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Localization in the self-interaction-corrected density-functional formalism

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We show that the self-interaction-corrected (SIC) local spin-density (LSD) approximation can describe localization in a system where the Coulomb interaction is large compared with the bandwidth. In contrast with the normal LSD approximation, the SIC approximation can be used for a band with orbital degeneracy, even if the band is not half filled. The method is applied to the one-dimensional Hubbard model for which there is an exact solution. The total energy, the band gap, the local moment, and the momentum distribution are substantially better described than in the LSD approximation. For some of these properties the SIC approach is shown to compare favorably with the Gutzwiller ansatz.

The basic physics of localization in, e.g., a Mott insulator or in the $\alpha-\gamma$ transition in Ce, is well understood. The quantitative description of these effects in an *ab initio* theory, such as the density functional (DF) formalism, is, however, difficult. In the α phase of Ce the $4f$ spin is screened by the conduction electrons due to the Kondo mechanism. This increases the cohesive energy and gives a negative contribution to the pressure.[1] In the γ phase, on the other hand, the $4f$ contribution to the cohesion is very small.[1] In a DF calculation in the local spin-density (LSD) approximation, Glötzel found that Ce becomes ferromagnetic at a lattice parameter which approximately corresponds to γ Ce.[2] Minority spin $4f$ electrons in bonding states are then transferred to less bonding majority spin states, and there is a partial loss of the $4f$ contribution to the pressure. Since, however, the $4f$ band is far from being half full, the spin-up band in the ferromagnetic phase is only partly occupied and a substantial $4f$ pressure remains. The total pressure is far from zero, and the LSD approximation does not predict a stable γ phase.[2] In the $3d$-oxide series, the $3d$ electron shows localized behavior in MnO and in the systems to the right of MnO. In the LSD approximation the corresponding loss of cohesion is well described as an increase in the lattice parameters.[3] In MnO, which has a half-filled $3d$ band, the $3d$ pressure is negligible, and the gap is sizable. For FeO, CoO, and NiO, where the $3d$-band is more than half full, the gap is, however, much too small or zero.[4] In analogy to MnO, the LSD approximation seems to describe localization well for Am, which has a half-filled $5f$ shell.[5]

An alternative way of describing localization in the DF formalism is provided by the self-interaction-corrected (SIC) LSD approximation.[6] The exchange-correlation (XC) energy functional is approximated as

$$E_{XC}^{SIC}[n]=E_{XC}^{LSD}[n]-\sum_i^{\mathrm{occ}}\left(\int d^3r\,d^3r'\frac{n_i(\mathbf{r})n_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+\int d^3r\,n_i(\mathbf{r})\varepsilon_{XC}(n_i(\mathbf{r}),0)\right)\,, \tag{1}$$

where $n_i(\mathbf{r})$ is the charge density corresponding to orbital i and $\varepsilon_{XC}(n_\uparrow,n_\downarrow)$ is the XC energy of a homogeneous system with the spin densities $n_\uparrow$ and $n_\downarrow$. The second term subtracts the nonphysical Coulomb interaction of an electron with itself as well as the corresponding LSD XC energy. The corresponding XC potential for orbital i with spin σ is

$$v_{XC,\sigma,i}^{SIC}(\mathbf{r})=v_{XC,\sigma}^{LSD}(n_\uparrow(\mathbf{r}),n_\downarrow(\mathbf{r}))-\int d^3r'\frac{n_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}-v_{XC,\uparrow}^{LSD}(n_i(\mathbf{r}),0)\,, \tag{2}$$

where $v_{XC,\sigma}^{LSD}(n_\uparrow,n_\downarrow)$ is the LSD XC potential. An important property of the SIC potential is its orbital dependence, which may lead to broken-symmetry solutions, where, for instance, one orbital localizes on each site. In contrast, the LSD approximation gives delocalized solutions for periodic systems. To be more specific, let us assume that there is one electron and one orbital with the degeneracy M per atom. The on-site Coulomb interaction is U and the hopping integral is t. We now form a trial solution, where the ith one-particle solution of the Kohn-Sham equation is assumed to be the m_ith orbital on the l_ith site. The potential for the ith solution is then zero on the l_ith site and repulsive on all other sites. In the first iteration this solution expands somewhat and it obtains weight on neighboring sites. This raises the potential on the central site and lowers it on the neighboring sites. If $U\gg t$ the solution can, however, stay essentially localized when the problem is iterated to convergence. This solution reduces the Coulomb interaction at the cost of an increase in kinetic energy, as one expects for the proper solution in this $U\gg t$ limit. This approach works also for a band filling which differs from $\frac{1}{2}$ (here $1/M$), since the $M-1$ unoccupied orbitals feel a repulsive potential on all sites and form extended states at higher energies than the occupied ones. In the limit $t\rightarrow 0$ for the simple model discussed above, SIC gives the exact result for the interaction energy and the ionization potential, while the LSD approximation in particular fails for the latter property.

