Electronic Structure of NiO: Antiferromagnetic Transition and Photoelectron Spectra in the Ordered Phase

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The thermodynamics of the antiferromagnetic ordering transition in NiO and the photoelectron spectra in the antiferromagnetic phase are studied by the Variational Cluster Approximation. Using realistic Racah parameters to describe the Coulomb interaction in the Ni 3d shell and a Slater-Koster parameter \((p\sigma)\) which is slightly (10%) increased over the band structure estimate the calculated Néel temperature is 481 Kelvin (experimental value: 523 Kelvin). The magnetic susceptibility above \(T_N\) has Curie-Weiss form. A significant contribution to the stabilization of the antiferromagnetic phase comes from electron hopping between oxygen which would be missed in theories that consider superexchange along a single bond only. The single particle spectral function in the ordered phase is in good agreement with experiment, in particular a number of dispersionless bands which are not reproduced by most calculations are obtained correctly. These flat bands are shown to be direct experimental evidence for a dispersionless electronic self-energy with several poles in the energy range of the valence band which originate from the multiplets of the Ni\(^{3+}\) ion. Small but possibly experimentally detectable changes of the photoelectron spectra with temperature are discussed, in particular a widening of the insulating gap in the paramagnetic phase by approximately 10% is predicted.

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I. INTRODUCTION

Nickel Oxide has received attention over several decades because it is the prototype of a correlated insulator. As early as 1937 this material was cited as a counterexample to the Bloch theory of solids[1]: assuming strong ionicity, oxygen will be O\(^{2-}\) leaving Nickel to be Ni\(^{2+}\) or [Ar]3d\(^8\). This means that 4 electrons/spin direction have to be distributed over five Ni 3d bands which could result in an insulating ground state only if one of the five bands were split off from the others over the entire Brillouin zone. This is impossible, however, because at \(\Gamma\) the five Ni 3d bands converge into one 3-fold degenerate \((t_{2g})\) and one 2-fold degenerate \((e_g)\) level. Band structure calculations for the paramagnetic phase of NiO confirm this, showing three O 2p derived bands well below the Fermi energy and a group of five Ni 3d bands which are intersected by the Fermi energy.

This simple picture is modified in that NiO undergoes an antiferromagnetic ordering transition at \(T_N = 523\) Kelvin. Thereby Ni-ions in planes perpendicular to \((1,1,1)\) allign their magnetic moments parallel to each other, with the ordered moment in successive planes being antiparallel (type II antiferromagnetism). This structure is consistent with the Goodenough-Kanamori rules because all 180° Ni-O-Ni bonds are antiferromagnetic in this way. Band structure calculations within the framework of Density Functional Theory (DFT) for the antiferromagnetic phase reproduce the insulating ground state, but the band gap is only \(G \approx 0.3\) eV[2] whereas the experimental value is \(G \approx 4.3\) eV[3]. It should be noted, however, that DFT does indeed give a rather accurate estimate of \(G = 4.1\) eV for the single-particle gap in NiO[2] if one does not use the band structure of Kohn-Sham eigenvalues - which have no true physical significance anyway - but calculates the ground state energy \(E_0\) of finite clusters as a function of electron number \(N\) and uses \(G = E_0(N+1) + E_0(N-1) - 2E_0(N)\). The crucial point is, however, that NiO remains an insulator even above \(T_N\) so that the insulating nature of NiO cannot be explained by antiferromagnetic ordering.

There is general agreement by now that the true origin of the insulating nature of NiO is the strong Coulomb interaction between electrons in the Ni 3d shell so that an adequate description requires a more accurate treatment of the electron-electron interaction. Accordingly, a wide variety of methods for treating interacting electrons have been applied to NiO over the years. Amongst others there are calculations using the self-interaction corrected density functional theory[6, 7], the LDA+U formalism[8, 9] and the GW approximation[10, 11] which more recently, was also combined with the LDA+U formalism[12]. NiO was also treated in the framework of the three-body scattering formalism[13, 14] and dynamical mean-field theory (DMFT), both for the paramagnetic[15, 16] and antiferromagnetic[18] phase. Moreover it was shown recently that within DFT the agreement between calculated and measured band gap for antiferromagnetic NiO is improved considerably if a more accurate density functional is used[19].

A quite different - but very successful - approach was initiated by Fujimori and Minami[20]. These authors showed that good agreement between theory and experiment could be obtained for angle-integrated valence band photoemission spectra if one focused on local physics by considering an octahedron-shaped NiO\(^6^-\) cluster comprising of a single Ni-ion and its six nearest neighbor oxygen ions. The eigenstates and eigenenergies of such a
finite cluster can be calculated exactly by the configuration interaction (CI) (or exact diagonalization) method and the single-particle spectral function can be obtained from its Lehmann representation. The CI method was subsequently applied to the calculation of the angle-integrated valence band photoemission spectra of a number of transition metal compounds and was extended to simulate X-ray absorption spectra. In all cases the agreement with experiment is excellent and in the case of X-ray absorption spectroscopy the comparison of simulated and measured spectra by now is in fact becoming a routine tool for determining the valence and spin state of transition metal ions in solids.

The reason for the success of the cluster method is that it takes into account the full Coulomb interaction between electrons in the transition metal 3d shell in the framework of atomic multiplet theory. Introducing the compound index \( \nu = (n, l, m, \sigma) \) (where \( n = 3 \) and \( l = 2 \) for a 3d-shell) the Coulomb interaction between electrons in atomic shells can be written as:

\[
H_1 = \frac{1}{2} \sum_{i,j,k,l} V(\nu_i, \nu_j, \nu_k, \nu_l) c_i^{\dagger} c_j^{\dagger} c_k c_l,
\]

\[
V(\nu_1, \nu_2, \nu_3, \nu_4) = \delta_{\sigma_1, \sigma_4} \delta_{\sigma_2, \sigma_3} \delta_{m_1+m_2, m_3+m_4} \sum_k F_k^{l c_1(\nu_1+m_1) c_2(\nu_3+m_3) c_3(\nu_2+m_2)}.
\]

(1)

Here the \( c^k(lm_1;lm_2) \) denote Gaunt coefficients the \( F^k \) Slater integrals and for a d-shell the multipole index \( k \in \{0, 2, 4\} \). The Hamiltonian was derived originally to explain the line spectra of atoms and ions in vacuum, see Ref. for an extensive list of examples. There are various simplified expressions in the literature where the Hamiltonian is approximated in terms of Hubbard-U and Hund’s rule \( J \) and sometimes additional parameters (see Ref. for the relation between Hubbard-U and Hund’s rule \( J \) and the Slater integrals) but the Hamiltonian is the only one that can actually be derived from first principles and gives correct results for free ions (an instructive comparison of the eigenvalue spectra of the original Hamiltonian and various simplified versions was given by Haverkort). \( H_1 \) contains diagonal terms such as

\[
(V(\nu_1, \nu_2, \nu_1, \nu_2) - V(\nu_1, \nu_2, \nu_2, \nu_1)) n_{\nu_1} n_{\nu_2}
\]

(2)

but also off-diagonal terms where all four \( \nu_i \) in are pairwise different. The off-diagonal matrix elements are frequently discarded in DMFT calculations because they exchange electrons and thus exacerbate the minus-sign problem in quantum Monte-Carlo calculations. On the other hand the matrix elements of these terms are of the same order of magnitude (namely proportional to the Slater integrals \( F^2 \) and \( F^4 \)) as the differences between the various diagonal matrix elements in [2] so that there is no justification for discarding them but keeping different diagonal matrix elements. As will be seen below the Variational Cluster Approximation (VCA) proposed by Potthoff allows to extend the scope of the CI method of Fujimori and Minami once more, to the calculation of thermodynamical quantities and band structures for strongly correlated electron systems. Since the VCA is based on exact diagonalization and therefore free from the minus-sign problem the full Coulomb Hamiltonian including the off-diagonal matrix elements can be included. As could have been expected on the basis of the considerable success of the CI method in reproducing experimental spectra the VCA achieves good agreement with experiment.

