Nonadiabatic exchange-correlation kernel for strongly correlated materials

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Abstract

We formulate a rigorous method for calculating a nonadiabatic (frequency-dependent) exchange-correlation (XC) kernel appropriate for accurate description of both equilibrium and nonequilibrium properties of strongly correlated systems within the time-dependent density functional theory (TDDFT) via the charge susceptibility, which is in turn obtained from dynamical mean field theory (DMFT) based on the effective multi-orbital Hubbard model. Application to the simple case of the one-orbital Hubbard model already shows the importance of the nonadiabatic kernel as it leads to significant modification of the excitation spectrum—shifting the (adiabatic) peak and disclosing another that is reminiscent of the solution from DMFT. The impact of dynamical effects, naturally included through the nonadiabaticity of the XC kernel, becomes even more transparent in our consideration of the nonequilibrium charge-density response of a multi-orbital perovskite, YTIO\(_3\), to a perturbation by a femtosecond (fs) laser pulse. These initial results indicate that electron–electron correlations and nonadiabatic features may significantly affect the spectrum and nonequilibrium properties of strongly correlated systems. We also propose an algorithm for extension of the approach to non-linear response. The transparency and computational efficiency of this non-adiabatic TDDFT+DMFT approach opens the door to examination of the spectra and response of multi-orbital systems with many nonequivalent atoms—bulk material, films and nanostructures.

Keywords: strongly correlated materials, time-dependent density-functional theory, ultrafast dynamics

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

1. Introduction

Strong electron correlations and nonadiabatic features, such as time-resolved electron–electron interactions, can significantly affect the energy spectrum and nonequilibrium response of materials that demonstrate unusual properties with many potential applications from high-temperature superconductivity and giant magneto-resistance [1] to antiferromagnetism in small Fe chains [2] and other exotic effects [3–6] at the nanoscale. Accurate theoretical description of experimentally observed properties as well as predictive modeling of strongly correlated systems with desired properties is, however, not a trivial task.

In recent times, DMFT [7, 8], combined with DFT (DFT+DMFT) [9, 10], with its successful description of extended, homogeneous systems, has been proposed as an optimal approach for describing strongly correlated systems: for nanostructures [11], thin films and bulk systems [12, 13]. In DFT+DMFT the ‘non-correlated’ properties of the system, such as geometry and energy spectrum, are obtained via DFT, while correlation effects are taken into account by post-processing the self-consistent solution of the corresponding effective Hubbard model. Unfortunately, DFT+DMFT is computationally demanding even for systems which are in equilibrium (not to mention systems out-of-equilibrium) and can be described with computational super-cells that contain only tens of non-equivalent atoms [14, 15]. On the other hand, TDDFT [16] being the theory of a single variable, the charge density, allows examination of properties of systems containing hundreds of atoms in the super cell [17]. Development
of a pure TDDFT approach for strongly correlated systems, with rigorously derived XC potential, is thus very desirable.

Some progress in devising schemes beyond DFT (or TDDFT) for strongly correlated materials has already been made. Several groups [18–23] have resorted to the Bethe ansatz [24] and DMFT [7, 8] in developing an adiabatic (non-retarded) XC potentials for the one-band Hubbard model, which when combined with TDDFT may be applied to study time-dependent phenomena. However, as shown by Karlsson et al usage of such an adiabatic XC potential [23] in TDDFT for strongly correlated systems yields results that deviate significantly from the exact solution (at large Coulomb repulsion and/or close to half-filling), suggesting the importance of nonadiabatic (memory, frequency-dependence) effects. Indeed, as we have recently shown by analyzing the exact solution for the Hubbard dimer [25], non-adiabaticity of the XC kernel is essential for obtaining an electronic spectrum with the characteristic Hubbard satellite peaks (and also the zero-energy quasi-particle peak in the case of extended systems) resulting from dynamical (time-resolved) local interactions between the electrons. For the case of small clusters, a nontrivial frequency dependence of the XC kernel was found numerically by Aryasetiawan and Gunnarsson [26].

In this paper, we formulate a rigorous approach for calculating the nonadiabatic XC kernel for strongly correlated systems from the DMFT solution of the multi-band Hubbard model. We develop the formalism first in the linear response regime and then extend it non-linear response of multi-orbital systems. For the latter, we derive a generalized Sham–In the linear-response approximation DMFT calculations.

In section 2, we present some details of the formalism in the linear response regime. This is followed in section 3 with a discussion of the derivation of the XC kernel from DMFT. In section 4 we apply the formalism to examine the ultrafast charge dynamics in two systems. Our conclusions are summarized in section 5. In appendix A, we develop the formalism for non-linear response, while in appendix B we provide details of TDDFT calculations of the excitation spectrum for the one-band Hubbard model, and in appendix C we include some details of our non-equilibrium DMFT calculations.

2. General formalism of TDDFT in the linear-response approximation

To begin with, one solves the time-dependent Kohn–Sham (KS) equation for the electron wave function:

\[
\frac{i}{\hbar} \frac{\partial \psi^\sigma_i(r,t)}{\partial t} = \left[ -\frac{\nabla^2}{2m} + V_{\text{ion}}(r) + V_H[n](r,t) + V_{\text{XC}}[n](r,t) \right] \psi^\sigma_i(r,t),
\]

where \( \sigma \) and \( l \) are the spin and orbital indices, \( V_{\text{ion}}(r) \), \( V_H[n](r,t) \), \( V_{\text{XC}}[n](r,t) \) are the ion, Hartree and external potentials, respectively, and \( V_{\text{XC}}[n](r,t) \) is the XC potential which takes into account all effects of electron–electron interactions. Finding the exact expression for \( V_{\text{XC}}[n](r,t) \) is a daunting task. On the other hand, unless the perturbation is very strong, it is sufficient to assume that the XC potential is proportional to linear fluctuations of the charge density:

\[
V_{\text{XC}}[n](r,t) \approx V_{\text{XC,0}}[n](r,t = -\infty) + \int_{-\infty}^{t} \int_{-\infty}^{t} f_{\text{XC}}(r, r', t, t') \, \delta n(r, t') \, \, dt' \, dt.
\]

(2)

where \( V_{\text{XC,0}}[n](r,t = -\infty) \) is the static XC potential (of the non-perturbed system) and

\[
f_{\text{XC}}(r, r', t, t') = \frac{\delta V_{\text{XC}}[n](r,t)}{\delta n(r', t')}
\]

(3)

is the XC kernel. Note that the explicit expression for \( V_{\text{XC,0}}[n](r,t = -\infty) \), as well as the function itself, is not needed to study the nonequilibrium or steady-state properties of the perturbed system. Indeed, the main role of this function is to modify the spectrum of the non-correlated system (e.g. by opening a Mott gap). On the other hand, the ‘correlation correction’ to the KS spectrum is included in the DFT+DMFT [12, 13] solution of the static problem. Note also that as the XC potential depends on the fluctuation of the electronic density: \( \delta n(r,t) = \sum_{l,\sigma} \left[ |\psi^\prime\sigma_i(r,t)|^2 - |\psi^\sigma_i(r, t = -\infty)|^2 \right] \) equations (1)–(3) must be solved self-consistently.

