# First-principles optical response of semiconductors and oxide materials

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(Received 22 March 2011; published 31 May 2011)

The calculation of the optical gaps of a series of nonmagnetic direct and indirect semiconductors and simple oxides is addressed using an all-electron perturbative method based on density-functional theory. Hybrid exchange, in both the Kohn-Sham spectrum and the perturbative response, is shown to be essential to achieve an accuracy comparable to experimental estimates for all systems studied, including those exhibiting excitonic transitions at the absorption edge. In agreement with existing evidence it is shown that a proper description of excitonic features relies crucially on the nonlocality of the response equations.

DOI: 10.1103/PhysRevB.83.195325 PACS number(s): 78.20.−e, 71.15.Mb, 71.35.−y, 78.40.Fy

## I. INTRODUCTION

The ability of density-functional theory[1,2] (DFT) to address reliably, and often quantitatively, the calculation of ground-state properties of molecules and condensed-phase systems (including structure, dynamics, and thermodynamic stability) is widely documented. With few, if important, cases in which poor performance of standard DFT implementations is expected (e.g., strongly correlated materials, spin-unsaturated systems, bond breaking processes), DFT is usually considered a *predictive* theory of the electronic structure of wide classes of materials. Additionally, at variance with higher-level "*ab initio*" methods, DFT offers a number of advantages, including ease of implementation within a variety of basis sets and numerical schemes, excellent scaling with system size, and unparalleled generality in its range of applications.[3]

The extension of DFT to excited states is far less developed, especially in condensed-phase calculations. Rigorously, standard DFT is *exclusively* a theory of the ground state.[4] Frequently, however, and without further justification, empty levels or bands (obtained from the lowest canonical eigenvalues of a local, self-consistent, Kohn-Sham potential) are nonetheless interpreted as excited electronic states, within the Born-Oppenheimer and classical-nuclei approximations. This approximation often yields surprisingly accurate results, not only in molecules, but also in periodic systems,[5,6] provided sufficiently accurate models for the exchange-correlation functional are used, or semiempirical corrections applied to the Kohn-Sham excitation spectrum. Evidence has in fact been put forward that, in finite systems and for exchange-correlation potentials approaching the exact limit, differences in energy between virtual and occupied Kohn-Sham levels can rigorously be interpreted as physically meaningful "relaxed" one-particle excitation energies, similar to quasiparticle energies in Green's-function theory.[7,8] This last finding points to the existence of interesting and potentially far-reaching analogies between exact Kohn-Sham theory and quasiparticle theory.[9,10] At the same time it highlights the inadequacy of DFT, even in its exact limit, as a theory for excited states beyond the independent-particle approximation. A consistent description of the full optical response of a molecular or condensed-phase system therefore necessarily implies extending DFT beyond its one-particle (Kohn-Sham) formulation, to include one- (quasiparticle screening) and two-particle (screened particle-hole attraction) correlations. Both contributions are important in modeling phenomena such as photoinduced electron transfer, exciton formation and charge migration in solids, and photoluminescence, as well as in predicting accurate optical-absorption spectra.

In the solid state, many-body perturbation theory extensions of DFT have been proposed since the late 1980s, and have now evolved to a high level of accuracy and generality. In these approaches, quasiparticle energies are typically estimated from a set of Kohn-Sham bands, computed within the local-density approximation (LDA), using approximate, possibly non-self-consistent, models for the electronic self-energy, as in the popular GW method.[11] Screened particle-hole interactions are then taken into account by solving the Bethe-Salpeter equation (BSE) for the two-particle Green's function. Two-particle correlations are therefore accounted for potentially very accurately in the full GW + BSE method, and optical spectra computed using this route are typically directly comparable to experimental data.[9,10]

As an alternative to Green's-function based methods, time-dependent DFT[9,12–15] (TD-DFT) was proposed in the early 1990s as a rigorous, formally exact theory for excited states, which, similar to the GW + BSE method accounts quantitatively for screened particle-hole interactions. Within the TD-DFT formalism, the many-body response of the electrons is described by a response kernel $f = f_{\mathrm{H}} + f_{\mathrm{xc}}$, containing the response (at all orders) of the Hartree ($f_{\mathrm{H}}$) and exchange-correlation ($f_{\mathrm{xc}}$) potentials to an external time-dependent perturbation. The latter quantity, which in general is unknown and has to be replaced by physically motivated models, is both nonlocal in space and frequency dependent.

Typical implementations of TD-DFT resort to the so-called adiabatic approximation,[16] in which the frequency dependence

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of $f_{xc}$ is neglected. In addition, the response of the Kohn-Sham potential is usually limited to first order (linear-response approximation). The calculation of excitation energies can then be cast as a generalized eigenvalue problem, using the well-known random-phase approximation (RPA)-matrix formalism[17] of molecular quantum physics, which is then solved either directly or using iterative algorithms. This approach has been found to be sufficiently accurate for computing optical properties of molecules (at least in those cases in which only valence excitations were involved), including excited-state energies,[13,14,18–20] structure,[21–25] and dynamics,[22,26,27] but to give considerably lower quality absorption spectra in infinite periodic systems. This "scale up catastrophe"[15] of TD-DFT has been attributed to the preponderance of the $f_{xc}$ contribution, for which only approximate forms are available, over the Hartree response kernel in periodic systems[9] (the opposite is true for molecules).

A second major hurdle in the application of the RPA-matrix formalism or its variants to crystalline periodic systems is the explicit simultaneous dependence of each element in the RPA-like coupling matrix on more than one **k** point of the first Brillouin zone, as shown in Ref. 17. This makes the size of the eigenvalue problem prohibitive for fully three-dimensional periodic systems. In this context, TD-DFT based methods that avoid construction and explicit diagonalization of large matrices coupling independent-particle excitations (see, e.g., Refs. 28–31) may be computationally preferable, and are therefore of potential major interest in solid-state applications.

