Optical response of extended systems from
time-dependent Hartree-Fock and time-dependent
density-functional theory

Leonardo Bernasconi¹, Ross Webster², Stanko Tomić³ and
Nicholas M Harrison¹,²
¹ STFC Rutherford Appleton Laboratory, Harwell Oxford, Didcot, OX11 0QX, UK
² Department of Chemistry, Imperial College London, London SW7 2AZ, UK
³ Joule Physics Laboratory, University of Salford, Manchester, M5 4WT, UK
E-mail: leonardo.bernasconi@stfc.ac.uk

Abstract. We describe a unified formulation of time-dependent Hartree-Fock (TD-HF) and
time-dependent density-functional theory (TD-DFT) for the accurate and efficient calculation
of the optical response of infinite (periodic) systems. The method is formulated within the
linear-response approximation, but it can easily be extended to include higher-order response
contributions, and, in TD-DFT, it can treat with comparable computational efficiency purely
local, semi-local or fully non-local approximations for the ground-state exchange-correlation
(XC) functional and for the response TD-DFT XC kernel in the adiabatic approximation. At
variance with existing methods for computing excitation energies based on the diagonalisation
of suitable coupling matrices, or on the inversion of a dielectric matrix, our approach exploits
an iterative procedure similar to a standard self-consistent field calculation. This results in
a particularly efficient treatment of the coupling of excitations at different \( k \) points in the
Brillouin zone. As a consequence, our method has the potential to describe completely from
first principles the optically induced formation of bound particle-hole pairs in wide classes of
materials. This point is illustrated by computing the optical gaps of a series of representative
bulk semiconductors, (non-spin polarised) oxides and ionic insulators.

1. Introduction
The development of accurate methods to account, fully from first principles, for the response
of a quantum system of nuclei and electrons to an electromagnetic radiation of optical or
UV frequency is currently a very active and complex area of research in solid state physics
and materials science. Technologically, predictive models of the optical response of extended
many-electron systems offer a potentially very powerful route to the design and optimisation of
new materials of relevance \( e.g. \) in photo-voltaics and solar light conversion, photo-catalysis,
and quantum control of single atoms. Theoretically, the \( ab\ initio \) description of electronic
excitations provides means to study fundamental issues in the quantum theory of condensed
phases, including, for instance, the effects of electron correlation in excited states \( and \) in the
ground state of a many-electron system.

TD-DFT [1] has emerged in recent years as a powerful and general approach to address
the computation of several excited state properties, including excitation energies, transition
probabilities, and excited state energy gradients with respect to nuclear displacements. [2–6]
TD-DFT is formally an exact theory of the time-evolution of a many-electron system in the presence of an external time-dependent perturbation. [7] As such, it allows one to study the real-time evolution of an interacting ensemble of electrons perturbed by the presence of the external field.

In the limit of a weak field, e.g. in the simulation of absorption spectra, TD-DFT can be formulated using a particularly elegant formalism [8, 9] that yields the interacting linear density response function $n^{(1)}(r''', \omega)$ in terms of the non-interacting (Kohn-Sham [10, 11]) response function $\chi_s(r, r'; \omega)$ via a Dyson-like equation,

$$
\int dr' \chi_s(r, r'; \omega) v^{(1)}(r', \omega) =
\int dr'' \left[ \delta(r - r'') - \int dr'' \chi_s(r, r''; \omega) \left\{ \frac{1}{|r' - r''|} + f^{xc}(r', r''; \omega) \right\} \right] n^{(1)}(r'', \omega).
$$

$v^{(1)}(r', \omega)$ describes an external field oscillating at a frequency $\omega$, and $f^{xc}(r, r'; \omega)$ is the frequency representation of the XC kernel $f^{xc}(r, t; r', t')$, describing the response of the XC component of the Kohn-Sham potential to the external perturbation,

$$
f^{xc}(r, t; r', t') = \frac{\delta^2 A^{xc}[n](r, t)}{\delta n(r, t) \delta n(r', t')} \bigg|_{n(r, t) = n^{(0)}(r)} = \frac{\delta n^{xc}[n](r, t)}{\delta n(r', t')} \bigg|_{n(r, t) = n^{(0)}(r)},
$$

with $A^{xc}[n](r, t)$ being the XC action functional, and $\delta / \delta n(r, t)$ indicating a functional derivative with respect to $n(r, t)$. The exact form of $f^{xc}(r, t; r', t')$ is, in general, unknown, and this quantity, similarly to the ground state XC functional of density-functional theory (DFT), has to be approximated. Frequently, practical applications of TD-DFT employ the adiabatic approximation, [12] in which the frequency dependence of the kernel is neglected and the functional derivative of the XC potential in Eqn. (2) replaced by the second functional derivative of an XC energy, e.g. the Local Density Approximation (LDA) XC energy, with respect to the density response. This leads to a purely local and frequency independent kernel. The poles of $n^{(1)}(r''', \omega)$ correspond to the many-body excitation energies of the system, whose modes couple with the external field.

