Correlated band structure of NiO, CoO and MnO by variational cluster approximation

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The variational cluster approximation proposed by Potthoff is applied to the calculation of the single-particle spectral function of the transition metal oxides MnO, CoO and NiO. Trial self-energies and the numerical value of the Luttinger-Ward functional are obtained by exact diagonalization of a TM3o-cluster. The single-particle parameters of this cluster serve as variational parameters to construct a stationary point of the grand potential of the lattice system. The stationary point is found by a crossover procedure which allows to go continuously from an array of disconnected clusters to the lattice system. The self-energy is found to contain irrelevant degrees of freedom which have marginal impact on the grand potential and which need to be excluded to obtain meaningful results. The obtained spectral functions are in good agreement with experimental data.

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I. INTRODUCTION

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 the electrons in the conduction bands formed from these shells becomes unusually strong and approximations which rely on a mapping of the physical electron system onto one of fictitious free particles in a suitably constructed effective potential - as is the case in density functional theory [1] in the local density approximation (LDA) - cannot even qualitatively describe the resulting state. A frequently cited example are the transition metal (TM) oxides NiO, CoO and MnO. Band structure calculations for the paramagnetic phase predict these materials to be metallic while experimentally they remain insulators well above their respective Néel temperature. For NiO and MnO an insulating ground state can be obtained in the framework of band theory by introducing antiferromagnetic order - for CoO on the other hand even the antiferromagnetic ground state is metallic [2]. From a comparison of X-ray photoemission spectroscopy (XPS) and bremsstrahlung isochromat spectroscopy (BIS) it was found [3] that the band gap predicted by LDA for antiferromagnetic is too small by a factor of ≈ 10. Moreover electron spectroscopy shows that the electronic structure remains essentially unchanged at the Néel temperature for both NiO[4] and CoO[5]. In both compounds there is practically no difference between the electronic spectra in the antiferromagnetic and paramagnetic phase. The same holds true for the related compound NiS where LDA band structure calculations on the contrary predict that the transition to the magnetically ordered phase is accompanied by a significant change of the electronic structure [6]. Failure to predict the insulating ground state and the magnitude of the insulating gap is not the only shortcoming of LDA. In valence band photoemission spectroscopy (PES) all three oxides NiO, CoO and MnO show a 'satellite' at an energy of ≈ 6 – 8eV below the valence band top[5, 7, 8]. The Fano-like intensity variation with photon energy at the TM 3p → 3d threshold identifies this feature as being due to dn → d(n−1) transitions[9]. This part of the electronic structure is not at all reproduced by band structure calculations which on the contrary would predict the dn → d(n−1) transitions near the valence band top. And finally experimental band structures measured by angle resolved photoelectron spectroscopy (ARPES) show that for all compounds, NiO, CoO and MnO, the TM-derived bands near the valence band top are almost dispersionless[10]. This is also in contradiction to LDA calculations which predicts band widths of around 2eV for the TM3d-derived bands.

Starting with the work of Hubbard[11] a variety of theoretical methods have been invented to deal with this problem[12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22]. Major progress towards a quantitative description of 3d TM oxides has been made by the cluster method initiated by Fujimori and Minami[22, 23, 24, 25, 26]. 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[23, 24] - the Coulomb interaction in the 3d-shell of a TM-ion in an octahedral ‘cage’ of nearest-neighbor oxygen atoms. The angle-integrated valence band photoemission spectra calculated by this method are in excellent agreement with experiment[23, 24, 25, 26, 27]. This is clear evidence that the atomic multiplets of the partly filled 3d-shell - suitably modified by the crystalline electric field (CEF) - persist in the solid and play an important part in the physics. On the other hand due to its ‘impurity’ character the cluster method can only give k-independent quantities.

Recently, however, ideas have been put forward to broaden the correlated ionization and affinity states of finite clusters into bands[28, 29, 30]. A particularly elegant way to do so - the variational cluster approximation (VCA) - has been proposed by Potthoff[31]. Building on field-theoretical work of Luttinger and Ward[32] who showed that the grand canonical potential Ω of an interacting Fermion system is stationary with respect to variations of the electron self-energy Σ(ω), Potthoff pro-
posed to generate trial self-energies numerically by exact diagonalization of finite clusters and use them in a variational scheme for $\Omega$. This amounts to finding the best approximation to the true self-energy of the lattice amongst the subset of ‘cluster representable’ ones, i.e. exact self-energies of finite clusters.

So far the VCA has been applied mainly to simplified systems such as the single-band Hubbard-model but the success of the cluster method for TM-oxides clearly suggests to apply the VCA also to a realistic model for TM-oxides thereby using the octahedral clusters introduced by Fujimori and Minami to generate self-energies. Here we outline such a calculation for NiO, CoO and MnO, which all have the rocksalt structure. For simplicity we neglect any of the lattice distortions observed in the actual compounds as well as the antiferromagnetic order at low temperature and study the ideal rocksalt structure in the paramagnetic phase. As already mentioned the single-particle spectra of these compounds do not change appreciably during the Néel transition so this is probably a reasonable assumption. A preliminary study for NiO using the VCA has been published elsewhere. Using clusters containing just a single TM-ion implies that the self-energy is site-diagonal, i.e. $k$-independent. The corresponding approximation thus is similar to the $\text{DMFT}$ calculations which have recently been applied to a variety of compounds. The relationship between DMFT and the VCA has been discussed in detail by Potthoff and a detailed comparison with recent DMFT calculations for NiO will be presented below.