Similar arguments apply to systems with several electrons per atom.

To study the SIC approach we perform calculations for the monoatomic hydrogen solid as a function of the lattice parameter. This system often serves as a model for a Mott insulator. Kelly, Rice, and Andersen[7] and Min, Oguchi, Jansen, and Freeman[8] have studied the hydrogen solid within the LSD approximation. Of particular interest is the Hubbard model of a hydrogen solid, since for the one-dimensional version there is an exact solution to compare with. Thus we study the one-dimensional Hamiltonian

$$H=\sum_{\sigma}\left(\sum_{i=1}^{N}\varepsilon_0\hat{n}_{i\sigma}+t\sum_{i=1}^{N}(\psi_{i+1\sigma}^{\dagger}\psi_{i\sigma}+\text{H.c.})\right)+U\sum_{i=1}^{N}\hat{n}_{i\uparrow}\hat{n}_{i\downarrow}\ , \tag{3}$$

where ε_0 is the energy of the $1s$ level, t is the hopping integral, and U is the Coulomb interaction. We use a cyclic chain, i.e., $N+1$ stands for 1 in (3). The $N=\infty$ model was solved exactly by Lieb and Wu.[9] We choose $\varepsilon_0=-1$ Ry and $U=0.945$ Ry, since in the atomic limit $t=0$ these parameters give the correct ionization energy and affinity energy of a H atom.[10] We use a discrete version of the DF formalism,[11] where the XC energy is a functional of the occupation numbers $n_{i\sigma}\equiv\langle\hat{n}_{i\sigma}\rangle$. For the LSD functional we take the form

$$E_{\text{XC}}^{\text{LSD}}[n_{i\sigma}]=U\sum_{i}(n_{i\uparrow}+n_{i\downarrow})^{4/3}\{-a-b[(1+\zeta_i)^{4/3}+(1-\zeta_i)^{4/3}-2]/(2^{4/3}-2)\}\ , \tag{4}$$

where $\zeta_i=(n_{i\uparrow}-n_{i\downarrow})/(n_{i\uparrow}+n_{i\downarrow})$. We use $a=0.3840$ and $b=0.0705$, since the functional (4) then reproduces the LSD results for the total energy ($E=-0.96$ Ry) and for the position of the spin-down eigenvalue $\varepsilon_{1s\downarrow}=-0.20$ Ry of a free H atom.[12] The adjustment to $\varepsilon_{1s\downarrow}$ is important, since it determines the affinity level for large lattice parameters.

The SIC potential (2) is orbital dependent, and the corresponding eigenstates are not automatically orthogonal. We therefore have to find an extremum of the SIC-LSD functional under the subsidiary condition that the orbitals are orthogonal. In the SIC N-electron state one localized orbital per atom is occupied. We find that the lowest energy is obtained for an antiferromagnetic (AF) occupation with a spin-up electron on every second site. The lowest LSD solution is also an AF solution. In Fig. 1 we compare the SIC total energy with the exact solution[9] and the AF-LSD solution. The SIC-LSD solution is very close to the exact result over the whole parameter range, while the AF-LSD solution is too low in energy for small values of $U/(4t)$ and too high for large values. The error for large values of $U/(4t)$ represents the well-known LSD error for an H atom, where the LSD approximation incorrectly gives a weak interaction of the electron with itself.[13] The SIC-LSD calculation is exact in the atomic limit ($t=0$), and the behavior for $t\rightarrow 0$ is well described. The binding energy per atom goes as $-At^2/U$ for small t, where $A=2.77$ and 2.35 in the exact and SIC-LSD calculations, respectively. The Gutzwiller ansatz, without the introduction of any further approximations in the evaluation of the expectation values,[14] gives a nonanalytical behavior $-1.621t^2/[U\ln(\pi U/4t)]$ for small t. A modification of the Gutzwiller approximation has been shown to give an analytical behavior with $A=2.75$.[15] Also for large values of t the SIC-LSD functional gives substantially better results than the AF-LSD calculation. The energy goes as $-4t/\pi+kU$, where $k=0.250$, 0.250, 0.247, and 0.116 in the exact, the Gutzwiller, the SIC-LSD, and the AF-LSD calculations, respectively.

