



# Are there two types of f-electrons in Pr-metal?

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## Abstract

We show that in order to properly describe the bonding properties of strongly correlated systems, here demonstrated for praseodymium metal, it is necessary to split the f-electron system into two parts. Using perturbation theory from the atomic limit we show that LDA-based calculations with f-electrons in the core can be considered as the limit of an infinite Hubbard  $U$ . Then, the correction to the total energy proportional to  $1/U$  makes the upper  $f^2 \rightarrow f^3$  intra-atomic transitions (IT) important. Mixing interaction and f–f-hopping delocalize these IT and some of them become populated. These IT give an additional contribution to the cohesive energy. This gain in energy is the reason for the separation of the f-electron system into localized (with reduced spectral weight) and delocalized ones. © 1999 Elsevier Science B.V. All rights reserved.

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For strongly correlated systems, state-of-the-art standard band structure calculations (SBSC), based on the local density approximation (LDA) fail to give a perfect description. The reason for the failure is well known: the strong intra-shell Hubbard repulsion,  $U$ , is underestimated in the calculations and this is most pronounced for the f-electron systems. The SBSC with f-electrons treated as delocalized give a too small lattice parameter and cannot describe the experimentally observed Curie–Weiss behavior of e.g. praseodymium at high temperature. When the f-electrons are treated as core electrons (no hybridization and overlap with the conduction bands), the localized moment is provided and the equilibrium volume becomes much closer to the experimental value. However, there is a slight overestimation of the equilibrium volume. A way to treat this defect of SBSC would be to split the f-system into two, one describing the localized part, and a second delocalized part contributing to the cohesive energy. The target of this paper is to show that this scenario indeed arises in a microscopical many-

body theory. The model, and its features, has been described earlier [1]. The main idea of this model is that in the light lanthanides the lower Hubbard band with a spectral weight  $1 - \eta$ , provides a local moment, while the upper Hubbard band, with spectral weight  $\eta$ , is delocalized due to mixing interaction. This provides the correct Curie–Weiss behavior of the magnetic susceptibility at high  $T$ . We are here using a perturbation theory from the atomic limit. The full many-electron Hamiltonian,  $H$ , of the system is written in terms of LDA calculated wave functions and defines an unperturbed Hamiltonian, and a perturbation. In short we write  $\mathcal{H} = \mathcal{H}_{\text{LDA}} + (\mathcal{H} - \mathcal{H}_{\text{LDA}}) = \mathcal{H}_0 + \mathcal{H}'$ . We choose the perturbation from the LDA reference point since it presents an opportunity to use accurate ab initio calculations which fully account for the structure of real materials.

Let us consider the single-site correction in the f-block,

$$H_U = \frac{1}{2} \sum_{m_1 m_2 m_3 m_4} f_{m_1 \sigma}^\dagger f_{m_2 \sigma'}^\dagger f_{m_3 \sigma'} f_{m_4 \sigma} - \sum_m v_m^{(LDA)} \sum_{\sigma} f_{m \sigma}^\dagger f_{m \sigma} \quad (1)$$

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and start our analysis from the itinerant-electron limit. The largest correction comes from the difference between the unscreened Hartree–Fock terms and Hartree plus exchange-correlation terms. The exchange-correlation potential,  $v_{xc}$ , in LDA takes into account RPA-screening, i.e., vertex corrections in the particle–hole channel. Thus it seems that the static part of these corrections from  $\mathcal{H}'_V$  for delocalized states should be equal to zero. Actually this is not so since the HF correction from the screened Coulomb interaction to the potential for the orbital  $\mu_i$  contains a contribution from all *other* orbitals,  $\mu_j \neq \mu_i$ , while  $v_{xc}$  contains also the interaction of a given orbital  $\mu_i$  with itself. The HF potential is the same for all orbitals only for the case of a non-polarized solution. The difference between the HF part of the screened  $\mathcal{H}'_V$ -interaction and  $v_{xc}f^\dagger f$  for a polarized solution gives the microscopically correct expression for the so-called LDA + U method. Physically, this negative correction to  $v_{xc}$  is equivalent to the self-interaction correction and for a sufficiently large  $U$  it leads to a localization of part of the f-electrons. Thus, the starting point is to have the f-electrons localized. In the case of Pr metal  $n_f = 2$  and any deviation from  $n_f = 2$  cannot arise. The existence of localized electrons makes it reasonable to inspect the picture also from the strong-coupling (atomic) limit. In Hubbard's picture the lower single-electron f-level  $E_1 = \varepsilon_f^0$  should be identified with the energy of the ( $f^2$ – $f^1$ )-transition, the upper level  $E_2 = \varepsilon_f^0 + U$  is the energy of the ( $f^2$ – $f^3$ )-transition, while the ( $f^0$ – $f^1$ ), and ( $f^3$ – $f^4$ ), etc. are not considered to contribute.

