

DENSITY-FUNCTIONAL PERTURBATION THEORY GOES TIME-DEPENDENT

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ABSTRACT. The scope of time-dependent density-functional theory (TDDFT) is limited to the lowest portion of the spectrum of rather small systems (a few tens of atoms at most). In the static regime, density-functional perturbation theory (DFPT) allows one to calculate response functions of systems as large as currently dealt with in ground-state simulations. In this paper we present an effective way of combining DFPT with TDDFT. The dynamical polarizability is first expressed as an off-diagonal matrix element of the resolvent of the Kohn-Sham Liouvillian super-operator. A DFPT representation of response functions allows one to avoid the calculation of unoccupied Kohn-Sham orbitals. The resolvent of the Liouvillian is finally conveniently evaluated using a newly developed non-symmetric Lanczos technique, which allows for the calculation of the entire spectrum with a single Lanczos recursion chain. Each step of the chain essentially requires twice as many operations as a single step of the iterative diagonalization of the unperturbed Kohn-Sham Hamiltonian or, for that matter, as a single time step of a Car-Parrinello molecular dynamics run. The method will be illustrated with a few case molecular applications.

Density-functional theory (DFT) is currently considered to be the state of the art for the quantum simulation of materials at the atomic (*nano*) scale [1]. Although its scope is limited by construction to the electronic ground state, many materials properties can be accurately and—with the aid of the powerful algorithms and computers presently available—inexpensively calculated through it. The establishment, twenty years ago, of density-functional perturbation theory (DFPT) [2] has considerably widened the scope of DFT, by allowing for the calculation of properties that can be expressed in terms static response functions, as well as of vibrational excitations in the harmonic Born-Oppenheimer approximation [3]. Thanks to these advances, it is now possible to predict the infrared, Raman, and inelastic neutron- or X-ray-diffraction spectra of materials with an accuracy which is often comparable with that achieved in the laboratory. Many other processes and properties that depend on the electron-phonon and phonon-phonon interactions (such as, *e.g.*, superconductivity [4, 5], thermo-elasticity [6, 7], or the width of spectral lines [8, 9, 10, 11]) can be simulated as well. Such an accuracy and flexibility open the way to the systematic use of *computational spectroscopy* as a powerful characterization tool: by comparing the dependence of the spectral features of a system on its atomic structure, which is readily simulated on a computer, with the spectra obtained in the laboratory, it is often possible to gain detailed information at the nano scale that would not be accessible by experimental means alone.

The situation is not as favorable for those spectroscopies, such as absorption in the visible or UV regions, or resonant Raman spectroscopy, for which the excitation of electrons across the energy gap plays an essential role. Extending the scope of DFT to electronic excitations is a very active field of research [12]. Time-dependent density-functional theory (TDDFT) [13] stands as a promising alternative to cumbersome many-body approaches to the calculation of the electronic excitation spectra of molecular and condensed-matter systems [14]. According to a theorem established in the mid eighties by Runge and Gross [13], for any given initial ($t = 0$) state of an interacting-electron system, the external time-dependent, potential acting on it is uniquely determined by the time evolution of the one-electron density, $n(\mathbf{r}, t)$, for $t > 0$. Using this theorem, one can formally establish a time-dependent Kohn-Sham (KS) equation that, once linearized, gives access to the dynamical susceptibility of the system, from which excitation energies and oscillator strengths can be obtained [15, 16]. Unfortunately, the computational methods available until very recently were so cumbersome that TDDFT could in practice be applied only to the low-lying portion of the spectrum of rather simple systems, consisting of a few tens inequivalent atoms at most [12]. New methods that would allow to simulate the spectra of complex molecular and nanostructured systems are therefore called for. One such method has indeed been recently proposed by scientists at the CNR-INFM DEMOCRITOS National Simulation Center in Trieste [17].