TD-DFT excitation energies can also be computed using an alternative procedure (which we will indicate here as the RPA-matrix formalism) based on the solution of a generalised anti-Hermitian eigenvalue equation, [13, 14]

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

The eigenvalues of this equation correspond to the free oscillations of the system, and the coupling with the external field is described by the left and right eigenvectors $X$ and $Y$, which yield the corresponding (possibly vanishing) transition intensities. The matrices $A$ and $B$ describe the coupling of independent-particle Kohn-Sham excitations $a \leftrightarrow i$ and $b \leftrightarrow j$ (with $i, j, \ldots$ and $a, b, \ldots$ labelling occupied and unoccupied Kohn-Sham orbitals respectively) via Coulomb and XC interaction,

$$
A_{ai,bj} = \delta_{ab} \delta_{ij} (\varepsilon_a - \varepsilon_i) + (ai|jb) + (ai|f^{xc}|jb)
$$

$$
B_{ai,bj} = (ai|bj) + (ai|f^{xc}|bj).
$$

The two-electron integrals $(pq|rs)$ are in Mulliken’s notation, [15] and the XC kernel integrals are given by

$$
(ai|f^{xc}|bj) = \int d^2r d^2r' \phi^*_a(r) \phi_i(r) f^{xc}(r, r'; \omega) \phi^*_b(r') \phi_j(r').
$$
This approach is formally analogous to the TD-HF method, [16] which leads to an eigenvalue equation identical to Eqn. (3) with the matrices $A$ and $B$ now given by

$$A_{ai, bj} = \delta_{ab}\delta_{ij}(\varepsilon_a - \varepsilon_i) + (ai|jb) - (ab|ji),$$

$$B_{ai, bj} = (ai|bj) - (aj|bi).$$  \hspace{1cm} (6)

Eqn. (4) and (6) can be therefore be combined to give the hybrid TD-DFT coupling matrices

$$A_{ai, bj} = \delta_{ab}\delta_{ij}(\varepsilon_a - \varepsilon_i) + (ai|jb) - c_{HF}(ab|ji) + (1 - c_{HF})(ai|f_{xc}|jb),$$

$$B_{ai, bj} = (ai|bj) - c_{HF}(aj|bi) + (1 - c_{HF})(ai|f_{xc}|bj),$$  \hspace{1cm} (7)

where $c_{HF}$ measures the fraction of Hartree-Fock exchange in the hybrid response (e.g. $c_{HF} = 0.2$ for TD-DFT at the B3LYP [17] level of theory). For infinite periodic systems, the Kohn-Sham orbitals have the Bloch form, $\langle r|\rho k \rangle = e^{ik\cdot r}u_p(r)$, with one-particle energies $\varepsilon_p^k$, and Eqns. (7) have to be generalised, to give [18]

$$A_{ai, bj} = \delta_{ij}\delta_{ab}\delta_{k_i,k_j}(\varepsilon^k_a - \varepsilon^k_i) + (ak_a|\rho k_j|jb) - c_{HF}(ak_a|bk_b|jk_jk_i) + (1 - c_{HF})(ak_a|f_{xc}|jb)\frac{(1)}{(8)},$$

$$B_{ai, bj} = (ak_a|\rho k_j|bj) - c_{HF}(ak_a|bk_b|k_jk_i) + (1 - c_{HF})(ak_a|f_{xc}|bk_b|k_j).$$

Eqn. (3) can then in principle be solved by iterative diagonalisation for a periodic system using the definitions given in Eqn. (8), to obtain an absorption profile from a discrete set of (several) many-body excitations. In practice, however, this approach rapidly becomes impractical as the size of the system increases, or if very fine meshes of $k$ points are used to sample the Brillouin zone.

In this paper, we describe a formulation of TD-HF, TD-DFT and hybrid TD-HF/TD-DFT for weak perturbations that obtains excitation energies without resorting to a diagonalisation of a large coupling matrix, as in Eqn. (3), and that does not require the calculation (and subsequent inversion, to obtain excitation energies) of $\chi_s(r, r'; \omega)$, as in Eqn. (1). The method is closely related to the (frequency-dependent) coupled-perturbed Hartree-Fock/DFT theories [19–21] widely used in quantum chemistry and molecular physics, which we generalise here to infinite periodic systems. Our approach is formulated in the Linear Combination of Atomic Orbital (LCAO) approximation, with an all-electron basis set of Gaussian functions, as implemented in the CRYSTAL [22–24] code. This choice allows us to compute analytically and extremely efficiently the two-electron integrals $\langle pq|r^s \rangle$, and to arrive at an algorithm that scales linearly with the number of $k$ points used to sample the Brillouin zone. [25]

The paper is organised as follows. In Section 2 we derive the working equations of our method, and we show how excitation energies can be determined from the poles of suitable response functions. We also show how the frequency-dependent dielectric tensor, and a number of related quantitites can be computed using our approach. In Section 3, we describe examples of the application of our method to the calculation of the optical gaps of a number of semiconductors and crystalline ionic systems, and show the level of accuracy achieved in each class of materials. We demonstrate that our method describes qualitatively weakly bound excitons in semiconductors, and, possibly, tightly bound excitons in crystalline materials. The more complex case of charge-transfer excitons in highly ionic systems is also briefly addressed.

2. Theory
2.1. Derivation of frequency-dependent coupled-perturbed Hartree-Fock and DFT equations
The equation of motion for the $k$-dependent Fock (or Kohn-Sham) matrix $F^k$ in the presence of an external time-dependent perturbation,

$$F^k C^k - i \frac{\partial}{\partial t} S^k C^k = S^k C^k E^k$$  \hspace{1cm} (9)
can be derived from Frenkel’s variational principle, [20, 26] subject to the orthonormality constraint
\[
\frac{\partial}{\partial t} C^k C^k = 0. \tag{10}
\]
Throughout this derivation, atomic units for all quantities are assumed. Here, \( C^k \) is a matrix of crystal orbital (CO) coefficients. The COs, \( \psi_i(r, k) \), are combinations of \( N \) Bloch functions (BFs) \( \phi_\mu(r, k) \),
\[
\psi_i(r, k) = \sum_\mu N^C_k C^k_\mu \phi_\mu(r, k). \tag{11}
\]

The elements of the overlap matrix \( S^k \) are given by
\[
S^k_{\mu \nu} = \int dr \phi_\mu(r, k) \phi_\nu(r, k), \tag{12}
\]
and \( E^k \) is the orbital energy matrix. The BFs are expressed in terms of a set of atom-centred Gaussian basis set functions, \( \chi_\mu(r - R) \),
\[
\phi_\mu(r, k) = N^{-\frac{1}{2}} \sum_R N^{-C} e^{i k \cdot r} \chi_\mu(r - R), \tag{13}
\]
where the sum runs on the real-lattice vectors \( R \), and \( N \to \infty \).

