CONSTRUCTION OF AN ACCURATE SELF-INTERACTION-CORRECTED CORRELATION ENERGY FUNCTIONAL BASED ON AN ELECTRON GAS WITH A GAP

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I. INTRODUCTION

The usual starting point of any first principles construction of an approximate electron correlation energy functional $E_c[\{n_\sigma\}]$ is the homogeneous electron gas weakly perturbed by an external potential. To lowest non-vanishing order in the gradient of the electron density, ∇n, the correlation energy density, per electron, $\epsilon_c(r_s, \zeta)$, may be written[1,2] as the usual local spin density (LSD) expression, ϵ_c^{LSD}, plus a term proportional to $|\nabla n|^2$. When perturbation theory is employed to calculate ϵ_c^{LSD}, the result diverges in each order of the electron-electron coupling due to the zero energy gap

between states at the Fermi energy and the neighboring unoccupied states in the continuum. By employing many body perturbation theory techniques, this series may be summed in the high density limit to yield a finite result[3]. Other numerical calculations have been employed to calculate ϵ_c^{LSD} for arbitrary uniform density[4].

However, when the resulting $\epsilon_c^{LSD}(r_s, \zeta)$ is employed to calculate E_c for atoms, the results are generally too large in magnitude by approximately a factor of two. Thus the gradient corrections to E_c^{LSD} must be approximately equal to $-E_c$, suggesting that a simple gradient expansion of E_c is inadequate to describe the contribution from the rapid variation in electron density in these physical systems. This has prompted the construction of generalized gradient approximations (GGA's) which reduce to the gradient expansion approximation (GEA) results in the slowly varying limit, but are constructed to satisfy certain important scaling properties[6] known to be satisfied by the exact $E_c[n]$ but not satisfied by a simple GEA gradient or by an expansion including higher order derivatives of the density. Perhaps the most interesting GGA is the recent one by Perdew, Burke and Enzerhof[7] (PBE), who employ only the $\epsilon_c^{LSD}(r_s, \zeta)$, the lowest order term in the gradient expansion and an ingenious ansatz to obtain an expression for $E_c[\{n_\sigma\}]$ that yields results for molecular dissociation energies which are nearly identical to those predicted by the much more complicated PWGGA.[5] However, although these results reduce the error in the LSD calculations by a factor of four, the PBE dissociation energies still exhibit an average error of $\approx$ 8 kcal/mole, which is eight times larger than the quantum-chemistry accuracy criterion. Moreover, from a more theoretical point of view, the PBE correlation energy functional may be criticized because, as with other pure spin density functionals, it is not self-interaction-free[8] i.e. for the hydrogen atom it predicts[9] $E_c \approx$ −6 mhartree $\approx$ −4 kcal/mole.

It has long been understood that the LSD overestimate of the magnitude of the correlation energy for localized electrons arises primarily from the fact that the ground state of such systems is separated from the higher lying states by a non-zero energy with the gap to the continuum given by the ionization energy. Thus, if one employs perturbation theory taking the zeroth order wavefunction to be either the Hartree-Fock (Moller-Plesset perturbation theory) or the exchange-only Kohn-Sham ground state, the calculation of E_c for atoms converges after only a few orders to nearly the same result as that obtained by configuration interaction techniques. Moreover, early work by Tong[10] demonstrated that if electrons were confined to a box of atomic dimensions such that the density was equivalent to that found in atoms, the existence of discrete states with resulting energy gaps led to results for E_c that were about a factor of two smaller than that given by the local density approximation. The foregoing observations therefore suggest that a more appropriate model to employ in performing density functional calculations of E_c is one that includes an appropriately chosen energy gap.

Generally, it is not possible to define a local potential that yields a homogeneous electron gas with a non-zero energy gap at the Fermi level for an infinite system. However, Rey and Savin[11] have employed a non-local one body operator to shift the virtual (non-interacting) levels by an arbitrary energy gap G. They then performed calculations of the correlation energy density of a homogeneous unpolarized electron gas as a function of both r_s and G i.e. $\epsilon_c(r_s, G, \zeta = 0)$ which reduces to the usual local density approximation when $G = 0$. In addition, they have obtained an accurate analytic representation of $\epsilon_c(r_s, G, \zeta = 0)$ so that this functional may be employed to calculate

E_c for any spin unpolarized system once a prescription is given to determine G for the system of interest.

In section II we discuss their results and propose that, to a first approximation, $G[n]$ be taken as the simplest function of the gradient of the electron density that reduces to the ionization energy in the large r limit, i.e. the energy gap to the continuum. It then follows that $\epsilon_c(r_s, G[n], \zeta = 0) \to 0$ as $|\nabla n| \to \infty$ and that $\epsilon_c(r_s, G[n], \zeta = 0)$ saturates under uniform scaling to the high density limit without the need to introduce any further ansatz to construct a GGA. The correlation energy density for any ζ is then obtained by employing the von Barth-Hedin[12] interpolation formula between the $\zeta = 0$ and $\zeta = 1$ results, the latter having recently been obtained by Savin[13]. When the resulting $\epsilon_c(r_s, G[n], \zeta)$ is employed to calculate E_c for atoms and positive ions for $Z \leq 18$, we find that the discrepancy from highly accurate CI calculations[14] is less than half that obtained by employing the LSD with $G = 0$.

