\right)^{l+2k} \tag{9}$$

is an identity.

From the identity relation in Eq. (9), we can further infer that:

$$\textstyle\sum_{k=0}^{k_{max}\to\infty} \frac{(2l+4k-1)!!}{(2k)!!(2l+2k+1)!!}\left(\frac{\tilde{t}}{1+\tilde{t}^2}\right)^{2k} = \frac{(1+\tilde{t}^2)^{l+\frac{1}{2}}}{2l+1}, \tag{10}$$

$$\tilde{j}_l(\tilde{t}) = \tfrac{\tilde{t}^l}{2l+1}\sqrt{1+\tilde{t}^2}, \tag{11}$$

$$\tilde{j}_l(\tilde{t}) = \left(\tfrac{2l-1}{2l+1}\right)\tilde{t}\,\tilde{j}_{l-1}(\tilde{t}) \tag{12}$$

$$\tilde{j}_l(\tilde{t}) = \tfrac{\tilde{t}^l}{2l+1}\,\tilde{j}_0(\tilde{t}) \tag{13}$$

Using the relations given by Eq. (8), we have analytically tested and confirmed the inferences given by Eqs. (10)-(11) for the first two orders of the spherical Bessel-like functions herebelow. The zeroth-order spherical Bessel-like function simplifies to:

$$\begin{aligned}\tilde{j}_0(\tilde{t}) &= \frac{\sqrt{1+2t}-\sqrt{1-2t}}{2t}\\ &= \frac{\sqrt{1+\frac{2\tilde{t}}{1+\tilde{t}^2}}-\sqrt{1-\frac{2\tilde{t}}{1+\tilde{t}^2}}}{\frac{2\tilde{t}}{1+\tilde{t}^2}}\\ &= \frac{\sqrt{1+\tilde{t}^2}\left[\sqrt{1+2\tilde{t}+\tilde{t}^2}-\sqrt{1-2\tilde{t}+\tilde{t}^2}\right]}{2\tilde{t}}\\ &= \frac{\sqrt{1+\tilde{t}^2}\left[(1+\tilde{t})-(1-\tilde{t})\right]}{2\tilde{t}} = \sqrt{1+\tilde{t}^2}\end{aligned} \tag{14}$$

Likewise, the first-order spherical Bessel-like function simplifies to:

$$\begin{aligned}\tilde{j}_1(\tilde{t}) &= -\frac{1}{3!!}\frac{d}{dt}\left\{\frac{1}{2t}\left[(1+2t)^{\frac{3}{2}}-(1-2t)^{\frac{3}{2}}\right]\right\}\\ &= \frac{1}{6t^2}\left[(1+2t)^{\frac{3}{2}}-(1-2t)^{\frac{3}{2}}\right]-\frac{1}{2t}\left[(1+2t)^{\frac{1}{2}}+(1-2t)^{\frac{1}{2}}\right]\\ &= \frac{\sqrt{1+\tilde{t}^2}}{6\tilde{t}^2}\left[(1+\tilde{t})^3-(1-\tilde{t})^3\right]-\frac{\sqrt{1+\tilde{t}^2}}{2\tilde{t}}\left[(1+\tilde{t})+(1-\tilde{t})\right]\\ &= \sqrt{1+\tilde{t}^2}\left[\frac{1}{\tilde{t}}+\frac{\tilde{t}}{3}-\frac{1}{\tilde{t}}\right] = \frac{\tilde{t}}{3}\sqrt{1+\tilde{t}^2}.\end{aligned} \tag{15}$$

The use of the recurrence relations given by Eqs. (12) and (13) can be useful in eliminating singularities associated with the analytical expression of the spherical Bessel-like functions, $\tilde{j}_l(\tilde{t})$,[11] as $\tilde{t}\to 0$.

As a practical example, we use the Laplace and the alternative multipole expansion series, within a meanfield approximation, to estimate the Slater double integrals $F^l(r_i,r_j)$[18]

$$\begin{aligned}F^l_{1s,nl}(r_i,r_j) &= \langle\tilde{t}\rangle^l\int_0^\infty r_i^2\,dr_i\,R_{n,l}(r_i)R_{n',l'}(r_i)\\ &\times\left[\frac{1}{r_i}\int_0^{r_i} r_j^2\,dr_j\,R_{n',l'}(r_j)R_{n,l}(r_j)+\int_{r_i}^\infty r_j\,dr_j\,R_{n',l'}(r_j)R_{n,l}(r_j)\right]\end{aligned} \tag{16}$$

for helium-like systems, where the higher-order terms involve the exchange of angular momentum quantum number between the s and the l^{th} orbital. The optimization is based on the root mean value of t,

$$\langle t\rangle = \left\langle\frac{\tilde{t}}{1+\tilde{t}^2}\right\rangle = \frac{1}{4\pi\sqrt{2}}, \tag{17}$$

per solid angle, obtained by determining the root mean square value of t scaled by 2π as given by Eq. (32) of ref.[16]. This, consequently, yields

$$\langle\tilde{t}\rangle = 5.6426216557\times 10^{-2}. \tag{18}$$

Unscreened hydrogenic radial orbitals are employed as the trial wavefunctions in evaluating Eq. (16).

