

Electron removal energies in Kohn-Sham density-functional theory

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Talman and co-workers have presented a realization of the *exact* Kohn-Sham density-functional theory, neglecting correlation. From their numerical results we conclude that the occupied orbital energy eigenvalues of the local-spin-density (LSD) approximation for exchange and correlation are close to the *exact* Kohn-Sham orbital energies (apart from a constant shift), but that the latter do *not* accurately predict the removal energies of tightly-bound electrons in atoms, molecules, and solids. For the calculation of these removal energies, we propose an add-on, single-shot self-interaction correction (SIC) to the LSD orbital energies, based on a simplification and representation-invariant transformation of the original SIC method. This correction's relationship to the Dyson mass operator is briefly discussed.

I. INTRODUCTION

Self-consistent-field theories of atoms, molecules, and solids commonly identify the energy needed to create a hole of quantum numbers $-\alpha, -\sigma$ (where the spin $\sigma = \uparrow$ or \downarrow) with $-\epsilon_{\alpha\sigma}$, where $\epsilon_{\alpha\sigma}$ is the energy eigenvalue of orbital $\psi_{\alpha\sigma}(\vec{r})$. This identification is made, not only in band-structure calculations for solids, but also in calculations of the local density of states

$$\rho(\vec{r}, \epsilon) = \sum_{\alpha\sigma} |\psi_{\alpha\sigma}(\vec{r})|^2 \delta(\epsilon - \epsilon_{\alpha\sigma}) \quad (1)$$

for clusters and disordered systems. The hope is that a single solution for the ground state will yield all the electron-removal energies, without recourse to a separate calculation for each excited state (which may lack the symmetry of the ground state).

Kohn and Sham¹ and von Barth and Hedin² have proposed a self-consistent-field theory which in principle yields the exact ground-state energy E , electron density n , and spin densities n_\uparrow and n_\downarrow , where

$$n(\vec{r}) = \int_{-\infty}^{\mu} d\epsilon \rho(\vec{r}, \epsilon) = n_\uparrow(\vec{r}) + n_\downarrow(\vec{r}) . \quad (2)$$

The orbitals are solutions of the equation (in atomic units where $\hbar = m = e^2 = 1$)

$$\left\{ -\frac{1}{2} \nabla^2 + v_{\text{eff}}^\sigma([n_\uparrow, n_\downarrow]; \vec{r}) \right\} \psi_{\alpha\sigma}(\vec{r}) = \epsilon_{\alpha\sigma} \psi_{\alpha\sigma}(\vec{r}) , \quad (3)$$

but no theorem identifies the orbital energies $\epsilon_{\alpha\sigma}$ with physical removal energies. The effective potential is

$$v_{\text{eff}}^\sigma = v_{\text{ext}}(\vec{r}) + u([n]; \vec{r}) + v_{\text{xc}}^\sigma([n_\uparrow, n_\downarrow]; \vec{r}) , \quad (4)$$

where v_{ext} is the external or nuclear potential,

$$u([n]; \vec{r}) = \int d^3r' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} \quad (5)$$

is the direct electrostatic potential, and v_{xc}^σ is the exchange-correlation potential. In practice the latter must be approximated, e.g., in the local-spin-density (LSD) approximation^{1,2}

$$v_{\text{xc}}^{\sigma, \text{LSD}} = \mu_{\text{xc}}^\sigma(n_\uparrow(\vec{r}), n_\downarrow(\vec{r})) , \quad (6)$$

where $\mu_{\text{xc}}^\sigma(n_\uparrow, n_\downarrow)$ is obtained from calculations for the uniform electron gas.

In actual calculations for atoms and solids, the LSD approximation yields rather good total energies and electron densities.³ The LSD values of $-\epsilon_{\alpha\sigma}$ are also good for the removal energies from valence bands in metals,^{4,5} and the LSD errors of the aforementioned properties are small enough that one may hope they will be corrected by recent improvements⁶ in the approximate density functionals. (Some calculations⁷ for valence and conduction bands of metals and semiconductors, using improved density functionals, have recently been reported.) However, the LSD values of $-\epsilon_{\alpha\sigma}$ seriously underestimate the removal energies from tightly-bound orbitals as well as the energy-band gaps in crystals.⁸

