Non-local and non-adiabatic effects in the charge-density response of solids: a time-dependent density functional approach

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The charge-density response of extended materials is usually dominated by the collective oscillation of electrons, the plasmons. Beyond this feature, however, intriguing many-body effects are observed. They cannot be described by one of the most widely used approaches for the calculation of dielectric functions, which is time-dependent density functional theory (TDDFT) in the adiabatic local density approximation (ALDA). Here we propose an approximation to the TDDFT exchange-correlation kernel which is non-adiabatic and non-local. It is derived in the homogeneous electron gas and implemented in the real system in a simple mean density approximation. This kernel contains effects that are completely absent in the ALDA; in particular, it correctly describes the double plasmon in the dynamic structure factor of sodium, and it shows the characteristic low-energy peak that appears in systems with low electronic density. It also leads to an overall quantitative improvement of spectra.

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The response to an external perturbation is an important tool to probe materials, and spectroscopic experiments play a crucial role [1]. Response properties are also of interest for applications: examples are the linear response to photons, which governs optical properties and hence the color of materials and their capability to absorb the sunlight, or the response to a beam of fast charges, which determines the stopping power [2]. A first attempt to interpret experimental findings or to predict response properties is based on the band structure, in an independent-particle picture. However, collective effects and signatures of strong correlation influence and sometimes even dominate electronic spectra, making their calculation a formidable intellectual challenge and a crucial tool for technological applications. In optical absorption spectra, the Coulomb interaction can lead to bound electron-hole pairs that create sharp excitonic peaks in the fundamental gap [3]. Other important spectroscopic quantities are the loss function and the dynamic structure factor as measured in electron energy loss spectroscopy or inelastic x-ray scattering (IXS) [3]; for example, the loss function exhibits the plasmon excitations and is therefore a key ingredient for plasmonics [4]. It is also crucial for theory, since the density-density response function enters the calculation of the correlation energy in the adiabatic connection formula [3, 6] and it is one of the main building blocks of many-body perturbation theory [7].

At first sight, spectra are often dominated by classical electrostatic (Hartree) effects for which the random phase approximation (RPA) is sufficient to capture the essential trends [1]. Beyond the RPA, the adiabatic local density approximation (ALDA) to time-dependent density functional theory (TDDFT) yields in general a small quantitative improvement [8]. However, for today’s needs often the resulting rough overall agreement is not sufficient. Details of the loss function are responsible for the shape of the satellite spectra in photoemission, and transmit therefore precious information, for example about doping [3]. Especially in correlated materials, even weak low-energy structures can dramatically influence materials properties [10]. Loss spectra can exhibit many-body effects such as lifetime broadening [11, 12] or double-plasmon excitations [13, 14], and in the low-density regime the spectral shape can be very different from the naively expected single plasmon peak, even in the homogeneous electron gas (HEG) [15].

To capture those intriguing effects, one has to go beyond the RPA and ALDA. Many advanced density functionals have been developed which can be directly applied to real materials; some of them are non-local [16, 18], others are non-adiabatic [19, 21]. However, most of them are meant to improve just one of the shortcomings of the ALDA; for example, long-range corrected functionals are often adiabatic [22, 23]. On the other side, more advanced calculations in the TDDFT framework exist in the HEG [15, 22, 24], but without an indication of how to use them in a real material. Interestingly, even beyond density functionals non-adiabatic effects are difficult to capture; in particular the widely used Bethe-Salpeter equation within many-body perturbation Green’s function theory is usually applied in an adiabatic approximation [3].

The aim of the present work is to close this gap. In the spirit of ground-state density functionals such as the LDA [30], our strategy consists of two parts: first, an advanced calculation in the HEG, and second, a ”connector”, namely a prescription of how to use the result in real materials. The enormous advantage of such a procedure is that the advanced calculation is done only once and forever; indeed our HEG results are freely available [31]. By using the very simple “connector” proposed in
this work, results for real materials are then obtained with a computational effort that is similar to the RPA. They show features that are extremely difficult to obtain otherwise, in particular double-plasmon excitations and the double-peak structure which characterizes strong correlation in the low-density regime.