II. HAMILTONIAN

We start by defining the Hamiltonian which describes the correlated TMO lattice. We use a linear combination of atomic orbitals (LCAO) parameterization of the non-interacting Hamiltonian with hybridization integrals obtained from a fit to a LDA band structure thereby closely following the procedure outlined by Mattheiss. The parameters so obtained are listed in Table I. To give an impression about what accuracy can be expected from such a fit Figure II shows the actual LDA band structure and the LCAO-fit for CoO. Following Mattheiss an $O2s$ orbital was included into the basis set in addition to the $O2p$ and $TM3d$ orbitals. This turned out to be crucial for a correct fit of the dispersion of some $TM3d$-like bands along $\Gamma - X$. The energy of the $O2s$ orbital has no particular impact on the dispersion of the bands near the Fermi level and was kept at 14 eV below the $O2p$ energy. The fit can be improved substantially by also including nonvanishing overlap integrals between $O2p$ and $TM3d$ orbitals - since, however, the VCA needs well defined $TM3d$ orbitals to which the self-energy can be added these overlap integrals were omitted. The hybridization element $(d\delta d\delta)$ turned out to be meaningful only in combination with these overlap integrals - a fit without overlap produced a positive value of $(d\delta d\delta)$ - and hence was set to be zero. By and large the variation of the hybridization integrals along the series NiO→MnO is consistent with the increasing lattice constant on one hand and the increasing $d$-shell radius on the other. The parameters are similar to previous estimates in the literature.

The Coulomb interaction within the $d$-shell can be written as

$$H_1 = \sum_{\kappa_1,\kappa_2,\kappa_3,\kappa_4} V^{\kappa_1,\kappa_2}_{\kappa_1,\kappa_2} d^\dagger_{\kappa_1} d_{\kappa_2} d_{\kappa_3} d^\dagger_{\kappa_4}.$$  

(1)

Here we have suppressed the site label $i$ and $\kappa = (\alpha, \sigma)$ where $\alpha \in \{d_{xy}, d_{xz}, d_{yz}, d_{3z^2-r^2}\}$ denotes the CEF-level. The matrix elements $V^{\kappa_1,\kappa_2}_{\kappa_1,\kappa_2}$ can be expressed in terms of the 3 Racah-parameters, $A$, $B$ and $C$. Due to the ‘breathing’ of the 3d radial wave function these parameters should be taken to depend on the $d$-shell occupation. This, however, would create an ‘implicit’ interaction containing terms higher than quartic in the Fermion operators and also an interaction between $d$ and $p$-electrons. This would defeat our formalism and we therefore do not take the dependence on $d$-shell occupation into account. Whereas $B$ and $C$ can be estimated from atomic Hartree-Fock wave functions the parameter $A$ is reduced substantially from its atomic value by solid state screening. This parameter can in principle be obtained from density functional calculations. In the cluster calculations for TM oxides the parameter $A$ is usually treated as an adjustable parameter and hence we do the same. Adjusting $A$ is equivalent to adjusting the ‘Hubbard $U$’ $E(d^{n+1}) + E(d^{n-1}) - 2E(d^n)$ where $E(d^n)$ denotes the energy of a $d$-shell with $n$ electrons. There is some ambiguity as to what exactly is to be understood by the energy of $d^n$ - here we follow Refs. and take $E(d^n)$ to be the Coulomb energy of the Hund’s rule ground state of the free ion i.e. calculated without CEF splitting. $E(d^n)$ - and hence $U$ - then can be expressed in terms of the Racah parameters. Another way to define a Hubbard $U$ would be to note that the average Coulomb

|                | NiO  | CoO  | MnO  |
|----------------|------|------|------|
| $(pp\sigma)$   | 0.695| 0.627| 0.542|
| $(pp\pi)$      | -0.118| -0.111| -0.108|
| $(sd\sigma)$   | -1.210| -1.210| -1.319|
| $(pd\sigma)$   | -1.289| -1.276| -1.275|
| $(pd\pi)$      | 0.614| 0.596| 0.587|
| $(dd\sigma)$   | -0.255| -0.274| -0.331|
| $(dd\pi)$      | 0.060| 0.067| 0.097|
| $\epsilon(O2s)$| -14.000| -14.000| -14.000|
| $\epsilon(O2p)$| 0.000| 0.000| 0.000|
| $\epsilon(TM3d)$| 2.822| 3.400| 3.899|
| 10Dq           | 0.138| 0.142| 0.069|

TABLE I: Hybridization integrals and site-energies $\epsilon$ (in eV) obtained by a LCAO fit to paramagnetic LDA band structures. The site-energies have been shifted so as to have $\epsilon(O2p) = 0$. 


FIG. 1: LDA band structure (top) and LCAO-fit (bottom) for CoO.

energy of the \(d^n\) multiplets is \[1, 29 \]

\[ E = \frac{n(n-1)}{2}(A - \frac{14}{9}B + \frac{7}{9}C) \] (2)

which would suggest to define \(U_{av} = A - \frac{14}{9}B + \frac{7}{9}C\).