Recently a self-interaction correction (SIC) to the LSD approximation has been shown to yield orbital energies for atoms which may be interpreted as elec-

tron removal energies.⁸ The formal justification for this interpretation has been presented elsewhere⁸; here we will simply observe that in SIC (Ref. 8) as in many other self-consistent-field theories (e.g., Kohn-Sham⁹ and Hartree Fock⁸)

$$\epsilon_{\alpha\sigma} = \frac{\partial E}{\partial f_{\alpha\sigma}}, \quad (7)$$

where E is the total self-consistent-field energy including relaxation of the other orbitals in response to the change of occupation $f_{\alpha\sigma}$ of orbital $\alpha\sigma$. But in SIC, E varies almost linearly with $f_{\alpha\sigma}$ (see Fig. 1 of Ref. 10), making the electron removal energy $\sim \Delta E \approx -\epsilon_{\alpha\sigma}$ for $\Delta f_{\alpha\sigma} = -1$.

In SIC the exchange-correlation potential is orbital dependent,

$$v_{xc}^{\alpha\sigma, \text{SIC}}(\vec{r}) = \mu_{xc}^{\sigma}(n_{\uparrow}(\vec{r}), n_{\downarrow}(\vec{r})) - u([n_{\alpha\sigma}]; \vec{r}) - \mu_{xc}^{\uparrow}(n_{\alpha\sigma}(\vec{r}), 0), \quad (8)$$

where $n_{\alpha\sigma}$ is the orbital density:

$$n_{\alpha\sigma}(\vec{r}) = f_{\alpha\sigma} |\psi_{\alpha\sigma}(\vec{r})|^2. \quad (9)$$

The original SIC calculations were for atoms, but the method has been extended to rare-gas⁸ and ionic¹¹ crystals as well.

Since the exact Kohn-Sham exchange-correlation potential must also, like Eq. (8), be self-interaction free, the hope has been rekindled that the exact Kohn-Sham orbital energies might closely approximate physical removal energies. With regret we have come to the conclusion that this hope is in vain, and that the unphysical LSD orbital energies closely approximate the exact Kohn-Sham values, apart from an overall constant shift of all the occupied levels (roughly equal to the LSD self-interaction of the least-bound electron). In other words, a local effective potential of the Kohn-Sham type can yield the correct density but *not* also the correct removal energies; only an orbital-dependent (or nonlocal) potential can do both. Our conclusion

is based on the “exchange-only” approximation, which is justified for tightly bound orbitals where correlation is negligible compared to exchange.

Talman and co-workers¹² have constructed an *exact* realization of the Kohn-Sham potential for “exchange-only” in atoms, i.e., they have found the *local* potential $v_{\text{eff}}(\vec{r})$ whose orbitals yield an absolute minimum of the Hartree-Fock total energy functional. (The Hartree-Fock orbitals, which arise from a *nonlocal* effective potential, yield a lower minimum, but only by less than 50 ppm.¹²) In Table I we compare the exact Kohn-Sham orbital energies¹² $\epsilon_{\alpha\sigma}$ with LSD approximate values and with removal energies, all calculated for “exchange-only” in the Ar atom. (Similar results were found for other open- and closed-shell atoms.) The removal energies $\Delta E_{\alpha\sigma}|_{\text{rel}}$ were taken from Hartree-Fock total-energy differences, calculated with relaxed Hartree-Fock orbitals.¹³ The ground-state Hartree-Fock orbital energies,¹³ which by Koopmans’s theorem equal the unrelaxed total energy differences $\Delta E_{\alpha\sigma}|_{\text{unrel}}$, are also displayed. Note that when the LSD orbital energies are all shifted by the same constant, the results are close to the exact Kohn-Sham orbital energies, but the latter do not accurately predict the removal energies. From these results we can conclude in particular that LSD will give an accurate approximation to the occupied Kohn-Sham energy bands in solids, but this band structure will not predict the correct removal energies.

By construction the Talman¹² effective potential tends to zero as $r \rightarrow \infty$, like the LSD, SIC, and Hartree-Fock potentials. However, the exact Kohn-Sham potential whose orbital energies satisfy Eq. (7) tends to a small positive constant in this limit.¹⁴ The exact Kohn-Sham orbital energies ϵ_{nl} of Table I were obtained from the Talman¹² orbital energies by adding 0.05 hartrees, a value chosen to make $-\epsilon_{nl} = \Delta E_{nl}$ for the least-bound occupied orbital. This condition is an exact one¹⁴ within the

TABLE I. Orbital energies ϵ_{nl} and electron removal energies $\Delta E_{nl}|_{\text{rel}}$ for the Ar atom. HF: Hartree-Fock (Ref. 13). KS-X: Exact Kohn-Sham for “exchange only” (Ref. 12). LSD-X: Local spin-density approximation for exchange only. (All energies in hartrees.)