In general, a time dependent perturbation of the Hamiltonian operator can be expressed as a sum of oscillatory contributions with frequencies \( \pm \omega \)
\[
\lambda_\omega = \lambda_+ e^{i \omega \tau} + \lambda_- e^{-i \omega \tau}, \tag{14}
\]
\( \lambda_\pm = (\lambda_{x}^\pm, \lambda_{y}^\pm, \lambda_{z}^\pm) \) are the electric field Cartesian components oscillating at frequencies \( \pm \omega \). The coupling between the electrons and the external field is described by the perturbation Hamiltonian
\[
\hat{H}' = \lambda_{\pm} \hat{r}, \tag{15}
\]
where \( \hat{r} \) is the position operator. For finite systems, this corresponds to the standard position operator \( \hat{r}^F = (x, y, z) \). For an infinite periodic system, \( \hat{r}^F \) is unbound, and it has to be replaced by its generalised, translational-invariant form [20, 27–29]
\[
\hat{r} = i e^{i k \cdot r} \nabla r e^{-i k \cdot r}. \tag{16}
\]
We remark that using the definition of Eqn. (16) for \( \hat{r} \) is formally equivalent to introducing an electric field in the Hamiltonian via a vector potential \( A(t) \), to replace the kinetic energy operator \( \hat{p}^2/2 \) with \( |\hat{p} + A(t)|^2/2 \). Both approaches maintain the translational invariance of the Hamiltonian, and they are related by a gauge transformation. [20, 29] Ultimately, they can be shown to lead to the same set of coupled-perturbed equations.

The matrices \( F^k, C^k, E^k \) and \( S^k \) in Eqn. (9) can be expanded in the perturbative parameters \( \lambda_\pm \), and, for \( \lambda_\pm \to 0 \), the linear response approximation for a pair of fixed frequencies \( \pm \omega \) leads to
\[
\begin{align*}
F^k_+ &= F^k + \lambda_+^a F^k_+ e^{i \omega t} + \lambda_-^a F^k_- e^{-i \omega t}, \\
C^k_+ &= C^k + \lambda_+^a C^k_+ e^{i \omega t} + \lambda_-^a C^k_- e^{-i \omega t}, \\
E^k_+ &= E^k + \lambda_+^a E^k_+ e^{i \omega t} + \lambda_-^a E^k_- e^{-i \omega t}, \\
S^k_+ &= S^k + \lambda_+^a S^k_+ e^{i \omega t} + \lambda_-^a S^k_- e^{-i \omega t},
\end{align*} \tag{17}
\]
where \( a \) represents the Cartesian component of the applied field, and \( \mathbf{F}^k, \mathbf{C}^k, \mathbf{E}^k \) and \( \mathbf{S}^k \) are the matrices solving the unperturbed Hartree-Fock (or Kohn-Sham) equation

\[
\mathbf{F}^k \mathbf{C}^k = \mathbf{S}^k \mathbf{C}^k \mathbf{E}^k. \tag{18}
\]

In Eqn. (17) we have defined the response matrices

\[
\begin{align*}
F_{\pm \omega}^{k,a} &= \partial \mathbf{F}^k / \partial \lambda_{\pm \omega}^a \\
C_{\pm \omega}^{k,a} &= \partial \mathbf{C}^k / \partial \lambda_{\pm \omega}^a \\
E_{\pm \omega}^{k,a} &= \partial \mathbf{E}^k / \partial \lambda_{\pm \omega}^a \\
S_{\pm \omega}^{k,a} &= \partial \mathbf{S}^k / \partial \lambda_{\pm \omega}^a
\end{align*} \tag{19}
\]

representing the gradients of the Fock/Kohn-Sham matrix, CO coefficients, orbitals energies and overlap matrix respectively to the external perturbation. Assuming that the nuclei are at fixed positions (i.e. that the electronic and nuclear motions are decoupled) leads to \( \partial \mathbf{S}^k / \partial \lambda_{\pm \omega}^a = 0 \), i.e. \( \mathbf{S}^k = \tilde{\mathbf{S}}^k \). In practice, this entails that excitation energies will be obtained here in the Franck-Condon approximation. [30]

