A DFT+nonhomogeneous DMFT approach for finite systems

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Abstract

For reliable and efficient inclusion of electron–electron correlation effects in nanosystems we formulate a combined density functional theory/nonhomogeneous dynamical mean-field theory (DFT+DMFT) approach which employs an approximate iterated perturbation theory impurity solver. We further apply the method to examine the size-dependent magnetic properties of iron nanoparticles containing 11–100 atoms. We show that for the majority of clusters the DFT+DMFT solution is in very good agreement with experimental data, much better compared to the DFT and DFT+U results. In particular, it reproduces the oscillations in magnetic moment with size as observed experimentally. We thus demonstrate that the DFT+DMFT approach can be used for accurate and realistic description of nanosystems containing about hundred atoms.

Keywords: magnetism, strong electron correlations, nanostructures

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(Some figures may appear in colour only in the online journal)

1. Introduction

Magnetic nanoparticles are promising ingredients for several modern and future technologies. For example, nanoparticles with controllable magnetic moment may be used as contrast agents in magnetic-resonance imaging techniques and in cancer therapy by hyperthermia \[1\]. Furthermore, magnetic particles with high anisotropic energy are needed for energy-harvesting technologies \[2\] as well as for ultra-high-density recording media \[3\]. In most cases, these promising new applications call for a microscopic understanding of magnetic and other characteristics of nanoparticles. Not surprisingly, electron–electron correlations are expected to play a role in determining the magnetic properties of nanoparticles \[4\]. It is thus important to extend to nanoparticles theoretical and computational techniques that take such correlations into account.

In theoretical examination of systems in which electron correlations have to be included beyond that in density functional theory (DFT), often the DFT+U method, where U the on-site Coulomb repulsion term, is employed \[5,6\]. However, this method, based on the static mean field approximation, has its limitations. In particular, for bulk systems it is limited to describing only long-range spin and orbital order and hence fails for paramagnetic insulators \[7\]. It may fail even for cases in which correlations are not strong, as in bulk transition metals. Furthermore, it may lead to wrong prediction of spin-ordering temperatures (see \[8\], and references therein). Another shortcoming is the neglect of time-resolved local interactions. The last point suggests dynamical mean-field theory (DMFT) as an alternative approach. An important step in the analysis of the correlation effects in real materials was thus taken when DMFT was incorporated into DFT \[9,10\]. This combined method has been successfully applied to study the spectral, optical and magnetic properties of bulk systems \[7,8\].

Following Florens’ suggestion of the suitability of DMFT for nanosystems \[11\], several groups applied it to model systems containing a few to several hundred atoms \[12–17\]. The concept of local correlations which works well for extended systems was thus shown to be applicable also at the nanoscale. Most relevant for our purposes are the relatively few studies directed towards realistic description of the properties of nanoparticles \[13,18–20\]. For example, using DFT+DMFT
Boukhvalov et al [20] were able to reproduce the energy gap in the Mn$_4$ molecular magnet correctly. Our recently proposed DFT+DMFT approach, in which we used a quantum Monte Carlo (QMC) based solver for the Anderson impurity problem proved to be appropriate for examining the magnetic properties of small (2–5 atom) iron and iron-platinum clusters [18, 19]. However there are technical issues with the application of the QMC solver to low temperatures and to systems containing more than a few atoms. Note that although Valli et al [12] and Lin et al [14] applied DFT+DMFT to systems containing 110 and 50 atoms, respectively, the description was limited to a single atomic orbital, which may not be adequate for describing properties of realistic systems. Since the interest in nanoscience is in accurate description of systems containing tens to hundreds and thousands of atoms, the development of a DFT+DMFT methodology for the purpose is highly desirable.

Here we propose a formalism which allows one to introduce an approximate nano-DMFT, generalized IPT solution for the impurity problem. It is already known that IPT, which is a second order perturbative approximation in U, succeeds in capturing many important effects in bulk correlated systems, including zero-energy quasiparticle resonance and the upper and lower incoherent Hubbard bands in the electron spectral function [8]. While it is faster than most other solvers, it also gives results in good agreement with the more accurate QMC and exact diagonalization solutions, both at and away from half filling [8].

