

Relativistic self-interaction-free density-functional formalism

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We present a relativistic self-interaction-free density-functional formalism based on the local-density approximation with additional correction terms, and propose an algorithm for its numerical solution. The rigorous foundations of the scheme in density-functional theory and the resulting effective one-electron picture are discussed. Calculations for several atoms are shown as a practical example.

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I. INTRODUCTION

In the past 15 years, self-interaction corrections to approximative density-functional schemes have been successful in the prediction of the electronic properties of atoms [1–3], small molecules [4,5], transition metal compounds including high-temperature superconductors [6,7], and in the study of model systems [8,9].

The predominant method has been the self-interaction-corrected local-spin-density approximation (SIC-LSD) that goes back to the work of Perdew and Zunger [1] in 1981. Most of the published calculations have not taken relativistic effects into account. This is certainly of little importance for the first through third row elements, for which the bulk of the atomic calculations was done, but is of increasing significance in heavier elements. Cole and Perdew [10] have employed a scalar relativistic approximation, but they worked with nonorthogonal orbitals, which amounts to an incomplete minimization of the total energy functional.

The aim of the present paper is twofold. First, we develop a fully self-consistent relativistic self-interaction-corrected local-density-functional formalism. Second, we give a comprehensive description of the foundations of the scheme within density-functional theory, since this is a point which has been disputed [11], and we demonstrate that equations for one-electron-type wave functions can be formulated that completely parallel the Kohn-Sham equations of the local density approximation (LDA) and possess a *state-independent* effective potential with a small, short-range nonlocal component. The respective eigenvalues turn out to be good approximations to true excitation energies.

The paper is structured as follows: the theoretical foundations of the self-interaction correction scheme and the one-electron picture are introduced nonrelativistically in Sec. II, in Sec. III the relativistic formalism is laid out, and in Sec. IV the actual atomic calculations are described and results presented and discussed. The Appendix contains details of the numerical algorithm developed for the present calculations. Atomic units are used throughout the paper.

II. SELF-INTERACTION-CORRECTED LOCAL-DENSITY APPROXIMATION

A. The total energy functional

Density-functional theory (for a review see Ref. [12]) has been established by the pioneering work of Hohenberg and Kohn [13]. The basic tool is a functional of the density,

$$E^{DFT}[\rho] = F[\rho] + \int \rho(\mathbf{r})v_{ext}(\mathbf{r})d^3r, \quad (2.1)$$

which assumes at a density ρ_0 its minimum E_0 , that equals the total energy of a many-electron system of density ρ_0 under the influence of an external potential $v_{ext}(\mathbf{r})$. The Hohenberg-Kohn theorem [13] postulates that there exists a unique and invertible map between the ground state density and the external potential and that the functional $F[\rho]$ is universal in the sense that it is independent of v_{ext} . The formulation of Levy [14,15] and Lieb [16] for F is

$$F[\rho] = \min_{\{\Phi\} \rightarrow \rho} \langle \Phi | T + W | \Phi \rangle, \quad (2.2)$$

meaning that for a given density ρ , $F[\rho]$ corresponds to the minimum of the expectation value of the sum of kinetic energy operator T and electron-electron interaction operator W over all possible antisymmetric wave functions Φ yielding the density ρ .

Most practical applications are based on the theorem of Kohn and Sham [17]. It states that for a ground state density ρ_0 there is an auxiliary local potential $v^s([\rho]; \mathbf{r})$ such that ρ_0 minimizes the functional

$$F^{KS}[\rho] = T^s[\rho] + \int \rho(\mathbf{r})v^s([\rho]; \mathbf{r})d^3r, \quad (2.3)$$

which fulfils $F^{KS}[\rho_0] = F[\rho_0]$;

$$T^s[\rho] = \min_{\{\phi_i\} \rightarrow \rho} \sum_{i=1}^N \langle \phi_i | T | \phi_i \rangle \quad (2.4)$$

is the minimum of the sum of the expectation values of T over a set $\{\phi_i\}$ of N orthonormal one-electron wave functions (N being the number of electrons in the system) whose squared absolutes sum up to ρ . It is important in this context to note that the same density can be achieved by quite different function sets that need not be connected by an orthogonal transformation [18].

The by far most widely used approximation for $v^s[\rho]$ is the local-density approximation [17], or its spin-polarized variant, the local spin-density approximation (LSD) [19]. The differences between LDA and LSD concern only the splitting up of the total density into two spin-polarized parts, which enter separately into the approximation to the exchange-correlation energy. This affects the principal theory as subsequently laid out in no way, and we will argue in a formalism without spin-polarization, thus saving the additional indices. The generalization to SIC-LSD is in any case straightforward.

