# The electronic structure of NiO in the $GW$ approximation

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**Abstract**

We present a method for calculating the self-energy in the $GW$ approximation that can be applied to systems containing $3d$ and $4f$ electrons. The method is applied to NiO and a gap of $\sim 5.5$ eV is obtained, which is in reasonable agreement with the experimental value of 4.0 eV. The local density O $p$-band is also improved. The high binding energy satellite at 8 eV, however, is not obtained and there is no substantial increased of O $p$-character at the top of the valence band compared to the local density result. Based on our results, we discuss to which extent the $GW$ approximation is capable of describing highly correlated systems such as NiO.

The electronic structure of NiO has been the subject of controversy for several decades. It was pointed out by Mott[1] in the 1940's that a system with a Coulomb energy $U$ much larger than the band width is an insulator, due to strong correlation effects. Alternatively, Slater[2] proposed that the band gap could be opened by an interplay of antiferromagnetism and crystal-field effects. Band structure calculations in the local density approximation (LDA)[3] of the density functional formalism[4] indeed produced such a gap[5]. The gap ($0.2\ eV$) was, however, much smaller than the experimental gap ($4\ eV$)[6, 7, 8] and the magnetic moment ($\sim 1\ \mu_B$) was also too small compared with experiment ($1.7 - 1.9\ \mu_B$)[9]. The bands derived from the O $2p$-level agreed rather well with photoemission experiments, while a satellite below the O $2p$-band naturally could not be reproduced[10]. A third approach is based on the Anderson impurity or cluster models, treating a Ni atom as an impurity in an O $2p$ host [11, 8]. The model takes into account the Coulomb correlation on the Ni atom and the hopping between the Ni $d$-level and the O $2p$ band. These model studies suggest that the gap in NiO is a charge transfer gap meaning that if a hole with a small binding energy is created on the Ni site, it is then with a large probability filled by a transfer of an electron from the O site, i.e. the hole residing in the highest valence state has a large O $p$-character. The lowest conduction state is of $d$-character so that the gap is formed between states with large O $p$ and Ni $d$-character. This model has gained a wide acceptance because it is able to explain experimental data which would be difficult to understand in the other two models. In particular, resonant photoemission of the related compound CuO shows a giant Cu $2p$ resonance[12] which identifies a large amount of Ni $d$ spectral weight below rather than above the O $p$ band as predicted by the LDA and the Mott-Hubbard picture. Also, X-ray absorption measurements on similar doped high $T_c$ compounds[13] show that the holes at the top of the valence band have a large O $p$-character.

Model calculations, while providing insight into the physical mechanism behind a phenomenon, have a drawback of relying on adjustable parameters. In addition the model itself may be too simple to represent the real system. For example, the bandstructure is largely neglected in the Anderson impurity model and long-range correlation is only included implicitly by renormalizing the value of $U$. Progress in *ab initio* calculations on the other hand has been slow. Only recently such *ab initio* calculations were performed, within the self-interaction correction (SIC) scheme[14, 15], LDA+U[16], and Hartree-Fock (HF) theory[17]. These theories, however, do not take into account the effects of correlation properly.

A working method for introducing correlation effects in *ab initio* calculations is the so-called $GW$ approximation (GWA),[18, 19, 20] where the self-energy is calculated to lowest order in the screened interaction $W$. The GWA has been successful in predicting the quasiparticle energies in weakly and moderately strongly correlated systems such as free-electron like metals and semiconductors. For these systems, the calculations can be carried out in a plane wave basis. Systems with strong correlations usually contain $3d$ or $4f$ states, which make a plane wave expansion impractical. For this reason the GWA has not been applied to such systems. The purpose of the present paper is to present a computational scheme which is applicable also to systems containing $3d$ and $4f$ electrons, to apply the method to NiO, and to test how well the GWA works for such a strongly correlated system.