In this work we propose a straightforward and consistent approach for the calculation of optical spectra of crystalline systems that addresses some of the issues of TD-DFT and related theories for periodic systems, improving their reliability, computational efficiency, and scaling with system size. Our approach is formally equivalent to the solution of a TD-DFT RPA-matrix equation within the adiabatic and linear-response approximations (as we explicitly prove in the Appendix). The coupling between **k** points is, however, accounted for through the self-consistent determination of the response potential and (linear) density-matrix response at each frequency.[32] This is similar to a standard self-consistent coupled-perturbed calculation, as in common quantum chemical applications,[33–35] extended to an infinite periodic system. This scheme is also related to the method proposed by Petersilka and coworkers[18,36] for the calculation of excitation energies from the poles of a many-body susceptibility function obtained from the solution of a Dyson-like equation. In our case, however, direct inversion of a large matrix is not required. Our method is also closely related to the well-known coupled-perturbed Hartree-Fock (CP-HF) approach of molecular physics,[37] and formally (although not practically) equivalent to the recently developed Liouvillian superoperator approach for the calculation of the dynamical polarizability of Refs. 29–31.

The paper is organized as follows. In Sec. II we provide a brief derivation of the working equations used in this work. Details of the calculation are given in Sec. III. The main results are discussed in Sec. IV. In the Appendix we demonstrate the equivalence of our method with the standard coupling-matrix formulation of TD-DFT (and therefore, indirectly, with the approach of Refs. 29–31).

## II. THEORY

The equation of motion of the Fock (or Kohn-Sham) operator $\mathbf{F}^{\mathbf{k}}$ in the presence of an external time-dependent perturbation is given by[35]

$$\mathbf{F}^{\mathbf{k}}\mathbf{C}^{\mathbf{k}} - i\frac{\partial}{\partial t}\mathbf{S}^{\mathbf{k}}\mathbf{C}^{\mathbf{k}} = \mathbf{S}^{\mathbf{k}}\mathbf{C}^{\mathbf{k}}\mathbf{E}^{\mathbf{k}}, \tag{1}$$

where $\mathbf{C}^{\mathbf{k}}$ is a matrix of crystal orbital (CO) coefficients, $\mathbf{S}^{\mathbf{k}}$ is the overlap matrix, and $\mathbf{E}^{\mathbf{k}}$ contains the orbital energies. All matrices are in the atomic-orbital (AO) representation, with **k** indicating the crystal quasimomentum quantum number. We use atomic units, and we have set $\hbar = 1$ for convenience of notation. Each CO $\psi_i(\mathbf{r},\mathbf{k})$ is a combination of $N$ Bloch functions (BFs) $\phi_\mu(\mathbf{r},\mathbf{k})$,

$$\psi_i(\mathbf{r},\mathbf{k}) = \sum_{\mu}^{N} C_{\mu i}^{\mathbf{k}}\phi_\mu(\mathbf{r},\mathbf{k}). \tag{2}$$

The BFs are properly symmetrized linear combinations of atomic orbitals, each of which is expressed in terms of a set of atom centered Gaussian basis set functions $\chi_\mu(\mathbf{r}-\mathbf{g})$,

$$\phi_\mu(\mathbf{r},\mathbf{k}) = N^{-1/2}\sum_{\mathbf{g}}^{N} e^{i\mathbf{k}\cdot\mathbf{r}}\chi_\mu(\mathbf{r}-\mathbf{g}), \tag{3}$$

where the sum is over the real-lattice vectors **g**, and $N \to \infty$. Greek indices are used throughout for AOs, and Roman indices for COs. Equation (1) is formally derived from Frenkel's variational principle, and it has therefore to be solved subject to the orthonormalization condition

$$\frac{\partial}{\partial t}\mathbf{C}^{\mathbf{k}\dagger}\mathbf{S}^{\mathbf{k}}\mathbf{C}^{\mathbf{k}} = \mathbf{0}. \tag{4}$$

In the presence of a monochromatic optical field oscillating at a frequency $\pm\omega$,

$$\lambda_\omega^a = \lambda_{+\omega}^a e^{+i\omega t} + \lambda_{-\omega}^a e^{-i\omega t} \tag{5}$$

(with $a = x,y,z$), the coupling between electronic motion and the external (electric) field components $\lambda_{\pm\omega}^a$ introduces an additional term in the electronic Hamiltonian given by (again in atomic units)

$$\hat{H}' = \lambda_{\pm\omega}^a \hat{r}^a, \tag{6}$$

where $\hat{r}^a$ is a Cartesian component of the dipole operator. For periodic systems, this is given by[38,39]

$$\hat{r}^a = i e^{i\mathbf{k}\cdot\mathbf{r}}\nabla_{k_a} e^{-i\mathbf{k}\cdot\mathbf{r}}. \tag{7}$$

A working expression for matrix elements of this operator is given below [see Eq. (27)], and its formulation with a Gaussian basis set is described, e.g., in Ref. 40.

For clarity, we remark that in Eq. (5) and in all equations below, $\pm\omega$ have to be interpreted as *fixed* frequencies at which all other $\omega$-dependent properties have to be determined. In the linear-response approximation, the matrices appearing in Eq. (1) are expanded in the perturbative parameters $\lambda_{\pm\omega}^a$ according to

$$\mathbf{M}_\omega^{\mathbf{k}} = \underline{\mathbf{M}}^{\mathbf{k}} + \lambda_{+\omega}^a \mathbf{M}_{+\omega}^{\mathbf{k},a} e^{+i\omega t} + \lambda_{-\omega}^a \mathbf{M}_{-\omega}^{\mathbf{k},a} e^{-i\omega t}, \tag{8}$$

where $\mathbf{M}^{\mathbf{k},a}_{\pm\omega} = \mathbf{F}^{\mathbf{k},a}_{\pm\omega}, \mathbf{C}^{\mathbf{k},a}_{\pm\omega}, \mathbf{E}^{\mathbf{k},a}_{\pm\omega}$, and $\underline{\mathbf{M}}^{\mathbf{k}} = \underline{\mathbf{F}}^{\mathbf{k}}, \underline{\mathbf{C}}^{\mathbf{k}}, \underline{\mathbf{E}}^{\mathbf{k}}$ are the matrices solving the stationary, unperturbed Schrödinger equation

$$\underline{\mathbf{F}}^{\mathbf{k}}\underline{\mathbf{C}}^{\mathbf{k}} = \underline{\mathbf{S}}^{\mathbf{k}}\underline{\mathbf{C}}^{\mathbf{k}}\underline{\mathbf{E}}^{\mathbf{k}}, \tag{9}$$

and $\mathbf{M}^{\mathbf{k},a}_{\pm\omega} \equiv \partial \boldsymbol{M}^{\mathbf{k}}/\partial\lambda^{a}_{\pm\omega}$. For fixed nuclei, $\partial\mathbf{S}^{\mathbf{k}}/\partial\lambda^{a}_{\pm\omega} = \mathbf{0}$, therefore $\mathbf{S}^{\mathbf{k}} = \underline{\mathbf{S}}^{\mathbf{k}}$.

