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

S. Goedecker,

Max-Planck Institute for Solid State Research, Stuttgart, Germany

C. J. Umrigar,

Cornell Theory Center and Laboratory of Atomic and Solid State Physics,
Cornell University, Ithaca, NY 14853, USA

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 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 scheme can been found in the literature [11], 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 [4] where self-interaction terms are subtracted out in a straightforward way (SIC-LDA). Even though this scheme is appealing because of its conceptional simplicity, it has not been widely used possibly because it leads to a numerically more complicated scheme since the potential becomes orbital dependent. The minimization of this functional therefore cannot anymore be considered as an eigenvalue problem in a self-consistent potential and the total energy is not any more 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 [5, 20], and then present results that we obtained for atomic and molecular systems.

Studies of periodic systems using SIC-LDA have mainly concentrated on systems where the LDA approximation gives qualitatively wrong results (such as transition metal oxides [6]) and where the electronic structure undergoes qualitative changes in response to changing external conditions [7, 8]. Most of these calculations involving heavy atoms were done with the LMTO method. The gap in insulators is also improved compared with the LDA case [9]. In the case of atoms and molecules most papers [10, 12, 13] investigated the properties of excited states of atoms and molecules at the experimental geometry and found that the SIC-LDA improves upon LDA. Instead, we concentrate on the ground state properties such as the equilibrium geometries of small molecules and find that SIC-LDA is less accurate than 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

$$
\begin{aligned}
E_{\text{tot}}[\Psi_i(\mathbf{r})] &= \sum_i \int \Psi_i(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 + V_{\text{ext}}\right) \Psi_i(\mathbf{r}) d\mathbf{r} \\
&+ \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' - \frac{1}{2}\sum_i \int \int \frac{\rho_i(\mathbf{r})\rho_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\
&+ \int \epsilon(\rho(\mathbf{r}))\rho(\mathbf{r}) d\mathbf{r} - \sum_i \int \epsilon(\rho_i(\mathbf{r}))\rho_i(\mathbf{r}) d\mathbf{r}
\end{aligned}
\tag{1}
$$

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:

$$
d_j(\mathbf{r}) = \frac{1}{2}\frac{\partial E}{\partial \tilde{\Psi}_j(\mathbf{r})} = \left(-\frac{1}{2}\nabla^2 + V_{\text{ext}}\right)\tilde{\Psi}_j(\mathbf{r})
\tag{5}
$$

$$+ \left(\int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' - \int \frac{\rho_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right) \tilde{\Psi}_j(\mathbf{r})$$

$$+ \ \left(\mu(\rho(\mathbf{r})) - \mu(\rho_j(\mathbf{r})) \right) \tilde{\Psi}_j(\mathbf{r})$$

$$= \ H_j \tilde{\Psi}_j(\mathbf{r}) \ ,$$

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

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

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

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

The above gradient expression is different from what is found in the literature [12, 15, 7].

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

In numerical applications, it was apparent that the gradient expression in Eq. 8 does not lead to the correct minimum [15] 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 people added a second minimization step which is based on a relation derived by Pederson et al [10]

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

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 7. The DIIS method [19] was used as a convergence accelerator. In the molecular case the gradient was preconditioned using the scheme by Teter et al. [20], in the atomic case the operator $Im(\frac{1}{H-z})$ was used as a preconditioner [21] , where z is a suitably chosen complex energy. All the calculations were done for a spin unpolarized system where the spin up orbital is required to have the same spatial form as the matching spin down electron orbital, $\Psi_{2i-1}(\mathbf{r}) = \Psi_{2i}(\mathbf{r})$

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 give in the following 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 us consider a set of orbitals $\Psi_i(\mathbf{r}, \vec{\mathbf{R}}')$ which are the solutions of the SIC-LDA equations for a molecule, whose atomic positions are given by $\vec{\mathbf{R}}'$. We consider $\vec{\mathbf{R}}'$ to be a super vector, i.e. for a system comprising N atoms it will have $3N$ components. By construction these orbitals are orthonormal for all values of $\vec{\mathbf{R}}'$. 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 $\vec{\mathbf{R}}'$ will vanish at that point.

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

Let us now calculate the force acting on the nuclei which 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 $\vec{\mathbf{R}}$.