The $\epsilon_c(r_s, G[n], \zeta)$ functional is further improved by performing an orbital dependent self-interaction-correction similar to one first suggested by Becke.[15] The resulting ϵ_c^{SIC} is invariant under a unitary transformation among the occupied orbitals. We find that the corresponding E_c^{SIC} for both atoms and positive ions with $Z \leq 18$ are significantly improved being approximately 10 to 20% too large in magnitude.

Finally, in order to ensure that $\epsilon_c(r_s, G[n], \zeta)$ for $\zeta = 0$ and $\zeta = 1$ yields the correct small gradient expansion in the high density limit, we construct the simplest possible $\epsilon_c^{GGA}(r_s, |\nabla n|, \zeta)$ to replace $\epsilon_c^{LSD}(r_s, \zeta)$ in the analytic representation of $\epsilon_c(r_s, G, \zeta)$. This GGA is constructed by requiring the correct small gradient expansion as well as satisfying the conditions that $\epsilon_c^{GGA} \to 0$ for $|\nabla n| \to \infty$ and ϵ_c^{GGA} saturates under uniform scaling in the high density limit (the three conditions required by PBE).

With this modification, the resulting $\epsilon_c^{GGASIC}(r_s, |\nabla n|, G[n], \zeta)$ yields results for E_c/N the average energy per electron, in atoms and positive ions with $Z \leq 18$, that are on average in error by ≈ 1 mhartree compared to an average error of ≈ 40 mhartree when the LSD approximation is employed. Our results for E_c generally lie between those given by the PWGGA and PBE functionals and are closer to the latter with the PWGGA calculations generally lying deeper and the PBE calculations always lying more shallow than the exact results for atoms and ions with more than three electrons.

II. CONSTRUCTION OF THE CORRELATION ENERGY FUNCTIONAL

A) Local Density Approximation for a Homogeneous Electron Gas with an Energy Gap

In order to account explicitly for the fact that the perturbation theory calculation of the correlation energy for systems containing localized electrons depends on the energy gap between the ground state and the higher lying states of the non-interacting (Kohn-Sham) system, Rey and Savin[11] have performed detailed calculations of $\epsilon_c(r_s, G)$, the correlation energy per particle for an unpolarized uniform electron gas with energy gap G separating the Fermi energy from the continuum. The results of their calculations have been tabulated for a wide range of densities $0.1 \leq r_s \leq 10$ relevant to atomic and molecular electron densities with $0 \leq G \leq 20\epsilon_F$ where ϵ_F is the Fermi energy of the homogeneous electron

gas. In addition, they have provided an analytic fit to $\epsilon_c(r_s,G)$ which is accurate to a few tenths of a milli-hartree when compared to their numerical results.

They find that

$$\epsilon_c(r_s,G) = \frac{\epsilon_c^{LDA}(r_s) + C_1(r_s)G}{1 + C_2(r_s)G + C_3(r_s)G^2} \tag{1}$$

where C_1, C_2, C_3 are given as analytic functions of r_s. Obviously, in the limit $G = 0$, $\epsilon_c(r_s,G) \to \epsilon_c^{LDA}(r_s)$.

In order to apply eq. (1) to physical systems, in addition to the usual local density approximation for $r_s = r_s[n(r)]$, it is necessary to choose an approximate ansatz for G.

If in the zeroth approximation we neglect any contribution to the correlation energy calculation from unoccupied localized KS orbitals then the smallest excitation energy is given by the ionization energy to the continuum, I. However, it is clear that such a choice for G is not consistent with the condition that the E_c for two dissimilar atoms that are very far apart must be the sum of the two separate correlation energies. This follows from the fact that E_c for each separate atom will depend on its own I, but the composite system with large interatomic distance will have only a single I, that of the atom with the lowest ionization energy. We therefore seek a definition of $G[n]$ which is local so that the E_c of two sub-systems far apart will be the sum of the separate correlation energies and that for any isolated system, $G \to I$ as $r \to \infty$. In addition we require that $G \to 0$ when applied to a homogeneous electron gas so that $\epsilon_c(r_s,G) \to \epsilon_c^{LDA}$ in that limit. This suggests that G depends on gradients of the density. Moreover, since $G \geq 0$, the latter suggests that G is a function of $|\nabla n|^2$.

But for any KS system of non-interacting electrons for which the external potential vanishes as $r \to \infty$, $V_{KS} \to 0$ as $r \to \infty$ [16] so the density for large r is dominated by the highest lying occupied orbital corresponding to

$$n(r) \underset{r \to \infty}{\sim} \exp -2[(-2\epsilon_m)^{1/2}r] \tag{2}$$

Consequently if we define

$$G^0[n] \equiv \frac{1}{8}|\nabla \ln n|^2 \tag{3}$$

then it follows from eqs. (2) and (3) that

$$G^0[n] \underset{r \to \infty}{\to} -\epsilon_m \tag{4}$$

But in an exact KS theory [17], $-\epsilon_m = I$ so

$$G^0[n] \underset{r \to \infty}{\to} I \quad . \tag{5}$$

We also note that since

$$n(r) \underset{r \to 0}{\sim} \exp(-2Zr) \tag{6}$$

near the nucleus of an atom of atomic number Z, then

$$G^0[n] \underset{r \to 0}{\to} Z^2/2 > I \quad \text{for } Z > 1 \,, \tag{7}$$

so that G^0 tends to increase in the atomic core and approximates the excitation energy necessary to move an electron to the continuum from these deeper levels i.e. approximates the energy denominators appearing in a perturbation theory treatment. In taking $G^0 = G^0[n]$ we are of course depending on the fundamental theorem of density functional theory[18] which guarantees that $E_c = E_c[n]$ so that in applying eq.(1) to real physical systems, it should be possible to write $G = G[n]$.