To find the appropriate expression for \( f_{\text{XC}}(r, r', t, t') \), we turn to the approximate, but broadly used, Hubbard Hamiltonian:

\[
H = - \sum_{ijlm,\sigma} \delta n^\sigma_{ij} c^\dagger_{i\sigma} c_{j\sigma}^\sigma - \mu \sum_{ij} n_{i\sigma}^\sigma c^\dagger_{i\sigma} c_{i\sigma}^\sigma + U \sum_{ij} n_{i\uparrow}^\sigma n_{i\downarrow}^\sigma + (U - J) \sum_{ijlm} n_{i\sigma}^\sigma n_{j\sigma}^\sigma + (U - 2J) \sum_{ijlm,\sigma} n_{i\sigma}^\sigma n_{j\sigma}^\sigma
\]

(4)

where \( c, c^+ \) and \( n \) are the electron annihilation, creation and number operators with the respective orbital, spin and space indices, \( \delta n^\sigma_{ij} \) are the corresponding inter-(intra-) site and hopping parameters (\( i,j \)—the site-, \( l,m \)—the orbital-, and \( \sigma \)—the spin indices), \( U \) is the orbital Coulomb repulsion at each site, \( U-J \) and \( U+2J \) are the corresponding inter-orbital, opposite-spin and same-spin Coulomb repulsions (\( J \) is the exchange energy parameter), and \( \mu \) is the chemical potential. In the above many-body approach, most of the single-particle properties, collective excitations and response can be obtained from the spin and orbital dependent single-particle Green’s function

\[
G_{\sigma\sigma'}^{\mu}(r,t; r', t') = - \langle T c_{\sigma'}(r,t) c_{\sigma'}^\dagger(r',t') \rangle
\]

and two-particle susceptibility
\[ \chi_{\sigma\sigma'}^{\mu}(r,t; r',t') = -\langle \hat{T} n_{\mu}(r,t) n_{\mu}^{\prime}(r',t') \rangle, \]  
where \( \hat{T} \) is the time-ordering operator. It is the latter that can be also used to find the TDDFT XC kernel, through the relationship:

\[ \chi(r,t; r',t') = -\langle \hat{T} n(r,t) n(r',t') \rangle = \sum_{\mu,\sigma,\sigma'} \chi_{\sigma\sigma'}^{\mu}(r,t; r',t') \]  

as:

\[ f_{xc}(r,r',\omega) = \chi_{0}^{-1}(r,r',\omega) - \chi^{-1}(r,r',\omega) - \frac{1}{|r-r'|} \]  

(in the real frequency representation). In equation (8), \( \chi_{0}^{-1} \) is the inverse susceptibility for the ‘non-interacting’ (DFT) case. Thus, provided the functions \[ \chi_{\sigma\sigma'}^{\mu}(r,t; r',t') \]  
are known, one can find the total-charge XC kernel from equations (7) and (8).

3. XC kernel: the DMFT approximation

In this section, after summarizing the basic features of DMFT (section 3.1), we proceed with the general set of equations that define the local-in-space DMFT XC kernel (section 3.2), and eventually obtain an approximate (ladder-approximation) solution of these equations that yields the sought kernel which we then apply to model systems.

3.1. Main DMFT equations

To find the functions (5) and (6), and hence the XC kernel (8), we shall use the DMFT solution for the Hubbard model (4). In DMFT, to calculate the Green’s function in equation (5), one neglects the momentum-dependence (spatial inhomogeneity) of the electron self-energy \( \hat{\Sigma}(k,\omega) \), i.e. the problem is reduced to that of an electron(s) in an atom, embedded in a bath of other electrons, described by the dynamical mean-field \( G_{ab}(\omega) \) [8–12]. The above approximation allows one to obtain the exact numerical solution of the problem and appears to be quite accurate for systems with large atomic coordination number, i.e. for the great majority of bulk solids and also materials with reduced dimensionality. More specifically, to find the Green’s functions in equation (5), one needs to solve the following system of equations involving the self-energy and the dynamical mean-field:

\[ G_{ab}(i\omega_{n}) = \sum_{k} \left[ i\omega_{n} - \hat{\epsilon}_{k} + \mu - \hat{\Sigma}(i\omega_{n}) \right]_{ab}^{-1}, \]  

\[ G_{ab}^{-1}(i\omega_{n}) = G_{ab}^{-1}(i\omega_{n}) - \Sigma_{ab}(i\omega_{n}), \]  

\[ G_{ab}(\tau) = \int D[\psi] D[\psi^{\dagger}] \psi_{a}(\tau) \psi_{b}^{\dagger}(0) \]  

\[ \times \exp \left[ -\int_{0}^{\beta} d\tau \int_{0}^{\beta} d\tau' \sum_{c,d} \psi_{c}^{\dagger}(\tau') G_{ab}^{-1}(\tau' - \tau) \psi_{d}(\tau') + \int_{0}^{\beta} d\tau \sum_{c,d} U_{cd} n_{c}(\tau)n_{d}(\tau') \right], \]  

where \( \omega_{n} = \pi T(2n + 1) \) and \( \beta = 1/T \)—inverse temperature, \( n \)—integer number) are the Matsubara (imaginary) frequency and time, respectively. In equations (9)–(11) and below, indices \( a-d \) represent collectively the orbital and spin indices. The elements of the local Coulomb interaction matrix \( U_{cd} \) in equation (11) can be easily identified from the last three terms of the Hamiltonian in equation (4). In equation (9), hats are placed over the free electron energy, \( \hat{\epsilon}_{k} \) (momentum), and the self-energy \( \hat{\Sigma} \) functions to emphasize that these are matrix functions. In equation (11), path integration is performed over fermionic Grassman fields \( \psi_{a} \) and \( \psi_{a}^{\dagger} \) (see, e.g. [8]). Note that in DMFT, it is much easier to solve the equations in the Matsubara representation than in the real-frequency space. Once such a solution has been found, one can obtain the corresponding real-frequency dependencies of the functions by performing analytic continuation \( i\omega_{n} \to \omega + i\delta \). Below, to obtain the real-frequency electron self-energy and other functions we use the Padé approximation algorithm [29].