II. HAMILTONIAN AND METHOD OF CALCULATION

The method of calculation has been described in detail in Ref. so we give only a brief description. The Hamiltonian describing the NiO lattice is

\[
H = H_0 + H_1
\]

\[
H_0 = \sum_{i \sigma} \epsilon_i d_{i \sigma}^{\dagger} d_{i \sigma} + U \sum_{i} n_{i \sigma} n_{i \sigma} + H_{dd}
\]

\[
H_{pd} = \sum_{i \alpha, j \beta} \sum_{\sigma} (t_{i \alpha, j \beta} d_{i \alpha \sigma} p_{j \beta \sigma} + H.c.)
\]

(3)

where e.g. \( d_{i \alpha \sigma}^{\dagger} \) creates an electron with \( z \)-spin \( \sigma \) in the Ni 3d orbital \( \alpha \in \{xy, xz, \ldots, 3z^2-r^2\} \) at the Ni-site \( i \) whereas \( p_{j \beta \sigma}^{\dagger} \) creates an electron in the O 2p orbital \( \beta \in \{x, y, z\} \) at the O-site \( j \). The energy of the O 2p orbitals is the zero of energy. The terms \( H_{pp} \) and \( H_{dd} \) describe hopping between two O 2p orbitals or two Ni 3d orbitals, respectively, and their form is self-evident. The parameters in this Hamiltonian have been obtained from a fit to an LDA band structure and are listed in Table I of Ref. One noteworthy detail is that the energies \( \epsilon_{\alpha} \) have to be subject to the ‘double-counting correction’: \( \epsilon_{\alpha} \rightarrow \epsilon_{\alpha} - nU \) with \( U \) the Hubbard U - see Ref. for a detailed discussion. The interaction Hamiltonian \( H_1 \) has the form [11] for each Ni 3d shell, the Racah parameters were \( A = 7 \) eV, \( B = 0.13 \) eV \( C = 0.6 \) eV, resulting in the Slater integrals \( F^0 = 7.84 \) eV, \( F^2 = 10.57 \) eV and \( F^4 = 7.56 \) eV. An important detail is that there is a nonvanishing interaction only between Ni 3d orbitals in the same Ni ion.

For a multiband system such as the imaginary time Green’s function \( G(k, i\omega_N) \) and self-energy \( \Sigma(k, i\omega_N) \) are matrices of dimension \( 2n_{orb} \times 2n_{orb} \) with \( n_{orb} \) the number of orbitals/unit cell. In the following we will often omit the \( k, i\omega_N \) argument on these quantities for brevity. The starting point for the VCA is an expression for the Grand Canonical Potential of an interacting Fermi sys-
\[
\Omega = - \frac{1}{\beta} \sum_{\mathbf{k}, \nu} e^{i \omega_{\nu} 0^+} \left[ \ln \det (-\mathbf{G}^{-1}) + \text{tr} \, \Sigma \mathbf{G} \right] + \Phi[\mathbf{G}].
\]

(4)

Here \(\Phi[\mathbf{G}]\) denotes the so-called Luttinger-Ward functional which was defined originally as a sum over infinitely many closed, connected, skeleton diagrams with the noninteracting Green’s function \(\mathbf{G}_0\) replaced by the argument of the functional, \(\mathbf{G}\). A nonperturbative construction of \(\Phi[\mathbf{G}]\) has been given by Potthoff. Luttinger and Ward derived two important results: first, \(\Phi[\mathbf{G}]\) is the generating functional of the self-energy

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

(5)

and, second, \(\Omega\) is stationary under variations of \(\Sigma\)

\[
\frac{\partial \Omega}{\partial \Sigma_{\alpha\beta}(\mathbf{k}, i \omega_{\nu})} = 0.
\]

(6)

The first of these equations can be used to define the Legendre transform \(F[\Sigma]\) of \(\Phi[\mathbf{G}]\) via

\[
F[\Sigma] = \Phi[\mathbf{G}[\Sigma]] - \frac{1}{\beta} \sum_{\mathbf{k}, \nu} \text{tr} \, \Sigma \, \mathbf{G}.
\]

Introducing the noninteracting Green’s function \(\mathbf{G}_0\), \(\Omega\) thus can be expressed as a functional of \(\Sigma\):

\[
\Omega = - \frac{1}{\beta} \sum_{\mathbf{k}, \nu} e^{i \omega_{\nu} 0^+} \left[ \ln \det (-\mathbf{G}_0^{-1} + \Sigma) \right] + F[\Sigma]
\]

(7)

which is known to be stationary at the exact \(\Sigma(\omega)\) by virtue of \(\Omega\). The problem one faces in the practical application of this stationarity principle is that no explicit functional form of \(F[\Sigma]\) is known.

In the framework of the VCA this problem is circumvented as follows: first, we note that \(\Phi[\mathbf{G}]\) involves only the interaction part \(H_I\) of the Hamiltonian (via the interaction lines in the skeleton diagrams) and the Green’s function \(\mathbf{G}\) (via the Green’s function lines) - the latter, however, is the argument of the functional. This implies that the functional \(\Phi[\mathbf{G}]\) and its Legendre transform \(F[\Sigma]\) are the same for any two systems with the same interaction part \(H_I\) (Potthoff has derived this property without making any reference to diagrams).

In the application to NiO we accordingly consider two systems: System I is the original NiO lattice described by the Hamiltonian \(H\) whereas System II - termed the reference system by Potthoff - is an array of clusters, each of which consists of the five Ni 3d orbitals of one Ni ion of the original NiO lattice plus five Ligands or bath sites which hybridize with these. The single-particle Hamiltonian of such a cluster is

\[
\tilde{H}_0 = \sum_{\alpha, \sigma} (\epsilon_d(\alpha) \, d_{\alpha, \sigma}^\dagger \, d_{\alpha, \sigma} + \epsilon_L(\alpha) \, l_{\alpha, \sigma}^\dagger \, l_{\alpha, \sigma}) + \sum_{\alpha, \sigma} (V(\alpha) \, d_{\alpha, \sigma}^\dagger \, l_{\alpha, \sigma} + H.c.),
\]

(8)

where \(\alpha \in \{xy, xz, 3z^2 - r^2\}\) whereas the interaction part \(H_I\) for each cluster is again given by \(\Omega\). In the CI method by Fujimori and Minami the Ligand \(l_{\alpha}\) would be the linear combination of O 2p orbitals on the 6 oxygen ions surrounding the Ni ion under consideration which hybridizes with the d-orbital \(d_{\alpha}\). In the case of the VCA the Ligands are purely mathematical objects which have no counterpart in the physical system and which are introduced solely for the purpose of constructing self-energies. Accordingly, there are no terms coupling the clusters centered on neighboring Ni ions in system II which therefore consists of completely disconnected finite clusters. The crucial point is, that since the interaction parts of systems I and II are identical by construction they have the same Luttinger-Ward functional \(F[\Sigma]\). Since the individual clusters of system II are relatively small - they comprise 10 orbitals/spin direction - they can be treated by exact diagonalization and we can obtain all eigenstates of \(H - \mu N\) within \(\approx 20k_BT\) above the minimum value. Using these the Grand Potential \(\Omega\) can be evaluated numerically (quantities with \(\tilde{\cdot}\) refer to a cluster in the following) and the full Green’s function \(\mathbf{G}(\omega)\) can be calculated (e.g. by using the Lanczos algorithm). Next, \(\mathbf{G}(\omega)\) can be inverted numerically for each \(\omega\) and the self-energy \(\Sigma(\omega)\) be extracted. Thereby we have in real-space representation \(\tilde{\Sigma}_{\alpha\beta}(i, j, \omega) = \hat{\Sigma}_{\alpha\beta}(\omega) \, \delta_{ij}\) where \(i, j\) are the indizes of the individual disconnected clusters and moreover \(\tilde{\Sigma}_{\alpha\beta}(\omega) \neq 0\) only if both indizes \(\alpha\) and \(\beta\) refer to Ni 3d orbitals. The resulting self-energy thus is \(\mathbf{k}\)-independent and bears no more reference to the fictitious Ligands.

Using \(\Omega\) and \(\Sigma(\omega)\) the equation - now applied to a single cluster - can be reverted to obtain the numerical value of \(F[\Sigma]\) for the self-energy \(\Sigma(\omega)\). By taking the disgregation to the reference system of clusters it is thus possible to generate self-energies for which the exact numerical value of the Luttinger-Ward functional is known. Next, these self-energies are used as ‘trial self-energies’ for the lattice i.e. we approximate

\[
\Omega \approx - \frac{1}{\beta} \sum_{\mathbf{k}, \nu} e^{i \omega_{\nu} 0^+} \left[ \ln \det \left( -\mathbf{G}_0^{-1} + \tilde{\Sigma} \right) \right] + NF[\tilde{\Sigma}]
\]

(9)

where \(\mathbf{G}_0\) now is the noninteracting Green’s function of the physical NiO lattice and \(N\) the number of Ni-sites in this.

