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A critical assessment of the Self-Interaction Corrected Local Density Functional method and its algorithmic implementation

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ABSTRACT

We calculate the electronic structure of several atoms and small molecules by direct minimization of the Self-Interaction Corrected Local Density Approximation (SIC-LDA) functional. To do this, we first derive an expression for the gradient of this functional under the constraint that the orbitals be orthogonal and then show that previously given expressions do not correctly incorporate this constraint. In our atomic calculations, the SIC-LDA yields total energies, ionization energies and charge densities that are superior to results obtained with the Local Density Approximation (LDA). However, for molecules, SIC-LDA gives bond lengths and reaction energies that are inferior to those obtained from LDA. The nonlocal BLYP functional, which we include as a representative GGA functional, outperforms both LDA and SIC-LDA for all ground state properties we considered.

Introduction

The Local Density Approximation (LDA) [1] has become one of the most popular tools for electronic structure calculations. The reason for this is that it gives good accuracy for structural properties and is computationally less costly than traditional quantum chemistry methods such as Hartree-Fock, Configuration Interaction and Coupled Cluster methods. With the rapid increase in computer power and the development of low complexity algorithms, the limits on the system size are being pushed up steadily. However, in many cases LDA is not sufficiently accurate. A primary concern is therefore to improve upon the accuracy of the LDA approximation at the expense of a moderate increase in computational cost. The Generalized Gradient Approximations such as the Becke-Lee-Yang-Parr (BLYP) scheme [2, 3] fall into this category and are now widely used. Numerous other schemes to improve upon the LDA can been found in the literature [4], but very few of them have been systematically tested in atomic and molecular calculations. A major deficiency of the LDA and also to a lesser extent of the GGA is the fact that there is an unphysical self-interaction in these functionals. To cure this, several years ago, Perdew and Zunger proposed a scheme [5] where self-interaction terms are subtracted out in a straightforward way (SIC-LDA). Even though this scheme is appealing because of its conceptual simplicity, it has not been widely used possibly because it is numerically more complicated since the potential is orbital dependent. Consequently the minimization of this functional is no longer an eigenvalue problem in a self-consistent potential and the total energy is not invariant under unitary transformations among the occupied orbitals. In this paper, we first derive the gradient of the SIC-LDA functional, which is necessary for minimization algorithms [6, 7], and then present the results we obtained for atomic and molecular systems.

The SIC-LDA functional has been used mostly to study excitation energies. Studies of periodic systems using SIC-LDA have concentrated mainly on systems where the LDA approximation gives qualitatively wrong results (such as transition metal oxides [8]) and where the electronic structure undergoes qualitative changes in response to changing external conditions [9, 10]. Most of these calculations involving heavy atoms were done with the LMTO method. SIC-LDA yields larger band gaps than LDA, in substantially better agreement with experiment. [11]. In the case of atoms and molecules also, SIC-LDA yields improved excitation energies [5, 12, 13, 14]. However, most calculation of molecules were performed at the experimental geometry, there being very few SIC-LDA studies of equilibrium geometries [14, 15]. Hence, in this paper, we concentrate on the ground state properties and find that whereas atomic properties are more accurately predicted by SIC-LDA than LDA, equilibrium geometries of small molecules and reaction energies are less accurate in SIC-LDA.

The SIC-LDA functional and its gradient

In all the following formulae we consider the orbitals Ψ_i to be real and the subscripts of the orbitals run over all the occupied orbitals. The SIC-LDA functional is given by

$$E_{\rm tot}[\Psi_i(\mathbf{r})] = \sum_i \int \Psi_i(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 + V_{\rm ext}\right) \Psi_i(\mathbf{r}) d\mathbf{r} \tag{1}$$

$$\begin{aligned} &+ \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' + \int \epsilon(\rho(\mathbf{r}))\rho(\mathbf{r})d\mathbf{r} \\ &- \frac{1}{2}\sum_i \int\int \frac{\rho_i(\mathbf{r})\rho_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' - \sum_i \int \epsilon(\rho_i(\mathbf{r}))\rho_i(\mathbf{r})d\mathbf{r}, \end{aligned}$$

where

$$\rho_i(\mathbf{r}) = \Psi_i(\mathbf{r})\Psi_i(\mathbf{r}), \quad \rho(\mathbf{r}) = \sum_i \rho_i(\mathbf{r}),$$

and $\int \epsilon(\rho)\rho d\mathbf{r}$ is the local approximation of the exchange correlation functional.