The time-dependent Kohn-Sham equations of Runge and Gross can be conveniently cast into an operator equation for the one-electron density matrix, $\hat{\rho}(t)$:

$$(1) \quad i \frac{d\hat{\rho}(t)}{dt} = [\hat{H}_{KS}(t), \hat{\rho}(t)],$$

where

$$(2) \quad \hat{H}_{KS}(t) = -\frac{1}{2} \frac{\partial^2}{\partial \mathbf{r}^2} + v_{ext}(\mathbf{r}, t) + v_{HXC}(\mathbf{r}, t)$$

is a time-dependent KS Hamiltonian, $v_{ext}(\mathbf{r}, t)$ and $v_{HXC}(\mathbf{r}, t)$ being the time-dependent external and Hartree-plus-exchange-correlation potentials, respectively, and the square brackets indicate a commutator. In the above equation, as well as in the following, quantum-mechanical operators are denoted by a hat, “ $\hat{}$ ”, and Hartree atomic units ($\hbar = m = e = 1$) are used. When no confusion can arise, local operators, such as one-electron potentials, \hat{V} , will be indicated by the diagonal of their real-space representation, $v(\mathbf{r})$, as in Eq. (2). Linearization of Eq. (1) with respect to the strength of an external perturbation leads to:

$$(3) \quad i \frac{d\hat{\rho}'(t)}{dt} = [\hat{H}_{KS}^\circ, \hat{\rho}'(t)] + [\hat{V}'_{HXC}(t), \hat{\rho}^\circ] + [\hat{V}'_{ext}(t), \hat{\rho}^\circ],$$

where $\hat{\rho}^\circ$ is the unperturbed density matrix, $\hat{\rho}'(t) = \hat{\rho}(t) - \hat{\rho}^\circ$, \hat{V}'_{ext} is the perturbing external potential, and \hat{V}'_{HXC} is the variation of the HXC potential linearly induced by

$n'(\mathbf{r}, t) = \rho'(\mathbf{r}, \mathbf{r}; t)$ that, in the adiabatic approximation,¹ reads:

$$(4) \quad v'_{HXC}(\mathbf{r}, t) = \int \kappa(\mathbf{r}, \mathbf{r}') n'(\mathbf{r}', t) d\mathbf{r}',$$

where $\kappa(\mathbf{r}, \mathbf{r}') = \frac{1}{|\mathbf{r}-\mathbf{r}'|} + \left. \frac{\delta v_{XC}(\mathbf{r})}{\delta n(\mathbf{r}')} \right|_{n(\mathbf{r})=n^\circ(\mathbf{r})}$. By inserting Eq. (4) into Eq. (3), one sees that the linearized Liouville equation can be cast into the form:

$$(5) \quad i \frac{d\hat{\rho}'(t)}{dt} = \mathcal{L} \cdot \hat{\rho}'(t) + [\hat{V}'_{ext}(t), \hat{\rho}^\circ],$$

where the action of the *Liouvillian super-operator*, \mathcal{L} , onto $\hat{\rho}'$, $\mathcal{L} \cdot \hat{\rho}'$, is defined as:

$$(6) \quad \mathcal{L} \cdot \hat{\rho}' \doteq [\hat{H}_{KS}^\circ, \hat{\rho}'] + [\hat{V}'_{HXC}[\hat{\rho}'], \hat{\rho}^\circ],$$

and $\hat{V}'_{HXC}[\hat{\rho}']$ is the linear operator functional of $\hat{\rho}'$ whose (diagonal) kernel is given by Eq. (4). By Fourier analysing Eq. (5), we obtain:

$$(7) \quad (\omega - \mathcal{L}) \cdot \tilde{\rho}'(\omega) = [\tilde{V}'_{ext}(\omega), \hat{\rho}^\circ].$$

The expectation value of any one-electron operator can be expressed as the trace of its product with the one-electron density matrix. The Fourier transform of the dipole linearly induced by the perturbing potential, \hat{V}'_{ext} , for example, reads:

$$(8) \quad \mathbf{d}(\omega) = \text{Tr}(\hat{\mathbf{r}}\tilde{\rho}'(\omega)),$$

where $\hat{\mathbf{r}}$ is the quantum-mechanical position operator, and $\tilde{\rho}'$ is the solution to Eq. (7). Let us now suppose that the external perturbation is a homogeneous electric field:

$$(9) \quad \tilde{v}'_{ext}(\mathbf{r}, \omega) = -\mathbf{E}(\omega) \cdot \mathbf{r}.$$

