Dynamical Mean Field Theory for Diatomic Molecules and the Exact Double Counting

Juho Lee and Kristjan Haule
Department of Physics & Astronomy, Rutgers University, Piscataway, NJ 08854-8019, USA
(Dated: March 12, 2014)

The Dynamical Mean Field Theory (DMFT) in combination with the Local Density Approximation (LDA) is widely used in solids to predict properties of correlated systems. Here we use the simplest strongly correlated system, the H$_2$ molecule, to test its applicability to quantum chemistry problems. We show that the total energy accuracy of LDA+DMFT in its single site version is around 0.2% around equilibrium distance, provided a good projector to correlated subspace, and the exact double-counting is used. We introduce the exact intersection of the two methods, which leads to highly accurate subtraction of the correlations counted in both methods. We propose the extension of the exact double-counting to solid state applications.

I. INTRODUCTION

Quantum mechanics has long sought deeper insight into correlation effects because they lie at the heart of understanding atomic, molecular and solid state electronic structure. Very useful methods which approximate correlation effects were devised during the past decades including Density Functional Theory (DFT) [1, 2], GW [3], Density Matrix Renormalization Group (DMRG) [4] and recently Dynamical Mean Field Theory (DMFT) [5, 6] and its cluster extensions [7, 8]. The beauty of DFT is that its formalism is exact yet efficient, with one determinant describing the electron density. All of the complexity is hidden in one term, the exchange-correlation functional. Practical implementations of DFT heavily rely on approximate functionals which are local or semi-local in real space $r$, such as local density approximations (LDA) and generalized gradient approximation (GGA). In situations with large number of near-degenerate many body states, methods that implement only static correlations have extreme difficulty in handling these degeneracies, and hence fail to address the regime of strong correlations and the Mott transition. DMFT method brought about a revolution in the theory of strong correlations, because its exact treatment of local dynamic correlations successfully described the Mott transition in lattice models, such as the Hubbard model [9]. Since the method is very flexible and versatile, and scales linearly with the system size, it was quickly adapted for many problems in the solid state, including electronic structure calculations in solids. The most commonly used DMFT approximation in solid state is combination of LDA and DMFT (LDA+DMFT) [10], where some selected correlated orbitals are treated by DMFT while the rest of the electronic states are treated by LDA. The LDA+DMFT method was very successful in a large number of problems involving strong electronic correlations in solids and very recently it has been also applied to molecules [11, 12] and nano-systems [13, 14]. However, the combination of the two methods in solid state problems has a few ambiguities, which limits the precision of the method: i) the DMFT method needs the partially screened Coulomb interaction, which is hard to satisfactory predict from first principles, ii) the part of the correlations included in both LDA and DMFT – called double-counting – is not known exactly, and a phenomenological form [15] is most often used (for discussion see [16] and [17]).

The study of correlations in small molecules can be a testbed for the quality of electronic structure methods, because numerically exact results exist. For DMFT method, this has a particularly strong appeal because the screening of the Coulomb repulsion can be ignored, and hence the ambiguities due to screening, present in solid state, can be decoupled from the issues concerning the construction of the functional and its precision. The simplest case of H$_2$ molecule, which shows very strong correlations at large nuclear separation, was not yet used to test quality of DMFT or LDA+DMFT.

Here we use a complete basis set, which is the exact solution of H$_2^+$ molecule, to address the quality of the Dynamical Mean Field method in describing correlations in H$_2$ molecule. We propose a double-counting functional for LDA+DMFT, which is an exact intersection of the two methods, and results in highly precise electronic structure method with no ambiguity in subtracting double-counted correlation effect. We propose the extension of this double-counting functional to the solid state calculations, where additional complexity of screening will need to be addressed for the new functional to become useful.

To construct appropriate complete basis set, we solve exactly the single electron problem of H$_2^+$ by following the methodology of Ref. 18. We denote the ground state and the first excited state by $|\sigma_U\rangle$ and $|\sigma_M\rangle$, respectively. The complete set of H$_2^+$ states is enumerated by $|m\rangle$. We typically keep between 20-30 states to converge the results. In this basis, we then evaluate matrix elements of the Coulomb interaction, as explained in the Supplementary material. The DMFT is basis set dependent approximation, and its quality crucially depends on the choice of the projector [19-24], which maps the continuous problem to a discrete set of sites (lattice), each consisting of only a few important degrees of freedom (orbitals). Here we restrict our discussion to the simplest
possible DMFT approximation, treating only a single hydrogen atom by impurity solver, which contains only one correlated orbital. This choice leads to the one-band impurity problem, which is solved to very high precision by the continuous time quantum Monte Carlo method [25], as implemented in Ref. 26.