In LDA, the total energy is expressed as

$$E^{LDA}[\rho] = T^s[\rho] + U_H[\rho] + E_{xc}^{LDA}[\rho] + \int \rho(\mathbf{r})v_{ext}(\mathbf{r})d^3r, \quad (2.5)$$

where $T^s[\rho]$ is given by Eq. (2.4),

$$U_H[\rho] = \frac{1}{2} \int d^3r d^3r' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (2.6)$$

is the electronic Hartree energy, and

$$E_{xc}^{LDA} = \int \rho(\mathbf{r})\epsilon_{xc}(\rho(\mathbf{r}))d^3r, \quad (2.7)$$

with the exchange-correlation energy density $\epsilon_{xc}(\rho)$ of an homogeneous electron gas of density ρ . The potential $v^s([\rho], \mathbf{r})$ can be straightforwardly derived from these expressions.

One striking feature of this approximation is that it yields by construction the correct result in the homogeneous electron gas, but fails completely in the limit of a simple one-electron system (e.g. H, He⁺), as there remains a spurious electron-electron interaction energy connected with the density of the one electron in the system. Errors of varying degrees occur in finite, inhomogeneous many-electron systems. Perdew and Zunger [1] have suggested an alternative expression for the total energy [20] which enforces the correct behavior in both limiting cases:

$$E_{\phi}^{SIC-LDA}[\{\phi_i\}] = \sum_{i=1}^N \langle \phi_i | T | \phi_i \rangle + U_H[\rho] + E_{xc}^{LDA}[\rho] - \sum_{i=1}^N \left(U_H[|\phi_i|^2] + E_{xc}^{LDA}[|\phi_i|^2] \right) + \int \rho(\mathbf{r})v_{ext}(\mathbf{r})d^3r. \quad (2.8)$$

The second sum in Eq. (2.8) subtracts in an approximate manner (or even exactly in a system with a single electron) the electronic self-interactions contained in E^{LDA} , hence the name "self-interaction-corrected LDA" (SIC-LDA). The correct limit in the homogeneous electron gas

is preserved, since completely delocalized states produce no self-interaction correction and so SIC-LDA reduces to LDA.

As it stands, Eq. (2.8) does not represent a functional of the total density alone, but also of the individual orbital densities. This has often been held against the SIC-LDA and led to the perception that it stands outside rigorous density-functional theory. But there is a proper density functional [1,21,20]

$$E^{SIC-LDA}[\rho] = \Theta^{LDA}[\rho] + U_H[\rho] + E_{xc}^{LDA}[\rho] + \int \rho(\mathbf{r})v_{ext}(\mathbf{r})d^3r, \quad (2.9)$$

$$\Theta^{LDA}[\rho] = \min_{\{\phi_i\} \rightarrow \rho} \sum_{i=1}^N \left\{ \langle \phi_i | T | \phi_i \rangle - U_H[|\phi_i|^2] - E_{xc}^{LDA}[|\phi_i|^2] \right\}, \quad (2.10)$$

which fulfils

$$E^{SIC-LDA} \left[\sum_{i=1}^N |\phi_i|^2 \right] \leq E_{\phi}^{SIC-LDA}(\{\phi_i\}). \quad (2.11)$$

The equality holds for the set $\{\phi_i\}$ that minimizes $E_{\phi}^{SIC-LDA}$.

Instead of minimizing $E^{SIC-LDA}$ with respect to the density, it is easier and nevertheless exact to minimize $E_{\phi}^{SIC-LDA}$ with respect to the orbitals, thus obtaining at the same time a knowledge of the minimum value of $E^{SIC-LDA}$ and the ground state density ρ_0 . This is the way that has been chosen in virtually all works on SIC-LDA or SIC-LSD and is correct from a density-functional theoretical point of view.

Equation (2.9) does not contain $T^s[\rho]$, since the orbitals involved in Eq. (2.10) may be quite different from those in Eq. (2.4). However, the use of $T^s[\rho]$ is a specific feature of the Kohn-Sham formalism and not of density-functional theory in general, as may be seen by comparison with Eq. (2.2). SIC-LDA therefore stands outside the Kohn-Sham formalism, but is nevertheless a valid density-functional approximation [21]. Still, in any theory with an exchange-correlation functional having the property $U_H[|\phi|^2] + E_{xc}[|\phi|^2] = 0$, $\Theta[\rho]$ equals $T^s[\rho]$. This is true in particular for the (unknown) exact functional [22].