III. RESULTS

Our goal in this work is to test the convergence of the Laplace and the alternative multipole expansion series and also to compare the performance of both methods in estimating the exact function given by Eq. (1). The spherical Bessel-like functions, $\tilde{j}_l(\tilde{t})$, used in the alternative multipole expansion can be evaluated perturbatively as given by Eqs. (5) and (6) or analytically as given by Eq. (7). Our calculations for convergence and performance are computed both perturbatively and analytically.

In Fig. 1, we plot the convergence of the first two orders of the Laplace functions, $\tilde{t}^l$, relative to the alternative multipole expansion functions, $h_l(\tilde{t})$, as given by Eq. (9). The domain $0\le\tilde{t}\le 1$ has been chosen to coincide with the regime of convergence of the Laplace multipole expansion series. The convergence tests should confirm the validity of the identity relations given by the stated equation. Since $h_l(\tilde{t})$ is an infinite series function, it can be seen that only three terms (with $k_{max} = 2$) of the summation series already yield reasonable trend of convergence, albeit slowly. In subsequent figures, we use $h_l^{k_{max}=2}(\tilde{t})$ as our best converged perturbative results. From Eqs. (**??**)-(**??**), it can be seen that the divergence between the Laplace functions and the perturbative alternative multipole expansions stems from the approximation of the factor $\sqrt{1+\tilde{t}^2} \to 1$ as $k_{max} \to 0$.

In Fig. 2a, we compare the convergence of the perturbative results with the corresponding analytical, $h_l(\tilde{t})$, functions and the Laplace basis functions as given by Eqs. (9) and (11) for the first six orders of l. As already shown in Fig. 1, except at lower values of $\tilde{t}$, the perturbative basis functions do not agree fully with the corresponding Laplace basis functions in all the cases considered. As expected, the analytical basis functions, on the other hand, show an excellent agreement with the corresponding Laplace basis functions. In Fig. 2b, we show the relative deviation between the analytical and the Laplace basis functions. The relative deviations are calculated as the absolute difference between the analytical $h_l(\tilde{t})$ and the Laplace $f_l(\tilde{t}) = \tilde{t}^l$ functions divided by the Laplace functions. The observed relative deviations can be attributed to numerical noise as well as the divergences due to singularities in the analytical function as $\tilde{t} \to 0$.

Because of the slow convergence of the perturbative functions, it became of importance to test the performance of the expansions in approximating the value of the analytic function given by Eq. (1) for various values of $\tilde{t}$ across the angular spectrum. The performance results are summarized in Fig. 3 for all values of $x = \cos\theta$. For lower values of $\tilde{t}$, fewer angular momentum values are necessary for convergence. For $\tilde{t} = 0.75$, reasonable convergence is obtained with $l_{max} = 10$. The perturbative expansion on the other hand converges faster with fewer values of l_{max} and k_{max}, although the expected results are underapproximated to some extent using this approximation. In particular, complete convergence for the perturbative expansion is obtained using $l_{max} = 5$ and $k_{max} = 2$ only. As $\tilde{t} \to 1$, a higher number of angular momenta are necessary for convergence if the Laplace or the analytical multipole functions are used. In Fig. 4, we show that for $\tilde{t} = 1$ convergence of the expected function is not yet achieved even with $l_{max} = 30$ for the Laplace and the analytical multipole expansion. It can also be observed in Fig. 4 that as the angular momenta increases, the period and the amplitude of oscillation of the Laplace and the analytical multipole expansion results reduces. The perturbative expansion, on the other hand, is converged with less angular momenta and shows remarkable stability in the approximation of the expected function. The perturbative results offer the possibility to isolate features that are dependent on the lower order terms of the multipole expansion of the Coulomb potential.

