Novel Approaches to Spectral Properties of Correlated Electron Materials: From Generalized Kohn-Sham Theory to Screened Exchange Dynamical Mean Field Theory

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The most intriguing properties of emergent materials are typically consequences of highly correlated quantum states of their electronic degrees of freedom. Describing those materials from first principles remains a challenge for modern condensed matter theory. Here, we review, apply and discuss novel approaches to spectral properties of correlated electron materials, assessing current day predictive capabilities of electronic structure calculations. In particular, we focus on the recent Screened Exchange Dynamical Mean-Field Theory scheme and its relation to generalized Kohn-Sham Theory. These concepts are illustrated on the transition metal pnictide BaCo₂As₂ and elemental zinc and cadmium.

1. Introduction

Technological progress has been intimately related with progress in materials science since its very early days. The last century has seen the development of refined capabilities for materials elaboration, characterisation and control of properties, culminating among others in the unprecedented possibilities of the digital age: materials properties have become an object of theoretical simulations, stimulating systematic searches for systems with desired characteristics. This branch of condensed matter physics is continuously evolving into a true new pillar of materials science, where the theoretical assessment of solid state systems becomes a fundamental tool for materials screening.

Obviously, the success of this program hinges on the degree of predictive power of modern simulation techniques, which have to allow for performing calculations without introducing adjustable parameters. This requirement is even more severe since the most popular branch of \textit{ab initio} calculations, the Density Functional Theory (DFT) approach, is restricted to ground state properties of the solid, while most properties of potential technological interest stem from excited states: the calculation of any type of transport phenomenon, for example electric, thermal, thermoelectric or magnetoelectric transport, of optical or spectroscopic properties, or of magnetic, charge- or orbital susceptibilities requires the accurate assessment of highly non-trivial response functions within a finite-temperature description.

It is not a coincidence that the materials with the most exotic features are also most challenging to get to grips with from a theoretical point of view: both the complexity of their properties and the difficulty of their description are in fact a consequence of the very nature of the underlying electronic structure: typically, one is dealing with transition metal, lanthanide or actinide compounds, where the electrons in partially filled \textit{d}- or \textit{f}-shells strongly interact with each other through electron-electron Coulomb interactions, leading to highly entangled many-body quantum states.

Even when using a simplified description of the solid in terms of an effective lattice model, assessing these quantum correlated states is a tremendous challenge. If \textit{local} quantum fluctuations on a given atomic site are dominant, dynamical mean-field theory (DMFT)¹,² yields an accurate description of the system. In particular, DMFT captures both the strong coupling Mott-insulating limit and the weakly interacting band limit of the Hubbard model, and is able to describe the salient spectral features of a correlated metal with coexisting quasi-particle and Hubbard peaks even in the intermediate correlation regime. In the multi-orbital case, additional degrees of freedom can lead to even richer physics with unconventional (e.g. orbital-selective) behavior,³ or complex ordering phenomena.⁴⁻⁹

In order to recover the material-specific character of the calculations, DMFT has been combined with DFT¹⁰,¹¹ into the so-called “DFT+DMFT” scheme, which is nowadays one of the most popular workhorses of electronic structure theory for correlated electron materials. Successful applications include transition metals,¹²⁻¹⁴ transition metal oxides,¹⁵⁻¹⁹ lanthanide²⁷,²⁸ or actinide²⁹⁻³² systems. Comparisons be-
between calculated and measured spectral functions have sometimes led to impressive agreement.\textsuperscript{33,34} However, despite these successes the construction of the Hamiltonian used in these calculations is rather \textit{ad hoc} and remains a limitation to the predictive power of the approach. Therefore, the elaboration of more systematic interfaces between electronic structure and many-body theory has become an active area of research.\textsuperscript{35}

In this work, we review a recent scheme combining screened exchange and DMFT.\textsuperscript{36–38} We discuss its relation to many-body perturbation theory and generalized Kohn-Sham (KS) Theory and analyse the effects included at the different levels of the theory. As an illustration we describe its application to the low-energy spectral properties of the cobalt pnictide BaCo\textsubscript{2}As\textsubscript{2}.