The variation of \(\tilde{\Sigma}\) is performed by varying the single particle parameters \(\lambda_i\) of the cluster single-particle Hamiltonian \(H\), that means \(\epsilon_d(\alpha), \epsilon_L(\alpha)\) and \(V(\alpha)\). These
parameters are not determined as yet because the only requirement for the equality of the Luttinger-Ward functionals of the two systems was that the interaction parts \( H_I \) be identical. In this way the approximate \( \Omega \) becomes a function of the \( \lambda_i \), \( \Omega = \Omega(\lambda_1, \ldots, \lambda_n) \) and the stationarity condition (6) is replaced by a condition on the \( \lambda_i \):

\[
\frac{\partial \Omega}{\partial \lambda_i} = 0. \quad (10)
\]

The physical interpretation would be that the VCA amounts to seeking the best approximation to the true self-energy of the NiO lattice amongst the ‘cluster representable’ ones. Since its invention by Potthoff the VCA has been applied to study the Hubbard model in various dimensions [54–64] for 3d transition metal compounds [65–69] and interacting Bosons [70, 71]. For the present application to NiO and in the paramagnetic case cubic symmetry reduces the number of parameters \( \lambda_i \) to be varied to only six: for each \( \alpha \) the Hamiltonian (5) contains 3 parameters and there is one such set for the \( e_g \) orbitals and one for the \( t_{2g} \) orbitals. The equation system (10) is solved by the Newton method, see Refs. [54, 68] for details. The proposal of Balzer and Potthoff [55] to use rotated and rescaled coordinate axis for the calculation of the derivatives of \( \Omega \) with respect to the \( \lambda_i \) turned out to be of crucial importance for successful Newton iterations.

The paramagnetic phase of NiO was studied in some detail in the preceeding paper Ref. [50]. There are only a few differences as compared to this study: first, a reduced value of the Racah-parameter \( A = 7.0 \text{ eV} \) (\( A = 8.25 \text{ eV} \) in Ref. [50]) and consequently a readjustment of the Ni 3d-orbital energy \( \epsilon_d = -52 \text{ eV} \) (whereas \( \epsilon_d = -62 \text{ eV} \) in Ref. [50]) to account for the different double-counting correction. Moreover, the Ni 3d-to-O 2p hopping parameter \( (pd\sigma) \) was increased by 10\% to \(-1.4178 \text{ eV}\).

Due to improved computer power it was now moreover possible to optimize all relevant single particle parameters of the octahedral cluster. Thereby it turned out that \( V(t_{2g}) = 0 \) is a stationary point irrespective of the values of the other parameters. The energy of the \( t_{2g} \)-like Ligand, \( \epsilon_L(t_{2g}) \) then is irrelevant so that only the four parameters \( \epsilon_d(e_g), \epsilon_L(e_g), V(e_g) \) and \( \epsilon_d(t_{2g}) \) remain to be solved for. The resulting paramagnetic solution, however, is stationary with respect to all six possible parameters. Some results for the paramagnetic phase will be presented later in comparison to the antiferromagnetic one.

### III. MAGNETIC SUSCEPTIBILITIES AND ANTIMAGNETIC TRANSITION

We discuss the staggered and uniform magnetic susceptibility. Within the VCA the Grand Canonical Potential may be thought of as being expressed as a function of a number of parameters

\[
\Omega = \Omega(\zeta_1, \ldots, \zeta_m, \lambda_1, \ldots, \lambda_n), \quad (11)
\]

were the \( \zeta_i \) are the parameters of the physical lattice system - such as the physical hopping integrals and orbital energies or certain external fields - and the \( \lambda_i \) are the single-electron parameters of the reference system which parameterize the self-energy. We assume that amongst the \( \zeta_i \) there is also a uniform or staggered magnetic field \( h \) along the z-direction. This implies that the values of all single-particle parameters of the reference system must be taken as spin-dependent:

\[
\lambda_i, \sigma = \lambda_i, + \text{sign}(\sigma)\lambda_i, -,
\]

which results in a spin-dependent self-energy, \( \Sigma_\uparrow(\omega) \neq \Sigma_\downarrow(\omega) \). For a staggered field we switch to the antiferromagnetic unit cell and assume that the \( \lambda_i, - \) have opposite sign at the two Ni-ions in this cell. This means that the self-energy for an \( \uparrow \)-electron is \( \Sigma_\uparrow(\omega) \) at the first Ni-ion and \( \Sigma_\downarrow(\omega) \) at the second Ni-ion in the antiferromagnetic cell and vice versa for a \( \downarrow \)-electron (k-sums now have to be performed over the antiferromagnetic Brillouin zone).

For a uniform field we retain the orginal unit cell and use the spin dependent self-energy at the single Ni-ion in this cell.

We assume that we have found a stationary point \( \lambda_i^* \) for \( h = 0 \) i.e.

\[
\frac{\partial \Omega}{\partial \lambda_i} \bigg|_{\lambda_i^*} = 0 \quad (12)
\]

for all \( i \) and denote the Grand Potential for this solution by \( \Omega_0 \). Since this is the paramagnetic stationary point all spin-odd parameters \( \lambda_i, - \) are zero. Upon applying a small finite \( h \) in the lattice system, \( \Omega \) therefore can be expanded as

\[
\Omega = \Omega_0 + \frac{1}{2} \sum_{i,j} \lambda_i \hat{A}_{i,j} \hat{A}_{j,i} + \sum_i \hat{\lambda}_i B_i h + \frac{1}{2} C h^2, \quad (13)
\]

where the shifts \( \hat{\lambda}_i = \lambda_i - \lambda_i^* \) and \( A, B \) and \( C \) are second derivatives of \( \Omega \) at the point \( \lambda_i = \lambda_i^*, h = 0 \). There are no terms linear in the \( \hat{\lambda}_i \) because of (12) and there is no term linear in \( h \) because \( \Omega \) must be an even function of \( h \). The second derivatives can be evaluated numerically whereby the fact that the \( \lambda_i \) are parameters of the reference system whereas the staggered field \( h \) is one of the \( \zeta_i \) in (11) causes no problem. Moreover, all derivatives are to be evaluated in the paramagnetic phase, so no calculation in a finite field is necessary. Demanding stationarity we obtain for the shifts \( \hat{\lambda}_i \):

\[
\frac{\partial \Omega}{\partial \hat{\lambda}_i} = \sum_j A_{i,j} \hat{\lambda}_j + B_i h = 0, \quad (14)
\]
and reinserting into (13) we obtain $\Omega$ as a function of $h$

$$\Omega(h) = \Omega_0 - \frac{h^2}{2} \chi$$

$$\chi = \sum_{i,j} B_i A_{ij}^{-1} B_j - C. \quad (15)$$

$\Omega$ must be invariant under a simultaneous sign change of $h$ and all spin-odd parameters $\lambda_i$, so that $\lambda_{i,+} = 0$ for all $i$ and the sums over $i$ and $j$ in (15) extend only over the spin-odd parameters.

Figure 1 shows the staggered and uniform susceptibilities obtained in this way as a function of temperature. Thereby the term

$$H_m = -\hbar \sum_i e^{iQ \cdot R_i} (n_{i\uparrow} - n_{i\downarrow})$$

was added to the lattice Hamiltonian, so that the physical susceptibilities are given by

$$\chi_Q = -\mu_B^2 \frac{\partial^2 \Omega}{\partial h^2}.$$ 

The staggered susceptibility can be fitted accurately by

$$\chi_s(T) = \frac{\mu_B^2 C_s}{T - T_N} \quad (16)$$

with $T_N = 481.03$ K and $C_s = 24805 \cdot eV^{-1}$ whereas the uniform susceptibility can be fitted by

$$\chi_0(T) = \frac{\mu_B^2 C_0}{T + \Theta_{CW}} \quad (17)$$

with $\Theta_{CW} = 491.62$ K and $C_0 = 30923 \cdot eV^{-1}$. The divergence of $\chi_s(T)$ at $T_N$ is due to an eigenvalue of the Hessian $A$ crossing zero at $T_N$.

