Optical spectra of solids obtained by time-dependent density functional theory with the jellium-with-gap-model exchange-correlation kernel

Paolo E. Trevisanutto,^{1,2} Aleksandrs Terentjevs,¹ Lucian A. Constantin,³ Valerio Olevano,^{2,4} and Fabio Della Sala^{1,3}

¹National Nanotechnology Laboratory, Istituto Nanoscienze-CNR, Via per Arnesano 16, I-73100 Lecce, Italy

²European Theoretical Spectroscopy Facility (ETSF)

³Center for Biomolecular Nanotechnologies @UNILE, Istituto Italiano di Tecnologia, Via Barsanti, I-73010 Arnesano, Italy

⁴Institut Néel, CNRS and UJF, Grenoble, France

(Received 24 October 2012; revised manuscript received 31 January 2013; published 31 May 2013)

Within the framework of *ab initio* time-dependent density functional theory (TD-DFT), we propose a static approximation to the exchange-correlation kernel based on the jellium-with-gap model. This kernel accounts for electron-hole interactions, and it is able to address both strongly bound excitons and weak excitonic effects. TD-DFT absorption spectra of several bulk materials (both semiconductor and insulators) are reproduced in very good agreement with the experiments and with a low computational cost.

DOI: 10.1103/PhysRevB.87.205143

PACS number(s): 78.20.-e, 71.10.-w, 71.45.Gm

I. INTRODUCTION

The theoretical description of the optical properties of materials by first-principles calculations is one of the classical issues in solid-state physics. After photon absorption, the excitonic effects, driven by the electron and hole (e-h) interactions, are principal actors, rendering the *ab initio* computational description demanding. The most successful approach is, so far, based on many-body perturbation theory: the *GW* self-energy accounts for electron-electron (e-e) many-body effects in the band structure calculations, whereas the Bethe-Salpeter equation (BSE) is solved to introduce the electron-hole (e-h) interactions.¹ This accurate method has a limited applicability to large systems due to its high computational cost.

Time-dependent density functional theory (TD-DFT) is another theory for the exact treatment of excited states. Similar to ground-state DFT, its main drawback is to properly approximate the unknown dynamic exchange-correlation (xc) kernel f_{xc} , which should account for both e-e and e-h interactions. From the very first attempt, the homogeneous electron gas (HEG) model system had been employed in construction of xc kernels,^{2,3} and one of the most used approaches was derived from local-density approximation (LDA) xc potential v_{xc} in the *static* regime, i.e. the adiabatic LDA (ALDA).² ALDA has been successfully applied to molecules and clusters, but it usually becomes inappropriate in solids, where the improvements with respect to the random-phase approximation (RPA; with the trivial $f_{xc} = 0$) are negligible. The introduction of short-range nonlocality, as in a generalized gradient approximation $(GGA)^4$ or in a non-LDA $(NLDA)^5$ approach, does not improve the charge-charge interaction description with respect to LDA or RPA optical spectra. The main reason for this failure resides in the missed ultralongrange behavior, $1/|\mathbf{r} - \mathbf{r}'|$ or $1/q^2$ in reciprocal space, which is absent in HEG and HEG-based kernels. On the other hand, the introduced empirical long-range contribution (LRC) kernel, $f_{xc} = (\alpha/q^2),^{6-8}$ with α found to be related to the screening, correctly reproduces e-h excitonic effects, but it is limited to semiconductors and small gap insulators. Very recently, renewed interest in this issue has been boosted by two new approaches. In the first one, the *bootstrap* kernel⁹ extends the LRC kernel to a matricial form and proposes a heuristic form for the LRC weight in terms of the screening which has to be calculated self-consistently. This method has been successfully applied to a wide range of bulk materials. In Refs. 10 and 11, starting from the meta-GGA xc functional, the authors derive an f_{xc} which presents an α/q^2 term, with α calculated from the meta-GGA parametrizations. Finally, the *nanoquanta* kernel,^{12–16} adapted from the four-point BSE kernel in the TD-DFT framework, achieves high accuracy, although with much higher computational cost than the other aforementioned kernels.