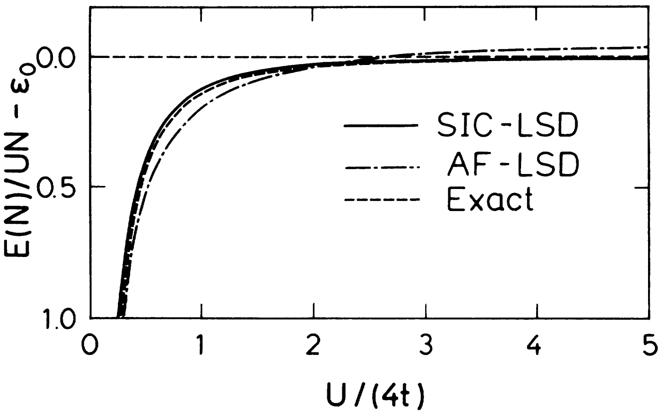

FIG. 1. The total energy $E(N)/N$ per site as a function of $U/(4t)$, where $4t$ is a measure of the bandwidth in a one-particle calculation and $N=256$. The full curve shows the SIC-LSD result, the dashed curve represents the exact result for an infinite chain (Ref. 9), and the dashed-dotted curve represents the AF-LSD result. Here $U=0.945$ Ry and $\varepsilon_0=-1$ Ry.

In Fig. 2 the energy gap E_g is shown as a function of

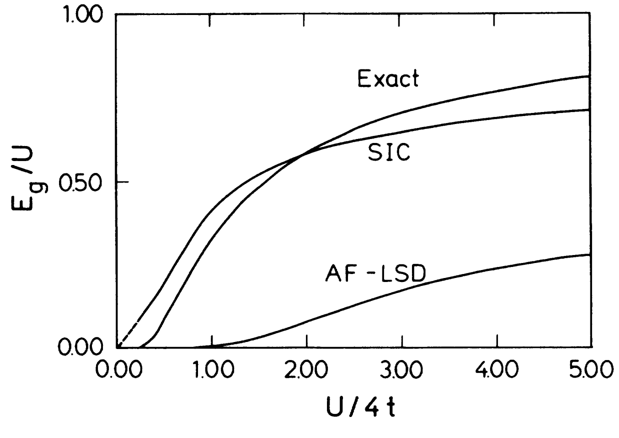

FIG. 2. The band gap E_g as a function of $U/(4t)$.

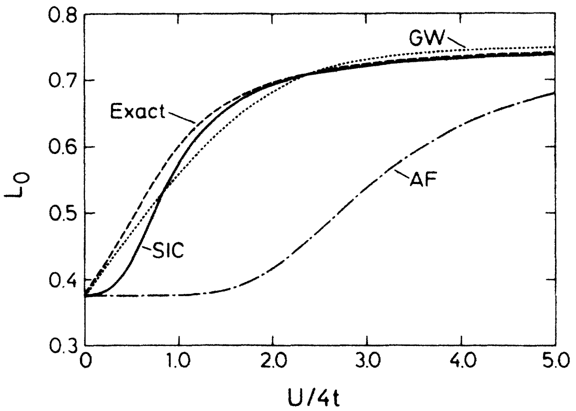

FIG. 3. The local moment L_0 [see (6)] as a function of $U/(4t)$. The notations are the same as in Fig. 1. The Gutzwiller (GW) result (Ref. 14) is shown by the dotted curve.

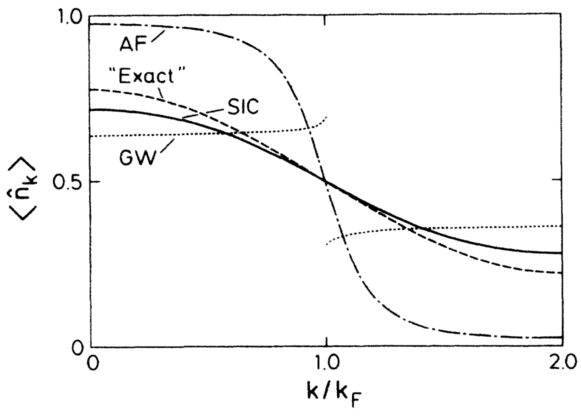

FIG. 4. The momentum distribution $\langle \hat{n}_k \rangle$ as a function of k/k_F for $U/t=10$ according to the SIC-LSD (full curve); Takahashi ("Exact"), shown by the dashed curve (Ref. 16); the AF-LSD, shown by the dashed-dotted curve; and the Gutzwiller (GW) calculations, represented by the dotted curve (Ref. 14).

