Fast Track Communication

Nonadiabatic time-dependent spin-density functional theory for strongly correlated systems

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Abstract

We propose a nonadiabatic time-dependent spin-density functional theory (TDSDFT) approach for studying single-electron excited states and the ultrafast response of systems with strong electron correlations. The correlation part of the nonadiabatic exchange–correlation (XC) kernel is constructed by using exact results for the Hubbard model of strongly correlated electrons. We demonstrate that the corresponding nonadiabatic XC kernel reproduces the main features of the spectrum of the Hubbard dimer and the 2D, 3D and infinite-dimensional Hubbard models, some of which are impossible to obtain within the adiabatic approach. The formalism may be applied for *ab initio* examination of strongly correlated electron systems in- and out-of-equilibrium within the TDSDFT, extending it beyond the metallic and semiconductor structures with plasmons, excitons and other excitations.

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

1. Introduction

Reliable description of the electronic properties of systems that contain localized d- and f-orbitals remains a challenging problem in condensed-matter physics for both extended and finite systems. Extended systems form a large class of materials with many exotic properties which in turn lead to many potential technological applications. Examples include cuprate high-temperature superconductors, heavy fermion materials and manganites. One may also expect unusual properties in the much less explored case of molecules and nanostructures, in which correlation effects may be even more enhanced owing to space confinement. Moreover, in nanotechnological applications, in which the distance between the atoms can be tuned (for example, by putting the atoms on a substrate), even s- and p-electron systems may find themselves in a strongly correlated regime when the interatomic separation is appropriately large. These nanoscale systems show many surprises, such as the recently observed unusual antiferromagnetic ordering in small Fe chains [1], and the metal–insulator transition in Au and Fe chains [2]. The excited states and the nonequilibrium properties of such systems, including their ultrafast (femto- and atto-second) response, are very relevant to the modern trend of designing ‘smaller and faster’ systems. Correct understanding of nanosystems and molecules with strong electron correlations may also shed light on the general properties of strongly correlated materials, including local correlations and nonhomogeneous order in extended systems.

Most of the progress in studies of correlated systems has been made by using many-body approaches. Two of the most powerful are the Bethe ansatz for 1D systems and dynamical mean-field theory (DMFT), which is exact in the limit of infinite dimensions [3] and appears to be also a good approximation for 2D and 3D systems (reviews of both approaches are given in [4, 5], respectively). These methods have also been generalized for the nonequilibrium case.
In this paper, we propose—on the basis of some exact results for the Hubbard model—a simple form of the nonadiabatic XC kernel, which results in the single-electron spectrum of the Hubbard model that reproduces the main features of the spectra of both finite (dimer) and extended (infinite-dimensional) systems. This kernel can be easily implemented within the standard TDDFT codes for use for strongly correlated systems.

2. The Hubbard dimer

In order to obtain the XC kernel $f_{\text{XC},\sigma}(r, r', \omega)$ for the Hubbard dimer, we map the eigenvalue equation (which defines the positions of the spectral peaks) derived from the dimer Green’s function onto the corresponding TDDFT Casida eigenenergy equation [29], which has the following general form:

$$\det \left[ \begin{array}{cc} \epsilon^2_0 + 2\epsilon_0 K_{\downarrow\uparrow}(\omega) - \omega^2 & 2\epsilon_0 K_{\downarrow\downarrow}(\omega) \\ 2\epsilon_0 K_{\uparrow\downarrow}(\omega) & \epsilon^2_0 + 2\epsilon_0 K_{\uparrow\uparrow}(\omega) - \omega^2 \end{array} \right] = 0,$$

(1)

where

$$K_{\sigma,\sigma'}(\omega) = \int \int \psi_\sigma^*(r) \psi_{\sigma'}(r) \times \left( \frac{1}{|r - r'|} + f_{\text{XC},\sigma,\sigma}(r, r', \omega) \right) \times \psi_\sigma^*(r') \psi_{\sigma'}(r') \, dr \, dr'$$

(2)

(the first part being the Hartree term, and $f_{\text{XC},\sigma,\sigma}(r, r', \omega)$ the Fourier transform of $\delta V_{\text{XC}}[n](r,t) / \delta n_{\sigma}(r',t)$ with respect to $t$-$t'$), $\epsilon_0 = \epsilon_u - \epsilon_g$ is the excitation energy of the free electron, and $\psi_{\sigma,\sigma'}(r)$ and $\psi_{\sigma,\sigma'}^*(r)$ are the corresponding bonding- and anti-bonding energies and wavefunctions. This equation has two solutions

$$\omega^2 = \epsilon_0 (\epsilon_0 + 2 (K_{\downarrow\uparrow} \pm K_{\uparrow\downarrow})).$$

(3)

where $+$ corresponds to the singlet state, and $-$ to the triplet one. Since the ground state of this system is a singlet and the total spin of the isolated system is conserved, for definiteness we shall focus on the singlet state.

