Self-interaction correction for the Wannier representation of the uniform electron gas

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The self-interaction correction (SIC) to the local-density approximation is evaluated for the total energy in the Wannier representation of plane waves and is found to be a small, but positive, number. This indicates that the delocalized plane waves are the correct solution of the SIC equations for a uniform electron gas, and thus this calculation provides a good consistency check on the SIC method.

The self-interaction correction to the local-density approximation (LDA) is a state-dependent correction that explicitly subtracts off the spurious self-interaction present in the LDA potential.[1] It has been applied with success to atoms[1] and insulators.[2,3] In the Bloch representation, the SIC correction to the average energy of an electron in the uniform electron gas vanishes. This can easily be shown as follows (we ignore correlation). The SIC correction to the total energy in hartrees is

$$E_{\rm SIC}=-\frac{1}{2}\sum_{\alpha}\int\frac{\rho_\alpha(\vec{r})\rho_\alpha(\vec{r}')}{|\vec{r}-\vec{r}'|}d^3r\,d^3r' +0.9305\sum_{\alpha}\int\rho_\alpha^{4/3}(\vec{r})d^3r \quad , \tag{1}$$

the first piece being the self-Coulomb term and the second being the self-exchange term where ρ_α is the density of orbital α and the sum is over all occupied orbitals. For plane-wave orbitals with wave functions $\Psi_\alpha(\vec{r})=V^{-1/2}e^{i\vec{k}\cdot\vec{r}}$, where $\vec{k}$ is a wave vector and V the volume of the crystal and density $\rho_\alpha(\vec{r})=V^{-1}$, we have

$$E_{\rm SIC}=-\tfrac{1}{2}V^{-2}\sum_{\sigma,\vec{k}}\int\frac{d^3r\,d^3r'}{|\vec{r}-\vec{r}'|} +0.9305\,V^{-4/3}\sum_{\sigma,\vec{k}}\int d^3r \quad . \tag{2}$$

The sum over $\vec{k}$, σ yields N, the number of electrons (σ is the spin). Thus the average SIC energy per electron, $E_{\rm SIC}/N$, clearly vanishes as $V^{-1/3}$ in the limit as V goes to infinity.

Since the SIC equations are not invariant under unitary transformations, the big question is whether there exists another solution to the SIC equations for the uniform electron gas which is localized and has a lower average energy than the plane waves. Such a solution would be erroneous because the LDA is already exact for a uniform electron gas. We thus propose to do a Wannier transformation on the plane waves and evaluate the SIC correction for this localized representation. For this purpose we introduce a fictitious close-packed lattice with two electrons per unit cell.

The Wannier transformation of the plane wave is[4]

$$\Phi(\vec{r}-\vec{R})=V_0^{-1}\int_{V_0}d^3k\,e^{-i\vec{R}\cdot\vec{k}}\Omega_0^{-1/2}e^{i\vec{k}\cdot\vec{r}} \quad , \tag{3}$$

where $\vec{R}$ is a lattice site vector, V_0 is the volume of the first Brillouin zone, and Ω_0 is the unit-cell volume (chosen so as to correctly normalize the Wannier solution). We choose a spherical zone for computational simplicity and thus let $V_0=\frac{4}{3}\pi k_F^3=8\pi^3/\Omega_0$, where k_F is the radius of the spherical zone. The integral in Eq. (3) is easily evaluated to yield

$$\Phi(\vec{r}-\vec{R})=3\,\Omega_0^{-1/2}(\sin x-x\cos x)/x^3 \quad , \tag{4}$$

where $x=k_F|\vec{r}-\vec{R}|$.

We examine the exchange integral first:

$$E_{\rm SIC}^{x}=0.9305\sum_{\vec{R},\sigma}\int\rho^{4/3}(\vec{r}-\vec{R})d^3r \tag{5}$$

where $\rho=\Phi^2$. The sum over $\vec{R}$, σ yields N. Using $\Omega_0=6\pi^2/k_F^3$ and changing variables to x we obtain

$$E_{\rm SIC}^{x}/N=0.9305\left(\frac{9k_F^3}{6\pi^2}\right)^{4/3}\left(\frac{4\pi}{k_F^3}\right) \times\int_0^\infty x^2(\sin x-x\cos x)^{8/3}x^{-8}dx \quad . \tag{6}$$

The integral was evaluated numerically and yielded $\simeq 0.1442$. Thus $E_{\rm SIC}^{x}/N\simeq 0.1368k_F$ (note we are in atomic units with $\hbar=m=e^2=1$).

We next evaluate the Coulomb integral

$$E_{\rm SIC}^{\rm Coul}=-\tfrac{1}{2}\sum_{\vec{R},\sigma}\int\frac{\rho(\vec{r}-\vec{R})\rho(\vec{r}'-\vec{R})}{|\vec{r}-\vec{r}'|}d^3r\,d^3r' =-\frac{N}{2}\int\frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}d^3r\,d^3r' \quad . \tag{7}$$

We write this as

$$E_{\mathrm{SIC}}^{\mathrm{Coul}}/N = -\tfrac{1}{2}\int 4\pi r^2 \rho(r)\phi(r)\,dr \ , \tag{8a}$$

$$\phi(r) = \int \frac{d^3\vec{r}'\rho(r')}{|\vec{r}-\vec{r}'|} = \int_r^\infty E(r')\,dr' \ , \tag{8b}$$

$$E(r') = \left(\frac{1}{r'}\right)^2 \int_0^{r'} dr\, 4\pi r^2 \rho(r) \ . \tag{8c}$$

Again numerically evaluating these integrals we obtain $E_{\mathrm{SIC}}^{\mathrm{Coul}} \simeq -0.1308 k_F$.

The addition of these two terms yields $0.0060 k_F$, a positive number. For a face-centered cubic lattice with $\Omega_0 = a^3/4$ and $a = 6.8309$ a.u. (corresponding to copper) we obtain $E_{\mathrm{SIC}}/N \simeq 0.0054$ hartrees, a small energy. The inclusion of correlation will only make this number more positive. Thus localizing the plane waves via a Wannier transformation raises the total energy and therefore it is not a variational minimum. This is a good indication that the orbitals which minimize the SIC total energy for the uniform electron gas are indeed plane waves.

We have looked at Lin's method[3] for solving the SIC equations for extended systems. Lin's method involves using the Wannier representation to evaluate the SIC correction to the total energy, but minimizes the total energy with respect to the Bloch orbitals. For the electron gas, we found that Lin's method gave a slightly nonuniform solution (i.e., a spurious charge-density wave with small amplitude). This can trivially be seen since any variation of the coefficients of the Wannier expansion will lead to a nonconstant amplitude in the density. The SIC correction to the energy would be lower than our result, but, we suspect, not by much. Except at abnormally low densities, such a charge-density wave will also raise the LDA piece of the energy,[5] in further support of our conclusions.

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