$U/(4t)$, where E_g is defined as

$$E_g=\mu_+-\mu_- \\ =E(N+1)-E(N)-[E(N)-E(N-1)] \ , \quad (5)$$

and $E(K)$ is the energy of a system with K electrons. In the SIC $N+1$ electron state, an itinerant state is occupied in addition to the N localized states. For $t \rightarrow 0$, this state has weight only on atoms where the localized state has the opposite spin, and its energy is given by the LSD energy eigenvalue $\varepsilon_{1s\downarrow}=-0.20$ Ry (Ref. 12) of a free H atom. For $t \rightarrow 0$, $\mu_+=\varepsilon_{1s\downarrow}$ according to both the AF-LSD and SIC-LSD calculations, which differs by 0.14 Ry from the exact result -0.06 Ry.[10] For the $N-1$ electron SIC state, we find that, except for very small values of t, the lowest energy is obtained for a state with the occupation $\uparrow\downarrow\uparrow\downarrow \cdots \downarrow\uparrow\downarrow\uparrow$. Here "$\cdots$" denotes a spin-up solution, which is essentially localized to two sites. In the limit $t \rightarrow 0$ the SIC calculation gives $\mu_-=-1$ Ry, which is the exact result, while the AF-LSD result is $\mu_-=0.63$ Ry. Figure 2 shows that the SIC-LSD functional correctly predicts a gap for the whole parameter range. The gap goes to zero too slowly for small values of $U/(4t)$ and it is somewhat too small for large values of $U/(4t)$. The latter deviation reflects the error in μ_+ discussed above. The results are substantially better than in the AF-LSD approximation. It has been found earlier that SIC improves the gaps of ionic and rare-gas solids. In these cases, the valence and conduction bands have different characters, and the SIC improvement of the gap is due to the SIC corrections being different for the different types of levels, e.g., for the Ne $2p$ and $3s$ levels in a Ne rare-gas solid. For the Hubbard model there is only one type of level, and it is then crucial for the band gap that the SIC potential is allowed to determine the spatial extent of the one-particle solutions of the system.

Figure 3 shows results for the local moment defined as

$$L_0=\langle S^2\rangle=\tfrac{3}{4}\langle \hat{n}_{i\uparrow}+\hat{n}_{i\downarrow}-2\hat{n}_{i\uparrow}\hat{n}_{i\downarrow}\rangle \ , \quad (6)$$

which is a measure of the localization. For a completely localized system $\langle \hat{n}_{i\uparrow}\hat{n}_{i\downarrow}\rangle=0$ and $L_0=\frac{3}{4}$, while for $t \gg U < \hat{n}_{i\uparrow}\hat{n}_{i\downarrow}\rangle \approx 0.25$ and $L_0 \approx \frac{3}{8}$. The SIC-LSD results for L_0 grow too slowly for small values of $U/(4t)$, but are otherwise close to the exact ones. This is in contrast with the AF-LSD solution, which has substantial errors for almost the whole parameter range. The Gutzwiller calculation[14] agrees well with the exact results for small values of $U/(4t)$, but it gives too small values of L_0 for intermediate values of U and too large values for large U.

Figure 4 shows results for the momentum distribution $\langle \hat{n}_k\rangle$. The SIC-LSD, the AF-LSD, and the Gutzwiller[14] calculations are compared with a calculation of Takahashi,[16] which is correct to second order in t/U. The SIC-LSD result is close to the calculation of Takahashi, which should be very close to the exact results for the small value of t/U ($=0.1$) considered here. The Gutzwiller calculation incorrectly gives a large discontinuity, although the system is an insulator.

We have shown that the SIC-LSD approximation can describe localization for a system with one (or several) electron(s) per atom, even if the system has a band with orbital degeneracy. This appears to be the greatest advantage over the traditional LSD approximation. In the present paper we have applied the formalism to the one-dimensional Hubbard model without orbital degeneracy, for which the exact solution is known, and demonstrated that also in this case the SIC-LSD approximation gives substantially more accurate results than the LSD approximation for quantities such as the total energy, the energy gap, the local moment, and the momentum distribution. For some of these properties a comparison was also made with the Gutzwiller ansatz.[14] While the Gutzwiller ansatz gives accurate results for small values of $U/(4t)$, the SIC-LSD calculation is generally more accurate for large values of $U/(4t)$. In a future publication we plan to show results for the two-dimensional Hubbard model, a hydrogen solid, and Ce metal, where the latter case is an example of a system with orbital degeneracy.

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