The dipole given by Eq. (8) reads:

$$(10) \quad d_i(\omega) = \sum_j \alpha_{ij}(\omega) E_j(\omega),$$

where the dynamical polarizability, $\alpha_{ij}(\omega)$, is defined by:

$$(11) \quad \alpha_{ij}(\omega) = -\text{Tr}(\hat{r}_i(\omega - \mathcal{L})^{-1} \cdot [\hat{r}_j, \hat{\rho}^\circ]).$$

Traces of products of operators can be seen as scalar products defined on the linear space of quantum mechanical operators. Eq. (11) can therefore be formally written as:

$$(12) \quad \alpha_{ij}(\omega) = -\langle \hat{r}_i | (\omega - \mathcal{L})^{-1} \cdot \hat{s}_j \rangle,$$

where

$$(13) \quad \hat{s}_j = [\hat{r}_j, \hat{\rho}^\circ]$$

is the commutator between the position operator and the unperturbed one-electron density matrix. The results obtained so far and embodied in Eq. (12) can be summarized by saying that *within TDDFT the dynamical polarizability can be expressed as an off-diagonal matrix element of the resolvent of the Liouvillian super-operator.*

¹In the adiabatic approximation, it is assumed that the exchange-correlation potential depends only on the charge density at the same time at which it is evaluated, and that this functional dependence is the same as in the electronic ground state.

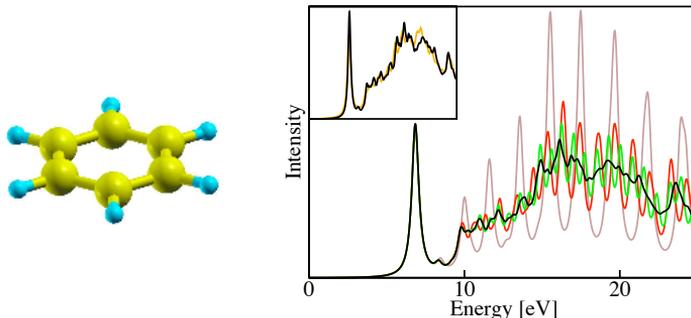


FIGURE 1. Absorption spectrum of benzene calculated using the Lanczos method with different numbers of recursion steps: 1000 (plum), 2000 (red), 3000 (green), and 6000 (black). The inset compares the 6000-step spectrum (black) with that obtained using the real-time propagation method (orange).

The calculation of the polarizability using Eqs. (11) or (12) implies our ability compute $(\mathcal{L} - \omega)^{-1} \cdot [\hat{r}_j, \hat{\rho}^\circ]$ in a super-operator linear system. The latter task, in turn, requires an explicit representation for the density-matrix response, $\tilde{\rho}'$, for its commutator with the unperturbed Hamiltonian, for local operators, such as \hat{r}_j of \hat{V}'_{HXC} , for their commutators with the unperturbed density matrix, as well as for the Liouvillian super-operator, or at least for its product with any relevant operators, \hat{A} , such as $\mathcal{L} \cdot \hat{A}$. All these tasks can efficiently be achieved by extending to the dynamical regime the representation of response functions adopted in DFPT [2, 3, 17]. In Ref. [17] it was also shown how the matrix element of Eqs. (11) and (12) can be conveniently calculated using a block-matrix variant of the non-symmetric Lanczos algorithm [18].

In Fig. 1 we display the absorption spectrum of benzene, as calculated for light polarized in the molecular plane [17]. We see that a few thousands Lanczos iterations are enough to obtain a spectrum that is very well converged up to frequencies of a few tens eV. After this innovative approach to the simulation of optical spectra was proposed in 2006 [17], a number of improvements have been devised [19, 20]. First of all, it was noticed that the number of iterations necessary to achieve convergence scales linearly with the condition number of the Liouvillian super-operator. By reducing such condition number (e.g. by reducing the width of the one-electron spectrum by employing ultra-soft pseudopotentials [21]) does allow for a considerable reduction of the computational burden of the simulation. In addition, a new extrapolation technique based on the *scalar* (rather than *matrix* as used before) non-Hermitian Lanczos algorithm allows one to limit the number of Lanczos iterations necessary to achieve well converged spectra to a few hundreds (or a couple of thousands in the less favorable cases). This is allowing us to calculate the absorption spectrum over a wide energy range for systems of hundreds of inequivalent atoms, a task that was thought to be formidable until very recently. As an example of the capabilities of