We want to obtain its gradient under the constraint that the orbitals be orthonormal. Following the ideas outlined by Arias et al. [16] , we consider a more general functional that is also defined with respect to nonorthogonal functions Ψ_i. First we construct a set of orthonormal orbitals $\tilde{\Psi}_i$ by a symmetric Löwdin orthogonalization of the non-orthogonal set Ψ_i

$$\tilde{\Psi}_i = \sum_j S_{i,j}^{-1/2}\Psi_j \tag{2}$$

where $S_{i,j} =< \Psi_i|\Psi_j >= \int \Psi_i(\mathbf{r})\Psi_j(\mathbf{r})d\mathbf{r}$ is the overlap matrix among the occupied orbitals. The functional we are interested in is just the SIC-LDA functional evaluated for the orthonormal orbitals $\tilde{\Psi}_i$. In our actual calculation, for reasons of numerical stability, we use orthogonal orbitals. Hence, in our derivations it is necessary to consider only infinitesimally nonorthogonal orbitals . Then $S^{-1/2} = (I + (S - I))^{-1/2} \approx I - (1/2)(S - I)$ and Eq. (2) simplifies to

$$\tilde{\Psi}_i = \sum_j (\frac{3}{2}\delta_{i,j} - \frac{1}{2}S_{i,j})\Psi_j \tag{3}$$

The gradient of the total functional is then obtained by applying the chain rule:

$$\frac{\partial E}{\partial \Psi_i(\mathbf{r})} = \sum_j \int \frac{\partial E}{\partial \tilde{\Psi}_j(\mathbf{r}')}\frac{\partial \tilde{\Psi}_j(\mathbf{r}')}{\partial \Psi_i(\mathbf{r})}d\mathbf{r}' \tag{4}$$

where each part of Eq. (4) can easily be calculated. Denoting the unconstrained gradient by $d_j(\mathbf{r})$ we obtain:

$$\begin{aligned} d_j(\mathbf{r}) = \frac{1}{2}\frac{\partial E}{\partial \tilde{\Psi}_j(\mathbf{r})} &= \left(-\frac{1}{2}\nabla^2 + V_{\text{ext}}\right)\tilde{\Psi}_j(\mathbf{r}) \qquad (5) \\ &+ \left(\int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' - \int \frac{\rho_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'\right)\tilde{\Psi}_j(\mathbf{r}) \\ &+ \left(\mu(\rho(\mathbf{r})) - \mu(\rho_j(\mathbf{r}))\right)\tilde{\Psi}_j(\mathbf{r}) \\ &= H_j\tilde{\Psi}_j(\mathbf{r}) \ , \end{aligned}$$

where the orbital dependent Hamiltonian H_j is

$$\begin{aligned} H_j &= (-\frac{1}{2}\nabla^2 + V_{\text{ext}}) \\ &+ \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' - \int \frac{\rho_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' \\ &+ \mu(\rho(\mathbf{r})) - \mu(\rho_j(\mathbf{r})). \end{aligned}$$

The second part of Eq. (4) gives

$$\begin{aligned}\frac{\partial\tilde{\Psi}_j(\mathbf{r}')}{\partial\Psi_i(\mathbf{r})} &= \frac{3}{2}\delta_{i,j}\delta(\mathbf{r}-\mathbf{r}') - \frac{1}{2}S_{i,j}\delta(\mathbf{r}-\mathbf{r}') - \frac{1}{2}\sum_l \Psi_l(\mathbf{r}')\frac{\partial}{\partial\Psi_i(\mathbf{r})}\int \Psi_j(\mathbf{r}'')\Psi_l(\mathbf{r}'')d\mathbf{r}'' \\ &= \frac{3}{2}\delta_{i,j}\delta(\mathbf{r}-\mathbf{r}') - \frac{1}{2}S_{i,j}\delta(\mathbf{r}-\mathbf{r}') - \frac{1}{2}\sum_l \Psi_l(\mathbf{r}')\left(\delta_{i,j}\Psi_l(\mathbf{r}) + \delta_{i,l}\Psi_j(\mathbf{r})\right) \\ &= \delta_{i,j}\delta(\mathbf{r}-\mathbf{r}') - \frac{1}{2}\Psi_i(\mathbf{r}')\Psi_j(\mathbf{r}) - \frac{1}{2}\delta_{i,j}\sum_l \Psi_l(\mathbf{r}')\Psi_l(\mathbf{r})\ . \qquad (6)\end{aligned}$$