A second parameter which of importance for charge transfer systems \[1, 29 \] which is usually adjusted to experiment is the \(d\)-level energy or equivalently the charge transfer energy \(\Delta = E(d^{n+1}) - E(d^n)\). Expressing the \(E(d^n)\) in terms of Racah-parameters \(\Delta\) can be expressed in terms of these and the difference of site energies \(\epsilon(TM3d) - \epsilon(O2p)\). The values used in the present calculation are given in Table II as well. It should be noted that while the LCAO-fit actually gives an energy for these site energies - see Table II - these values of \(\epsilon(TM3d)\) already incorporate the Coulomb interaction between \(d\)-electrons. Since in our formalism the Coulomb interaction is described by the Hamiltonian \[1, 29 \] one would have to subtract it off to avoid double counting. Namely if one considers the Hubbard \(U\) known one may estimate the ‘bare’ value of \(\epsilon(TM3d)\) from the LDA site-energy \(\epsilon(TM3d)_{LDA}\) and the \(d\)-level occupancies \(n_d\) as \[20 \]

\[ \tilde{\epsilon}_d = \epsilon(TM3d)_{LDA} - 9U_{av}n_d. \] (3)

The estimates obtained in this way are also given in Table II. For NiO and CoO these corrected LDA values are close to the adjusted parameters used in the actual calculation. The situation is different for MnO but for this compound the \(U\) obtained from ground state energies also differs strongly from the multiplet average \(U_{av}\). The reason is the strong exchange stabilization in the high-spin ground state of \(d^5\) and one may not hope to obtain agreement between the two estimates for the site energy either. The reason is simply that a ‘Hubbard \(U\)’ is not uniquely defined in the presence of strong multiplet splitting. Finally, any Coulomb interaction between electrons which are not in the same \(TM3d\)-shell is neglected.

### III. VARIATIONAL CLUSTER APPROXIMATION

Having specified the strongly correlated problem under discussion we outline the variational cluster approximation. This is based on an expression for the grand potential \(\Omega\) of an interacting many-Fermion system derived by Luttinger and Ward \[34 \]. 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 in the unit cell, it reads \[42 \]

\[ \Omega = -\frac{1}{\beta} \sum_{k, \nu} \epsilon_{\nu, k} e^{\omega_{\nu}/\beta} \ln \det (-G^{-1}(k, \omega_{\nu}) + F[\Sigma]) \] (4)

where \(\omega_{\nu} = (2\nu + 1)\pi/\beta\) with \(\beta\) the inverse temperature are the Fermionic Matsubara frequencies,

\[ G^{-1}(k, \omega) = \omega + \mu - t(k) - \Sigma(k, \omega). \] (5)

with \(\mu\) the chemical potential and the functional \(F[\Sigma]\) is the Legendre transform of the Luttinger-Ward functional \(\Phi[G]\). The latter is defined \[34 \] as the sum of all

| Compound | \(A\) | \(B\) | \(C\) | \(\epsilon(TM3d)\) | \(U\) | \(\Delta\) | \(U_{av}\) | \(n_d(LDA)\) | \(\tilde{\epsilon}_d\) |
|----------|------|------|------|-----------------|------|--------|--------|----------------|---------|
| NiO      | 8.25 | 0.13 | 0.60 | -62.0           | 8.38 | 7.42   | 8.51   | 0.85           | -60.53  |
| CoO      | 7.2  | 0.14 | 0.54 | -45.5           | 7.34 | 11.48  | 7.40   | 0.76           | -45.81  |
| MnO      | 6.1  | 0.12 | 0.41 | -23.3           | 10.07| 10.07  | 6.23   | 0.56           | -26.91  |

TABLE II: Racah parameters, \(d\)-level energy, Hubbard \(U\) and charge transfer energy \(\Delta\). Also given are the ‘average Hubbard \(U\)’ according to \[2 \] the electron number per \(d\)-orbital as obtained from the LDA calculation and the estimate for the \(d\)-level energy according to \[3 \]. All energies are in eV.
closed linked skeleton diagrams with the non-interacting Green’s functions replaced by the full Green’s functions. A nonperturbative derivation of a functional with the same properties as \( \Phi \) has recently been given by Potthoff \cite{12}. \( \Phi[G] \) is the generating functional of the self-energy \( \Sigma \) i.e.

\[
\frac{1}{\beta} \Sigma_{ij}(k, \omega_\nu) = -\frac{\partial \Phi}{\partial G_{ij}(k, \omega_\nu)},
\]

and \( F[\Sigma] \) is obtained by Legendre-transform to eliminate \( G \) in favour of \( \Sigma \):

\[
F[\Sigma] = \Phi[G] - \frac{1}{\beta} \sum_{k, \nu} \text{trace} \left( (G(k, \omega_\nu) \Sigma(k, \omega_\nu) \right).
\]

By virtue of being a Legendre transform it obeys

\[
\frac{1}{\beta} G_{ij}(k, \omega_\nu) = -\frac{\partial F}{\partial \Sigma_{ji}(k, \omega_\nu)},
\]

and using the identity

\[
\frac{\partial}{\partial A_{ij}} \ln \det A = (A^{-1})_{ji}
\]

which holds for any matrix \( A \) with \( \det A \neq 0 \) as well as the Dyson equation \( \Sigma \) we find that \( \Omega \) is stationary with respect to variations of \( \Sigma \):

\[
\frac{\partial \Omega}{\partial \Sigma_{ij}(k, \omega_\nu)} = 0.
\]

The crucial obstacle in exploiting this stationarity property in a variational scheme for the self-energy \( \Sigma \) is the evaluation of the functional \( F[\Sigma] \) for a given ‘trial \( \Sigma \)’. Potthoff’s solution \cite{12} makes use of the fact that just like \( \Phi[G] \), \( F[\Sigma] \) has no explicit dependence on the single-particle terms of \( H \) and therefore is the same functional of \( \Sigma \) for any two systems with the same interaction part of the Hamiltonian. This is easily seen from the diagrammatic representation of \( \Phi[G] \) because the expression associated with a given Feynman diagram involves only the interaction matrix elements and the Green’s function itself.