Note also that equation (9) is the expression for the local (in the site index) Green’s function in terms of the matrix elements of the free electron energy and the interacting electron self-energy matrices \( \hat{\Sigma}(\omega) \). In DMFT it is assumed that the Green’s functions \( G_{ab}(\omega) \) and self-energies \( \Sigma_{ab}(\omega) \) in the many-site problem are the same as the corresponding functions in the one-site (impurity) case. Therefore, for the single-site problem one can write down a (Dyson) equation (10) that connects the one-site electron Green’s function and the self-energy with the ‘bath’ dynamical mean-field function \( G_{ab}(\omega) \). Finally, equation (11)—the only non-trivial equation in the set above—is the path-integral expression for the impurity Green’s function \( G_{ab}(\tau) \) defined by the dynamical mean-field function and the Coulomb repulsion parameters. The impurity problem equation (11) can be solved in principle exactly [30, 31]. Below, to solve it we use the computationally inexpensive second-order self-consistent iterative perturbation theory (IPT) approximation [32], which gives

\[ \sum_{n} (i\omega_{n}) = U_{ab} n_{b} - U_{ab}^{2} \sum_{n,m} G_{ab}(i\omega_{n}) G_{ab}(i\omega_{m}) G_{ab}(i\omega_{n} + i\omega_{m} - i\omega_{l}), \]  

where the first (linear) term corresponds to the static (Hartree) approximation, while the second, frequency-dependent, term describes non-trivial dynamical effects which often play a dominant role in the behavior of strongly correlated systems.

IPT is exact in the limits of large \( U \)’s and high frequencies and is very accurate in the other extreme of small \( U \)’s. It is also regarded as a valid approximation for intermediate values of \( U \)’s as it reproduces important features, such as the central quasiparticle peak and the Hubbard bands in the density of states, of the bulk Hubbard model [8, 33], in agreement with more accurate solutions. The IPT single-particle Green’s function and self-energy satisfy the spectral sum rules. As a number of recent studies show, one can obtain very encouraging results with the IPT approximation also for systems with reduced size and dimensionality, including the multi-orbital systems with non-local interactions (see, e.g. [34–36]).

As we show below, the IPT solution is sufficient to provide the
3.2. XC kernel: dynamical vertex approximation

In TDDFT+DMFT, the two-particle susceptibilities (6), necessary for calculation of the XC kernel, are approximated by the local-in-space DMFT susceptibilities. To calculate the last functions, one can use the Bethe–Salpeter formalism (see, e.g. [17]). In this approach, one begins with calculating a generalized four-time orbital susceptibility (in the imaginary time representation):

\[ \chi_{abcd}(\tau_1, \tau_2, 0) = -\langle T \epsilon_{a\sigma}^+ (\tau_1) \epsilon_{b\sigma}^+ (\tau_2) \epsilon_{b\sigma} (\tau_2) \epsilon_{a\sigma} (\tau_1) \rangle \]

where the suffix \( i \) corresponds to the (impurity) site and the other letters (\( a-f \)) are the spin–orbital indices. We put the last time argument above as zero because of time translation invariance. It is important to stress that such a choice is relevant only in the linear response regime. In the general non-linear case, one should keep four time arguments in equation (13).

As the next step, one substitutes the resulting frequency-transformed function (13),

\[ \chi_{abcd}(\omega_m, \omega_l, \omega_n) = T^2 \int_0^\beta d\tau_1 \int_0^\beta d\tau_2 \times \int_0^\beta d\tau_3 \text{e}^{-i\omega_0 \tau_3} \sum_{\tau_4} \chi_{abcd}(\tau_3, \tau_1, \tau_2, 0) \]

into the equation for the local vertex function \( \Gamma(\omega_m, \omega_l, \omega_n) \):

\[ \chi_{abcd}(\omega_m, \omega_l, \omega_n) = \frac{\delta \Gamma}{\delta x} \chi_{abcd}(0)(\omega_m, \omega_n) - \chi_{abcd}(0)(\omega_m, \omega_n) \Gamma(\omega_m, \omega_l, \omega_n) \chi_{abcd}(0)(\omega_l, \omega_n), \]

where

\[ \chi_{abcd}(0)(\omega_m, \omega_n) = G_{\text{dd}}(\omega_m + \omega_n) G_{\text{dd}}(\omega_m). \]

Finally, the result for the vertex function \( \Gamma(\omega_m, \omega_l, \omega_n) \) obtained from equation (15) has to be substituted into the following equation, which gives the expression for the local susceptibility, needed to calculate the XC kernel with equation (8):

\[ \chi(\omega_n) = 2 T \sum_m \chi^0(\omega_m, \omega_n) - 2T^2 \sum_{m,l} \chi^0(\omega_m, \omega_n) \times \Gamma(\omega_m, \omega_l, \omega_n) \chi^0(\omega_l, \omega_n), \]

where \( \chi^0 \) are defined in equation (16).

In DMFT, the above methodology is known as the dynamical vertex approximation (DFA), that was originally proposed [37] to calculate the local vertex function \( \Gamma \) needed to determine the momentum-dependent correction to the electron self-energy.

3.3. XC kernel: static (ladder) vertex approximation

To demonstrate the capabilities of the above approach of infusing DMFT susceptibility into TDDFT, we consider a computationally inexpensive static, or ladder, approximation [33,38,39] for the vertex in equation (17),

\[ \Gamma(\omega_m, \omega_l, \omega_n) \equiv U_{\text{ch}}, \]

where \( U_{\text{ch}} \) is an effective (‘ch’ for the ‘charge susceptibility’) parameter, such that the resulting charge susceptibility

\[ \chi(\omega_n) = \frac{\chi^0(\omega_n)}{1 + U_{\text{ch}} \chi^0(\omega_n)}, \]

satisfies the sum rule

\[ T \sum_m \chi(\omega_n) = n(1 - n) + 2 T. \]

In the last two equations, \( \chi(\omega_n) \) is the one-loop susceptibility \( G(\omega_n) \) is the local Green’s function, equation (9),

\[ D = \langle n \rangle^2 = T \sum_a \sum_{a \neq a} (\omega_n) G_{aa}(\omega_n). \]

is the one-site electron double occupancy and \( n \) is the average number of electrons per site.

