



Design of effective kernels for spectroscopy and molecular transport: Time-dependent current–density-functional theory

Matteo Gatti

Citation: *J. Chem. Phys.* **134**, 084102 (2011); doi: 10.1063/1.3558738

View online: <http://dx.doi.org/10.1063/1.3558738>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v134/i8>

Published by the [American Institute of Physics](http://www.aip.org).

Related Articles

Hybrid density functional/molecular mechanics studies on activated adsorption of oxygen on zeolite supported gold monomer

J. Chem. Phys. **135**, 244703 (2011)

Structure, electronic, and optical properties of TiO₂ atomic clusters: An ab initio study

J. Chem. Phys. **135**, 244704 (2011)

An empirical law for the band gaps of MgZnO nanowires

J. Appl. Phys. **110**, 124315 (2011)

Effects of composition and compositional distribution on the electronic structure of ZnSe_{1-x}Te_x ternary quantum dots

J. Appl. Phys. **110**, 123509 (2011)

A density functional theory study of structural, mechanical and electronic properties of crystalline phosphorus pentoxide

J. Chem. Phys. **135**, 234513 (2011)

Additional information on *J. Chem. Phys.*

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT



AIP Advances

Submit Now

Explore AIP's new
open-access journal

- Article-level metrics now available
- Join the conversation! Rate & comment on articles

Design of effective kernels for spectroscopy and molecular transport: Time-dependent current–density-functional theory

Matteo Gatti^{a)}

Nano-Bio Spectroscopy group, Dpto. Física de Materiales, Universidad del País Vasco, Centro de Física de Materiales CSIC-UPV/EHU-MPC and DIPC, E-20018 San Sebastián, Spain, European Theoretical Spectroscopy Facility (ETSF) and Laboratoire des Solides Irradiés, École Polytechnique, CNRS-CEA/DSM, F-91128 Palaiseau, France

(Received 21 December 2010; accepted 3 February 2011; published online 24 February 2011)

Time-dependent current–density-functional theory (TDCDFT) provides an, in principle, exact scheme to calculate efficiently response functions for a very broad range of applications. However, the lack of approximations valid for a range of parameters met in experimental conditions has so far delayed its extensive use in inhomogeneous systems. On the other side, in many-body perturbation theory accurate approximations are available, but at a price of a higher computational cost. In the present work, the possibility of combining the advantages of both approaches is exploited. In this way, an exact equation for the exchange–correlation kernel of TDCDFT is obtained, which opens the way for a systematic improvement of the approximations adopted in practical applications. Finally, an approximate kernel for an efficient calculation of spectra of solids and molecular conductances is suggested and its validity is discussed. © 2011 American Institute of Physics. [doi:10.1063/1.3558738]

The theoretical description of the response of an electronic system to a time-dependent perturbation is a key problem for many areas of physics and chemistry. Most spectroscopic experiments probe the elementary excitations of an electronic system through its linear response to an external electromagnetic field. Their theoretical interpretation is of primary interest for technological applications in condensed-matter physics, nanosciences, photochemistry, or biophysics. Similarly, response functions are essential, among many possible applications, also for the determination of the electrical conductivity or other transport coefficients in molecular electronic devices.

Therefore, one would like to devise a reduced theoretical framework, that is, at the same time, *reliable* and *efficient*, by calculating only the information needed to interpret and predict specific experimental measurements. Two prominent examples of such reduced approaches are many-body perturbation theory (MBPT) and density-functional-based theories. Key variables of the former are one- and two-particle Green's functions, $G(1, 2)$ and $G_2(1, 2, 3, 4)$ (1 is a shorthand notation for space, time, and spin indices $\mathbf{r}_1, t_1, \sigma_1$). Methods based on the Green's-function formalism reduce the complexity of the many-body wavefunction into the propagation and the interaction of renormalized quasiparticles. Their intuitive, direct contact with the initial problem of real interacting electrons makes it rather *easy* to introduce working approximations. A remarkably successful example is the solution of the Bethe–Salpeter equation (BSE) for the two-particle correlation function $L(1, 2, 3, 4) = -G_2(1, 2, 3, 4) + G(1, 3)G(2, 4)$ which has led to an important breakthrough by permitting, for in-