Substitution of the relevant matrices from Eq. (8) into Eq. (1) and truncation of the resulting expression to first order in $\lambda^{a}_{\pm\omega}$ gives the two equations

$$\mathbf{F}^{\mathbf{k},a}_{+\omega}\underline{\mathbf{C}}^{\mathbf{k}} + \underline{\mathbf{F}}^{\mathbf{k}}\mathbf{C}^{\mathbf{k},a}_{+\omega} + \omega\mathbf{C}^{\mathbf{k},a}_{+\omega} = \underline{\mathbf{S}}^{\mathbf{k}}\mathbf{C}^{\mathbf{k},a}_{+\omega}\underline{\mathbf{E}}^{\mathbf{k}} + \underline{\mathbf{S}}^{\mathbf{k}}\underline{\mathbf{C}}^{\mathbf{k}}\mathbf{E}^{\mathbf{k},a}_{+\omega}, \tag{10}$$

$$\mathbf{F}^{\mathbf{k},a}_{-\omega}\underline{\mathbf{C}}^{\mathbf{k}} + \underline{\mathbf{F}}^{\mathbf{k}}\mathbf{C}^{\mathbf{k},a}_{-\omega} - \omega\mathbf{C}^{\mathbf{k},a}_{-\omega} = \underline{\mathbf{S}}^{\mathbf{k}}\mathbf{C}^{\mathbf{k},a}_{-\omega}\underline{\mathbf{E}}^{\mathbf{k}} + \underline{\mathbf{S}}^{\mathbf{k}}\underline{\mathbf{C}}^{\mathbf{k}}\mathbf{E}^{\mathbf{k},a}_{-\omega} \tag{11}$$

for $+\omega$ and $-\omega$, respectively. By multiplying on the left by $\underline{\mathbf{C}}^{\mathbf{k}\dagger}$, CO matrices of general form

$$\tilde{\mathbf{M}}^{\mathbf{k},a}_{\pm\omega} = \underline{\mathbf{C}}^{\mathbf{k}\dagger}\mathbf{M}^{\mathbf{k},a}_{\pm\omega}\underline{\mathbf{C}}^{\mathbf{k}} \tag{12}$$

are obtained. Using the definitions

$$\mathbf{1} = \underline{\mathbf{C}}^{\mathbf{k}\dagger}\underline{\mathbf{S}}^{\mathbf{k}}\underline{\mathbf{C}}^{\mathbf{k}}, \tag{13}$$

$$\tilde{\mathbf{C}}^{\mathbf{k},a}_{\pm\omega} = \underline{\mathbf{C}}^{\mathbf{k}}\mathbf{U}^{\mathbf{k},a}_{\pm\omega}, \tag{14}$$

$$\tilde{\mathbf{G}}^{\mathbf{k},a}_{\pm\omega} = \underline{\mathbf{C}}^{\mathbf{k}\dagger}\mathbf{F}^{\mathbf{k},a}_{\pm\omega}\underline{\mathbf{C}}^{\mathbf{k}} \tag{15}$$

and rearranging, Eqs. (10) and (11) are then recast as a set of coupled-perturbed Hartree-Fock or Kohn-Sham (CP-KS) equations,

$$\tilde{\mathbf{U}}^{\mathbf{k},a}_{+\omega}\tilde{\underline{\mathbf{E}}}^{\mathbf{k}} - \tilde{\underline{\mathbf{E}}}^{\mathbf{k}}\tilde{\mathbf{U}}^{\mathbf{k},a}_{-\omega} + \omega\tilde{\mathbf{U}}^{\mathbf{k},a}_{+\omega} = \tilde{\mathbf{G}}^{\mathbf{k},a}_{+\omega} - \tilde{\mathbf{E}}^{\mathbf{k},a}_{+\omega}, \tag{16}$$

$$\tilde{\mathbf{U}}^{\mathbf{k},a}_{-\omega}\tilde{\underline{\mathbf{E}}}^{\mathbf{k}} - \tilde{\underline{\mathbf{E}}}^{\mathbf{k}}\tilde{\mathbf{U}}^{\mathbf{k},a}_{+\omega} - \omega\tilde{\mathbf{U}}^{\mathbf{k},a}_{-\omega} = \tilde{\mathbf{G}}^{\mathbf{k},a}_{-\omega} - \tilde{\mathbf{E}}^{\mathbf{k},a}_{-\omega}. \tag{17}$$

From the solution of these equations, unitary matrices $\tilde{\mathbf{U}}^{\mathbf{k},a}_{\pm\omega}$ are obtained that transform the unperturbed one-particle orbitals into their linear orbital responses [Eq. (14)]. The matrix $\tilde{\mathbf{G}}^{\mathbf{k},a}_{\pm\omega}$ contains matrix elements of the external perturbation and of the two-electron response of the Fock matrix (both in CO representation),

$$\tilde{\mathbf{G}}^{\mathbf{k},a}_{\pm\omega} = \underline{\mathbf{C}}^{\mathbf{k}\dagger}\boldsymbol{\Omega}^{\mathbf{k},a}\underline{\mathbf{C}}^{\mathbf{k}} + \underline{\mathbf{C}}^{\mathbf{k}\dagger}\mathbf{B}^{\mathbf{k},a}_{\pm\omega}\underline{\mathbf{C}}^{\mathbf{k}}. \tag{18}$$