5

It is given by

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

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 their original paper, Perdew and Zunger [4] do several atomic calculations. They however did not minimize the SIC-LDA functional under the orthogonality constraint, but instead employed the eigen orbitals of the orbital dependent potential. Since the orbitals are the eigenfunctions for different Hamiltonians, they are not orthogonal but they assume that this will 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 aspects from the atomic orbitals obtained in a non-orbital dependent potential. First their nodal structure is different as shown in Fig.1. All orbitals (even the 1s core states) have the same number of nodes. Second all the orbitals decay with the same exponent (see Fig. 2). A set of orbitals with a behaviour appropriate for a local potential can however be obtained by forming the new linear combinations

$$\Phi_i = \sum_j C_{ij} \Psi_j \qquad (13)$$

where C is the matrix containing the eigenvectors of the (hermitian) matrix $< \Psi_i | H_j \Psi_j >$.

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 behaviour from the approximate orbitals calculated by Perdew and Zunger (which show the behaviour of eigenorbitals in a local potential and look therefore similar to the orbitals Φ_i of Fig.1), 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. [4], 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) and the Perdew-Wang '92 (PW92-LDA) parametrizations, the Becke-Lee-Yang-Parr GGA (BLYP) 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
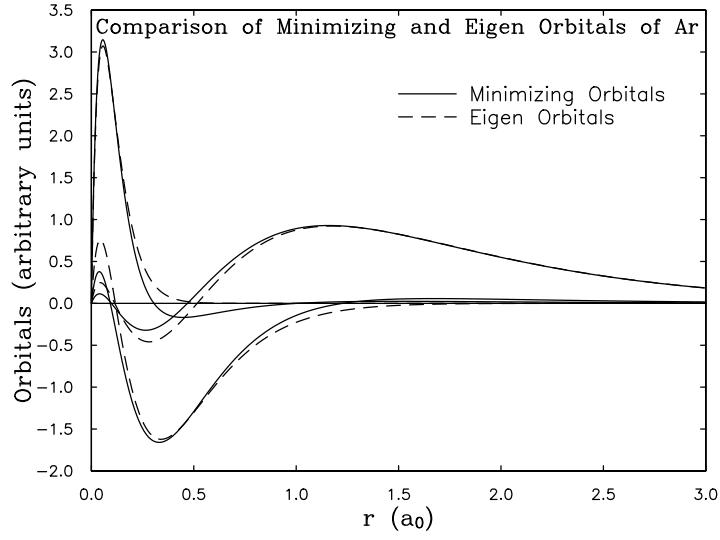
Figure 1: 1s, 2s, and 3s orbitals of Argon. Solid line: The orbitals Ψ that minimize the SIC-LDA functional, dashed line: the linear combinations Φ of Eq.13.
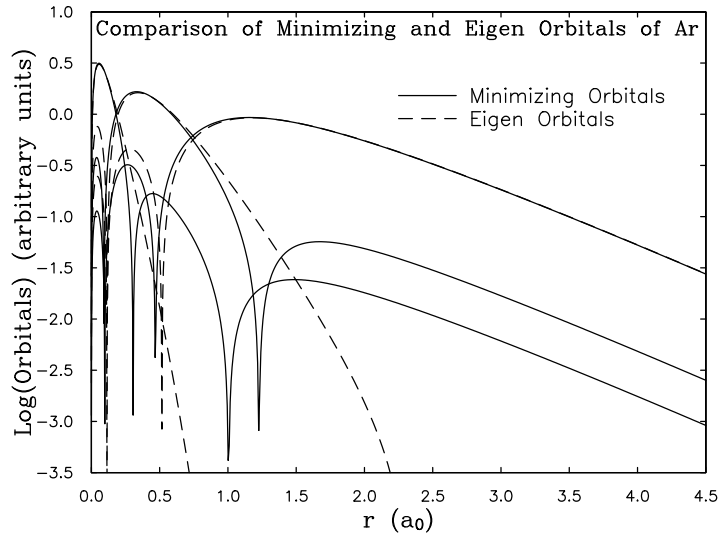

Figure 2: Same as Fig.1 but on a logarithmic scale. The 3s orbitals Ψ and Φ are nearly indistinguishable on this plot beyond $r = 1$.

to facilitate comparison with Ref. [4]. 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.

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.

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. [17]. We have used a factor of 27.2112 eV/Hartree for converting most of the energies but for consistency with Ref. [4] 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. [18].