In this paper, we propose a nonempirical static xc kernel based on the *jellium-with-gap* model (JGM).^{17–22} In the past, this model was used to determine qualitative and quantitative insights for semiconductors. Hereafter we assess that, in spite of its simplicity, this model forcing the jellium to have a gap extends the ALDA kernel, reaching very good agreement with experimental findings. Moreover, in the spirit of DFT, this kernel is a *density functional* $f_{xc}[n](E_g)$. The approach is *ab* initio in the same regard as the LRC, bootstrap, and nanoquanta methods, once first-principles calculations (like GW) are used to estimate good E_g . We show that this kernel properly describes both weak excitonic effects in semiconductors and bound excitons in ionic insulators, without requiring any frequency dependence. It provides absorption spectra in good agreement with experiments. Moreover, this approach is as computationally expensive as standard ALDA. This paper is organized as follows. In Secs. II and III we introduce the theoretical derivation of the model and computational details. In Sec. IV we present and discuss the JGM results. Finally, conclusions are drawn in Sec. V.

II. THEORETICAL DERIVATION

In linear-response TD-DFT, the central quantity is the density-density response function $\chi(q,\omega)$ (written in reciprocal space q and frequency ω), which is calculated by the Dyson equation:

$$\chi^{-1}(q,\omega) = \chi_0^{-1}(q,\omega) - f_{xc}(q,\omega) - v(q),$$
(1)

where $\chi_0(q,\omega)$ is the independent-particle Kohn-Sham response function and $v(q) = 4\pi/q^2$ is the Coulomb potential.

The dielectric function ϵ is related to the density-density response via the relation $\epsilon = 1 - v\chi$.

For the HEG (or jellium) model, which is the most important reference for simple metals, very accurate f_{xc} kernels have been developed^{23–25} by fulfilling important exact constraints (e.g., compressibility and the third-frequency-moment sum rules) and using diffusion Monte Carlo input.

Here we extend those parametrizations to the case of the JGM model. In this work, we restrict ourselves to the static $\omega = 0$ case and work in the adiabatic approximation. In the JGM model at density *n* and with energy gap E_g , the RPA static dielectric constant (i.e., with $f_{xc} = 0$) is²⁰

$$\epsilon_0^{\text{JGM}-\text{RPA}}(q \to 0; n, E_g) = 1 + \frac{4\pi n}{E_g^2}.$$
 (2)

Equation (2) is qualitatively different from the HEG counterpart, being *finite* for a nonzero band gap. Similar models are widely used to describe dielectric properties of semiconductors.²⁶

In analogy to Eqs. (20) and (21) of Ref. 27, a static kernel for the JGM kernel (f_{xc}^{JGM}) is approximated as

$$f_{xc}^{\text{JGM}}(q \to 0; n, E_g) \simeq -\frac{4\pi}{q^2} \frac{1}{\left(\epsilon_0^{\text{JGM}-\text{RPA}} - 1\right)} = -\frac{E_g^2}{nq^2}.$$
 (3)

We then extend the kernel of Ref. 23 to the JGM imposing condition (3), obtaining

$$f_{xc}^{\text{JGM}}(q;n,E_g) = \frac{4\pi}{q^2} B'(n,E_g) \Big[e^{-k'_{n,E_g}q^2} - 1 \Big] - \frac{4\pi}{k_F^2} \frac{C'(n,E_g)}{1+1/q^2},$$
(4)

with

$$B'(n, E_g) = \frac{B(n) + E_g}{1 + E_g}, \quad C'(n, E_g) = \frac{C(n)}{1 + E_g},$$
 (5)

$$k'_{n,E_g} = k_n + \frac{1}{4\pi q^2} \frac{E_g^2}{nB'(n,E_g)},$$
(6)

where k_n , B(n), and C(n) are defined in Ref. 23, constructed from exact HEG constraints $[k_n \text{ and } C(n)]$ and from HEG diffusion Monte Carlo data²⁴ [B(n)]; k_F is the Fermi wave vector.