In the minimum of the functional Eq. (2.9) all $\delta E_{\phi}^{SIC-LDA} / \delta \phi_i^*$ ($i = 1, \dots, N$) must vanish. This, together with the orthogonality constraint on the wave functions, leads to the set of equations

$$H_i \phi_i(\mathbf{r}) = \left(-\frac{1}{2} \nabla^2 + v_{ext}(\mathbf{r}) + v_H([\rho]; \mathbf{r}) + v_{xc}^{LDA}([\rho]; \mathbf{r}) + v_i^{SIC}(\mathbf{r}) \right) \phi_i(\mathbf{r}) = \sum_{j=1}^N \lambda_{ij} \phi_j(\mathbf{r}), \quad (2.12)$$

$$\begin{aligned}
v_H([\rho]; \mathbf{r}) &= \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \\
v_{xc}^{LDA}([\rho]; \mathbf{r}) &= \frac{d}{d\rho} \left(\rho(\mathbf{r}) \epsilon_{xc}(\rho(\mathbf{r})) \right), \\
v_i^{SIC}(\mathbf{r}) &= -v_H(|\phi_i|^2; \mathbf{r}) - v_{xc}^{LDA}(|\phi_i|^2; \mathbf{r}). \quad (2.13)
\end{aligned}$$

The Lagrange multipliers $\lambda_{ij} = \langle \phi_j | H_i | \phi_i \rangle$ guarantee the orthogonality of the orbitals ϕ_i . Unlike in the LDA, the off-diagonal λ_{ij} cannot be eliminated by a simple rotation among the orbitals, since the left hand side of Eq. (2.8) is state dependent as well.

In the absolute minimum of the energy functional (2.8) the relationship

$$\langle \phi_i | v_j^{SIC} - v_i^{SIC} | \phi_j \rangle = 0 \quad (2.14)$$

holds, since $E_{\phi}^{SIC-LDA}$ is stationary with respect to any variations of the ϕ_i . This can be seen by specifically examining the condition that the functional derivatives with respect to rotations among the orbitals must vanish [4]. Equation (2.14) implies that the matrix λ is Hermitian, since

$$\begin{aligned}
\lambda_{ij} - \lambda_{ji}^* &= \langle \phi_j | H_i - H_j | \phi_i \rangle \\
&= \langle \phi_j | v_i^{SIC} - v_j^{SIC} | \phi_i \rangle = 0. \quad (2.15)
\end{aligned}$$

B. The one-electron picture

The Kohn-Sham scheme leads to a Schrödinger-type equation, yielding eigenvalues that are, however, rather poor approximations to excitation energies, as is well-known. Perdew and Zunger [1] derived a set of one-electron equations from the functional (2.8), but neglected the requirement that the resulting orbitals be orthogonal. Their equations have several appealing features: first and foremost, the eigenvalues are good approximations to relaxed total energy differences. Furthermore, the effective potential for a given state of a neutral atom shows the correct long-range limit $\lim_{r \rightarrow \infty} (rv_{eff}^i) = -1$. Unfortunately, these equations contain an orbital-dependent potential and this has led to the SIC-LDA or SIC-LSD being often regarded with some suspicion.

The one-electron picture is lost if the minimization of

the functional (2.8) is rigorously done with the inclusion of nondiagonal Lagrange multipliers, as in Eq. (2.12). In fact, the latter equations do not even contain scalar eigenvalues. Pederson and co-workers [4,5,23] have shown that the eigenvalues of the Lagrange multiplier matrix are again good approximations to total energy differences and satisfy Janak's theorem [24]. They also found [4] that the "localized orbitals," which minimize the functional (2.8), in general do not reflect the symmetry of the system, whereas the "canonical orbitals," which are connected with the localized ones by the unitary transformation that diagonalizes the Lagrange multiplier matrix, do possess the full symmetry.

We show in the following that the self-interaction-corrected LDA can be formulated in such a way that the equations resulting from the variational minimization procedure lend themselves to a very suggestive effective one-particle interpretation. The features of these equations are:

- (i) The eigenfunctions obey a single, state-independent Hamiltonian of the Schrödinger type (or, relativistically, Dirac type) with a small short-range nonlocal component in the potential.
- (ii) In the long range, the equations for a neutral atom reduce to the form

$$(T - 1/r)\Psi_i = \epsilon_i \Psi_i. \quad (2.16)$$

- (iii) The eigenvalues are good approximations to electron binding energies.

The limit (ii) is the proper one, since, intuitively, a single electron far away from the center of an atom of atomic number Z is expected to "see" a spherical Coulomb potential of net charge -1 caused by the nucleus screened by the remaining $Z - 1$ electrons, and not to interact otherwise. This property could also be shown rigorously by Gunnarson *et al.* [25] by an investigation of the exact exchange-correlation potential.