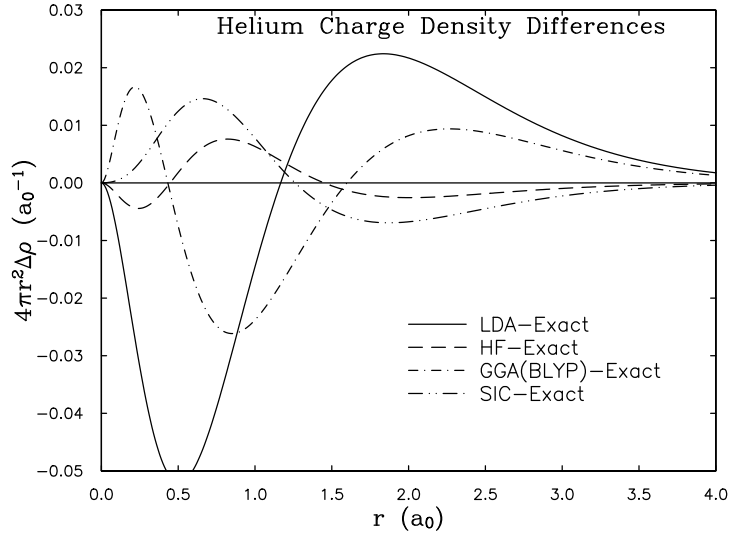|	SIC-LDA	PZ	PZ-LDA	PW92-LDA	BLYP	HF	exper
He	-25.8	-25.8	-15.5	-15.5	-15.8	-25.0	-24.6
Be	-9.1		-5.6	-5.6	-5.4	-8.4	-9.3
Ne	-22.8	-22.9	-13.5	-13.5	-13.2	-23.1	-21.6
Ar	-15.9	-15.8	-10.4	-10.4	-10.0	-16.1	-15.8

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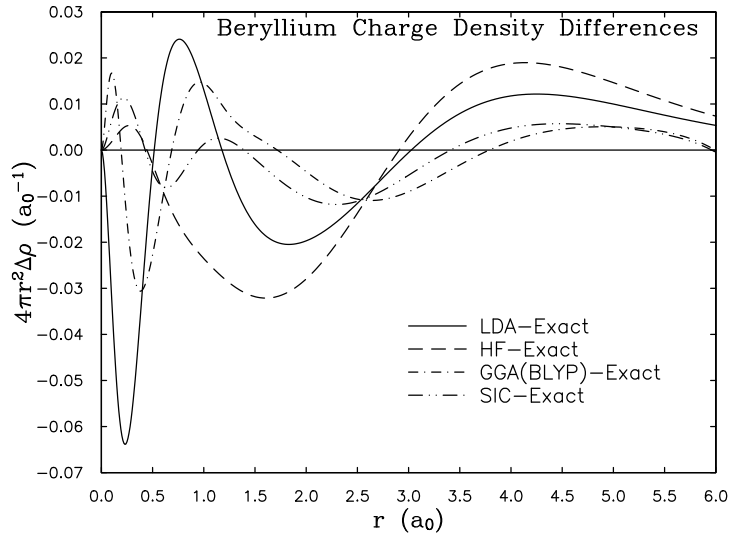

Figure 4:   Comparison of the charge density of Be obtained by different methods with the quasi exact charge density from a Quantum Monte Carlo calculation.
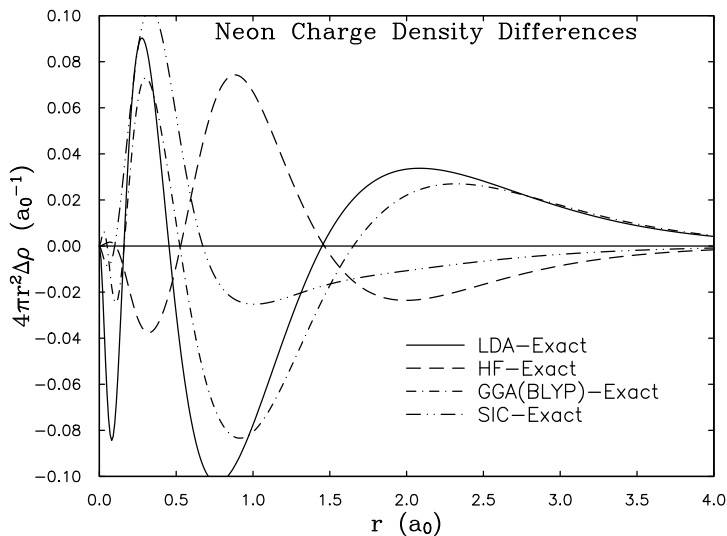
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Figure 5: Comparison of the charge density of Ne obtained by different methods with the quasi exact charge density from a Quantum Monte Carlo calculation.