In the VCA this independence of \( F[\Sigma] \) on the single-particle terms of the Hamiltonian is used to construct trial self-energies by exact diagonalization of finite clusters and thereby obtain the exact numerical value of \( F[\Sigma] \). In a first step one chooses a so-called reference system, which has the same interaction part as the lattice problem under study but consists of disconnected finite clusters. If the interaction terms are short ranged - which is the reason for keeping only the Coulomb interaction between electrons in the same d-shell - this can always be achieved by suitable choice of the single-particle terms. The disconnected finite clusters of the reference system then are solved by exact diagonalization, which gives the eigenenergies \( \epsilon_\nu \) and wave functions \( \{ \Phi_\nu \} \) for all particle numbers in the cluster. Of course this sets some limit on the size of the clusters. Next, the Green’s function \( G(\omega) \) and grand potential \( \Omega \) of the reference system are calculated numerically and equation \ref{eq:1} is reverted to express the exact numerical value of \( F[\Sigma] \) in terms of these. This simply means that the summation of infinitely many Feynman diagrams and Legendre transform is done implicitly in the course of the exact diagonalization of the reference system. Then, the self-energy \( \Sigma(\omega) \) of the reference system - which is readily extracted from the Dyson equation for \( G(\omega) \) - can be used as a trial self-energy for the lattice system. Thereby the numerical value of \( F[\Sigma] \) calculated in the cluster is simply inserted into the Luttinger-Ward formula \cite{43} for the grand potential of the physical (i.e. lattice) system. The variation of \( \Sigma(\omega) \) is performed by varying the single-electron parameters - such as hybridization integrals or site-energies - of the reference system.

In applying this procedure one frequently has to evaluate expressions of the type (the momentum \( k \) is suppressed for brevity)

\[
S = -\frac{1}{\beta} \sum_\nu e^{\omega_\nu} \ln \det (-G^{-1}(\omega_\nu)).
\]

To evaluate this we closely follow Luttinger and Ward \cite{34} and first convert the sum into a contour integral

\[
-\frac{1}{\beta} \sum_\nu g(\omega_\nu) \rightarrow \frac{1}{2\pi i} \int_{C_0} f(\omega) g(\omega) d\omega
\]

where \( f(\omega) \) is the Fermi function and \( C_0 \) is the standard contour encircling the singularities of the Fermi function in counter-clock-wise direction. Next we deform the contour so that it encircles the singularities of the logarithm, which are all located on the real axis (see the Appendix). Following Luttinger and Ward we then use

\[
f(\omega) = -\frac{1}{\beta} \frac{d}{d\omega} \log(1 + e^{-\beta\omega})
\]

and integrate by parts. Using \ref{eq:5} we thus obtain

\[
S = \frac{1}{2\pi \beta i} \int_C d\omega \log(1 + e^{-\beta\omega})
\]

\[
\text{trace \left( [1 - \frac{d\Sigma(\omega)}{d\omega}] G(\omega) \right)}
\]

where \( C \) is a contour that encircles the singularities of \text{trace} in clockwise fashion. This can now be evaluated by numerical contour integration. To derive the expression given by Potthoff we note the alternative expression

\[
S = -\frac{1}{2\pi \beta i} \int_C d\omega \log(1 + e^{-\beta\omega}) \sum_i \frac{1}{\lambda_i(\omega)} \frac{\partial \lambda_i(\omega)}{\partial \omega}
\]

where \( \lambda_i(\omega) \) are the eigenvalues of \( G(\omega) \). There are two types of singularities of this expression: a) zeroes of an eigenvalue, i.e.

\[
\lambda_i(\omega) \approx a_\nu (\omega - \zeta_\nu) \rightarrow \frac{1}{\lambda(\omega)} \frac{\partial \lambda(\omega)}{\partial \omega} = \frac{1}{\omega - \zeta_\nu}
\]
b) singularities of an eigenvalue, i.e.

\[ \lambda(\omega) \approx \frac{\partial \lambda(\omega)}{\omega - \eta_\mu} \rightarrow \frac{1}{\lambda(\omega)} \frac{\partial \lambda(\omega)}{\partial \omega} = -\frac{1}{\omega - \eta_\mu} \]

Whence

\[ S = -\frac{1}{\beta} \left( \sum_\mu \log(1 + e^{-\beta \eta_\mu}) - \sum_\nu \log(1 + e^{-\beta \eta_\nu}) \right), \]

i.e. the expression derived by Potthoff \[33\].

For the numerical evaluation of \( S \) a slightly different procedure is more convenient. For Matsubara frequencies \( \omega_\nu \) with \( |\nu| \leq \nu_{\text{max}} \) the respective terms in the sum \([10]\) are evaluated directly by computing the eigenvalues of \( G^{-1}(\omega) \). For \( |\nu| > \nu_{\text{max}} \) we switch to a contour integral using \([11]\) and deform the integration contour as indicated in Figure 2. Along \( C_1 \) and \( C_4 \) the integral is evaluated numerically again by calculating the eigenvalues of \( G^{-1}(\omega) \). Along the positive real axis the integrand thereby is cut off by the Fermi function. Along \( C_2 \) and \( C_3 \) we integrate by parts using again \([12]\) and deform the two pieces into the short piece \( C_5 \) - which is possible because the contour encloses no more singularities of the integrand. It is not possible to integrate by parts along \( C_1 \) and \( C_4 \) because these contours cross the lines - indicated by dashed lines in Figure 2 - where \( \log(1 + e^{-\beta \omega}) \) has branch cuts. The advantage of this procedure is that the resulting integration contour \( C_1 - C_5 - C_4 \) can be kept far from the singularities of the Greens function and self-energy on the real axis so that the integrand will always be a smooth function and a numerical integration with relatively few mesh points (of order 10\(^3\)) gives accurate results.