The equivalence between the Laplace and the analytical alternative multipole expansion methods provides a wider choice of techniques to use when dealing with the Coulomb repulsion term. The Laplace basis functions appear simpler,

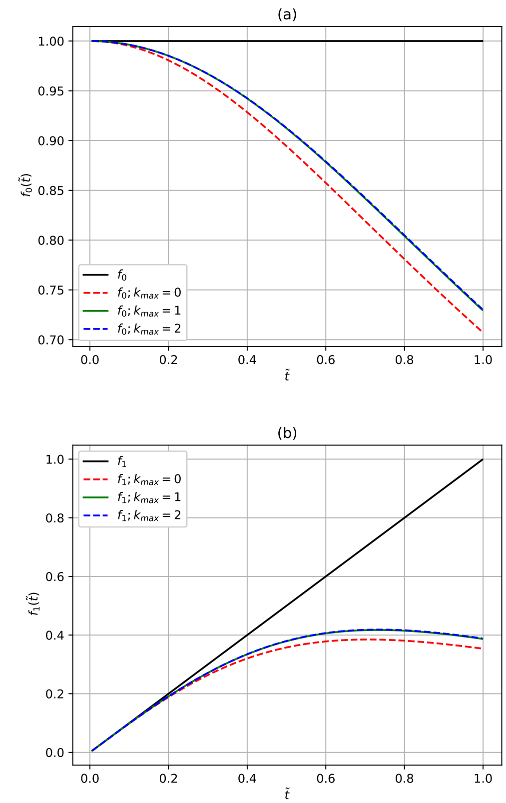

FIG. 1. (Color online) Comparison of the functions (a)$f_0(\tilde{t}) = 1$ and $h_0(\tilde{t}) = f_0^{k_{max}}(\tilde{t})$ and (b) $f_1(\tilde{t}) = \tilde{t}$ and $h_1(\tilde{t}) = f_1^{k_{max}}(\tilde{t})$, summed up to the maximum value (k_{max}), plotted using left and right hand side of Eq. (9) respectively. The black solid line corresponds to the Laplace basis functions, $\tilde{t}^l$.

in comparison with the analytical functions, but the underlying difficulty lies in the uncertainty of $r_>$ and $r_<$ variables. In the analytical expansion, on the other hand, it is not necessary to distinguish between the $r_>$ and $r_<$ variables because they are treated on an equal footing. Additionally, as already shown in references[15,16], the correlated term becomes separable in the alternative multipole expansion within some mean-field approximation making it quite favourable to use for computations.

As a practical example, we have compared the Slater integrals[18] for the $1s - nl$ interacting states estimated using the Laplace and the lowest-order perturbative alternative multipole expansion series for two electron systems as expressed in Eq. (16). The results are presented in table I. The calculations have been done using unscreened hydrogenic radial wavefunctions. As expected the analytical alternative multipole expansion yields results equivalent to the Laplace multipole expansion results. The lowest-order perturbative alternative multipole expansion results are slightly less by a constant factor. From the results presented in the table, it is evident that the higher order multipole interactions are negligible and only become important when the lower order interactions vanish.

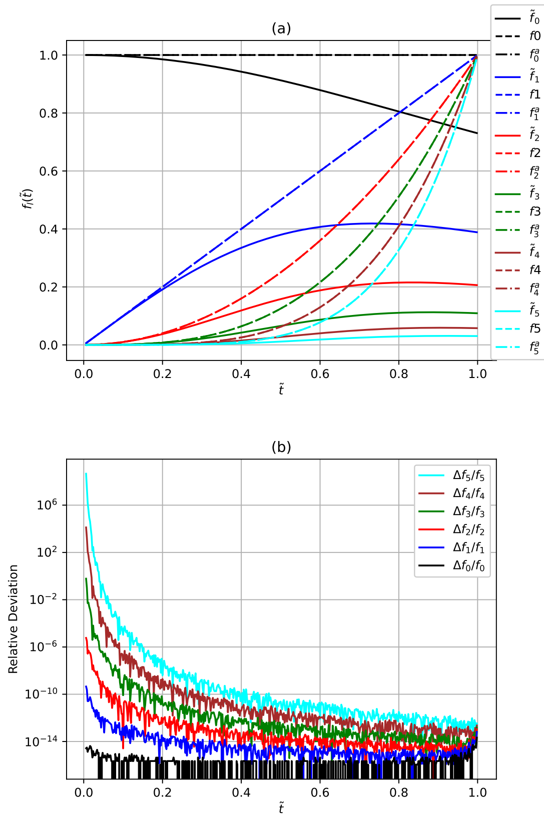

FIG. 2. (Color online) (a) Comparison of the six functions of $f_l(\tilde{t}) = t^l$, $h_l(\tilde{t}) = \tilde{f}_l^{k_{max}}(\tilde{t})$ with the value $k_{max} = 2$, and the analytical $h_l(\tilde{t}) = \tilde{f}_l(\tilde{t})$, plotted using left and right hand side of Eq. (11) respectively. The solid and the dash-dot lines represent the perturbative and the analytical $h_l(\tilde{t})$ functions, as given by Eqs. (5) - (7), while the dashed lines represent the Laplace basis functions, $f_l(\tilde{t}) = \tilde{t}^l$, respectively. (b) The relative deviation given as the absolute difference between the analytical $h_l(\tilde{t})$ and the Laplace $f_l(\tilde{t}) = \tilde{t}^l$ functions divided by the Laplace functions.