For an illustration we concentrate on sodium as a prototype material. Fig. 1 shows experimental and various theoretical results for a moderate momentum transfer. In agreement with literature, the RPA dynamic structure factor exhibits one plasmon peak that is blue shifted with respect to experiment. The ALDA exhibits one plasmon peak that is not access spectra. Details of the method that we denote by the fact that even in sodium the effects of the crystal are not negligible: Fig. 1 shows that the ALDA result for the HEG is significantly different from the ALDA in sodium. In order to distinguish effects of the crystal from the description of many-body effects, let us first look at the HEG.

The first task is to calculate the density-density response function $\chi(q, \omega, n)$, which is a function of wavevec-
which satisfies many exact conditions, is wavevector- and frequency dependent. However, it has been derived for imaginary frequencies, and while it yields significant improvement in correcting RPA correlation energies \[^{[40]}\], its performance for spectroscopy is less obvious. We thus expect that the observed corrections with respect to the RPA are relevant, while there may still be small deviations from the (unknown) exact spectrum. In any case, Takada’s result represents probably today the best available benchmark. It is remarkably different from the RPA: there is a strong shift of spectral weight to lower energies, and a double peak structure appears.

The shift of spectral weight is at the origin of the so-called “ghost plasmon” (called “ghost exciton” in Ref. \[^{[14]}\]), which has been introduced by Takayanagi and Lipparini \[^{[41]}\] as a pole of the irreducible polarizability on the imaginary axis. It manifests itself through a negative frequency dependent. However, it has been derived for \[^{[17]}\], which contains the information about the non-interacting system, whereas the exchange-correlation kernel \(f_{xc}^{hom}\) describes interaction effects. Of course, it also depends on the system, i.e. in the case of the HEG \(f_{xc}^{hom}\) is a function of the density. Still, focusing on \(f_{xc}\) instead of the full \(\chi\) allows us to separate materials- and interaction-effects to a significant extent. Using the 2p2h results for \(\chi\), we therefore calculate \(f_{xc}^{hom}\) for densities ranging from \(r_s = 1\) to \(r_s = 6\) according to Eq. \[^{[1]}\]. Only the \(q \to 0\) limit is delicate because of lack of precision in the fitting procedure of the MC data. The easiest solution is to correct this limit using the static \(f_{xc}^{COEDF}(q)\) of Corradini et al. \[^{[17]}\], which should be close to exact in the static limit \[^{[42]}\].

The resulting table of 2p2h \(f_{xc}^{hom}\) \[^{[31]}\] has now to be used in the real systems: we have to devise the connector. In the case of ground-state calculations the canonical choice for the exchange-correlation potential \(v_{xc}(\mathbf{r})[n]\) is the LDA, based on the nearsightedness principle \[^{[43]}\]. Extensions based on some suitable density average around the local point \(\mathbf{r}\) have been also proposed \[^{[44, 45]}\]. The kernel \(f_{xc}(\mathbf{r}, \mathbf{r}'; \omega)\), however, is non-local and at least two regions (around \(\mathbf{r}\) and around \(\mathbf{r}'\)) or even a whole area indicated by these two points should give important contributions. If the pertinent area is larger than the scale of the density variation in the system, the canonical approximation should be to take the mean density \(\bar{\rho}\) of the system, rather than a somehow defined local density. Since a wavevector \(q \approx 0.5/a_0\) as used in Fig. \[^{[1]}\] would roughly correspond to a distance of \(2\pi/q = 4\pi a_0\), which is already large compared to the interatomic distance of \(7a_0\) in Na, we propose to adopt the mean density approximation (MDA) as simplest connector to import \(f_{xc}\) from the HEG into extended systems \[^{[16]}\]. In practice, this means that in the real system one has to solve the Dyson equation for \(\chi\) using the inhomogeneous \(\chi_0\) and \(f_{xc}^{hom}\) calculated at the mean density \(\bar{\rho}\) of the real system. This is the time-dependent MDA (TDMDA).