The trouble with the nondiagonal Lagrange multipliers arises because the functional (2.8) is not invariant under orbital rotations. So let us formulate an alternative functional that possesses the same minimum at the same overall density but is *invariant* under unitary transformations of the wave functions:

$$\begin{aligned}
E_{\Psi}^{SIC-LDA}[\{\Psi_i\}] &= \sum_{i=1}^N \langle \Psi_i | T | \Psi_i \rangle + U_H[\rho] + E_{xc}^{LDA}[\rho] + \int \rho(\mathbf{r}) v_{ext}(\mathbf{r}) d^3r \\
&+ \min_{\mathbf{M}} \sum_{i=1}^N \left(-U_H \left[\left| \sum_j M_{ji}^* \Psi_j \right|^2 \right] - E_{xc}^{LDA} \left[\left| \sum_j M_{ji}^* \Psi_j \right|^2 \right] \right). \quad (2.17)
\end{aligned}$$

The minimization on the right hand side of Eq. (2.17) is over all unitary matrices \mathbf{M} . The particular matrix that yields the minimum in Eq. (2.17) will be denoted by \mathcal{M} . The variational conditions $\delta E_{\Psi}^{SIC-LDA}/\delta\Psi_i^* = 0$, coupled with the orthogonality constraint, lead to the single-particle equations

$$\left(T + v_H[\rho] + v_{xc}[\rho] + v_{ext} + \bar{v}^{SIC} + \sum_k^{occ} (v^{SIC}[\rho_k] - \bar{v}^{SIC}) |\phi_k\rangle\langle\phi_k| \right) |\Psi_i\rangle = \epsilon_i |\Psi_i\rangle, \quad (2.18)$$

$$\phi_k = \sum_j \mathcal{M}_{jk}^* \Psi_j, \quad (2.19)$$

$$\rho_k = |\phi_k|^2, \quad (2.20)$$

$$v^{SIC}[\phi_k] = -v_H[\rho_k] - v_{xc}[\rho_k], \quad (2.21)$$

$$\bar{v}^{SIC} = \frac{1}{N} \sum_k v^{SIC}[\rho_k]. \quad (2.22)$$

The average SIC potential, \bar{v}^{SIC} , has been purposefully introduced to underline the short-range nature of the nonlocal term. The operator on the left hand side of Eq. (2.18) will be investigated in greater detail in the Appendix, where a scheme for practical calculations is presented.

One can easily check that Eq. (2.18) has the first two of the above postulated properties and that furthermore the orbitals ϕ_i are identical to the localized orbitals of Eq. (2.12), the orbitals Ψ_i are equal to the earlier mentioned canonical orbitals, and the ϵ_i are the eigenvalues of the matrix λ . The third postulate about the agreement between eigenvalues and electronic binding energies is confirmed by the results presented in Sec. IV and discussed there.

From Eq. (2.18) one finds immediately that

$$\lim_{r \rightarrow \infty} \Psi_i \sim e^{-\sqrt{-2\epsilon_i} r}, \quad (2.23)$$

which means that the ϵ_i control the decay of the canonical wave functions in a way that is characteristic of one-electron eigenvalues. Thereby their interpretation as electronic binding energies is supported. The localized orbitals, on the other hand, being a mixture of the canonical ones, have a limit

$$\lim_{r \rightarrow \infty} \phi_k = \lim_{r \rightarrow \infty} \sum_j \mathcal{M}_{jk}^* C_j e^{-\sqrt{-2\epsilon_j} r} = \mathcal{M}_{mk}^* C_m e^{-\sqrt{-2\epsilon_m} r}, \quad (2.24)$$

where m labels the state with the largest eigenvalue contained in the sum. Consequently it is underlined that the canonical orbitals, and not the localized ones, possess single-electron qualities.

III. RELATIVISTIC FORMALISM

A. Relativistic LDA

A relativistic variant of the LDA formalism (RLDA) has been derived in complete analogy to the nonrelativistic

one by MacDonald and Vosko [26]. We will give a short account of the modifications required in comparison to the nonrelativistic case.

The total energy functional retains its general form

$$E^{RLDA}[\rho] = T_{rel}^s[\rho] + U_H[\rho] + E_{xc}^{RLDA}[\rho] + \int \rho(\mathbf{r}) v_{ext}(\mathbf{r}) d^3r. \quad (3.1)$$

The density ρ is given by

$$\rho = \sum_{i=1}^N \phi_i \phi_i^\dagger, \quad (3.2)$$

where the ϕ_i are now the four-component spinor functions belonging to the N lowest positive eigenvalues of the Dirac-type equation

$$(H_D - c^2 + v_{ext} + v_H + v_{xc}^{RLDA})\phi_i = \epsilon_i \phi_i, \quad (3.3)$$

$$H_D = -i\alpha\nabla + \beta c^2, \quad (3.4)$$

with the Dirac matrices α and β (the notation follows Ref. [28]) and the speed of light c . The subtraction of the electronic rest energy $-c^2$ on the left hand side serves to make the eigenvalues ϵ_i comparable to their nonrelativistic counterparts;

$$T_{rel}^s[\rho] = \min_{\{\phi_i\} \rightarrow \rho} \sum_{i=1}^N \langle \phi_i | H_D | \phi_i \rangle \quad (3.5)$$

is the kinetic energy (plus rest energy) of the noninteracting relativistic electron gas. The terms resulting from the external charges and the interelectronic Coulombic energy retain their form as described in the previous section. In the relativistic local-density approximation, the exchange energy density of the homogeneous relativistic electron gas is approximated by [26]

$$\epsilon_x^{rel} = \epsilon_x^{nonrel} \times \left(1 - \frac{3}{2} \frac{\beta \sqrt{1 + \beta^2} - \ln(\beta + \sqrt{1 + \beta^2})}{\beta^2} \right), \quad (3.6)$$

