Multiplet ligand-field theory using Wannier orbitals

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Many electronic properties of solids can now be described *ab initio*, thanks to the advent of powerful computers and the development of ingenious methods, such as density-functional theory (DFT) with local density (LDA) or generalized gradient (GGA) approximations, LDA+Hubbard U (LDA+U), quantum chemical methods, dynamic mean-field theory, quantum Monte-Carlo simulations, and exact diagonalization for finite clusters. Nevertheless, for correlated open-shell systems with several local orbital and spin degrees of freedom, electronic-structure calculations remain a challenge.

We demonstrate how *ab initio* cluster calculations including the full Coulomb vertex can be done in the basis of the localized, Wannier orbitals which describe the low-energy density functional (LDA) band structure of the infinite crystal, *e.g.* the transition metal $3d$ and oxygen $2p$ orbitals. The spatial extend of our $3d$ Wannier orbitals (orthonormalized Nth order muffin-tin orbitals) is close to that found for atomic Hartree-Fock orbitals. We define Ligand orbitals as those linear combinations of the O $2p$ Wannier orbitals which couple to the $3d$ orbitals for the chosen cluster. The use of ligand orbitals allows for a minimal Hilbert space in multiplet ligand-field theory calculations, thus reducing the computational costs substantially. The result is a fast and simple *ab initio* theory, which can provide useful information about local properties of correlated insulators. We compare measurements of d-d excitations in NiO with inelastic x-ray scattering experiments. The multiplet ligand field theory parameters found by our *ab initio* method agree within $\sim 10\%$ to known experimental values.
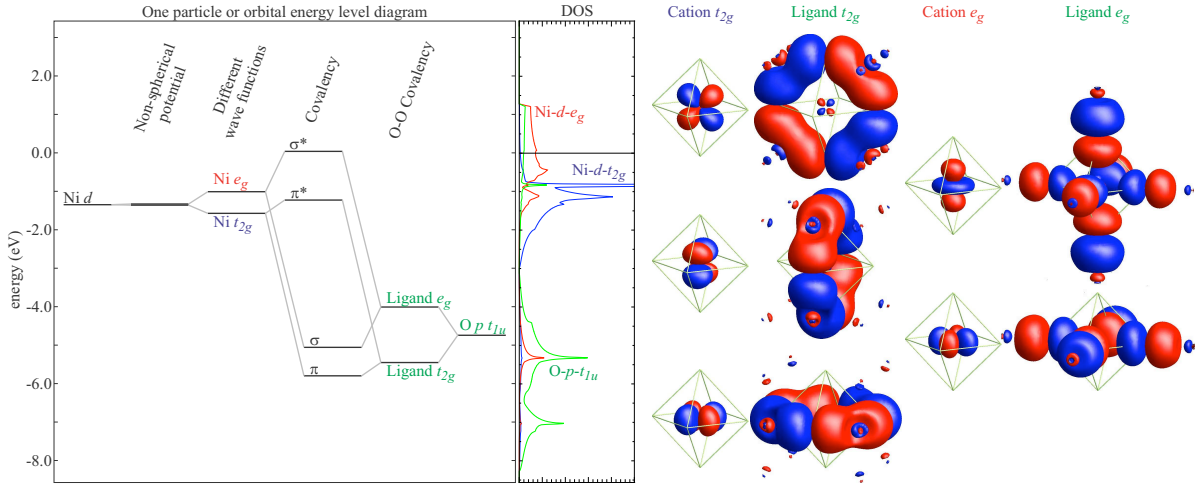

Figure 1: Left panel: Orbital energy level diagram for the NiO_6 cluster. Middle panel: LDA density of states on the same energy scale as the orbital energy level diagram shown in the left panel. The Fermi level is the zero of energy. Right panel: Constant-amplitude contours of the Ni d Wannier orbitals and of the Ni-centered ligand orbitals. The latter are symmetrized linear combinations of the O p Wannier orbitals.

We start our *ab initio* calculations with a conventional charge-selfconsistent LDA calculation for the experimental infinite crystal structure. The LDA density of states can be seen in the middle panel of Fig. 1. Within the LDA, NiO is a metal, in strong contrast to experiments where NiO is found to be a good insulator with a room-temperature resistance of $\sim 10^5 \, \Omega$cm and an optical band-gap of about 3.0-3.5 eV. This is one of the most noticeable failures of the LDA. For the current paper, this is not a problem. Although the LDA cannot reproduce the correct electronic structure near the nickel atom, the minimal set of localized Ni d and O p orbitals which together span the low-energy solutions of Schrödinger's equation for the LDA crystal potential exactly, are expected to constitute a good single-particle basis set for many-body calculations. These orbitals, as well as the corresponding tight-binding Hamiltonian we use for the NiO_6 cluster. The band structure in such a cluster reduces to the O p like π- and σ-levels and the Ni d like π^*- and σ^*-levels shown in the central part of the left-hand panel of Fig. 1. The onsite energy difference of the Ni t_{2g} and e_g Wannier orbitals is a result of an interplay of potential and kinetic energy related to the different radial wave-functions of these orbitals. The O $2p$ Wannier orbitals can, within the NiO_6 cluster be recombined to form Ligand orbitals of either e_g or t_{2g} symmetry. (see left hand side of Fig. 1) The Ligand e_g (t_{2g}) orbital forms an σ (π) bonding and anti-bonding state with the Ni e_g (t_{2g}) Wannier orbital.