Interestingly the Curie-Weiss temperature $\Theta_{CW}$ is somewhat higher than the Néel temperature $T_N$. This can be understood as a consequence of the type-II antiferromagnetic structure and (weak) antiferromagnetic exchange between Ni-ions connected by a 90°-degree Ni-O-Ni bond (an example would be two Ni-ions at distance $(a, a, 0)$). For such a pair of Ni ions there is a competition between the direct antiferromagnetic exchange (mediated by the direct Ni-Ni hopping as described by Slater-Koster parameters such as $(dd\sigma)$) and the ferromagnetic exchange due to Hund’s rule coupling on oxygen. Let us assume that the net exchange constant between such a pair of Ni ions is antiferromagnetic (this is certainly true for the present calculation which does not include Hund’s rule exchange on oxygen). Then, any given Ni ion has 12 neighbors of that type and in the type-II antiferromagnetic structure the ordered moment of one half of these neighbors is parallel to the moment of the ion at the center whereas it is antiparallel for the other half. The exchange fields due to these 12 neighbors therefore cancel and the Néel temperature is determined solely by the antiferromagnetic superexchange with the 6 neighbors connected by 180°-degree Ni-O-Ni bonds. On the other hand the parameter $\Theta_{CW}$ is a measure as to how strongly the antiferromagnetic exchange between spins opposes a uniform ferromagnetic polarization. For the case of a uniform ferromagnetic polarization, however, the exchange fields from all 12 $(a, a, 0)$-like neighbors are parallel and therefore do contribute to $\Theta_{CW}$. The discrepancy between $T_N$ and $\Theta$ obtained in the VCA calculation thus is to be expected. The experimental value $\Theta_{exp} = 2000$ K was given in Ref. [72] but being almost four times the experimental Néel temperature this appears somewhat high.

For a Heisenberg antiferromagnet the constant $C$ would be given by

$$C = \frac{S(S+1)}{3k_B} (g S_{eff})^2$$
Using the values from the fits in Figure 1 with $S = 1$ we obtain the reasonable values $S_{eff} = 1.000$ for $\chi_0$ and $S_{eff} = 0.895$ from $\chi_s$. The smaller value for $S_{eff}$ in the staggered case likely is due to the fact that in the computation of $\chi_0$ the magnetic field is applied to all orbitals in the unit cell whereas it acts only on the Ni 3d orbitals in the case of $\chi_s$. 

Lastly we point out an interesting feature of these results: the matrix $A$ of second derivatives of $\Omega$ with respect to the spin-odd parameters $\lambda_i$ is obviously the same in the case of staggered and uniform susceptibility. Only the quantities $B$ and $C$ are different. Still, the resulting susceptibilities have a completely different but physically reasonable temperature dependence.

IV. ANTIFERROMAGNETIC PHASE

To obtain the results presented so far only the paramagnetic solution was needed. If we want to discuss the antiferromagnetic phase itself we need to find stationary points with spin dependent parameters $\lambda_i$ and this doubling of the number of parameters complicates the numerical problem of finding the stationary point. We recall that in the paramagnetic case a total of 4 parameters were varied: $\epsilon_d(e_g), \epsilon_{L}(e_g), V(e_g)$ and $\epsilon_d(t_{2g})$ (moreover, $V(t_{2g}) = 0$ always was a stationary point and with that value the last parameter $\epsilon_L(t_{2g})$ is irrelevant). Doubling all of the nonvanishing parameters would result in a total of 8 parameters. Using the Newton method this is still numerically manageable but it turned out that a more severe problem appears. While it might seem that the more parameters $\lambda_i$ one is varying the better an approximation for the self-energy results, calculations showed that the opposite is true. Introducing too many symmetry-breaking parameters $\lambda_i$ leads to unphysical solutions - one example is discussed in detail in Appendix A. In fact it turned out that retaining more than 2 - out of the 4 possible $\lambda_i$ leads to unphysical solutions. Accordingly, in the following we present solutions obtained with 6 parameters $\lambda_i$. In choosing the $\lambda_i$ to be kept we heuristically use the staggered susceptibility $\chi_s$ as a guidance. Namely we can restrict the set of the $\lambda_i$ in the expression (15) for $\chi_s$ to only 2 and examine which combination still gives a $\chi_s$ which is closest to the one obtained with the full set of 4 $\lambda_i$. It turned out that retaining only the spin-odd part of the $e_g$-like hopping integral $V_-(e_g)$ and the $t_{2g}$-like $d$-level energy $\epsilon_d(t_{2g})$ the staggered susceptibility $\chi_s$ - and in particular the Néel temperature - remain practically unchanged. This appears plausible because the physical mechanism that stabilizes antiferromagnetism in NiO is the enhanced hopping for the $e_g$ electrons of one spin direction along the 180°-degree Ni-O-Ni bonds connecting sites on different sublattices. A spin dependent $d$-level-to-Ligand hopping then clearly is the best way to simulate this effect in a cluster with only a single Ni-ion. Since we have set $V(t_{2g}) = 0$ in the paramagnetic case, $\epsilon_d(t_{2g})$ moreover is the only remaining parameter pertinent to the $t_{2g}$ orbitals. In the following, the resulting solution will be referred to as AF-I.

In addition there is a second type of antiferromagnetic solution where $V_+(e_g) = V_-(e_g)$ so that the hopping for one spin direction of $e_g$ electrons is exactly zero. In this case the only remaining spin-odd parameters to be varied are $\epsilon_d^-(t_{2g})$ and $\epsilon_d^+(t_{2g})$ (since one spin direction of the $e_g$ electrons has zero hopping, the spin splitting of the $e_g$-like ligand, $\epsilon_L^-(e_g)$ is irrelevant and can be set to zero). It should be stressed that in this case $\Omega$ is stationary also with respect to $V_-(e_g)$, and the values $V_+(t_{2g}) = V_-(t_{2g}) = 0$ remain stationary as in the paramagnetic case. Despite the fact that only 6 parameters are actually varied, the corresponding solution therefore is stationary with respect to all 12 possible parameters of the cluster. This solution will be referred to as AF-II.

Figure 2 shows $\Omega$ as a function of temperature for the paramagnetic, AF-I and AF-II solutions. For the paramagnetic phase to good approximation $\Omega(T) = \Omega_0 - k_B T \log(3)$ where $k_B \log(3)$ is the entropy due to the 3-fold degenerate $^3A_{2g}$ ground state of a single Ni$^{2+}$ ion with configuration $t_{2g}^2e_g^2$. At $T_N$ the solution AF-I branches off as would be expected for a 2$^{nd}$ order phase transition. At $237.5 \text{ K}$ there is a crossing with finite difference of slopes between the AF-I and the AF-II solutions. This would imply a 1$^{st}$ order phase transition which most probably is unphysical. Rather, this may be the way in which the VCA approximates a continuous but rapid change of the electronic state.

We discuss the phase transition at $T_N$. As usual we introduce the staggered magnetization $m_s$

$$m_s = -\frac{\partial \Omega}{\partial h_s}$$

(18)
and switch to the Legendre-transformed potential \( \Omega'(m_s) = \Omega(h_s) + m_s \cdot h_s \) which, using \( \Omega(h_s) = \frac{1}{2} n_B^2 \chi_s^{-1} m_s^2 + O(m_s^4) \), is

\[
\Omega'(m_s) = \frac{1}{2} n_B^2 \chi_s^{-1} m_s^2 + O(m_s^4).
\]

In the present situation where the chemical potential is within the sizeable insulating gap this equals the Gibbs free energy up to an additive constant. Comparison with \( \Omega(h_s) \) shows that the lowest order term in the expansion of \( \Omega'(m_s) \) has the form expected from Landau theory:

\[
\Omega'(m_s) = a(T - T_N)m_s^2 + \frac{b}{2} m_s^4
\]

with \( a = 1/(2C_s) \). To carry this further we use

\[
h_s = \frac{\partial \Omega'}{\partial m_s} = 2a(T - T_N)m_s + 2bm_s^3.
\]

The dependence of \( h_s \) on \( m_s \) can be obtained within the VCA by increasing the staggered field \( h_s \) in small steps starting from \( h_s = 0 \), thereby always using the converged AF-I solution for the preceding step as starting point for the Newton algorithm for the next \( h_s \). After convergence, \( m_s \) is obtained from \( \Omega(h_s) \). The resulting curves are shown in Figure 3. At 470 K the magnetization is opposite to \( T_N \) and hence also the states ‘close’ to it are unstable and in fact this behaviour is precisely what is expected from Landau theory. Namely \( h_s(m_s) \) can be fitted by a third order polynomial \( h_s = c_1 m_s + c_2 m_s^3 \). Evaluating \( c_1 \) from \( c_1 = 2a(T - T_N) \) gives \( c_1 = -0.484 \text{ meV} \), \( c_2 = 2.339 \text{ meV} \) at 470 K and \( c_1 = 0.322 \text{ meV} \), \( c_2 = 2.458 \text{ meV} \) at 480 K. From the rather similar values of \( c_2 \) we can conclude that \( b \approx 1.20 \text{ meV} \). Evaluating \( c_1 \) from \( c_1 = 2a(T - T_N) \) gives \( c_1 = -0.447 \text{ meV} \) at 470 K and \( c_1 = 0.362 \text{ meV} \) at 490 K, reasonably consistent with the values extracted from \( m_s(h_s) \). Figure 4 shows the difference \( \Omega_{\text{para}} - \Omega_{\text{AF}} \). Since both are calculated in zero external field we have \( \Omega' = \Omega \) and expect

\[
\Omega_{\text{para}}(T) - \Omega_{\text{AF}}(T) = A(T - T_N)^2.
\]

The fit gives \( A = 1.746 \times 10^{-4} \text{ meV} K^{-2} \) whereas using \( a^2/(2b) = 1.694 \times 10^{-4} \text{ meV} K^{-2} \). Figure 4 also shows the ordered moment \( m_s = \langle n_{d,\uparrow} \rangle - \langle n_{d,\downarrow} \rangle \) versus temperature. Close to \( T_N \) this can be fitted by \( m_s(T) = B\sqrt{T_N - T} \) with \( B = 0.131 K^{-1/2} \). The symmetry-breaking parameters \( V_{-}(e_g) \) and \( e_{d,-}(e_g) \) have a similar \( T \)-dependence \( \propto \sqrt{T_N - T} \) close to \( T_N \). All in all the phase transition is described well by Landau theory and the VCA allows to extract the parameters of the theory from the original Hamiltonian.