Orbital nl	HF		KS-X $-\epsilon_{nl}$	LSD-X	
	$-\epsilon_{nl}$	$\Delta E_{nl} _{\text{rel}}$		$-\epsilon_{nl}$	$-\epsilon_{nl} + 0.21$
1s	118.60	117.42	114.40	113.71	113.92
2s	12.31	11.94	11.10	10.73	10.94
2p	9.56	9.15	8.68	8.38	8.59
3s	1.28	1.22	1.04	0.83	1.04
3p	0.59	0.54	0.54	0.33	0.54

exact Kohn-Sham theory.

The Kohn-Sham formalism with its orbital-independent local effective potential is very convenient for self-consistent calculations. In particular, if we compare the LSD and original SIC schemes for a crystal, we find that only in the former scheme do we have a periodic effective potential, Bloch's theorem, strict orbital orthogonality, etc. We therefore ask whether there is some simple way to take the $-\epsilon_{\alpha\sigma}$ of a Kohn-Sham self-consistent calculation (e.g., in the LSD approximation) and correct them to yield physical removal energies.

In Sec. II we present a simplification and transformation of the original SIC method which does just this, and display the results. Section III connects our new expression to the Dyson mass operator and summarizes our conclusions.

II. SIMPLIFICATION OF THE SELF-INTERACTION CORRECTION

In this section we will consider the self-interaction correction for an atom, one of the building blocks of real systems. We will reduce the SIC method⁸ by approximations to its simplest viable form and then generalize the result to solids and other extended systems of interest.

We begin by noting that the self-exchange correction of Eq. (8) is simply

$$-\mu_x^1(n_{\alpha\sigma}(\vec{r}), 0) = 1.241n_{\alpha\sigma}^{1/3}(\vec{r}). \quad (10)$$

The self-direct correction is $-u([n_{\alpha\sigma}]; \vec{r})$ where

$$u([n]; \vec{r}) = \frac{\delta}{\delta n(\vec{r})} U[n] \quad (11)$$

and

$$U[n] = \frac{1}{2} \int d^3r \int d^3r' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|}. \quad (12)$$

The direct electrostatic energy $U[n]$ also has a local-density approximation¹⁵

$$U[n] \approx 1.085N^{2/3} \int d^3r n^{4/3}(\vec{r}), \quad (13)$$

where $N = \int d^3r n(\vec{r})$. Equation (13) is exact for exponential densities $n(r) = ae^{-br}$, and a good approximation for many other spherically symmetric densities. The functional derivative from Eq. (11), applied to Eq. (13), tells us that

$$u([n]; \vec{r}) \approx \frac{4}{3}(1.085)N^{2/3}n^{1/3}(\vec{r}) + \frac{2}{3}(1.085)N^{-1/3} \int d^3r' n^{4/3}(\vec{r}'). \quad (14)$$

The second term on the right-hand side of Eq. (14) is just a constant—it represents the attempt of the local approximation to imitate the long-range ($\propto N/r$) behavior of $u([n]; \vec{r})$. We now evaluate (14) for the orbital density $n_{\alpha\sigma}(\vec{r})$, for which $N=1$, and combine this with Eq. (10) to estimate the complete self-interaction correction to the potential seen by orbital $\alpha\sigma$:

$$-0.206n_{\alpha\sigma}^{1/3}(\vec{r}) - \mu_c^1(n_{\alpha\sigma}(\vec{r}), 0) - \frac{2}{3}(1.085) \int d^3r' n_{\alpha\sigma}^{4/3}(\vec{r}'). \quad (15)$$

The first term here is the small residue of the cancellation of two larger terms. It tends to cancel further against $-\mu_c^1(n_{\alpha\sigma}(\vec{r}), 0)$, the negative of the correlation potential which is also small. Neglecting these terms, we are left with a self-interaction correction to the effective potential which is *constant in space* but *orbital dependent*. This correction shifts each unphysical LSD eigenvalue into better agreement with the physical removal energy,

$$\begin{aligned} \Delta E_{\alpha\sigma} |_{\text{rel}} &\approx -\epsilon_{\alpha\sigma}^{\text{SIC}} \\ &\approx -\epsilon_{\alpha\sigma}^{\text{LSD}} + 0.723 \int d^3r n_{\alpha\sigma}^{4/3}(\vec{r}), \end{aligned} \quad (16)$$

while it leaves each LSD orbital $\psi_{\alpha\sigma}(\vec{r})$ unchanged. We have tested Eq. (16) in numerical calculations for atoms; it works about as well as the full, original, self-consistent SIC orbital energy (see Table II).