The JGM kernel has been constructed in order to satisfy the following properties: (i) $f_{xc}^{\text{JGM}}(q;n,E_g=0) \equiv f_{xc}^{\text{HEG}}(q;n)$, where $f_{xc}^{\text{HEG}}(q,n)$ is the HEG static kernel defined by Eq. (12) of Ref. 23, which is very accurate for the HEG correlation energy per particle *at every* wave vector q and recovers the accurate (exact) RPA long-range effective interaction. (ii) $f_{xc}^{\text{JGM}}(q;n,E_g \to \infty) \to -v(q)$, such that this kernel gives a vanishing correlation energy (E_c) in the limit of *perfect* insulators $(E_g \to \infty)$. Moreover, due to the construction of $B'(n,E_g)$ and $C'(n,E_g)$, we observe, by applying the so-called adiabatic-connection fluctuation-dissipation theorem,²³ that $E_c \approx \text{const}/E_g + O(E_g^{-2})$ in the limit of large band gap. This is one of the most important exact constraints for the JGM which was derived from perturbation theory.²¹ (iii) $\lim_{q\to 0} f_{xc}^{\text{JGM}}(q;n,E_g) \approx -\alpha^{\text{JGM}}(n,E_g)/q^2$, where

$$\alpha^{\text{JGM}}(n, E_g) = 4\pi B'(n, E_g) [1 - e^{-E_g^2/4\pi n B'(n, E_g)}].$$
(7)

Equation (7) approaches E_g^2/n [see Eq. (3)] for small E_g (semiconductor case). Thus, in the $q \to 0$ optical limit, we recover an LRC α/q^2 behavior. (iv) $\lim_{q\to\infty} f_{xc}^{\text{JGM}}(q; n, E_g) =$

 $-\frac{4\pi}{k_F^2}C'(n,E_g)$. This limit is unknown in the JGM, with the exception of the cases $E_g \to 0$ and $E_g \to \infty$, for which the behavior of our kernel becomes exact. We recall that both RPA and ALDA fail badly in this limit.²³

In order to use the JGM kernel equation (4) for real inhomogeneous bulk systems, we first consider its real-space form $f_{xc}^{\text{JGM}}(|\mathbf{r} - \mathbf{r}'|; n, E_g)$. We then use the DFT density $n(\mathbf{r})$ in place of the constant density n, whereas as a first approximation (valid for bulk systems investigated in this work) we approximate E_g to the fundamental band gap of materials; thus the kernel in the real space depends explicitly on the position [i.e., $f_{xc}^{\text{JGM}}(|\mathbf{r} - \mathbf{r}'|, \mathbf{r}; E_g)$]. Then, we obtain the Fourier transform in the reciprocal space with the shape $\tilde{f}_{xc}^{\text{JGM}}(|\mathbf{q} + \mathbf{G}|, \mathbf{G} - \mathbf{G}'; E_g)$, with \mathbf{q} being a vector in the first Brillouin zone and \mathbf{G} , \mathbf{G}' being reciprocal lattice vectors. The kernel still needs symmetrization in \mathbf{G}, \mathbf{G}' . In previous works^{5,6} the symmetrization adopted for the Coulombian term of the dielectric matrix,²⁸ we perform the symmetrization in reciprocal space:

$$f_{xc}(\mathbf{q}, \mathbf{G}, \mathbf{G}'; E_g) = \tilde{f}_{xc}^{\text{JGM}}(\sqrt{|\mathbf{q} + \mathbf{G}||\mathbf{q} + \mathbf{G}'|}, \mathbf{G} - \mathbf{G}'; E_g).$$
(8)