Approximation (18) becomes exact in the ‘linear in \( U \) theory’, when \( U_{\text{ch}} = U \). At large \( U \)’s it corresponds to summation of ladder diagrams when one calculates the charge susceptibility. Despite its simplicity, its is capable to reproduce many important features of the exact DMFT solution, including such a nontrivial effect as superconductivity in the 2D Hubbard model (for details and references on the results in the one-orbital case, see, e.g. [33], and for a multi-orbital generalization of the approach—[39]).

As we show below, already at this level of approximation the theory correctly describes the main features of the spectrum and nonequilibrium response of correlated materials.

As a consequence of choosing the local in space susceptibilities, the frequency-dependent (and analytically-continued) part of the XC kernel (8) is also local in space:

\[ f_{\text{XC}}(r, r') = A \delta(r - r') f_{\text{XC}}(\omega). \]

where \( f_{\text{XC}}(\omega) \) is the frequency-dependent (dynamical) part obtained from equation (8) by using local susceptibilities (at \( r = r' \)). In equation (23), the spatial part of the kernel \( A \delta(r - r') \) (A is a parameter) is a simple static local XC kernel (we will neglect the Hartree (adiabatic) term in equation (8), assuming it to be smaller than the local (strongly correlated, dynamical) part of the kernel). The above approximation corresponds to the case when only the local charge dynamics is taken into account, which may be regarded as a reasonable choice for localized d- and f-orbitals. Such an approximation is also sufficient to grasp a qualitative understanding of the non-adiabatic structure of \( f_{\text{XC}}(r, r', \omega) \) defined by the time-resolved local-in-space charge correlations.
take into account spatially-resolved effects, i.e. the space-(momentum-) dependence of the kernel, one needs to go beyond the $D\Gamma_A$ (i.e. to calculate the spatially nonlocal susceptibilities in equation (13)).

Finally, one can generalize the methodology above on the non-linear case, where the XC potential can be obtained from solving the Sham–Schluter equation that connects the XC potential and the electron (in our case DMFT) self-energy of electron (see appendix A).

4. Application: examining ultrafast charge dynamics with TDDFT+DMFT

In this section, we demonstrate some applications of the above formalism to two systems: a one band Hubbard model and a multi-orbital Mott insulator YTiO$_3$. To begin with we show that for the one-band Hubbard model the TDDFT+DMFT excitation spectrum is in a reasonable agreement with the DMFT spectrum which is known to demonstrate several characteristic peaks for strongly correlated materials. As the next step, we compare the time-dependence of a laser-pulse excited charge density obtained with the TDDFT+DMFT and non-equilibrium DMFT in this model system. The TDDFT+DMFT solution was obtained by using the non-adiabatic and adiabatic XC kernels. We show that the non-adiabatic solution is in a better agreement with that obtained from the nonequilibrium DMFT, i.e. memory effects play an important role in the charge dynamics. Finally, to demonstrate the capabilities of the approach we apply it to analyze the ultrafast charge dynamics in a more complex system, YTiO$_3$. In particular, we show that in this case too there is a qualitative difference between the non-adiabatic and adiabatic TDDFT+DMFT solutions.

4.1. The one-band Hubbard model

The excitation spectrum of the one-band Hubbard model at half-filling (one electron per site) is obtained within DMFT (imaginary part of the local susceptibility in equation (19)) and TDDFT+DMFT (eigen-energies of equation (1)). We take the free electron density of states (DOS) to be described by a Gaussian function: $\rho(\varepsilon) = \frac{1}{\sqrt{2\pi}t} \exp\left(\frac{-\varepsilon^2}{2t^2}\right)$, where $t$ is the hopping parameter [8], which corresponds to the ‘infinite-dimensional’ system, when each atom has infinite number of nearest neighbors. In the DMFT calculations, we used temperature $T = 0.01t$ and six hundred Matsubara frequencies. The results for the DMFT DOS, $-(1/\pi)\text{Im} G(\omega)$, and the excitation spectrum at different values of $U$ are presented in figure 1(a) (inset). For small values of $U$, the DMFT DOS is similar to that of the free-electron with the peak at zero energy (inset figure 1(a), red curve). When $U$ increases,
the peak splits into three: a central peak and two side peaks, separated approximately by \( U \) (inset figure 1(a), green curve). The two side peaks correspond to two Hubbard bands centered around \( \omega = \pm U/2 \) and the central peak is the zero energy quasi-particle peak, which gets suppressed at large values of \( U \) [8, 40, 41] (insert figure 1(a), blue curve). The central peak, a very important feature of the spectrum of many systems in which electron correlations cannot be ignored [8, 12], is a characteristic of the DMFT solution. This peak is missed in the oft-used static mean-field, or unrestricted Hartree–Fock (HF, or ‘DFT + U’) approximation, in which only the frequency-independent part of the electron self-energy (linear in \( U \) in equation (12)) is taken into account.

The features of the DMFT single-electron DOS mentioned above are also reflected in the DMFT excitation spectrum, already in the one-loop approximation (figure 1(a)). Indeed, at small values of \( U \) the excitation spectrum is dominated by low energy excitations near the Fermi energy (solid red curve). In the case of larger values of \( U \) with the three-peak DOS (solid green curve), the corresponding excitation spectrum demonstrates two characteristic features: low-energy excitation shoulder related to low-energy transitions (short green arrow) and the peak at \( \sim U \) (long green arrow) that corresponds to excitations from the Fermi-energy to the upper Hubbard band. Finally, at large values of \( U \) (solid blue curve), the excitation spectrum has one peak at \( \sim U \), that corresponds to the excitations between the Hubbard bands (marked blue). In order to estimate the role of the vertex correction to the susceptibility in the excitation spectrum, we calculated the corresponding excitation spectrum with the results shown in figure 1(b) (the vertex parameters \( U_{ch} \) for used values of \( L = 1, 2.5 \text{ and } 6 \) are 0.339, 4.265 and 55.734, correspondingly).