How does a theory that has been designed for strongly correlated materials reduce to an \textit{a priori} simpler version in the case of a weakly correlated system? For methods based on DFT that include only the static on-site Coulomb interaction between localized states, like DFT+U\textsuperscript{39} or DFT+DMFT, the spectrum in the limit of vanishing Hubbard interactions reduces trivially to the Kohn-Sham spectrum of DFT. For more complex interfaces of electronic structure and many-body theory which we will discuss here, however, it is a non-trivial question and allows for interesting possibilities to check their consistency. Here, we will discuss this issue on the example of the transition metals zinc and cadmium. This also allows us to comment on the challenge of including states in a wider energy range, identifying a challenging problem on these seemingly “simple” systems.

The paper is organised as follows: in section 2 we review how Screened Exchange Dynamical Mean Field Theory derives from the combined many-body perturbation theory + dynamical mean field scheme “GW+DMFT”. In section 3 we analyse the relation of screened exchange schemes to generalized KS theory. Section 4 provides an example of the application of such methods to BaCo\textsubscript{2}As\textsubscript{2}, while section 5 discusses the electronic structure of elemental zinc and cadmium within a simplified approach. Finally, we conclude in section 6.

2. From GW+DMFT to Screened Exchange Dynamical Mean Field Theory

Improving the predictive power of methods that combine electronic structure and many-body theory poses the challenge of properly connecting the two worlds, without double counting of interactions or screening. At the heart of this challenge lies the mismatch between the density-based description of DFT and the Green’s function formalism used at the many-body level, as well as the difficulty of incorporating the feedback of high-energy screening processes governed by the unscreened Coulomb interaction onto the low-energy electronic structure. Conceptually speaking, these difficulties can be avoided by working on a large energy scale in the continuum with the full long-range Coulomb interactions, and a Green’s function-based formalism even at the level of the weakly correlated states. These features are realised within the combined many-body perturbation theory and dynamical mean field theory scheme “GW+DMFT\textsuperscript{36–38}” screening is assessed by the random phase approximation in the continuum, augmented by a local vertex correction, while the starting electronic structure for the DMFT calculation can be roughly interpreted as a “non-local GW” calculation.\textsuperscript{50}

Screened Exchange Dynamical Mean Field Theory\textsuperscript{36–38} can be understood as an approximation to this full GW+DMFT scheme. It is based on the recent observation\textsuperscript{36,50} that within the GW approximation the correction to LDA can be split into two contributions: a local dynamical self-energy $\Sigma_{\text{loc}}(\omega)$ and a $k$-dependent but static self-energy $\Sigma_{\text{nonloc}}(k)$, which does not contain any local component. If such a separation was strictly valid in the full energy range, the non-local static part of the full self-energy would be given by the non-local Hartree-Fock contribution, since the dynamical part vanishes at high frequency. In many realistic systems such a decomposition holds to a good approximation in the low-energy regime that we are interested in, where the static part $\Sigma_{\text{nonloc}}(k)$ is quite different from the Fock exchange term. It is approximately given by a screened exchange self-energy, leading to a decomposition of the GW self-energy into $\Sigma_{GW} = [GW(\nu = 0)]_{\text{nonloc}} + [GW]_{\text{loc}}$. Here, the first term is a screened exchange contribution arising from the screened interaction $W(\nu)$ evaluated at zero frequency $W(\nu = 0)$. The second term is the local projection of the GW self-energy. It is simply given by the GW self-energy evaluated using a local propagator $G_{\text{loc}}$ and the screened Coulomb interaction $W_{\text{loc}}$. Exactly as in GW+DMFT, Screened Exchange Dynamical Mean Field Theory replaces this term by a non-perturbative one: it is calculated from an effective local impurity problem with dynamical interactions. In current practical applications of Screened Exchange + DMFT the RPA-screened Coulomb potential $W$ has been replaced by its long-wavelength limit, which reduces to a simple Yukawa-form.\textsuperscript{36}

Quite generally the dynamical character of the interactions results in an additional renormalization $Z_B$ of the hopping amplitudes, which can be understood as an \textit{electronic polaron} effect: the coupling of the electrons to plasmonic screening degrees of freedom leads to an effective mass enhancement corresponding to the hopping reduction, manifesting itself as a narrowing of the band. This effect can be estimated from the plasmon density of modes as given by the imaginary part of the frequency dependent interaction $W$. An explicit expression for $Z_B$ has been derived in Ref. 51.