Moreover, if eq.(3) is employed to approximate G in eq.(1), then it not only follows that

$$\epsilon_c(r_s, G^o[n]) \to \epsilon_c^{LDA}(r_s) \quad \text{for } |\nabla n| \to 0 \tag{8}$$

but in addition

$$\epsilon_c(r_s, G^o[n]) \to 0 \quad \text{for } |\nabla n| \to \infty \,. \tag{9}$$

Furthermore, under uniform scaling i.e. $n(r) \to n_\lambda(r) = \lambda^3 n(\lambda r)$ in the high density limit $(\lambda \gg 1)$ $r_s \sim \lambda^{-1}$, $\epsilon_c^{LDA} \sim -\gamma \ln\lambda$, $G^0[n] \sim \lambda^2$, and employing the analytical behavior[11] of C_1, C_2, C_3 in eq.(1) we find

$$\epsilon_c(r_s, G^0[n]) \underset{\lambda \to \infty}{\to} \frac{C_1}{C_3 G^0} \sim \frac{1}{r_s^2 G^0} \sim \lambda^0 \tag{10}$$

i.e. the correlation energy saturates. Thus $\epsilon_c(r_s, G^o[n])$ automatically satisfies some of the important exact scaling properties often imposed in constructing approximate GGA's for the correlation energy[7].

B) Extension to Spin Polarized System

In order to perform calculations on spin polarized systems, we require $\epsilon_c(r_s, G, \zeta)$ which is not yet available for partial spin polarization i.e. $0 < \zeta < 1$. However, since the results for $\zeta = 0$ [11] and $\zeta = 1$ [13] have been calculated, we can employ the von Barth-Hedin[12] interpolation formula to obtain the results for intermediate ζ i.e.

$$\epsilon_c(r_s, G, \zeta) = \epsilon_c(r_s, G, \zeta = 0) + f(\zeta)[\epsilon_c(r_s, G, \zeta = 1) - \epsilon_c(r_s, G, \zeta = 0)] \tag{11}$$

where

$$f(\zeta) \equiv \frac{(1 + \zeta)^{4/3} + (1 - \zeta)^{4/3} - 2}{2(2^{1/3} - 1)} . \tag{12}$$

In order to employ eq. (11) for continuous values of r_s and G, we require an analytic fit to Savin's numerical results for $\epsilon_c(r_s, G, \zeta = 1)$. Taking the same functional form given by eq. (1) we find $C_1(r_s, \zeta = 1) = 0.70\, C_1(r_s, \zeta = 0)$, $C_2(r_s, \zeta = 1) = 1.50\, C_2(r_s, \zeta = 0)$, and $C_3(r_s, \zeta = 1) = 2.59\, C_3(r_s, \zeta = 0)$ yields $\epsilon_c(r_s, G, \zeta = 1)$ which are within 1 mhartree for $0.1 \leq r_s < 10$ and $0 \leq G \leq 20\,\epsilon_F$. Although the accuracy of the von Barth-Hedin formula cannot be tested for arbitrary G, we have compared the results of employing this interpolation to those given by a more precise spin polarized fit to numerical calculations for $G = 0$. We find that when the two $\epsilon_c^{LSD}(r_s, \zeta)$ are employed to calculate the correlation energy for atoms using exact exchange-only densities[19], the two results for E_c are within a few tenths of one percent for atoms with $Z \leq 18$ with the exception of nitrogen for which they differ by 1%.

When the local density approximation is made for r_s and G is given by eq.(3), we shall refer to eq.(10) as the LSDGAP approximation.

C) Inclusion of Self-Interaction-Correction

The exact correlation energy functional must vanish indentically for any one-electron system independent of the form of the external potential. As in the case of the LSD approximation, the LSDGAP expression for $E_c[n]$ does not satisfy this condition and thus a self-interaction correction (SIC) must be introduced.

Early work by Perdew and Zunger[20] employed an ad hoc SIC for E_c which consisted of subtracting the sum of the separate orbital contributions to E_c of each electron. The resulting expression for E_c^{SIC} was self-interaction free and significantly reduced the overestimate of E_c^{LSD}. However, this method is not invariant under a unitary transformation of the occupied orbitals and thus does not yield a unique E_c for different orbital representations of the same density. Subsequently, Becke[15] showed that the correlation energy of any system of electrons may be written as the sum of the contribution from interactions between electrons with opposite spins and a contribution from electrons with parallel spin, the latter being proportional to an orbital dependent factor $D_\sigma \equiv \sum_i |\nabla \phi_{i\sigma}|^2 - |\nabla n_\sigma^{1/2}|^2$. D_σ is invariant under a unitary transformation of the occupied orbitals and is identically zero if there is only one occupied orbital of a given spin.