In the last transformation step, we have used the fact that we calculate the derivative for a set of orthonormal orbitals and therefore $S = I$. In order to take account of the orthogonality constraint we are of course allowed to put $S = I$ only after calculating the derivative. Finally, we obtain the gradient expression

$$\begin{aligned}\frac{1}{2}\frac{\partial E}{\partial\Psi_i(\mathbf{r})} = d_i(\mathbf{r}) \quad &- \quad \frac{1}{2}\sum_j\left(\int d_j(\mathbf{r}')\Psi_i(\mathbf{r}')d\mathbf{r}'\right)\Psi_j(\mathbf{r}) \\ &- \quad \frac{1}{2}\sum_j\left(\int d_i(\mathbf{r}')\Psi_j(\mathbf{r}')d\mathbf{r}'\right)\Psi_j(\mathbf{r}). \qquad (7)\end{aligned}$$

The above gradient expression is different from what is found in the literature [12, 17, 9]:

$$\frac{1}{2}\frac{\partial E}{\partial\Psi_i(\mathbf{r})} = d_i(\mathbf{r}) - \sum_j\left(\int d_i(\mathbf{r}')\Psi_j(\mathbf{r}')d\mathbf{r}'\right)\Psi_j(\mathbf{r}). \qquad (8)$$

In numerical applications, it was apparent that the gradient expression in Eq. 8 does not lead to the correct minimum [17] of the functional. However, nobody seems to have drawn the logical conclusion that Eq. 8 is not the correct gradient of the LDA-SIC functional. Instead, a second minimization step, based on a relation derived by Pederson et al [15]

$$< \Psi_i|H_j\Psi_j > = < H_i\Psi_i|\Psi_j >, \qquad (9)$$

was added. This relation follows immediately by considering infinitesimal unitary transformations among the occupied orbitals and putting the gradient of the SIC-LDA functional with respect to these transformations equal to zero. We see that Eqs. 8 and 9 together are equivalent to Eq. 7. These difficulties appear only in the SIC-LDA case; in the LDA case, the potential is not orbital dependent, and therefore, the two gradient expressions are identical.

The results of the following two sections were obtained by direct minimization of the SIC-LDA functional, using the correct gradient of Eq. 7. The Direct Inversion in Iterative Subspace (DIIS) method [19] was used as a convergence accelerator. In the molecular case, the gradient was preconditioned using the scheme by Teter et al. [7]; in the atomic case, the operator $Im(\frac{1}{H-z})$ was used as a preconditioner [20], where z is a suitably chosen complex energy. All the calculations were done for spin unpolarized systems where the spin up orbitals are required to have the same spatial form as the matching spin down electron orbitals, $\Psi_{2i-1}(\mathbf{r}) = \Psi_{2i}(\mathbf{r})$.

To calculate the equilibrium geometries of small molecules, we relaxed the atoms in the direction of the forces until the forces vanished. The forces in the SIC-LDA scheme are given by the Hellman-Feynman theorem. This might not be quite obvious, since, in the usual derivation of the Hellman-Feynman theorem, one takes advantage of the fact that the orbitals are eigenfunctions of the self-consistent Hamiltonian, which is not the case in the SIC-LDA scheme. We therefore provide a derivation of the Hellman-Feynman theorem which does not require the orbitals to be eigenfunctions, but uses only the fact that the orbitals minimize the total energy for some fixed positions of the nuclei.

