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A SELF-INTERACTION CORRECTED APPROACH TO MANY-ELECTRON SYSTEMS: BEYOND THE LOCAL SPIN DENSITY APPROXIMATION

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A self-consistent self-interaction correction to the local spin density approximation is shown to remove many of the anomalies in the predicted exchange, correlation and total energies of atoms, stability of negative ions and band gaps of insulators. It also suggests a new interpretation of the calculated cohesive energies of transition metals.

DESPITE the striking success of the local density (LD) [1] and spin-density (LSD) [2] functional approaches to many-electron systems, some significant discrepancies remain. These include the facts that: (i) While the LSD total energy of a metal surface is *too low* when compared with the exact value [3], the LSD energy for atoms is *too high* [4]. Furthermore, the lowest-order correction to the LSD exchange-correlation energy predicted by many-body theory, i.e., the density-gradient correction [5], is positive, and so can only worsen the calculated energies of atoms. (ii) For atoms [4] the magnitude of the exchange energy in LSD is consistently underestimated by 10–15% while the magnitude of the correlation energy is overestimated by 100–200%. (iii) The experimentally stable negative ions (e.g. H^-, O^-, F^-) are predicted to be unstable [6]. (iv) Self-consistent LD band structure calculations underestimate the one-electron energy gap of insulators by as much as 40% (see [7–11]), and more generally the LSD one-electron eigenvalues are not close to physical removal energies from bound states. The conventional remedies have been delta-SCF or Slater transition-state type calculations, which are very tedious, especially for solids where they break the translational periodicity.

In this letter we show that these problems are interrelated and that a simple, physically transparent correction to LSD – the subtraction of spurious self-interaction – accounts for and corrects the qualitative as well as most of the quantitative discrepancies. This self-interaction correction is a "non-homogeneity correction" which vanishes for systems of uniform density, like the gradient correction [5], but unlike the latter it arises only for localized electronic states. A more detailed account of our work will be presented elsewhere [12].

Spin-density functional theory [1, 2] expresses the ground-state energy of a many-electron system, coupled to an external potential $V_{\text{ext}}(\mathbf{r})$ and characterized by electron density $\rho(\mathbf{r}) = \rho_\uparrow(\mathbf{r}) + \rho_\downarrow(\mathbf{r})$ and spin-polarization $\zeta(\mathbf{r}) = (\rho_\uparrow - \rho_\downarrow)/\rho$, as:

$$E = T[\rho, \zeta] + E_{\text{ext}}[\rho] + \tfrac{1}{2}E_{ee}[\rho] + E_{xc}[\rho, \zeta], \qquad (1)$$

where T is the non-interacting kinetic energy, $E_{\text{ext}} = \int d^3r\, \rho(\mathbf{r})V_{\text{ext}}(\mathbf{r})$ is the interaction of ρ with V_{ext}, E_{ee} is the interaction of ρ with the time-averaged Coulomb potential $V_{ee}([\rho];\mathbf{r}) = \int d^3r'\, \rho(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'|$, and E_{xc} is the sum of exchange and correlation energies. The self-consistent one-electron equation found variationally from equation (1) is

$$\{-\tfrac{1}{2}\nabla^2 + V^\sigma(\mathbf{r})\}\, \psi_{\alpha\sigma}(\mathbf{r}) = \epsilon_{\alpha\sigma}\psi_{\alpha\sigma}(\mathbf{r}), \qquad (2)$$

where the potential (with spin index σ) is implicitly a functional of ρ and ζ:

$$V^\sigma(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_{ee}([\rho];\mathbf{r}) + V^\sigma_{xc}([\rho, \zeta];\mathbf{r}), \qquad (3)$$

and the density is determined via $\rho(\mathbf{r}) = \Sigma_{\alpha\sigma}\, \rho_{\alpha\sigma}(\mathbf{r})$ from the spin–orbital densities $\rho_{\alpha\sigma}(\mathbf{r}) = N_{\alpha\sigma}|\psi_{\alpha\sigma}(\mathbf{r})|^2$. ($N_{\alpha\sigma}$ is an occupation number, 0 or 1). The exchange-correlation potential V^σ_{xc} is the functional derivative of E_{xc} with respect to $\rho_\sigma(\mathbf{r})$.