3. Relation to Generalized Kohn-Sham Theory

Screened Exchange Dynamical Mean Field Theory can also be viewed as a specific approximation to a spectral density functional theory based on the Generalized Kohn-Sham (GKS) scheme of Seidl \textit{et al.}\textsuperscript{52} In GKS theory, alternative choices for the reference system that are different than the familiar Kohn-Sham system of DFT are explored. In particular, a generalized Kohn-Sham scheme where the reference system is a screened exchange Hamiltonian can be constructed. The main motivation for the inclusion of screened
exchange in the literature has been to improve upon the band gap problem in semiconductors. Indeed, it can be shown that the screened exchange contribution, which corresponds to a non-local potential, effectively reintroduces to some degree the derivative discontinuity that is missing in the pure DFT description based on local exchange-correlation potentials.\(^{53}\)

Since the derivative discontinuity corresponds to the discrepancy between the true gap and the Kohn-Sham gap in exact DFT, a substantial improvement of the theoretical estimate for band gaps can be expected on physical grounds and has indeed been found. Here, our goal is somewhat different: motivated by the analysis of the role of screened exchange in GW+DMFT described above, we would like to connect the Screened Exchange DMFT scheme introduced above to generalized KS schemes making direct use of the non-local screened exchange potential.

With this aim in mind, we briefly review the generalized Kohn-Sham construction in the case an effective Kohn-Sham system including screened exchange. Hereby, we follow closely Seidl et al.\(^{53}\) both in notation and presentation. First, one defines a functional

\[
S [\Phi] = \langle \Phi | \hat{T} | \Phi \rangle + U_H [\{\phi_i\}] + E_{\text{xc}}^S [\{\phi_i\}] \tag{1}
\]

that includes, in addition to the familiar kinetic energy term \(\langle \Phi | \hat{T} | \Phi \rangle\) and the Hartree energy \(U_H [\{\phi_i\}]\) also the screened Fock term

\[
E_{\text{xc}}^S [\{\phi_i\}] = -\sum_{i<j} \int \frac{d\mathbf{r}d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \phi_i^*(\mathbf{r}) \phi_j^*(\mathbf{r}') e^{-k_{\text{FF}}|\mathbf{r} - \mathbf{r}'|} \phi_j(\mathbf{r}) \phi_i(\mathbf{r}') \tag{2}
\]

Here, \(\Phi\) are Slater determinants of single-particle states \(\phi_i\). \(k_{\text{FF}}\) is the Thomas Fermi wave vector. In order to derive a functional of the density Seidl et al. define a functional \(F^\text{S}\) via the minimisation

\[
F^\text{S} [\rho] = \min_{\Phi \sim \rho(r)} S [\Phi] = \min_{\{\phi_i\} \sim \rho(r)} S [\{\phi_i\}] \tag{3}
\]

Next we define the energy functional

\[
E^\text{S} [\{\phi_i\}; \nu_{\text{eff}}] = S [\{\phi_i\}] + \int d\nu_{\text{eff}}(r) \rho(r) \tag{4}
\]

where now the potential \(\nu_{\text{eff}}\) does not only include the external potential \(\nu\) as in usual DFT, but also a contribution by the exchange-correlation part

\[
\nu_{\text{eff}} = \nu + \nu_{\text{xc}}^\text{S} [\rho]. \tag{5}
\]

The additional contribution, the generalized (local) exchange-correlation potential

\[
\nu_{\text{xc}}^\text{S} = \frac{\partial E_{\text{xc}}^\text{S} [\rho]}{\partial \rho}. \tag{6}
\]

is the functional derivative of the generalized (local) exchange-correlation functional

\[
E_{\text{xc}}^\text{S} [\rho] = E_{\text{xc}} [\rho] - E_{\text{x}}^\text{S} [\rho] + T [\rho] - T_{\text{xc}}^\text{S} [\rho] \tag{7}
\]

which comprises the difference between the exchange-correlation potential of standard Kohn-Sham DFT and the non-local exchange energy defined above, as well as the difference between the kinetic energies of the standard and generalized Kohn-Sham systems. The functional derivative will eventually have to be evaluated self-consistently at the converged density.