The former derives from the AO representation of the dipole operator of Eq. (6),

$$\Omega^{\mathbf{k},a}_{\mu\nu} = i\langle\phi_\mu(\mathbf{r},\mathbf{k})|e^{i\mathbf{k}\cdot\mathbf{r}}\nabla_{k_a}e^{-i\mathbf{k}\cdot\mathbf{r}}|\phi_\nu(\mathbf{r},\mathbf{k})\rangle. \tag{19}$$

The two-electron AO response matrix $\mathbf{B}^{\mathbf{k},a}_{\pm\omega}$ is related to the linear density-matrix response $\mathbf{D}^{\mathbf{k},a}_{\pm\omega}$ by

$$\begin{aligned} B^{\mathbf{k},a}_{\pm\omega,\mu\nu} &= \sum_{\rho\tau}^{N} D^{\mathbf{k},a}_{\pm\omega,\rho\tau}(\mu\nu||\rho\tau) \\ &= \sum_{i}^{N_{\mathrm{occ}}}\sum_{j}^{N_{\mathrm{vir}}}\sum_{\rho\tau}^{N}\left(\left[\tilde{U}^{\mathbf{k},a}_{\pm\omega}\right]^{*}_{ij}\underline{C}^{\mathbf{k}*}_{\mu j}\underline{C}^{\mathbf{k}}_{\nu i} + \underline{C}^{\mathbf{k}*}_{\mu i}\left[\tilde{U}^{\mathbf{k},a}_{\pm\omega}\right]_{ij}\underline{C}^{\mathbf{k}}_{\nu j}\right) \\ &\quad\times(\mu\nu||\rho\tau). \end{aligned} \tag{20}$$

Here $N_{\mathrm{occ}}$ and $N_{\mathrm{vir}}$ are the number of occupied and unoccupied COs, respectively, and $N = N_{\mathrm{occ}} + N_{\mathrm{vir}}$.

$(\mu\nu||\rho\tau)$ are standard two-electron integrals in the AO basis, which, for CP-HF and CP-KS read, respectively,

$$\begin{aligned} (\mu\nu||\rho\tau)^{\mathrm{HF}} &= (\mu\nu|\rho\tau) - (\mu\rho|\nu\tau) \\ &= \int d\mathbf{r}d\mathbf{r}'\frac{\chi^{*}_{\mu}(\mathbf{r})\chi_{\nu}(\mathbf{r})\chi^{*}_{\rho}(\mathbf{r}')\chi_{\tau}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\ &\quad - \int d\mathbf{r}d\mathbf{r}'\frac{\chi^{*}_{\mu}(\mathbf{r})\chi_{\rho}(\mathbf{r})\chi^{*}_{\nu}(\mathbf{r}')\chi_{\tau}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}, \end{aligned} \tag{21}$$

$$\begin{aligned} (\mu\nu||\rho\tau)^{\mathrm{KS}} &= (\mu\nu|\rho\tau) + (\mu\nu|f_{\mathrm{xc}}|\rho\tau) \\ &= \int d\mathbf{r}d\mathbf{r}'\frac{\chi^{*}_{\mu}(\mathbf{r})\chi_{\nu}(\mathbf{r})\chi^{*}_{\tau}(\mathbf{r}')\chi_{\rho}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\ &\quad - \int d\mathbf{r}d\mathbf{r}'\chi^{*}_{\mu}(\mathbf{r})\chi_{\nu}(\mathbf{r})f_{\mathrm{xc}}\chi^{*}_{\rho}(\mathbf{r}')\chi_{\tau}(\mathbf{r}'), \end{aligned} \tag{22}$$

where $f_{\mathrm{xc}}$ is the functional derivative of the exchange-correlation potential with respect to the linear density response, which we compute here within the adiabatic approximation,

$$f_{\mathrm{xc}} \equiv f_{\mathrm{xc}}(\mathbf{r},\mathbf{r}';\omega) = \delta(\mathbf{r}-\mathbf{r}')\frac{\delta v_{\mathrm{xc}}(\mathbf{r})}{\delta\rho(\mathbf{r}')}\bigg|_{\rho(\mathbf{r}')=\rho_{\omega=0}(\mathbf{r}')}. \tag{23}$$

In hybrid CP-HF/CP-KS theory, the two above equations are combined to give

$$\begin{aligned} (\mu\nu||\rho\tau)^{\mathrm{hybrid}} &= (\mu\nu|\rho\tau) + c_{\mathrm{HF}}(\mu\nu|f_{\mathrm{xc}}|\rho\tau) \\ &\quad - (1-c_{\mathrm{HF}})(\mu\rho|\nu\tau), \end{aligned} \tag{24}$$

where $c_{\mathrm{HF}}$ represents the fraction of Hartree-Fock exchange admixed in the exchange-correlation functional, and $(\mu\nu|\rho\tau)$, $(\mu\nu|v_{\mathrm{xc}}|\rho\tau)$, and $(\mu\rho|\nu\tau)$. In the implementation used in this work, all integrals of Eqs. (21)–(22) and (24) are computed analytically,[41,42] and $c_{\mathrm{HF}}$ is set to the value used in the standard B3LYP[43] exchange-correlation functional (i.e. $c_{\mathrm{HF}} = 0.20$).

The solutions of Eqs. (16) and (17) are formally given by

$$\tilde{U}^{\mathbf{k},a}_{\pm\omega,ij} = \frac{\tilde{G}^{\mathbf{k},a}_{\pm\omega,ij}}{\varepsilon^{\mathbf{k}}_{j} - \varepsilon^{\mathbf{k}}_{i} \mp \omega} = \frac{\left[\underline{\mathbf{C}}^{\mathbf{k}\dagger}\left(\Omega^{\mathbf{k},a} + \mathbf{B}^{\mathbf{k},a}_{\pm\omega}\right)\underline{\mathbf{C}}^{\mathbf{k}}\right]_{ij}}{\varepsilon^{\mathbf{k}}_{j} - \varepsilon^{\mathbf{k}}_{i} \mp \omega}, \tag{25}$$