IV. REFERENCE SYSTEM

Given the excellent results obtained by the cluster method for angle-integrated spectra \([23, 24, 25, 26, 27]\) it seems natural to use clusters which are equivalent to TM06 octahedra as reference system. More precisely we choose a reference system where each TM3d orbital \( d_\alpha \) 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 \([11]\). The reference system thus is equivalent to an array of non-overlapping identical TM06 clusters where each ligand \( L_\alpha \) corresponds to the unique linear combination of \( 02p \) orbitals on the six nearest \( O \) neighbors of a given TM atom which hybridizes with the TM3d\( _\alpha \) orbital - see Figure 3. We write the single-particle Hamiltonian for a TML\( _6 \) cluster as

\[ H_{\text{single}} = \sum_{\alpha, \sigma} V(\alpha) \left( \hat{d}_{\alpha, \sigma}^\dagger L_{\alpha, \sigma} + \text{H.c.} \right) \]

\[ + \sum_{\alpha, \sigma} \left( E(\alpha) \hat{d}_{\alpha, \sigma}^\dagger \hat{d}_{\alpha, \sigma} + e(\alpha) L_{\alpha, \sigma}^\dagger L_{\alpha, \sigma} \right). \]

\[ (14) \]

The variational parameters thus are the hopping matrix elements \( (V_\alpha) \), the ligand energies \( e(\alpha) \) and the \( d \)-level energies \( E(\alpha) \) in total we thus have 6 parameters. It is convenient to rewrite the site-energies in the reference system as follows

\[ E(\epsilon_g) = \epsilon_0 - \epsilon_1 + 3\epsilon_2/5 + \epsilon_4, \]

\[ E(\epsilon_g) = \epsilon_0 - \epsilon_1 - 2\epsilon_3/5 + \epsilon_4, \]

\[ e(\epsilon_g) = \epsilon_0 + \epsilon_1 + 3\epsilon_3/5, \]

\[ e(\epsilon_g) = \epsilon_0 + \epsilon_1 - 2\epsilon_3/5. \]
As shown by Aichhorn et al., optimization of the ‘center of gravity’ $\epsilon_0$ ensures that the electron number obtained by differentiating $\Omega$ with respect to $\mu$ is equal to the result obtained by integrating the spectral function. The search for the stationary point of a function of 6 variables $\lambda_i$ is a difficult task - even more so because the stationary point is not a global minimum or maximum and is in fact not even a local extremum but a saddle point (see below). This problem has motivated the search for functionals other than $\Omega[\Sigma]$ which take an extremum for functionals other than $\Omega[\Sigma]$ which take an extremum. We can solve this problem in the following way, however: if we have a set of parameters which is sufficiently close to the stationary point we can evaluate the derivatives $\partial \Omega / \partial \lambda_i$ and $\partial^2 \Omega / \partial \lambda_i \partial \lambda_j$ numerically and use the Newton method to find the point where $\partial \Omega / \partial \lambda_i = 0$. Next, instead of the true lattice system we choose our ‘physical system’ to be a ‘hybrid system’ which contains both, the true lattice system we choose our ‘physical system’ to be the result obtained by integrating the spectral function.

Having found the stationary point we can calculate the form of second derivatives $\partial^2 \Omega / \partial \lambda_i \partial \lambda_j$ numerically and use the Newton method to find it. Second there are certain directions in parameter space where $\Omega$ shows only an extremely weak variation. This turned out to be true in all other cases studied as well. This weak variation may either stem from a near-invariance of the self-energy under changes of the cluster-parameters or the change of the self-energy is appreciable but irrelevant in that it does not change the lattice $\Omega$. The presence of such ‘nearly invariant lines’ in parameter space clearly is undesirable in that it may induce numerical instabilities. It may happen that small changes of $\Omega$ due to e.g. a slightly wrong LCAO band structure or even numerical inaccuracies may drive the stationary point along these lines in parameter space to compensate for them. To simplify matters the number of parameters therefore was reduced. Inspection of the eigenvectors associated with the ‘nearly invariant lines’ showed, that these were predominantly combinations of the parameters $\epsilon_1$ and $\epsilon_3$ in [15]. These parameters have almost no influence on $\Omega$ and hence were not subject to variation. The parameter $\epsilon_1$ was set equal to zero. In the cluster calculation the value for $\epsilon_3$ would be $2(pp\sigma) - 2(pp\pi)$ [24] - for simplicity the value $\epsilon_3 = 1.4eV$ was used for all three compounds. Including $\epsilon_1$ and $\epsilon_3$ into the set of parameters to be optimized actually turned out to give unsatisfactory results for the single particle spectrum. $\epsilon_1$ tended to take on large positive values whereas $\epsilon_3$ usually took large negative values. As a net effect this produced spurious photoemission peaks with very small spectral weight which were split off by one or two $eV$ from the remainder of the photoemission spectrum resulting in too small gaps and poor agreement with experiment. Clearly this is a feature of the variational cluster approximation which needs to be clarified. It should be noted that reducing the number of parameters which are optimized simply amounts to restricting the space of trial self-energies. Since op-
Optimization of these parameters hardly changes $\Omega$ this is similar to restricting the degrees of freedom in a trial wave-function to the most relevant ones. It then seems that an ‘overoptimization’ of parameters leads to poor results but on the other hand the inclusion of irrelevant degrees of freedom into a variational wave function may also be detrimental for properties of the wave function other than the ground state energy.