Let $\Psi_i(\mathbf{r},\vec{\mathbf{R}}')$ be the SIC-LDA orbitals for a molecule, whose nuclear positions are given by the $3N$-dimensional vector $\vec{\mathbf{R}}'$. By construction, these orbitals are orthonormal for any $\vec{\mathbf{R}}'$. Let us now consider the SIC-LDA total energy $E_{\text{tot}}[\Psi_i(\mathbf{r},\vec{\mathbf{R}}');\vec{\mathbf{R}}]$ for a set of atomic positions $\vec{\mathbf{R}}$. The dependence on $\vec{\mathbf{R}}$ stems from the fact that the external potential V_{ext} depends on the atomic positions $\vec{\mathbf{R}}$. Obviously, the functional will be minimized if $\Psi_i(\mathbf{r},\vec{\mathbf{R}}') = \Psi_i(\mathbf{r},\vec{\mathbf{R}})$ and its gradient with respect to $\vec{\mathbf{R}}'$ vanishes at that point:

$$\left.\frac{\partial E_{\text{tot}}[\Psi_i(\mathbf{r},\vec{\mathbf{R}}');\vec{\mathbf{R}}]}{\partial\vec{\mathbf{R}}'}\right|_{\vec{\mathbf{R}}'=\vec{\mathbf{R}}} = 0. \tag{10}$$

The force acting on the nuclei is given by

$$\frac{\partial E_{\text{tot}}[\Psi_i(\mathbf{r},\vec{\mathbf{R}});\vec{\mathbf{R}}]}{\partial\vec{\mathbf{R}}} = \left.\frac{\partial E_{\text{tot}}[\Psi_i(\mathbf{r},\vec{\mathbf{R}});\vec{\mathbf{R}}'']}{\partial\vec{\mathbf{R}}''}\right|_{\vec{\mathbf{R}}''=\vec{\mathbf{R}}} + \left.\frac{\partial E_{\text{tot}}[\Psi_i(\mathbf{r},\vec{\mathbf{R}}');\vec{\mathbf{R}}]}{\partial\vec{\mathbf{R}}'}\right|_{\vec{\mathbf{R}}'=\vec{\mathbf{R}}}. \tag{11}$$

The first term on the right side of Eq. (11) takes into account that the external potential V_{ext} depends on the atomic positions $\vec{\mathbf{R}}$ but freezes the dependence of the orbitals on $\vec{\mathbf{R}}$. It is given by

$$\sum_i \int \Psi_i(\mathbf{r},\vec{\mathbf{R}})\frac{\partial V_{\text{ext}}}{\partial\vec{\mathbf{R}}}\Psi_i(\mathbf{r},\vec{\mathbf{R}})d\mathbf{r}. \tag{12}$$

The second term freezes the dependence on the external potential but takes into account the dependence of the orbitals . This second term is however equal to the left hand side of Eq. (10) and therefore vanishes. So we are just left with the first term which can be immediately transformed to the usual Hellman-Feynman form.

Atomic results

In the original paper on the SIC-LDA method, Perdew and Zunger [5] performed several atomic calculations. They, however, did not minimize the SIC-LDA functional under the orthogonality constraint, but instead employed the eigenorbitals of the orbital dependent potential. Since the orbitals are the eigenfunctions for different Hamiltonians, they are not orthogonal but the authors assumes that this did not change their results appreciably. We therefore repeated some of the atomic calculations to check this assumption and in fact find it to be true.

The orbitals that one obtains from a minimization solution differ in two important respects from the atomic orbitals obtained by solving a single-particle Schrodinger equation. First their nodal structure is different as shown in Fig. . All orbitals (even the 1s core states) have the same number of nodes. Second all the orbitals decay with the same exponent (see Fig.). A set of orbitals, which have the characteristic behavior of eigenfunctions of a local potential can be obtained, from the minimizing orbitals Ψ_i, by forming the linear combinations

$$\Phi_i = \sum_j U_{ji} \Psi_j \tag{13}$$

where U is the unitary matrix that diagonalizes the matrix $< \Psi_i | H_j \Psi_j >$, which is hermitian by Eq. (9). The Krieger-Li-Iafrate approximation [21] to the SIC-LDA functional would, for instance, give orbitals of similar form, but also the non-orthogonal set of orbitals used by Perdew and Zunger [5] look rather similar. As can be seen from Figs. and these eigenorbitals are rather different from the minimizing orbitals Ψ_i.