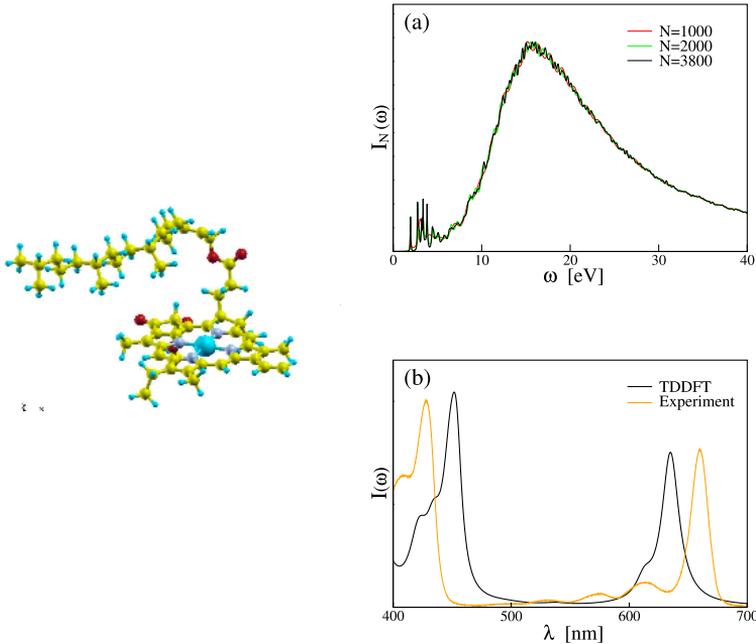


FIGURE 2. (a) Convergence of the chlorophyll a (left)absorption spectrum between 0 and 40 eV. (b) Chlorophyll absorption spectrum in the visible region for wavelengths between 400 and 700 nm compared with the experimental data in di-ethyl ether of Ref. [22].

the new method, in Fig. 2 we report the absorption spectrum calculated for chlorophyll-a (a 137-atom molecule: $C_{55}H_{72}O_5N_4Mg$).

In this paper we have presented a new algorithmic approach to linearized TDDFT that results from the combination of many elements which are individually not new in different communities, ranging from condensed matter and quantum chemistry, to control theory/engineering and signal processing. In particular our method is the natural extension to the dynamical regime of DFPT, a technique made popular in the condensed-matter community by the calculation of static properties (such as dielectric, piezoelectric, elastic) and by the calculation of phonons and related properties in crystals. The main features of the new method are that it is tailored to the calculation of *specific responses* to *specific perturbations* and that the computational burden for the calculation of the *complete* spectrum of a given response function in a wide frequency range is comparable to that of a *single* static ground-state or response-function calculation. We believe that, from the algorithmic point of view, the new method is close to optimal in its application range and that it opens thus the way to the simulation of the dynamical properties of large and very large molecular and condensed-matter systems. Assuredly, it cannot yield any better results than granted by the quality of the exchange-correlation functional used to implement it. Devising new

functionals capable of properly describing the electron-hole interaction responsible, *e.g.*, of Rydberg and excitonic effects in the low-lying portion of the spectrum of molecular and extended systems, respectively, remains a major problem to be addressed and solved.