where $\varepsilon^{\mathbf{k}}_{i}$ and $\varepsilon^{\mathbf{k}}_{j}$ are matrix elements of $\underline{\mathbf{E}}^{\mathbf{k}}$ in Eq. (9), i.e., unperturbed one-particle energies at $\mathbf{k}$. Since, from Eq. (20), $\mathbf{B}^{\mathbf{k},a}_{\pm\omega}$ depends explicitly on $\tilde{\mathbf{U}}^{\mathbf{k},a}_{\pm\omega}$, this equation has to be solved self-consistently. From the solutions at given energies $\pm\omega_I$, the energy-dependent polarizability tensor $\alpha_{ab}(\pm\omega_I)$ can then be computed using[32,44]

$$\alpha_{ab}(\pm\omega_I) = -2\sum_{\mathbf{k}}^{N_{\mathbf{k}}} w_{\mathbf{k}}\sum_{i}^{N}\sum_{j}^{N_{\mathrm{occ}}}\left[\tilde{U}^{\mathbf{k},a}_{\pm\omega_I}\right]_{ji}\tilde{\Omega}^{\mathbf{k},b}_{ij} + \tilde{\Omega}^{\mathbf{k},b}_{ji}\left[\tilde{U}^{\mathbf{k},a}_{\pm\omega_I}\right]_{ij}, \tag{26}$$

where $N_{\mathbf{k}}$ is the number of $\mathbf{k}$ points in the Brillouin zone, and $w_{\mathbf{k}}$ are $\mathbf{k}$-point integration weights. The matrix $\tilde{\Omega}^{\mathbf{k},b}_{ij}$ is the CO representation of Eq. (19),

$$\tilde{\Omega}^{\mathbf{k},a}_{ij} = i\langle\psi_i(\mathbf{r},\mathbf{k})|e^{i\mathbf{k}\cdot\mathbf{r}}\nabla_{k_a}e^{-i\mathbf{k}\cdot\mathbf{r}}|\psi_j(\mathbf{r},\mathbf{k})\rangle, \tag{27}$$

and contains the Cartesian components $a$ of the dipole matrix elements between independent-particle states $i$ and $j$ at $\mathbf{k}$.

Equation (26) also yields the mean dynamical polarizability (MDP):

$$\overline{\alpha}(\pm\omega) = \tfrac{1}{3}\mathrm{tr}\{\boldsymbol{\alpha}(\pm\omega)\}. \tag{28}$$

The latter quantity has poles at those *true* (i.e., many-body) electronic excitation energies $\omega_I$ which are optically allowed. We can determine the position of the poles by solving self-consistently Eqs. (16) and (17) for a set of discrete positive energies $\{\omega_l = \omega_0 + l\delta\omega\}$ where $\delta\omega$ is a sufficiently small energy increment. Since we are only interested here in estimating the lowest-energy optically allowed electronic excitation, we restrict the values of $\omega_i$ to a range $[0, E_g)$, where $E_g$ is a rough estimate (obtained, e.g., from experimental data) of the optical gap of the bulk material under study. We then interpolate the resulting values of the self-consistent MDP $\{\overline{\alpha}(\omega_i)\}$ with an inverse law,

$$\tilde{\alpha}(\omega_i) = [A + B(\omega_i - C)]^{-1}, \tag{29}$$

where $A$, $B$, and $C$ are constants to be determined by regression, and we locate the energy of the pole by computing the asymptotic limit $\tilde{\alpha} \to \infty$ of Eq. (29) as $\tilde{\omega} = -A/B + C$. It is clear that the calculation of the linear density-matrix response via Eq. (20) is linear in the number of **k** points, as is the calculation of the MDP starting from Eq. (26). Also, the formalism can be adapted to work with one-dimensional (1D)- and 2D-periodic systems, as well as with finite (molecular) systems. In the latter case, Eqs. (16) and (17) are equivalent to the standard RPA-like coupling matrix diagonalization problem of molecular TD-DFT, as we show in the Appendix.

## III. DETAILS OF CALCULATIONS

Equations (16) and (17) were solved at the LDA, Hartree-Fock, and hybrid-DFT (B3LYP) levels of theory, with all electrons (including core ones) explicitly included in the calculations, and the Brillouin zone sampled using a uniform Monkhorst-Pack mesh of $8 \times 8 \times 8$ **k** points. Atomic orbitals were expanded in a Gaussian basis set of triple-$\zeta^\star$ or quadruple-$\zeta^\star$ quality.[46] Calculations were carried out with a locally modified version of the CRYSTAL09 code.[41,42]

A considerable reduction in the calculation cost was achieved by exploiting crystal symmetry in the estimation of the MDP. For instance, for materials with zinc-blende structure ($\alpha_{xx} = \alpha_{yy} = \alpha_{zz}$), the CP-HF/KS self-consistent determination of the MDP was restricted to one diagonal component of $\boldsymbol{\alpha}$. Similarly, for wurtzite materials ($\alpha_{xx} = \alpha_{yy} \neq \alpha_{zz}$) only the $\alpha_{xx}$ and $\alpha_{zz}$ components were calculated. Since the calculation of all independent components of $\boldsymbol{\alpha}$ requires up to three CP-HF/KS self-consistent cycles (one for each Cartesian direction in the external perturbation), this resulted in a decrease of roughly 2/3 and 1/3 in the overall computational cost for zinc-blende and wurtzite materials, respectively.

## IV. RESULTS AND DISCUSSION

Results from the application of this method to crystalline silicon are shown in Fig. 1. Extrapolation from Eq. (29) yielded the lowest pole in the MDP at 2.52, 3.44, and 4.86 eV for LDA, Hartree-Fock, and B3LYP, respectively. Experimental

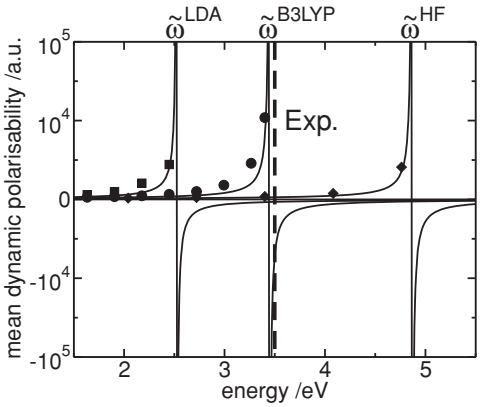



FIG. 1. MDPs $\overline{\alpha}(\omega_I)$ for silicon at the experimental lattice parameter calculated by solving Eqs. (16) and (17) at the LDA (squares), Hartree-Fock (diamonds), and B3LYP (dots) levels of theory for a series of values of the energy $\omega_I$. Inverse regression of the calculated values, as from Eq. (29), are indicated by continuous curves, each of which has a discontinuity at the energy corresponding to the lowest pole of $\overline{\alpha}(\omega_I)$ (situated at the intersection with the horizontal axis and indicated by $\tilde{\omega}^{\mathrm{LDA,HF,B3LYP}}$). The dashed vertical line represents the experimental energy[45] of the optical-absorption gap.