stance, an accurate calculation of electronic spectra of solids and nanosystems.¹ On the other hand, practical calculations at this level remain very demanding, even for nowadays' computers. An alternative pathway is instead based on the extension of the density-functional theory (DFT) to scalar time-dependent external potentials, $V_{\text{ext}}(\mathbf{r}, t)$, as in the time-dependent density-functional theory (TDDFT),² or to time-dependent vector potentials, $\mathbf{A}_{\text{ext}}(\mathbf{r}, t)$, as in the time-dependent current-density-functional theory (TDCDFT).^{3,4} When one needs only charge or current densities, $\rho(\mathbf{r}, t)$ and $\mathbf{j}(\mathbf{r}, t)$, these density-based methods identify the minimum content of information that one has to calculate in order to provide the searched answers. In the Kohn–Sham (KS) scheme,⁵ the many-body problem is reformulated very efficiently into a set of self-consistent noninteracting one-particle equations. For this reason, in the KS scheme the solution of the full many-body problem is made *simple* and its computational cost is very convenient. The main drawback is that it is generally very difficult to improve upon the simplest local-density approximations⁵ for the exact density functionals of the formal theory. In fact, after the first promising results,⁶ the development of TDCDFT in this field has been delayed by the lack of adequate approximations to the exchange–correlation (xc) vector potential \mathbf{A}_{xc} , beyond the local functional in the current density of Vignale and Kohn (VK),^{4,7} which is unfortunately valid only in a range of parameters that is often not met in experiments performed on inhomogeneous systems.^{8,9}

The present work aims at overcoming the limitations of the VK functional, by applying to TDCDFT the emerging successful strategy of combination of MBPT and density-functional approaches, in order to profit from the complementary advantages of both.^{10–14} In particular, we will derive an exact relation linking the unknown exchange–correlation tensor kernel f_{xc} to quantities that can be, in principle, accurately

^{a)} Author to whom correspondence should be addressed. Electronic mail: matteo.gatti@ehu.es. Present address: Centro Joxe Mari Korta, Avenida de Tolosa, 72, E-20018 San Sebastián, Spain.

calculated in MBPT. Moreover, we will show how it is possible to introduce suitable approximations to this exact relation opening the way to a broad class of applications and to a systematic way to improve the approximations adopted in TDCDFT calculations.

The Bethe–Salpeter equation for the irreducible polarization function $\tilde{L}(1, 2, 3, 4)$ reads¹⁵ (throughout the paper, integrals and sums are always done on repeated indices and atomic units are adopted)

$$\tilde{L}(1, 2, 3, 4) = L_0(1, 2, 3, 4) + L_0(1, 2, 5, 6)\tilde{\Xi}(5, 6, 7, 8)\tilde{L}(7, 8, 3, 4). \quad (1)$$

Here, $L_0(1, 2, 3, 4) = -iG(1, 3)G(4, 2)$ is the two-particle correlation function for independent particles and $\tilde{\Xi}(5, 6, 7, 8) = i\delta\Sigma(5, 6)/\delta G(7, 8)$ is the BSE kernel, which, e.g., accounts for excitonic effects in optical spectra. In standard BSE implementations the GW approximation¹⁶ for the self-energy Σ is adopted, where Σ is evaluated as a product of the one-electron Green's function G and the screened Coulomb interaction W . $\tilde{\Xi}$ is usually approximated as $\tilde{\Xi}(5, 6, 7, 8) = -W(5, 6)\delta(5, 7)\delta(6, 8)$. This amounts to neglecting the term $iG\delta W/\delta G$, which contains information about the change of the screening in the excitation and is considered to be small. Moreover, for W , one generally considers only a static screening of the Coulomb interaction v and L_0 is built with GW quasiparticle (QP) energies and KS wavefunctions. \tilde{L} is then linked to the correlation function L by a Dyson equation: $L = \tilde{L} + \tilde{L}vL$. Whereas the quantities of spectroscopic interest are, for instance, the two-point density–density and current–current response functions, $\chi_{\rho\rho}(1, 2) = \delta\rho(1)/\delta V_{\text{ext}}(2)$ and $\hat{\chi}(1, 2) = \delta\mathbf{j}(1)/\delta\mathbf{A}_{\text{ext}}(2)$, the BSE is an intrinsically four-point equation. In fact, in the BSE scheme, these two-point response functions can be obtained only as contractions of the four-point correlation function L , which has to be calculated in a first step. In many situations, as the ones we are interested herein, this clearly reveals to be a computational waste that one would like to avoid.

