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Structure, magnetism and Coulomb correlations: From bulk systems to nanoclusters

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Abstract

An account is given of the role of electronic correlations in bulk materials and in systems of reduced dimensions like nanoparticles. In case of bulk materials we encounter diversity as well as universality regarding the response of materials to strong local on-site Coulomb correlations. In order to describe the momentum and energy resolved corrections to the single particle energies arising from charge and spin fluctuations, it has become state of the art to combine density functional calculations with calculations based on characteristic many-body Hamiltonians like the multi-band Hubbard and Anderson lattice models. For example, in case of bulk materials this procedure allows to describe the physical properties of transition metal oxides like $\alpha$-Fe$_2$O$_3$ correctly. In case of magnetic nanoparticles this method proves to be necessary in order to obtain their magnetic properties, which are in agreement with Hund’s empirical rules.
1. Introduction to electronic correlations

Quantum chemical methods allow to calculate the chemical and physical properties of small molecules with an accuracy which allows direct comparison with experiments. These so called ab initio methods, which make no use of empirical information, usually rely on specific implementations of the configuration interaction (CI) method, Møller-Plesset perturbation theory (MP2 or MP4), coupled cluster (CC) approaches and multi-configuration or complete active space self-consistent field (SCF) methods (MCSCF or CASSCF), see [1] for a compact discussion of the different methods and [2] for more general discussions and comparison to implementations of density functional theory (DFT). These approaches allow to calculate the correlation energy after Hartree-Fock (HF) calculations (post-HF methods). The limitation of the HF method is that, due to the independent particle approximation, the instantaneous correlation of the moving electrons is neglected. Hence, with respect to quantum chemical methods the difference between the exact energy and the HF energy is known as correlation energy,

\[ (\langle H \rangle = E_{\text{exact}}) - E_{\text{HF}} < 0, \]

where \( H \) is the Hamiltonian of the system. These methods, of which the most accurate ones are CC approaches, are very powerful since they allow to study ground- and excited-state properties. However, the accuracy comes at a price because of the scaling in the range of \( M^5 \) to \( M^7 \), where \( M \) is the number of basis functions. Therefore, already very early molecular modeling in quantum chemistry has been performed, in which only valence electrons are considered. To the most popular methods used today belong MNDO, AM1 and PM3, in which zero differential overlap is applied to basis functions on different atoms, as well as atomic force-field methods like Amber and Charmm.

Alternative methods of electronic structure calculations rely on different implementations of DFT, which is based on the Hohenberg-Kohn-Sham theorems allowing to map the many-body Hamiltonian onto an effective one-electron problem, see, for example, [3]. The theorem states that the exact total energy of the many-body Hamiltonian is a functional of the electron density, \( E = E(\rho) \), and that any trial density \( \tilde{\rho}(\mathbf{r}) \) fulfills \( E[\tilde{\rho}] \geq E[\rho] \). So the importance of the theorems is related to the fact that not the full many-particle wavefunction needs to be calculated, but only the total electron density \( \rho(\mathbf{r}) \) with the total number of electrons given by \( N = \int d^3 \rho(\mathbf{r}) \). This reduces the computational cost which scales from \( M^3 \) to \( M \) in the most favorable cases. This means that with DFT methods much larger systems can be computed without too much loss of accuracy compared to the case when using ab initio quantum chemical methods. Advantages and short-comings of DFT studies relying on different approximative schemes like spin-polarized local density approximation (LDA) or generalized gradient approximation (GGA) depend on the system under investigation, for different case studies see [4]. In DFT the total energy can be written as

\[ E[\rho] = T[\rho] + \int d^3 \mathbf{r} \left[ V_{\text{ext}}(\mathbf{r}) + V_{\text{C}}(\mathbf{r}) \right] + E_{\text{ex}}[\rho], \]