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References

- [1] N. Marzari, *Realistic modeling of nanostructures using density functional theory*, MRS BULLETIN **31**, 681 (2006).
- [2] S. Baroni, P. Giannozzi, and A. Testa, *Green's function approach to linear response in solids*, Phys. Rev. Lett. **58**, 1861 (1987).
- [3] S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, *Phonons and related crystal properties from density-functional perturbation theory*, Rev. Mod. Phys. **73**, 515 (2001).
- [4] K.-P. Bohnen, R. Heid, H. J. Liu, and C. T. Chan, *Lattice Dynamics and Electron-Phonon Interaction in (3,3) Carbon Nanotubes*, Phys. Rev. Lett. **93**, 245501 (2004).
- [5] M. Calandra and F. Mauri, *Theoretical Explanation of Superconductivity in C_6Ca* , Phys. Rev. Lett. **95**, 237002 (2005).
- [6] J. Xie, S. de Gironcoli, S. Baroni, and M. Scheffler, *Temperature-dependent surface relaxations of Ag(111)*, Phys. Rev. B **59**, 970 (1999).
- [7] B.B. Karki, R.M. Wentzcovitch, S. de Gironcoli, and S. Baroni, *High-pressure lattice dynamics and thermoelasticity of MgO*, Phys. Rev. B **61**, 8793 (2000).
- [8] K.A. Mäder and S. Baroni, *Vibrational broadening of x-ray emission spectra: A first-principles study on diamond*, Phys. Rev. B **55**, 9649 (1997).
- [9] S. Pisana, M. Lazzeri, C. Casiraghi, K.S. Novoselov, A.K. Geim, A.C. Ferrari, and F. Mauri, *Breakdown of the adiabatic Born-Oppenheimer approximation in graphene*, Nature Mat. **6**, 198 (2007).
- [10] M. Lazzeri, M. Calandra, and F. Mauri, *Anharmonic phonon frequency shift in MgB_2* , Phys. Rev. B **68**, 220509 (2003).
- [11] A. Debernardi, S. Baroni, and E. Molinari, *Anharmonic Phonon Lifetimes in Semiconductors from Density-Functional Perturbation Theory*, Phys. Rev. Lett. **75**, 1819 (1995).
- [12] M.A.L. Marques, C.L. Ullrich, F. Nogueira, A. Rubio, K. Burke, and E.K.U. Gross, *Time-Dependent Density Functional Theory*, Lecture Notes in Physics, v. 706 (Springer-Verlag, Berlin and Heidelberg, 2006).
- [13] E. Runge and E.K.U. Gross, *Density-Functional Theory for Time-Dependent Systems*, Phys. Rev. Lett. **52**, 997 (1984).
- [14] G. Onida, L. Reining, and A. Rubio, *Electronic excitations: density-functional versus many-body Green's-function approaches*, Rev. Mod. Phys. **74**, 601 (2002).
- [15] M.E. Casida, *Recent Advances in Density Functional Methods, Part I*, (World Scientific, Singapore, 1995), p. 155.
- [16] M. Petersilka, U.J. Gossmann, and E.K.U. Gross, *Excitation Energies from Time-Dependent Density-Functional Theory*, Phys. Rev. Lett. **76**, 1212 (1996).
- [17] B. Walker, A.M. Saitta, R. Gebauer, and S. Baroni, *Efficient Approach to Time-Dependent Density-Functional Perturbation Theory for Optical Spectroscopy*, Phys. Rev. Lett. **96**, 113001 (2006).
- [18] Y. Saad, *Iterative Methods for Sparse Linear Systems*, second edition (SIAM, Philadelphia, 2003).
- [19] D. Rocca, *Time-dependent density-functional perturbation theory: new algorithms with applications to molecular spectra*, SISSA PhD thesis, unpublished; available on the web at URL: <http://www.sissa.it/cm/thesis/2007/Dario.Rocca.PhD.Thesis.pdf>.
- [20] D. Rocca, R. Gebauer, Y. Saad, and S. Baroni, *Turbocharging time-dependent density-functional theory with Lanczos chains*, J. Chem. Phys. **128**, 154105 (2008).
- [21] B. Walker and R. Gebauer, *Ultrasoft Pseudopotentials in Time-Dependent Density Functional Theory*, J. Chem. Phys. **127**, 164106 (2007).

[22] H. Du, R. C. A. Fuh, J. Li, L. A. Corkan, and J. S. Lindsey, *PhotochemCAD: A computer-aided design and research tool in photochemistry* Photochem. Photobio. **68**, 141 (1998).

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