UV spectra of Si exhibit two sharp absorption peaks at ∼3.5 and ∼4.2 eV, both of which arise from exciton transitions. The optical-absorption gap can be identified with the lowest of these peaks, and it is therefore well reproduced (to within 0.1 eV) by our CP-KS (B3LYP) estimate. CP-KS (LDA) underestimates the gap by 1.0 eV and CP-HF overestimates it by 1.4 eV.

It is important to realize that the accuracy of the CP-KS (B3LYP) optical gap is a consequence of the proper description of the self-consistent *response* of the density matrix

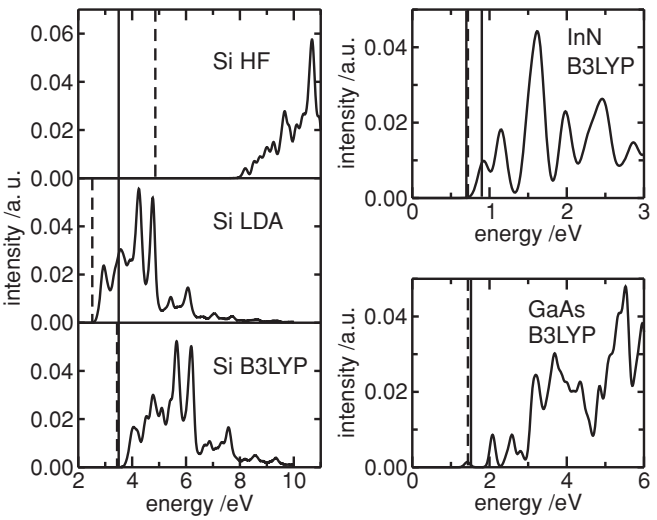



FIG. 2. Hartree-Fock (HF), LDA, and B3LYP independent-particle spectra of Si (left), and B3LYP independent-particle spectra of GaAs, and InN (right). Vertical continuous (dashed) lines represent the experimental (calculated) values of the optical gap. In the case of InN, experimental gaps fall between the two continuous vertical lines.

TABLE I. Calculated and experimental (Refs. 45 and 46) optical gaps in eV. n/a indicates that the calculated band gap is lower than 0.1 eV.

| | CP-HF | TD-KS (LDA) | TD-KS (B3LYP) | Expt. |
|---|---|---|---|---|
| Si | 4.86 | 2.52 | 3.44 | 3.5 |
| GaAs | 4.94 | 0.21 | 1.44 | 1.52 |
| InSb | 3.15 | n/a | 0.25 | 0.24 |
| GaN (wz) | 8.83 | 1.91 | 3.52 | 3.51 |
| InN (wz) | 4.95 | n/a | 0.72 | 0.7–0.9 |
| MgO | 13.61 | 4.87 | 7.02 | 7.16 |
| ZnO | 8.65 | 0.95 | 3.02 | 3.4 |

in Eq. (20), which explicitly includes nonlocality in the form of the exchange integrals contributing to $(\mu\nu||\rho\tau)$.[47,48] This is consistent with the previous observation that the onset of the optical absorption in silicon has excitonic character, and its proper account thus necessarily requires nonlocal response prescriptions.[49] Consistent with this fact, the independent-particle spectrum deduced from the B3LYP Hamiltonian (Fig. 2 does *not* show any nonvanishing absorption at the energy of the optical gap.

In addition to crystalline silicon, which is known to have an indirect band gap in the vicinity of the $X$ point of the Brillouin zone, we applied our approach to a series of more technologically relevant direct-gap III-V semiconductor binaries, and to two simple oxides. These systems were selected to represent wide classes of optically active materials: a small-$E_g$ III-V zinc-blende system (InSb); a small-$E_g$ wurtzite III-V material (InN); a material with a moderately large $E_g$ (GaAs). For these systems it is well known that LDA or generalized gradient approximation to the exchange-correlation DFT functional yield significantly underestimated band gaps at the $\Gamma$ point.[46] Among materials with optical absorption in the ultraviolet we considered III-V wurtzite GaN and II-VI wurtzite ZnO. Although the last two materials have very similar band gaps $E_g$ (∼3.5 eV GaN, ∼3.4 eV ZnO), the exciton binding energy in ZnO is substantially larger than in the GaN (∼60 meV vs ∼25 meV), and much larger than the thermal energy at room temperature (∼26 meV). Finally we considered MgO in the rocksalt structure, which is the II-VI oxide with the largest $E_g$. As for crystalline silicon, in all systems examined TD-KS (B3LYP) was found to perform significantly better than TD-KS (LDA) and CP-HF (cf. Fig. 2, and typically to yield estimates of the optical gap within 0.2 eV of those observed in experiment, with the possible exception of ZnO, which shows a slightly larger discrepancy (Table I). Again in analogy with crystalline silicon, LDA and CP-KS (LDA) were found to underestimate the band and/or optical gap consistently throughout the series of materials examined, and, similarly, HF and CP-HF to yield highly overestimated gaps.

## V. CONCLUSIONS

We have presented a simple, general, and computationally convenient approach for the calculation of optical properties of infinite and finite quantum systems. This method is formally equivalent to TD-DFT, time-dependent Hartree-Fock, or hybrid TD-DFT, but overcomes some of the computational problems that limit the application of these theories to infinite periodic systems. We have showed that our approach can be used to address the calculation of optical gaps of various classes of semiconductors and oxides to good accuracy, including those involving exciton transitions at or near the absorption edge.