Then, if $\epsilon_c[n_\alpha, n_\beta]$ is the uncorrected correlation energy density,

$$E_{copp} = \int d\tau \{ n\epsilon_c[n_\alpha, n_\beta] - \sum_\sigma n_\sigma \epsilon_c[n_\sigma, 0] \} \tag{13}$$

and

$$E_{c\sigma\sigma} = \int d\tau \sum_\sigma \frac{\sum_i |\nabla \phi_{i\sigma}|^2 - |\nabla n_\sigma^{1/2}|^2}{\sum_i |\nabla \phi_{i\sigma}|^2} n_\sigma \epsilon_c[n_\sigma, 0] . \tag{14}$$

The only difference between eqs.(13) and (14) and Becke's prescription is the choice of the denominator in eq. (14). In Becke's original treatment, the kinetic energy density in the LSD approximation was employed as a normalizing factor so the factor multiplying $n_\sigma \epsilon_c[n_\sigma,0]$ should reduce to unity in the homogeneous gas limit. However, he found that for atoms with large interatomic distances, this could lead to an enhancement of $E_{c\sigma\sigma}$ due to this SIC which was unphysical. The choice of the exact kinetic energy density as the normalizing factor obviously ensures that the fraction is always ≤ 1[21].

Adding eqs.(13) and (14) yields

$$E_c^{SIC} = \int d\tau \{ n\epsilon_c[n_\alpha,n_\beta] - \sum_\sigma \frac{|\nabla n_\sigma^{1/2}|^2}{\sum_i |\nabla \phi_{i\sigma}|^2} n_\sigma \epsilon_c[n_\sigma,0] \} \qquad (15)$$

When the LSDGAP expression given by eq.(11) is employed for ϵ_c in eq. (15), we shall refer to this approximation as LSDGAPSIC. As in the case of the LSD approximation for $E_c[\{n_\sigma\}]$, the correlation energy functional given by the LSDGAP and LSDGAPSIC approximations have no adjustable parameters, depending only on results of calculations on the homogeneous electron gas with a gap.

D) Inclusion of Gradient Correction to ϵ_c^{LSD}

In the limit of high but slowly varying density it has been shown[1,2] that

$$\epsilon_c^{LSD}(r_s,\zeta,t) = \epsilon_c^{LSD}(r_s) + \beta\phi^3 t^2 + \ldots \qquad (16)$$

where

$$\beta = 0.066725 \frac{e^2}{a_0} \quad , \quad \phi(\zeta) \equiv \frac{[(1+\zeta)^{2/3} + (1-\zeta)^{2/3}]}{2},$$

$$t \equiv \frac{|\nabla n|}{2\phi k_s n} \quad , \quad k_s \equiv \left[\frac{4k_F}{\pi a_0} \right]^{1/2} \qquad (17)$$

However, if we take the small G expansion of the LSDGAP approximation discussed in Sec. IIB, employ eq. (3) and write the result in terms of t^2 instead of G, we find that the correction to $\epsilon^{LSD}(r_s)$ of order t^2 vanishes in the high density limit.

The simplest approach to ensure the correct small t^2 expansion of ϵ_c^{LSDGAP} is to modify the $\epsilon_c^{LDA}(r_s)$ term appearing in eq. (1) for $\zeta = 0$ and in the corresponding expression for $\zeta = 1$ so that $\epsilon_c(r_s,G,\zeta)$ given by eq.(11) exactly reduces to eq.(16) at least for $\zeta = 0$ and 1. As in the case of the LSD approximation, it is not possible to simply employ eq.(16) to describe the inhomogeneous electron gas for arbitrary t^2 because for

sufficiently large t^2 in the high density limit the expansion for ϵ_c would become positive.

Alternatively, we consider the construction of $\epsilon_c(r_s,G,\zeta,t)$ for extended states such that in the $t = 0$ limit, the resulting $\epsilon_c(r_s,G,\zeta)$ is identical to ϵ_c^{LSDGAP} given by eq.(11), and in the $G = 0$ limit is identical to eq.(16) for $t^2 \ll 1$ (at least for $\zeta = 0$ and $\zeta = 1$), and in addition satisfies the three conditions required by PBE in constructing a suitable GGA[7].

In the simplest approximation this can be accomplished by replacing $\epsilon_c^{LDA}(r_s)$ in eq.(1) (and in the corresponding expression for $\zeta = 1$[13]) by an $\epsilon_c^{GGA}(r_s,\zeta,t)$ that satisfies the conditions given by eqs. (9,10) and reduces to $\epsilon_c(r_s,\zeta,t)$ given by eq.(16) for $t^2 \ll 1$.

We consider a GGA of the form

$$\epsilon_c^{GGA}(r_s,\zeta,t) = \frac{\epsilon_c^{LSD}(r_s,\zeta)}{1 + f(r_s,\zeta,t)} \tag{18}$$

Then, under uniform scaling in the high density limit[7]

$$\epsilon_c^{LSD} \underset{\lambda \to \infty}{\sim} -\gamma ln\lambda \quad \text{and} \quad t^2 \underset{\lambda \to \infty}{\sim} \lambda \tag{19}$$

so that if ϵ_c^{GGA} saturates in the limit $\lambda \to \infty$, then

$$f \underset{\lambda \to \infty}{\sim} ln\lambda \sim ln t^{2p} \tag{20}$$

where p can be taken as a constant > 0. Furthermore, if we take

$$f = \beta ln \left[1 + \frac{\phi^3 t^2}{p|\epsilon_c^{LSD}(r_s,\zeta)|}\right]^p \tag{21}$$

with $p > 0$, then it follows from eq.(18) that $\epsilon_c^{GGA} \to 0$ as $t^2 \to \infty$, and for $t^2 \ll 1$, the expansion of ϵ_c^{GGA} satisfies eq.(16) independent of the choice of p. In addition, since $f \geq 0$, $\epsilon_c^{GGA} \leq 0$ for all r_s and t.