This construction leads to the generalized Kohn-Sham equations

\[
-\nabla^2 \phi_i(\mathbf{r}) + v(\mathbf{r}) \phi_i(\mathbf{r}) + u (\{\rho\}; \mathbf{r}) \phi_i(\mathbf{r})
- \int d\mathbf{r}' \nu_{\text{xc}}^\text{NL}(\mathbf{r}, \mathbf{r}') \phi_i(\mathbf{r}') + \nu_{\text{xc}}^\text{S} (\{\rho\}; \mathbf{r}) \phi_i(\mathbf{r}) = \epsilon_i \phi_i \tag{8}
\]

with the Hartree potential \(u\) and the non-local screened Fock potential

\[
\nu_{\text{xc}}^\text{NL}(\mathbf{r}, \mathbf{r}') = -\sum_{j=1}^N \phi_j(\mathbf{r}) e^{-k_{\text{FF}}|\mathbf{r} - \mathbf{r}'|} \phi_j(\mathbf{r}) \tag{9}
\]

and the effective (local) generalized Kohn Sham potential \(\nu_{\text{xc}}^\text{S}\) defined above. The generalized Kohn-Sham equations have the form

\[
\hat{O} [\{\phi_i\}] \phi_j + \nu_{\text{eff}} \phi_j = \epsilon_j \phi_j \tag{10}
\]

where \(\hat{O}\) is a non-local operator, generalizing the standard Kohn-Sham operator consisting solely of kinetic energy and Hartree potential.

The ground state energy for a system in the external potential \(\nu\) is then given by the expression

\[
E_{\text{SEX-DFT}} [\nu] = F^\text{S} [\rho_0^\text{S} [\nu_{\text{eff}}]] + E_{\text{xc}}^\text{S} [\rho_0^\text{S} [\nu_{\text{eff}}]]
+ \int d\mathbf{r} \nu(r) \rho_0^\text{S} [\nu_{\text{eff}}] \tag{11}
\]

Now, the relation to Screened Exchange DMFT is becoming clear: one may construct a spectral density functional in the same spirit as in DFT+DMFT,\(^{54}\) but starting from the generalized KS functional. In 55, the expression for the total energy within the standard DFT+DMFT case was derived to be

\[
E = E_{\text{DFT}} - \sum_i \epsilon_i^{\text{KS}} + \langle H_{\text{KS}} \rangle + \langle (H_{\text{int}} - H_{\text{dc}}) \rangle \tag{12}
\]

where \(\sum_i \epsilon_i^{\text{KS}}\) is the sum of the occupied Kohn-Sham eigenvalues, \(\langle H_{\text{KS}} \rangle = \text{tr} [H_{\text{KS}} \hat{G}]\), and \(H_{\text{int}}\) and \(H_{\text{dc}}\) denote the local interaction part of the Hamiltonian and the corresponding double counting term, respectively.

Instead of using the usual Kohn-Sham Hamiltonian for the construction of the one-body part, Screened Exchange DMFT relies on the generalized Kohn-Sham reference system that includes the screened exchange potential. The generalization of (12) to the present case thus replaces the Kohn-Sham Hamiltonian \(H_{\text{KS}}\) in the expression for the energy by its non-local form, keeping track of the effective potential part:

\[
E = E_{\text{SEX-DFT}} - \sum_i \epsilon_i^{\text{SEX-KS}} + \langle \hat{O} + \nu_{\text{eff}} \rangle
\]
Furthermore, the local interaction term is taken in the more general form of a dynamical interaction, thus corresponding to a local Hubbard term with unscreened interactions and local Einstein plasmons of energy $\omega_s$ coupling to the electrons via coupling strength $\lambda_s$.