The imperfectly-known exchange-correlation functional E_{xc} is usually replaced by the local (LSD) approximation [1, 2]: $E^{\text{LSD}}_{xc} = \int d^3r\, \rho(\mathbf{r})\, \epsilon_{xc}[\rho(\mathbf{r}), \zeta(\mathbf{r})]$, where $\epsilon_{xc}(\rho, \zeta)$ is the exchange-correlation energy per particle of a uniform electron gas; this approach reduces to the LD approach in the unpolarized

Table 1. (− 1) × *total energy in* eV *for atoms*

Atom	Exact	SIC	LSD
H	13.6	13.6	13.0
He	79.0	79.4	77.1
Li	203.5	204.2	199.8
Be	399.1	399.8	393.0
B	670.8	672.0	662.5
N	1485.3	1489.0	1472.8
F	2713.5	2720.9	2696.7
Ne	3507.9	3517.9	3489.1

limit $\zeta = 0$. In the present study we use Ceperley's correlation [13], which we have matched to the exact high-density limit and generalized to arbitrary spin polarization [12]; we have used an *accurate* $\epsilon_{xc}(\rho, \zeta)$, in order to uncover the real errors of LSD and of our self-interaction-corrected scheme.

We note that $\frac{1}{2}E_{ee}[\rho]$ and $E_{xc}^{\rm LSD}[\rho, \zeta]$ in equation (1) contain spurious electron self-Coulomb $\frac{1}{2}E_{ee}[\rho_{\alpha\sigma}]$ and self exchange-correlation $E_{xc}^{\rm LSD}[\rho_{\alpha\sigma}, 1]$ contributions from each spin orbital, which are negligible only for very diffuse orbitals. (By $\zeta = 1$ we express the fact that each orbital is fully spin-polarized.) The partial success of LSD in describing localized states (atoms, molecules, deep impurities, etc.) rests on the fact that often most of the *positive* self-Coulomb energy is cancelled by the *negative* self-exchange-correlation energy. The corresponding spurious contributions to the potential of equation (3) in LSD are $V_{ee}([\rho_{\alpha\sigma}]; \mathbf{r})$ and $V_{xc}^{\uparrow\rm LSD}([\rho_{\alpha\sigma}, 1]; \mathbf{r})$. Retention of these self-interactions results in a misrepresentation of the long-range behavior of the potential for systems with localized orbitals (e.g. the large r electrostatic limit $-(Q + 1)/r$ of the potential for ions of charge Q is not realized).

To generalize the LSD formalism for systems with localized states, we propose a self-interaction corrected (SIC) energy functional:

$$E^{\rm SIC} = E^{\rm LSD}[\rho, \zeta] - \sum_{\alpha\sigma} \delta_{\alpha\sigma}, \qquad (4)$$

with $E^{\rm LSD}$ given by the LSD version of equation (1). We have explicitly subtracted the self-interaction $\Sigma_{\alpha\sigma}\,\delta_{\alpha\sigma}$, where

$$\delta_{\alpha\sigma} = \tfrac{1}{2}E_{ee}[\rho_{\alpha\sigma}] + E_{xc}^{\rm LSD}[\rho_{\alpha\sigma}, 1]. \qquad (5)$$

(The SI correction term in equation (4) belongs to E_{xc}.) The corresponding variational one-electron potential is

$$V_{\rm SIC}^{\alpha\sigma}(\mathbf{r}) = V_{\rm LSD}^{\sigma}(\mathbf{r}) - V_{ee}([\rho_{\alpha\sigma}]; \mathbf{r}) - V_{xc}^{\uparrow\rm LSD}([\rho_{\alpha\sigma}, 1], \mathbf{r}), \qquad (6)$$

where the $\rho_{\alpha\sigma}(\mathbf{r})$ are now the orbital densities that are self-consistent with the potential (6). This kind of scheme was used by Lindgren [14] as a way to obtain better trial orbitals for the Hartree–Fock total energy; its application to the LSD energy functional has been proposed by Zunger and Cohen [15] and Perdew [16]. In the present approach, we solve the one-electron Schrödinger equation self-consistently in a central field approximation. (As in the Hartree approximation, the resulting orbitals are not automatically orthogonal. At each iteration we have performed a Schmidt orthogonalization of the orbitals, which we find has only a very small effect on the density and total energy (e.g. 10^{-2} eV for second-row atoms).)

The scheme proposed above is an ansatz which will be used to test the utility of self-interaction corrections to LSD. It is an orbital functional [16] and *not* a density functional scheme, and we will defer to the end of this letter the problem of incorporating self-interaction corrections within a true density-functional scheme. (Furthermore, even within an orbital-functional scheme the absolute minimum of equation (4) over all orthogonal orbitals will be given, not by our self-consistency scheme, but by the introduction of off-diagonal Lagrange multipliers into the Euler equation for the orbitals.)

Figure 1 shows $rV_{\rm SIC}^{\alpha\sigma}(\mathbf{r})$ for Ni in the $3d^8 4s^2$ configuration, compared with the LSD potential $rV_{\rm LSD}^{\sigma}(\mathbf{r})$. The removal of self-interaction (SI) has resulted in a pronounced orbital dependence (decreasing with the delocalization of the orbital), an overall deepening of the potential, a reduced spin-dependence, and correct $r \to \infty$ behavior.