## ACKNOWLEDGMENTS

We thank S. Kümmel, E. J. Baerends, and O. Gritsenko for useful discussions. Computing resources were provided by STFC Rutherford-Appleton Laboratory.

## APPENDIX: DERIVATION OF TD-DFT EQUATIONS FROM CP-KS THEORY FOR FINITE SYSTEMS

We show here how the calculation of excitation energies in CP-HF and CP-KS methods, Eqs. (16) and (17), can be recast as a (non-Hermitian) generalized eigenvalue problem, well known from time-dependent Hartree-Fock (TD-HF) theory in molecular physics (see, e.g., Refs. 50 and 14). The derivation is restricted to a finite, isolated system. The resulting equation is thus appropriate for atomic or molecular systems in the gas phase. It can also be extended to periodic systems in the single $\mathbf{k}$-point ($\Gamma$) approximation, as shown, e.g., by Hutter and co-workers.[22,51] A generalization for polymers and 3D periodic systems with full Brillouin-zone sampling has also been proposed.[17]

0D or single $\Gamma$-point versions of Eqs. (16) and (17) can immediately be derived by setting $\mathbf{k} = \mathbf{0}$ in all expressions following Eq. (1). For simplicity we therefore drop the $\mathbf{k}$ index, to obtain

$$\tilde{\mathbf{U}}^a_{+\omega}\underline{\tilde{\mathbf{E}}} - \underline{\tilde{\mathbf{E}}}\tilde{\mathbf{U}}^a_{-\omega} + \omega\tilde{\mathbf{U}}^a_{+\omega} = \tilde{\mathbf{G}}^a_{+\omega} - \tilde{\mathbf{E}}^a_{+\omega}, \tag{A1}$$

$$\tilde{\mathbf{U}}^a_{-\omega}\underline{\tilde{\mathbf{E}}} - \underline{\tilde{\mathbf{E}}}\tilde{\mathbf{U}}^a_{+\omega} - \omega\tilde{\mathbf{U}}^a_{-\omega} = \tilde{\mathbf{G}}^a_{-\omega} - \tilde{\mathbf{E}}^a_{-\omega}. \tag{A2}$$

In Eqs. (A1) and (A2), and throughout this Appendix, a tilde indicates that the corresponding matrix is written in the molecular orbital (MO) basis for a finite system, or in the CO basis for single $\mathbf{k}$-point sampling of a periodic system.

The response matrix $\tilde{\mathbf{G}}^a_{\pm\omega}$ [ cf. Eq. (18)] is now given by

$$\tilde{\mathbf{G}}^a_{\pm\omega} = \underline{\mathbf{C}}^\dagger\mathbf{\Omega}^a\underline{\mathbf{C}} + \underline{\mathbf{C}}^\dagger\mathbf{B}^a_{\pm\omega}\underline{\mathbf{C}}, \tag{A3}$$

with

$$\Omega^a_{\mu\nu} = \langle\phi_\mu(\mathbf{r})|\hat{r}_a|\phi_\nu(\mathbf{r})\rangle \tag{A4}$$

and

$$B^a_{\pm\omega,\mu\nu} = \sum_{\rho\tau}^{N} D^a_{\pm\omega,\rho\tau}(\mu\nu||\rho\tau) = \sum_{i}^{N_{\rm occ}}\sum_{j}^{N_{\rm vir}}\sum_{\rho\tau}^{N}\left(\left[\tilde{U}^a_{\pm\omega}\right]^*_{ij}\underline{C}^*_{\mu j}\underline{C}_{\nu i} + \underline{C}^*_{\mu i}\left[\tilde{U}^a_{\pm\omega}\right]_{ij}\underline{C}_{\nu j}\right)(\mu\nu||\rho\tau), \tag{A5}$$

$\underline{\mathbf{C}}$ being matrices of MO (or CO) coefficients. In a finite system, the dipole operator $\hat{r}_a$ of Eq. (7) needs to be replaced, in Eq. (A4), by its nonperiodic counterpart

$$\hat{r}^x = x; \quad \hat{r}^y = y; \quad \hat{r}^z = z. \tag{A6}$$

For a periodic system in the single ($\Gamma$) $\mathbf{k}$-point approximation, an analytic expression for Eq. (7) has also been derived,[51]

which does not involve explicit derivatives over **k** points, and can be used in place of Eq. (A6).

Substitution of Eqs. (A4) and (A5) into Eq. (A3) gives

$$\tilde{G}^a_{\pm\omega,ai} = \sum_{\mu\nu\rho\tau}^{N} \underline{C}^*_{\mu a} \sum_{l}^{N_{\rm vir}} \sum_{m}^{N_{\rm occ}} \Big( \big[\tilde{U}^a_{\pm\omega}\big]^*_{ml} \underline{C}^*_{\tau l} \underline{C}_{\rho m} + \underline{C}^*_{\tau m} \big[\tilde{U}^a_{\pm\omega}\big]_{lm} \times \underline{C}_{\rho l} \Big)(\mu\nu||\rho\tau) \underline{C}_{\nu i} + \sum_{\mu\nu} \underline{C}^*_{\mu a} \Omega^a_{\mu\nu} \underline{C}_{\nu i}$$

$$= \sum_{l}^{N_{\rm vir}} \sum_{m}^{N_{\rm occ}} \big[(ai||lm)\big[\tilde{U}^a_{\pm\omega}\big]_{lm} + (ai||lm)\big[\tilde{U}^a_{\pm\omega}\big]^*_{ml}\big] + \tilde{\Omega}^a_{ai} \equiv \tilde{B}^a_{\pm\omega,ai} + \tilde{\Omega}^a_{ai}, \tag{A7}$$

where the two-electron MO (CO) integrals $(ai||lm)$ are given by expressions similar to Eqs. (21)–(24), with MOs $\psi_i(\mathbf{r})$ replacing AOs $\chi_\mu(\mathbf{r})$, and $\tilde{\Omega}^a_{ai}$ are Cartesian components of the dipole matrix elements between MOs (COs) $i$ and $a$.