In the GWA the self-energy is given by

$$\Sigma(\mathbf{r},\mathbf{r}';\omega)=\frac{i}{2\pi}\int d\omega G(\mathbf{r},\mathbf{r}';\omega+\omega')W(\mathbf{r},\mathbf{r}';\omega') \tag{1}$$

From the self-energy we obtain the quasiparticle energies and the spectral functions. In practice, the self-consistent Green function $G$ is replaced by a zeroth order Green function $G_0$. The screened potential $W$ is given by

$$W(\mathbf{r},\mathbf{r}';\omega)=\int d^3r''\epsilon^{-1}(\mathbf{r},\mathbf{r}'';\omega)v(\mathbf{r}''-\mathbf{r}') \tag{2}$$

where $\epsilon^{-1}$ is an inverse dielectric matrix and $v$ is a bare Coulomb potential. In a previous publication[21], we have presented a method for calculating $\epsilon^{-1}$. For the bandstructure calculations, we use the linear muffin-tin orbital (LMTO)[22] method which can be applied to systems with $d$ and $f$ electrons. The LMTO basis within the atomic sphere approximation[22] has the following form:

$$\chi_{\mathbf{R}L}=\phi_{\mathbf{R}L}+\sum_{\mathbf{R}'L'}\dot{\phi}_{\mathbf{R}'L'}h_{\mathbf{R}'L',\mathbf{R}L} \tag{3}$$

where $\mathbf{R}L$ denote the site and angular momentum $(l,m)$ respectively, $\phi$ is the solution to the Schrödinger equation inside the muffin-tin sphere and $\dot{\phi}$ is its energy derivative taken at some fixed energy $\epsilon_\nu$. When calculating the response function within the random phase approximation (RPA)[23], we have products of Bloch states so that the Hilbert space spanned by the response function consists of products of the type $\phi\phi$, $\phi\dot{\phi}$, and $\dot{\phi}\dot{\phi}$. Some of these products are linearly dependent and we construct an optimized basis for $\epsilon^{-1}$ by forming linear combinations of these product functions. The number of basis functions per atom is typically 50-100.[21]

We have performed a self-energy calculation for NiO within the GWA. The zeroth order Green function is constructed from the LDA wavefunctions and eigenvalues which are calculated by using the LMTO method. The screened potential $W$ is calculated within the RPA without using plasmon-pole or other similar approximations. Starting from the LDA antiferromagnetic bandstructure with a gap of 0.2 $eV$, the self-energy correction increases the gap to $\sim 1$ $eV$. The increase of the gap leads to a substantial change in the wavefunctions. This suggests that the self-energy calculation should be performed self-consistently using the self-energy $\Sigma$ from one iteration to construct the Green function $G$ for the next iteration. This is, however, beyond our computational resources, and we have used a simplified version of self-consistency. Some of the important effects of the self-energy correction are to raise and reduce the width of the Ni unoccupied $e_g$ band. These effects can be well simulated in the LMTO method by applying a non-local potential to the $e_g$ orbital. This does not simply lead to a rigid shift of the corresponding band but it also alters the wavefunctions. This shift is chosen so that the band gap of $G_0$ used in Eq. ( 1) agrees with the band gap obtained from $\Sigma$ in the previous iteration, and the iterations are continued to self-consistency. The shift is only used to construct $G_0$, and the resulting $\Sigma$ minus the LDA $V_{xc}$ is added to the *unshifted* LDA bandstructure. The final non-local potential corresponding to the $e_g$ orbital is $\sim 6\ eV$, slightly larger than the final gap because of the hybridization with other orbitals.

In Fig. 1b we compare the $GW$ quasiparticle bandstructure and the LDA bandstructure along the (1 0 0) and (1 1 1) directions. The bands between $-3$ and $0\ eV$ have mainly Ni $d$-character and the ones between $-7$ and $-3\ eV$ O $p$-character. The effects of the self-energy correction on the valence bandstructure are not very large. The bottom part of the $d$-bands along $\Gamma X$ is narrowed by $\sim 0.3\ eV$ and the top of the valence bands along $\Gamma L$ is pushed down by $\sim 0.3\ eV$. Apart from these changes, the $d$-bands are essentially unaffected. As can be seen in Fig. 1b, the top and the bottom of the O $p$ bands are affected significantly so that the separation between the top and the bottom of the bands at the $\Gamma$ point is reduced by $\sim 1.0\ eV$. The bottom of the O $p$ band is pushed up relative to the LDA one as the self-energy correction reduces the hybridization with the unoccupied Ni $3d$ states. Comparison with photoemission data shows that this is indeed an improvement on the LDA. The lowest conduction band is of Ni $e_g$ character and it lies just below the Ni $4s$. The band gap is found to be $\sim 5.5\ eV$ which is in reasonable agreement with experiment ($4\ eV$). As a check, we have also performed a self-energy calculation for the ferromagnetic state. We obtain a gap of $\sim 5.2\ eV$ which is very close to the value for the antiferromagnetic case. Thus, in contrast to the Slater model, the gap does not depend on the antiferromagnetic ordering in any essential way, and the results correctly suggest that NiO should remain an insulator also above the Neel temperature.