Next we consider the specific heat \( C(T) \) which is shown in Figure 5. The top panel shows experimental data for
NiO taken from Refs. 73, 74. Also shown is the phonon contribution which was calculated from the phonon spectrum measured by inelastic neutron scattering at room temperature75. The electronic heat capacity $C_{el}$ is compared to the VCA result in the lower part of the figure. The VCA of course does not reproduce the divergence of $C_{el}$ at the ordering transition which follows the critical exponents for a 3D Heisenberg antiferromagnet75. Apart from that the result from the VCA is roughly consistent with the measured values, especially the solution AF-II agrees quite well with the data at low temperature. In fact, this solution appears to match the experimental data considerably better up to $\approx 0.7 T_N$. This may be an indication that in NiO this solution is realized even at temperatures well above the transition between AF-I and AF-II at 237.5 $K$ (which is indicated by the vertical line in Figure 5). In fact, as will be seen below, the single particle spectral function for this solution matches the experimental photoelectron spectra - which are usually taken at room temperature - quite well.

The apparently large value of $C_{el}$ above $T_N$ probably is an artefact: the phonon spectrum was measured at room temperature that means where the lattice was deformed by magnetostriction. Above $T_N$ this deformation is absent and the phonon spectrum may change so that using the low temperature phonon spectrum gives an incorrect estimate for the phonon contribution. The electronic heat capacity per mole obeys the sum rule

$$\int_0^{T_h} \frac{C_{el}(T)}{T} dT = R \log(3)$$

where $T_h$ is well above the Néel temperature. It turns out that the experimental data exhaust this sum rule at $T_h \approx 660$ $K$.

Finally, Table I compares the parameter values for the paramagnetic and AF-II solutions at 200 Kelvin, as well as various observables. The expectation value of any term $H_{part}$ in the Hamiltonian can be calculated by replacing $H_{part} \rightarrow \zeta H_{part}$ and using

$$\langle H_{part} \rangle = \left. \frac{\partial \Omega}{\partial \zeta} \right|_{\zeta=1} .$$

The numerical calculation of the derivative thereby is simplified considerably by taking into account that due to the stationarity condition for the $\lambda_i$ their variation with $\zeta$ can be neglected59. The antiferromagnetic unit cell and k-mesh were used also for the paramagnetic calculation to avoid artefacts.

A somewhat surprising feature is that the quite different

| AF      | Para   | $\Delta$ |
|---------|--------|----------|
| $e_d(e_g) \uparrow$ | -51.4113 | -51.5278 |
| $e_d(e_g) \downarrow$ | -50.9896 | -51.5278 |
| $V(e_g) \uparrow$   | -1.4880  | -1.7260  |
| $V(e_g) \downarrow$  | 0.0000   | -1.7260  |
| $e_L(e_g) \uparrow$  | 4.3633   | 3.4089   |
| $e_L(e_g) \downarrow$ | 4.3633   | 3.4089   |
| $e_d(t_{2g}) \uparrow$ | -51.1777 | -51.2256 |
| $e_d(t_{2g}) \downarrow$ | -51.0794 | -51.2256 |
| $\Omega + \mu N$  | -244.0363 | -244.0235 | -0.0128 |
| $\langle H \rangle$ | -244.0344 | -244.0046 | -0.0299 |
| $S/k_B$  | 0.1090   | 1.0977   | -0.0988 |
| $\langle H_0 \rangle$ | -457.9924 | -457.3822 | -0.6102 |
| $\langle H_1 \rangle$ | 213.9579 | 213.3776 | 0.5803 |
| $\langle H_{pd} \rangle$ | -3.5283 | -3.4380 | -0.0903 |
| $\langle H_{pp} \rangle$ | -0.1915 | -0.1757 | -0.0158 |
| $\langle H_{gl} \rangle$ | -0.0030 | -0.0034 | 0.0004 |
| $\langle n_{e_{g,\uparrow}} \rangle$ | 0.2241 | 1.0945 | -0.8698 |
| $\langle n_{e_{g,\downarrow}} \rangle$ | 1.9738 | 1.0945 | 0.8793 |
| $\langle n_{d} \rangle$ | 8.1985 | 8.1890 | 0.0095 |
| $\langle n_{t_{2g,\uparrow}} \rangle$ | 3.0000 | 3.0000 | 0.0000 |
| $\langle n_{t_{2g,\downarrow}} \rangle$ | 3.0000 | 3.0000 | 0.0000 |

Table I: Top: Parameters of the AF-II (AF) and paramagnetic (Para) solution at 200 Kelvin. $\Delta$=AF-Para. Center part: Various contributions to $\Omega$ (energies in eV per Ni) Bottom part: Occupation numbers of the Ni 3d shell.
cluster parameters for the two different solutions give only slightly different $\Omega$. As expected, $\Omega$ is lower for the antiferromagnetic phase due to the lower energy $\langle H \rangle$. This is partly compensated by the almost complete loss of entropy in the AF phase but at the low temperature considered this does not result in a higher $\Omega$. As already mentioned the entropy in the paramagnetic phase is close to $S/k_B = \log(3) = 1.0986$ as expected for a system of localized $S = 1$ spins. While this may seem trivial it should be noted that the spin degeneracy can only be reproduced if a spin rotation invariant Hamiltonian is used. Discarding the off-diagonal matrix elements of the Coulomb interaction [1] breaks the spin-rotation symmetry so that the entropy of the paramagnetic phase cannot be obtained correctly.

The considerably lower value of $\langle H_0 \rangle$ in the AF phase comes about because the $d$-occupancy increases slightly, by 0.0095. With the orbital energy $v_d = -52$ eV this lowers $\langle H_0 \rangle$ by $-0.494$ eV. This is more than compensated, however, by the increase of the Coulomb energy $\langle H_1 \rangle$ in the AF phase by 0.5803 eV. Eventually, the energy in the antiferromagnetic phase becomes lower due to the $dp$-hybridization which is lowered by $-0.0903$ eV in the AF phase. Consistent with the theory of superexchange the driving force behind the antiferromagnetic ordering is not the lowering of the Coulomb energy but a gain of kinetic energy. Interestingly there is also a significant - on the scale of the change of $\langle H \rangle$ - gain in the direct $O$ 2p-O 2p hopping energy $\langle H_{pp} \rangle$ in the AF phase. This is due to the increased charge transfer to Ni 3d which reduces the filling of the O 2p orbitals and thus allows for enhanced O 2p-O 2p hopping. This contribution is missed in models for superexchange which consider only a single Ni-O-Ni bond.

To summarize the results of the two preceding sections: the description of the magnetic properties and phase transition of NiO as obtained by the VCA is very similar to what would be obtained from a simple mean-field treatment of a localized spin system. It should be noted, however, that the Hamiltonian does not contain any exchange terms nor is there any molecular field in the physical system. Rather, the Hamiltonian is the one for the full NiO lattice [3], the self-energy is calculated in a cluster containing a single Ni-ion and the coupling between Ni-ions is solely due to the lattice kinetic energy. Still, the VCA even captures subtle details such as the presence of different exchange channels as manifested by the different values of $T_N$ and $\Theta_{CW}$. It should also be kept in mind that all parameters in the original Hamiltonian are several orders of magnitude larger than the differences in energy in Table [1] but still the calculated Néel temperature is quite close to the experimental value. The VCA thus appears successful in correctly extracting the low energy scales relevant for ordering phenomena and thermodynamics from the high energy scales of Hubbard $U$, charge transfer energy, and hopping parameters.