Since the matrix $\underline{\tilde{\mathbf{E}}}$ contains unperturbed Hartree-Fock or Kohn-Sham one-particle energies $\varepsilon_i$, the solutions to Eqs. (A1)–(A2) can be written as

$$(\varepsilon_a - \varepsilon_i + \omega) U^a_{-\omega,ia} = \Omega^a_{ia} + B^a_{-\omega,ia}, \tag{A8}$$

$$(\varepsilon_a - \varepsilon_i - \omega) U^a_{+\omega,ia} = \Omega^a_{ia} + B^a_{+\omega,ia}, \tag{A9}$$

which, using the relations

$$\Omega^a_{ia} = \Omega^{a*}_{ai}, \tag{A10}$$

$$B^a_{\pm\omega,ia} = B^{a*}_{\pm\omega,ai} \tag{A11}$$

and[35]

$$\mathbf{U}^a_{+\omega} = \mathbf{U}^{a\dagger}_{-\omega} \equiv \mathbf{U}^a_{\omega} \tag{A12}$$

give

$$(\varepsilon_a - \varepsilon_i + \omega) U^a_{\omega,ia} = \Omega^a_{ia} + B^a_{-\omega,ia}, \tag{A13}$$

$$(\varepsilon_a - \varepsilon_i - \omega) U^{a*}_{\omega,ai} = \Omega^{a*}_{ai} + B^{a*}_{+\omega,ai}. \tag{A14}$$

Substituting Eq. (A7) into Eqs. (A13) and (A14) yields

$$\sum_{l}^{N_{\rm vir}} \sum_{m}^{N_{\rm occ}} [\delta_{il}\delta_{am}(\varepsilon_a - \varepsilon_i + \omega) - (ia||lm)] U^a_{\omega,lm} - \sum_{l}^{N_{\rm vir}} \sum_{m}^{N_{\rm occ}} (ia||ml) U^{a*}_{\omega,ml} = \Omega^a_{ia}, \tag{A15}$$

$$\sum_{l}^{N_{\rm vir}} \sum_{m}^{N_{\rm occ}} [\delta_{il}\delta_{am}(\varepsilon_a - \varepsilon_i - \omega) - (ai||lm)^*] U^{a*}_{\omega,lm} - \sum_{l}^{N_{\rm vir}} \sum_{m}^{N_{\rm occ}} (ai||ml)^* U^a_{\omega,ml} = \Omega^{a*}_{ai}. \tag{A16}$$

$$A_{ia,lm} = \delta_{il}\delta_{am}(\varepsilon_a - \varepsilon_i) - (ia||lm), \tag{A17}$$

$$B_{ia,lm} = -(ia||ml) \tag{A18}$$

allows us to finally rewrite these equations in supermatrix form, giving

$$\left[ \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} - \omega \begin{pmatrix} -\mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix} \right] \begin{pmatrix} \mathbf{U}^a \\ \mathbf{U}^{a*} \end{pmatrix} = \begin{pmatrix} \mathbf{\Omega}^a \\ \mathbf{\Omega}^{a*} \end{pmatrix}. \tag{A19}$$

When $\omega$ corresponds to a true excitation $\omega_I$, it follows from Eq. (25) that elements of the matrices $\mathbf{U}^a$ and $\mathbf{U}^{a*}$ diverge, whereas $\Omega^a$ and $\Omega^{a*}$ remain finite. Therefore for $\omega = \omega_I$ the quantity in square brackets in the left-hand side of Eq. (A19) has to be singular. In this formalism, excitation energies are therefore solutions of the generalized non-Hermitian eigenvalue equation

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} -\mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}. \tag{A20}$$

It is frequently possible to simplify this eigenvalue problem, which is of order $2N_{\rm vir}N_{\rm occ}$ [ cf. Eqs. (A15) and (A16)], using a $2 \times 2$ unitary transformation,[52] to obtain

$$(\mathbf{A} - \mathbf{B})(\mathbf{A} + \mathbf{B})(\mathbf{X} + \mathbf{Y}) = \omega^2 (\mathbf{X} + \mathbf{Y}), \tag{A21}$$

which is a non-Hermitian eigenvalue problem of size $N_{\rm vir}N_{\rm occ}$. If $(\mathbf{A} - \mathbf{B})$ is positive definite (as is always the case, except when the system exhibits singlet-triplet instabilities[50,53]), multiplication on the left by $(\mathbf{A} - \mathbf{B})^{-1/2}$ gives

$$(\mathbf{A} - \mathbf{B})^{1/2}(\mathbf{A} + \mathbf{B})(\mathbf{A} - \mathbf{B})^{1/2}\mathbf{T} = \omega^2 \mathbf{T}, \tag{A22}$$

with

$$\mathbf{T} = (\mathbf{A} - \mathbf{B})^{-1/2}(\mathbf{X} + \mathbf{Y}), \tag{A23}$$

which is a Hermitian eigenvalue problem of the same size. In TD-DFT, this equation is usually cast as

$$\mathbf{\Omega F}_i = \omega_i^2 \mathbf{F}_i, \tag{A24}$$

which is known as *Casida's equation*.[14] The matrix elements of $\mathbf{\Omega}$ are given by

$$\Omega_{ia,lm} = \delta_{il}\delta_{am}(\varepsilon_a - \varepsilon_i)^2 + 2(\varepsilon_a - \varepsilon_i)^{1/2} K_{ia,lm} (\varepsilon_m - \varepsilon_l)^{1/2}, \tag{A25}$$

where the *coupling matrix* $\mathbf{K}$ is defined by

$$K_{ia,lm} = (ia|ml) + (ia|f_{\rm xc}|ml). \tag{A26}$$

To summarize, we have proved in this Appendix that excitation energies obtained from the solution of the coupled-perturbed equations (16) and (17) are equivalent, in the $\Gamma$-point approximation, to those obtained from the solution of standard RPA-like eigenvalue problems at the relevant (TD-DFT, TD-HF, hybrid TD-DFT) level of theory. Following Ref. 29, the latter formalism can further be developed to yield an expression for a generalized susceptibility function in terms of Liouvillian superoperator matrix elements, from which the full excitation spectrum can be determined recursively *via* the Lanczos chain scheme.[31]


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