$\beta(\rho) = v_F(\rho)/c$, where $v_F(\rho)$ is the nonrelativistic uniform-system Fermi velocity at the density ρ . The correlation energy is assumed to be the same as in the nonrelativistic case. The exchange-correlation potential in the relativistic local-density approximation (RLDA) is accordingly

$$v_{xc}^{RLDA} = v_x^{LDA} \left[-\frac{1}{2} + \frac{3 \ln(\beta + \sqrt{1 + \beta^2})}{2 \beta \sqrt{1 + \beta^2}} \right] + v_c^{LDA}. \quad (3.7)$$

B. Relativistic SIC-LDA

We have generalized the argument of the previous section and applied a self-interaction correction to the

RLDA total energy functional (SIC-RLDA):

$$E^{SIC-RLDA}[\rho] = \Theta_{rel}[\rho] + U_H[\rho] + E_{xc}^{RLDA}[\rho] + \int \rho(\mathbf{r})v_{ext}(\mathbf{r})d^3r. \quad (3.8)$$

$$\Theta_{rel}[\rho] = \min_{\{\phi_i\} \rightarrow \rho} \sum_{i=1}^N \left\{ \langle \phi_i | H_D | \phi_i \rangle - U_H[\rho_i^2] - E_{xc}^{RLDA}[\rho_i^2] \right\}, \quad (3.9)$$

$$\rho_i = \phi_i \phi_i^\dagger. \quad (3.10)$$

Variation of this functional with respect to the orbitals ϕ_i leads again to an equation of the same form as Eq. (2.12),

$$H_i \phi_i(\mathbf{r}) = \sum_{j=1}^N \lambda_{ij} \phi_j(\mathbf{r}),$$

but now

$$H_i = H_D - c^2 + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}^{RLDA}(\mathbf{r}) + v_i^{SIC}(\mathbf{r}), \quad (3.11)$$

$$v_i^{SIC}(\mathbf{r}) = -v_H(\rho_i(\mathbf{r})) - v_{xc}^{RLDA}(\rho_i(\mathbf{r})). \quad (3.12)$$

The relativistic analogue of Eq. (2.18) is

$$\left(H_D - c^2 + v_H[\rho] + v_{xc}^{RLDA}[\rho] + v_{ext} + \bar{v}^{SIC} + \sum_k^{occ} (v^{SIC}[\rho_k] - \bar{v}^{SIC}) |\phi_k\rangle \langle \phi_k| \right) |\Psi_i\rangle = \epsilon_i |\Psi_i\rangle. \quad (3.13)$$

Here the Ψ_i are, of course, four-component spinors.

IV. APPLICATION TO FREE ATOMS

A. Formalism

In this section we stay in the relativistic formalism throughout. For atoms of atomic number Z , the external potential has the simple form

$$v_{ext}(r) = -\frac{Z}{r}. \quad (4.1)$$

In order to keep the full effective potential rotationally invariant and to take advantage of the resulting simplifications in the Dirac equation, we work only with spherically averaged densities. This approximation is widely

used in density-functional calculations for atoms and has been discussed in some detail by Pederson and Lin [27] for the nonrelativistic case. With this simplification, the wave functions separate into the product of a radial and an angular part. The former, multiplied by r , is composed of major component G and minor component F , which obey the differential equations [28]

$$\begin{aligned} -c \frac{d}{dr} F_{m\kappa}(r) + \frac{c\kappa}{r} F_{m\kappa}(r) \\ + v_{eff}(r) G_{m\kappa}(r) = \epsilon_{m\kappa} G_{m\kappa}(r), \\ c \frac{d}{dr} G_{m\kappa}(r) + \frac{c\kappa}{r} G_{m\kappa}(r) \\ + [v_{eff}(r) - 2c^2] F_{m\kappa}(r) = \epsilon_{m\kappa} F_{m\kappa}(r). \end{aligned} \quad (4.2)$$

c is again the speed of light, given by $c = 137.037$ in atomic units, and κ is connected with the quantum numbers of orbital angular momentum l and total angular momentum j by the relation

$$\kappa = \begin{cases} -(l+1) & \text{if } j = l + \frac{1}{2} \\ l & \text{if } j = l - \frac{1}{2}. \end{cases} \quad (4.3)$$