We thus find that there is a family of ϵ_c^{GGA}, each corresponding to a different choice of the parameter p, that satisfy the PBE conditions for an acceptable GGA. This result suggests that it may not be possible to derive a unique ϵ_c^{GGA} even if more scaling conditions are imposed and that the only way to obtain a highly accurate ϵ_c^{GGA} by employing only scaling properties and the small t^2 expansion of ϵ_c is to bias the choice of parameters that enter ϵ_c^{GGA}. It is clear that the PBEGGA yields results close to those of PWGGA, not simply because it satisfies the conditions given by eq.(9,10,16) but because it was constructed to mimic the PWGGA which is not a unique theoretical fit but is somewhat biased toward atoms by the use of a sharp real-space cut-off of the gradient expansion for the correlation hole[9].

However, as long as we employ the exact exchange-only functional[22], we can in principle determine the best p based on purely theoretical considerations by requiring the ionization theorem be satisfied i.e. the self consistently calculated $-\epsilon_m$ and $I \equiv E(N-1) - E(N)$ agree as closely as possible. Such a method has been successfully employed to calculate the best exchange-mixing coefficient[23]. For simplicity, the

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calculations reported here employ the simplest choice of p in eq.(21) i.e. $p = 1$.

In the following we shall refer to the method in which $\epsilon_c^{LSD}(r_s,G,\zeta)$ is replaced by $\epsilon_c^{GGA}(r_s,G,\zeta,t)$ in the LSDGAPSIC approximation as the GGAGAPSIC approximation.

III. DISCUSSION OF NUMERICAL RESULTS

It is interesting to study the effect on the calculated correlation energy density as the sequence of approximations described in Section II are implemented. All calculations reported here are performed by employing the KLI approximation[22] for the exact exchange-only single particle wavefunctions.

Figure 1 is a graph of the radial correlation energy density for helium versus the distance from the nucleus so that the area under the horizontal axis is the corresponding E_c in each approximation. For helium, the exact[14] $E_c = -0.0420$ a.u. and $E_c^{LSD} = -0.1125$ a.u. using the PW[24] parametrization of $\epsilon_c^{LSD}(r_s)$ which will be employed throughout these calculations. We see that when the LSDGAP for ϵ_c is employed with G given by eq.(3), the resulting radial correlation energy density is significantly smaller in magnitude with the resulting $E_c^{LSDGAP} = -0.0715$ a.u., thus reducing the error in the LSD result by $\approx 60\%$. In addition, when the self-interaction correction is included, the correlation energy density is further everywhere reduced with $E_c^{LSDGAPSIC} = -0.0470$ a.u. which corresponds to an error of $\approx 7\%$ of the original LSD error. Finally, the implementation of the GGAGAPSIC approximation leads to a further, smaller, decrease in the magnitude of the correlation energy density yielding $E_c^{GGAGAPSIC} = -0.0408$ a.u., thus overshooting the exact result and leaving an error of only 1.2 mhartree which is less than 2% of the LSD error.
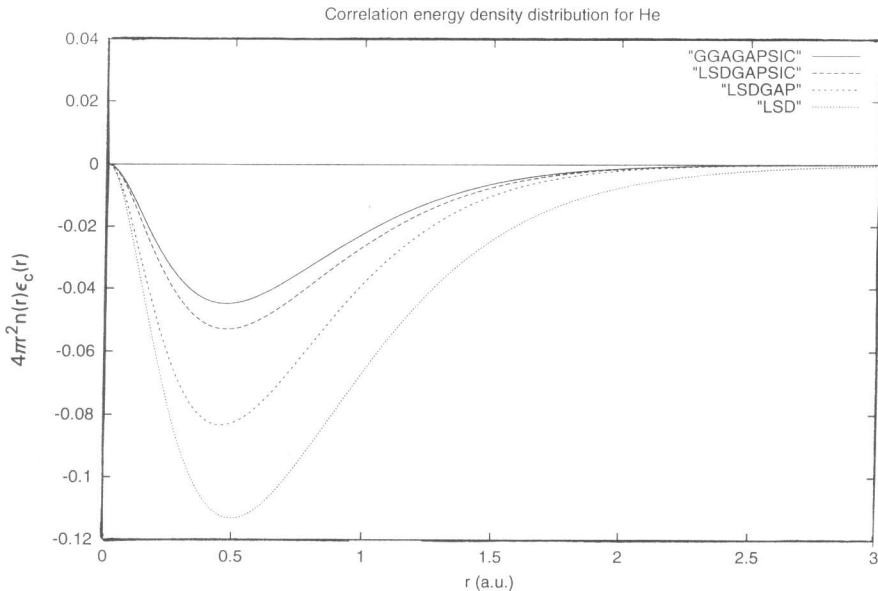

Fig. 1 The radial correlation energy density for the helium atom in several approximations vs. the distance from the nucleus. Results are exhibited in the local spin density (LSD) approximation as well as approximations described in Section II.