Substituting the matrix expansions of Eqn. (17) into Eq. (9) and neglecting all resulting terms that are of order 2 or higher in \( \lambda_{\pm \omega}^a \) gives the pair of equations

\[
F_{\pm \omega}^{k,a} \mathbf{C}^k + F_{\pm \omega}^{k,a} \mathbf{C}^k \pm \omega \mathbf{C}_{\pm \omega}^{k,a} = S_{\pm \omega}^{k,a} \mathbf{E}^k + \tilde{S}_{\pm \omega}^{k,a} \mathbf{C}^k \mathbf{E}^k \tag{20}
\]

for \( +\omega \) and \( -\omega \). These equations can be converted to CO representation by multiplying on the left by \( \mathbf{C}^{k\dagger} \). Using the definitions

\[
1 = \mathbf{C}^{k\dagger} \tilde{\mathbf{S}}^k \mathbf{C}^k \tag{21}
\]

\[
\tilde{C}^{k,a}_{\pm \omega} = \mathbf{C}^{k\dagger} \mathbf{U}^{k,a}_{\pm \omega} \tag{22}
\]

\[
\tilde{G}^{k,a}_{\pm \omega} = \mathbf{C}^{k\dagger} \tilde{F}^{k,a}_{\pm \omega} \mathbf{C}^k \tag{23}
\]

for the expressions resulting from Eqn. (20) gives the frequency-dependent coupled-perturbed equations

\[
\tilde{U}^{k,a}_{\pm \omega} \mathbf{E}^k - \mathbf{E}^k \tilde{U}^{k,a}_{\pm \omega} \pm \omega \tilde{U}^{k,a}_{\pm \omega} = \tilde{G}^{k,a}_{\pm \omega} - \tilde{E}^{k,a}_{\pm \omega}. \tag{24}
\]

A tilde indicates that the corresponding matrix is in CO representation. The matrix \( \mathbf{U}^{k,a}_{\pm \omega} \) introduced in Eqn. (22) has to be interpreted as a unitary matrix that transforms the unperturbed CO coefficients into their linear response by linearly combining occupied and unoccupied one-particle states of the unperturbed Hamiltonian. As will be shown below, various frequency-dependent response functions can directly be determined from \( \mathbf{U}^{k,a}_{\pm \omega} \). The RPA-matrix formalism, Eqn. (3), can easily be derived from Eqns. (24), [25] This will allow us to identify the poles of response functions computed via Eqns. (24) corresponding to the optically allowed (forced) resonances described by Eqn. (3) with fictitious transitions between stationary electronically excited states. [16]

The matrix \( \tilde{G}^{k,a}_{\pm \omega} \) is the sum of the response of the Fock/Kohn-Sham matrix, \( \mathbf{B}^{k,a}_{\pm \omega} \), and of the matrix representation of the external perturbation \( \mathbf{\Omega}^{k,a}_{\pm \omega} \) from Eqn. (15), i.e.

\[
\tilde{G}^{k,a}_{\pm \omega} = \mathbf{C}^{k\dagger} \mathbf{D}^{k,a}_{\pm \omega} \mathbf{C}^k + \mathbf{C}^{k\dagger} \mathbf{\Omega}^{k,a}_{\pm \omega} \mathbf{C}^k. \tag{25}
\]

The response matrix \( \mathbf{B}^{k,a}_{\pm \omega} \) is related to the linear density matrix response \( \mathbf{D}^{k,a}_{\pm \omega} \) by

\[
B^{k,a}_{\pm \omega,\mu\nu} = \sum_{\rho\tau} D^{k,a}_{\pm \omega,\rho\tau} (\mu\nu||\rho\tau) \tag{26}
\]
where we have used the standard notation for the two-electron integrals, which are defined:

1) for Hartree-Fock:

\[
(\mu\nu||\rho\tau)^{\text{HF}} = (\mu\nu|\rho\tau) - (\mu\rho|\nu\tau)
\]

\[
= \int d\mathbf{r} d\mathbf{r'} \frac{\chi^{\dagger}_\mu(\mathbf{r})\chi_\nu(\mathbf{r})\chi_\rho(\mathbf{r'})\chi^{\dagger}_\tau(\mathbf{r'})}{|\mathbf{r} - \mathbf{r'}|} - \int d\mathbf{r} d\mathbf{r'} \frac{\chi^{\dagger}_\mu(\mathbf{r})\chi_\nu(\mathbf{r})\chi^{\dagger}_\rho(\mathbf{r'})\chi_\tau(\mathbf{r'})}{|\mathbf{r} - \mathbf{r'}|},
\]

(27)

2) for pure DFT:

\[
(\mu\nu||\rho\tau)^{\text{KS}} = (\mu\nu|\rho\tau) + (\mu\nu|f_{\text{xc}}|\rho\tau)
\]

\[
= \int d\mathbf{r} d\mathbf{r'} \frac{\chi^{\dagger}_\mu(\mathbf{r})\chi_\nu(\mathbf{r})\chi^{\dagger}_\rho(\mathbf{r'})\chi_\tau(\mathbf{r'})}{|\mathbf{r} - \mathbf{r'}|} + \int d\mathbf{r} d\mathbf{r'} \frac{\chi^{\dagger}_\mu(\mathbf{r})\chi_\nu(\mathbf{r})f_{\text{xc}}^{\dagger}\chi^{\dagger}_\rho(\mathbf{r'})\chi_\tau(\mathbf{r'})}{|\mathbf{r} - \mathbf{r'}|},
\]

(28)

3) for hybrid Hartree-Fock/DFT:

\[
(\mu\nu||\rho\tau)^{\text{hybrid}} = (\mu\nu|\rho\tau) + (1 - c_{\text{HF}})(\mu\rho|f_{\text{xc}}|\rho\tau) - c_{\text{HF}}(\mu\nu|\nu\tau).
\]

(29)

The linear density matrix response in Eqn. (26) can be computed from the matrix \( U^{k,a}_{\pm\omega} \) appearing in Eqn. (24):

\[
D^{k,a}_{\pm\omega,\mu\nu} = \sum_i \sum_d \sum_{\rho\tau} \left( \langle \tilde{U}^{k,a}_{\pm\omega} | \xi^{\dagger}_d | \phi_{\rho\tau} \rangle + \langle \tilde{U}^{k,a}_{\pm\omega} | \phi_{\rho\tau} \rangle | \xi^{\dagger}_d \rangle \right)
\]

(30)

Here \( N_{\text{occ}} \) and \( N_{\text{vir}} \) are the number of occupied and unoccupied COs respectively, and \( N = N_{\text{occ}} + N_{\text{vir}} \). Finally, the matrix of the external perturbation \( \Omega^{k,a}_{\mu\nu} \) in the right hand side of Eqn. (25) is the atomic orbital representation of the the operator \( \mathbf{r} \) of Eqn. (16), i.e.