Gunnarsson and Lundqvist [2] have argued that LSD gives reasonable total energies outside its domain of formal validity (densities that vary slowly in space) because it satisfies the sum rule that the exchange-correlation hole $n(\mathbf{r}, \mathbf{r}')$ around an electron at r must contain -1 electrons: $\int d^3r'\, n(\mathbf{r}, \mathbf{r}') = -1$. The LSD and SIC holes may be constructed by inspection of

$$E_{xc} = \tfrac{1}{2}\int d^3r\, \rho(\mathbf{r}) \int d^3r'\, n(\mathbf{r}, \mathbf{r}')/|\mathbf{r} - \mathbf{r}'|.$$

The SIC hole so constructed clearly satisfies the sum rule (for occupation numbers 0 or 1). Unlike the LSD hole but like the true one, it is not spherically symmetric. Details will be presented elsewhere [12].

Total energy calculations for atoms (Table 1) show that, while the LSD values are substantially higher than the experimental ones [17, 18], the SIC values are slightly *lower*. Thus SIC brings the atomic results into line with LSD calculations on the jellium surface (for which the orbitals are de-localized and the LSD = SIC energy is slightly lower than the exact value [3]).

Table 2 compares the self-consistent SIC exchange

Table 2. (− 1) × exchange and (− 1) × correlation energies in eV *for atoms*

	Exchange			Correlation		
Atom	Exact	SIC	LSD	Exact	SIC	LSD
H	8.5	8.5	7.3	0.0	0.0	0.6
He	27.9	28.6	23.4	1.1	1.5	3.0
Be	72.6	72.9	62.3	2.5	3.1	6.0
Ne	329.5	338.1	298.4	10.0	11.4	19.9

Table 3. SI *corrections* Δ_{SIC} *to the* LSD *band-structure error* ΔE_g *in the band gaps of rare-gas solids and the core ionization in* LiF (eV)

Solid	E_g^{exper}	E_g^{LSD}	ΔE_g	Δ_{SIC}
Ne	21.4(a)	11.2(c)	− 10.2	9.9
Ar	14.2(a)	8.3(c)	− 5.9	5.8
Kr	11.6(a)	6.8(d)	− 4.9	4.9
Xe	9.3(a)	–	–	4.2
LiF(Li 1*s*)	64.4(b)	47.2(e)	− 17.2	18.0
LiF(F 2*s*)	37.6(b)	30.1(e)	− 7.5	7.9

(a)Ref. [7]; (b)Ref. [8, 11]; (c)Ref. [9]; (d)Ref. [10]; (e)Ref. [11].

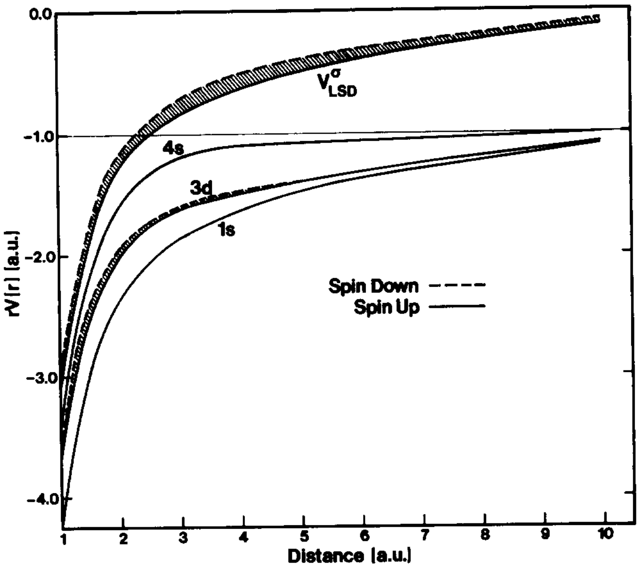

Fig. 1. The LSD and SIC atomic potentials for Ni $3d^8 4s^2$. Shaded areas indicate the spin splitting.

E_x and correlation E_c energies with LSD and exact values [17, 18]. The long-known [4] 10–15% discrepancy of E_x^{LSD} from the exact value is largely corrected. Similarly, the large (100–200%) errors in E_c^{LSD}, which have been attributed [19] to the effect of the discrete atomic energy spectrum on E_c, are reduced by a factor of 5.

We also find that the SIC approach correctly predicts the stability of negative ions, in contrast to LSD which often has no self-consistent negative-ion solution [6], and to Hartree–Fock which seriously underestimates the binding. The observed electron affinities, and the ΔSCF- calculated affinities from the SIC and Hartree–Fock approaches, are respectively (in eV): H^- 0.8, 0.9, − 0.3; O^- 1.5, 1.6, − 0.5; F^- 3.4, 3.6, 1.4; Cl^- 3.6, 3.8, 2.6.