Similarly, Figure 2 is a graph for the magnesium atom for which the shell structure is apparent due to the weighting of the correlation energy density by the radial density. Here the best available estimate of the correlation energy[14] (see also eq. (23)) is $E_c = -0.4424$ a.u., and $E_c^{LSD} = -0.8876$ a.u. We see that the application of the LSDGAP energy functional decreases the depth of ϵ_c in the vicinity of the $n = 1$ shell i.e. near $r \approx 0.1$ a.u., to about 60% of its LSD value whereas the corresponding decrease for r near the $n = 2$ radial density maximum i.e. $r \approx 0.5$ a.u., is to approximately 85% of its LSD value. This is a general characteristic of the LSDGAP functional: the core electron contribution to E_c is reduced by a greater factor than that from the higher lying electron shells and for atoms with larger Z, the radial correlation energy density near the $n = 2$ shell is deeper than that near the $n = 1$ shell. For magnesium, $E_c^{LSDGAP} = -0.6183$ a.u. which corresponds to a reduction in the LSD error of $\approx 60\%$. As in the $Z = 2$ case, the implementation of the LSDGAPSIC approximation further reduces the magnitude of ϵ_c everywhere with the greatest depth of the radial correlation energy density now in the vicinity of the $n = 2$ subshell, with $E_c^{LSDGAPSIC} = -0.5029$ a.u. corresponding to an error of $\approx 14\%$ of the LSD error. Finally, the application of the GGAGAPSIC approximation results in a further decrease in the magnitude of ϵ_c everywhere and a value of $E_c^{GGAGAPSIC} = -0.4362$ a.u. thus overshooting the needed correction by less than 2% of the LSD error.
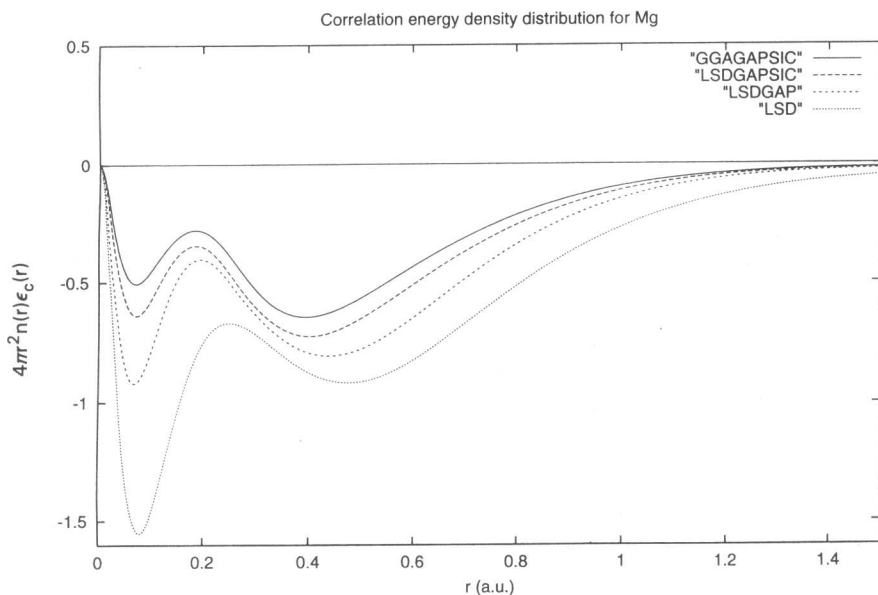

Fig. 2 The radial correlation energy density for the magnesium atom vs. the distance from the nucleus. The approximations employed are the same as in Fig. 1.

Figures 3 and 4 exhibit the correlation energy per electron for atoms and positive ions versus the number of electrons in each system for which accurate CI calculations have been performed[14] i.e. $Z \leq 18$. We see that as each successive correction is made to the correlation energy functional, the calculated E_c more closely approximate the most accurate available E_c^{DFT} results with the GGAGAPSIC yielding a discrepancy of ≈ 1 mhartree on average for the correlation energy per electron compared to an average error of ≈ 40 mhartree for E_c/N when the LSD approximation is employed.
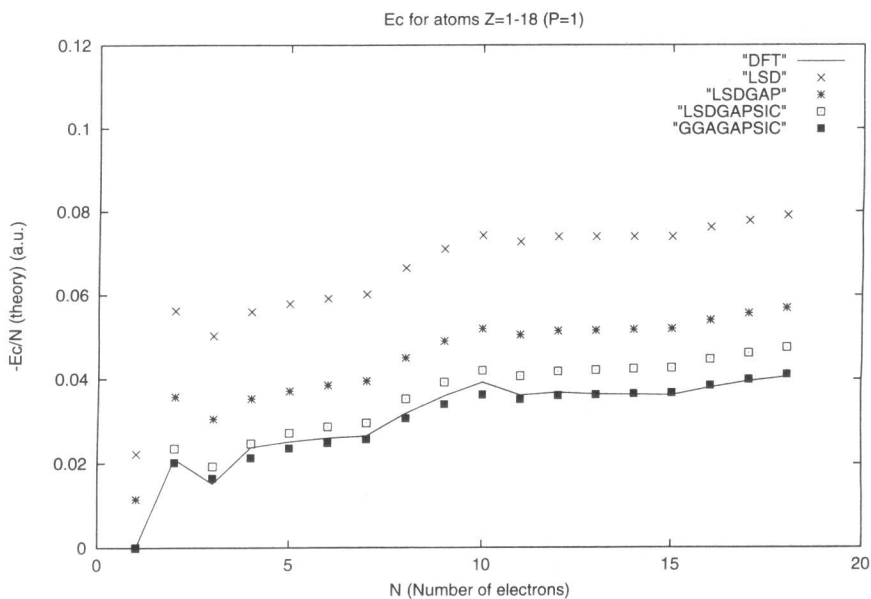
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Ec for atoms Z=1-18 (P=1)