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

(31)

### 2.2. Self-consistent solution of the coupled-perturbed equations

The coupled-perturbed equations, Eqns. (24), can be solved symbolically to give

\[
\tilde{U}^{k,a}_{\pm\omega,\mu\nu} = \frac{\tilde{G}^{k,a}_{\pm\omega,\mu\nu}}{\varepsilon^{k}_{d} - \varepsilon^{k}_{i} + \omega} = \frac{[C^{k}]^{\dagger}\Omega^{k,a}_{\mu\nu} + B^{k,a}_{\pm\omega}]C^{k}_{\mu\nu}}{\varepsilon^{k}_{d} - \varepsilon^{k}_{i} + \omega},
\]

(32)

where \( \varepsilon^{k}_{i} \) and \( \varepsilon^{k}_{d} \) are matrix elements of \( E^{k} \) in Eqn. (18), i.e. unperturbed one-particle energies at \( k \) corresponding to occupied (i) and unoccupied (d) states. Since, from Eqn. (26), \( B^{k,a}_{\pm\omega} \) depends explicitly on \( \tilde{U}^{k,a}_{\pm\omega} \), Eqn. (32) defines an infinite recursion, which can be solved e.g. using diagrammatic techniques (see e.g. Ref. [31]). Here we adopt a different approach, and we recast Eqn. (32) as a self-consistent procedure, exploiting the ground-state self-consistent field solver implemented in the CRYSTAL code. [21] Considering a pair of fixed frequencies \( \pm \omega = \pm \omega_f \), we start by computing a zeroth order matrix \( \tilde{U}^{k,a}_{\pm\omega} \) in the absence of inter-electron contributions by setting \( B^{k,a}_{\pm\omega} = 0 \) in Eqn. (32). In Hartree-Fock approximation, this iteration corresponds to the so-called “uncoupled Hartree-Fock” perturbation theory. [31] From the resulting \( \tilde{U}^{k,a}_{\pm\omega} \) we compute the density matrix response \( D^{k,a}_{\pm\omega} \) using Eqn. (30), and this allows us now to estimate the two-electron response matrix from Eqn. (26). We can then in turn compute the first-iteration
Figure 1. Convergence of coupled mean dynamical polarisability for crystalline silicon with TD-HF at $\omega_I = 0$ and 2.7 eV during the self-consistent solution of Eqn. (32).

coupled-perturbed matrix $\tilde{U}_{k,a}^{\pm \omega}$, and we then repeat the same procedure for all subsequent iterations. At each iteration we estimate a (coupled) polarisability tensor, \cite{20, 25, 32, 33}

$$\alpha_{ab}(\pm \omega_I) = -\sum_k N_k \sum_i \sum_d (\tilde{U}_{k,a}^{\pm \omega_I} \tilde{\Omega}_{id}^{k,b} + \tilde{\Omega}_{di}^{k,b} \tilde{U}_{k,a}^{\pm \omega_I})$$ \hspace{1cm} (33)

where $a$ and $b$ indicate Cartesian components, $N_k$ is the number of $k$-points in the Brillouin zone, with $w_k$ the weight of $k$ in Brillouin zone integrals. $\tilde{\Omega}_{id}^{k,b}$ is the CO representation of Eqn. (31),

$$\tilde{\Omega}_{id}^{k,b} = i \langle \psi_i(r, k) | e^{ik \cdot r} \nabla_k e^{-ik \cdot r} | \psi_d(r, k) \rangle$$ \hspace{1cm} (34)

and contains the Cartesian component $b$ of the position operator matrix elements between independent-particle states $i$ and $d$ at $k$. We then use the mean dynamical polarisability

$$\bar{\alpha}(\pm \omega_I) = \frac{1}{3} \text{tr} \{ \alpha(\pm \omega_I) \}$$ \hspace{1cm} (35)

to define a convergence criterion for self-consistency in Eqn. (32), see Figure 1. From the self-consistent polarisability, the frequency dependent dielectric tensor $\epsilon(\omega)$, the first-order dielectric susceptibility $\chi^{(1)}(\omega)$ and the (complex) refractive index $n(\omega)$ can also be computed using the relations \cite{21}

$$\epsilon_{ab}(\pm \omega_I) = n_{ab}^2(\pm \omega_I) = 1 + \chi_{ab}^{(1)}(\pm \omega_I) = 1 + \frac{4\pi}{V} \alpha_{ab}(\pm \omega_I),$$ \hspace{1cm} (36)

where $V$ is the unit cell volume.

2.3. Excitation energies

At iteration 0, the uncoupled matrix $\tilde{U}_{k,a}^{\pm \omega}$ at $\omega = \omega_I$ is given by

$$\tilde{U}_{\omega_I, id}^{k,a} = \frac{\tilde{\Omega}_{id}^{k,a}}{\varepsilon_d - \varepsilon_k - \omega_I},$$ \hspace{1cm} (37)

where Eqns. (32) and (34) have been used. It is clear from this expression that $\tilde{U}_{\omega_I, id}^{k,a}$ diverges whenever $\omega_I$ approaches an independent-particle energy difference $\varepsilon_d - \varepsilon_k$, provided
the corresponding independent-particle free oscillation couples to the external field, i.e. \( \hat{\Omega}_{\text{td}}^{k,a} \neq 0 \). Because of Eqn. (33), independent-particle dipole allowed electronic transitions therefore correspond to the poles of the polarisability tensor \( \alpha(\omega) \), or equivalently of the mean dynamical polarisability \( \overline{\alpha}(\pm \omega) \), with non-zero residues.