Over 96% of the electronic charge of the DMFT solution is contained in the two lowest energy states \(|1\sigma_u\rangle\) and \(|1\sigma_d\rangle\) of \(H^2_+\) problem, hence a natural choice of the DMFT projector is the linear combination of these two states, which we define as the “left” (L) and the “right” (R) localized orbital

\[
|\chi_L\rangle = \frac{1}{\sqrt{2}}(|1\sigma_u\rangle - |1\sigma_d\rangle),
\]

\[
|\chi_R\rangle = \frac{1}{\sqrt{2}}(|1\sigma_u\rangle + |1\sigma_d\rangle).
\]

We define the DMFT local Green’s function for left atom by the following projection \(g^{L}_{local}(\omega) \equiv \hat{P}_L G = |\chi_L\rangle \langle \chi_L| G(r',\omega) |\chi_L\rangle \langle \chi_L|\) and similarly for the right atom. The impurity self-energy is embedded into real space by the inverse of the projection, i.e., \(\Sigma(r,\omega) = |\chi_L\rangle \Sigma^{L}(\omega) \langle \chi_L| + |\chi_L\rangle \Sigma^{R}(\omega) \langle \chi_R|\). Due to the symmetry of the problem, \(\Sigma^L = \Sigma^R\) and \(G^L = G^R\), the two impurity problems, describing the left and the right H atom, are equivalent and only a single impurity problem needs to be solved.

We mention in passing that alternative definition of projector, which selects as the correlated orbital 1s state of the hydrogen atom, leads to results of much worse quality than presented here, because such choice does not capture the majority of the active degrees of freedom at equilibrium internuclear separation. Consequently, more time consuming cluster-DMFT method needs to be used to get similar quality results, as recently found in Ref. 11.

To define DMFT approximation, we resort to the Baym-Kadanoff formalism [27, 28], which defines a functional of the exact Green’s function by (see also [10])

\[
\Gamma[G] = \text{Tr} \log(G) - \text{Tr}((G^0_1^{-1} G^{-1}) G) + \Phi[G]. \tag{2}
\]

Here \(G_0(r, r'; i\omega) = [(i\omega + \mu + \nabla^2 - V_{\text{ext}}(r))\delta(r - r')]^{-1}\), and \(V_{\text{ext}}\) is the potential created by the two nucleons. When Luttinger functional \(\Phi[G]\) is the sum of all skeleton Feynman diagrams constructed by \(G\) and Coulomb interaction \(U_C\), the extremum of the functional gives the exact Green’s function \(G\), and \(\Gamma\) gives the exact free energy of the system.

The Hartree-Fock approximation can be defined by approximating \(\Phi[G]\) by \(\Phi^H[p] + \Phi^X[p]\), where \(\Phi^H[p] = \frac{1}{2} \int dr' \rho(r) U_C(r - r') \rho(r')\) and \(\Phi^X[p] = \frac{1}{2} \sum \int dr' \rho^2(r, r') U_C(r - r') \rho^2(r', r)\). Here \(U_C\) is the Coulomb repulsion, and \(\rho(r) = \rho(r, r)\) is the electronic density.

In the LDA approximation, \(\Phi[G]\) is approximated by the sum of the Hartree \(\Phi^H[p]\), local exchange \(\Phi^{\text{LDA},X}[\rho]\), and local correlation \(\Phi^{\text{LDA},C}[\rho]\)

\[
\Phi^{\text{LDA},X}[\rho] = \int \rho(r) \varepsilon_x(\rho(r))\text{ and local correlation } \Phi^{\text{LDA},C}[\rho] = \int \rho(r) \varepsilon_c(\rho(r))\text{ functional, where } \varepsilon_x(\rho) = -\frac{3}{4} \frac{\varepsilon}{\rho}\text{, and we used Vosko and Wilk parametrization of } \varepsilon_c(\rho)\text{ [29].}
\]