To see if the self-interaction correction to the LSD effective potential is really constant in space, we have plotted it [from Eq. (8)] for the copper atom in Fig. 1. Over the radial extent of the orbital to which it belongs, the variation of this potential is indeed small.

In atoms the LSD and SIC orbitals $\psi_{\alpha\sigma}(\vec{r})$ are closely similar, but this is *not* true in crystals, where the LSD orbitals are extended Bloch functions while the self-consistent SIC orbitals are localized on one or a few atoms. In crystals, Eq. (16) may continue to work for SIC orbital densities, but cannot work for LSD orbital densities. The latter are periodically extended over the volume Ω of the crystal and yield a correction of order $\Omega^{-1/3}$ which vanishes as $\Omega \rightarrow \infty$.

In order to correct the LSD orbital energies in *both* atoms and extended systems, we seek an addition correction similar to Eq. (16) with the following properties: (a) Like Eq. (16), it should scale as an exchange energy [i.e., as γ under the scale transformation $n_{\alpha\sigma}(\vec{r}) \rightarrow \gamma^3 n_{\alpha\sigma}(\gamma\vec{r})$], and it should in this way measure the degree to which orbital $\psi_{\alpha\sigma}(\vec{r})$ is

TABLE II. Experimental electron removal energies $\Delta E_{nl} |_{\text{rel}}$ (from Ref. 16) in atomic Ni $3d^8 4s^2$, compared with LSD and original SIC (Ref. 8) orbital energies ϵ_{nl} and with the results of Eqs. (16) and (17). (All energies in hartrees. To facilitate comparison with experiment, the calculations were done relativistically using the expressions summarized in Ref. 19. All energies were averaged over the magnetic quantum numbers.)

Orbital	$\Delta E_{nl} _{\text{rel}}^{\text{exper}}$	$-\epsilon_{nl}^{\text{LSD}}$	$-\epsilon_{nl}^{\text{SIC}}$	Eq. (16)	Eq. (17)
1s	306.8	300.2	307.8	306.0	306.1
2s	37.63	35.92	37.24	37.21	37.18
2p	32.2	30.97	32.64	32.28	32.21
3s	4.59	4.05	4.44	4.65	4.45
3p	3.01	2.61	2.99	3.11	2.98
3d	0.62	0.34	0.68	0.65	0.63
4s	0.330	0.215	0.321	0.360	0.313

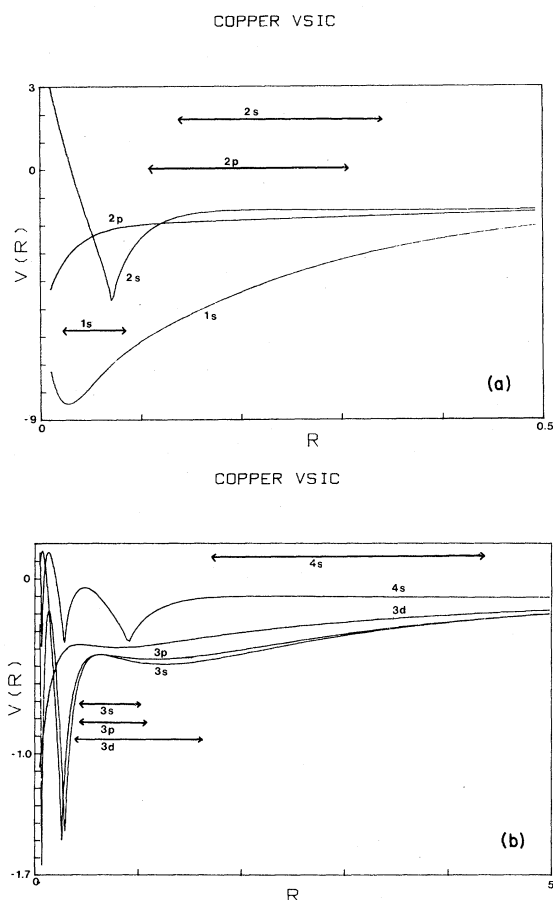


FIG. 1. Orbital-dependent self-interaction correction to the LSD effective potential in the copper atom (atomic units). The radial extent of each orbital, $\langle r \rangle \pm \Delta r$ where $\Delta r = (\langle r^2 \rangle - \langle r \rangle^2)^{1/2}$, is indicated by a horizontal bar. (a) Inner core orbitals. (b) Outer core and valence orbitals.