In the spirit of Koopmans' theorem, we would like to identify the eigenvalues of the one-electron Schrödinger equation with physical removal energies, at least for the more loosely-bound electrons for which relaxation effects are expected to be small. However, the change in the total energy functional due to removal of an electron from orbital $\alpha\sigma$, including relaxation, is strictly [16, 20] $-\int_0^1 dN_{\alpha\sigma}\epsilon_{\alpha\sigma}(N_{\alpha\sigma})$, and not $-\epsilon_{\alpha\sigma}(1)$ (the eigenvalue at full occupancy). Even for rather weakly-bound electrons, $\epsilon_{\alpha\sigma}$ depends strongly on $N_{\alpha\sigma}$ in LSD because of the spurious self-interaction in the one-electron potential. But in our SIC approach, since an electron is "forbidden" to interact with itself, $\epsilon_{\alpha\sigma}$ can depend on $N_{\alpha\sigma}$ only indirectly (hence less strongly), through the reflection back onto orbital $\alpha\sigma$ of its self-consistent effect on the other orbitals. Thus, to the extent that *physical* relaxation effects are small, the SIC eigenvalue gives the change in total energy functional due to removal of an electron.

The energy eigenvalues of the SIC approach do in fact approximate the corresponding ionization energies better than the LSD eigenvalues do. For example, the measured first ionization potentials [17] and the negatives of the corresponding SIC and LSD eigenvalues are respectively (in eV): He 24.6, 25.8, 15.3; Kr 14.0, 14.0, 9.4; Li 5.4, 5.4, 3.2; Cr 6.8, 6.7, 4.0.

Turning now to solids, we note that LD and LSD band calculations have had some striking successes in relating the band eigenvalues and related spectral functions to observed excitations. However, in many of the calculations for insulators, if additional approximations such as artificial exchange scaling are avoided, anomalously small optical gaps E_g are frequently obtained in LSD (e.g. [7–11]). We show in Table 3, along with the LD band structure error ΔE_g, the difference Δ_{SIC} between the LSD and SIC eigenvalue of the outermost atomic orbital forming the valence band edge (e.g. $2p$, $3p$, $4p$ for Ne, Ar, Kr respectively). Clearly the SI of this orbital accounts for almost 100% of the LSD error in the insulating gap of the solid. We also show in Table 3 the error of the LSD band structure prediction of the energy of core electrons, relative to vacuum, in the insulator LiF; again SI correction of the eigenvalue removes most of the discrepancy.

We next consider the implications of SIC for calculations of the cohesive energy E_B of metals within LSD [21]. These assume that E_B is the difference between the calculated atomic and solid LSD total energies, and agree closely with experiment except in the 3*d* transition series (e.g. E_B is overestimated by 70, 45, 45 and 25% for Mn, Fe, Co and Ni respectively [21]). It seems reasonable to assume that the *core* SI corrections are similar in the atom and the solid, and nearly cancel in E_B. This still leaves the SI corrections $-\delta_{\alpha\sigma}$ for the *valence* orbitals, which we find are sizeable for atomic 3*d* electrons (-0.1 to -1 eV/electron) on the scale of E_B (1–6 eV/atom). One is then tempted to analyze the discrepancies between the LSD and observed E_B as the result of incomplete cancellation between the SI corrections of the atomic 3*d* orbitals and the lesser SI corrections of the more diffuse Wannier-like orbitals in the solid. Using the LSD and observed E_B and our $\delta_{\alpha\sigma}$ values for atoms, we find that the valence SI in the *solid* ranges from 10% at the beginning to as much as 80% of the atomic value at the end of the 3*d* series. The same analysis yields negligible valence SI for the alkali metals (10^{-2}–10^{-3} eV), in accord with their free-electron character. This suggests that SI effects may be important in transition metal physics.

The numerical results of our orbital-functional calculations suggest that self-interaction corrections can dramatically improve the LSD approximation in atoms and in solids. In contrast to an orbital functional [16], a self-interaction-corrected density functional formalism would have several advantages, including the full sanction of the Hohenberg–Kohn–Sham theorems [1] and the computational convenience of a single, local one-electron potential for all orbitals. Such a formalism can be defined in principle as follows: (i) To each pair of trial spin densities $\rho_\sigma(\mathbf{r})$ there corresponds a pair of trial potentials $V^\sigma(\mathbf{r})$ which produce the same spin densities in a non-interacting system. Solve equation (2) using these potentials. (ii) Perform a unitary transformation (which leaves the spin densities invariant) of the resulting occupied molecular or Bloch orbitals to localized orbitals having maximal self-interaction, and so minimize the SI corrected total energy of equation (4). The result of this first minimization is the energy corresponding to $\rho_\uparrow$ and $\rho_\downarrow$; a further minimization over $\rho_\uparrow$ and $\rho_\downarrow$ gives the ground-state energy.

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