In order to get a better idea about the importance of dynamical effects in DMFT (described by the second, frequency-dependent, term in the self-energy in equation (12)), we compare the static, HF, and full DMFT excitation spectra, in figure 1(a). The spectra agree at small and large values of \( U \), while there is an important difference for intermediate \( U \)'s (green curves) as revealed by the missed low-energy quasi-particle peak in the HF spectrum. In fact, the HF solution is particle peak in the HF spectrum. In fact, the HF solution is

\[
\chi_{\sigma\sigma}(\omega) = \frac{\epsilon_{\text{g}}(1-n_{\text{g}})}{\omega^2 - U^2 + \beta},
\]

that has only one peak at \( \omega = U \). Thus, while at large values of \( U \) one can use a simplified HF solution for the XC kernel, in the most complex and very important case of ‘intermediate’ \( U \)'s, when the local Coulomb repulsion and the electron kinetic energies are of the same order of magnitude, the exact DMFT expression for the kernel is needed.

The corresponding XC kernels (figure 1(b)) demonstrate peaks at values close to those of the excitation spectrum (figure 1(a)), indicating that the system responds with resonance at perturbations close in energy to the electronic excitations. To find the TDDFT+DMFT excitation spectrum, we solved the eigenenergy equation (1) by transforming it to the Casida eigenvalue problem [42]. To obtain the electron eigenfunctions we carried out DFT calculation for solid hydrogen with the ‘free-electron’ spectrum close to the Gaussian DOS that we used above in one-band Hubbard model (details of the TDDFT+DMFT calculations are given in appendix B).

As seen from figure 2(a), TDDFT+DMFT is capable of reproducing the main peaks of the DMFT excitation spectrum shown in solid lines in figure 1(b). Some discrepancies between the width of the TDDFT+DMFT and DMFT spectra can be attributed to the finite number of the energy points used to solve the Casida equation.

We have also compared the nonadiabatic and adiabatic solutions versus the second order in \( U \) nonequilibrium DMFT solution for time-dependent cases. Namely, we have calculated the excited charge density as a function of time in the case of a laser pulse perturbation (figure 2(b)). The nonequilibrium calculations were performed at the same initial pumped excited charge (the initial condition) as in the TDDFT+DMFT case. We find that the nonadiabatic TDDFT+DMFT result is in much better agreement with the nonequilibrium DMFT solution than the adiabatic case, suggesting the important role of memory effects in the response of the system. Much larger overestimation of the scattering effects in the adiabatic case may be explained by stronger scattering of excited electrons by ‘frozen ground state charges’ (in the non-adiabatic case, they are ‘moving’, which reduces the on-site scattering effects).

Our analysis shows that the difference between the nonadiabatic and adiabatic TDDFT+DMFT solutions increases with increase of the perturbation field. It is important to notice that the PT results are valid up to times \( \sim \frac{\hbar}{eV} \approx 5 \text{ fs} \), i.e. the slight deviation between the TDDFT+DMFT and nonequilibrium
DMFT results at the right end of the time axis can be attributed to not very high accuracy of the last approach for these times. The details of the nonequilibrium DMFT calculations are given in appendix C.

4.2. YTiO₃

As application to a real material consisting of several orbitals, we consider the Mott insulator YTiO₃ in the paramagnetic phase. DFT calculations [43] predict a metallic ground state with three isolated, partially occupied, narrow t₂g bands around the Fermi level with approximate total electron occupation number \( n \approx 1 \) (shown as dashed line (obtained with \( U = J = 0 \)) in figure 3(a)). Contrary to DFT, DMFT calculations [43, 44], including our results (figure 3(a), show that YTiO₃ is a Mott insulator with the bandgap \( \sim 1 \) eV in agreement with experimental optical spectra [45, 46].

The positions of the Hubbard band peaks in the DFT + DMFT DOS separated by \( \sim 3.3 \) eV are also in agreement with (room temperature) experimental results [47] (squares in figure 3(a)) and theoretical calculations (see, e.g., work by Pavarini et al [43]). Our calculated peak width is, however, much smaller than that in experiments. This difference could be attributed to the difference in temperature and other broadening effects (experimental measurements were performed at temperatures three times higher than that in our calculations, and hence involving larger phonon broadening; bands other than t₂g could also be contributing). The width of the high-energy peak obtained by Pavarini et al is also narrower than that in the experimental data, but broader than ours. This latter difference may have resulted from the different impurity solvers used in the IPT DMFT approximation. The broadening effect might be included by adding an imaginary parameter \( i\delta \) in the denominator of the spectral function (which will not affect essentially the low-energy excitation spectrum). We prefer not to do it, since our nonequilibrium results for the YTO₃ were obtained by using the given DMFT DOS. Moreover, since the low-excited charge density response (studied in the used linear response approximation) is defined mainly by the low-energy parts of the ‘valence’ and ‘conduction bands’, it is not seriously affected by the band peak widths.

It should be also noted that the used second-order IPT expression for the self-energy (equation (12)) is a reasonable approximation for purposes here. More accurate solvers are required when, for example, one is interested in evaluating detailed changes of the magnetic order in systems crossing the metal–insulator transition point [43].

Finally, we applied the TDDFT + DMFT (XC kernel equation (23) with different values of parameter \( A \)) to examine the charge dynamics in YTiO₃ as perturbed by an external Gaussian laser pulse (magnitude \( 0.1 \) eV/Bohr, duration \( \tau = 0.82 \) fs). We calculated the time-dependent orbital occupancy from equation (1) by expanding the wave function in terms of the t₂g KS wave functions. As displayed in figure 3(b), non-adiabatic effects play a very important role in the response when the parameter \( A \), describing the spatial overlap of the different orbitals, is not small. While a more general non-adiabatic solution (frequency-dependent kernel in equation (23)) practically coincides with the non-interacting and MF ones at short times, it demonstrates different response at longer times. (The negligible difference between such solutions at short times is due to dominating effect of strong electric field chosen for the calculations). Indeed, one may expect memory effects to affect the post-pulse dynamics, in particular because of fluctuations in orbital occupancies. The difference between the non-adiabatic and adiabatic solutions with \( A \), or spatial overlap of charges/correlation, increases. Another interesting result is a beating solution for the current at large value of \( A (A = 15) \), due to charge transitions between occupied and empty levels. Of course, these conclusions await experimental verification. It is important to emphasize though that the second-order IPT approximation (equation (12)) is capable of correctly describing the dynamics of the system only for times below \( \tau / U^2 \) [48] (femtoseconds in our case). Analysis of longer-time response requires the exact expression for the electron self-energy, which is beyond the scope of this work.
5. Summary