The Dynamical Mean Field Theory approximates the exact Luttinger functional \(\Phi[G]\) by its local counterpart \(\Phi_{\text{DMFT}} = \sum_i \Phi_{\text{local}}[\rho_i]\) [10], which contains all skeleton Feynman diagrams constructed from local Green’s function \(\Phi_{\text{local}}\) centered on atom (or cluster) \(i\), and Coulomb repulsion \(U_C\). Notice that only the local Coulomb repulsion \(U_{\text{local}}(\chi_i \chi_i^\dagger U_C(r - r') \chi_{\text{local}}(r) \chi_{\text{local}}(r')\) enters the functional. Notice also that the exact Luttinger functional \(\Phi\) and the DMFT functional \(\Phi_{\text{DMFT}}\) have exactly the same form (can be expanded in exactly the same set of Feynman diagrams), the only difference is that \(\Phi\) is a functional of total \(G\), while \(\Phi_{\text{DMFT}}\) is a functional of projected \(\Phi_{\text{local}}\). The Luttinger functional \(\Phi_{\text{DMFT}}\) is evaluated by solving an auxiliary quantum impurity problem.

The flexibility of the DMFT approximation allows one to treat exactly some parts of the functional, such as the Hartree term. We first choose to treat exactly the Hartree-Fock part, while the correlation part is treated by DMFT. This approximation is denoted by HF+DMFT, i.e., \(\Phi_{\text{HF+DMFT}} = \Phi_H[p] + \Phi_X[p] + \sum \Phi_{\text{DMFT}}[\rho_{\text{local}}] - \sum \Phi_{\text{DC}[\rho_{\text{local}}]}\). Since local part of the Hartree and exchange term is present also in DMFT, we have to subtract terms counted twice \(\Phi_{\text{DC}[\rho_{\text{local}}]} = \Phi_H[p_{\text{local}}^i] + \Phi_X[p_{\text{local}}^i]\), where \(p_{\text{local}}^i = \langle \chi_i | (\chi_i^\dagger \rho | \chi_i) | (\chi_i^\dagger \rho | \chi_i)\rangle\).

Finally, we define the combination of LDA+DMFT, in which the DMFT dynamic correlations truncated to small subset of important degrees of freedom, and LDA static correlations complement each other. The functional is \(\Phi_{\text{LDA+DMFT}} = \Phi_H[p] + \Phi_X[p] + \Phi^{\text{LDA},X}[\rho] + \sum \Phi_{\text{DMFT}}[\rho_{\text{local}}] - \sum \Phi_{\text{DC}[\rho_{\text{local}}]}\). The terms which are double-counted are contained in \(\Phi_{\text{DC}[\rho_{\text{local}}]} = \Phi_H[p_{\text{local}}^i] + \Phi_X[p_{\text{local}}^i] + \Phi^{\text{LDA},X}[\rho_{\text{local}}^i] + \Phi^{\text{LDA},C}[\rho_{\text{local}}^i]\), where \(\Phi_H\) and \(\Phi_X\) are the defined above, and the double-counted correlations are

\[
\Phi^{\text{LDA},C}[\rho_{\text{local}}] = \int \varepsilon_c(\rho_{\text{local}}(r)) \rho_{\text{local}}^2(r). \tag{3}
\]

This is the exact intersection between LDA and DMFT approximation, since it parallels the derivation of the DMFT approximation starting from the exact functional. It is hence a "DMFT"-like approximation to the LDA correlation functional. Namely, the replacement of the total \(G\) by its local counterpart \(G_{\text{local}}\) in the exact functional leads to the DMFT approximation, hence replacing total \(\rho\) by \(\rho_{\text{local}}\) in LDA functional gives the intersection of the two methods.

Although LDA+DMFT is very often used in solid-state electronic structure calculations, such exact double-counting term was not proposed before. This is because in the solids, there is additional complexity of screening, whereby the core, semicore and other states eliminated from the DMFT model screen the Coulomb interaction of
the equilibrium distance is overestimated by LDA ($R \approx 1.46$) and the total energy at equilibrium is similar to its Hartree-Fock value. We also include in the plot the results of the self-consistent GW calculation from Ref. 30, which give quite accurate equilibrium distance, but the energy at equilibrium is substantially too low, and the dissociation energy is severely overestimated, similarly to LDA.