In Table 1, we compare our total energies for several closed shell atoms with the ones from Perdew and Zunger. In spite of the fact that the minimizing orbitals Ψ_i have a quite different behavior from the orbitals employed by Perdew and Zunger, the total energies are nevertheless very similar. In fact the small differences in the total energy in the columns labelled SIC-LDA and PZ are not due to their approximate solution method but are instead probably due to the use of an insufficiently dense grid in Ref. [5] since we find the same differences in comparing the LDA results too.

In Table 1, we also give the results obtained from the Perdew-Zunger (PZ-LDA) [5] and the Perdew-Wang '92 (PW92-LDA) [22] parametrizations of LDA, the Becke-Lee-Yang-Parr GGA (BLYP) [2] and Hartree Fock (HF). Of the two LDA functionals, PZ-LDA and PW92-LDA, the latter is the more accurate parametrization of the correlation energy of a homogeneous electron gas and yields slightly more accurate total energies. We include the former only to facilitate comparison with Ref. [5]. As observed in earlier papers, LDA yields total energies that are not sufficiently negative while SIC-LDA gives too deep total energies. The absolute value of the error is significantly smaller in SIC-LDA than in LDA, but not as small as for BLYP.

In Table 2, we compare the highest occupied eigenvalues of closed shell atoms. Here the SIC-LDA functional outperforms all the others. This comes from the fact that in SIC-LDA the orbitals experience the correct long range Coulomb potential whereas the potentials in the other density functional methods decay too fast giving rise to too weakly bound eigenstates.

In Figs. 3, 4 and 5, we show the error in the self consistent charge densities from the different methods. The SIC-LDA density is somewhat more accurate than the LDA density except in a region around 0.3 a_0 for Neon.

Molecular results

A very attractive feature of the SIC-LDA scheme is that the minimizing orbitals can usually be easily interpreted in physical terms. They either represent bonds or lone electron pairs. For instance, in the case of the CH_4 molecule, one obtains 4 localized orbitals (each containing a spin-up and spin-down electron), which are centered on the 4 lines linking the 4 hydrogens to the central carbon, and therefore representing bonds. The H_2O molecule also has 4 localized orbitals in nearly uniform tetrahedral positions. However, in this case, only the two orbitals on the two lines linking the oxygen with the two hydrogens represent bonds; the

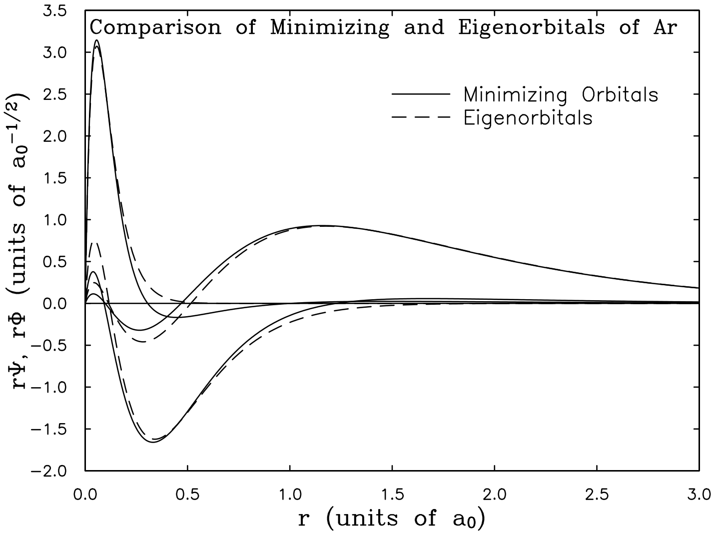

Figure 1: 1s, 2s, and 3s orbitals of Argon. Solid line: the orbitals $r\Psi$ that minimize the SIC-LDA functional; dashed line: the linear combinations $r\Phi$ of Eq.13.