concentrated close to the nuclei. (b) Like Eq. (16), it should be a self-interaction correction, dependent mainly on the orbital density $n_{\alpha\sigma}(\vec{r}) = |\psi_{\alpha\sigma}(\vec{r})|^2$ or at most on the local density of states $\rho(\vec{r}, \epsilon)$ of Eq. (1), evaluated at $\epsilon = \epsilon_{\alpha\sigma}^{\text{LSD}}$. Other desirable properties are suggested by the Dyson mass operator discussed in Sec. III: (c) The correction should vanish for an electron gas of uniform density. (d) Unlike Eq. (16), it should be expressible as the expectation value for the orbital $\psi_{\alpha\sigma}(\vec{r})$ of a *representation-invariant* object such as $n(\vec{r})$ or $\rho(\vec{r}, \epsilon)$. (Both are invariant under unitary transformations which mix degenerate occupied orbitals, such as the transformations among traveling plane waves, standing plane waves, and free spherical waves in a uniform electron gas.)

A simple expression which realizes these properties is

$$\Delta E_{\alpha\sigma} |_{\text{rel}} \approx -\epsilon_{\alpha\sigma}^{\text{LSD}} + 0.104 \times \int d^3r |\psi_{\alpha\sigma}(\vec{r})|^2 \frac{\hat{u} \cdot \vec{\nabla} \rho(\vec{r}, \epsilon)}{\rho(\vec{r}, \epsilon)} \Big|_{\epsilon = \epsilon_{\alpha\sigma}^{\text{LSD}}}, \quad (17)$$

where \hat{u} is a unit vector in the direction of $\vec{\nabla} n(\vec{r})$. In this expression all the required inputs may be taken directly from the outputs of an LSD calculation.

If the orbital $\psi_{\alpha\sigma}(\vec{r})$ belongs to a closed subshell of an isolated atom, then $\rho(\vec{r}, \epsilon)$ becomes [apart from the constant factor $\rho(\epsilon) = \sum_{\alpha\sigma} \delta(\epsilon - \epsilon_{\alpha\sigma})$] the spherical average of the orbital density $n_{\alpha\sigma}(\vec{r}) = |\psi_{\alpha\sigma}(\vec{r})|^2$. For practical reasons, all SIC calculations to date have employed this spherical average. The constant 0.104 in Eq. (17) was chosen to make (17) identically equal to (16) for the special

case of hydrogenic 1s orbitals.

Equation (17) has in fact only been “derived” for 1s orbitals, just as the LSD approximation is only derived for an electron gas of slowly varying density. However, the actual range of validity of each is far greater. We have tested Eq. (17) in numerical calculations for 16 atoms ranging from hydrogen to mercury; in comparison with experimental values¹⁶ for the electron removal energies $\Delta E_{\alpha\sigma}|_{\text{rel}}$ from all occupied orbitals, it agrees as well as the full, original, self-consistent SIC orbital energy $-\epsilon_{\alpha\sigma}^{\text{SIC}}$. Typical results for the nickel atom are shown in Table II.

Equation (17) may also be applied to crystals. It is instructive to consider the deep core orbitals, which in LSD are tight-binding Bloch orbitals [i.e., $\alpha = n', \vec{k}$ in Eq. (17)]. For these orbitals the orbital density

$$|\psi_{n',\vec{k}}(\vec{r})|^2 = |\psi_{nl}(\vec{r})|^2 / N_a$$

is distributed periodically over all N_a atoms in the crystal, so the correction of Eq. (17) is *size consistent*, i.e. independent of N_a . Note that previous versions of SIC for crystals^{8,11} have had to appeal to a special, localized orbital representation in order to avoid a size-consistency problem. Note further that if we *did* decide to use localized Wannier functions (i.e., $\alpha = n, l$) in Eq. (17), the orbital density would be $|\psi_{nl}(\vec{r})|^2$ on *one* atom and zero elsewhere, and we would obtain the *same* self-interaction correction that was found in the Bloch representation. The physical analog of this invariance is the fact that a long-lived deep core hole would remain localized on one atom for a long time on the microscopic scale, and yet become delocalized over longer times as it hopped to neighboring atoms.