To illustrate the effects of correlations, we have also calculated the HF bandstructure using the LDA wavefunctions. The band gap is very large ($\sim 10\ eV$) as expected because there is no screening. The occupied Ni $d$ bands are found to be at the bottom of the O $p$ band so that the top of the valence band has an O $p$-character, similar to a self-consistent HF result, although the Ni $d$-bands are not pushed down as much as in the latter case. We can regard the GWA as a HF approximation but with dynamical (RPA) screening. This screening leads to a large reduction of the gap and is primarily due to long-range correlations, included in the GWA.

To analyze the $GW$ result, we have calculated the spectral function at $\mathbf{k} = 2/3(1,0,0)2\pi/a$ which should be representative of other $\mathbf{k}$-points. To study the character of the top of the valence band, we project the spectral function onto the Ni and O sites, i.e. we calculate the weight of the Ni $d$ and O $p$ states contained in the spectral function. The results are shown in Fig. 2. As can be seen from the figure, there is no marked increase of the O $p$-character at the top of the valence band and the main character is primarily Ni $d$. This is due to the small off-diagonal elements $\Sigma_{dp}$. It is also found in other systems that the $GW$ self-energy is almost diagonal. The small structure around $\sim 7\ eV$ is due to a single-particle state which is already present in the LDA. The experimentally observed high binding energy satellite at $\sim 8\ eV$ associated with the $d^8 \rightarrow d^7$ transition is not found.

To obtain a better understanding of the results, we make a comparison with an Anderson impurity calculation of the spectrum. The hopping matrix elements $V_{nk}$ were deduced from ab initio calculations[24], and the self-energy was determined by

$$G^{-1}(\omega) = \omega - \epsilon_d - \Gamma(\omega) - \Sigma(\omega) \tag{4}$$

where $G(\omega)$ is the Green function of the Anderson model, $\epsilon_d$ is the $d$-level position and

$$\Gamma(\omega) = \sum_{nk} |V_{nk}|^2/(\omega - \epsilon_{nk} - i0) \tag{5}$$

describes the effects of hopping. Fig. 3 shows $Re\ \Sigma(\omega)$ and the line $w - \epsilon_d$ for the majority spin $e_g$ states. The $t_g$ self-energies are similar, while the $e_g$ minority spin $\Sigma \sim 6\ eV$ is rather constant, leading to only one peak at $\omega \sim 4\ eV$. The corresponding $d$-spectral weight has a peak at about $-7$ to $-8\ eV$, where both $\omega - \epsilon_d - Re\ \Sigma(\omega)$ and $Im\ \Sigma(\omega)$ (not shown in the figure) are small. This peak corresponds to a transition from the $d^8$-like ground state to a final $d^7$-state. The spectral function also has a peak close to $\omega = 0$. This peak has a relatively small $d$-character, and a substantial $d^8L^-$ character where $L^-$ indicates that a $O\ 2p$ electron has filled the $3d$ hole created in photoemission. The self-energy obtained from the $GW$ calculation is also shown in Fig. 3. In this case, $Re\ \Sigma(\omega)$ varies more slowly with $\omega$, and there is only one crossing with the line $\omega - \epsilon_d$ close to $\omega = 0$. The corresponding peak in the spectral function is then mainly of $d$-character. Compared with the Anderson impurity model calculation, the $d^8 \to d^7$ satellite is missing and the peak close to $\omega = 0$ has too much $d$-weight. The shoulder structure at $\sim 8\ eV$ in $Im\ \Sigma(\omega)$ that lowers $Re\ \Sigma(\omega)$ can be traced back to the small peak in $Im\ W(\omega)$ at about the same position. To get a lowering of $Re\ \Sigma(\omega)$ as much as in the Anderson impurity model would require a much larger peak in $Im\ W(\omega)$.