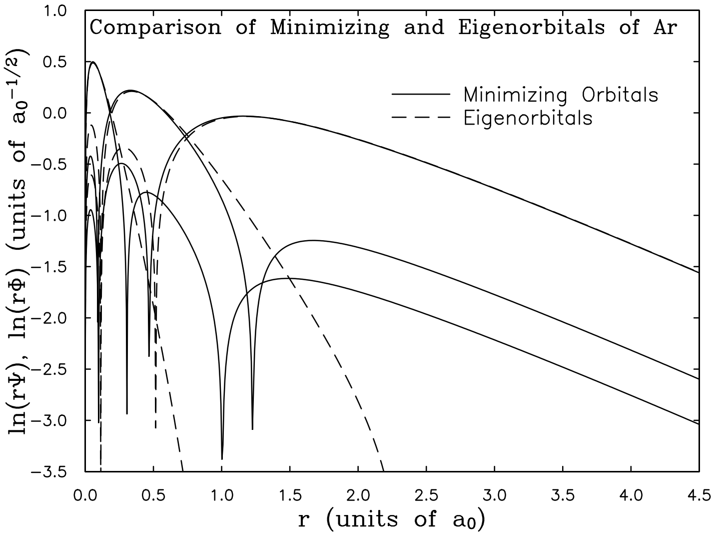

Figure 2: Same as Fig.1 but on a logarithmic scale. The 3s orbitals $r\Psi$ and $r\Phi$ are nearly indistinguishable on this plot beyond $r = 1$.

Table 1: Total energies of closed shell atoms in eV. Our results using direct minimization and the PZ parametrization (SIC-LDA) are compared with the results obtained by Perdew and Zunger (PZ) for the same functional using an approximate solution method. The next two columns show the LDA results with the Perdew-Zunger (PZ-LDA) and the Perdew-Wang '92 (PW92-LDA) parametrizations. The final three columns are the Becke-Lee-Yang-Parr GGA (BLYP), Hartree Fock (HF) and the exact value. The exact values are from Ref. [18]. We have used a factor of 27.2112 eV/Hartree for converting most of the energies but, for consistency with Ref. [5], a factor of 27.21 eV/Hartree for converting the SIC-LDA energies.

	SIC-LDA	PZ	PZ-LDA	PW92-LDA	BLYP	HF	exact
He	-79.4	-79.4	-77.1	-77.1	-79.1	-77.9	-79.0
Be	-399.9	-399.8	-393.1	-393.1	-398.9	-396.6	-399.1
Ne	-3517.9	-3517.6	-3489.1	-3489.3	-3509.2	-3497.9	-3508.6
Ar	-14378.8	-14378.3	-14307.9	-14311.6	-14352.4	-14335.4	-14354.6

Table 2: Highest occupied eigenvalues of closed shell atoms in eV. Our results using direct minimization and the PZ parametrization (SIC-LDA) are compared with the results obtained by Perdew and Zunger (PZ) for the same functional using an approximate solution method. The next two columns show the LDA results with the Perdew-Zunger (PZ-LDA) and the Perdew-Wang '92 (PW92-LDA) parametrizations. The final three columns are the Becke-Lee-Yang-Parr GGA (BLYP), Hartree Fock (HF) and experiment. The experimental values are from Ref. [23].

	SIC-LDA	PZ	PZ-LDA	PW92-LDA	BLYP	HF	exper
He	-25.8	-25.8	-15.5	-15.5	-15.8	-25.0	-24.6
Be	-9.1		-5.6	-5.6	-5.4	-8.4	-9.3
Ne	-22.8	-22.9	-13.5	-13.5	-13.2	-23.1	-21.6
Ar	-15.9	-15.8	-10.4	-10.4	-10.0	-16.1	-15.8

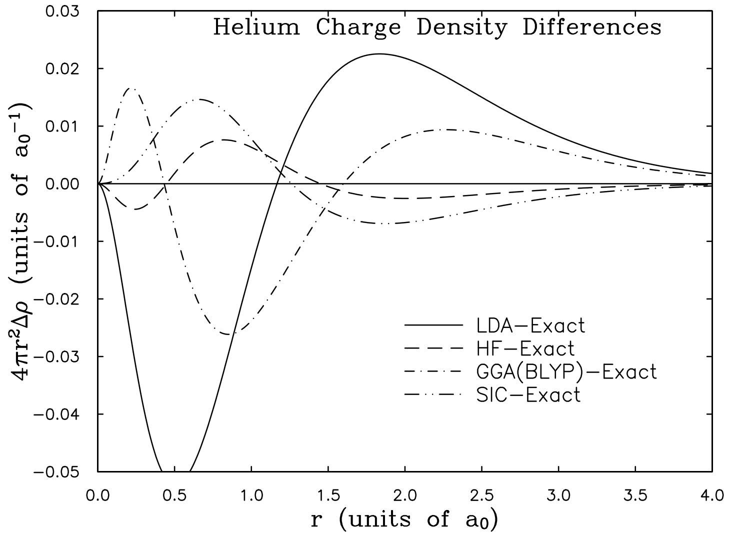

Figure 3: Comparison of the charge density of He obtained by different methods with the quasi exact charge density from a Hylleras-type calculation.