where \( T \) is the kinetic energy, \( V_{\text{ext}}(\mathbf{r}) \) is the external potential of electrons moving in the field of the nuclei, \( V_{\text{C}}(\mathbf{r}) \) the classical electrostatic Coulomb energy of the electrons (Hartree term), and \( E_{\text{ex}}[\rho] \) is the so called exchange-correlation energy. Kohn et al. introduced a simplification by replacing \( T \) by the kinetic energy of \( N \) non-interacting
quasi-electrons moving in a different external potential $V_{\text{eff}}(\mathbf{r})$. This allows to solve the Schrödinger equation separated into $N$ single-particle equations of the form

$$
\left(-\frac{\hbar^2}{2m} \nabla^2 + [V_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_{\text{C}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r})] \right) \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}).
$$

(3)

The DFT can also be extended to allow evaluation of excited states dynamics at zero temperature either within the time-dependent density functional theory (TDDFT) [13] or by using a Green’s function approach (GW) [14].

Moreover, ab initio quantum chemical and empirical methods as well as DFT can be extended to finite temperatures by including the entropy, which retains the influence of excitations in a mean-field like manner. This allows to treat gas-phase reactions, where the vibrational, rotational and $pV$ terms can be approximated using expressions for ideal gases.

However, the independent-electron model of DFT together with its approximative treatment by using the LDA or GGA are not accurate enough for certain classes of materials like, for example, transition metal oxides or other systems, where on-site Coulomb effects dominate the low-energy excitations of the electrons leading to a metal-insulator transition for strong enough Coulomb repulsion (note that this type of correlation is different from the corresponding notion used in quantum chemistry). Here, two remedies have emerged over the last years for resolving this problem.

The so-called LDA + U or GGA + U methods allow to retain most of the correlation effects of the multi-band Hubbard model in a mean-field like manner [5, 6] leading to

$$
E_{\text{LDA/GGA}+U} = E_{\text{LDA/GGA}} + \frac{1}{2}(U - J) \sum_{m\sigma}(n_{m\sigma} - n_{m\sigma}^2)
$$

(4)

for the total energy and to

$$
\varepsilon_{m\sigma} = \varepsilon_{m\sigma}^{\text{LDA/GGA}} + (U - J) \left( \frac{1}{2} - n_{m\sigma} \right),
$$

(5)

for the corresponding Kohn-Sham eigenvalues, where $m$ and $\sigma$ denote magnetic quantum number and spin. The relation shows that unoccupied and occupied states are separated by $(U - J)$. This method will be applied below to discuss the impact of correlation effects on bulk $\alpha$-Fe$_2$O$_3$ and on Fe nanoparticles.

An advanced treatment of local Coulomb correlation effects is based on the dynamical mean-field theory which allows to solve model Hamiltonians like the Hubbard and Anderson impurity model in infinite dimensions numerically by means of Monte Carlo simulations, for a review see [7, 8, 9]. Here, the dynamical field $\Delta(\omega)$ is related to the self energy of the Anderson impurity model in second order perturbation theory by

$$
\Delta(\omega) = \sum_{\mu} \frac{|V_\mu|^2}{\omega - \varepsilon_\mu},
$$

(6)

where $\varepsilon_\mu$ corresponds to the LDA variational parameters, $\mu$ stands for spin and orbital and $V_\mu$ is the hybridization matrix element.

This method can be combined in three dimensions with LDA which is called the “LDA ++ approach” [10, 11, 12]. In this approach, by analogy to DFT, an exact functional
of both the charge density and the local Green’s function of the correlated electrons can be introduced as
\[
E[\rho(r), G] = T[\rho(r), G] + \int d^3 r V_{\text{ext}}\rho(r) + \frac{1}{2} \int d^3 r \int d^3 r' \frac{\rho(r) \rho(r')}{|r - r'|} + E_{\text{sc}}[\rho(r), G].
\] (7)

Here, the kinetic energy is no longer that of free electrons but corresponds to the kinetic energy of a system with given density \(\rho(r)\) and local Green’s function \(G\). Investigations of strongly correlated electron systems with LDA++ can be found, for example, in [15, 20]. For a very compact and concise overview as well as further important references we refer to [16].