The index m labels different eigenstates having the same quantum number κ and must not be confused with a magnetic quantum number. After introducing the radial functions

$$u_{m\kappa}(r) = \begin{pmatrix} G_{m\kappa}(r) \\ F_{m\kappa}(r) \end{pmatrix}, \quad (4.4)$$

one can, with the help of Eq. (4.2), transform Eq. (3.13) into a two-dimensional matrix equation purely for the radial functions:

$$H_\kappa u_{m\kappa} = \epsilon_{m\kappa} u_{m\kappa}, \quad (4.5)$$

$$\begin{aligned} H_\kappa = H_D^\kappa - c^2 + v_{eff}^{loc}(r) \\ + \sum_m (v^{SIC}[\rho_{m\kappa}] - \bar{v}^{SIC}) P_{m\kappa}, \end{aligned} \quad (4.6)$$

$$H_D^\kappa = c \begin{pmatrix} c & -\frac{d}{dr} + \frac{\kappa}{r} \\ \frac{d}{dr} + \frac{\kappa}{r} & -c \end{pmatrix}. \quad (4.7)$$

The local part of the effective potential, including the local SIC contributions, is

$$\begin{aligned} v_{eff}^{loc}(r) = -\frac{Z}{r} + v_H([\rho]; r) + v_{xc}^{RLDA}(\rho(r)) \\ + \bar{v}^{SIC}([\{\rho_i\}]; r), \end{aligned} \quad (4.8)$$

where the ρ_i are averaged orbital densities

$$\rho_i(r) = \frac{1}{r^2} [G_i^2(r) + F_i^2(r)]. \quad (4.9)$$

Here, all quantum numbers have been lumped together

into i . The total density is consequently given by

$$\rho(r) = \sum_{i=1}^Z \rho_i(r). \quad (4.10)$$

$P_{m\kappa}$ is the projector onto the function

$$w_{m\kappa}(r) = \sum_{m'} \mathcal{M}_{m'm}^* u_{m'\kappa}(r), \quad (4.11)$$

which constitutes the radial part, multiplied by r , of the respective localized orbital. All the other symbols in Eqs. (4.6) – (4.11) are chosen as in Eq. (3.13).

A sketch of the algorithm we have developed for the self-consistent solution of Eq. (4.5) is given in the Appendix. We use the spin-unpolarized parametrization of Perdew and Zunger [1] of the results of Ceperley and Alder [29] for the nonrelativistic exchange-correlation potential and modify it relativistically according to Eq. (3.7).

B. Results

Table I and Fig. 1 show the results of SIC-RLDA calculations of the eigenvalues of the outermost shell states of six atoms, compared to self-consistently computed total energy differences and experimental electron binding energies. We find good agreement for these three quantities in all cases considered. This is in line with earlier observations [1,30] that self-interaction-corrected LDA eigenvalues are a good approximation to relaxed energy differences and are much closer to experimentally measured binding energies than mere LDA eigenvalues. The energy differences in the RLDA do not deviate all that much from their self-interaction-corrected counterparts.

The improved eigenvalues may be understood to result from the attractive SIC potential, which moves the

TABLE I. Detailed predicted valence energies compared to experiment. Displayed are the relativistically calculated eigenvalues of the valence states, with (RSIC) and without (RLDA) self-interaction corrections, and the differences in the total energy upon removal of the specified electron. The theoretical eigenvalues are weighted averages over $j_+ = l + 1/2$ and $j_- = l - 1/2$, such that $\epsilon(l) = [(l+1)\epsilon(j_+) + l\epsilon(j_-)]/(2l+1)$. All values are in eV.

	Al	Si	P	Ga	Ge	As
$-\epsilon^{RSIC}(s)$	11.87	15.66	19.49	13.38	16.67	19.91
$-\Delta E_{tot}^{RSIC}(s)$	12.36	16.03	19.76	13.81	16.99	20.15
$-\epsilon^{RLDA}(s)$	7.83	10.88	14.02	9.17	11.95	14.70
$-\Delta E_{tot}^{RLDA}(s)$	11.67	15.24	18.89	13.38	16.48	19.48
$-\Delta E_{tot}^{exp}(s)^*$	11.32	14.95	18.39	12.61	16.06	18.21
$-\epsilon^{RSIC}(p)$	5.73	7.82	9.94	5.67	7.52	9.31
$-\Delta E_{tot}^{RSIC}(p)$	5.94	8.40	10.46	6.00	8.06	9.83
$-\epsilon^{RLDA}(p)$	2.79	4.17	5.60	2.74	4.05	5.35
$-\Delta E_{tot}^{RLDA}(p)$	5.85	7.83	9.82	5.90	7.70	9.32
$-\Delta E_{tot}^{exp}(p)^*$	5.98	7.75	9.58	5.93	7.77	8.46

*Configuration averaged values from Ref. [33].