The dimer Green’s function can be found from the exact solution for the Hubbard model with the Hamiltonian

$$H = -t \sum_{\langle i,j \rangle \sigma} c^\dagger_{i\sigma} c^\sigma_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow},$$

(4)

where $c^\dagger_{i\sigma}$ and $c^\sigma_{i\sigma}$ are the creation and annihilation operators of the electron with spin $\sigma$ on site $i$, $n_{i\sigma}$ is the corresponding number operator, and $t$ is the hopping parameter. The exact single particle dimer Green’s function has the following form in the singlet (or, more generally, the ‘non-magnetic’) case:

$$\hat{G}^{-1}(\omega) = \begin{bmatrix} \omega - \Sigma_{11}(\omega) - t - \Sigma_{21}(\omega) \\ t - \Sigma_{12}(\omega) - \omega - \Sigma_{22}(\omega) \end{bmatrix},$$

(5)
where the self-energies are
\[
\Sigma_{11,\sigma\sigma'} = \Sigma_{22,\sigma\sigma'} = \delta_{\sigma\sigma'} \frac{U^2}{8} \left( \frac{1}{\omega - 3t + i\delta} + \frac{1}{\omega + 3t + i\delta} \right),
\]
(6)
and
\[
\Sigma_{12,\sigma\sigma'} = \Sigma_{21,\sigma\sigma'} = \delta_{\sigma\sigma'} \frac{U^2}{8} \left( \frac{1}{\omega - 3t + i\delta} - \frac{1}{\omega + 3t + i\delta} \right).
\]
(7)
Substitution of equations (6) and (7) into (5) leads to the following eigenvalue equation:
\[
\omega^2 = \frac{t^2 + \frac{U^2}{2} + \frac{U^2}{2} \left( \frac{6t^2 - U^2/4}{\omega^2 - 9t^2} \right)}{4tA},
\]
(8)
From equations (3) and (8), one can then obtain an equation for the XC kernel for the Hubbard dimer,
\[
K_{\uparrow\uparrow}(\omega) + K_{\downarrow\downarrow}(\omega) = \frac{U^2}{4t} \left( 1 + \frac{6t^2 - U^2/4}{\omega^2 - 9t^2} \right),
\]
(9)
where \(K_{\sigma\sigma'}(\omega)\) is in equation (2). Since we are interested in the contribution to the energy from correlation effects, we assume that the Hartree (\(-1/|r-r'|\)) and the exchange (\(K_{\uparrow\uparrow}\)) parts simply lead to the renormalization of the free-particle energy \(\omega_0 \rightarrow \omega\) in equation (1).

Furthermore, from equations (2) and (9), one can arrive at the following separable form of the correlation portion of the local XC kernel:
\[
f_{C_{\uparrow\uparrow}}(r, r', \omega) = \delta(r - r') \frac{U^2}{4tA} \left( 1 + \frac{6t^2 - U^2/4}{\omega^2 - 9t^2} \right),
\]
(10)
where \(A = \int \int |\psi_{\uparrow\uparrow}(r)|^2 |\psi_{\uparrow\uparrow}(r')| dr dr'\). This kernel results in the exact excitation spectrum (or more precisely, positions of the spectral function peaks) of the Hubbard dimer [28],
\[
\omega = \pm t \pm \sqrt{4t^2 + \frac{U^2}{4}}.
\]
(11)
The spectra obtained from equation (11), presented in figure 1(a), show two extra states: Hubbard satellite peaks with energy \(\pm 3t\) at small \(U\)s. These states appear only at finite \(U\) and arise from the redistribution of the single-electron spectral weight. It is easy to see that one cannot obtain these new states from equation (1) with the static XC kernel.

In the case of extended systems, considered below, the DMFT approximation \(\Sigma_{ij}(\omega) \simeq \delta_{ij} \Sigma(\omega)\) is valid. Even though in the case of the dimer this approximation is not sufficiently accurate, we present the corresponding expression for the kernel for the discussion below,
\[
f_{C_{\uparrow\uparrow}}(r, r', \omega) = \delta(r - r') \frac{U^2}{32A} \left( 8 + \frac{72t^2 - U^2}{\omega^2 - 9t^2} \right)
\]
\[
- \frac{9t^2 U^2}{(\omega^2 - 9t^2)^2}.
\]
(12)
As follows from equations (10) and (12), they have the same expression in the high-frequency limit, but as \(\omega \rightarrow 0\) they differ. The DMFT solution has an extra energy peak around zero energy, which is a characteristic of this approach (figure 1).