2. The generic phase diagram of the single-band Hubbard model

In order to illustrate the influence of strong on-site Coulomb correlations we briefly recall results for the single-band Hubbard model defined by
\[
H = - \sum_{\langle ij \rangle \sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \text{H.c.} + \frac{1}{2} \sum_{\nu \sigma} U_{\nu} n_{\nu\sigma} n_{\nu\sigma-\sigma}
\] (8)

with nearest-neighbor hopping. This model can be solved “exactly” for electrons on a hypercube with connectivity \(z = 2d\) in the limit \(d = \infty\) with \(t_{ij} = t^*/\sqrt{2z}\) [17, 18, 19]. The corresponding generic phase diagram is shown in Fig. 1.

The density of states (DOS) of the single-band Hubbard model is shown in Fig. 2 for increasing values of \(U\) showing the typical feature of the quasi-particle peak of metallic electrons centered around the Fermi energy together with the “atomic” excitations (broadened by the hopping of electrons), which appear for sufficiently strong \(U\).

This three-peak structure of the DOS of strongly correlated metals can actually be observed in the photoemission spectrum of \(V_2O_3\) near the metal-insulator transition [20]. In the following we discuss first-principles calculations of correlation effects in another bulk oxide system, i.e., in hematite, \(Fe_2O_3\) [21].

3. Correlation effects in hematite (\(Fe_2O_3\))

Hematite, \(Fe_2O_3\), is an oxide system, for which it is important to take the local Coulomb interactions at the lattice sites of the transition metal element rigorously into account. Although the Coulomb interaction at the iron sites is only of moderate strength (approximately half of the d-electron band width), we will show that it leads to a vanishing antiferromagnetic-ferromagnetic phase transition under pressure, which is in agreement with the experimental findings.

Figure 3 shows the complex unit cell of \(Fe_2O_3\) with two different iron sites (each surrounded by six oxygen atoms) forming two-dimensional layers. Calculations have been done for different ground states including nonmagnetic (NM), ferromagnetic (FM) and three distinct antiferromagnetic (AF) states, see Ref. [21] for details. In contrast to metallic systems transition metal oxides can exhibit antiferromagnetic order with a lattice constant being larger than the corresponding one belonging to the ferromagnetic phase, see Fig. 4.

The results have been obtained with VASP [22, 23] employing GGA and are in agreement with previous calculations. Experimentalists have tried in vain to induce a magnetic
phase transition (AF \rightarrow FM) under external pressure, whereas theory predicts such a transition as indicated by the tangent in Fig. 4.

Therefore, we have performed GGA + U calculations in order to check in how far local Coulomb interactions can alter the physics. Figure 5 shows that indeed correlation effects at moderate values of $U$ cause the AF \rightarrow FM transition to vanish in accordance with the experimental observation, here seen as an abrupt change of the $c/a$ ratio dependent on pressure. Furthermore, by retaining Coulomb correlation effects, we obtain the correct band gap and spectroscopic data for $\alpha$-Fe$_2$O$_3$ which are in agreement with experiment [21, 24]. This is another example, besides the calculations for vanadium oxide by Held [15], which shows that correlation effects induced by local Coulomb interactions are important in order to obtain accurate physical properties of transition metal oxides. In the following we briefly discuss the importance of such correlation effects in small iron clusters.