We have formulated a nonadiabatic TDDFT+DMFT approach to examine spectral properties and nonequilibrium response of strongly correlated systems. Simplicity of the algorithm allows its application to complex materials which consist of multiorbital and several nonequivalent atoms—from bulk materials to nanostructures, inaccessible so far to many-body approaches. We demonstrate that the nonadiabatic effects are important for determining both the excitation spectrum and the response of the system. Since the DMFT approach is now regarded as a method of choice in the many-body strongly correlated community, our results establish that the corresponding XC kernel can be successfully used for the time-dependent ab initio applications as well for such strongly correlated systems. We look forward to many applications of the methodology presented here. Furthermore, through analysis of the results TDDFT+DMFT results for the XC kernel and XC potential for a variety of systems, it should be possible to establish the general structure of these nonadiabatic functions valid for majority of the materials with strong electron-electron correlations.

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Appendix A. Extension of the TDDFT+DMFT formalism to the nonlinear case

In this appendix, we describe a possible way to generalize the formalism to nonlinear system response, i.e. the scheme to obtain the expression for the XC potential for a multi-orbital system \( V_{XC}(r,t) \) within DMFT, which will allow one to solve the KS TDDFT equations exactly.

As the first step to achieve this goal, one has to generalize the time-dependent Sham-Schlueter equation [27,28], that connects the XC kernel with the electron self-energy, for the multi-orbital system. For this, we begin with equations for the KS \( G_{KS}(r_1,t_1, r_2,t_2) \) and many-body (orbital-dependent) \( G_{lm}(r_1,t_1, r_2,t_2) \) Green’s functions [17]:

\[
\left( \frac{\partial}{\partial t_1} + \vec{v}_{KS}(r_1,t_1) - v_{XC}(r_1,t_1) \right) G_{KS}(r_1,t_1, r_2,t_2) = \delta(r_1-r_2) \delta(t_1-t_2), \tag{A.1}
\]

\[
\left( \frac{\partial}{\partial t_1} + \frac{\nabla}{2} \right) \delta(r_1-r_2) \delta(t_1-t_5) \delta_{\mu\nu} - \delta_{\mu\nu} \Sigma_{\nu\nu}(r_1,t_1, r_3,t_3) \right) G_{lm}(r_3,t_3, r_2,t_2) = \delta(r_1-r_2) \delta(t_1-t_2) \delta_{lm}. \tag{A.2}
\]

In these equations and below in this appendix, the time arguments are defined on the complex (Keldysh) time contour. To obtain the ‘physical’ results for the susceptibility and other functions one has to use the results for these functions for the real times arguments on the first branch of the contour (see, e.g. [17]).

Multiplication of equations (A.1) and (A.2) from the left by \( G_{lm}(r_3,t_3, r_1,t_1) \) and \( G_{KS}(r_3,t_3, r_2,t_2) \), integration over \( (r_1,t_1) \) and subtraction of one equation from the other gives the equation that connects the KS and many-body Green’s functions:

\[
G_{lm} (r_1,t_1, r_2,t_2) = \delta_{lm} G_{KS}(r_1,t_1, r_2,t_2) + \int dr_3 dr_4 dr_5 dr_6 \times \left\{ G_{KS}(r_1,t_1, r_2,t_2) \Sigma_{\nu\nu}(r_3,t_3, r_4,t_4) G_{lm}(r_4,t_4, r_5,t_5) \right. \\
\left. - G_{lm}(r_1,t_1, r_2,t_2) \left[ v_{\nu\nu}(r_3,t_3) + v_{XC}(r_3,t_3) \right] \delta(r_3-r_4) \times \delta(t_5-t_4) \right\} G_{KS}(r_4,t_4, r_2,t_2). \tag{A.3}
\]

Next putting, \( r_2 = r_1, t_2 = t_1^*, l = m \), performing summation over orbital index \( l \), and taking into account the fact that the electron charge density is \( n(r_1,t_1) = G_{KS}(r_1,t_1, r_1^*,t_1^*) = \sum_l G_{ll}(r_1,t_1, r_1^*,t_1^*) \), one gets the time-dependent Sham-Schlueter equation generalized on the multi-orbital case:

\[
\int dr_3 dr_2 \left( \sum_l G_{ll}(r_1,t_1, r_2,t_2) \right) \left[ v_{\nu\nu}(r_3,t_3) + v_{XC}(r_3,t_3) \right] G(r_2,r_3) = \left( N_{\text{orb}} - 1 \right) n(r_1,t_1) + \int dr_3 dr_4 dr_5 dr_6 G_{KS}(r_1,t_1, r_5,t_5) \times \sum_l G_{ll}(r_2,t_2) G_{lm}(r_4,t_4, r_1^*,t_1^*) \tag{A.4}
\]

where \( N_{\text{orb}} \) is the number of orbitals.

Equation (A.4) can be formally solved as:

\[
v_{XC}(r_1,t_1) = (N_{\text{orb}} - 1) \int dr_2 v_{\nu\nu}(r_2,t_2) + v_{XC}(r_2,t_2) G_{KS}(r_1,t_1, r_2,t_2) + \int dr_2 dr_4 dr_5 dr_6 G_{KS}(r_1,t_1, r_2,t_2) \Sigma_{\nu\nu}(r_2,t_2, r_3,t_3) G_{ll}(r_3,t_3, r_4,t_4) \chi(r_4,t_4, r_1^*,t_1^*), \tag{A.5}
\]

where

\[
\chi(r_1,t_1, r_2,t_2) = \left( \sum_l G_{ll}(r_1,t_1, r_2,t_2) \right) G_{KS}(r_2,r_1^*,t_1^*). \tag{A.6}
\]

As seen from equations (A.5) and (A.6), to find the XC potential one needs three functions: the KS and many-body Green’s function and the XC self-energy. For the last function, we use the DMFT result:

\[
\sum_l G_{lm}(r_1,t_1, r_2,t_2) \approx \delta(r_1-r_2) \Sigma_{lm}(t_1,t_2), \tag{A.7}
\]

where \( \Sigma_{lm}(t_1,t_2) \) is the momentum-independent nonequilibrium DMFT self-energy that can be obtained by solving the DMFT problem for given external perturbation.