In TDCDFT the linear response of the current \mathbf{j} to an external vector potential \mathbf{A}_{ext} is⁴

$$\delta j_{\alpha}(1) = \frac{1}{c}\hat{\chi}_{s,\alpha\beta}(1, 2)\delta A_{s,\beta}(2), \quad (2)$$

where the Kohn–Sham vector potential \mathbf{A}_s is the sum of the external, Hartree, and exchange–correlation potentials: $\mathbf{A}_s(1) = \mathbf{A}_{\text{ext}}(1) + \mathbf{A}_{\text{H}}(1) + \mathbf{A}_{\text{xc}}(1)$, and $\hat{\chi}_s$ is the Kohn–Sham current–current response function. Similarly, the linear variation of the current can be calculated through the knowledge of the irreducible current–current response function $\hat{\chi}$:

$$\delta j_{\alpha}(1) = \frac{1}{c}\hat{\chi}_{\alpha\beta}(1, 2)[\delta A_{\text{ext},\beta}(2) + \delta A_{\text{H},\beta}(2)]. \quad (3)$$

Combining these two definitions, one immediately gets to a Dyson equation linking $\hat{\chi}_s$ with $\hat{\chi}$:

$$\hat{\chi}_{\alpha\beta}(1, 2) = \hat{\chi}_{s,\alpha\beta}(1, 2) + \hat{\chi}_{s,\alpha\lambda}(1, 3)\hat{f}_{\text{xc},\lambda\kappa}(3, 4)\hat{\chi}_{\kappa\beta}(4, 2), \quad (4)$$

where the exchange–correlation tensor kernel

$$\hat{f}_{\text{xc},\alpha\beta}(1, 2) = \frac{\delta A_{\text{xc},\alpha}(1)}{\delta j_{\beta}(2)} \quad (5)$$

has been introduced. Once, thanks to Eq. (4), the irreducible $\hat{\chi}$ has been calculated, the (reducible) response function $\hat{\chi}$ (hence, the spectra) can be obtained through

$$\hat{\chi}_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2, \omega) = \hat{\chi}_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2, \omega) - \hat{\chi}_{\alpha\lambda}(\mathbf{r}_1, \mathbf{r}_3, \omega) \times \frac{1}{\omega^2}\nabla_{3\lambda}\frac{1}{|\mathbf{r}_3 - \mathbf{r}_4|}\nabla_{4\kappa}\hat{\chi}_{\kappa\beta}(\mathbf{r}_4, \mathbf{r}_2, \omega). \quad (6)$$

The quality of the approximation adopted for the xc kernel Eq. (5) is, hence, fundamental for the accuracy of the final results.

As in TDDFT, also in TDCDFT, the effect of the xc kernel on the spectra calculated from the independent KS-particle response is twofold. The Kohn–Sham eigenvalues are known to underestimate the quasiparticle band gap of insulating systems due to the derivative discontinuity of the DFT xc potential.¹⁷ Hence, the xc kernel first has to provide a consistent band gap opening. And, second, as the BSE kernel $\tilde{\Xi}$, it has to describe electron–hole interactions. So, following Refs. 12 and 13, in order to make explicit these two aspects here we set $\hat{f}_{\text{xc},\alpha\beta} = \hat{f}_{\text{xc},\alpha\beta}^{(1)} + \hat{f}_{\text{xc},\alpha\beta}^{(2)}$, where $\hat{f}_{\text{xc},\alpha\beta}^{(1)}$ has the task of overcoming the KS band gap problem, while $\hat{f}_{\text{xc},\alpha\beta}^{(2)}$, for instance, accounts for excitonic effects in optical spectra, or dynamical corrections to the Landauer formula for the electronic conductance in quantum transport.¹⁸ Formally, we will now introduce a contraction operator $\Pi_{\alpha\beta}$:

$$\Pi_{\alpha\beta}L_0(1, 1', 2, 2') = \frac{1}{2i}\frac{1}{2i}[(\nabla_{1\alpha} - \nabla_{1\alpha}')(\nabla_{2\beta} - \nabla_{2\beta}')L_0(1, 1', 2, 2')]_{1'=1+, 2'=2+}, \quad (7)$$

in such a way that $\hat{\chi}_0$ is¹⁵

$$\hat{\chi}_{0,\alpha\beta}(1, 2) = \rho(1)\delta(1, 2)\delta_{\alpha\beta} + \Pi_{\alpha\beta}L_0(1, 1', 2, 2'). \quad (8)$$

$\hat{\chi}_0$ is built with QP ingredients instead of KS ones. In this way one has

$$[\hat{\chi}_s^{-1}]_{\alpha\beta}(1, 2) - [\hat{\chi}_0^{-1}]_{\alpha\beta}(1, 2) = \hat{f}_{\text{xc},\alpha\beta}^{(1)}(1, 2), \quad (9)$$

and then

$$[\hat{\chi}_0^{-1}]_{\alpha\beta}(1, 2) - [\hat{\chi}^{-1}]_{\alpha\beta}(1, 2) = \hat{f}_{\text{xc},\alpha\beta}^{(2)}(1, 2). \quad (10)$$

In many semiconductors, the difference between KS and QP can be accounted for by using a scissor operator that shifts rigidly upward the eigenvalues of the conduction with respect to valence bands. The use of a scissor operator is also a common practice in TDCDFT.^{9,19} The main point of interest in our discussion here is, hence, about $\hat{f}_{\text{xc},\alpha\beta}^{(2)}$.

Equation (10) leads to

$$\hat{\chi}_{\alpha\beta}(1, 2) = \hat{\chi}_{0,\alpha\beta}(1, 2) + \hat{\chi}_{0,\alpha\lambda}(1, 3)\hat{f}_{\text{xc},\lambda\kappa}^{(2)}(3, 4)\hat{\chi}_{\kappa\beta}(4, 2). \quad (11)$$

By definition, both TDCDFT and BSE yield the exact two-point response function $\hat{\chi}_{\alpha\beta}(1, 2) = \rho(1)\delta(1, 2)\delta_{\alpha\beta} + \Pi_{\alpha\beta}\tilde{L}(1, 1', 2, 2')$. Therefore, applying the contraction $\Pi_{\alpha\beta}$

to Eq. (1) and comparing the result with Eq. (11), one obtains

$$\hat{\chi}_{0,\alpha\lambda}(1, 3) \hat{f}_{xc,\lambda\kappa}^{(2)}(3, 4) \hat{\chi}_{\kappa\beta}(4, 2) = \Pi_{\alpha\beta} \{L_0(1, 1', 3, 4) \tilde{\Xi}(3, 4, 5, 6) \tilde{L}(5, 6, 2, 2')\}, \quad (12)$$

which can be solved for the TDCDFT kernel $\hat{f}_{xc,\alpha\beta}^{(2)}$ giving

$$\hat{f}_{xc,\alpha\beta}^{(2)}(1, 2) = [\hat{\chi}_0^{-1}]_{\alpha\lambda}(1, 3) \Pi_{\lambda\kappa} [L_0(3, 3', 4, 5) \times \tilde{\Xi}(4, 5, 6, 7) \tilde{L}(6, 7, 8, 8')] [\hat{\chi}^{-1}]_{\kappa\beta}(8, 2). \quad (13)$$

Equation (12) is a generalized Sham–Schlüter equation,^{17,20} which relates in an *exact* manner TDCDFT quantities with MBPT ones, opening the way to possible systematic improvements in the design of new approximations for the xc kernel of TDCDFT. The design of operative approximations is, in fact, easier in the context of MBPT, as proved by the accurate results obtained from the solution of the BSE.¹ Then, thanks to Eq. (13), working approximations of MBPT can be mapped into the more efficient TDCDFT scheme, where one would prefer to solve the equations. In particular, when approximating Eq. (13), no assumptions of locality in the current density for functional dependence of the vector potential \mathbf{A}_{xc} are explicitly needed, leading to approximate kernels that can be employed also in the range of parameters where the VK func-

tional is formally not valid, namely, for ground-state densities and induced current densities not slowly varying in space, and in the region below the particle–hole continuum of the homogeneous electron gas.