4. Correlation effects in small Fe$_n$ clusters

The magnetic moments of Fe$_n$ clusters as function of the cluster size have been measured at low temperatures by Billas [25]. However, we observe that the experimental magnetic moments of tiny Fe$_n$ clusters as well as corresponding theoretical values (see, for example, [26]) obtained so far by ab initio methods appear to be too small when comparing the values with what one would expect from Hund’s empirical rules. Although the experi-
Figure 2: Density of states of the single-band Hubbard model at half filling (one electron per lattice site) as a function of the local Coulomb interaction. From top to bottom the corresponding values are (a) $U = 0$ (semi-elliptic model density of states of uncorrelated electrons), (b) $U/W = 0.5$, (c) $U/W = 1.2$ and (d) $U/W = 2$, where $W$ is the band width (figure adapted from [16]). For large $U$ broadened (due to electron hopping) atomic like excitations appear at $(E_F \pm U/2)$ (lower and upper Hubbard subbands) with simultaneous narrowing of the quasi-particle peak near $E_F$. The metal-insulator transitions occurs for sufficiently strong Coulomb interaction (when $U$ is of the order of the band width) causing the quasi-particle peak to vanish.

Typical values for tiny systems like the dimer Fe$_2$ are rather insecure, we would expect, on the basis of Hund’s rules, magnetic moments being close to the corresponding value in the atomic limit, which is 4 $\mu_B$ per atom.

Without going into too much detail, we briefly summarize the ab initio results obtained so far for small Fe$_n$ clusters without and with local Coulomb correlations. Sophisticated quantum chemical calculations for the Fe dimer reveal the possibility of different ground states lying close in energy [27, 28]. However, the results are not converged with respect to basis set size and treatment of correlation, so a precise statement cannot be made. We have repeated calculations for the dimer and find similar trends for states of different symmetry lying close in energy. Including local Coulomb interactions of moderate strength allows indeed to reproduce magnetic moments corresponding to the atomic limit value.

For larger Fe$_n$ clusters, in the absence of local Coulomb interactions, we observe a subtle competition between the structural arrangement of the iron atoms in the cluster.
Figure 3: Rhombohedral crystal structure of hematite, in which the iron atoms form two-dimensional sheets. Each of the iron atoms is surrounded by six oxygen atoms (distorted FeO₆ cages). The unit cell shown in the right panel contains 4 Fe and 6 O atoms (figure adapted from [21]).

Figure 4: Calculated nonmagnetic (NM), antiferromagnetic (AF) and ferromagnetic (FM) states of hematite in the absence of additional local Coulomb correlations. The tangent shows that the system can undergo a magnetic phase transition from the AF ground state to the FM state under an external pressure of about 14 GPa (figure adapted from [21]).

(Jahn-Teller distortions) and resulting magnetic moments. Figure 6 shows results for the corresponding level sequence in the two spin channels for the case of a symmetric and Jahn-Teller distorted Fe₅ cluster.

The interesting effect if local Coulomb interactions are switched on is that the distortions of the transition metal clusters investigated so far are reduced, because the artificial energetic degeneracies can now be lifted by the Coulomb repulsion. In addition we obtain
Figure 5: Tetragonal distortion as a function of pressure for pure GGA and GGA + U with $U = 2$ and $4$ eV (figure adapted from [24]).

Figure 6: Gaussian broadened level sequence of the Fe$_5$ cluster for the two spin channels [29]. The symmetric bi-pyramidal structure leads to an energetic degeneracy in the spin-up and spin-down channels which can be partially lifted when allowing for a Jahn-Teller distortion.

values for the magnetic moments which we expect on the basis of Hund’s rules.

5. Conclusions

In the present work the effect of local Coulomb correlations has been discussed on the basis of different implementations of DFT. Our own calculations were performed with VASP, which allows highly efficient and accurate calculations of transition metal and
oxide compounds as well as a serious discussion of correlation effects in metallic clusters. The results for the clusters show that DFT GGA + U calculations are of comparable accuracy when comparing with corresponding results obtained by sophisticated and time consuming quantum chemical calculations. In summary, this paper shows that in systems like transition metal oxides and clusters of transition metals local Coulomb interactions and resulting correlation effects cannot be neglected.

References


[29] G. Rollmann et al., to be published.