\section{PHOTOELECTRON SPECTRA IN THE ANTIFERROMAGNETIC PHASE}

We proceed to a discussion of ‘high energy physics’ and consider the single particle spectral function. Figure 6 shows the $k$-integrated spectral density

\begin{equation}
A(\omega) = -\frac{1}{\pi} \sum_{k\alpha} G_{\alpha,\alpha}(k, \omega + i\eta),
\end{equation}

where the sum over $\alpha$ runs over either the Ni 3d or the O 2p orbitals. This was calculated for the antiferromagnetic solution AF-II at 200 Kelvin. Experiments are usually done at room temperature but the specific heat data in Figure 7 suggest that the AF-II solution may be relevant also at higher temperature. The Figure also shows different experimental angle-integrated spectra: First, hard x-ray photoelectron spectroscopy (HAXPES) with a photon energy of $h\nu = 6500$ eV [77] - at this energy the photoionization cross section for Ni 3d is approximately 10 times larger than that for O 2p so that predominantly the Ni 3d density of states is observed. Second, an x-ray photoemission (XPS) spectrum taken with a photon energy of $h\nu = 67$ eV [78]. This is close to the Ni 3p$\to$3d absorption threshold so that the satellite region around $-10$ eV is resonantly enhanced [79]. And, third, an x-ray emission (XES) spectrum which shows predominantly the O 2p density of states [80]. Several peaks in the theoretical spectra can be identified.
in the various experimental spectra: these are the peaks $A$ and $B$ which have Ni 3d character and thus appear in HAXPES and XPS (although at $h\nu = 67\text{eV}$ the peak $A$ is anti-resonantly suppressed). The peak $A$ also has some oxygen admixture so that together with peak $C$ it can also be seen in the XES spectrum. Peak $C$ also corresponds to a weak feature observed in HAXPES and in the XPS spectrum. Peak $D$ can be seen both in HAXPES and XPS and the tail of the XES spectrum towards negative energy also shows an indication of the additional shoulder $E$ which corresponds to a similar feature in the theoretical O 2p spectrum. Finally the rather broad feature $F$ can be seen very well in the XPS spectrum. By and large there is good agreement between calculated and measured spectra. It has to be kept in mind, however, that as far as the Ni 3d density is concerned a similar degree of agreement has been obtained earlier by Fujimori and Minami\cite{20} and van Elp et al.\cite{26} by the cluster method. The discussion so far shows mainly that as far as the Ni 3d density is concerned a similar agreement has been obtained earlier by Fujimori and Minami\cite{20} and van Elp et al.\cite{26} by the cluster method.

We therefore turn to the quantity which allows for the most detailed comparison to experiment, namely the $k$-resolved spectral density

\begin{equation}
A(k, \omega) = -\frac{1}{\pi} \sum_\alpha G_{\alpha,\alpha}(k, \omega + i\eta),
\end{equation}

where the sum over $\alpha$ now runs over both, the Ni 3d and the O 2p orbitals. The dispersion of peaks in $A(k, \omega)$ can be compared to the band structure as measured in angle resolved photoemission spectroscopy (ARPES). To date there are two ARPES studies of NiO, one by Shen et al.\cite{81} and the other by Kuhlenbeck et al.\cite{82}. Shen et al. give three different sets of data points: the bands from $\Gamma$ to $X = (\frac{2\pi}{a}, 0, 0)$ (i.e. the $(1, 0, 0)$-direction) measured in normal and off-normal emission and the bands from $\Gamma$ to $X_1 = (\frac{2\pi}{a}, 0, 0)$ (i.e. the $(1, 1, 0)$-direction) measured in off-normal emission. The two data sets along $\Gamma - X$ agree for some bands but differ for others due to matrix element effects. If a given band is observed in any one experimental geometry it obviously does exist and if it is not observed in another geometry this can only be a matrix-element effect. The true band structure along $\Gamma - X$ thus should comprise at least the superposition of the two sets of bands for normal and off-normal emission. Figure 7 compares $A(k, \omega)$ and the respective experimental band dispersions. For both directions the top of the band structure is formed by a complex of several closely spaced bands with high spectral weight in the range $-0.5 \rightarrow -1.5 \text{eV}$, labeled $a$ in the Figure. In the angle-integrated spectrum in Figure 6 these bands produce the intense peak $A$. The high spectral weight of these bands can also be seen in the experimental spectra in Figures 7 and 8 of Shen et al.. Below this group of bands there is a gap of approximately $1 \text{eV}$. In the range $-2.5 \rightarrow -3.5 \text{eV}$ there are several essentially dispersionless bands with weak intensity, labeled $b$. In the angle integrated spectrum in Figure 6 these bands produce the weak feature B. Shen et al. resolved two such bands along $(1, 0, 0)$ but only one along $(1, 1, 0)$ - since the dispersions must match at $\Gamma$ there probably are more than one of these dispersionless bands also along $(1, 1, 0)$. Such (nearly) dispersionless bands can be seen also at even more negative energies, but there they are superimposed over and mix with the strongly dispersive O 2p derived bands which results in more $k$-dependence.

First, there is the dispersive band $c$ along $(1, 0, 0)$ and $e$ along $(1, 1, 0)$. In experiment band $c$ shows a relatively strong upward bend near $X$ - this may indicate that there rather a part of the dispersionless band which starts at

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure7.png}
\caption{Single particle spectral density $A(k, \omega)$ for the antiferromagnetic solution AF-II at 200 Kelvin compared to ARPES data by Shen et al.\cite{81}. The three panels show the data for off-normal emission along $\Gamma - X$ (top), normal emission along $\Gamma - X$ (middle) and off-normal emission along $\Gamma - X_1$ (bottom).}
\end{figure}
\( \Gamma \) at \( \approx -4.6 \, eV \) has been observed. This dispersionless band and its ‘avoided crossing’ with a strongly dispersive O 2p derived band \( c \) as predicted by the VCA may also have been observed near \( \Gamma \), see the region labeled \( f \) in the top panel. Along \((1,1,0)\) this dispersionless band can be followed over the full \( k \)-range, see the band labeled \( d \) in the bottom panel. In normal emission (middle panel) it moreover becomes apparent that the strongly downward dispersing O 2p band indeed splits into two bands with opposite curvature - see the region labeled \( g \) - which would be similar to the VCA bands. Lastly, at \( \approx -6.6 \, eV \) another dispersionless band - labeled \( g \) and \( h \) in the middle and bottom panel - is observed which would correspond to the nearly dispersionless band which starts out from \( \Gamma \) at slightly below \(-6 \, eV\) (and which gives rise to the peak \( D \) in the angle-integrated spectrum in Figure 8).

Some of the above interpretations are corroborated in Figure 8 which shows a comparison to the band structure deduced by Kuhlenbeck et al. along \( \Gamma - X \) [82]. There the dispersionless bands \( a \), \( b \) and \( c \) obviously correspond to the bands with the same labels in the data by Shen et al. - and the corresponding bands predicted by the VCA. Particularly interesting is the band portion labeled \( d \) in Figure 8 which also shows a peculiar downward curvature and corresponds exactly to the part labeled \( g \) in Figure 7 - which in turn had some counterpart in the VCA bands (plotting the two experimental band structures on top of each other shows the exact correspondence of these two bands). Finally, the dispersionless band portion \( e \) is precisely the continuation towards \( \Gamma \) of the dispersionless band labeled \( h \) in Figure 7 - which also has its counterpart in the VCA band structure.

Generally speaking for all bands which should be easy to observe because they either have a high intensity or are relatively isolated from other bands there is an essentially one-to-one correspondence between VCA and experiment. The VCA predicts a multitude of dispersive low-intensity bands below \( \approx -4 \, eV \) and only a few of these seem to have been observed. Combining the three experimental spectra along \( \Gamma - X \) indicates, however, that the experimental band structure in this energy range does not consist just of the three strongly dispersive O 2p-derived bands obtained by band structure calculations\[2\] which are also predicted by many ‘correlated’ calculations as well\[16, 17\]. Rather, additional bands, both dispersive and non-dispersive, appear to be observed. In the next section it will be shown that the dispersionless bands are in fact the very fingerprints of the atomic multiplets in the ARPES spectra.