Fig. 3 The negative of the correlation energy per electron vs. the number of electrons, N, for atoms with nuclear charge $Z \leq 18$. The DFT results are obtained from eq. (23) and ref. 14. The straight lines connecting the DFT results for integer values of N have no physical significance. The approximations employed are the same as in Fig. 1.
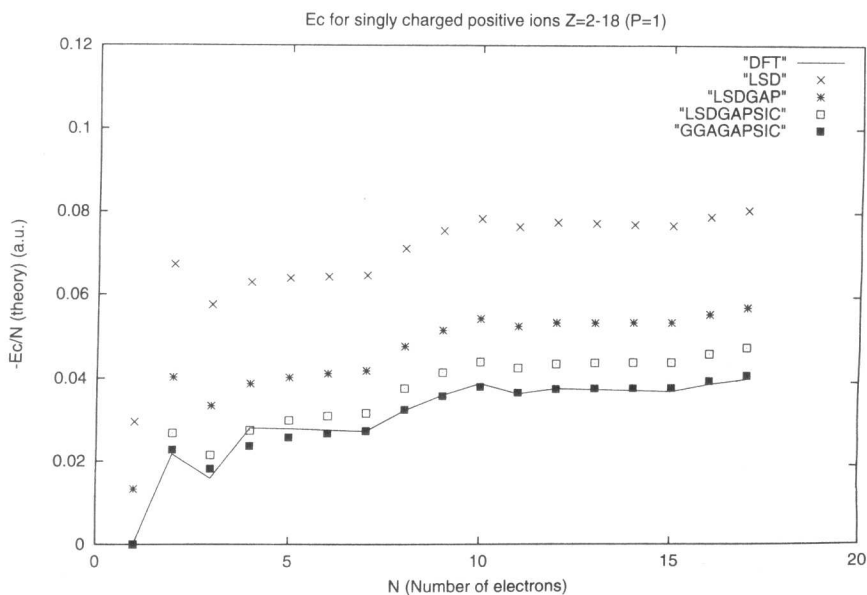
Ec for singly charged positive ions Z=2-18 (P=1)

Fig. 4 The negative of the correlation energy per electron vs. the number of electrons, N, for singly charged positive ions with nuclear charge $Z \leq 18$. The methods employed are the same as in Fig. 3.

Table 1. Comparison of calculations of the correlation energy (-E_c in hartrees) of neutral atoms for Z=1 to 18 with accurate DFT results

Z	DFT	PWGGA	PBEGGA	GGAGAPSIC
1	0.0000	0.0066	0.0060	0.0000
2	0.0420	0.0459	0.0420	0.0408
3	0.0455	0.0574	0.0514	0.0498
4	0.0950	0.0941	0.0854	0.0860
5	0.1255	0.1269	0.1158	0.1187
6	0.1561	0.1599	0.1473	0.1499
7	0.1858	0.1932	0.1797	0.1804
8	0.2553	0.2583	0.2383	0.2466
9	0.3249	0.3217	0.2956	0.3085
10	0.3929	0.3822	0.3510	0.3665
11	0.3988	0.4061	0.3711	0.3903
12	0.4424	0.4497	0.4104	0.4362
13	0.4740	0.4896	0.4466	0.4756
14	0.5094	0.5316	0.4856	0.5153
15	0.5447	0.5742	0.5258	0.5548
16	0.6095	0.6406	0.5865	0.6209
17	0.6728	0.7062	0.6467	0.6843
18	0.7314	0.7702	0.7060	0.7452

Table 2. Comparison of calculations of the correlation energy (-E_c in hartrees) of singly charged positive ions for Z=2 to 18 with accurate DFT results

Z	DFT	PWGGA	PBEGGA	GGAGAPSIC
2	0.0000	0.0074	0.0062	0.0000
3	0.0435	0.0506	0.0448	0.0461
4	0.0477	0.0620	0.0541	0.0551
5	0.1119	0.1028	0.0919	0.0955
6	0.1394	0.1368	0.1236	0.1298
7	0.1658	0.1703	0.1556	0.1614
8	0.1909	0.2039	0.1885	0.1922
9	0.2590	0.2733	0.2506	0.2626
10	0.3257	0.3384	0.3091	0.3261
11	0.3906	0.3999	0.3654	0.3852
12	0.4028	0.4222	0.3838	0.4085
13	0.4548	0.4669	0.4238	0.4557
14	0.4897	0.5085	0.4619	0.4961
15	0.5257	0.5507	0.5014	0.5359
16	0.5596	0.5932	0.5417	0.5753
17	0.6266	0.6621	0.6045	0.6436
18	0.6884	0.7286	0.6655	0.7079

Tables 1 and 2 provide a comparison between our results and those of both the PWGGA and PBE approximations. The E_c^{DFT} results are obtained from reference 14 adjusted for the fact that the spin-density functional theory definition of the correlation energy is slightly different from that employed in quantum chemistry (QC) i.e. we define E_c^{DFT} by

$$E_{tot} = E^{RHF} + E_c^{QC} = E^{UOEPX} + E_c^{DFT} \quad . \tag{22}$$

Therefore

$$E_c^{DFT} = E_c^{QC} + (E^{RHF} - E^{UOEPX}) \tag{23}$$

i.e. the adjustment is the difference between the total energy in the restricted Hartree Fock (RHF) approximation and the corresponding exact unrestricted optimized effective potential[19] result for exchange-only (UOEPX) which corresponds to exact KS exchange-only theory. (This definition of E_c^{DFT} is slightly different from the conventional E_c^{KS} which would employ the expectation value of the Hamiltonian, H, with a determinant of the exact KS orbitals rather than E^{UOEPX}, which is the expectation value of H with a determinant of the exact exchange-only KS orbitals. E_c^{DFT} given by eq. (23) is then easy to calculate because E^{UOEPX} is available for any atom, whereas $<H>^{KS}$ is not because the exact KS orbitals are difficult to obtain. We expect that the different DFT definitions of E_c lead to $|E_c^{KS}| > |E_c^{DFT}|$ by ≤ 1 mhartree.)