A core SBSC does not include mixing between the f-electrons and the conduction band. Since corrections to LDA from correlations lead to the multi-orbital periodical Anderson model, we calculate the total energy in a simplified version of it,

$$\begin{aligned} \mathcal{H} = & \sum_{k,\mu} \varepsilon_{k\mu} c_{k\mu}^\dagger c_{k\mu} + \sum_{i,\mu} \varepsilon_i^0 \hat{n}_{i\mu} + \frac{U}{2} \sum_{i,\nu \neq \mu} \hat{n}_{i\nu} \hat{n}_{i\mu} \\ & + \sum_{\mu,k,i} (V_\mu(\mathbf{k}) e^{i\mathbf{k}R_i} c_{k\mu}^\dagger f_{i\mu} + V_\mu^*(\mathbf{k}) e^{-i\mathbf{k}R_i} f_{i\mu}^\dagger c_{k\mu}). \end{aligned} \quad (2)$$

Using a diagram technique we construct a mean field theory for the population numbers of the transitions between different f-configurations,  $P^a$ , and for the energies of these transitions,  $\Delta_a$  [1]. We solved the equations for the  $P^a$ 's and  $\Delta_a$ 's self-consistently, using a density of states from a SBSC-calculation. Two different scenarios were investigated, first the mixing constant,  $V_k = V^0$ , and second  $V_k = V^0 * (\varepsilon_k - \varepsilon_0)$ , where  $\varepsilon_0 (= \sum_k \varepsilon_k)$  is added to assure that the local mixing should vanish ( $\langle \psi_{s,p,d} | \mathcal{H} | \psi_f \rangle = \sum_k V_k = 0$ ). The renormalization of the  $\Delta_a$ 's is actually a renormalization of Hubbard  $U$  due to correlations, however, this effect is very small, the driving force for changes in the total energy is the

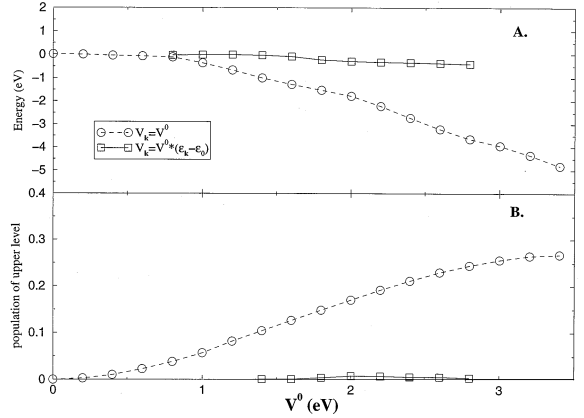


Fig. 1. Total energy when mixing delocalizes part of the f-electrons. (A) The total energy as a function of  $V_{\text{mix}}$  for the cases of constant and  $\mathbf{k}$ -dependent mixing. (B) The corresponding population of the upper transition  $P^{2 \rightarrow 3}$ .  $V^0 = 0$  corresponds to completely localized electrons.

changes in population numbers. The total energy of the self-consistent solution was extracted, the result is presented in Fig. 1A and B where we plot the total energy as a function of  $V^0$  (Fig. 1A), and the population for the upper transition (Fig. 1B), for the two cases of mixing. When depopulating the lower level, the decrease in energy (i.e. in  $\sum_\mu \varepsilon^0 \hat{n}_\mu + U/2 \sum_{\nu \neq \mu} \hat{n}_\nu \hat{n}_\mu$ ) is compensated by a contribution to the total energy from mixing interaction,  $(\sum_{\mu,k,i} V_\mu^k e^{i\mathbf{k}R_i} c_{k\mu}^\dagger f_{i\mu})$ . Thus the total energy is actually *lowered* compared to the completely localized case (seen in Fig. 1 when  $V^0 = 0$ ). If we treat all electrons as delocalized the total energy will be much higher than the energies given in the plot. In the simulations  $U$  was chosen to be 10 eV and the conduction bandwidth was 19 eV. At large depopulation, the energy for the system is increased, and the curve in Fig. 1A turn upwards. Therefore, it is only at *moderate* populations of the upper transitions that the energy is lowered compared to the completely localized case. To summarize we have presented evidence that a splitting of the f-shell of strongly correlated materials, and in particular Pr metal, into a lower Hubbard band, providing a local moment, and delocalized states close to the Fermi level, gives a more correct description of strongly correlated materials. Further details will be presented elsewhere.

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## References

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