To conclude this section we discuss the temperature dependence of the spectra. The bottom part of Figure 9 compares the angle integrated Ni 3d-like spectral function for the AF-II solution at 200 K and for the paramagnetic solution at 520 K. Also shown are experimental spectra by Tjernberg et al. measured below and above the experimental Néel temperature of 523 K.
Figure 9 also shows the experimental spectrum taken by Tjernberg et al. 78 at 615 K - which is well above \( T_N \) - and a modified version of the spectrum at 300 K. More precisely, the 300 K spectrum was broadened by convolution with a Gaussian to simulate the enhanced thermal broadening and fitted to the high-temperature spectrum whereby both spectra were normalized to unity 78. Due to the relatively low photon energy \( h\nu = 65 \text{ eV} \) the experimental spectrum also contains a considerable amount of O 2p weight, which gives rise to the intense peak \( C \) (compare Figure 4). Accordingly Figure 9 also shows the sum of Ni 3d-like and O 2p-like spectral functions. In the experimental spectrum the peak \( A \) looses weight in the paramagnetic phase whereas the opposite is predicted by the calculation. In experiment the spectral weight in the energy range between the two large peaks \( A \) and \( C \) increases in the paramagnetic phase and a similar change occurs in the theoretical spectra were the relatively well-defined gap between the peaks \( A \) and \( C \) is partly filled in the paramagnetic spectrum, although the effect seems less pronounced in experiment. In experiment the peak \( C \) looses a small amount of spectral weight and is shifted to slightly less negative energy in the paramagnetic phase. A similar tendency can be seen in the theoretical spectra but considerably exaggerated. Lastly, in experiment the spectral weight increases slightly at various positions in the satellite region below \( -8 \text{ eV} \) but no decrease is observed anywhere. In contrast to this in the theoretical spectra there is a drastic change in the satellite region where a considerable amount of weight disappears around \( -10 \text{ eV} \) and a new strong peak appears at approximately \( -8 \text{ eV} \). Summarizing, the VCA is only partly successful in predicting the changes of the photoemission spectrum across the \( \text{Néel} \) temperature. It has to be kept in mind, however, that the photon energy of 65 \text{ eV} used in the experiment is close to the \( 3p \rightarrow 3d \) absorption threshold so that the satellite (peak \( A \)) is resonantly enhanced (antiresonantly suppressed). In fact, the intensities of the various peaks are quite different from the HAXPES spectrum in Figure 6. Accordingly, additional effects may come into play which determine the intensity of these features and this might be one explanation why discrepancies with theory occur precisely for peak \( A \) and the satellite. In any way some of the observed changes with temperature - or actually: between antiferromagnetic and paramagnetic phase - appear to be reproduced qualitatively by the VCA. Lastly, Figure 9 also shows a somewhat surprising difference between the single particle spectra in the antiferromagnetic and paramagnetic phase: namely the insulating gap in the paramagnetic phase is larger than in the antiferromagnetic phase. More precisely, the peak-to-peak distances are 4.65 \text{ eV} and 4.05 \text{ eV} so that the gap increases by \( \approx 10 \% \). So far the temperature dependence of the insulating gap in NiO has not been studied experimentally. As will be discussed in the next section, however, there is a clear physical reason for this discrepancy namely the fact that the mechanism which opens the insulating gap in the two phases is quite different.

VI. DISCUSSION OF THE SELF ENERGY

We discuss some of the results presented in the preceding section from the ‘self-energy perspective’. Luttinger has shown 83 that for a single band system the self-energy has a spectral representation of the form

\[
\Sigma(\omega) = \eta + \sum_i \frac{\sigma_i}{\omega - \zeta_i} \tag{21}
\]

where \( \eta, \sigma_i > 0 \) and \( \zeta_i \) are real. In the following we assume these parameters to be \( k \)-independent. The equation for the poles of the Green’s function reads

\[
\omega_k - \epsilon_k = \sum_i \frac{\sigma_i}{\omega_k - \zeta_i} \tag{22}
\]

where for brevity of notation we have replaced \( \epsilon_k + \eta - \mu \rightarrow \epsilon_k \). Let us first assume that we have only a single pole with a large weight, Figure 10 shows the resulting \( \Sigma(\omega) \) for real \( \omega \). Also shown is the noninteracting density of states for the band \( \epsilon_k \), the two straight lines correspond to \( \omega - \epsilon_- \) and \( \omega - \epsilon_+ \) where \( \epsilon_- \) and \( \epsilon_+ \) are the bottom and top of the noninteracting band \( \epsilon_k \). The intersections of these lines with \( \Sigma(\omega) \) give the solutions of the equation 22 and there is one solution for any \( k \) in between these. A single isolated pole of \( \Sigma(\omega) \) thus splits the noninteracting band into the two Hubbard bands and opens a gap in the spectral function. Such an isolated pole with a residuum \( \propto N^0 \) in the self-energy obviously is the very essence of a Mott insulator - this can also be seen in the self-energy of the 2-dimensional Hubbard model 84.
Figure 11 shows the $e_g$-like self-energy $\Sigma(\omega)$ for the paramagnetic solution at 520 K and for the antiferromagnetic AF-II solution at 200 K. For the paramagnetic solution there is indeed an isolated intense peak of the self-energy - labelled $G$ in the Figure - within the insulating gap. In contrast no such ‘gap-opening-peak’ exists in the self-energy for the antiferromagnetic solution. There the mechanism which opens the gap is the different values of the additive constants $\eta_{\uparrow}$ and $\eta_{\downarrow}$ in the spin-dependent self-energy, which has the effect of an oscillating potential

$$V_{SDW}(i) = e_i^2 Q \cdot R_i \frac{\eta_{\uparrow} - \eta_{\downarrow}}{2},$$

which opens a gap in the same way as in spin-density-wave mean-field theory. For the AF-II solution at 200 K $\eta_{\uparrow}(e_g) = 59.89$ eV, $\eta_{\downarrow}(e_g) = 50.69$ eV (whereby the large average $(\eta_{\uparrow} + \eta_{\downarrow})/2 \approx 55.3$ eV cancels the double-counting correction to the Ni 3d-level energy). Since the insulating gaps in the paramagnetic and antiferromagnetic phase are created by different mechanisms it is not too surprising that they have different values (see Figure 9). For completeness we mention that the $t_{2g}$-like self-energy has no such ‘gap-opening-peak’ in either the paramagnetic or insulating phase. This is special for NiO because in the $^3A_{2g}$ ground state of d$^8$ in cubic symmetry, which is $t_{2g}^6e_g^2$, the $t_{2g}$ orbitals are completely filled and thus comprise a ‘band-insulating’ subsystem. Very probably this is also the reason why $V(t_{2g}) = 0$ is a stationary point.

The AF-I solution which branches off the paramagnetic solution at $T_N$ and crosses with the AF-II solution at 237.5 K (see Figure 2) interpolates between these two types of insulating gap: Figure 12 shows $\Sigma(\omega)$ for the AF-I solution at different temperatures. With decreasing temperature
If a given pole has a small
the self-energy there is one complete quasiparticle band.
This shows that in between any two successive poles of
νΣ(ζ) in any interval [ζ,ζ+i], however, Σ(ω) drops almost
vertically near the corresponding ζi, so that the width of
the respective band becomes small. Replacing
\[ ∑ i \frac{σ_i}{ω - ζ_i} \rightarrow C + \frac{σ_0}{ω - ζ_0} \]
in the neighborhood of such a pole ζ0, the resulting dis-

crption and quasiparticle weight Z = \(1 - \frac{∂Σ}{∂ω})^{-1}\) are
\[ \omega_k ≈ ζ_0 + \frac{σ_0}{ζ_0 - C - ε_k}, \]
\[ Z_k ≈ \frac{σ_0}{(ζ_0 - C - ε_k)^2}. \]

Therefore, unless the denominator happens to cross zero
near ζ0 this results in a band with little dispersion and
low spectral weight close to ζ0. Whether the band is on
the high or low energy side of ζ0 depends on the sign of
the denominator ζ0 - C - εk. Figure 14 compares partial
ARPES spectra along (1,0,0), where the sum in (20) is
restricted to either eg-like or t2g-like Ni 3d orbitals and
the respective self-energies. Although the situation in
NiO is more complicated due to the multi-band situation
and the hybridization with the O 2p bands it is quite
obvious how the various dispersionless bands can be as-
associated with poles of the self-energy. In the case of NiO
these poles describe the multiplet splitting of the final
state of the photoemission process, i.e. mainly the Ni3+ ion.
In the absence of the Coulomb interaction a single
Ni 3d shell would have eigenstates obtained by distribut-
ing the electrons over the eg and t2g levels and the single
particle spectral function A(ω) would have few peaks cor-
responding to the energies of these CEF levels. The con-
siderably larger number of CEF-split multiplet states in
the presence of Coulomb interaction - as given e.g. in the
Tanabe-Sugano diagrams - increases the number of peaks
in A(ω) and the interacting peak structure is generated
by the poles of the self-energy of the Ni 3d electrons in
exactly the same way as in Figure 13. In the solid these
poles of the self-energy then generate the dispersionless
bands observed in ARPES as discussed above. In that
sense one can literally see the dispersionless self-energy of
the Ni 3d electrons directly in the experimental data
of Shen et al. and Kuhlenbeck et al.

