

Method for evaluation of density functional integrals in molecular calculations

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Abstract. Numerical methods for computing variationally optimized molecular orbitals within the Hartree–Fock approximation are augmented to include correlation functionals of the density in the energy and the numerical methods for carrying this out are described. The approach is applied explicitly to the Colle–Salvetti correlation energy functional. It is found that the gradient terms in the Colle–Salvetti functional present numerical problems associated with the low-density behavior, but also that they make a relatively small contribution to the correlation energy. In the three cases considered, HF, H₂O and N₂, it is found that the Colle–Salvetti correction considerably underestimates the correlation energies obtained in coupled-cluster theory.

Keywords: Molecular integrals – Density functional theory – Colle – Salvetti functional

1 Introduction

Most quantum chemical calculations employ expansions, in one form or another, of molecular orbitals in terms of Gaussian-type orbitals (GTOs). Their ubiquity speaks decisively to their utility. The fact that the calculations are essentially all analytic eliminates many of the uncertainties associated with other numerical methods. In recent years, however, the popularity of density functional theory (DFT) methods has required the development of numerical methods that depart from the standard purely analytic methods. Explicitly, the local exchange–correlation potential, V_{xc} , is usually also expanded in terms of Gaussian functions; however, its expression as a function of $F(\rho(\mathbf{r}))$ or $F(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \nabla^2\rho(\mathbf{r}))$ requires at some step a pointwise evaluation of the density and its derivatives. There appear to be a large number of approaches to this numerical

problem of expanding V_{xc} . One such, due to Becke [1], is the partitioning of space into subsets with points in intersecting subsets assigned different weights depending on the subset to which they are attributed, but this approach is far from unique.

In recent years a purely numerical approach to the calculation of molecular orbitals has been pursued by one of us [2, 3, 4]. (See also Ref. [5]). In this approach, the GTOs centered at each nucleus are replaced by orbitals defined numerically on a radial mesh for a spherical coordinate system centered at that nucleus. It is then possible to solve the variational equations for the basis orbitals thereby approaching the Hartree–Fock limit with a much smaller basis set than in the usual GTO methods. In fact, variational optimization of GTO basis functions is rarely attempted beyond atomic calculations. A reasonably robust numerical program has been developed to construct and solve these equations and has been applied to a number of small molecules [4, 6].

In the philosophy of DFT, it should be possible to go beyond the Hartree–Fock approximation by including a correlation functional of the density in the Hamiltonian. In the usual DFT, a local exchange functional is also included, but the case can be made that exchange is essentially a nonlocal effect and should be included at the Hartree–Fock level [7]. An early estimate for a correlation functional is that of Colle and Salvetti (CS) [8], although this is not an explicit functional of the density. This prescription was modified to an explicit functional of the density by Lee, Yang and Parr [9], and this approximation is now being widely applied. Another widely applied approximation is that of Perdew and Wang (PW91) [10].

It appears to be a natural extension of the optimized numerical orbital approach to the Hartree–Fock problem for molecules to include an estimate for the correlation correction in the Hamiltonian. This procedure can be construed to be the DFT approach with the exact nonlocal exchange. Although this appears to be a reasonable method, it runs somewhat counter to conventional DFT methodology, which would

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prescribe also a local exchange approximation. It is the purpose of this article to describe some initial results for this approach.

In these calculations, the Hamiltonian was modified by adding the CS estimate for the correlation energy. It has been found, however, that this causes intractable numerical difficulties associated with its behavior at low density. These problems are discussed in Sect. 2 and a slight modification that eliminates them is described. The numerical techniques that have been developed are explained in Sect. 3 and results are given for a number of small molecules in Sect. 4.

In the numerical orbital approach, molecular orbitals are expressed as a linear combination of numerical ‘atomic’ orbitals:

$$\psi_i(\mathbf{r}) = \sum_j c_{ji} \chi_j(\mathbf{r}) , \quad (1.1)$$

where the $\chi_j(\mathbf{r})$ are functions of the form $F_{lm}(\mathbf{r} - \mathbf{R}_n)$ and F_{lm} is the product of a radial factor and a spherical harmonic and \mathbf{R}_n is a nuclear coordinate. The radial factors in F_{lm} are numerically optimized on the radial mesh centered at \mathbf{R}_n . The degree to which the Hartree–Fock equations are satisfied depends on the number of polarization orbitals included in the variational calculation.