Molecular results

Using pseudo-potentials and plane waves as basis set, we did a series of molecular calculations. We examined the bond lengths of several small molecules and the energy released in a chemical reaction. We generated SIC-LDA pseudo-potentials according to the procedure described in reference [22] where however the eigenvalues and charge distributions of the reference configuration were the ones from an atomic SIC-LDA calculation. As is to be expected from the concept of pseudo-potentials representing physical ions [14] these pseudo-potentials are very similar to the pure LDA pseudo-potentials and substituting a LDA pseudo-potential in a SIC-LDA calculation has only a very minor effect. For consistency, we used however always the SIC-LDA pseudo-potential. With this kind of pseudo-potential it is possible to get the correct LDA bond length to within a few thousands of a Bohr for first row molecules [22]. We expect the same accuracy for the SIC-LDA pseudo-potentials. A very attractive feature of the SIC-LDA scheme is that the minimizing orbitals can usually easily be interpreted in physical terms. They represent either bonds or lone electron pairs. In the case of the CH_4 molecule for instance, 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 with the central carbon and representing therefore bonds. In the case of the H_2O molecule one obtains again 4 localized orbitals in nearly tetragonal positions. In this case however only the two sitting on the two lines linking the O with the two H represent bonds, the other two which are in the half-space

not containing any H are lone electron pairs. In the case of double or triple bonds, the minimizing functions are banana shaped localized functions distributed around the line linking the two atoms. We found that in the case of a Si crystal also, the minimizing orbitals are bond-centered Wannier type functions. In some cases such as the CO molecule we found two very close minima, the lowest one corresponding to a triple bond, the other one to a single bond. The charge density was however very similar in both cases. Unfortunately, as can be seen from table 3, the bond lengths we obtain for small molecules are systematically too short, and the error was significantly larger than the error of the LDA bond length. The error for triple bonds are particularly large.

Table 3: Comparison of the LDA and SIC-LDA bond lengths (a.u.) for several small molecules. The experimental bond lengths (exper.) [23] and the differences between the theoretical and experimental bond lengths are given.

	exper.	SIC 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 in this context is the atomization energy, which is the difference between the molecular total energy and the sum of the total energies of its constituent atoms. To calculate the energy of an open-shell atom one has to decide whether one wants to spherically symmetrize the atom by introducing fractional occupation numbers. In the case of GGA is has been found [24] that the non-spherical atom gives better results. The theoretical foundation of this empirical observation is however not quite clear and it can not be predicted which scheme would give better results in the case of SIC-LDA. To check the accuracy of the SIC-LDA total energy differences and avoid at the same time the above mentioned symmetry problems we looked therefore at the energy released in the chemical reaction $3\,H_2 + N_2 \rightarrow 2\,NH_3$. All the total energies were calculated after a full relaxation of the atomic positions within each scheme. In the case of SIC-LDA, we also calculated the energy difference using the more accurate LDA geometries of the molecules. As can be seen from Table 4, the SIC-LDA scheme did worse than

the other schemes examined. By far the best results were obtained with the BLYP [3] scheme. To check the accuracy of the pseudo-potential plane wave method we calculated the LDA result both with this method and with the Gaussian 94 (G94) [25] program package, getting extremely close agreement. The BLYP calculation was done with the Gaussian 94 software. In all the Gaussian 94 calculations mentioned in this paper we used a 6-311G++(3df,3pd) basis set.

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 [26].

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 ground state energies and molecular geometries with sufficient precision. Whereas the atomic results are superior to the LDA results, the molecular results are clearly worse. A good GGA scheme such as the BLYP scheme outperforms both of them in all test cases considered. It is surprising how well the simple LDA scheme works compared to more sophisticated schemes that one would expect to give superior results. Charlesworth recently came to similar conclusions when he systematically examined several weighted density functional schemes [27]. All these schemes satisfy sum rules [28] that are generally believed to be responsible for the accuracy of the LDA scheme. Thus it might well be that we actually do not yet fully understand the true reasons for the success of the LDA scheme.