3. Extended systems

In these cases the DMFT with the local self-energy approximation can be applied. We shall use the following exact result for the high-frequency electron self-energy for the Hubbard model:
\[
\Sigma_{ij}(\omega) = \delta_{ij} \left( U_{\uparrow\uparrow} + \frac{U^2}{2} \frac{n_{\uparrow\downarrow}(1 - n_{\downarrow\uparrow})}{\omega} \right)
\]
(13)
(see, for example [30, 31]). In the homogeneous case, one can construct the XC kernel by mapping the eigenvalue equation
\[
\omega - \epsilon_k - \Sigma(\omega) = 0,
\]
(14)
or
\[
\epsilon_k^2 + 2\epsilon_k \text{Re} \Sigma(\omega) + |\Sigma(\omega)|^2 = \omega^2,
\]
(15)
onto the corresponding Casida equation. As in the dimer case one can find the equation which connects the XC kernel with the self-energy,
\[
K_{\uparrow\downarrow}(\omega) \sim \text{Re} \Sigma(\omega).
\]
(16)
A more straightforward way to find the expression for the XC kernel is to compare the TDDFT and DMFT correlation energies,
\[
E_{\text{TDDFT}}^C = \frac{1}{2} \int \int \delta n(r, t) f_{\text{XC}}(r, t; r', t') \delta n(r', t') dr dr' dr' dt'
\]
(17)
\[
E_{\text{DMFT}}^C = \int \int \psi^*(r, t) \Sigma(t - t') \psi(r, t') dr dt dr' dt'.
\]
(18)
The square of the kinetic energy $\varepsilon^2$ of electrons per site. It is important to note that we do not model: split (by energy $U$) the Hubbard bands and the zero energy quasi-particle peak, which disappears as $U$ increases.

With this XC kernel one can reproduce the main features of the spectrum of the infinite-dimensional Hubbard model: split (by energy $U$) Hubbard bands and the zero energy quasi-particle peak, which disappears as $U$ increases (figure 2).

It is important that the above frequency dependence (nonadiabaticity) of the correlation kernel describes the main properties of the spectrum of the dimer and the infinite-dimensional model. The spatial dependence of the kernel is essential.

In order to demonstrate that the proposed kernel can also reproduce the main features in the cases intermediate between the infinite dimensions and the dimer, we performed calculations for the cases of 3D and 2D Hubbard models. The results in figure 3 demonstrate that the nonadiabatic kernel reproduces the Hubbard band peaks at $\omega = \pm U/2$ and the zero energy quasi-particle peak, in agreement, for example, with DMFT calculations [32, 33].

4. Conclusions

It is already known from the DFT + DMFT study of real materials that the main effects of strong electron correlations can be described by local, temporally resolved electron interaction. Here we have shown that a spatially local, nonadiabatic XC kernel is sufficient for the description of strongly correlated systems within the TDSDFT. From our analysis above it follows that one may use the following nonadiabatic XC kernel to describe the main effects of strong electron–electron correlations within TDDFT:

$$f_{\text{XC}1;1m}(\mathbf{r}, \mathbf{r}', \omega) = \frac{U^2}{4t} \delta(\mathbf{r} - \mathbf{r}') \frac{n_m(1 - n_m)\omega}{\omega^2 - B^2_{\text{im}}}.$$

Equations (13), (17) and (18), together with the result for the dimer, equation (10), can be used to construct the following "universal" (DMFT) function for the correlation part of the XC kernel for the extended systems:

$$f_{\text{C}1}(\mathbf{r}, \mathbf{r}', \omega) = \frac{U^2}{4t} F(\sigma)(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \frac{n_m(1 - n_m)\omega}{\omega^2 - B^2_{\text{im}}},$$

where $F(\sigma)(\mathbf{r})$ is a functional of the ground state density $n_0(\mathbf{r})$ (in general, of the spin parts) and $B \sim 3t$ in the case of the dimer, while one can choose $B^2$ to be equal to the mean square of the kinetic energy $\frac{1}{2}\sum_i \epsilon_i^2$, or more generally $B^2 = \alpha \frac{1}{2}\sum_i \epsilon_i^2$, where $\alpha \sim 1$. Here $n_m$ is the average number of the spin-down electrons per site. It is important to note that we do not include the contribution of the static Hartree term $U n_m$ to the self-energy, since it is canceled by the chemical potential at half-filling. With this XC kernel one can reproduce the main features of the spectrum of the infinite-dimensional Hubbard model: split (by energy $U$) Hubbard bands and the zero energy quasi-particle peak, which disappears as $U$ increases (figure 2).