Within the TDDFT framework, such a mapping strategy has already demonstrated to be a successful approach and has led to the introduction of an xc kernel, known as Nanoquanta kernel,^{10–14,20} which has shown to provide the same level of accuracy as the BSE in a wide range of spectroscopy applications, from solids to finite molecular chains.^{21,22} Therefore, by discussing a first practical application of the exact Eq. (13), here we will show that a similar approach for the design of new approximations to the tensor xc kernel of TDCDFT is also possible. In fact, one expects to find a similar level of accuracy also for current–current response functions. By a first-order linearization of Eq. (13), where for the various response functions one uses the independent-particle versions, and taking for $\tilde{\Xi}$ the statically screened W , as usually done in BSE, one obtains

$$\hat{f}_{xc,\alpha\beta}^{(2)}(1, 2) = -[\hat{\chi}_0^{-1}]_{\alpha\lambda}(1, 3) \Pi_{\lambda\kappa} [L_0(3, 3', 4, 5) \times W(4, 5) L_0(4, 5, 6, 6')] [\hat{\chi}_0^{-1}]_{\kappa\beta}(6, 2). \quad (14)$$

More explicitly,

$$\hat{f}_{xc,\alpha\beta}^{(2)}(1, 2) = -[\hat{\chi}_0^{-1}]_{\alpha\lambda}(1, 3) \lim_{3' \rightarrow 3} \left[\frac{1}{2i} (\nabla_{3\lambda} - \nabla_{3'\lambda}) L_0(3, 3', 4, 5) W(4, 5) \frac{1}{2i} (\nabla_{6\kappa} - \nabla_{6'\kappa}) L_0(4, 5, 6, 6') \right] [\hat{\chi}_0^{-1}]_{\kappa\beta}(6, 2), \quad (15)$$

where the presence of three-point current–density and density–current response functions, $\chi_{j\rho}^3(3; 4, 5)$ and $\chi_{\rho j}^3(4, 5; 6)$, becomes apparent. Hence, the kernel Eq. (15) can be also be rewritten in a compact way as

$$\hat{f}_{xc}^{(2)} = -\hat{\chi}_0^{-1} \chi_{0,j\rho}^3 W \chi_{0,\rho j}^3 \hat{\chi}_0^{-1}. \quad (16)$$

This is a new approximation of the TDCDFT \hat{f}_{xc} kernel that has to be understood as an orbital functional, hence an implicit functional of the ground-state density. In this sense it is more flexible than the VK approximation to the vector potential \mathbf{A}_{xc} , which instead is an explicit functional of the induced current and the ground-state density. In practical applications, the response functions appearing in Eq. (16) are built using QP energies, calculated in the GW approximation or using a scissor-operator correction to KS eigenvalues, and KS wavefunctions (which in many situations are a good approximation to QP wavefunctions). The product $\hat{\chi}_0 \hat{f}_{xc}^{(2)} \hat{\chi}_0$ is then inserted in a symmetrized version of the Dyson equation (11): $\hat{\chi} = \hat{\chi}_0 (\hat{\chi}_0 - \hat{\chi}_0 \hat{f}_{xc}^{(2)} \hat{\chi}_0)^{-1} \hat{\chi}_0$, which can be solved for $\hat{\chi}$.

The spatial derivatives that appear in Eq. (15) do not modify the structure of the poles of the response functions in the frequency domain. Therefore, this approximation of the TDCDFT tensor xc kernel can benefit from the same cancellation of poles and zeroes of the response functions that

has been shown to be essential for the Nanoquanta kernel of TDDFT (Ref. 23) [provided that the response functions entering Eq. (15) are built with QP energies]. Since any scalar potential with a gauge transformation can be represented by a longitudinal vector potential, Eq. (15) can be thought as a generalization of the Nanoquanta TDDFT f_{xc} kernel to the calculation of the response to any kind of time-dependent external vector potential.