Finally, NiO turned out to be a special case. Since the ground state of $d^8$ in cubic symmetry is $t^{2g}_{2g}$, the hopping integral $V(t^{2g})$ has practically no impact on $\Omega$ because it connects filled orbitals. In fact, derivatives of $\Omega$ with respect to $V(t^{2g})$ turned out to be of order $10^{-10}$, i.e. well beyond the numerical accuracy of the whole procedure. $V(t^{2g})$ was therefore kept at $2(pd\pi)$ which again is the value expected in the cluster calculation. In a previous VCA-study of NiO[36] a different approach was chosen. There the hopping integral $V(t^{2g})$ was set equal to zero. This implies that the $t^{2g}$-like ligands are irrelevant altogether and can be discarded from the reference system, so that also the parameters $E(t^{2g})$ and $e(t^{2g})$ play no more role. Although slightly different LCAO- and Racah-parameters were used in this calculation the results obtained in Ref. [36] are very similar to the ones in the present study, in particular the bands in the valence band top are essentially identical.

V. RESULTS

The parameters at the stationary point of $\Omega$ have practically no dependence on temperature. Figure 6 shows the temperature dependence of $\Omega$ for CoO. This can be fitted very well by $\Omega(T) = \Omega_0 - k_B T \log(12)$. The second term thereby is the entropy due to the degeneracy of the $^{4}T_{1g}$ ground state of $d^7$ in cubic symmetry. In a system with a wide gap this is the expected behaviour of $\Omega$. This is clearly a trivial result but it should be noted that for the discussion of a phase transition to a magnetically or orbitally ordered state the correct description of this entropy is important because this competes with the energy gain due to ordering.

Next we consider the resulting self-energy. Figure 7 shows the spectral density of the CoO$_6$ cluster and the self-energy at the stationary point for $T = 150$ Kelvin. Due to the cubic symmetry of the cluster only the diagonal elements of the self-energy are non-vanishing and these are identical between all $e_g$ and $t^{2g}$ orbitals, respectively. Luttinger has shown[46] that the self energy has a spectral representation of the form

$$\Sigma(\omega) = \eta + \sum_{\nu} S_{\nu} \frac{1}{\omega - \zeta_{\nu}}$$

where the real matrix $\eta$ is actually the Hartree-Fock potential and the poles $\zeta_{\nu}$ are all on the real axis. The spectral density of the cluster has a well-defined gap around $\omega = 0$ between a charge-transfer peak and the upper Hubbard band. The self-energy for both $e_g$ and $t^{2g}$ electrons has a strong central peak (indicating a pole $\zeta_{\nu}$ with large residuum $S_{\nu}$) in this gap. Using the Dyson-equation it
is easy to convince oneself that such a strong peak in the self-energy indeed ‘pushes open’ a gap in the pole structure of the Green’s function. Several other prominent peaks create additional gaps in the spectral density and thus split off the satellite below $-9\text{eV}$. In addition there are many small peaks near the top of the valence band. Since the poles of the Green’s function are ‘sandwiched’ between the poles of the self-energy we thus expect a large number of 3d-derived bands with very small dispersion in this energy range.

Next, we proceed to a comparison of $G(k,\omega)$ to experiment and begin with NiO. Figure 8 compares $k$-integrated spectral densities at $T = 150$ Kelvin to angle-integrated valence band photoemission spectra taken by Oh et al.\cite{oh2001} at two different photon energies. It is known\cite{oh2001} that with decreasing photon energy the intensity of $O2p$ derived states increases relative to that of $TM3d$ derived states - the change of the spectra with photon energy thus allows to draw conclusions about the character of individual peaks. Moreover, final states with $d^{n-1}$ character are enhanced at a photon energy just above the $TM3p \rightarrow TM3d$ absorption threshold so that such energies are particularly suited to identify this type of final state. Accordingly, at $h\nu = 150\text{eV}$ the experimental spectrum mostly resembles the $d$-like spectral density, whereas at $h\nu = 67\text{eV}$ the states at the valence band top are anti-resonantly suppressed - whence $O2p$-derived features become more clearly visible - and the ‘satellite’ at $-10\text{eV}$ is resonantly enhanced. Figures 9 and 10 compare the $k$-resolved spectral function for momenta along $\Gamma-X$ in NiO. Lorentzian broadening $0.05\text{eV}$, $d$-like weight is multiplied by factor of 2.
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 $\approx -3.5$ eV and $\approx -2$ eV, which was shown to consist of several sub-peaks by Shen et al.\cite{10}. These authors did not actually resolve the dispersion of the individual sub-peaks although the data seem to indicate a weak overall ‘upward’ dispersion as one moves $\Gamma \rightarrow X$ which would be consistent with theory. Proceeding to more negative binding energy the experimental band structure shows a gap of $\approx 1$ eV and then a group of dispersionless bands between $-6$ eV and $-4$ eV. This is bounded from below by a weakly dispersive band which resembles one of the $O2p$ derived bands. In the angle-integrated spectrum, Figure 8, the topmost of these dispersionless bands produces the ‘shoulder’ at $-4$ eV. The gap between the topmost band complex and the group of dispersionless bands in the theoretical spectra is not as wide as in experiment but there are clearly several dispersionless bands in approximately the right energy range. The agreement would be very good if the peaks at $\approx -3.5$ eV in Figures 9 and 10 were shifted by $\approx 0.5$ eV to more negative binding energy. In addition, the $O2p$ derived band can be seen clearly. As can be seen from the band structure in Figure 11 this band actually has a saddle point at $X$ - this gives rise to a van Hove-singularity in the angle-integrated spectrum which matches very well the peak at $\approx -5.5$ eV in Figure 8. The sole strongly dispersive feature in the spectrum, namely an $O2p$-derived band at binding energies between $-6$ eV $\rightarrow -9$ eV is again well reproduced by theory. Finally the ‘satellite’ at binding energies $-8$ eV $\rightarrow -12$ eV consists of at least two sub-peaks as can be seen in Figure 8 and also in the ARPES data.

