



Addressing the Coulomb potential singularity in exchange-correlation energy integrals with one-electron and two-electron basis sets

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ABSTRACT

Nonlocal functionals for the exchange-correlation energy like the weighted density approximation require evaluating six-dimensional integrals with a Coulomb singularity. The convergence of a straight-forward grid-based approach is linear in the number of grid points, because grid points where the integrand's magnitude exceeds a threshold must be neglected. This slow convergence makes extrapolation to the infinite-grid limit problematic. We introduce an alternative approach, based on basis-set expansion using either conventional three-dimensional basis functions or explicitly-correlated basis functions. The approach using explicitly-correlated GAUSSIAN geminal basis functions converges particularly rapidly.

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1. Motivation

In quantum many-body theory, one often needs to evaluate six-dimensional integrals with the form,

$$W[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r})K(\mathbf{r}, \mathbf{r}')\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \quad (1)$$

where $\rho(\mathbf{r})$ is the electron density. For many interesting choices of the correlation factor, $K(\mathbf{r}, \mathbf{r}')$, this integral cannot be performed analytically and numerical methods must be used. Six-dimensional numerical integration is challenging numerically, especially when the integrand is singular. If one uses the standard approach based on the direct product of two three-dimensional numerical integration grids [1], or even a sparse-grid approach using a Smolyak-type construction [2], the integration grid will include points where the two particles' coordinates are the same ($\mathbf{r} = \mathbf{r}'$). These points must be omitted from the numerical quadrature. Omitting these points, however, results in a quadrature that converges only with the slow rate of n_{grid}^{-1} , where n_{grid} is the number of grid points. There are other approaches to these integrals in the literature, including methods based on short-range/long-range decomposition [2,3], solution of the Poisson equation by eigenvector decomposition, Green's theorem tricks, and center-of-mass transformation [4]. In this Letter we will discuss methods using basis sets, which we believe to be the most promising technique overall, partly because it makes contact with the computational machinery of conventional molecular electronic structure theory.

Our interest in this type of integral stems from density functional theory (DFT), where integrals of this form appear in the expression for nonlocal exchange-correlation energy functionals,

$$E_{xc}[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r})\overline{h_{xc}(\mathbf{r}, \mathbf{r}')}\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \quad (2)$$

where

$$\overline{h_{xc}(\mathbf{r}, \mathbf{r}')} = \int_0^1 h_{xc}^\lambda(\mathbf{r}, \mathbf{r}') d\lambda \quad (3)$$

is the exchange-correlation hole averaged over the constant-density adiabatic connection [5,6]. This type of two-point exchange-correlation functional is as old as the weighted density approximation [7–9] and has recently reappeared in the context of direct correlation function [10–13], exchange-correlation hole functionals [14–16] and nonlocal density functionals for dispersion [17–23].

2. One-electron basis set approach

We start with a density-fitting basis set, $\{\eta_i(\mathbf{r})\}_{i=1}^{N_b}$, containing N_b basis functions. We define an associated potential-fitting basis set, $\{\xi_i(\mathbf{r})\}_{i=1}^{N_b}$, as the Coulomb potential of the density-fitting basis functions,

$$\xi_i(\mathbf{r}) = \int \frac{\eta_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (4)$$

As long as the density-fitting basis functions are chosen so that Eq. (4) can be evaluated analytically, the singularity in the integral (1) can be subsumed in the potential-like basis functions. This is the key idea of this Letter. It is not new; similar ideas arise throughout the density-fitting approaches associated with DFT and *ab initio*

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methods [24–37]. While the space of density-like functions is separable, and therefore amenable to basis-set expansion, the space of potential-like functions is not [38–41]. Expanding potentials in a basis set like Eq. (4) cannot give an expansion that converges in a strict mathematical sense.