At large internuclear separation, the static correlations are not adequate because of the near-degeneracy of many body states, which can not be well described by electron density alone. The DMFT uses the dynamical concept of the Green’s function and captures correctly the atomic limit, hence dissociation energy is exact. This is because at large internuclear distance the impurity hybridization function, which describes the hoping between the two ions, vanishes, and consequently the impurity solver recovers the exact atomic limit. The inclusion of dynamic correlations by DMFT (HF+DMFT) also substantially improves the total energy for all distances, including at equilibrium, and the error of the total energy is below 1% for almost all distance, except around $R \approx 3.6$, where error increases to 2%. This transition region close to dissociation is notoriously difficult, because correlations beyond single site have significant contribution, and only the two site cluster DMFT calculation avoids this error [11]. The predicted equilibrium distance is slightly overestimated ($R \approx 1.44$).

Finally, the combination of LDA and DMFT gives surprisingly precise total energies. Except around the transition to dissociation ($R \approx 3.6$), it predicts total energy within 0.2% of the exact result, and essentially exact equilibrium distance. Such success of LDA+DMFT is quite unexpected, and shows that LDA and DMFT capture complementary parts of correlations. While DMFT includes all dynamic correlations local to a single H-ion, it neglects Coulomb repulsion between electrons that are located at different ions, and poorly described the correlations in the regions close to the midpoint, where $\rho_{l}^{\text{local}}(r)$ and $\rho_{l}^{\text{local}}(r)$ are comparable in size. In this case, DMFT correlations are approximated by a linear sum of two independent terms, the left and right correlations, which misses the essential non-linearity of the electronic correlations. This situation is very common in solid state calculations, where only charge from the most localized orbitals (such as $d$ or $f$) is treated by DMFT, while majority of the electronic charge is described only by the LDA correlations. On the other hand, LDA adds correlations due to all electronic charge, but in a static and purely local approximation. The two methods are clearly complementary, and when correctly combined, lead to extremely precise total energy.

To gain deeper insight into correlation energy in the two methods, we plot in Fig. 2 the correlated part of the LDA and LDA+DMFT potential energy versus ion separation. The LDA correlation energy slightly decreases with increasing distance [92], in contrast to physical expectations. On the other hand, the LDA+DMFT poten-
The double-counting potential within LDA+DMFT, which is defined by
\[ \Phi_{LDA+DMFT} = \chi_{LDA+DMFT}^\dagger \sum_i \rho_{local,i} \chi_{LDA+DMFT,i} + \Phi_{DC}^{\text{local}} + \Phi_{\text{U}}^{\text{local}} \],
where \( \Phi_{DC}^{\text{local}} \) and \( \Phi_{\text{U}}^{\text{local}} \) are the local double-counting and Hartree-Fock contributions, respectively.

In the lower panel of Fig. 2, we show the double-counting potential within LDA+DMFT, which is defined by \( V_{DC} = \langle \chi_i | \delta \Phi_{DC} / \delta \rho_{local,i} | \chi_i \rangle \). The often used phenomenological form first introduce in the context of LDA+U [15] is also shown for comparison. The exact double-counting is somewhat smaller than the proposed phenomenological form, and its variation is almost entirely due to variation of local Coulomb repulsion \( U = \langle \chi_i \chi_i | U_C(r - r') | \chi_i \chi_i \rangle \), with proportionality constant \( V_{DC} = 0.412 U \). In the solid state calculations, the self-consistent form of the double-counting \( U(n-1/2) \) is also often found too large and is many times reduced (see discussion in Ref. 16).

The ionization energy (IE) is usually substantially underestimated by LDA, and the electron affinity (EA) requires precise description of highly excited states, which are not well described by static mean field theories, such as Hartree-Fock or LDA. The DMFT spectral functions contains information about the single-particle excitations, and hence we expect a sharp peaks at HOMO energy, and a resonance at the energy of \( H_2^+ \) molecule. In Fig. 3 we show the plot of the DMFT spectral function at equilibrium distance, analytically continued to the real axis by Pade approximation. With the vertical line we mark the exact IE and EA, as well as LDA+DMFT IE, which is obtained as the difference between the total energy of \( H_2^+ \) and \( H_2 \) molecules. Because the total energy...