Next we consider CoO. Figure 11 compares the angle integrated spectra at different photon energies and the $k$-integrated spectral function obtained by the VCA, Figure 12 shows the dispersion along $\Gamma \rightarrow X$ and ARPES data from Shen et al.\cite{5} and Brookes et al.\cite{48}. The XPS spectrum for CoO starts out with a prominent peak at $-3$ eV.
followed by three ‘humps’ at $-5eV$, $-8eV$ and $-12eV$. The VCA gives peaks of $d$-like spectral weight at roughly these energies although the peak at $-5eV$ is at slightly too negative energy. The PES spectrum at $40eV$ shows additional peaks at $-6.5eV$ and $-9eV$ which were interpreted as $O2p$-derived by Shen et al. These peaks are also reproduced by the VCA. A little more problematic is the angle resolved spectrum. Along (100) the VCA predicts a split peak at the the top of the valence band at $-4eV$. This splitting is not seen in experiment - on the other hand, the spectra were taken at low photon energy where the Co3d states have relatively small weight. There is another $d$-derived band at $-6eV$ which corresponds to the second ‘hump’ in the angle integrated spectrum. This is crossed by and mixes with one of the $O2p$ derived bands, which start at $\Gamma$ at an energy of $-5eV$. The presence of these two crossing bands may explain the ‘wiggly’ nature of the bands observed experimentally in this energy range. The presence of more than one band and a possible crossing between these is clearly seen in the data of Shen et al. Finally there is the strongly dispersive $O2p$ derived band at energies of around $-8eV$. Surprisingly the experimental dispersions for this band differ somewhat - this may be due to the crossing of this band with the dispersionless Co3d derived band at $-7.5eV$ which leads to a hybridization gap in the $O2p$ derived band.

Finally we consider MnO. Figure 13 shows the angle integrated photoemission spectra compared to the result from the VCA. At high photon energy the experimental spectrum matches well the $d$-derived density of states. The single-particle gap and the structure of the valence band spectrum are reproduced well. At a photon energy of $20eV$ the intense peak at $-5.5eV$ almost disappears and another large peak at $-6.5eV$ appears, which accordingly must have $O2p$ character. In the theoretical spectra this is reproduced well, the peak at $-6.5eV$ again is due

FIG. 12: Top: Experimental band structure along (100) as seen in ARPES by Shen et al. and by Brookes et al. in CoO. Bottom: $k$-dependent spectral function for momenta along $\Gamma - X$ for CoO. Lorentzian broadening $0.05 eV$, $d$-like weight is multiplied by factor of 2.

FIG. 13: Single particle spectral densities obtained by VCA for MnO compared to valence band photoemission data. Experimental data in (a) from Ref. [26], in (b) from Ref. [27].
FIG. 14: Spectral function for momenta along Γ − X in MnO. Lorentzian broadening 0.05 eV, d-like weight is multiplied by factor of 2. There are no ARPES results available.

FIG. 15: Dispersion of the ‘sub-peaks’ in the photoemission spectra of NiO (top) and CoO (bottom). Also shown are the energies of the poles of the self-energy.

to a van-Hove singularity at X. Figure [14] shows the \( k \)-resolved spectrum along (100). Lad and Heinrich\[^8\] performed ARPES measurements on MnO but did not perform any band mapping due to the broad nature of peaks so that an experimental dispersion unfortunately is not available.

Lastly we discuss the fine structure of the TM3d derived bands. This is shown in Figure [15]. The band structures of all three compounds have a similar structure: at the top of the band structure there is a group of dispersive bands which shows a rough similarity with the upper group of bands in the LDA band structure (see Figure [1]), which have mainly TM 3d-character. The total width of this band complex is reduced by a factor of \( \approx 0.5 \) as compared to LDA. These bands have high spectral weight and produce the intense peaks at the top of the angle-integrated spectra for NiO and CoO. Separated from this group of dispersive bands there is then a region with many almost dispersionless bands with relatively low spectral weight. This overall structure can be understood by considering the spectral representation of the self energy \[^1\] and the equation for the poles of the Green’s function

\[
\omega + \mu - \epsilon_k - Re \Sigma(\omega) = 0
\]

where we have considered the single band case for simplicity. Since \( Re \Sigma(\omega) \) takes any value between \( \infty \) and \( -\infty \) in between two successive poles \( \zeta_{\nu} \) and \( \zeta_{\nu+1} \) there is one band in between any two successive poles of the self energy. This implies that the distance between these two successive poles is an upper bound for the width of this band, which may be viewed as a kind of correlation narrowing. Moreover, if a pole \( \zeta_{\nu} \) has only a small residuum the resulting pole of the Green’s function will be almost ‘pinned’ very close to it - as can be seen repeatedly in Figure [15]. The topmost group of relatively strongly dispersive bands then is actually above the topmost pole of \( \Sigma(\omega) \) in the valence band region and the dominant ‘gap opening peak’ in the center of the insulating gap, see Figure [7]. Since the separation in energy between these peaks is large - of the order of the insulating gap - these bands still have an appreciable width. The similarity with the LDA band structure is due to the fact that the dispersion of these bands is largely due to direct \( d-d \) -hopping, which remains operative also when the self-energy is included.
While the fine structure of the valence band top is not really resolved experimentally as yet, at least experiment puts a quite low upper limit $\leq 0.5$ eV along (100) - on the width of the individual bands. The VCA would be consistent with that.

The large number of dispersionless bands at more negative binding energy is produced by the large number of densely spaced poles of the self-energy. These are in turn the consequence of the large number of CEF-split multiplet states in the TMO$_6$ cluster. Interestingly, at least in the case of NiO where detailed band mapping is available from ARPES, the experimental band structure is quite consistent with this overall structure, namely a group of dispersive bands at the top of the valence band and essentially dispersionless bands at more negative binding energy. The distance between the dispersive band complex and the dispersionless bands is underestimated somewhat by VCA.