The numerator of the integrand in Eq. (1) is a density-like quantity so we expand it in the density-like basis set,

$$h_x^{UEG}(\mathbf{r}) = -9 \left[\frac{\sin(k_F r) - k_F r \cos(k_F r)}{(k_F r)^3} \right]^2 \quad (5)$$

Substituting this expansion into the target integral, (1), gives

$$\begin{aligned} W[\rho] &\approx \frac{1}{2} \sum_i^{N_b} \sum_j^{N_b} L_{ij} \int \int \frac{\eta_i(\mathbf{r}) \eta_j(\mathbf{r}')}{\|\mathbf{r} - \mathbf{r}'\|} d\mathbf{r} d\mathbf{r}' \\ &= \frac{1}{2} \sum_i^{N_b} \sum_j^{N_b} L_{ij} \int \eta_i(\mathbf{r}) \xi_j(\mathbf{r}) d\mathbf{r} \end{aligned} \quad (6)$$

The potential-like basis functions (4) appear naturally here. Denoting the ‘overlap’ between the potential-like and density-like functions as

$$S_{ij} = \int \eta_i(\mathbf{r}) \xi_j(\mathbf{r}) d\mathbf{r} = \iint \frac{\eta_i(\mathbf{r}) \eta_j(\mathbf{r}')}{\|\mathbf{r} - \mathbf{r}'\|} d\mathbf{r} d\mathbf{r}' = S_{ji} \quad (7)$$

gives a compact matrix equation for the integral,

$$W[\rho] \approx \frac{1}{2} \sum_i^{N_b} \sum_j^{N_b} L_{ij} S_{ji} = \frac{1}{2} \text{Tr}[\mathbf{L}\mathbf{S}] \quad (8)$$

The only unknowns in this expression are the coefficients of expansion, L_{ij} . These are determined by projecting the density-like quantity $\rho(\mathbf{r})K(\mathbf{r}, \mathbf{r}')\rho(\mathbf{r}')$ onto the potential-like basis set,

$$\begin{aligned} K_{mn} &= \iint \xi_m(\mathbf{r}) \rho(\mathbf{r}) K(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}') \xi_n(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \\ &= \sum_{i=1}^{N_b} \sum_{j=1}^{N_b} L_{ij} \left[\int \xi_m(\mathbf{r}) \eta_i(\mathbf{r}) d\mathbf{r} \right] \left[\int \eta_j(\mathbf{r}') \xi_n(\mathbf{r}') d\mathbf{r}' \right] \\ &= \sum_{i=1}^{N_b} \sum_{j=1}^{N_b} S_{mi} L_{ij} S_{jn} \end{aligned} \quad (9)$$

In matrix notation,

$$\begin{aligned} \mathbf{K} &= \mathbf{S}\mathbf{L}\mathbf{S} \\ \mathbf{L} &= \mathbf{S}^{-1}\mathbf{K}\mathbf{S}^{-1} \end{aligned} \quad (10)$$

Substituting the second expression into Eq. (8) gives our working equation,

$$W[\rho] = \frac{1}{2} \text{Tr}[\mathbf{K}\mathbf{S}^{-1}] \quad (11)$$

The integrals that define K_{mn} must generally be done numerically, but they are nonsingular. In favorable cases, the integrals that define K_{mn} can be done analytically.

Since the point of this procedure is to avoid numerical integration of singular functions, it is important that the integrals that define the potential basis functions, (4), and the integrals in Eq. (7) can be performed analytically. As proposed by Köster [42,43], we decided to use the Hermite Gaussian functions centered on the atoms,

$$\eta_{NLM;\alpha_p}(\mathbf{r}, \mathbf{R}) = \Lambda_N(x - X, \alpha_p) \Lambda_L(y - Y, \alpha_p) \Lambda_M(z - Z, \alpha_p) e^{-\alpha_p |\mathbf{r} - \mathbf{R}|^2} \quad (12)$$

which can be rewritten as

$$\eta_{NLM;\alpha_p}(\mathbf{r}, \mathbf{R}) = \frac{\partial^N}{\partial X^N} \frac{\partial^L}{\partial Y^L} \frac{\partial^M}{\partial Z^M} (e^{-\alpha_p |\mathbf{r} - \mathbf{R}|^2}) \quad (13)$$

The integrals required can then be efficiently evaluated using the McMurchie–Davidson methodology [44]. The formulas for the integrals are presented in Appendix A. Our procedure for selecting the ‘angular labels’ and exponents in (13) is explained in Appendix B. Detailed derivations of the integral formulas are presented in the Supplementary material.