Equation (8) shows the following properties: (a) It reduces to Eq. (4) in the homogeneous case. (b) The head, $\mathbf{G} = \mathbf{G}' = 0$, element of the kernel matrix in the optical limit approaches $f_{xc}(q \to 0, 0, 0; E_g) \approx -\langle \alpha \rangle q^{-2}$, where

$$\langle \alpha \rangle \equiv \int \alpha^{\text{JGM}}(n(\mathbf{r}), E_g) d\mathbf{r},$$
 (9)

which differs from α^{JGM} evaluated with the average density \bar{n} . Thus, an explicit value for the LRC α parameter is provided as the mean value of α^{JGM} in the unit cell. $\langle \alpha \rangle$ depends on the band gap, and it is density functional (i.e., it depends on the density inhomogeneity). (c) In the $q \rightarrow 0$ limit, the wings of the kernel matrix $f_{xc}(q, 0, \mathbf{G'} \neq 0; E_g) = f_{xc}(q, \mathbf{G} \neq 0, 0; E_g) \propto$ $1/|\mathbf{q} + \mathbf{G}||\mathbf{q} + \mathbf{G'}|$ are O(1/q), and the remaining elements are regular.^{29,30} (d) The ALDA-HEG terms are present in the kernel, and they can play a role only at finite q, i.e., in energy-loss function calculations, where ALDA is already a good approximation.³¹ (e) The computational cost is very low, comparable to standard ALDA.

Finally, we note that, as in all previous approaches,^{7–9} in this paper we focus only on the e-h interaction, f_{xc}^{e-h} , excitonic effects part of the full f_{xc} , while we simulate the effect of the e-e, f_{xc}^{e-e} , self-energy effects part by calculating χ_0 with a scissor operator (so) band-gap-corrected DFT-LDA electronic structure, $E^{so} = E_g - E_g^{\text{LDA}}$, where E_g is set to the experimental band gap.³² The same parameter, E_g , is used in the JGM kernel. Instead of the experimental band gap, the *GW* one can be used as well, so as to refer to first-principles calculations. The use of scissor operator instead of *GW* energy corrections does not affect the final results for materials investigated in this work, as already shown in the literature.^{7–9,12} Nevertheless, the problem to find the f_{xc}^{e-e} kernel able to provide self-energy effects and the right E_g (which is also an input of the JGM kernel) is once again postponed. Hereafter, the RPA results are meant to be scissor operator shifted.

III. COMPUTATIONAL DETAILS

The absorption spectrum is calculated as the $q \to 0$ limit of the imaginary part of the macroscopic dielectric function $\text{Im}\epsilon^M(q,\omega)$, defined as $\epsilon^M(q,\omega) = 1/\epsilon_{G=G'=0}^{-1}(q,\omega)$.

We have implemented the f_{xc} kernel in the linear-response TD-DFT DP code.³³ The DFT ground-state calculations are performed utilizing ABINIT. All TD-DFT calculations are performed from LDA-DFT ground-state calculations sampled up to a (32 32 32) Monkhorst-Pack *k*-point-shifted grid except for LiF and MgO, where a (60 60 60) mesh grid was used. The experimental lattice parameters (in a.u.) used are Si, 10.217; LiF, 7.62; Ge, 10.70; GaAs, 10.68; SiC, 8.24; C, 6.75; MgO, 7.96. We used the Troullier-Martins norm-conserving pseudopotentials. In the LRC-type JGM, the number of **G** vectors for the spectrum calculations.^{8,34} In the full-kernel calculations we used up to $N_{\rm G} = 181$.

IV. RESULTS AND DISCUSSION

The JGM kernel and its extension to inhomogeneous periodic systems [Eq. (8)] is based on several well-defined and physical approximations which need to be tested in real situations. As a first test we applied Eq. (8) to calculate the optical absorption of several bulk systems.

In Fig. 1 we show our calculated spectra for semiconductors: Ge, Si, and GaAs. These materials present weakly bound excitons near the onset of the continuum. Previous works⁸ have shown that e-h excitonic effects increase the oscillator strength of the lowest-energy part of spectra.

Ge is the smallest band gap bulk system which we considered. Excitonic effects are modest, and the RPA calculation (dashed line) is already in good agreement with the experiment (green dots). Nevertheless, the TD-DFT JGM kernel (solid line) introduces improvements, enhancing the oscillator strength of the first peak at 2.2 eV.