In general, the relation between the tensor $\hat{f}_{xc}^{(2)}$ TDCDFT kernel and the scalar $f_{xc}^{(2)}$ TDDFT kernel is rather involved.²⁴ Its first-order linearization in $\hat{f}_{xc}^{(2)}$ reads²⁵

$$f_{xc}^{(2)} = -\frac{c}{\omega^2} \chi_{0,\rho\rho}^{-1} \nabla \hat{\chi}_0 \hat{f}_{xc}^{(2)} \hat{\chi}_0 \nabla \chi_{0,\rho\rho}^{-1}. \quad (17)$$

This approximation is consistent with the linearization of Eq. (13) that leads to Eq. (16). Hence, by inserting the TDCDFT kernel $\hat{f}_{xc}^{(2)}$ [Eq. (16)] in Eq. (17) and using the density continuity equation,²⁶ the TDDFT $f_{xc}^{(2)}$ kernel becomes

$$f_{xc}^{(2)} = -\chi_{0,\rho\rho}^{-1} \chi_{0,\rho\rho}^3 W \chi_{0,\rho\rho}^3 \chi_{0,\rho\rho}^{-1}, \quad (18)$$

which is, in a compact form, the Nanoquanta TDDFT kernel.^{10–14,20} This equivalence, to the first order in $\hat{f}_{xc}^{(2)}$, between the tensor kernel Eq. (16) and the scalar kernel Eq. (18) supports the validity of the new approximation for the TDCDFT kernel (16), thanks to the excellent results found

using the Nanoquanta TDDFT kernel Eq. (18).²¹ Moreover, this represents a further alternative derivation of the expression (18) of the Nanoquanta kernel that exploits the possibility of mapping approximations developed in the framework of TDCDFT into scalar TDDFT kernels.^{24,25,27,28}

In situations where the screening of the Coulomb interaction is ineffective, W can be approximated with v and the GW approximation reduces to Hartree–Fock. In this case, Eq. (15) reduces to an exact-exchange approximation for $\hat{f}_{xc}^{(2)}$ (which has been already worked out for the homogeneous electron gas in Ref. 14). On the other side, it has been demonstrated within the TDDFT framework that the lack of screening of the long-range contribution of the Coulomb interaction in the kernel implicitly overestimates both QP band gaps and excitonic effects, leading to pathologies in optical spectra of semiconductors.²⁹ These pathologies can be cured by taking into account the screening of the Coulomb interaction, as done in Eq. (15).

For optical spectra of solids, relevant is the long-wavelength limit $\mathbf{q} \rightarrow 0$ of the $\mathbf{G} = \mathbf{G}' = 0$ element of the xc kernel written in the reciprocal space: $\hat{f}_{xc,\alpha\beta}^{(2)}(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}', \omega)$, where \mathbf{G} and \mathbf{G}' are reciprocal lattice vectors. In this limit the $\hat{f}_{xc}^{(2)}$ kernel Eq. (15) in insulators becomes³⁰ $\hat{\alpha}/\omega^2$, where $\hat{\alpha}$ is a tensorial constant. Moreover, the static W is proportional to $1/\epsilon_\infty$, where ϵ_∞ is the static dielectric constant. This implies that for the $\mathbf{q} \rightarrow 0$ limit, also $\hat{\alpha}$ is proportional to $1/\epsilon_\infty$, suggesting that in isotropic systems α could be used as a fitting parameter for the calculation of optical spectra in solids.^{10,31} In this limit, the tensor kernel becomes completely local, contrary to the scalar TDDFT kernel that is ultranlocal³² and has a $1/q^2$ asymptotic behavior in the long-wavelength limit.^{10,33}

Here, it is interesting also to note that even though for the BSE kernel a static approximation for W is adopted, the resulting $\hat{f}_{xc}^{(2)}$ kernel in Eq. (15), in general, is naturally frequency dependent.³⁴ This is a consequence of the conversion of the spatial nonlocality into a frequency dependence,²⁰ associated to the reduction of the number of degrees of freedom, when one passes from the four-point \tilde{L} to the two-point $\tilde{\chi}$ and from the four-point $\tilde{\Xi}$ to the two-point \hat{f}_{xc} .

