From cluster to solid - the variational cluster approximation applied to NiO

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The variational cluster approximation is applied to the calculation of the single particle spectral function of NiO. Trial self energies and the numerical value of the Luttinger-Ward functional are obtained by exact diagonalization of NiO$_6$-clusters and the single particle parameters of the clusters serve as variational parameters to obtain a stationary point of the grand potential of the lattice system. Good agreement with experiment is obtained.

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The theoretical description of compounds containing partially filled 3d, 4f or 5f shells is a much-studied problem in solid-state theory. Due to the small spatial extent of these shells the Coulomb repulsion between conduction electrons in these compounds becomes unusually strong and approximations which rely on a mapping of the physical electron system onto one of fictious free particles in a suitably constructed effective potential cannot even qualitatively describe the resulting state. Starting with the work of Hubbard[1] a variety of theoretical methods have been invented to deal with this problem. Major progress towards a quantitative description of 3d transition metal (TM) oxides has been made by the cluster method initiated by Fujimori and Minami[10, 11]. This takes the opposite point of view as compared to band theory, namely to abandon translational invariance and instead treat exactly - by means of atomic multiplet theory[12, 13] - the Coulomb interaction in the 3d-shell of a TM-ion in an octahedral 'cage' of nearest-neighbor oxygen atoms. Recently ideas have been put forward to broaden the spectra of finite clusters into bands[14, 15, 16]. In particular, building on field-theoretical work of Luttinger and Ward[17] who showed that the grand canonical potential $\Omega$ of an interacting Fermion system is stationary with respect to variations of the electronic self-energy $\Sigma$, Potthoff has recently proposed[18] the variational cluster approximation (VCA) where trial self energies are generated numerically by solving finite clusters and used in a variational scheme for $\Omega$. So far the VCA has been applied mainly to simplified systems such as the single-band Hubbard-model[18, 19] but the success of the cluster method for TM-oxides suggests to apply the VCA also to a realistic model for TM-oxides thereby using the octahedral clusters discussed above to generate self-energies. Here we outline such a calculation for the frequently studied compound NiO. Using clusters containing just a single TM-ion implies that the self-energy is site-diagonal, i.e. $\kappa$-independent. The corresponding approximation thus is similar to the dynamical mean-field calculations which have recently been applied to a variety of compounds[20]. We start by defining the Hamiltonian which describes the NiO lattice and denote by $d^\dagger_{i,\alpha,\sigma}$ an operator which creates a spin-$\sigma$ electron in the $d$-orbital $\alpha \in \{xy, xz, yz, \ldots \}$ on metal site $i$ and $p_{j,\lambda,\sigma}$ annihilates an electron in $p$-orbital $\lambda \in \{x, y, z\}$ on oxygen site $j$. Taking the O2p-level energy $\epsilon_p$ as the zero of energy the single-particle terms read

$$H_0 = \sum_{i,\alpha,\lambda,\sigma} \sum_{\sigma'} (t_{i,\alpha,\lambda}^{\dagger}) \alpha_{i,\sigma} d^\dagger_{i,\alpha,\sigma} p_{j,\lambda,\sigma} + H.c.) + \sum_{i,\alpha,\sigma} (\epsilon_d + \epsilon_0) d^\dagger_{i,\alpha,\sigma} d_{i,\alpha,\sigma}. \quad (1)$$

The Hamiltonian also contains terms which describe hybridization between next-nearest neighbors, i.e. O2p-O2p and Ni3d-Ni3d. The numerical values of the different hopping integrals have been obtained by an LCAO-fit to a paramagnetic LDA band structure of NiO[21]. They are quite similar to those used by Fujimori and Minami[10] and van Elp et al.[17]. Also included - via the $\epsilon_0$ - is a CEF-splitting of 10.7eV[10, 11]. The Coulomb interaction within the $d$-shell reads

$$H_1 = \sum_{\lambda_1,\lambda_2,\lambda_3,\lambda_4} V^\lambda_{\lambda_1,\lambda_2} d^\dagger_{\lambda_3} d_{\lambda_4} \quad (2)$$