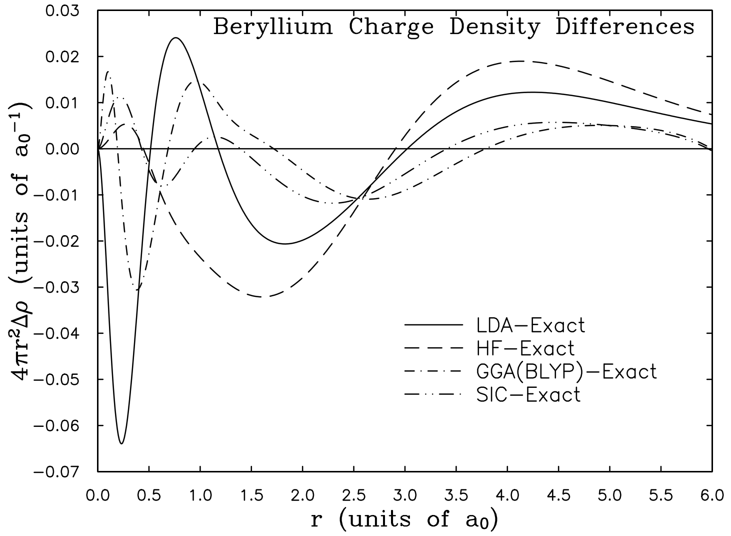

Figure 4: Comparison of the charge density of Be obtained by different methods with the quasi exact charge density from a Quantum Monte Carlo calculation.

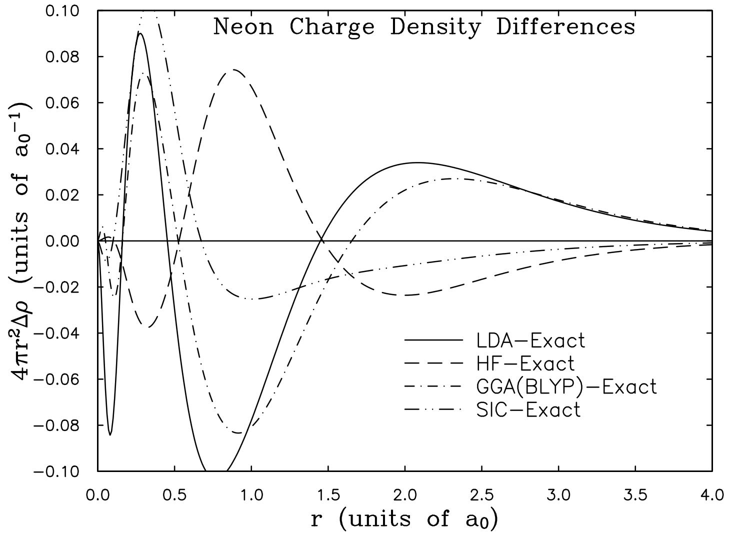

Figure 5: Comparison of the charge density of Ne obtained by different methods with the quasi exact charge density from a Quantum Monte Carlo calculation.

other two, which are in the half-space not containing any hydrogen, are lone electron pairs. In the case of double or triple bonds, the minimizing functions are banana-shaped localized functions surrounding the line linking the two atoms. Even for an infinite Si crystal, we find that the minimizing orbitals are localized bond-centered functions. In some cases such as the CO molecule we find two very close minima, the lower one corresponding to a triple bond, the upper one to a single bond. However, the two solutions have very similar charge densities.