VII. CONCLUSION

In summary, the Variational Cluster Approximation
proposed by Potthoff allows to combine the classic field
theoretical work of Luttinger and Ward with the very
successful cluster method due to Fujimori and Minami re-
sulting in an efficient band structure method for strongly
correlated electron systems. Since the VCA is based on
eax diagonalization which is free from the minus-sign
problem it allows to take into account the full Coulomb
interaction in the TM 3d-shell which is known to be
crucial for reproducing the correct multiplet structure

FIG. 13: Top: Spectral density of the ‘model self-energy’
Σ(ω).
Bottom: Graphical solution of equation (22) for the quasipar-
ticle energies ωk with the ‘model self-energy’ Σ(ω).

Next, we discuss the origin of the dispersionless bands
observed in the ARPES spectra of both Shen et al. and
Kuhlenbeck et al. For the sake of illustration
we consider a ‘model self-energy’ obtained by arbitrar-
ily choosing a few σi and ζi in (21). Figure 13 shows the
imaginary part of the resulting Σ(ω) for ω slightly off the
real axis (top) and Σ(ω) for real ω (bottom). The bottom
part again shows the density of states of the noninter-
acting band εk as well as the lines ω - ε- and ω - ε+.
For real ω Σ(ω) takes any value in [−∞, ∞] precisely once
in any interval [ζi,ζi+1] so that the line ω - εk intersects
Σ(ω) once for each εk. The point of intersection thereby
is between those of the lines ω - ε- and ω - ε+.
This shows that in between any two successive poles of
the self-energy there is one complete quasiparticle band.
If a given pole has a small σi, however, Σ(ω) drops almost
and for obtaining agreement with experiment for angle-integrated valence band photoemission [21–29] and X-ray absorption [30–40]. As might have been expected on the basis of the success of the cluster method in describing it produces a number of nearly dispersionless bands observed there. The VCA moreover delivers an estimate for the experimental quantities which probe energy scales from meV range up to \( \approx 10 \) eV.

In the case of NiO, using realistic values of the Hubbard-\( U \) and charge transfer energy \( \Delta \) - as demonstrated by the position of the satellite and the magnitude of the insulating gap - and a moderately adjusted value of the Slater-Koster parameter \( (pd\sigma) \) (increased by 10\% as compared to the LDA band structure estimate) the theoretical Néel temperature is 481 Kelvin (experimental value: 523 Kelvin). The behaviour near \( T_N \) is consistent with a 2\(^{nd}\) order phase transition in a local-moment system, with quite accurate Landau behaviour of the free energy and ordered moment below \( T_N \) and a Curie-Weiss susceptibility above \( T_N \). Consistent with experiment the angle-integrated density of states is very similar for the paramagnetic and antiferromagnetic phase. The angle-integrated spectrum and band structure in the antiferromagnetic phase agree well with experiment, whereby the band structure shows a considerable number of both dispersive and dispersionless bands and again shows the massive impact of the strong correlations in NiO in that it differs strongly from the band structure obtained within DFT.

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VIII. APPENDIX A

In this Appendix we discuss an unphysical solution which appears when 7 parameters are varied. Thereby all 4 spin-even parameters were varied and in addition to the spin-odd parameters \( V_- (\epsilon_g) \) and \( \epsilon_{\sigma} (t_{2g}) \) which are used in the AF-I solution, also the spin-odd part of the \( \epsilon_g \) level energy, \( \epsilon_{\sigma} (\epsilon_g) \). The upper part of Figure 15 shows the temperature dependence of the spin-odd d-Level-to-Ligand hopping \( V_- (\epsilon_g) \). We could have chosen any other spin-odd parameter but this one is sufficient to discuss what is happening. The lower part of the Figure shows two new solutions appear, see point C. The second solution emerging from the bifurcation C can be followed up to temperatures far above \( T_N \). As can be seen in the bottom part, the solution along \( A \rightarrow C \) has a higher \( \Omega \) than the one extending from \( C \) to high temperatures (the part above 430 K is omitted for this solution in the bottom part of Figure 15 to keep the range of \( \Omega \) sufficiently small). In fact, \( \Omega \) for this solution turns out to be even lower than for the paramagnetic solution so that we have an antiferromagnetic solution which gives the lowest \( \Omega \) up to the highest temperatures studied. Moreover, the magnetic solution \( A \rightarrow C \) appearing at \( T_N \) - which would be consistent with the staggered susceptibility - would be an unstable state which never should be realized. One of the two solutions emerging from the bifurcation B intersects the unphysical antiferromagnetic solution at \( \approx 420 \) K. The bottom part also shows \( \Omega'(T) \) for the solution AF-I with 6 varied parameters. Over almost the entire temperature range this solution is very close in energy (the deviation is \( \propto 10^{-5} \) eV between 300 K and 420 K and
changes visible the function different solutions with 7 parameters (lines). To make small
tom: Grand Potential as a function of temperature for the
different solutions, and from Figure 16 which compares
‘closeness’ is not restricted to Ω can be seen in Table
2 parameters. In fact, it seems to interpolate between
16 was subtracted from Ω. Also shown
FIG. 15: Top: Spin-odd hopping parameter $V_{-}(e_g)$ for the
solution with 7 parameters as a function of temperature. Bot-
tween the two solutions as far as observable quantities are
TABLE II: Comparison of the AF-I solution with 6 parame-
ters and the solution for 7 parameters at 400 K. All energies
As already mentioned, the unphysical solution has lower
TABLE III compares some observ-
parameters to be varied is superfluous. For completeness
we note that keeping $e_{d,-}(t_{2g}) = 0$ so that $V_{-}(e_g)$ re-
ains as the only spin-odd parameter to be varied, gives
results which are almost identical to those for the solu-
tion AF-I. From the above it looks very much as if already
with 6 parameters the solution is converged with respect
to the number of parameters and that adding an addi-
tional spin-odd parameter results in no more significant
to physical observables but creates a new branch of un-
physical solutions.
We now discuss the artificial antiferromagnetic solution
at high temperatures. Table III compares some observ-
able parameters for this solution and the paramagnetic one at 600 K.
As already mentioned, the unphysical solution has lower
Ω than the paramagnetic phase and in addition also a
higher entropy. There are no large differences in the
various ground state expectation values. Although the
symmetry breaking parameters $V_{-}(e_g)$ and $e_{d,-}(e_g)$ are
substantially larger than those for the antiferromagnetic
solutions at 400 K given in Table III the ordered moment
is much smaller. This shows again that the symmetry
breaking effect of the different spin-odd parameters cancels
almost completely in this solution.
The above example shows that including too many sym-
metry breaking parameters into the subset of variational
parameters for this solution and the paramagnetic one at 600 K.
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substantially larger than those for the antiferromagnetic
solutions at 400 K given in Table III the ordered moment
is much smaller. This shows again that the symmetry
breaking effect of the different spin-odd parameters cancels
almost completely in this solution.
the VCA appear to converge rather well with the number of variational parameters. In any way it seems desirable to find criteria which allow to identify unphysical solutions or methods to regularize the variational procedure so that unphysical solutions are suppressed.

\[
\begin{array}{c|c|c}
\hline
\text{AF} & \text{Para} \\
\hline
\langle H \rangle & -244.0046 & -244.0045 \\
\langle H_0 \rangle & -457.3758 & -457.3815 \\
\langle H_1 \rangle & 213.3712 & 213.3770 \\
\langle H_{pd} \rangle & -3.4373 & -3.4379 \\
\langle H_{pp} \rangle & -0.1756 & -0.1757 \\
\langle H_{dd} \rangle & -0.0034 & -0.0034 \\
\langle n_{e_g,\uparrow} \rangle & 1.1138 & 1.0945 \\
\langle n_{e_g,\downarrow} \rangle & 1.0757 & 1.0945 \\
\langle n_d \rangle & 8.1889 & 8.1890 \\
\langle m_s \rangle & 0.0376 & 0.0000 \\
\hline
\end{array}
\]

TABLE III: Comparison of the unphysical AF solution and the paramagnetic solution at 600 K. All energies in eV.

FIG. 16: Comparison of the k-integrated spectral densities for the AF-I solution with 6 varied parameters and the solution with 7 varied parameters at 400 K.