where we have suppressed the site label $i$ and $\lambda = (\alpha, \sigma)$. The matrix elements $V_{\lambda_1,\lambda_2}^{\lambda_3,\lambda_4}$ can be expressed in terms of the 3 Racah parameters, $A$, $B$ and $C$. To avoid an ‘implicit’ interaction between electrons these are assumed to be independent of the $d$-shell occupation. $B$ and $C$ can be estimated from atomic Hartree-Fock wave functions and the values used here, $B = 0.13$eV and $C = 0.6$eV are standard ones[10, 11]. The parameter $A$ is reduced substantially by solid state screening and is usually adjusted to match experiment - here we do the same and choose $A = 9$eV. The ‘Hubbard’ $U = E(d^6) + E(d^-) - 2E(d^5) - 2E(d^5) - 2E(d^5) - 2E(d^5)$ - calculated from ground state energies of free ions without CEF-splitting is $13$U = $A + B = 9.1$eV. Previous estimates range from $U = 6.7$eV - by fit of cluster spectra to experiment[10, 11] to $U = 8$eV by density functional calculations[22]. The present value thus is somewhat large which will be discussed below in more detail. Next, we choose - again by adjusting to experiment - $\epsilon_q = -68.5$ eV so that the charge transfer energy $\Delta = E(d^6) - E(d^5)$ is $13$ $\Delta = \epsilon_q - \epsilon_p + 8A - 6B + 7C = 6.9$eV. These values are consistent with the notion that NiO is a charge transfer insulator but close to the intermediate regime.
of the Zaenan-Sawatzky-Allen diagram. Finally, any Coulomb interaction between electrons which are not in the same Ni3d-shell is neglected.

The VCA is based on an expression for the grand potential $\Omega$ of an interacting many-Fermion system due to Luttinger and Ward. In a multi-band system where the Green’s function $G(k,\omega)$, the noninteracting kinetic energy $t(k)$ and the self-energy $\Sigma(k,\omega)$ for given energy $\omega$ and momentum $k$ are matrices of dimension $2n \times 2n$, with $n$ the number of orbitals/unit cell, it reads

$$\Omega = -\frac{1}{\beta} \sum_{k,\nu} e^{\omega_{\nu}0^+} \ln \det (-G^{-1}(k,\omega_{\nu})) + F[\Sigma] \quad (3)$$

where $\omega_{\nu} = (2l + 1)\pi/\beta$ are the Matsubara frequencies,

$$G^{-1}(k,\omega) = \omega + \mu - t(k) - \Sigma(k,\omega) \quad (4)$$

and the functional $F[\Sigma]$ is the Legendre transform of the Luttinger-Ward functional $\Phi[\Sigma]$. A definition of $\Phi[G]$ in terms of Feynman diagrams was given by Luttinger and Ward, a nonperturbative derivation has recently been given by Pothoff. $\Omega$ is stationary with respect to variations of the self-energy by $\delta \Omega = 0 \quad (5)$

but a prohibitive obstacle in exploiting in a variational scheme for $\Sigma$ is the evaluation of $F[\Sigma]$ for a given ‘trial $\Sigma$’. Pothoff has suggested to restrict the domain of $\Sigma$ to ‘cluster representable’ ones, i.e. exact self-energies of finite clusters, for which $F[\Sigma]$ can be determined numerically from $\Phi[G]$. The key observation is that $\Phi[G]$ and hence its Legendre transform $F[\Sigma]$ have no explicit dependence on the single-particle terms of $H$ whence $F[\Sigma]$ is the same functional of $\Sigma$ for any two systems with the same interaction part of the Hamiltonian. Under the assumption that only interconnection lines connecting orbitals in the same d-shell are relevant we can therefore use a numerically solvable system of disconnected finite clusters - the so-called reference system - to generate trial self-energies $\Sigma(\omega)$ together with their exact $F[\Sigma]$. More precisely we choose a reference system where each Ni3d orbital $d_n$ is coupled to one ‘ligand’ orbital $L_{\alpha}$ with these ligands in turn decoupled from each other and the interaction within the d-shell given by $\Sigma$. The reference system thus is equivalent to an array of non-overlapping identical NiO$_6$ clusters where each ligand $L_{\alpha}$ corresponds to the unique linear combination of $O2p$ orbitals on the six nearest $O$ neighbors of a given Ni atom which hybridizes with the Ni3d$_{\alpha}$ orbital. After numerical diagonalization of the cluster Hamiltonian for all possible electron numbers we obtain the grand potential $\Omega$ and Green’s function $G(\omega)$ of the cluster whence equations and give $\Sigma(\omega)$ and $F[\Sigma]$. Next we insert the $\Sigma(\omega)$ and $F[\Sigma]$ so obtained into equations and for the lattice system and obtain an approximate $G(k,\omega)$ and $\Omega$ for the infinite system. Variation of $\Sigma(\omega)$ is performed by varying the single-electron parameters - such as hybridization integrals or site-energies - of the reference system and the best approximation to $\Sigma(\omega)$ is obtained by demanding that $\Omega$ be stationary with respect to such variations. We write the single-particle Hamiltonian for a Ni$_5$ cluster as

$$H_{\text{single}} = \sum_{\alpha,\sigma} V(\alpha) \left( d_{\alpha,\sigma}^{} L_{\alpha,\sigma}^{} + \text{H.c.} \right) + \sum_{\alpha,\sigma} (E(\alpha) d_{\alpha,\sigma}^\dagger d_{\alpha,\sigma}^{} + \epsilon(\alpha) L_{\alpha,\sigma}^\dagger L_{\alpha,\sigma}^{}) \quad (6)$$

and have the following variational parameters:

1) The hopping integrals $V(\alpha)$. Since the ground state of $d^8$ in cubic symmetry has the configuration $t_{2g}^6e_g^2$, $V(t_{2g})$ connects mainly occupied orbitals. To simplify the problem we therefore discard the three $t_{2g}$-like ligands altogether and write the remaining $V(e_g) = \lambda \tilde{t}$ where $\tilde{t} = \sqrt{3}pda$ is the hopping integral in the cluster calculation for a NiO$_6$-cluster.

2) The site energy of the $e_g$-like ligands $\epsilon(\alpha)$.

3) The site energies $E(\alpha)$ of the $e_g$ and $t_{2g}$-like d-orbitals. By numerical scan a set of these 4 parameters where $\Omega$ is stationary can be found for each temperature $T$. For temperatures between 100 and 1000K the expression $\Omega(T) = \Omega_0 - k_B T \log(3)$ - expected for a gapped, paramagnetic spin-1 system - gives an excellent fit to the calculated $\Omega(T)$. The constant $\Omega_0$ thereby is the ground state expectation value $\langle H - \mu N \rangle$. Since the VCA also gives the lattice Green’s function $G(k,\omega)$, $\langle H - \mu N \rangle$ can alternatively be computed from its $0^{th}$ and $2^{nd}$ moments. There is no reason why these two results should agree - the formalism of the VCA would not necessitate this. Still the two values agree quite well - -148,649 eV/unit cell versus -418,684 eV/unit cell - indicating that the VCA is a quite ‘intrisically consistent’ approximation. Next, we proceed to a comparison of $G(k,\omega)$ to experiment. Figure compares k-integrated spectral densities calculated at room temperature (300 Kelvin) to angle-integrated valence band photoemission spectra taken by Oh et al. at two different photon energies. At $h\nu = 150$ eV the experimental spectrum essentially resembles the $d$-like spectral density, whereas at $h\nu = 67$ eV the states at the valence band top are anti-resonantly suppressed - whence $O2p$-derived features become more clearly visible - whereas the ‘satellite’ at $-10$ eV is resonantly enhanced. Figure compares the k-resolved spectral function for momenta along (100) ($\Gamma \rightarrow X$) to the experimental band dispersion by Shen et al.

The spectral density has gap of approximately 4eV around the chemical potential. This is consistent with experiment but has of course been achieved by the choice of $A$ and $\Delta$. At the top of the photoemission spectrum $E < 0$ there is a high-intensity band complex at binding energies between $\approx -4$ eV and $\approx -2$ eV, which was shown to consist of several sub-peaks by Shen et al. These authors did not actually resolve the dispersion of the individual sub-peaks although the data
FIG. 1: Single particle spectral densities obtained by VCA compared to valence band photoemission data (XPS).