FIG. 1. (Color online) Imaginary part of the macroscopic dielectric function $\epsilon_2(\omega)$ for bulk Ge, Si, and GaAs. Red dashed line: RPA results with scissor-operator shifting. Black solid line: TD-DFT with the JGM kernel. Green dots are the experimental absorption spectra: Ge from Ref. 35, Si from Ref. 36, and GaAs from Ref. 37. The same notation has been utilized in the following figures. Ge and Si are obtained with relative Gaussian and Lorentzian broadening of 0.02. Absolute Gaussian broadening of 0.1 eV was used for GaAs.



FIG. 2. (Color online) As in Fig. 1, but for SiC and diamond bulk. Experimental absorption spectra are SiC from Ref. 38 and diamond from Ref. 39. Absorption spectra are obtained with absolute Lorentzian broadening: SiC, 0.3 eV; diamond, 0.2 eV.

On the other hand, in Si e-h interactions have important effects on the spectral weight of excitations, and they determine a different absorption shape with respect to RPA. The JGM kernel increases the oscillator strength of the first feature at 3.4 eV, where the RPA shoulder becomes a well-defined peak, as in the experiment.

Similar to Si, in GaAs excitonic effects shift the spectral weight to lower energies. The JGM kernel moves the peak near 5 eV towards the experimental position, and it increases the intensity of the structure at 3 eV, therefore achieving a very good agreement with the experiment.

More severe tests are diamond and SiC (Fig. 2), where the larger band gap E_g increases the JGM kernel strength of excitonic effects. In SiC, the RPA peak at 8 eV is enhanced and redshifted in the TD-DFT result, achieving an almost perfect overlap with the experimental peak. The higher-energy peak at 9 eV is reproduced at the correct experimental position, although it is quite overestimated.

In diamond, the position of the main RPA peak is correctly redshifted by the TD-DFT, overlapping the experimental position, whereas the left shoulder is slightly too intense. Overall, TD-DFT calculations show a smooth and realistic description of optical spectra of both SiC and diamond.

LiF and MgO are wide-gap insulators, with a strongly bound exciton occurring in the band gap.^{8,13} They represent a severe test for any TD-DFT kernel. In Fig. 3, we show the calculated absorption spectra for LiF and MgO in comparison with the experiment. Here we report the results for both the full matrix JGM kernel (solid line) and also its $\mathbf{G} = \mathbf{G}'$ diagonal part only (dot-dashed line) in order to show the effect of nondiagonal elements. As a result of the strong excitonic effects on the absorption spectra, the RPA calculations completely miss both the main peaks (LiF: 12.6 eV and MgO: 7.2 eV) and the resonant-state features at higher energy.

In LiF, the diagonal TD-DFT JGM kernel is able to conjure the main excitonic peak, although it is blueshifted by 0.5 eV with respect to the experiment and the intensity



FIG. 3. (Color online) As in Fig. 1, but for LiF and MgO. Experimental absorption spectra are LiF from Ref. 40 and MgO from Ref. 41. Here the dot-dashed magenta line is JGM TD-DFT with only diagonal f_{xc} . Absorption spectra are obtained with an absolute Gaussian broadening of 0.3 eV for both LiF and MgO. The BSE absorption (blue dash-dotted line) spectra have been added from Refs. 13 and 42, respectively, for LiF and MgO.

is overestimated. The second experimental peak at 14.5 eV is well captured as a shoulder, and the remaining part of the experimental absorption spectrum is well reproduced. High-energy features at about 20 eV are present, whereas the spurious BSE (blue dash-dotted line) peak at 21 eV (Ref. 13) is absent here. When inserting nondiagonal kernel elements, we have further excitonic strength that redshifts the main peak up to 12.80 eV, improving the agreement with the experiment. The frequency dependence of f_{xc} has been considered crucial for the correct description of the absorption spectra of wide-band-gap insulators where the strongly bound excitons are appearing.^{13,34} However, as shown in Ref. 9 and in this work, a static nonlocal kernel can also correctly address the e-h interactions in solid-state systems.