The absence of the satellite in the GWA is as anticipated. This can be understood by noting that the imaginary part of the self-energy in the GWA is essentially a convolution of the Green function and the imaginary part of the screened potential $W$:[20]

$$\begin{aligned} Im\ \Sigma(\mathbf{r}, \mathbf{r}'; \omega) &= \sum_{\mathbf{k}n}^{occ} \psi_{\mathbf{k}n}(\mathbf{r}) \psi^*_{\mathbf{k}n}(\mathbf{r}') Im\ W(\mathbf{r}, \mathbf{r}'; \epsilon_{\mathbf{k}n} - \omega) \\ &\times \quad \theta(\epsilon_{\mathbf{k}n} - \omega), \quad \omega < \mu \end{aligned} \tag{6}$$

Thus the structure of the imaginary part of the self-energy is given by the structure of $Im\ W$. The loss spectra, which is proportional to $Im\ W$, shows no sharp peak around $8\ eV$ that would correspond to the existence of a satellite. It seems clear that the satellite structure arises from higher order terms in the self-energy. The satellite is likely of atomic origin, due to short-range correlation associated with the interaction between two or more holes in the same site. This is more appropriately described by the ladder type diagrams, rather than bubble type diagrams as in the GWA. For probably similar reasons, previous self-energy calculation for Ni metal[20] did not reproduce the well-known $6\ eV$ satellite either.

Corrections to the GWA, say ladder diagrams, which lead to the $d^8 \to d^7$ satellite at about $8\ eV$, would also remove $d$-spectral weight from the states at the top of the valence band, approaching the Anderson impurity model result. It is less clear if such diagrams would also increase the O $p$-character of these states. We note, however, that in the solution of the Anderson impurity model, the hopping between the $d^7$ and $d^8L^-$ configurations is increased by a degeneracy factor ($\sim 3$).[14] A proper treatment of the strong Coulomb repulsion on the Ni site in the ab initio calculation may therefore be expected to also enhance the $d^7 - d^8L^-$ coupling, leading to a substantial contribution to $\Sigma_{dp}$.

We have also estimated the magnetic moment from the spectral function shown in Fig. 2 yielding a value of $1.6\ \mu_B$ which is in good agreement with the experimental value of $1.7 - 1.9\ \mu_B$. The same value is obtained from two other $\mathbf{k}$-points along $\Gamma X$ indicating that it has little $\mathbf{k}$ dependence. The estimate has been obtained down to an energy of $-20\ eV$. We have found, however, that the contribution to the magnetic moment from $-10$ to $-20\ eV$ is only about $5 - 10$ % so that contribution from below $-20\ eV$ is not expected to be very significant. The improvement over the LDA result is due to the the self-energy correction which pushes up the unoccupied $e_g$-states. This reduces the hybridization so that the unoccupied $e_g$ band has a more pure $e_g$ character, thereby increasing the local moment.

We have presented a new method for performing $GW$ calculations, which allows the applications to systems with $3d$ and $4f$ electrons. This makes it possible to test the GWA for strongly correlated systems like NiO studied here. We have found that the GWA gives a rather good description of the size of the band gap and that it also improves the description of the O $p$-band compared with the LDA. However, it probably gives the top of the valence band too much $d$-character. From the structure of the self-energy, it seems clear that the GWA would not give a satellite structure apart from that due to the plasmon which is of the order of $\sim 25 - 30\ eV$. This appears to be quite a general result for real systems. It would be highly interesting to introduce ladder diagrams, which may describe the $8\ eV$ satellite and thereby reduce the $d$-character of the top of the valence band.

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**Figure 1**

(a) Comparison between the LDA (solid line) and experimental bandstructure[10]. (b) Comparison between the LDA bandstructure (solid line) and the quasiparticle bandstructure in the GWA (filled circles).

**Figure 2**

Spectral function at $\mathbf{k} = 2/3(1\ 0\ 0)2\pi/a$ within the GWA projected on the O $p$-orbitals (solid line) and Ni $d$-orbitals (the dotted line is for majority spin and the dashed line is for minority spin).

**Figure 3**

Comparison between the self-energy in the GWA and the Anderson impurity model (AIM).