Figure 2. The density of states (DOS) (arbitrary units) for the infinite-dimensional Hubbard model with the hypercubic free-electron DOS $A(\epsilon) = (1/\sqrt{2\pi t^2}) \exp(-\epsilon^2/t^2)$ ($t^2 = 2dt$ is the renormalized hopping, $d$ is the dimensionality of the system) and $F(n_0)(\mathbf{r}) = 1, A = 1, B = \epsilon_0$. The frequency on the x-axis is given in units of $t^*$.

Figure 3. (a) The DOS (arbitrary units) for (a) the cubic lattice 3D and (b) the square lattice 2D Hubbard models, at different values of $U$. The kernel parameters are $F(n_0)(\mathbf{r}) = 1, A = 1, B = r, \alpha = 1$.
where $l$ and $m$ are the orbital indices, and $B_{lm}$ is a parameter proportional to the kinetic energy of band $m$ ($B = 3t$ in the case of the dimer). The functional $F[n_{s\sigma}](r)$, the ‘strength’ of spatially local correlations, is defined by the static (‘non-correlated’ DFT) spin-density distributions. It must have maximum at the points of the d- and f-charge localization, i.e. in a close vicinity to the atom where the dynamical interaction takes place. Therefore, in order to model strong on-site correlations it can be chosen to be proportional to the corresponding static d- and f-electron spin density. On the other hand, it can in most general cases of very complex material systems (including the case of strong density fluctuations), the spatial form of the correlation kernel may be nonlocal. The frequency power $\alpha$ in the numerator is introduced heuristically in order to obtain a universal formula for small and large systems, and is expected to lie between zero (for small systems, such as dimers) and 1 (for the extended (DMFT) case).

It is important to notice that equation (20) contains a proposed generalized kernel to include (heuristically) multi-orbitals, which is more relevant for real materials. Namely, the correlation potential is the sum of the terms which correspond to the intra-orbital, $\sim U_{\text{intra}}^2$, and inter-orbital, $\sim U_{\text{inter}}^2$, spin-density interactions. In the case of several-electrons per site, one also needs to take into account the Hund coupling ($J$-) terms, even though typically $J$ is one order of magnitude smaller than the local Coulomb repulsion $U$. In the last case, one can take into account the effects of $J$ in a mean-field approximation. In particular, the spin flip $J$-terms in the Hubbard model can be taken into account by using the Hartree–Fock type splitting of the four fermion-operator terms. This will lead to a renormalization of the free electron bandstructure. Such approximation is used in the DFT + $U$ case. Therefore, it will correspond to static $J$-dynamic $U$ interaction in the theory presented in this paper. Moreover, the contribution of $J$ can be taken into account through renormalized $U$ which correspond to the repulsion between one-orbital opposite-spin electrons and different-orbital same-spin electrons (see, e.g., [11]). Therefore, the proposed kernel (20) should capture the main properties in the multi-orbital system in the case of single-electron per site and in the majority of cases of several-electrons per site (when $J$ is small compared to $U$).

Most general cases of large $J$, however, require additional studies on the form of the XC kernel. Moreover, the frequency dependence of the corresponding kernel at large frequencies is the same as the exact dependence of the intra- and inter-orbital electron self-energy (equation (13)), thereby supporting the form of proposed XC kernel in equation (20).

The most essential features of the proposed XC kernel are spatial locality, proportionality to the local Coulomb repulsion, and the oscillating in time interaction of the electrons with opposite spin, $\sim \exp(\pm iBt)$, where the frequency of oscillations $B$ is proportional to the hopping (kinetic) energy. While further tests of the validity of the methodology presented here for larger scale systems, both in- and out-of-equilibrium, are on-going, the frequency-dependent XC kernel of type equation (20) is able to describe the main features of single-orbital correlated systems. On the other hand, it is important to mention that, while we stress the importance of the nonadiabaticity, spatial nonlocality of the kernel is another important direction to explore. In particular, it was recently shown that one can get rather accurate values for the excitation energies in several types of systems by using nonlocal orbital-dependent functionals with nonlocal Hartree–Fock exchange as a function of inter-electronic distance [34, 35].

We expect the approach presented in this paper to open the possibility of describing strongly correlated materials within the standard TDDFT framework, extending it beyond the metallic and semiconductor structures with plasmons, excitons and other excitations (see, e.g., [36, 37]).

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