Since the validity of the new $\hat{f}_{xc}^{(2)}$ kernel Eq. (15) is not confined to the weakly inhomogeneous limit, it could be, for instance, used also to study dynamical corrections in the weak bias limit of the Landauer formula in molecular transport for nanoscale junctions.¹⁸ In fact, so far the calculated corrections have been based on the VK functional, which is strictly valid only for slowly varying densities in a high-frequency regime. Therefore, an accurate estimate of these effects is still under debate.³⁵ On the other side, the renormalization of molecular electronic KS levels at metal–molecule interfaces³⁶ in the present context is accounted for by the term $\hat{f}_{xc}^{(1)}$.

In conclusion, in the present work we have derived an exact equation for the xc kernel \hat{f}_{xc} of TDCDFT, which allows one to map well established working approximation of MBPT into the more efficient TDCDFT scheme. Due the lack of an appropriate approximate xc kernel, so far, TDCDFT could not be used for calculating optical spectra in good agreement with experiments.^{8,9,19} So, in analogy with the successful results obtained in the TDDFT case,²¹ we have suggested a practical

approximation for \hat{f}_{xc} and discussed its validity for the calculation of electronic spectra of solids and nanosystems and dc conductances in molecular devices.

We are grateful to Lucia Reining, Valerio Olevano, and Ilya Tokatly for their comments and suggestions on many aspects of this work. We acknowledge the support from the European Union's (EU's) 7th framework program through the ETSF e-I3 infrastructure project (Grant No. 211956), the Spanish MEC (FIS2007-65702-C02-01), ACI Promociona (ACI2009-1036), Grupos Consolidados UPV/EHU del Gobierno Vasco (IT-319-07), and ETORTEK projects.