This concludes our description of the generalized Kohn-Sham interpretation of Screened Exchange DMFT, resulting in particular in an energy functional expression. However, in the practical calculations presented in the following we do not minimise the full energy expression as given above, but rather work at the converged DFT density and then investigate spectral properties using the Screened Exchange DMFT formalism. This amounts to a one-shot Screened Exchange-DFT+DMFT calculation that uses the DFT density as a starting point. The advantage of such an approach is obvious: Numerically, this procedure allows us to avoid the expensive evaluation of non-local exchange terms within the self-consistency cycle of GKS theory. Moreover, as is well-known, while severe deviations of the true spectrum from the Kohn-Sham spectrum are quite common, the ground state density obtained even from approximate DFT functionals is often a good representation of the true one. In the case of the exact DFT functional, our approach would also lead to the exact ground state density and energy, with additional improvements of the spectrum over standard Kohn-Sham DFT.

4. Results on BaCo$_2$As$_2$

As a first illustration of Screened Exchange DMFT, we review calculations on BaCo$_2$As$_2$, which is the fully Co-substituted representative of the so-called “122” family of the iron-based superconductors, isostructural to the prototypical parent compound BaFe$_2$As$_2$. The Fe → Co substitution has however important consequences: the nominal filling of the 3$d$ states changes from $d^6$ to $d^7$, which strongly reduces the degree of Coulomb correlations, making BaCo$_2$As$_2$ a moderately correlated compound. Indeed, the power-law deviations from Fermi liquid behavior above an extremely low coherence temperature discussed in the Fe-based compounds are a consequence of the $d^6$ configuration and strong intraatomic exchange interactions. This is no longer the case in the cobalt pnictides, where angle-resolved photoemission spectroscopy (ARPES) identifies well-defined and long-lived quasiparticle excitations with relatively weak mass renormalization. Nevertheless, the DFT-LDA derived Fermi surface differs from experiment. Therefore, BaCo$_2$As$_2$ provides an ideal testing ground for new approaches to spectroscopic properties. We do not discuss here the details of yet another interesting question, which is the absence of ferromagnetism despite a high value of the DFT density of states at the Fermi level, suggestive of Stoner ferromagnetism, but refer the reader to Ref. 36, where the solution to this puzzle was discussed in detail.

Fig. 1 shows the DFT band structure of BaCo$_2$As$_2$, in comparison to a screened exchange calculation. As in the iron-based pnictides, the dominantly 3$d$-derived states are located around the Fermi level; in this case in a window of about -3 eV to 2 eV. As compared to the parent iron pnictides with 3$d^6$ configuration of the Fe shell, the Fermi surface topology is modified due to the larger 3$d^7$ filling. The hole pocket at the $\Gamma$ point that is present in most Fe-based pnictide compounds is pushed below the Fermi level, as well as the band forming the electron pocket at M, which is now fully filled. In standard DFT-LDA (see Fig. 2), a characteristic flat band of dominant $x^2 - y^2$ character lies directly on the Fermi level around the M point, giving rise to a huge peak in the density of states.
The close proximity of this band to the Fermi level will render its energy highly sensitive to the details of the calculation and thus provides a perfect benchmark for improved computational techniques.

Comparison to angle-resolved photoemission experiments, as reproduced in Fig. 3, reveals that the overall bandwidth of the LDA band structure is too wide by roughly a factor of 1.5. In a DFT+DMFT calculation, as shown in Fig. 4, this band renormalization is reproduced, giving an overall occupied bandwidth of about 1.5 eV. The fine details of the Fermi surface, and in particular the position of the flat $x^2 - y^2$ band are however not well described. For a detailed comparison we refer the reader to Ref. 36.