For the fully coupled self-consistent matrix \( \mathbf{U}_{\pm \omega}^{k,a} \) solving Eqn. (32), we can identify the poles of \( \overline{\alpha}(\pm \omega) \) with the many-body excitation modes that couple with the external field (see Section 2.1). Therefore, similar to the method of Eqn. (1), Eqn. (32) determines the forced oscillations induced by the external field in the interacting electron system. Many-body excitation energies can then straightforwardly be computed by solving Eqn. (32) over a given frequency range. Adaptive algorithms based on the on-the-fly estimation of the derivative of \( \overline{\alpha}(\pm \omega) \) with respect to \( \omega \) can be devised to locate the frequency of the poles with an accuracy at least comparable to the iterative (e.g. Davidson-like [34, 35]) diagonalisation methods typically used to solve large eigenvalue problems like Eqn. (3).

It is interesting to observe that the calculation of the response matrix \( \mathbf{U}_{\pm \omega}^{k,a} \) in Eqn. (32) and of the polarisability in Eqn. (33) only involve vertical transitions between the occupied and unoccupied one-particle states at each \( k \) point. This is a consequence of the \( k \) factorisability of the linear density matrix response \( D_{\pm \omega, \rho \tau}^{k,a} \), and therefore of the two-electron contribution to the Kohn-Sham/Fock matrix response \( B_{\pm \omega, \mu \nu}^{k,a} \), cf. Eqn. (26). The matrix \( \hat{\Omega}_{\pm \omega}^{k,b} = \mathbf{C}_{k}^{b} \hat{\Omega}^{k,b} \mathbf{C}_{k}^{a} \) in the right hand side of Eqn. (32) is also factorisable, owing to the fact that matrix elements of \( \nabla_{\mathbf{k}} \) between Bloch orbitals,

\[
\langle k'|\nabla_{\mathbf{k}}|k\rangle = \langle u_{k'm} | e^{i (\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}} \nabla_{\mathbf{k}} | u_{kn} \rangle,
\]

are zero unless \( k' = k \), since \( u_{k'm}(\mathbf{r})\nabla_{\mathbf{k}} u_{kn}(\mathbf{r}) \) is lattice periodic. [27, 28] The scaling of the self-consistent procedure used to solve Eqn. (32) is therefore linear in the number of \( k \) points.

3. Results and discussion

We show in Figure 2 the dependence of the coupled mean dynamical polarisability on the absorption energy in crystalline silicon, computed by including only the lowest optical excitation. Details of the calculations are as from Ref. [25]. In these examples, the energy of the lowest allowed excitation, corresponding to the optical gap of the system, was determined by solving Eqn. (32) at several values of \( \omega_I \) (filled shapes in Figure 2) and interpolating the results with an inverse law, \( \overline{\alpha}(\omega_I) = [A + B(\omega_I - C)]^{-1} \) (continuous lines). We remark that the profile of the mean dynamical polarisability extrapolated for \( \omega > \omega_I \) assumes that only one many-body excitation at \( \omega_I \) contributes to the absorption process, and does not therefore necessarily

**Figure 2.** Energy dependence of the mean dynamical polarisability of crystalline silicon with TD-LDA, TD-B3LYP and TD-HF, showing the position of the pole corresponding to the lowest optically-allowed many-body excitation. The dashed vertical line is the experimental value of the optical gap.
correspond to a physical situation. The three approximations used here, TD-HF, TD-LDA, and TD-B3LYP use the two-electron integrals of Eqsns. (27), (28) and (29) respectively in Eqn. (26). For the exchange-correlation kernel $f_{xc}$ in Eqsns. (28) and (29) we used the adiabatic local density approximation [12] (ALDA). The calculated values of the optical gaps are $E_{o}^{\text{HF}} = 4.86 \text{ eV}$, $E_{o}^{\text{LDA}} = 2.52 \text{ eV}$, $E_{o}^{\text{B3LYP}} = 3.44 \text{ eV}$, whereas the experimental estimate is $E_{o} = 3.5 \text{ eV}$. [36, 37]

In Figure (3) (left) we compare the calculated optical gaps for silicon with the corresponding independent-particle absorption spectra,

$$I(\omega) = \sum_{\mathbf{k}} w_{\mathbf{k}} \sum_{i} \sum_{d} \Gamma_{i}^{k,b} \delta(\varepsilon_{d}^{k} - \varepsilon_{i}^{k} - \omega).$$

(39)

TD-HF yields a large negative shift in the optical gap relative to the lowest energy Hartree-Fock absorption ($\sim 2.5 \text{ eV}$), but the resulting optical gap remains far too large compared to the experimental value. The huge overestimation of the independent-particle gap is a consequence of the virtual Hartree-Fock states lying at too high energies, owing to the fact that an electron promoted to an empty state experiences repulsion with $N$ (rather than $N-1$) electrons. [15]