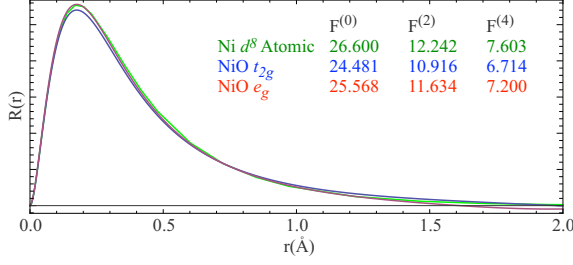|	$F^{(0)}$	$F^{(2)}$	$F^{(4)}$
Ni d^8 Atomic	26.600	12.242	7.603
NiO t_{2g}	24.481	10.916	6.714
NiO e_g	25.568	11.634	7.200

Figure 2: Angular averaged radial wave functions, $R(r)$, for the Ni e_g and Ni t_{2g} Wannier orbitals compared with the Hartree-Fock radial wave function for a Ni^{2+} ion in a $3d^8$ configuration. For Ni$^+$ $3d^8 s^1$ and Ni $3d^8 s^2$, the radial functions are similar. The distance to the nearest oxygen is 2.09 Å, which is consistent with the sum of the ionic radii of 0.72 Å for Ni^{2+} and 1.40 Å for O^{2-}.

The five Ni Wannier orbitals and their corresponding O Ligand orbitals, $w_i(\mathbf{r})$, are shown on the right-hand side of Fig. 1 as those surfaces where $|w_i(\mathbf{r})| = \text{const}$ and which incorporate 90% of the charge, $\int_S |w_i(\mathbf{r})|^2 d^3r \equiv 0.9$. The red/blue color of a lobe gives its sign. As one can see, the Ni d orbitals are extremely well localized. This is a necessary condition for several many-body models which implicitly assume such an orbital basis set. In order to visualize the localization of the Ni $3d$ Wannier orbitals at a more quantitative level, we computed the effective radial wave-functions for the t_{2g} and e_g orbitals by multiplying with the corresponding spherical harmonics and averaging over all solid angles. These radial functions are compared in Fig. 2 with that of a Ni atom in the d^8 configuration as calculated with the Hartree Fock method. Although there are slight differences, the agreement is astonishing. The local Ni d Wannier orbitals in NiO are rather similar to atomic Ni wave-functions.

Knowing the one particle energies we turn to the Coulomb interaction. The spherical part of the Coulomb repulsion, often parametrized by U, is strongly screened in a solid. If a Ni d electron is removed, there will be a charge-flow into the Ni $4s$ orbital, for example, which reduces the energy cost of such an excitation. Although several calculations of the screened U have been presented in the past, we here present charge neutral excitations for a model containing only one Ni atom. The results are therefore independent of the value of U.

The non-spherical parts of the Coulomb interactions we can easily calculate because the multipole interactions between two d electrons are hardly screened. For example, the Coulomb repulsion between two $d_{x^2-y^2}$ electrons is obviously larger than that between a $d_{x^2-y^2}$ electron and a d_{3z^2-1} electron, but to screen this difference requires electrons with high angular momentum around the Ni site; a Ni $4s$ electron, for instance, could *not* do it. Also electrons on neighboring sites are inefficient in screening the multipole because it decays fast ($\propto r^{-k-1}$). Multipole interactions are the cause of the Hunds-rule energy. For example, two $d_{x^2-y^2}$ electrons must have different spins, whereas two electrons in different d orbitals, and hence less repulsive, may be in a spin-triplet state, as well as in the spin-singlet state.