Expectation values of single-particle operators are given by

$$\langle \hat{O} \rangle = \sum_{kl} w_{kl} \langle \chi_k | \hat{O} | \chi_l \rangle , \quad (1.2)$$

where w_{kl} is an element of the density matrix

$$w_{kl} = \sum_i n_i c_{ki} c_{li} , \quad (1.3)$$

n_i being the occupation number of orbital i . The integrations required for the matrix elements of Eq. (1.2) can be carried out about any center; however, a more accurate way to make the calculation is described in Sect. 3.

2 CS Correlation functional

The CS expression for the correlation energy is

$$E_c = -a \int \rho(\mathbf{r}) \frac{1}{1 + dt(\rho)} \left[1 + bt(\rho)^8 e^{-ct(\rho)} W \right] d\mathbf{r} , \quad (2.1)$$

where $a = 0.04918$, $b = 0.132$, $c = 0.2533$, $d = 0.349$ and $t(\rho) = \rho^{-1/3}$. W depends on the derivatives of ρ and the kinetic energy density, and is explicitly

$$W(\mathbf{r}) = \frac{1}{8} \rho(\mathbf{r}) \nabla^2 \rho(\mathbf{r}) - \frac{1}{4} |\nabla \rho(\mathbf{r})|^2 + \rho(\mathbf{r}) T(\mathbf{r}) , \quad (2.2)$$

where

$$T(\mathbf{r}) = \frac{1}{2} \sum_i |\nabla \psi_i(\mathbf{r})|^2 . \quad (2.3)$$

The two terms in E_c , depending on ρ alone, and depending on the derivatives, will be denoted by E_{c1} and E_{c2} .

The origin of the parametric form for Eq. (2.1) is somewhat obscure; however, the parameters in the result are obtained by applying the form to an expression for the correlation energy of the He atom. Although the parametric form was fit to an integral involving ρ and W it appears that the parameters may also have been adjusted to fit estimates for the correlation energies of six atoms and ions, i.e. He, Li⁺, Be⁺⁺, Be, B⁺ and Ne as well as CH₄ and H₂O, since this set does not in fact minimize the root mean square deviation obtained from their data set as given in their Table 1. The CS prescription has been criticized on a variety of grounds by Singh et al. [11], Caratzoulas and Knowles [12] and Tao et al. [13]. The latter two criticisms are that the CS formalism underestimates long-range correlations in the He case and the uniform electron gas problem; this may not be too relevant to the molecular problem. The first criticism is of the normalization of the CS wave function, and the nature of the Coulomb hole. These problems can perhaps be attributed to an apparent inconsistency in the CS derivation at low densities, in that the function $\Phi(\mathbf{R})$ is assumed to vary slowly relative to the function $e^{-\beta r^2}$, where $\beta \sim \rho^{1/3}$.

The numerical problems with the CS expression mentioned in the Introduction arise at small values of the density, and occur in the second term involving W in Eq. (2.1). The numerical difficulties probably result from the function $t^8 e^{-ct}$, which reaches a very large maximum (around 3×10^8) at a large value (around 32) of t . Since W varies as ρ^2 or t^{-6} , it may be more realistic to consider the product $t^8 e^{-ct} W$, which varies as $t^2 e^{-ct}$, but this has a maximum of about 8 at $t = 8$ or $\rho = 0.002$. The problems have been substantially reduced by arbitrarily including with W a factor $\rho^2/(1 + \rho^2)$ which maintains the high-density behavior but screens the low-density

Table 1. Terms in the correlation energy (in hartrees) for six atoms or ions using the Colle–Salvetti (CS) expression and the present modification

System	E_{c1}	E_{c2} (CS)	E_{c2} (mod)	E_c (CS)	E_c (mod)	Ref. [15]
He	-0.05812	0.01655	0.00345	-0.04157	-0.05467	-0.420
Li ⁺	-0.06813	0.02424	0.01045	-0.04389	-0.05768	-0.435
Be ⁺⁺	-0.7403	0.02982	0.01685	-0.04421	-0.05718	-0.443
Be	-0.11019	0.01762	0.01687	-0.09257	-0.09332	-0.0940
B ⁺	-0.12327	0.01730	0.02102	-0.10597	-0.10225	-0.112
Ne	-0.36015	-0.01521	-0.01745	-0.37536	-0.37760	-0.372

behavior. In Table 1 we show, for the six systems considered using the CS, the contribution E_{c2} computed in the CS formalism and in the modified formalism. It is evident that the modification produces a substantial change in the two-electron systems and a relatively insignificant change in the other cases. This is the case both in the rather diffuse system Be, and in the more tightly bound systems B^+ and Ne.