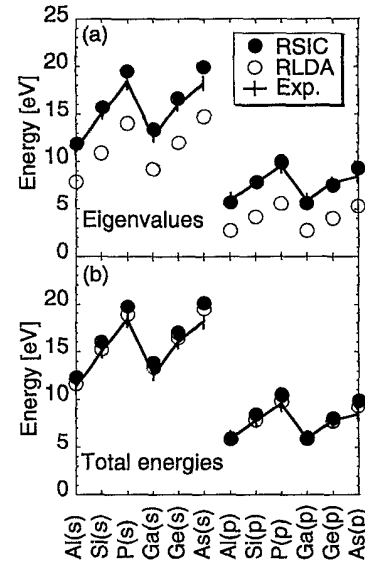


FIG. 1. Theoretical relativistic eigenvalues and total energy differences for atomic s - and p -type valence states, calculated with (RSIC, full circles) and without (RLDA, open circles) self-interaction correction. These results are compared to experimental binding energies that are configuration averaged values from Ref. [33]. (a) The RSIC eigenvalues shadow closely the experimental electronic binding energies, while the RLDA values are way off. (b) The total energy differences, on the contrary, are in both types of calculations close to experiment. The experimental data points have been interconnected by a solid line to guide the eye.

SIC eigenvalues a long way in the right direction towards the more negative total energy differences. The relative contribution of the SIC potential is strongest in the long range, where it restores the right one-electron-type $-1/r$ asymptotics and completely dominates the other contributions to the effective potential. In the total energy differences the effects of the self-interactions largely cancel out, so even in LDA they are fairly reliable. Only the self-interaction of the electron which is removed remains uncanceled, which is why the absolute LDA energy differences are still smaller than those of SIC-LDA.

The canonical wave functions of SIC-RLDA and RLDA are fairly similar and in particular they exhibit the same nodal structure. This is not true for the localized orbitals, which are a mixture of the canonical orbitals and hence possess in general as many nodes as the canonical orbital with the largest number of nodes of those involved. There is, however, a clear difference in the long-range behavior between the canonical wave functions of the SIC-RLDA and RLDA, due to the distinctly altered eigenvalue [cf. Table I]. This shows up when we look at the logarithm of a particular wave function with index i (Fig. 2), which approaches asymptotically a straight line with slope $-\sqrt{-2\epsilon_i + \epsilon_i^2/c^2}$ [cf. Eq. (2.21)].

To highlight the improvements the relativistic SIC-LDA calculations yield over nonrelativistic ones, we look at two relatively heavy elements, krypton and xenon,

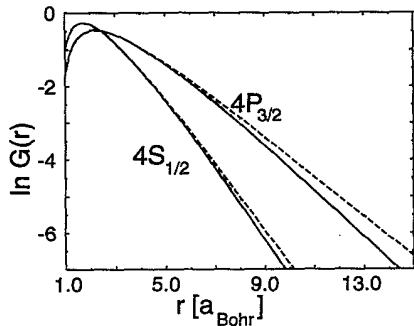


FIG. 2. Logarithm of the major component G of the radial $4S_{1/2}$ and $4P_{3/2}$ wave functions u beyond the last maximum in Ge. The solid lines are calculated with, the dashed lines without, self-interaction corrections to the relativistic LDA. Units on the ordinate: $\ln(1/\sqrt{a_{Bohr}})$.

which show sizeable relativistic effects. In noble gases there is no spin polarization, so the neglect of spin-polarization effects is perfectly justified. Table II compares calculated eigenvalues to experimental binding energies and Fig. 3 illustrates this graphically for Xe.

For all s and p core levels, the relativistic corrections lower the eigenvalues. Since most core levels are too weakly bound in the LDA, this causes improved agreement with experiment in these cases. Only the $2p$ core level in Kr and the $4p$ core level in Xe have in the SIC-LDA eigenvalues that are already lower than the measured binding energies, so here the relativistic corrections lead to an increased error. The same is true for the valence levels. Very little effect is seen for the valence p electrons, which are rather far removed from the nucleus in whose vicinity the relativistic effects work strongest, but the valence s electrons, which penetrate the core, get too low an eigenvalue.

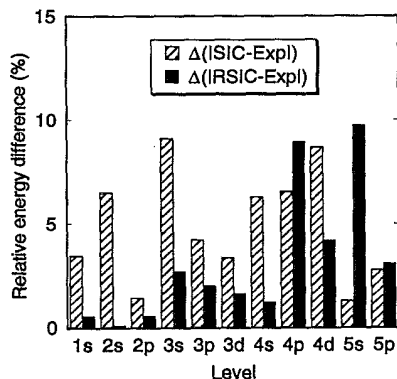


FIG. 3. Relative deviation between the calculated nonrelativistic (SIC) and relativistic (RSIC) self-interaction-corrected LDA eigenvalues on the one hand and the experimentally measured binding energies [32] of Xe on the other. All s and p eigenvalues are lowered by relativistic effects, the d states are moved upwards. With the exception of the $4p$ state, all core levels are better described by the RSIC. The valence electrons, in particular the $5s$ one, are too strongly bound.