Since Eq. (17) clearly works well for deep core levels, we also expect it to improve the LSD description of all the occupied bands in rare-gas and ionic crystals. Indeed, preliminary linearized augmented plane-wave (LAPW) calculations for LiCl using Eq. (17) display about the same improvement in the fundamental band gap that was found in a much more elaborate implementation¹¹ of SIC. However, it is not clear what to expect for the valence electrons in semiconductors and especially metals, where the sharp atomic levels have been smeared out into broad bands. Perhaps $\rho(\vec{r}, \epsilon)$ should be replaced by

$$\Delta^{-1} \int_{\epsilon-\Delta/2}^{\epsilon+\Delta/2} d\epsilon' \rho(\vec{r}, \epsilon'),$$

where Δ is the bandwidth. Preliminary estimates

for metallic copper and nickel, using the renormalized-atom⁴ orbitals, suggest that Eq. (17) seriously overshoots the correction needed in the valence band, and that this overshoot is reduced but not eliminated by energy smearing of $\rho(\vec{r}, \epsilon)$. To clarify this situation, LAPW band-structure calculations with realistically delocalized orbitals are currently being set up.

III. DYSON MASS OPERATOR AND CONCLUSIONS

Dyson’s quasiparticle equation¹⁷ is

$$\begin{aligned} & -\frac{1}{2} \nabla^2 \chi_{\alpha\sigma}(\vec{r}, E) \\ & + \int d^3r' \Sigma_{\sigma}(\vec{r}, \vec{r}', E) \chi_{\alpha\sigma}(\vec{r}', E) \\ & = \epsilon_{\alpha\sigma}(E) \chi_{\alpha\sigma}(\vec{r}, E), \end{aligned} \quad (18)$$

where E and $\epsilon_{\alpha\sigma}(E)$ are complex. The real part of E which minimizes $|E - \epsilon_{\alpha\sigma}(E)|$ is the energy separation from the ground state of an approximate eigenstate of the $N-1$ particle system,¹⁷ corresponding to a hole of quantum numbers $-\alpha, -\sigma$.

Comparison of Eq. (18) with Eqs. (3)–(6) and (17) suggests the identification

$$\begin{aligned} \text{Re} \Sigma_{\sigma} & \approx \delta(\vec{r} - \vec{r}') \\ & \times \left[v_{\text{eff}}^{\sigma, \text{LSD}}(\vec{r}) \right. \\ & \left. - 0.104 \frac{\hat{u} \cdot \vec{\nabla} \rho(\vec{r}, \epsilon)}{\rho(\vec{r}, \epsilon)} \Big|_{\epsilon = \text{Re} E} \right] \end{aligned} \quad (19)$$

for tightly bound electrons in systems built up from atoms. Thus the mass operator Σ_{σ} differs from the LSD effective potential by a negative self-interaction correction proportional to $\hat{u} \cdot \vec{\nabla} \rho(\vec{r}, \epsilon) / \rho(\vec{r}, \epsilon)$, which is roughly constant over the radial extent of the atomic shell to which it belongs (as a consequence of the piecewise exponential¹⁸ character of the density in an atom). As a result, the quasiparticle orbital $\chi_{\alpha\sigma}(\vec{r}, E)$ is about equal to the LSD orbital $\psi_{\alpha\sigma}(\vec{r})$, but their respective orbital energies are different. Equation (17) then emerges by regarding $\Sigma_{\sigma} - v_{\text{eff}}^{\sigma, \text{LSD}}$ as a first-order perturbation on the LSD solution. Equation (17) also makes sense for a spin-unpolarized electron gas of *uniform* density n , where $\vec{\nabla} \rho(\vec{r}, \epsilon) / \rho(\vec{r}, \epsilon) = 0$ and where the exchange-correlation piece of the mass operator is known¹⁷ to be close to $\mu_{\text{xc}}^{\sigma}(n/2, n/2) \delta(\vec{r} - \vec{r}')$.

We summarize our conclusions as follows: (1) Apart from a constant shift of all the occupied lev-

els, the LSD orbital energies are close to the exact Kohn-Sham orbital energies. Further refinements⁶ of the Kohn-Sham exchange-correlation potential can only produce small changes in the orbital energy *differences* between occupied levels. (2) The exact Kohn-Sham orbital energies will not accurately describe electron removal energies from tightly bound levels. However, improved removal energies may be found from an LSD calculation by means of the add-on correction of Eq. (17). This correction may be thought of as a size-consistent self-interaction correction or as an approximation to the difference between the Dyson mass operator and the

LSD effective potential. It may be applied to all the orbitals of an atom, and to the more tightly bound orbitals in molecules and solids, with no need to appeal to a special, localized orbital representation.

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