The large negative shift in absorption energy brought about by TD-HF is related to the overestimation of the Coulomb attraction between the excited electron and the hole, which are only partially screened by many-body correlation effects. Overall, the TD-HF correction is however insufficient to correct the unphysically high virtual Hartree-Fock orbital energies. In LDA, the onset of the independent-particle absorption occurs at far too low energies. This is a consequence of the underestimation of the band gap in LDA. The TD-LDA correction, in the ALDA approximation, appears to be modest. Consistent with a number of studies on the performance of the ALDA kernel for extended systems in TD-DFT, we find here that the optical gap essentially occurs at the same energy as the lowest independent-particle LDA excitation, and both are largely underestimated relative to experiment. Finally, TD-B3LYP yields a moderate stabilisation of the particle-hole pair ($\sim 0.4 \text{ eV}$) relative to the independent-particle gap, [38, 39] and the resulting optical gap is in close agreement with experiment. This approach is therefore capable of reproducing the formation of bound excitonic pairs in silicon. [40]

TD-B3LYP yields accuracy comparable to the case of crystalline silicon ($\leq 0.1 \text{ eV}$ difference from experiment) for a number of other weakly bound excitonic semiconductors (Table 1), including technologically important direct-gap III-V semiconductors binaries. Satisfactory agreement with experiment is also observed in (at least some classes of) tightly bound excitons in
Table 1. Calculated optical gaps compared to experimental values. n/a indicates the optical gap is lower than 0.1 eV. Experimental data is from Refs. [36, 37] for all systems except SiO\textsubscript{2} (Ref. [41]) and LiF (Ref. [42]).

|       | TD-HF | TD-LDA | TD-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   | 8.83  | 1.91   | 3.52     | 3.51  |
| InN   | 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   |
| SiO\textsubscript{2} | -     | -      | 9.99     | 10.3  |
| LiF   | 16.3  | -      | 11.90    | 12.8  |

insulators, like SiO\textsubscript{2}, although self-trapping of the excitons can complicate the direct comparison with experiment in many cases. [43, 44] The ability of TD-B3LYP to describe accurately bound excitons in these cases is likely to be explained by the proper inclusion of the non-local interaction between an excited electron and a hole, which results in the appearance of an electron-hole Coulomb-like attraction term, \( f_{eh}(\mathbf{r}, \mathbf{r}') \propto -c_{HF}/|\mathbf{r} - \mathbf{r}'| \), in the response equations. This fact has been exploited in the construction of semi-empirical adiabatic response kernels that can account very accurately for the optical reponse of weakly bound excitonic systems. [2, 3, 40] In our formalism, the electron-hole Coulomb attraction term appears in consequence to the inclusion of the Fock exchange integrals, \(-\langle \mu \rho \nu \tau \rangle\), in Eqn. (29). [45, 46] It is interesting to observe that our approach, based on the self-consistent determination of the Kohn-Sham linear density matrix response (rather than solving directly for the linear density response, as is common in implementations of TD-DFT based on variational density-functional perturbation theory [29, 47–53]), treats the Fock exchange contribution, which can only be formulated as a non-adiabatic functional of the density, [16] as a purely adiabatic functional of the Kohn-Sham density matrix.

More complex appears to be the case of charge-transfer (CT) excitons, see e.g. LiF in Table 1, in which the electron and the hole localise in disconnected and possibly remote regions of space, or on different crystal sublattices. Similar to CT excitations in gas-phase molecules, [45, 54] TD-DFT with local, semi-local or hybrid XC functionals and adiabatic XC kernels yields CT energies that are far too low compared to experiment in the condensed phase. [29, 46, 55, 56] This failure may be interpreted in terms of the incorrect asymptotics of \( f_{eh} \), which, for \(|\mathbf{r} - \mathbf{r}'| \to \infty \), does not reproduce the proper Coulomb tail \(-1/|\mathbf{r} - \mathbf{r}'|\). Various methods have been proposed in the quantum-chemical literature to overcome this well-known limitation of (adiabatic) TD-DFT, typically based on imposing the correct asymptotics in the electron-hole attraction, e.g. using range-separated functionals in which the fraction of Fock exchange varies with the distance between particle and hole, [57–61] or via model response kernels describing the physical factors contributing to the CT process. [62–64] Our method can be extended to encompass these classes of approaches, which only require modifying the algorithm at the level of the calculation of the two-electron integrals, Eqns. (27)-(29). A more elegant and potentially much more far reaching approach that has been proved to describe accurately wide classes of excitons (including, in particular, the CT exciton of LiF) has recently been proposed by Sharma et al., [65] based on a bootstrap XC kernel that is computed self-consistently from the dielectric function during the
solution of the exact Dyson equation for the response.

4. Summary and conclusions

We have described a method for computing the electronic response of extended (crystalline) systems that accounts accurately and computationally efficiently for optical excitations, including those involving interactions between excited electrons and holes. Our approach can be implemented at various levels of theory (pure TD-DFT, TD-HF, hybrid TD-DFT) and shows a very favourable scaling with system size and/or number of $k$ points in Brillouin zone integrals. In its hybrid TD-DFT implementation, it achieves predictive accuracy for weakly bound excitonic semiconductors, without resorting to semi-empirical response kernels and/or a posteriori quasi-particle corrections of one-particle Kohn-Sham energies. Good agreement with experiment is also observed for tightly-bound excitons in insulators, whereas CT exciton energies are largely underestimated, similar to CT excitations in molecules. Possible generalisations to address these classes of excitations are currently being explored.