TABLE II. SIC-LDA and SIC-RLDA eigenvalues compared to experimental electron binding energies [32]. Both theoretical eigenvalues and experimental energies are weighted averages over $j_+ = l + 1/2$ and $j_- = l - 1/2$, such that $\epsilon(l) = [(l+1)\epsilon(j_+) + l\epsilon(j_-)]/(2l+1)$. All values are in eV.

	SIC-LDA	SIC-RLDA	Expt.
Kr			
1s	-14198.71	-14434.80	-14326.0
2s	-1871.62	-1928.65	-1921.0
2p	-1708.98	-1720.51	-1695.9
3s	-265.31	-275.02	-292.8
3p	-213.33	-215.23	-217.0
3d	-102.54	-100.37	-94.3
4s	-31.15	-32.23	-27.5
4p	-14.57	-14.56	-14.1
Xe			
1s	-33382.75	-34750.74	-34561.0
2s	-5098.90	-5447.33	-5453.0
2p	-4821.43	-4916.13	-4889.3
3s	-1044.23	-1118.12	-1148.7
3p	-920.56	-941.84	-961.1
3d	-703.86	-692.45	-681.4
4s	-199.80	-215.75	-213.2
4p	-155.44	-158.96	-145.9
4d	-74.23	-71.16	-68.3
5s	-23.59	-25.57	-23.3
5p	-12.84	-12.88	-12.5

The d levels tend to be overbound in the SIC-LDA and the SIC-RLDA gives an adjustment in the right direction. This is due to the fact that even the lowest d electron "sees" a nucleus that is already well screened by s and p electrons. Since the relativistic corrections concentrate the latter even more closely around the nucleus, this screening effect grows and the d levels move upward in the SIC-RLDA.

V. SUMMARY

We have pointed out the solid roots of the SIC-LDA in density-functional theory and derived a set of one-electron equations with an orbital-independent self-interaction-corrected exchange-correlation potential with a small, short-range nonlocal part. The equations completely parallel the Kohn-Sham equations of the LDA.

A fully relativistic self-interaction-corrected LDA formalism has been developed and an algorithm for its solution proposed. We have shown with the example of several atoms that the calculated eigenvalues of the SIC-RLDA equations do compare favorably both to experimental electronic binding energies and to calculated total energy differences.

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analogously. Lastly, the discretized matrix representation of the projectors $P_{m\kappa}$ onto the localized radial functions $w_{m\kappa}$ [Eq. (4.11)] is

$$P_{ij}^{m\kappa} = w_{m\kappa}(i)w_{m\kappa}(j). \quad (\text{A11})$$

With these definitions and with $\mathbf{1}$ denoting the unit matrix, H_κ can be written as

$$H_\kappa = R^{-1}A^\kappa - c^2\mathbf{1} + V^{loc} + \sum_k V_k^{nl} P_{m\kappa}^{nl}. \quad (\text{A12})$$

Next we apply the transformation (A1):

$$\tilde{H}_\kappa = H_\kappa P_{occ} + P_{occ} H_\kappa^T + P_\perp (R^{-1}A^\kappa - c^2\mathbf{1} + V^{loc}) P_\perp, \quad (\text{A13})$$

$$P_{occ} = \sum_m^{occ} P_{m\kappa},$$

$$P_\perp = \mathbf{1} - P_{occ}. \quad (\text{A14})$$

This matrix is still not symmetric, due to the last term, but can be transformed into a symmetric matrix \tilde{H}'_κ by the similarity transformation

$$\tilde{H}'_\kappa = R^{\frac{1}{2}} \tilde{H}_\kappa R^{-\frac{1}{2}}. \quad (\text{A15})$$

\tilde{H}'_κ possesses the same eigenvalues as \tilde{H}_κ and if q_i is an eigenvector of \tilde{H}'_κ , then $u_i = R^{-\frac{1}{2}} q_i$ is an eigenvector of \tilde{H}_κ . The need for this additional transformation arises purely out of the discretization procedure.

Within each iteration of the self-consistency cycle — that is between updates of the effective potential — we have to diagonalize all matrices \tilde{H}'_κ with a value of κ that occurs among the occupied orbitals. One has to keep in mind that all negative-eigenvalue solutions are discarded. In setting up \tilde{H}'_κ , we take the $u_{m\kappa}$ from the previous iteration and determine the localized orbitals by rotations among the occupied states with equal κ , with a method similar to that described in Ref. [5], until they fulfil the condition

$$\langle w_{m\kappa} | v_{m'\kappa}^{SIC} - v_{m\kappa}^{SIC} | w_{m'\kappa} \rangle = 0. \quad (\text{A16})$$

In the first iteration we make a guess for the $u_{m\kappa}$. In the spirit of the spherical approximation, we occupy states with the same quantum number l but different j [here both are concisely expressed by κ , see Eq. (4.3)] weighted with their degeneracy.

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