The expression for the KS Green’s function is [17]

\[
G_{KS}(r_1,t_1, r_2,t_2) = -i \sum_l \left[ \phi_l(r_1,t_1) \phi_{l^*}(r_2,t_2) \right] \left[ \theta(t_1-t_2) \theta(\varepsilon_F - \varepsilon_l) - \theta(t_2-t_1) \theta(\varepsilon_F - \varepsilon_l) \right], \tag{A.8}
\]

where \( \phi_l(r_1,t_1) \) is the TDDFT KS wave function \( l \) is the state index (orbital, momentum, spin, etc.), and \( \varepsilon_F \) is the Fermi energy.

Thus, with approximation equations (A.7) and expressions (A.6) and (A.8), equation (A.5) can be regarded as the expression for the XC potential in terms of \( G_{lm}(r_1,t_1, r_2,t_2) \). To find
the last function, and hence $v_{\text{XC}}(r_1 t_1)$, one can use a supplementary to equation (A.5) Dyson equation (A.3).

In principle, the system of equations (A.3) and (A.5) can be solved exactly for given $\phi_l(r_1 t_1)$ and $\Sigma_{l\nu}(t_1 - t_2)$. In practice, however, such a solution (that involves also calculation of $\phi_l(r_1 t_1)$ by solving the KS equation) is very computationally expensive. Similar, to the one-orbital case [17], a reasonable approximation for the many-body Green’s function is

$$G_{lm}(r_1 t_1, r_2 t_2) = \delta_{lm} G_{\text{KS}}(r_1 t_1, r_2 t_2). \quad (A.9)$$

Indeed, as seen from equation (A.4), one can look for the solution for $G$ iteratively expanding it ‘in powers’ of $\Sigma_{l\nu}(r_1 t_1, r_3 t_3) + v_{\text{XC}}(r_3 t_3) \delta(r_3 - r_1) \delta(t_3 - t_1)$.

In this case, equation (A.9) is the lowest-order approximation for the many-body Green’s function. From the solution of the static Sham-Schluter equation it follows that in many cases the approximation (A.9) is rather accurate (see, e.g. [49] and references therein). Thus, we propose to use it for TDDFT+DMFT as well. The above approximation thus gives:

$$v_{\text{XC}}(r_1 t_1) = (N_{\text{orb}} - 1) \int d r_2 d t_2 \tilde{\chi}^{-1} (r_1 t_1, r_2 t_2) \eta (r_2 t_2)$$

$$+ \int d r_2 d t_2 d r_3 d t_3 d r_4 d t_4 \tilde{\chi}^{-1} (r_1 t_1, r_3 t_4)$$

$$\times G_{\text{KS}} (r_4 t_4, r_2 t_2) \left( \sum_l \sum_{l\nu} (r_2 t_2, r_3 t_3) \right) G_{\text{KS}} (r_3 t_3, r_4 t_4^\dagger) .$$

(A.10)

where

$$\tilde{\chi} (r_1 t_1, r_2 t_2) = N_{\text{orb}} G_{\text{KS}} (r_1 t_1, r_2 t_2) G_{\text{KS}} (r_2 t_2, r_1 t_1^\dagger) .$$

(A.11)

To summarize, for practical purposes we propose an expression for the XC potential given by equation (A.5), where all unknown functions are defined by equations (A.6)–(A.9).

Further improvement of the accuracy of the potential can be systematically obtained by taking into account the higher-order term corrections for $G_{lm}(r_1 t_1, r_3 t_3)$ in equation (A.3), or possibly go beyond the perturbation theory algorithm. Again, to go beyond DMFT (to include the momentum-dependence of the self-energy), one can use the momentum-dependent Dynamical Vertex correction to $\Sigma_{l\nu}$ in equation (A.5).

### Appendix B. TDDFT and the excitation spectrum of the one-band Hubbard model

Below we give details of the calculation of the TDDFT excitation spectra in figure 2(a).

To calculate the spectra, we used the Casida equation [42] for excitations $\omega$, which can be written as

$$[\varepsilon - \varepsilon']^2 \delta_{ZZ} \delta_{Z'}^2 + 2 \sqrt{\varepsilon - \varepsilon'} K_{\varepsilon', \varepsilon'}(\omega) \sqrt{\varepsilon - \varepsilon'} = \delta_{z Z} \delta_{z' Z'} \omega^2 .$$

(B.1)

where $\varepsilon$, $\varepsilon'$ and $\varepsilon''$, $\varepsilon''$ are the DFT states with the energies above and below the Fermi level, correspondingly, and

$$K_{\varepsilon', \varepsilon'}(\omega) = \int \int \psi_\alpha^*(r') \psi_{\alpha'}(r') f_{\text{XC}}(r, r'; \omega) \psi_\alpha(r) \psi_{\alpha'}(r') d r d r'$$

(B.2)

are the matrix with respect to pairs of the occupied-unoccupied states, defined by the XC kernel $f_{\text{XC}}(r, r'; \omega)$ and the DFT KS wave functions $\psi$. We considered the paramagnetic case. In general, the indices $\alpha$, $\alpha'$ and $\varepsilon$, $\varepsilon''$ incorporate the values of the energy (momentum), spin, orbital momentum and other quantum numbers. To obtain the wave functions, we solved the DFT problem for the solid bulk cubic-cell hydrogen by
using the Quantum Espresso package [50] with the following input: cell dimension $a = 3.7807$ Bohr, LDA-PZ XC potential, US pseudopotentials, energy cutoff 60 Ry and $9 \times 9 \times 9$ $k$-point mesh. The resulting DOS (figure B1) is in a good agreement with the Gaussian DOS used in the case of the one-band Hubbard model in the main text.

Similarly, the spectrum of the lowest-energy band of the hydrogen system (corresponding to the one-band Hubbard model free band), figure B2, can be fitted with the hopping parameter $\tau = 1.3$ eV (figure B3). Thus the hydrogen wave function can be used for a rather accurate solution of the Casida equation for the Hubbard model.