We apply this formalism to Fe nanoparticles containing 11–100 atom. The good agreement of our results with the experimental data [21, 22] on the trends in the variation of the magnetic moment with nanoparticle size attests to the reliability of the DFT+DMFT approach. The stage is now set for further application of this approach.

2. Method

Usually, the effects of strong electron-electron correlations are studied by solving a model described by the Hubbard Hamiltonian:

\[ H = - \sum_{i,j,l,m} t_{i,j} c_{i,l}^\dagger c_{j,m} + \sum_{i,j,l,m} U_{i,j,l,m} n_{i,l} n_{j,m}, \]

where \( c_{i,l}^\dagger \) and \( c_{i,l} \) are the creation and annihilation operators of electron at site \( i \) with spin \( \sigma \) and other quantum number (orbital energy level, orbital momentum etc) \( l \); \( c_{i,l}^\dagger c_{i,l} = n_{i,l} \) is the particle number operator for state \( \sigma, l \) at site \( i \). The kinetic energy and the potential energy (short-range Coulomb repulsion) are defined by the hopping term \( t_{i,j} \) and the Coulomb repulsion matrices \( U_{i,j,l,m} \), respectively. The diagonal elements \( t_{i,l} \) define the energy of orbital \( l \) at site \( i \). The hopping parameters are obtained from the DFT(DFT+U)-optimized (relaxed) structures. The Coulomb repulsion energy is often chosen in the local approximation, \( U_{i,j,l,m} = \delta_{l,l} \delta_{\sigma,\sigma} \delta_{l,m} U \), as usually it is the dominant term in the interaction part of the Hamiltonian in equation (1). The values for \( U \) (\( l \) in this context being the orbital quantum number: s, p, d ...) are chosen as fitting parameters, though one can in principle obtain them from DFT calculations (see, e.g. [7]). It is important to mention that unsupported few-atom clusters may, in general, experience mechanical rotation, which may lead to spin-mechanical orbital interaction. Since such effects are beyond the scope of this work, we do not include the corresponding term in the Hamiltonian.

As is well known, a range of physical properties of systems described by the Hamiltonian in equation (1) can be obtained from the time-ordered Green’s function (GF) \( G_{i,o;l,j;m}(t,t') = -i \langle \tau \psi_{i,l}(t)c_{o,j;m}(t') \rangle \). In particular, the site- and the orbital-spin densities that define the magnetic properties of the system can be found from the following expression: \( n_{i,o,l} = -\int \frac{\text{d}\omega}{2\pi} \text{Im} G_{i,o,l}(\omega) \). Furthermore, (the inverse) time-ordered GF is connected to the single-particle self-energy \( \Sigma_{i,o;l,j;m}(t,t') \) via the Dyson equation (in frequency representation):

\[ G^{-1}_{i,o;l,j;m}(\omega) = \delta_{\sigma,\sigma'} \delta_{l,l'} \delta_{\omega} - \delta_{\sigma,\sigma'} \Gamma_{i,l} - \Sigma_{i,o;l,j;m}(\omega). \]  

Therefore, in order to obtain GF one needs to find the electron self-energy.

In DMFT for finite sized systems we assume that the electronic self-energy is local in site and quantum indices, but depends on their value: \( \Sigma_{i,o;l,j;m}(\omega) = \delta_{\sigma,\sigma'} \delta_{l,l'} \delta_{\omega} \Sigma_{i,o;l,j;m}(\omega) \). This approximation was proposed by Nolting and Potthoff in the generalization of DMFT for non-homogeneous extended systems [24, 25]. In extending this approach to finite systems (N sites, M orbitals), one needs to find the GF matrix of size \( 2 \times N \times M \) (2 stands for the number of spin degrees). As for extended systems, the problem can be mapped onto that of a single-impurity. Namely, in DMFT the many-site problem is reduced to one-site \( 2 \times N \times M \) independent problems in the nonhomogeneous case) described by one- orbital Hubbard Hamiltonian for an electron in the presence of a dynamical (time or frequency dependent) mean-field \( \Sigma_{i,o;l,j;m}(\omega) \). This effective (bath) field describes the effect of the rest of the electrons in the nanostructure on the electron at site \( i \) in orbital \( l \). This single-site (impurity) mapping means that the local GF \( G_{i,o;l,j;m}(\omega) \) and the local self-energy \( \Sigma_{i,o;l,j;m}(\omega) \) of the nanostructure are equal to the corresponding GF and the self-energy of the impurity. Provided \( \Sigma_{i,o;l,j;m}(\omega) \) is known, one can find the impurity GF from:

\[ G_{i,o;l,j;m}(\omega) = \int D[\psi] D[\psi^*] \psi_{i,l}^* \psi_{o,m} \exp \left( -\int_0^\beta \text{d}\tau \right) \times \int_0^\beta \text{d}\tau \int_0^\beta \text{d}\tau \psi_{i,l}(\tau) G_{i,o;l,j;m}^{-1}(\tau - \tau') \psi_{o,m}(\tau') + U_{i,l} \int_0^\beta \text{d}\tau n_{i,l}(\tau) n_{i,l}(\tau) \]

(3)
the solution is the impurity equation (3). While in principle, as for extended systems, the exact numerical solutions of this equation can be obtained (by using QMC [26] or continuous-time QMC [27] solvers), for multiple impurity problems it is much less computationally-demanding to solve the problem by using the generalized IPT approximation. [8] developed for extended systems:

\[ \Sigma_{\ell,\alpha}(\omega) = U n_{\ell\alpha} + \frac{A_{\ell\alpha} \Sigma^{(2)}_{\ell,\alpha}(\omega)}{1 - B_{\ell\alpha} \Sigma^{(2)}_{\ell,\alpha}(\omega)} \]  

(5)

where \( n_{\ell\alpha} \) is the mean-field on-site orbital occupation (of the HOMO, LUMO and other atomic orbital states) and \( \Sigma^{(2)}_{\ell,\alpha}(\omega) \) is the second-order self energy: \( \Sigma^{(2)}_{\ell,\alpha}(\omega) = -U^2 \int_0^\infty \mathrm{d}\tau G_{\ell,\alpha}(\tau) G_{\ell,\alpha}(\tau) G_{\ell,\alpha}(-\tau) \) in the Matsubara frequency representation (below we use orbital-independent parameter \( U \)). One may easily obtain the corresponding expression in the real frequency domain by applying analytical continuation. The coefficients \( A \) and \( B \) are chosen to be: \( A_{\ell\alpha} = n_{\ell\alpha}(1-n_{\ell\alpha})/|n_{\ell\alpha}(1-n_{\ell\alpha})| \), \( B_{\ell\alpha} = (1-2n_{\ell\alpha})/|n_{\ell\alpha}(1-n_{\ell\alpha})| \), where \( n_{\ell\alpha} = -(1/\pi) \int \mathrm{d}\omega \Im G_{\ell,\alpha}(\omega) \). The choice of \( A \) leads to the correct high-frequency behavior of the self-energy, while that of \( B \) leads to the correct atomic limit of this quantity. Generally speaking, for extended systems IPT is regarded as a valid approximation for small and largevalues of \( U \) (including correct atomic limit). For intermediate values of \( U \), IPT may still be valid as it reproduces important features, such as the central quasiparticle peak and the Hubbard bands in the density of states of extended systems [26] in agreement with more accurate solutions. (For validation of the IPT approximation for systems with reduced size/dimensionality and for the extension of the IPT approximation on the case of multi-orbitals with non-local interactions, see, e.g. [28–30].)