- ¹G. Onida, L. Reining, and A. Rubio, *Rev. Mod. Phys.* **74**, 601 (2002).
- ²E. Runge and E. K. U. Gross, *Phys. Rev. Lett.* **52**, 997 (1984); M. Petersilka, U. J. Gossmann, and E. K. U. Gross, *ibid.* **76**, 1212 (1996).
- ³S. K. Ghosh and A. K. Dhara, *Phys. Rev. A* **38**, 1149 (1988).
- ⁴G. Vignale and W. Kohn, *Phys. Rev. Lett.* **77**, 2037 (1996).
- ⁵W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- ⁶M. van Faassen, P. L. de Boeij, R. van Leeuwen, J. A. Berger, and J. G. Snijders, *Phys. Rev. Lett.* **88**, 186401 (2002).
- ⁷G. Vignale, C. A. Ullrich, and S. Conti, *Phys. Rev. Lett.* **79**, 4878 (1997).
- ⁸M. van Faassen, P. L. de Boeij, R. van Leeuwen, J. A. Berger, and J. G. Snijders, *J. Chem. Phys.* **118**, 1044 (2003); M. van Faassen and P. L. de Boeij, *ibid.* **120**, 8353 (2004); C. A. Ullrich and K. Burke, *ibid.* **121**, 28 (2004).
- ⁹J. A. Berger, P. L. de Boeij, and R. van Leeuwen, *Phys. Rev. B* **75**, 035116 (2007).
- ¹⁰L. Reining, V. Olevano, A. Rubio, and G. Onida, *Phys. Rev. Lett.* **88**, 066404 (2002).
- ¹¹F. Sottile, V. Olevano, and L. Reining, *Phys. Rev. Lett.* **91**, 056402 (2003); G. Adragna, R. Del Sole, and A. Marini, *Phys. Rev. B* **68**, 165108 (2003); A. Marini, R. Del Sole, and A. Rubio, *Phys. Rev. Lett.* **91**, 256402 (2003).
- ¹²R. Stubner, I. V. Tokatly, and O. Pankratov, *Phys. Rev. B* **70**, 245119 (2004).
- ¹³F. Bruneval, F. Sottile, V. Olevano, R. Del Sole, and L. Reining, *Phys. Rev. Lett.* **94**, 186402 (2005).
- ¹⁴U. von Barth, N. E. Dahlen, R. van Leeuwen, and G. Stefanucci, *Phys. Rev. B* **72**, 235109 (2005).
- ¹⁵G. Strinati, *Riv. Nuovo Cimento* **11**, 1 (1988).
- ¹⁶L. Hedin, *Phys. Rev.* **139**, A796 (1965).
- ¹⁷L. J. Sham and M. Schlüter, *Phys. Rev. Lett.* **51**, 1888 (1983).
- ¹⁸M. Koentopp, K. Burke, and F. Evers, *Phys. Rev. B* **73**, 121403(R) (2006); G. Vignale and M. Di Ventra, *ibid.* **79**, 014201 (2009).
- ¹⁹P. L. de Boeij, F. Kootstra, J. A. Berger, R. van Leeuwen, and J. G. Snijders, *J. Chem. Phys.* **115**, 1995 (2002).
- ²⁰M. Gatti, V. Olevano, L. Reining, and I. V. Tokatly, *Phys. Rev. Lett.* **99**, 057401 (2007).
- ²¹S. Botti, A. Schindlmayr, R. Del Sole, and L. Reining, *Rep. Prog. Phys.* **70**, 357 (2007).
- ²²D. Varsano, A. Marini, and A. Rubio, *Phys. Rev. Lett.* **101**, 133002 (2008).
- ²³F. Sottile, M. Marsili, V. Olevano, and L. Reining, *Phys. Rev. B* **76**, 161103(R) (2007).
- ²⁴V. U. Nazarov, J. M. Pitarke, Y. Takada, G. Vignale, and Y.-C. Chang, *Phys. Rev. B* **76**, 205103 (2007).
- ²⁵V. U. Nazarov, G. Vignale, and Y.-C. Chang, *J. Chem. Phys.* **133**, 021101 (2010).
- ²⁶The continuity equation is strictly valid only if conserving approximations for the response functions are used. See Ref. 15.
- ²⁷N. T. Maitra and M. van Faassen, *J. Chem. Phys.* **126**, 191106 (2007).
- ²⁸V. U. Nazarov, G. Vignale, and Y.-C. Chang, *Phys. Rev. Lett.* **102**, 113001 (2009); V. U. Nazarov, I. V. Tokatly, S. Pittalis, and G. Vignale, *Phys. Rev. B* **81**, 245101 (2010).
- ²⁹F. Bruneval, F. Sottile, V. Olevano, and L. Reining, *J. Chem. Phys.* **124**, 144113 (2006).

- ³⁰In the present approximation and considering for all the quantities only the $\mathbf{G} = \mathbf{G}' = 0$ element, while W is static and proportional to $1/q^2$, at low frequencies current–current response functions are proportional to ω^2 and density–current or current–density response functions are proportional to ω and q .
- ³¹S. Botti, F. Sottile, N. Vast, V. Olevano, L. Reining, H-C. Weissker, A. Rubio, G. Onida, R. Del Sole, and R. W. Godby, *Phys. Rev. B* **69**, 155112 (2004).
- ³²G. Vignale, *Phys. Lett. A* **209**, 206 (1995).
- ³³P. Ghosez, X. Gonze, and R. W. Godby, *Phys. Rev. B* **56**, 12811 (1997).
- ³⁴N. T. Maitra, K. Burke, and C. Woodward, *Phys. Rev. Lett.* **89**, 023002 (2002).
- ³⁵J. Jung, P. Bokes, and R. W. Godby, *Phys. Rev. Lett.* **98**, 259701 (2007); N. Sai, M. Zwolak, G. Vignale, and M. Di Ventura, *ibid.* **98**, 259702 (2007).
- ³⁶J. B. Neaton, M. S. Hybertsen, and S. G. Louie, *Phys. Rev. Lett.* **97**, 216405 (2006); K. S. Thygesen and A. Rubio, *ibid.* **102**, 046802 (2009).