Acknowledgments

References

[1] R. G. Parr and W. Yang, "Density-Functional Theory of Atoms and Molecules", Oxford University Press, 1989.

[2] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 13244 (1992) ;
J.P. Perdew, K. Burke, and Y. Wang, unpublished ;
J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).

[3] A. D. Becke, Phys. Rev. A **38**, 3098 (1988);
C. Lee, W. Yang and R. G. Parr, Phys. Rev. B **37**, 785 (1988);
B. Miehlich, A. Savin, H. Stoll and H. Preuss, Chem. Phys. Lett. **157**, 200 (1988).

[4] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[5] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1989)

[6] A. Svane and O. Gunnarsson Phys. Rev. Lett. **65**, 1148 (1990)
Z. Szotek, W. Temmerman, and H. Winter, Phys. Rev. B **47**, 4029 (1993)
M. Arai, T. Fujiwara, Phys. Rev. B **47**, 1477 (1995)

[7] A. Svane, Phys. Rev. B **53**, 4275 (1996).

[8] Z. Szotek, W. Temmerman, and H. Winter, Phys. Rev. Lett. **72**, 1244 (1994)

[9] R. A. Heaton, J. G. Harrison and C. C. Lin Phys. Rev. B **28**, 5992 (1983).

[10] M. R. Pederson, R. A. Heaton and C. C. Lin, J. Chem. Phys **80**, 1972 (1984), M. R. Pederson, R. A. Heaton and C. C. Lin, J. Chem. Phys **82**, 2688 (1985).

[11] O. Gunnarson, M. Jonson and B.I. Lundqvist, Phys. Rev. B **20**, 3136 (1979); O. Gunnarson and R.O. Jones, Phys. Scr. **21**, 394 (1980); H. Stoll, C.M.E. Pavlidou and H. Preuss, Theor. Chim. Acta **49**, 143 (1978); S.H. Vosko and L. Wilk, J. Phys. B **16**, 3687 (1983); S. Baroni and E. Tuncel, J. Chem. Phys. **79**, 6140 (1983); S. Baroni, *ibid.*, **80**, 5703 (1984).

[12] J. G. Harrison, R. A. Heaton and C. C. Lin, J. Phys B **16**, 2079 (1983).

[13] Y. Guo and M. A. Whitehead, J. Molec. Struc. **228**, 285 (1991).

[14] P. Focher, A. Lastri, M. Covi and G. B. Bachelet, J. Phys B **44**, 8486 (1991).

[15] E. S. Fois, J. I. Penman and P. A. Madden, J. Chem. Phys **98**, 6352 (1993).

[16] T. A. Arias, M. C. Payne and J. D. Joannopoulos, Phys. Rev. Lett. **69**, 1077 (1992).

[17] E. R. Davidson, S. A. Hagstrom, S. J. Chakravorty, V. M. Umar and C. F. Fischer, Phys. Rev. A **44**, 7071 (1991); S. J. Chakravorty, S. R. Gwaltney, E. R. Davidson, F. A. Parpia and C. F. Fischer, Phys. Rev. A **47**, 3649 (1993).

[18] C. E. Moore, Natl. Bur. Stand. (US) Ref. Data Ser. **34**, 1 (1970).

[19] J. Hutter, H.P. Lüthi and M. Parrinello, Comp. Mat. Sci. **2** 244 (1994).

[20] M. P. Teter, M. C. Payne and D. C. Allan, Phys. Rev. B **40**, 255 (1989).

[21] S. Goedecker, J. of Comp. Phys. **118**, 261 (1995).

[22] S. Goedecker, M. Teter and J. Hutter to be published in Phys. Rev. B

[23] R. M. Dickson and A. D. Becke, J. Chem. Phys. **99**, 3898 (1993).

[24] F. W. Kutzler and G. S. Painter, Phys. Rev. Lett. **59**, 1285 (1987).

[25] Gaussian 94, Revision B.2, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1995.

[26] J. A. Pople, M. Head-Gordon, D. J. Fox, K. Rahavachari and L. A. Curtiss, J. Chem. Phys. **90**, 5622 (1989)

[27] J. Charlesworth, Phys. Rev. B **53**, 12667 (1996)

[28] R. O. Jones and O. Gunnarson, Rev. of Mod. Phys. **61**, 689 (1989)