3 Numerical evaluation

The integral of Eq. (2.1) can be evaluated in a coordinate system centered on any of the nuclei. This is not satisfactory, however, since values of the integrand near nuclei other than that at the origin are badly determined. These values are determined by an angular momentum sum which requires an unfeasible number of terms. For example, in the HF and H_2O cases, results for the integration centered on the protons are totally incorrect. This problem is resolved by rewriting the modified Eq. (2.1) as

$$E_c = -a \sum_k \int \chi_k(\mathbf{r}) \left[\sum_l w_{kl} \chi_l(\mathbf{r}) \right] \frac{1}{1 + dt(\rho)} \times \left[1 + bt(\rho)^8 e^{-ct(\rho)} \frac{\rho(\mathbf{r})^2}{1 + \rho(\mathbf{r})^2} W \right] d\mathbf{r}. \quad (3.1)$$

The integral is then dominated by the behavior of the integrand near \mathbf{R}_k , for which basis functions located at the other nuclei does not make a large contribution.

Each term in Eq. (3.1) is obtained by expanding the various functions in angular momentum functions centered on \mathbf{R}_k . The methods for expansion of angular momentum functions centered at one point in terms of functions centered at another point and the multiplication of two such expansions have been extensively discussed in a recent article by one of us [14].

The expansion of the factor $\sum w_{kl} \chi_l(\mathbf{r})$ is straightforward, and is obtained in the Hartree–Fock phase of the calculation; however, the calculation of the density-dependent factor, which will be denoted by $F[\rho](\mathbf{r})$, requires some discussion. The density

$$\rho(\mathbf{r}) = \sum_{mn} w_{mn} \chi_m(\mathbf{r}) \chi_n(\mathbf{r}) \quad (3.2)$$

is expanded about \mathbf{R}_k , together with $W(\mathbf{r})$. The functions are evaluated on the surface of a sphere, at points (θ_i, ϕ_j) , with the sums truncated at a maximum l value, L_{\max} . The angular momentum expansion is recovered as

$$F_{lm}[\rho](r) = \sum_{ij} \hat{w}_{ij} F[\rho](r, \theta_i, \phi_j) Y_{lm}(\theta_i, \phi_j), \quad (3.3)$$

where \hat{w}_{ij} are the appropriate weights for the (θ, ϕ) integration.

The N_θ integration points θ_i are chosen to be the Gauss–Legendre integration points on $[-1, 1]$ in the variable $t = \cos \theta$. The N_ϕ integration ϕ_j points are uniform on $[0, 2\pi)$.

4 Numerical results

In order to illustrate the efficacy of the proposed methods, numerical results for the molecules HF and H_2O are presented in this section. These calculations were made using numerically determined orbitals, as developed in Ref. [14]. The minimal basis sets for the orbitals, $1s$ on H and $1s, 2s$ and $2p$ on F and O, were employed and the calculations were made at the experimental geometries. Energies are in atomic units, except where differences are explicitly shown in millihartrees.

The correlation energy for HF is shown for several values of L_{\max} and for three methods of calculation in Table 2. These are the CS form with no gradient terms (labeled $b = 0$), the modified CS form, and the unmodified CS form. The latter was computed using the direct form (Eq. 2.1) and the F atom as the center. Since the density is concentrated in the neighborhood of the F nucleus, these results should be reliable. This is supported by the dependence, or lack thereof, of E_c on L_{\max} . These calculations were made with $N_\theta = N_\phi = 20$. (Since the molecular axis is the z -axis, N_ϕ is actually irrelevant.) The Hartree–Fock energy in this case is -108.0386 , 0.032 mhartree above the essentially exact result given by Helgaker et al. (HJO) [15]. The correlation energy can also be estimated from their coupled-cluster results to be 0.389, about 0.031 mhartree more than the present result.

The interesting observation in Table 2 is that the gradient terms make only a small contribution, of about -12 mhartree, to the correlation energy. This is comparable to the result for Ne, and in the opposite direction to the lighter atoms. The low-density modification increases the correlation energy by a slight 2 mhartree.