To conclude we compare the results of the VCA for NiO with recent LDA+DMFT calculations$^{21, 22}$. Figure 16 compares the $k$-integrated spectra, Figure 17 shows the dispersion along (100). The DMFT-results are taken from Yin et al.$^{22}$ which have obtained essentially identical results as Kunes et al.$^{21}$. While the $k$-integrated spectra look similar at first sight, comparison with the band structure shows that there are major differences. In the DMFT spectrum the top of the valence band is formed by a split off peak $A'$ with low spectral weight. This corresponds to the two topmost bands labelled $A'$ in Figure 17. The intense peak $B$ in the DMFT spectrum on the other hand originates from the band $B$ in Figure 17. The DMFT bands moreover show a rather obvious correspondence with the LDA band structure, resulting in bands with quite strong dispersion. As already noted the VCA differs strongly from LDA and shows a larger number of bands, with several of them being practically dispersionless, i.e. corresponding to localized electrons. Comparing with experiment, the raw data of Shen et al.$^{10}$ show no indication for the split off bands $A$ with low spectral weight as predicted by DMFT. With the exception of the O2p derived bands ARPES moreover shows no indication of the wide bands predicted by DMFT - rather there is a number of dispersionless bands as expected on the basis of the VCA. One may say that there are major differences between DMFT and VCA so that further experiments might resolve this discrepancy.

VI. CONCLUSION

To summarize, the variational cluster approximation due to Potthoff allows to combine the powerful cluster configuration interaction method for transition metal compounds due to Fujimori and Minami with the field-theoretical work of Luttinger and Ward to implement a variational scheme for the electronic self-energy and construct an efficient band structure method for strongly correlated electron compounds. As demonstrated above, a realistic band structure and the full atomic multiplet interaction can be incorporated into the Hamiltonian without problems, the system can be studied at arbitrar-
ily low temperatures and the Green’s function be obtained with arbitrary energy resolution. The key numerical problem of finding the stationary point of the grand potential thereby can be solved efficiently by a simple crossover procedure. It has been shown that in the course of varying the self-energy there may exist redundant degrees of freedom which leave the grand potential almost unchanged. Such redundant degrees of freedom can be eliminated by simply reducing the number of parameters in the reference system.

The results are quite encouraging in that there is good agreement between the calculated Green’s function and electron spectroscopies at least to the extent that ARPES data are available. The good agreement also suggests that the band structure of NiO, CoO and MnO is ‘Coulomb generated’ in that the atomic multiplet structure survives with minor modifications. All in all the VCA appears to be a promising tool for the study of realistic models of correlated electron systems. The possibility to treat the multiplet and CEF-splitting of the electronic problem of finding the stationary point of the grand potential remains unchanged. Such redundant degrees of freedom can be eliminated by simply reducing the number of parameters in the reference system.

I would like to thank M. Potthoff for many instructive discussions.

VII. APPENDIX

We show that ln(det G(ω)) is analytical off the real axis, where G(ω) can be either the exact Green’s function of the reference system or the approximate Greens function form the VCA. It is sufficient to prove that all eigenvalues of G(ω) have a nonvanishing imaginary part for ω not on the real axis. This is proved in turn if we show that

$$\langle \nu | G(\omega) | \nu \rangle = \sum_{i,j} v_i^* G_{ij}(\omega) v_j$$

has a nonvanishing imaginary part for any normalized ν. For the exact Greens function we have - using the Lehman representation -

$$\langle \nu | G(\omega) | \nu \rangle = \frac{1}{Z} \sum_{\nu', \nu} \frac{\left| C_{\nu\nu'} \right|^2}{\omega - (E_{\nu'} - E_{\nu})} \left( e^{-\beta \epsilon_{\nu'}} + e^{-\beta \epsilon_{\nu}} \right)$$

where \( \epsilon_{\nu} = E_{\nu} - \mu N_{\nu} \) and

$$C_{\nu\nu'} = \langle \nu | \sum_i v_i c_i | \nu' \rangle$$

It follows that for \( \omega \) in the upper (lower) half plane all eigenvalues of G(ω) have a negative (positive) imaginary part and accordingly all eigenvalues of G\(^{-1}(\omega)\) have a positive (negative) imaginary part. The imaginary part could only be zero if all \( C_{\nu\nu'} \) were zero which is unlikely to occur. A similar proof has been given previously by Dzyaloshinskii[40]. Luttinger has shown that the self-energy \( \Sigma(\omega) \) has a spectral representation of the form

$$\Sigma(\omega) = g + \sum_{\nu} \frac{S_{\nu}}{\omega - \xi_{\nu}}$$

with a real g[40]. Since G(ω) is Hermitian for real \( \omega \) the matrices \( S_{\nu} \) are Hermitian too moreover positive definite. Namely if one of the matrices \( S_{\nu} \) had a negative eigenvalue \( \lambda \) then G\(^{-1}(\xi_{\nu} + i\epsilon)\) had the eigenvalue \( \frac{1}{2} \lambda \) plus terms which stay finite as \( \epsilon \to 0 \), whereas we have shown that all eigenvalues for \( \omega \) in the upper half-plane have positive imaginary parts. It follows immediately that

$$\langle \nu | \omega - \Sigma(\omega) | \nu \rangle$$

has a positive (negative) imaginary part for \( \omega \) in the upper (lower) half plane which proves that all eigenvalues of the approximate Greens functions off the real axis have nonvanishing imaginary parts as well.

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