 seem to indicate a weak overall ‘upward’ dispersion as one moves $\Gamma \rightarrow X$ which would be consistent with theory. It also has to be kept in mind that the calculation has been performed for the paramagnetic phase whereas the experiment was done below the Néel temperature and thus in the antiferromagnetically ordered phase. This may have an impact on the dispersive features. Proceeding to more negative binding energy both the experimental band structure and the theoretical spectra show a gap of $\approx 1\text{eV}$ and then a group of dispersionless bands between $-4.5\text{eV}$ and $-6.5\text{eV}$. In the angle-integrated spectrum, Figure 1b, the topmost of these bands produces the shoulder at $-4.5\text{eV}$. The spectrum in Figure 1b shows a peak at $-6\text{eV}$ which originates from states with essentially pure $O_{2p}$ character [26]. The corresponding peak in the theoretical spectrum originates from a saddle point singularity of the upper $O_{2p}$ derived band at the $X$-point. Comparison of the angle integrated spectrum, the experimental dispersion and an LDA band structure makes this a plausible explanation. The sole strongly dispersive feature in the spectrum, namely an $O_{2p}$-derived band at binding energies between $-6\text{eV} \rightarrow -9\text{eV}$ is again well reproduced by theory. Finally the ‘satellite’ at binding energies $-9\text{eV} \rightarrow -15\text{eV}$ consists of at least two sub-peaks as can be seen in Figure 1b and also in the ARPES data. Theory predicts several sub-peaks in the satellite but these may not have been resolved in experiment due to the strong broadening of the satellite. By and large we may say that there is essentially a one-to-one correspondence between theory and the measured bands (the $k$-integrated spectra also agree roughly with a recent LDA+DMFT(QMC)-calculation [9]). Finally we mention the values of the $d$-shell occupation $n_d = 8.16$ and the expectation value of the $d - p$ hybridization $\langle H_{pd}\rangle = -2.30 \text{eV/unit cell}$ (at $T = 300 \text{K}$ with negligible $T$-dependence). To put these in perspective we note that perturbation theory for a NiO$_6$ cluster with unrenormalized parameters gives $n_d = 8 + 2(\tilde{t}/\Delta)^2 = 8.21$ and $\langle H_{pd}\rangle = -4\tilde{t}^2/\Delta = -2.93\text{eV}$.
An issue that requires more detailed discussion is the spectral weight of the satellite: the fraction of d-like weight below the ‘gap’ around $-7 eV$ is $w = 61\%$. A recent LDA+DMFT calculation\cite{9} gave $w = 45\%$ with $U = 8 eV$. Van Elp et al.\cite{11} estimated $w = 30\%$ with $U = 6.7 eV$. As shown in Ref.\cite{11} the spectral weight of the satellite is directly related to the choice of $U$ - larger $U$ produces a more intense satellite. The relatively large value of $U = 9.1 eV$ in the present work was necessary to get the satellite below the bottom of the $O2p$-band - as suggested by ARPES\cite{27}. This raises the question why we need a larger value of $U$ as compared to the $6.7 eV$ in the cluster calculations\cite{11,11}. It turns out that the reason is the downward renormalization of the hopping integral $V(e_{p})$ in $\Omega$. The value of $\lambda$ at the stationary point is $0.812$ (at $300K$ with negligible $T$-dependence) and even such a small reduction leads to an appreciable upward shift of the satellite due to reduced level repulsion between satellite and valence band top (see e.g. Figure 11 of Ref.\cite{11}) - which must be compensated by a larger $U$.

On the other hand there is a simple physical argument for the value of $\lambda < 1$: in a NiO$_{2}$ cluster, the mixing strength between (say) a $N3d_{z^{2}-r^{2}}$ orbital and the bonding combination of $O2p_{x}$ orbitals on the two nearest neighbors in $x$-direction is $t/\sqrt{2}$. In a NiO lattice the matrix element between the Bloch states of momentum $k$ formed from the $N3d_{z^{2}-r^{2}}$ orbital and the $O2p_{x}$-orbital is $i\sin(k_{z},a)$ with $a$ the Ni-O distance. The Brillouin zone average of $|\sin(k_{z},a)|$ is $0.63 = 0.89/\sqrt{2}$ so that the value of $\lambda$ at least partly reflects the smaller average $d-p$ hybridization in the NiO lattice as compared to the NiO$_{2}$ cluster. Anisimov et al.\cite{3} gave a similar argument to improve the agreement of their LDA+$U$ calculation with the cluster calculations and in principle this should occur in any approximation where a $k$ independent self-energy is determined in an ‘impurity’-like calculation. More accurate knowledge about the total weight and width of the satellite probably will be needed to decide which is the more correct description. Finally it should be noted that the values of $U$ and $\Delta$ determine mainly the energies of the upper Hubbard band and satellite relative to the valence band top - the band structure above $-7eV$ is influenced hardly at all by these parameters.

In summary: the variational cluster approximation due to Potthoff allows to combine the powerful cluster or CI method for transition metal compounds with the field-theoretical work of Luttinger and Ward to implement a variational scheme for the electronic self-energy and construct a band structure method for strongly correlated electron compounds. Both, a realistic band structure and the full atomic multiplet interaction can be incorporated into the Hamiltonian without problems, the system can be studied at arbitrarily low temperatures and the Green’s function be obtained with arbitrary energy resolution. The results are quite encouraging in that there is an essentially one-to-one correspondence between calculated Green’s function and electron spectroscopies whereby a comparison of the fine structure of the broad band complex at the valence band top to experimental data of higher resolution would be desirable. The good agreement also suggests that the band structure of NiO is ‘Coulomb generated’ in that the atomic multiplet structure survives with minor modifications and gets broadened into weakly dispersive bands. All in all the VCA appears to be a promising tool for the study of transition metal compounds.

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