Motivated by our interest in the weighted density approximation, we chose to use the exchange hole of the uniform electron gas to test our approach,

$$\begin{aligned} K(\mathbf{r}, \mathbf{r}') &= h_x^{UEG}(k_F |\mathbf{r} - \mathbf{r}'|) \\ &= -9 \left[\frac{\sin(k_F |\mathbf{r} - \mathbf{r}'|) - k_F |\mathbf{r} - \mathbf{r}'| \cos(k_F |\mathbf{r} - \mathbf{r}'|)}{(k_F |\mathbf{r} - \mathbf{r}'|)^3} \right]^2 \end{aligned} \quad (14)$$

Since the exchange hole should be symmetric, we opted to use the arithmetic mean of k_F in this expression,

$$k_F(\mathbf{r}, \mathbf{r}') = \frac{k_F(\mathbf{r}) + k_F(\mathbf{r}')}{2} = (6\pi^2)^{1/3} \left(\frac{\rho^{1/3}(\mathbf{r}) + \rho^{1/3}(\mathbf{r}')}{2} \right) \quad (15)$$

The integral in Eq. (1) is an approximation to the exchange energy. It is a very poor approximation, but this does not matter here because the purpose is to test the algorithm, not evaluate accurate energies.

In Figure 1 we plot the error in the exchange energy for various numbers of basis functions for Helium, Beryllium, and Lithium Hydride. Accurate results were computed by evaluating Eq. (1), with $K(\mathbf{r}, \mathbf{r}')$ defined by Eqs. (14, 15), using very large six-dimensional Becke-Lebedev integration grids extracted from the integration routines we developed for integrals associated with population analysis [1,45]. The resulting approximation to the exchange energy is accurate to about 10^{-4} a.u., which is why the computed error in the basis-set methods in Figure 1 levels off at that level. The stair-step shape of the curves occurs because we do three runs with the same maximum degree for the Hermite basis functions, but increasing numbers of primitive Gaussians with that maximal degree, before increasing the maximum degree of the Hermite basis functions further. (See Appendix B for details about the construction of the basis set.) It is more challenging to get good results for heavier atoms because our routines use primitive Gaussian functions, not contracted Gaussian functions. Therefore it requires more sharply-peaked Gaussians to get good results for Be than for He. Using contracted Gaussian functions would lessen the cost, but change the trends.

Obtaining reasonable accuracy of 10^{-3} a.u. requires between 50 and 100 basis functions. This is prohibitive unless the integral in Eq. (9) can be evaluated very efficiently.

3. Two-electron basis set approach

The exchange hole depends explicitly on the interelectronic distance, $|\mathbf{r} - \mathbf{r}'|$. In general exchange-correlation holes, and also most other relevant integrals with the form Eq. (1), have a strong dependence on the interelectronic distance. This suggests using an explicitly correlated basis set of the form

$$\eta_i(\mathbf{r}, |\mathbf{r} - \mathbf{r}'|) = f_i(\mathbf{r}) g_i(|\mathbf{r} - \mathbf{r}'|) \quad (16)$$

With this type of basis set, all of the previous formulas still hold. The only difficulty is finding density-like basis functions for which all the integrals can still be performed analytically. The integrals can still be performed if the Hermite Gaussian functions in Eq. (12) are multiplied by a GAUSSIAN geminal basis function [46–49]

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