Including screened exchange in the form of a Yukawa potential on top of DFT, as shown in Fig. 1 widens the band by a considerable amount as compared to DFT-LDA. Even more striking are the modifications at the Fermi level: the $x^2 - y^2$ band has been shifted above the Fermi level, with an energy at the $M$ point of about 0.15 eV above $E_F$. While the lowering of the filling of this band improves the agreement between theory and experiment, the shift is too large to reproduce the experimental Fermi surface. However, when applying DMFT with dynamical interactions on top of the screened exchange Hamiltonian, equivalent to the one-shot Screened Exchange DMFT procedure described above, this band is renormalized by the electronic interactions and ends up again close (but above!) the Fermi level. Its energy is slightly higher than in DFT-LDA and is now in excellent agreement with the experimental Fermi surface. A more detailed analysis presented in Ref. 36 reveals that also the higher energy features such as the bands within the range of up to 2 eV are well reproduced in this one-shot Screened Exchange DMFT approach.

The comparison of the band structures and spectral func-
5. How does Screened Exchange Dynamical Mean Field Theory behave for weakly correlated materials?

Hamiltonians built as combinations of a DFT part and local Hubbard-type interaction terms trivially reduce to the DFT Kohn-Sham electronic structure when assuming that in weakly correlated materials the effective local interactions become negligible. The question of the recovery of the weakly interacting limit is, however, more interesting in the case of Screened Exchange DMFT. While the static part of the effective local interaction may be assumed to lose its importance, band widening by the replacement of the DFT exchange correlation potential by the non-local exchange-correlation GW self-energy persists. On the other hand, plasmonic effects are also present in weakly correlated materials and continue to renormalize the low-energy band structure through electron-plasmon coupling. This raises the question of what the resulting spectra for weakly correlated materials look like in screened exchange + DMFT.

In Ref. 38, this question has been studied for early transition metal perovskites, where it was found that the band widening effect induced by non-local exchange and the electronic polaron effect counteract each other and tend to approximately cancel, thus resulting in a low-energy electronic structure close to the DFT Kohn-Sham band structure as long as static Hubbard interactions are disregarded. Here, we address this question in the case of the seemingly “simple” transition metals zinc and cadmium.

Both elements nominally display a $d^{10}$ configuration, with fully occupied 3$d$ orbitals in the case of Zn and 4$d$ in the case of Cd, the dominantly $d$-derived bands being located several eV below the Fermi level. In Fig. 7 and Fig. 8 we show the band structure calculated within DFT for both materials. Here and in the following we use the experimental crystal structure. DFT puts the occupied $d$ states at around -8 eV in Zn and -9 eV in Cd. The conducting states of this transition metal are formed by dispersive 4$s$($5s$) in Zn(Cd) states around the Fermi level, that hybridize with the $p$-manifold.

These facts raise the immediate expectation of negligibly small correlation effects on the occupied $d$ shells. An effective Hubbard interaction calculated for the $d$-manifold within the constrained random phase approximation coincides with the fully screened interaction, since as a consequence of the
complete filling of the d-shell there are no intra-d transitions to be cut out as opposed to an open shell system, where transitions inside the shell contribute to screening effects.

Figs. 9 and 10 display the local component of this fully screened interaction projected on the $d$-manifold. The low-frequency limit approaches a value of 4.8 eV and 3.1 eV for Zn and Cd respectively. Even though this value is similar to their oxides, which are open shell systems, where correlations on the $d$ states are significant, the high binding energy of these states far away from the Fermi level effectively prevents dynamical fluctuations. This suggests that screened exchange + DMFT should in fact reduce to screened exchange renormalized by the bosonic factor $Z_B$ discussed above. Nevertheless, this does not mean that static effects of the interaction are properly treated in DFT. Even if this were the case, there is no reason that the DFT Kohn-Sham spectrum, being derived from an effective non-interacting system, provides an accurate description of the experimental situation.

Figs. 11 and 12 compare the experimental photoemission spectra\cite{61,62} from the literature to the density of states (DOS) derived from DFT and Hartree-Fock (HF) theory. The resulting discrepancy in terms of an underestimation of the binding energy of the $d$ states in DFT of several eV had been noted in the literature before.\cite{63-65} Norman et al.\cite{63} discussed it in terms of a self-interaction error, proposing a correction in
terms of an approximate subtraction of self-interaction contributions contained in DFT.\(^6\)\(^0\) Hartree-Fock calculations are, on the one hand, self-interaction free, but on the other hand – due to the absence of screening – widen all bands and place the d-bands far too low in energy, as can be seen in Figs. 11 and 12.