References

[1] Gross E K U and Kohn W 1990 Adv. Quant. Chem. 21 255
[2] Onida G, Reining L and Rubio A 2002 Rev. Mod. Phys. 74 601
[3] Botti S, Schindlmayr A, Sole R D and Reining L 2007 Rep. Prog. Phys. 70 357
[4] Burke K, Werschnik J and Gross E K U 2005 J. Chem. Phys. 123 062206
[5] Casida M E 2009 J. Mol. Struct. (THEOCHEM) 914 3
[6] Ullrich C 2012 Time-Dependent Density-Functional Theory: Concepts and Applications (Oxford University Press)
[7] Runge E and Gross E K U 1983 Phys. Rev. Lett. 52 997
[8] Petersilka M, Gossmann U J and Gross E K U 1996 Phys. Rev. Lett. 76 1212
[9] Petersilka M, Gross E K U and Burke K 2000 Int. J. Quant. Chem. 80 534
[10] Hohenberg P and Kohn W 1964 Phys. Rev. 136 B864
[11] Kohn W and Sham L J 1965 Phys. Rev. 140 A1133
[12] Zangwill A and Soven P 1981 Phys. Rev. B 24 4121
[13] Casida M E, Ipatov A and Cordova F 2006 Time-Dependent Density-Functional Theory ed Marques M A L, Ullrich C, Nogueira F, Rubion A and Gross E K U (Springer, Berlin)
[14] Drew A and Head-Gordon M 2005 Chem. Rev. 105 4009
[15] Szabo A and Ostlund N S 1964 Modern Quantum Chemistry (Dover Publications)
[16] McLachlan A D and Ball M A 1964 Reviews of Modern Physics 36 844
[17] Becke A D 1993 J. Chem. Phys. 98 1372
[18] Hirata S, Head-Gordon M and Bartlett R J 1999 J. Chem. Phys. 111 10774
[19] Hurst G J B and Dupuis M 1988 J. Chem. Phys. 89 385
[20] Kirtman B, Gu F L and Bishop D M 2000 J. Chem. Phys. 113 1294
[21] Ferrero M, Rérat M, Orlando R and Dovesi R 2008 J. Comput. Chem. 29 1450
[22] Dovesi R, Orlando R, Civalieri B, Roetti R, Saunders V R and Zicovich-Wilson C M 2005 Z. Kristallogr. 220 571
[23] Dovesi R et al., CRYSTAL09 User’s manual; http://www.crystal.unito.it/
[24] Bush I J, Tomic S, Searle B G, Mallia G, Bailey C T, Montanari B, Bernasconi L, Carr J M and Harrison N M 2011 Proc. Roy. Soc. A 467 2112
[25] Bernasconi L, Tomic S, Ferrero M, Rérat M, Orlando R, Dovesi R and Harrison N M 2011 Phys. Rev. B 83 195325
[26] Sokino H and Bartlett R J 1986 J. Chem. Phys. 85 976
[27] Blount E I 1962 Solid State Physics (Academic, New York)
[28] Otto P 1992 Phys. Rev. B 45 10856
[29] Bernasconi L, Sprik M and Hutter J 2003 J. Chem. Phys. 119 12417
[30] Atkins P W and Friedman R S 1999 Molecular Quantum Mechanics (Oxford University Press)
[31] Caves T C and Karplus M 1969 J. Chem. Phys. 50 3649
[32] Bishop D M and Kirtman B 1991 J. Chem. Phys. 95 2646
[33] Ferrero M, Rérat M, Orlando R and Dovesi R 2008 J. Chem. Phys. 128 014110
[34] Davidson E R 1975 Journal of Computational Physics 17 87
[35] Stratmann R E, Scuseria G E and Frisch M J 1998 J. Chem. Phys. 109 8218
3rd Workshop on Theory, Modelling and Computational Methods for Semiconductors

Journal of Physics: Conference Series 367 (2012) 012001
doi:10.1088/1742-6596/367/1/012001

[36] Madelung O 2004 *Semiconductors: Data Handbook* (Springer, Berlin)
[37] Heyd J, Peralta J E, Scuseria G E and Martin R L 2005 *J. Chem. Phys.* 123 174101
[38] Muscat J, Wander A and Harrison N M 2001 *Chem. Phys. Lett.* 342 397
[39] Tomič S, Montanari B and Harrison N M 2008 *Physica E* 40 2125
[40] Reining L, Olevano V, Rubio A and Onida G 2002 *Phys. Rev. Lett.* 88 066404
[41] Ramos L E, Furthmüller J and Bechstedt F 2004 *Phys. Rev. B* 69 085102
[42] Roessler D M and Walker W C 1967 *J. Phys. Chem. Solids* 28 1507
[43] Trukhin A N 1992 *Journal of Non-Crystalline Solids* 149 32
[44] Ismail-Beigi S and Louie S G 2005 *Phys. Rev. Lett.* 95 156401
[45] Dreuw A, Weisman J L and Head-Gordon M 2003 *J. Chem. Phys.* 119 2943
[46] Baroni S, de Gironcoli S, Corso A D and Giannozzi P 2001 *Rev. Mod. Phys.* 73 515
[47] Walker B, Saitta A M, Gebauer R and Baroni S 2006 *Phys. Rev. Lett.* 113001 113001
[48] Tozer D J, Amos R D, Handy N C, Roos B O, Lutnaes O B, Tozer D J and Handy N C 2006 *PhysChemChemPhys* 8 558
[49] Yanai T, Tew D P and Handy N C 2004 *Chem. Phys. Lett.* 393 51
[50] Rudberg E, Salek P, Helgaker T and Agren H 2005 *J. Chem. Phys.* 123 184108
[51] Casida M E, Gutierrez F, Guan J, Gadea F X, Salahub D and Daudé J P 2000 *J. Chem. Phys.* 113 7062
[52] Gritsenko O and Baerends E J 2004 *J. Chem. Phys.* 121 11885
[53] Sharma S, Dewhurst J K, Sanna A and Gross E K U 2011 *Phys. Rev. Lett.* 107 186401