The inset in Fig. 2 is a table of the values of the Slater integrals obtained using the Ni^{2+} ionic radial function, $R(r)$, as well as the radial functions obtained by averaging the Ni t_{2g} and e_g Wannier orbitals over solid angles. The Slater integrals for d orbitals are:

$$F^{(k)} = \int \int \frac{r_<^k}{r_>^{k+1}} R^2(r_1)R^2(r_2)\, r_1^2 dr_1\, r_2^2 dr_2. \tag{1}$$

where $r_< = \min(r_1, r_2)$, $r_> = \max(r_1, r_2)$, and $k = 0, 2,$ or 4. The bare $F^{(0)}$ as calculated from the Wannier orbitals is of the order of ~ 25 eV. This is clearly much too large because the monopole part of the Coulomb repulsion is strongly screened. The values of $F^{(2)}$ and $F^{(4)}$ are respectively ~ 11 and ~ 7 eV, in good agreement with experimental values, as we shall see. The multiplet interactions are quite large and lead to a multiplet splitting of the Ni-d^8 configuration of about 7.5 eV, which is the energy difference between the ^3F ground-state configuration and the highest excited singlet of ^1S character. This is larger then the Ni-d bandwidth and therefore *not* a small energy.
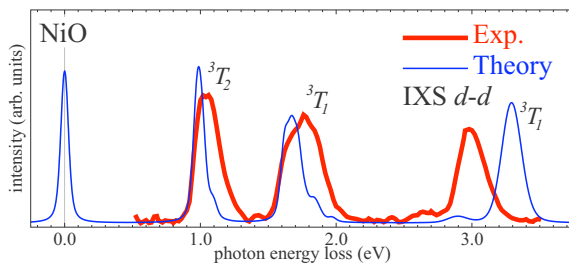

Figure 3: Comparison of the experimental (thick red) and MLFT (thin blue) non-resonant inelastic x-ray scattering intensity of low energy d-d excitations. The experimental spectra are reproduced from Verbeni *et al.*[2].

We now have all ingredients needed to perform MLFT calculations of experimentally observable quantities. In Fig. 3 we show the experimental [2] and theoretical non-resonant IXS spectra for a powder of NiO at large

momentum transfer (averaged over a transfer of $7.3 - 8.0$ Å $^{-1}$). These spectra are governed by quadrupole and hexadecapole transitions between the $3d$ orbitals. The non-resonant IXS excitations are spin-conserving. Locally the Ni ground-state configuration is d^8 with the t_{2g} orbitals fully occupied and the e_g orbitals half filled with $\langle S^2 \rangle = 2$, i.e. $S = 1$. In the one-electron picture, one can make a single excitation going from the t_{2g} shell to the e_g shell, which has an experimental energy of about 1.1 eV. This is the peak of T_{2g} final state symmetry in the experiment. In principle one could also excite two t_{2g} electrons simultaneously into the e_g sub-shell. This would give rise to a single peak at twice the energy. In a pure one-electron picture the double excitation is forbidden because non-resonant IXS couples a single photon to a single electron. Using full multiplet theory, however, both excitations have a finite intensity. This has to do with the strong t_{2g}-e_g multiplet interaction which mixes, for the excited states, the single Slater determinants. One even finds three peaks instead of two. The first peak indeed corresponds to an excitation of a single t_{2g} electron into the e_g sub-shell. The second peak is roughly the simultaneous excitation of two t_{2g} electrons into the e_g subshell. Finally, in order to understand the third peak, one should realize that the t_{2g} (xy) electron is Coulomb repelled more from an e_g $\left(x^2 - y^2\right)$ electron than from an e_g $\left(3z^2 - 1\right)$ electron because of the larger overlap of densities. This leads to multiplet splitting of the $t_{2g}^5 e_g^3$ states and to mixing of $t_{2g}^5 e_g^3$ and $t_{2g}^4 e_g^4$ states.

MLFT gets the lowest excitation $\left(^3T_2\right)$ 5% too low and the highest $\left(^3T_1\right)$ 10% too high. As the $^3T_2$ energy is mainly determined by one-electron interactions, we conclude that the $e_g - t_{2g}$ splitting due to covalency in our LDA based calculation is 5% underestimated. At the same time, the multiplet splitting due to the Coulomb repulsion, i.e. the values of the $F_{dd}^{(2)}$ and $F_{dd}^{(4)}$ Slater integrals, are 10% overestimated. The later could be a result of neglecting the screening of the multipole interactions, but not necessarily, because there are additional channels in which two $3d$ electrons can scatter into two higher excited states due to Coulomb repulsion. This gives rise to a multiplet-dependent screening, not easily described with a single screening parameter.

We have shown how MLFT calculations can be based on *ab-initio* LDA solid-state calculations, in a similar way as originally devised by Gunnarson *et al.* [3] and recently done for LDA+DMFT calculations. The resulting method could be named LDA+MLFT. The theory is very well suited for the calculation of local ground-state properties and excitonic spectra of correlated transition-metal and rare-earth compounds. Our TM d Wannier orbitals, which *together* with the O p Wannier orbitals span the LDA TM d- *and* O p-bands, are quite similar to atomic orbitals, and this justifies many previous studies using the latter.

References:

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