**Appendix C. Nonequilibrium DMFT calculations**

The nonequilibrium DMFT calculations on the Keldysh time contour were performed in order to obtain first the time-dependent distribution function

$$n(k,t) = -i \sum_\sigma G_{\sigma \sigma}^<(k,t,t+\delta),$$

(C.1)

where the lesser Green’s functions $G_{\sigma \sigma}^<(k,t_1,t_2)$ are obtained from the expressions for the retarded $G_{\sigma \sigma}^R(k,t_1,t_2) = -i \theta (t_1 - t_2) \left\{ \bar{c}_{\sigma}(t_1), c_{\sigma}(t_2) \right\}$, and the Keldysh $G_{\sigma \sigma}^K(k,t_1,t_2) = -i \left\{ \bar{c}_{\sigma}(t_1), c_{\sigma}(t_2) \right\}$ Green’s functions as

$$G_{\sigma \sigma}^<(k,t_1,t_2) = \frac{1}{2} \left[ G_{\sigma \sigma}^R(k,t_1,t_2) - G_{\sigma \sigma}^R(k,t_1,t_2) + G_{\sigma \sigma}^K(k,t_1,t_2) \right]$$

(C.2)

(in the expressions before the last equation, $\theta (t_1 - t_2)$ is the theta-function and $\left\{ \ldots \ldots \right\}$ and $\left[ \ldots \ldots \right]$ correspond to the anti-commutation and commutation of the operators, respectively).

To obtain the three functions on the right hand side of equation (C.2) one can use the perturbation theory solution for the Dyson equation for the time-ordered Green’s function on the Keldysh time contour

$$G_{\sigma \sigma}^>(k,t_1,t_2) = G_{\sigma \sigma}^{(0)}(t_1,t_2) + \Sigma_{\sigma \sigma}^{(2)}(k,t_1,t_2) G_{\sigma \sigma}^{(0)}(t_1,t_2),$$

(C.3)

where the contour-ordered matrix Green’s functions are

$$\tilde{G}_{\sigma \sigma}^>(k,t_1,t_2) = \left( \begin{array}{cc} G_{\sigma \sigma}^R & G_{\sigma \sigma}^K \\ 0 & G_{\sigma \sigma}^K \end{array} \right)(t_1,t_2),$$

(C.4)

and the local matrix self-energy in the second order perturbation theory is

$$\Sigma_{\sigma \sigma}^{(2)}(k,t_1,t_2) = U^2 (1 - n_\sigma) n_\sigma \sum_\delta \left( \begin{array}{cc} G_{\sigma \sigma}^{(0)} & G_{\sigma \sigma}^{(0)} \\ G_{\sigma \sigma}^{(0)} & G_{\sigma \sigma}^{(0)} \end{array} \right)(t_1,t_2).$$

(C.5)

The zero-order perturbation theory Green’s functions used in equations (C.3) and (C.4) are

$$G_{\sigma \sigma}^{(0)}(k,t_1,t_2) = G_{\sigma \sigma}^{(0)}(k,t_1,t_2) = i \left( -\theta (t_1 - t_2) - 2 \theta (t_2 - t_1) \right)$$

(C.6)

\[ e^{-i \oint_\gamma (\bar{\epsilon} - \delta \alpha (\bar{\epsilon})) d\bar{\epsilon} } \]

where $\bar{\alpha}(t) = -\theta (\tau - t) \theta (t) \bar{E}_{\sigma \sigma}$ is an external vector potential that corresponds to a pulse of duration $\tau$.

Finally, substituting the results of equations (C.2)–(C.6) into equation (C.1) and performing summation over the initially-unoccupied momenta one can obtain the excited charge density as function of time. In performing such a summation we can use the following decomposition:

$$\varepsilon (\bar{k} - \epsilon A(t)) = \varepsilon (\bar{k}) \cos (\epsilon A(t)) + \varepsilon (\bar{k}) \sin (\epsilon A(t)),$$

where $\varepsilon (\bar{k}) = -2i \sum_{i=1}^d \cos (k_i)$ and $\varepsilon (\bar{k}) = -2i \sum_{i=1}^d \sin (k_i)$ are two independent energy functions ($d$ is the system dimensionality), and then integrate over $\varepsilon$ and $\bar{k}$ that in the case of infinite dimensions have the Gaussian densities of states $\rho (\varepsilon) = 1/(\sqrt{2\pi}) \cdot \exp (-\varepsilon^2/\pi)$.

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**References**

[1] Anisimov V and Izyumov Yu 2010 *Electronic Structure of Strongly Correlated Materials* (Berlin: Springer) (https://doi.org/10.1007/978-3-642-04826-5)

[2] Loth S, Baumann S, Lutz C P, Eigler D M and Heinrich A J 2012 *Science* **335** 196

[3] Nakano M, Shibuya K, Okuyama D, Hatano T, Ono S, Kawasaki M, Iwasa Y and Tokura Y 2012 *Nature* **487** 459

[4] Tsunekawa S, Ishikawa K, Li Z, Kawazoe Y and Kasuya A 2000 *Phys. Rev. Lett.* **85** 3440

[5] Hailstone R K, Di Francesco A G, Leong J G, Allston T D and Reed K J 2009 *Phys. Chem. Chem. Phys.* **11** 13555

[6] Sundaresan A, Bhargavi R, Rangarajan N, Siddesh U and Rao C N R 2006 *Phys. Rev. B* **74** 161306

[7] Metzner W and Vollhardt D 1989 *Phys. Rev. Lett.* **62** 324

[8] Georges A, Kotliar G, Krauth W and Rozenberg M J 1996 *Rev. Mod. Phys.* **68** 13

[9] Anisimov V I, Poteryaev A I, Korotin M A, Anokhin A O and Kotliar G 1997 *J. Phys.: Condens. Matter* **9** 7359

[10] Lichtenstein A I and Katsnelson M I 1998 *Phys. Rev. B* **57** 6884

[11] Turkowski V, Kahir A, Nayyar N and Rahman T S 2012 *J. Chem. Phys.* **136** 114108

[12] Kotliar G, Savrasov S Y, Haule K, Oudovenko V S, Parcollet O and Marianetti C A 2006 *Rev. Mod. Phys.* **78** 865

[13] Held K, Nekrasov I A, Keller G, Eyert V, Blumer N, McMahan A, Pruschke T, Anisimov V I and Vollhardt D 2006 *Phys. Status Solidi b* **243** 2599

[14] Freericks J K, Turkowski V M and Zlatić V 2006 *Phys. Rev. Lett.* **97** 266408

[15] Aoki H, Tsuji N, Eckstein M, Kollar M, Oka T and Werner P 2014 *Rev. Mod. Phys.* **86** 779

[16] Ruge E and Gross E K U 1984 *Phys. Rev. Lett.* **52** 997

[17] Ullrich C A 2012 *Time-Dependent Density-Functional Theory: Concepts and Applications* (Oxford: Oxford