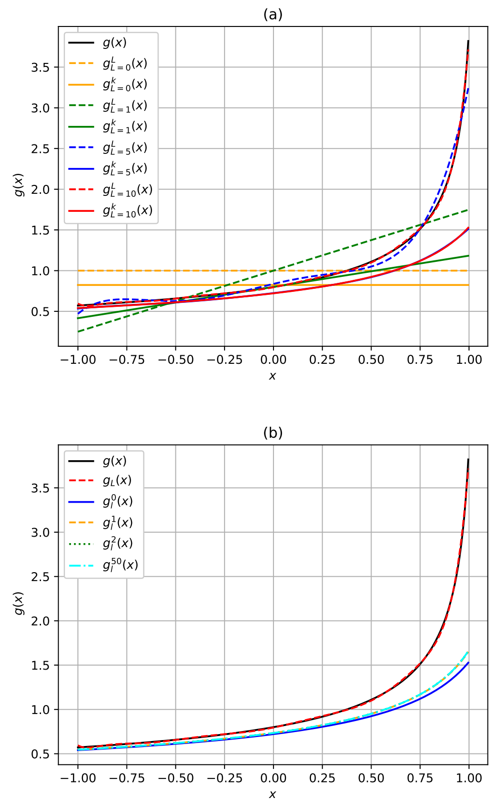

FIG. 3. (Color online) Convergence of the Laplace and the perturbative alternative multipole expansion series in comparison to the expected function $g(x,\tilde{t}) = (1 - 2x\tilde{t} + \tilde{t}^2)^{-\frac{1}{2}}$ given by Eq. (1) , at $\tilde{t} = 0.75$, as a function of: (a) the angular momenta L with $k_{max} = 2$ and, (b) k_{max} with $L_{max} = 10$. The black solid line is the expected curve. The Laplace functions are denoted by dashed lines in (a) and g_L in (b).

F^l	$1s-nl$	Laplace	Perturbative
F^0	1s-1s	$0.6250Z$	$0.6240Z$
F^1	1s-2p	$4.5409 \times 10^{-3} Z$	$4.5337 \times 10^{-3} Z$
F^2	1s-3d	$8.8323 \times 10^{-6} Z$	$8.8183 \times 10^{-6} Z$

TABLE I. Comparison of Slater integrals for the $1s-nl$ interacting states evaluated using Eq. (16) for the Laplace and the lowest-order perturbative alternative multipole expansion of the Coulomb repulsion term. The calculations have been done using the unscreened hydrogenic radial wavefunctions.

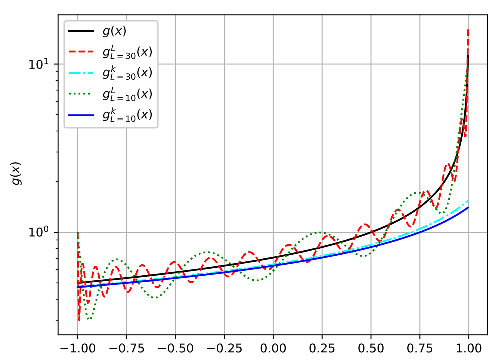

FIG. 4. (Color online) Convergence of the Laplace and the perturbative alternative multipole expansion series in comparison to the expected function $g(x,\tilde{t}) = (1 - 2x\tilde{t} + \tilde{t}^2)^{-\frac{1}{2}}$ given by Eq. (1) , at $\tilde{t} = 1.00$, as a function of the angular momenta ($L_{max} = 10$ and $L_{max} = 30$) with $k_{max} = 2$. The black solid line is the expected curve. The Laplace functions are denoted by g_L^L while the perturbative function by g_L^k. The logarithmic scale has been used for clarity.

IV. CONCLUSION

The convergence as well as the performance of the Laplace multipole expansion of the Coulomb potential, in comparison with our recently developed alternative multipole expansion series, is investigated in this study. We have confirmed that the Laplace and the analytical alternative multipole expansion series are indeed equivalent and offer a higher degree of accuracy if a larger l_{max} is used in the approximation. The perturbative alternative multipole expansion, on the other hand, converges with a much lower value of l_{max} and k_{max} and is stable against oscillations in results as $\tilde{t} \to 1$ but the converged results underapproximate the expected results to some extent at all angles. The stability of the perturbative results may be useful in isolating physically meaningful features even with less angular momenta in converged results.

DATA AVAILABILITY STATEMENT

All the data generated in the work are embedded as figures in the manuscript.

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