Since local dynamical correlations can assumed to be small as discussed before, an improved treatment of the screened interaction and the self-interaction correction at the same time is likely to improve the shortcomings of Hartree-Fock, resp. DFT. Here we will discuss the two possible extensions of Screened Exchange plus a bosonic renormalization factor \(Z_B\) and the GW approximation. The computationally cheaper option of screened exchange is including only static exchange contributions with a Yukawa-type interaction potential, and an effective renormalization \(Z_B\) which originates from the spectral weight transfer to plasmonic excitations. GW is computationally more demanding, but has the advantage of treating the dynamical part of the screening and correlation. Even though both methods include a self-interaction correction, the self-interaction contained in the Hartree term is not completely cancelled since the exchange contributions are derived from a screened interaction and not the bare one, as opposed to the Hartree term.

In Figs. 13 and 14 we show comparisons of the DOS of zinc and cadmium, calculated within DFT, screened Exchange\(+Z_B\) and GW\(^67\) to photoemission spectra. In the GW calculation we used \(7 \times 7 \times 3\) k-points and 5 additional high-energy local orbitals. Interestingly, while in both systems the GW approximation provides a significant correction of the DFT Kohn-Sham spectrum in the right direction, but still underestimates the binding energy, the screened exchange scheme places the d-states too low in energy for Zn while providing a slightly better estimate than GW in Cd. The addition of the bosonic renormalization factor \(Z_B\) merely renormalizes the d bandwidth but keeps the average level position constant.

This raises the interesting question of which effects are missing in screened exchange and GW? The incomplete cancellation of the self-interaction in both approaches is expected to lead to an overall underestimation of the binding energy, since the additional unphysical interaction increases the energy of the d states. A more accurate estimate of this term would lead to an improvement of GW in both systems, but an even larger error of screened exchange in Zn. Another effect neglected in screened exchange is the Coulomb hole contribution: this term, discussed by Hedin as part of the “Coulomb hole screened exchange (COHSEX)” approximation translates the fact that the presence of an electron at a position \(r\) pushes away charge at \(r\) (in the language of a lattice model, the charge-charge correlation function exhibits a reduction of the double occupancy), and the interaction of this effective positive charge with the electron presents an energy gain expressed in the form of an interaction of the electron with a “Coulomb hole”. This term, contained in GW but not in screened exchange, also increases the binding energy.

This leads to the overall picture that screened exchange with the inclusion of the static corrections just discussed has a tendency to overestimate the binding energy in general, while GW underestimates it. The obvious difference between the two methods is the dynamical treatment of the screened interaction, which is treated more appropriately in GW, but it is not clear a priori whether the static approximation of the screened interaction or the approximated form of the screened interaction in terms of a Yukawa potential gives rise to the difference between screened exchange and GW.

The GW description of zinc and cadmium is close to the experiment. The remaining discrepancy to experiment is likely...
explained by remaining self-interaction contributions and/or missing self-consistency. Self-consistency (or quasiparticle self-consistency) has been investigated in the homogeneous electron gas and various solid state systems. These questions are left for future work.

6. Conclusions

In this work we have reviewed and applied existing as well as novel approaches to obtain spectral properties of correlated electron materials. Guided by the need of a proper treatment of the long-range Coulomb interaction and non-local exchange effects we presented a lightweight version of the general GW+DMFT approach, the so-called Screened Exchange DMFT. It can be derived as a simplification to GW+DMFT in terms of a generalized screened exchange DFT scheme where local interactions are treated by dynamical DMFT.

Analysis and the application of a simplified form of this scheme to BaCo$_2$As$_2$ indeed showed that non-local exchange and electronic screening lead to significant corrections to the electronic spectrum which are necessary to obtain a proper description of the experimental observations.

Furthermore, we discussed the case of the elemental transition metals Zn and Cd, where strong local correlations are unimportant but the position of the occupied d manifold is very sensitive to a proper treatment of screened exchange effects.

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