3. Application to Fe nanoparticles

The initial geometry for the Fe19–Fe100 clusters was chosen from Cambridge Cluster Database [31], for which the global minimum (relaxed structure) was obtained using Finnis–Sinclair pair-potential [32] with initial bulk inter-atomic distances. To obtain smaller clusters we proceeded as follows. The initial structure for Fe17 cluster was obtained by removing two atoms from all possible surface sites of the relaxed (icosahedral) Fe19 cluster. Similarly, the structures Fe15–Fe11 were obtained by consequently removing atoms and relaxing the structures beginning from the relaxed Fe17 configuration. The ionic positions in the clusters were further relaxed using the conjugate gradient method and spin-polarized DFT as implemented in the Quantum Espresso code [33]. For the exchange and correlation potential the generalized gradient approximation (GGA) as parameterized by Perdew–Burke–Ernzerhof (PBE) [34] was used; ultra-soft pseudo-potentials were used for all atoms under consideration, the cut-off energy for the plane-wave expansion was 30 Ry. No symmetry constraints were imposed on the structural geometry of clusters during structural relaxation. The structures were relaxed until the atomic forces converged to less than 0.01 eV Å⁻¹. We used a cubic simulation box for the relaxation of isolated freestanding clusters, with at least 12 Å distance between the cluster and its periodic images in all three directions. The resulting relaxed geometries of the clusters are presented in figure 1.

Clearly, the atoms on the surface have much higher magnetization than the ones inside the cluster (figure 1) and that the magnetization of the surface atoms increases with decreasing cluster size. This can be explained by the fact that atoms inside the cluster are highly coordinated, accordingly hybridized and leaning towards itinerant-type ferromagnetism as in the bulk. In one case (Fe55), we find that some core atoms are anti-ferromagnetically coupled with the neighboring atoms (shown in pink). The bondlength distribution of the relaxed clusters are presented in figure 1 of the supplementary information (stacks.iop.org/JPCM/27/125601/mmedia),

The hopping parameters \( t \) for the \( s- \) and \( d- \) valence electrons of the structures presented in figure 1 were obtained using the Slater–Koster matrix approximation [35] (for details see [18, 19]). With \( t \) in hand (along with our already-chosen range of values for \( U \), we turn to DMFT using our nano-DMFT code (particulars described above). One virtue of the code is that it works for several hundreds atoms with modest computational resources.

Comparison of the results for the magnetic moment per atom obtained using the three theoretical approaches with the experimental data, in figure 2 (and in table 1 of the supplementary information (stacks.iop.org/JPCM/27/125601/mmedia)), leads to several conclusions. The first is that DFT+DMFT gives overall the best agreement with experimental data. The second is that only DFT+DMFT displays the peak in the magnetization observed in experiments for Fe14. Although the numerical value of the magnetic moment (~3.3 \( \mu_B \)) obtained by DFT and DFT+U for this cluster is in better agreement with the experimental result (~3.4 \( \mu_B \)), these two techniques find Fe13 to have higher magnetic moment (~3.4 \( \mu_B \)) than Fe14, in disagreement with experiments (~2.55 \( \mu_B \)). For Fe15 also
both DFT and DFT+U overestimate the magnetization, while DFT+DMFT gives good agreement with experimental data. Another large oscillation in the magnetization is seen in experiments for Fe_{14} and Fe_{55}. Here again DFT+DMFT fares better than DFT and also DFT+U. DFT predicts the magnetization to be larger for Fe_{14}, while DFT+U finds a smaller change (increase) in magnetization between Fe_{14} and Fe_{55}, as compared to experiments or DFT+DMFT. For the larger clusters (>55 atoms) both DFT+DMFT and DFT+U give similar results. In short, DFT+DMFT gives in general better agreement with experiments, particularly in depicting the trends in the variation of the magnetic moment with size. While DFT results deviate the most from the experimental values, DFT+U tends to overestimate the magnetic moments for small clusters. For the Fe_{11} and Fe_{12} clusters none of the approaches reproduces the high value extracted from the experiments, though the DFT+DMFT reproduces a local magnetization peak for Fe_{12}.