In MgO, the strongly bound exciton is accompanied by high-energy resonant peaks. The BSE absorption spectrum extracted from Ref. 42 has also been shown for comparison. JGM TD-DFT results display the strongly bound excitonic peak at 7.2 eV, in agreement with both experimental and BSE findings. As in the LiF case, the height of the exciton is very intensive. The similarity to LiF continues with the subsequent peak at 10.3 eV: in JGM TD-DFT calculations, this becomes an artifact shoulder which recovers the experimental peak shape only in the final part and where BSE results show a better agreement. The overall behavior at high energies is in better agreement with experiments than BSE results: both energy and intensity peaks are well described. Nondiagonal elements in the JGM kernel slightly decrease the intensity of the main peak at 7.2 eV, while the 13.50-eV peak is redshifted to 13.30 eV, in better agreement with the 13-eV experimental result.

Finally, we stress that the most important contribution to the absorption spectra is given by the head of the matrix kernel, which, in the case of a static kernel, such as the one presented in this work, is just an LRC-type α/q^2 , and all our results can be well reproduced by this simple (nonempirical) LRCtype kernel. In Table I, we show a comparison between JGM $\langle \alpha \rangle$ values and previous α estimations: Results are well in agreement each other. This agreement begins to deviate for wider-band-gap bulk systems where the inhomogeneity of the

TABLE I. The fundamental band gap E_g ,³² $\alpha_{\rm fit}$ from the best LRC fits, $\alpha_{\rm Boot}$ from the bootstrap kernel, and $\langle \alpha \rangle$ from Eq. (11).

	E_g (eV)	$\alpha_{\rm fit}{}^{\rm a}$	$\alpha_{\rm fit}{}^{\rm b}$	$\alpha_{\rm Boot}^{\rm c}$	$\langle \alpha \rangle$
Ge	0.74	0.08		0.036	0.06
Si	1.17	0.20	0.13	0.085	0.11
GaAs	1.42	0.22	0.15	0.1	0.22
SiC	2.36	0.50	0.20	0.327	0.23
С	5.48	0.60	0.28	0.487	0.68
MgO	7.67	1.8			3.33
LiF	14.2	2.15	1.5	6.65	7.76

^aReference 8 (LiF was estimated by the formula $\alpha = 4.615/\varepsilon^{\text{stat}} - 0.213$).

^bReference 34.

^cReference 9.

density is enhanced, resulting in much higher values of $\langle \alpha \rangle$ for MgO and LiF.

V. CONCLUSIONS

In conclusion, we have found that a simple, nonempirical, and physical static xc kernel derived from the jellium-with-gap model provides accurate optical absorption spectra of a wide range of bulk solids (from metals to strong insulators). The physics of this kernel relies on the validity of JGM, in spite of HEG, to represent real solids within TD-DFT. This kernel can be easily implemented in any solid-state code and with the same computational cost as TD-DFT ALDA calculations. In this work we tested bulk systems, but the JGM kernel can also be applied to more complex systems, such as heterostructures or metal-organic interfaces, where the energy gap itself will depend on the position. The JGM kernel will correctly modulate the LRC contribution according to the local value of the gap. Further investigation will be devoted to energy-loss spectra at finite q. As shown in Ref. 10, the meta-GGA rung of Jacob's ladder can provide, in principle, good absorption spectra due to the term α/q^2 present in the meta-GGA xc kernel. However, nonempirical functionals with exact constrains that ensure good optical properties are still lacking, whereas highly empirical kernels may provide good absorption spectra for regular semiconductors but not for insulators. On the other hand, both bootstrap and JGM kernels give a remarkable accuracy for the optical spectra of bulk materials even for wide-band-gap insulators with low computational costs. In particular, the JGM kernel, which relays on a well-known physical model system, provides a simple and analytical formula for the α coefficient [see Eq. (9)] that may also be useful in further development of more accurate meta-GGAs. The JGM kernel presented in this paper was constructed with only a few exact constraints. Moreover, diffusion Monte Carlo kernel calculations are needed for this model in order to insert the frequency dependence.

ACKNOWLEDGMENT

This work was partially funded by the ERC Starting Grant FP7 Project DEDOM (Grant No. 207441).

OPTICAL SPECTRA OF SOLIDS OBTAINED BY TIME- ...

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