Table 3 is similar to Table 2, but for the H_2O molecule. The CS value was computed with the center at the O nucleus. The Hartree–Fock energy in this case is -76.0177 , 50 mhartree above the HJO value. The results

Table 2. Correlation energy in hartrees of the HF molecule from the CS expression and two modifications, for different values of L_{\max} . Here $N_\theta = N_\phi = 20$

L_{\max}	CS	CS(mod)	$b = 0$
2	-0.3561	-0.3560	-0.3435
4	-0.3536	-0.3565	-0.3434
6	-0.3551	-0.3575	-0.3437
8	-0.3559	-0.3576	-0.3438
10	-0.3561	-0.3585	-0.3438

Table 3. The same as Table 2, but for the H_2O molecule

L_{\max}	CS	CS(mod)	$b = 0$
2	-0.3381	-0.3308	-0.3264
4	-0.3294	-0.3316	-0.3293
6	-0.3330	-0.3328	-0.3268
8	-0.3348	-0.3333	-0.3269
10	-0.3352	-0.3347	-0.3270

Table 4. Correlation energy in hartrees of H₂O calculated for several values of $N_\theta = N_\phi$. The calculations were made with the modified CS form with $L_{\max} = 6$ and $L_{\max} = 10$ and the gradient-independent ($b = 0$) form with $L_{\max} = 6$

$N_\theta = N_\phi$	CS(mod) $L_{\max} = 6$	CS(mod) $L_{\max} = 10$	$b = 0$ $L_{\max} = 6$
10	-0.3340	-0.3339	-0.3269
12	-0.3335	-0.3347	-0.3267
14	-0.3325	-0.3363	-0.3267
16	-0.3327	-0.3349	-0.3268
18	-0.3330	-0.3353	-0.3268
20	-0.3328	-0.3347	-0.3268

are quite similar to those of Table 2, not surprisingly since the systems are isoelectronic; however, the results suggest that there are no problems with going to a somewhat more complicated geometry. Again, the gradient terms make a small contribution, of about -8 mhartree, and the effect of the low-density modification is very small. The coupled-cluster estimate for the correlation energy is 0.372, about 40 mhartree more than the CS estimate.

The numerical dependence of E_c , in the H₂O case, on the choice of the spherical mesh used in Eq. (3.3) is shown in Table 4. Results are given for the modified CS form with $L_{\max} = 6$ and 10, and the gradient-independent case with $L_{\max} = 6$. It is evident that accuracy at a level of a few millihartree is obtainable almost independently of N_θ and N_ϕ , but that the gradient-independent case is considerably more consistent. This is not surprising, since the correlation functional is a reasonably smooth function of the density.

Calculations were also carried out for the N₂ molecule, both in the minimal basis for which the Hartree–Fock energy is -108.8188 and in a somewhat improved basis adding $3s$ orbitals, for which the energy is -108.8972 . The HJO estimate for the Hartree–Fock energy is -108.9930 . The correlation energy omitting the gradient terms is in each case about -0.455 . The gradient correction terms are again small, but show no indication of convergence in L_{\max} , varying from 0.010 at $L_{\max} = 2$ to -0.010 at $L_{\max} = 10$. The correlation energy as estimated from coupled-cluster calculations is about -0.549 .

5 Discussion

The calculations discussed here can be described as density functional calculations in the framework of nonlocal exchange and a local correlation functional of the density. This is not exactly correct, since the orbitals

are obtained in the Hartree–Fock approximation, i.e., without including the correlation in their determination and so do not solve the Kohn–Sham equations. The orbitals are obtained numerically and are variationally optimized, thus permitting much smaller basis sets than are required in GTO calculations.

The Hartree–Fock energies obtained here can obviously be improved by including polarization orbitals. Substantial improvement can probably be obtained without going to the very large polarized valence sixtuple-zeta basis employed in the results of HJO, but may require refinement of the numerical methods.

The CS functional and the modified form considered here underestimate the correlation energy in the cases considered here, and there is no reason to believe that these are atypical. A striking feature of these results is the smallness of the contribution of the gradient terms. This suggests that it may be possible to construct a reasonable correlation functional that is independent of the density and orbital derivatives. The numerical results presented indicate that evaluation of such a functional should present few difficulties, even for more complex systems.

Future work will include a study of the effect of the correlation potentials on the molecular orbitals and the role of the correlation energy on the determination of molecular geometries.

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