To get a deeper understanding of the oscillation of magnetization, in particular the peaks at \(N = 14\) and 55, we compared the DFT, DFT+U and DFT+DMFT spectral functions for all clusters (figures 3–9 in the supplementary information (stacks.iop.org/JPCM/27/125601/mmedia)). For spin-up electrons, we find the DFT+U spectral functions to be essentially the DFT functions shifted to lower energies, while the spin-down curves are not significantly affected by the U-correction. Since the spin-up orbitals are typically fully occupied, the change in the spin-down density of states is essentially responsible for any change of magnetization. Note that these conclusions are mainly valid for the d-orbitals, as the s-orbitals are not significantly affected by the U-correction because of their large kinetic energy. On the other hand, we find that the dynamical fluctuations associated with the DFT+DMFT results have a tendency to soften the DFT+U density of states, in a way that recovers the DFT shape. The above mentioned DMFT reduction of the clusters magnetization may indicate that the orbital position (through static shift of energy levels resulting from the self-energy correction) and/or their occupancy (due to the frequency-dependence of the self-energy) may change dramatically when dynamical effects are taken into account. Moreover, in DMFT one expects the presence of new orbitals (due to the frequency-dependence of the self-energy), as found in the DOS plotted in figure 3 for Fe_{14} with the different approaches. What is also important to note is that for both 14- and 55-atom clusters, the DFT+DMFT density of states (see figure 8 in the supplementary information (stacks.iop.org/JPCM/27/125601/mmedia)) for Fe_{55} for the spin-down electrons is strongly localized around the zero-level for all orbitals, as distinct from that for the other clusters. This sort of “universal-localization” of DOS is responsible for the large magnetization for these clusters. We attribute this effect to some sort of smearing, when d-orbitals become magnetically equivalent perhaps as a result of high cluster symmetry. Indeed, the DFT and DFT+U peaks in magnetization in the 55-atom case are often ascribed to symmetry effects.

Regarding some general trends in magnetization obtained with the with different approximation, one can distinguish three regimes. (1) Small clusters (11–19 atoms), for which DFT and DFT+U produce pretty similar magnetization, which is larger than that resulting from DFT+DMFT. The similarity of DFT and DFT+U results may be explained by large spin-up (fully occupied) and spin-down peak separations, due to small cluster size. (2) Large clusters (55–100 atoms), in which DFT+U and DFT+DMFT results are rather similar and in general are close to the experimental values. Similarity of these two results may be attributed to strong correlation effects in these clusters (due to larger average bondlength than that found for the smaller clusters, as shown in the supplementary information (stacks.iop.org/JPCM/27/125601/mmedia).). This suggests...
that fluctuation effects are less dramatic for this particular size of particles. (3) The ‘intermediate size’ particles (27–45 atoms), for which the three approximations give different results. Since DMFT results are more successful in reproducing the experimental magnetization for the clusters, it appears that the delicate balance of local repulsion and hopping processes taken into account by DMFT is important for obtaining the local peaks of magnetization as a function of cluster size. It must also be stressed that simple pictures of the Heisenberg exchange and itinerant-(Stoner-) like ferromagnetism in the clusters (based on the relation between the magnetization and the bondlength and number of nearest neighbor distributions) have limited application when understanding the size dependence of nanoparticle magnetization, as discussed in section 1 of the supplementary information (stacks.iop.org/JPCM/27/125601/mmedia) and that the DFT+DMFT approach seems to be able to capture the complexity in the size dependent variation of magnetism in these structures.

Finally, it is important to stress that further experimental work to clarify the geometry of the clusters considered in this work needs to be done. From the theoretical side, to test the dependence of our results on cluster geometry, we have performed DFT+U and DFT+DMFT calculations for Fe<sub>11</sub>–Fe<sub>19</sub> structures obtained from several different initial configurations (details in the supplementary information, figure 3 (stacks.iop.org/JPCM/27/125601/mmedia)). The trend for the magnetization is the same: DFT+DMFT improves the results as compared to DFT+U in all cases, except for Fe<sub>11</sub> and Fe<sub>12</sub> clusters for which none of the approaches reproduces the high values extracted from experimental data.

4. Conclusions

We have formulated a DFT+nonhomogenous DMFT approach using the generalized IPT impurity solver to study the physical properties of finite nanosized systems with strong electron–electron correlations. Application of the approach to examine the magnetic moment of 11–100 atom Fe clusters shows that in most cases the inclusion of dynamical correlations results in overall better agreement with experiment [21, 22]. This is to our knowledge the first demonstration that DFT+DMFT applied to experimentally realizable nanoparticles can produce accurate results. The methodology should have multiple applications as it can be readily applied to systems containing up to several hundred atoms. The computational speed of the developed code is such that the total computational time of the DFT+DMFT calculations is of the same order of magnitude as the corresponding time for the DFT calculations.

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