Using pseudo-potentials and a plane-wave basis set, we calculated the bond lengths of several small molecules and the energy released in a chemical reaction. The SIC-LDA pseudo-potentials were generated using the procedure described in reference [24], but with the eigenvalues and charge distributions of the reference configuration taken from an atomic SIC-LDA calculation rather than an LDA calculation. As expected, from the concept of pseudo-potentials representing physical ions [25], the SIC-LDA pseudo-potentials are very similar to the LDA pseudo-potentials, and substituting a LDA pseudo-potential in a SIC-LDA calculation has only a very minor effect. Nevertheless, for consistency, in both the LDA and the SIC-LDA molecular calculations we used the corresponding pseudo-potential. The LDA pseudo-potentials of reference [24] reproduce the true (all-electron) LDA bond lengths of first row molecules to within a few milli-Bohr. We expect the same accuracy for the SIC-LDA pseudo-potentials.

In Table 3 we show the errors in the LDA, SIC-LDA and BLYP geometries of several small molecules. Unfortunately the SIC-LDA bondlengths are systematically too short [26] and the magnitude of the errors are significantly larger than the LDA errors. The SIC-LDA errors for single bonds, with the exception of BH, are not as large as for double or triple bonds. The BLYP bond lengths, on the other hand, are somewhat more accurate than the LDA bond lengths.

Table 3: Comparison of the LDA and SIC-LDA bond lengths (a.u.) for several small molecules. The experimental bond lengths (exper.) [27] and the differences between the theoretical and experimental bond lengths are given.

	exper.	SIC-LDA error	LDA error	BLYP error
H_2	1.401	-.03	.05	.01
CH_4	2.052	-.05	.02	.02
C_2H_2 (CH)	2.005	-.05	.03	-.01
C_2H_2 (CC)	2.274	-.09	-.01	.00
NH_3	1.912	-.05	.02	.02
H_2O	1.809	-.05	.02	.03
BH	2.329	-.09	.04	.01
LiH	3.015	-.06	.01	.00
N_2	2.074	-.09	-.01	.01
CO	2.132	-.10	-.00	.02
CO_2	2.192	-.09	.00	.02
RMS deviation		.072	.024	.016

Another interesting quantity to compare is the atomization energy, which is the difference between the molecular total energy and the sum of the total energies of its constituent atoms. The energies of open-shell atoms are often calculated with a spherically symmetrized approximation to the density obtained by introducing fractional occupation numbers. In the case of GGA the non-spherical atom gives better atomization energies [28]. However one encounters, in LDA calculations of non-spherical atoms, the problem that orbitals that are occupied on one iteration of the self-consistency cycle become unoccupied on the next. To check the accuracy of the SIC-LDA total energy differences, and at the same time avoid this problem, we study the energy released in the chemical reaction 3 $H_2 + N_2 \rightarrow 2\ NH_3$. All the total energies are calculated after a full relaxation of the atomic positions within each scheme. In the case of SIC-LDA, we calculate also the energy difference using the more accurate LDA geometries of the molecules. As can be seen from Table 4, SIC-LDA does worse than the other schemes examined. By far the best results are obtained with the BLYP [3]. The SIC-LDA energies are calculated by the pseudo-potential plane wave method while the BLYP energies are obtained from the the Gaussian 94 (G94) program package [29] using a 6-311G++(3df,3pd) basis set. As a check of the accuracy of the pseudo-potential plane wave and the Gaussian 94 programs we calculated the LDA energies with both programs obtaining very close agreement.

Table 4: The experimental value and theoretical predictions for the energy (eV) released in the model chemical reaction 3 $H_2 + N_2 \rightarrow 2\ NH_3$.
The values are corrected for the zero point energy given in reference [30].

exp.	LDA (PSP)	LDA (G94)	SIC-LDA	SIC-LDA(LDA geom.)	BLYP
.76	2.1	2.1	2.6	2.9	.65

Conclusions

The SIC-LDA scheme, as proposed by Perdew and Zunger, does not give sufficiently accurate ground state energies and molecular geometries. Whereas the atomic results are superior to the LDA results, the molecular results are clearly worse. The BLYP functional, which we chose as representative of the various commonly used GGA functionals, yields more accurate ground state properties that both SIC-LDA and LDA for the atoms and molecules considered. It is surprising how well the simple LDA works compared to more sophisticated schemes that one would expect to be superior. Charlesworth recently came to similar conclusions after systematically examining several weighted density functionals [31]. All these schemes satisfy sum rules [32] that are generally believed to be responsible for the accuracy of the LDA. Thus it might well be that we actually do not yet fully understand the true reasons for the success of the LDA.

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