In order to get a feeling whether the choice between the local and the mean density is very delicate, we have calculated spectra for several systems using either the ALDA or the AMDA, which imports from the HEG the same static and local \(\delta(\mathbf{r} - \mathbf{r}')f_{xc}^{hom}(q \to 0, \omega = 0)\) as does the ALDA, but at the mean, instead of the local, density. In both cases \(\chi_0\) has been calculated using the LDA. For sodium (not shown) the spectra are on top of each other, which is not surprising. More interesting is silicon: it turns out that ALDA and AMDA are still very close, as can be seen in Fig. \[^{[6]}\]. If there is any difference, the tendency is rather in favor of the AMDA, which is confirmed by results in the supplemental material \[^{[39]}\]. This gives evidence that also in general the TDMDA is
FIG. 3. The dynamic structure factor of silicon at $q = 0.8 \, 1/a_0$ compared with IXS results of Weissker et al. [12]. Lines have the same meaning as in Fig. 4 but additionally the AMDA result is shown (blue dot-dashed).

an at least reasonable approximation, and we will adopt it in the following.

With the TDMDA, any whatsoever sophisticated interpolated or tabulated HEG kernel is easy to import and to use in real systems, including non-adiabatic ones. This allows us to calculate again sodium, now using our 2p2h kernel. For the ground-state calculation leading to $\chi_0$, we again adopt the LDA. The mean density used in $f_{xc}$ is that of the valence electrons, which are well separated from the core electrons. The result for $q = 0.532 \, a_0^{-1}$ is given in fig. The difference with respect to the 2p2h homogeneous result is mainly a significant redshift of the main plasmon. Of all the approximations shown, the 2p2h-TDMDA result has the best agreement with experiment. Since the double plasmon is only accessible by a frequency-dependent kernel, it merits particular attention; therefore the inset in Fig. 4 shows a zoom. The double plasmon contribution is clearly visible in the experiment and the theory, especially when we remove the gaussian broadening. The theoretical position is close to the homogeneous result and to experiment, and improves over the pioneering result of Sturm and Gusarov [13] by more than 1 eV.

In order to probe also the impact of the wavevector-dependence of the 2p2h-TDMDA kernel, Fig. 4 shows results for a larger wavevector, $q = 1.16 \, 1/a_0$. The 2p2h-TDMDA result is again better than the ALDA. In particular, it includes some lifetime damping. Similar improvement is obtained for silicon, as shown in the supplemental material [39].

In conclusion, we have shown that a nonlocal and dynamical 2p2h exchange-correlation kernel for TDDFT can be accurately built in the HEG and successfully used for the calculation of dynamic structure factors in real solids. The new kernel improves over existing approximations for the HEG, producing at the same time double-plasmon and “ghost-exciton” features that, so far, have been separately obtained through distinct approximations only [15, 34]. Moreover, our 2p2h kernel can be imported into real materials through a simple connector that is based on the mean electronic density. This severe approximation precludes its use in the present form in finite systems, and it cannot describe band gaps or bound excitons in insulators. However, it significantly improves the dynamic structure factor of simple metals and semiconductors, including double-plasmon resonances which are completely missed by standard TDDFT approximations. This implies that it could in principle also be used to improve many-body perturbation theory based on the screened Coulomb interaction, or total energy calculations using the adiabatic connection [3, 4]. Finally, we advocate that the very good quality of these results illustrates a general strategy that is very promising, as it allows one to separate dynamical correlation effects, which can be calculated and tabulated once for all in the HEG [31], from electronic structure features that are material specific but in principle easier to deal with.

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[1] W. Schülke, Electron Dynamics by Inelastic X-Ray Scattering, Oxford Series on Synchrotron Radiation (OUP Oxford, 2007).