We find that with few exceptions the PWGGA overestimates the magnitude of E_c and the PBE underestimates the same with the GGAGAPSIC results generally lying between the two and closely approximating the PBE results especially for first row atoms. For second row atoms, the GGAGAPSIC results always lie between the results of the other two approximations and generally are significantly closer to the DFT results.

One can attempt to improve the accuracy of the GGAGAPSIC approximation by treating p as a parameter and studying the p dependence of the calculated E_c. We find that in this approximation, $|E_c|$ is monotomically decreasing for increasing p for each atom and positive ion which follows from the observation that f increases with increasing p so ϵ_c^{GGA} given by eq. (18) decreases in magnitude with increasing p. As a result, for a choice of $p = 5/4$, all calculated E_c are reduced in magnitude by $\approx 2\%$ so the GGAGAPSIC calculation for $Z = 15$ to 18 yields results within 1 mhartree of E_c^{DFT} for atoms and within 6 mhartree for the positive ions. However, the decrease in $|E_c|$ for lighter atoms and ions generally yields results which are slightly further from the exact values. This negates the utility of simply increasing p because the largest percent errors in our calculated E_c for chemically active atoms and ions are for $N = 4, 5$, and 6, all of which are already too small in magnitude.

From a more fundamental point of view, we recognize that in constructing the correlation energy functionals discussed in Section II, we have neglected the contributions from the unoccupied orbitals with single particle energy eigenvalues lying in the gap when we required that $G^0 \rightarrow I$ rather than to an energy gap corresponding to the energy difference to the lowest lying unoccupied orbital. However, we find that no matter how we modify our definition of G^0 to include this contribution, the resulting GGAGAPSIC correlation energy functional always saturates for fixed N when $Z \rightarrow \infty$. On the other hand, it is well known[14] that E_c diverges for the isoelectronic series with $N = 4, 5$ or 6 electrons and converges for the other first row atoms. As can be seen from Moller- Plesset

perturbation theory, the reason for this is clear: for these isoelectronic series there are unoccupied $2p$ levels in both spin channels that are nearly degenerate with the highest lying occupied states in the $n = 2$ shell. As a result, the energy denominator in second order perturbation theory corresponding to two electrons from the $n = 2$ shell excited into these $2p$ states is proportional to Z in the large Z limit, while the matrix element in the numerator (which is squared) is proportional to Z. Thus, the contribution to E_c is $\sim Z^2/Z \sim Z$ instead of converging for other first row atom isoelectronic series for which the two particle excitation energy to the lowest lying states $\sim Z^2$. Although this behavior, as well as the saturation of the correlation energy under uniform scaling in the large λ limit, are both in principle properties of the exact DFT E_c, it is difficult to imagine how both properties can be obtained from any GGA which saturates such as our GGAGAPSIC or the PBE functional without explicitly including the contributions from nearly degenerate states. Although this divergence is not immediately relevant to questions concerning the binding of atoms or molecules, we believe the omission of contributions to E_c from low lying nearly degenerate electron states is the primary reason for the significant disparity between the calculated and exact E_c for atoms and ions with $N = 4,5$ or 6 electrons.

We therefore plan to investigate whether accurate values of E_c may be calculated by employing the GGAGAPSIC to approximate the contribution to E_c from states in the continuum and to employ second order perturbation theory (or a more sophisticated wavefunction approach) to include the contributions to E_c from the low lying KS states above the ground state which have been previously omitted for all atoms and ions. Preliminary calculations indicate that this latter contribution is generally small compared to the contributions to E_c from the continuum and is the correct order of magnitude to eliminate most of the discrepancy of the GGAGAPSIC results from the exact values. We anticipate that the inclusion of such terms will be of particular importance in improving the accuracy of calculations of E_c for molecules due to the frequent existence of low-lying unoccupied orbitals in such systems.

In concluding, we note that the inclusion of matrix elements involving unoccupied KS orbitals does not violate the Hohenberg-Kohn (HK) theorem that the correlation energy is a functional of the ground state electron density. This follows from the fact that the external potential and consequently all the orbitals, whether occupied or unoccupied, are in principle functionals of n. Thus any expression involving the single particle KS orbitals is an implicit functional of the density as in the case of exact KS exchange[22].

Finally, we observe that the suggestion that the correlation energy may be accurately calculated by making a density functional approximation for the large contribution from states that are relatively far from the highest occupied states and to include the contribution from nearby states by calculating matrix elements is similar to the work of Krieger *et al.*[25] on accurately calculating the ionization potential and electron affinity, A, in an exchange-only theory. They found that if the exchange energy for the interaction of the core electrons with each other, which is the greatest contribution to E_x, was approximated by a density functional and the interaction between the electrons in the two occupied subshells having the highest orbital energy with each other and with the core electrons was calculated by employing the exact exchange integrals, then I and A could be calculated with errors of only 0.1 mhartree compared with an exact KS exchange-only calculation. Moreover, they found that the KS exchange potential could be accurately calculated in the region occupied by the valence electrons with the correct asymptotic behavior as $r \to \infty$ leading to accurate highest occupied orbital energy eigenvalues as well.

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