PRL **109,** 153603 (2012) PHYSICAL REVIEW LETTERS week ending 12 OCTOBER 2012

Controlling the Dynamics of Many-Electron Systems from First Principles: A Combination of Optimal Control and Time-Dependent Density-Functional Theory

A. Castro,[1] J. Werschnik,[2] and E. K. U. Gross[3]

[1]*ARAID Foundation–Institute for Biocomputation and Physics of Complex Systems (BIFI)*
and Zaragoza Scientific Center for Advanced Modeling (ZCAM), University of Zaragoza, E-50018 Zaragoza, Spain
[2]*Jenoptik Optical Systems GmbH, Jena, Germany*
[3]*Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany*

(Received 14 September 2010; revised manuscript received 16 February 2012; published 12 October 2012)

Quantum optimal control theory (QOCT) provides the necessary tools to theoretically design driving fields capable of controlling a quantum system towards a given state or along a prescribed path in Hilbert space. This theory must be complemented with a suitable model for describing the dynamics of the quantum system. Here, we are concerned with many electron systems (atoms, molecules, quantum dots, etc.) irradiated with laser pulses. The full solution of the many-electron Schrödinger equation is not feasible in general, and therefore, if we aim for an *ab initio* description, a suitable choice is the time-dependent density-functional theory (TDDFT). In this Letter, we establish the equations that combine TDDFT with QOCT and demonstrate their numerical feasibility.

DOI: 10.1103/PhysRevLett.109.153603 PACS numbers: 42.50.Ct, 02.60.Pn, 31.15.ee, 32.80.Qk

The quest for systems able to perform quantum computing [1], the synthesis of design molecules by laser-induced chemical reactions [2], or the control of electron currents in molecular switches using light [3] may benefit from the recent advances in the field of design and synthesis of laser pulses specially tailored to perform specific tasks [4]. The laser pulse creation and shaping techniques have improved impressively over the last decades, and the area of experimental optimal control has therefore become a well-established field.

Such pulses can also be theoretically derived with the help of quantum optimal control theory (QOCT) [5]. This theory is rather general in scope, and its basic formulation makes no assumptions on the nature and modeling of the quantum system on which the pulse is applied. In practice, the solution of the QOCT equations requires multiple propagations, both forward and backward, for the system under study. Since these propagations are in general unfeasible for many-particle systems, few-level simplifications and models are typically postulated when handling the QOCT equations. Unfortunately, these simplifications are not always accurate enough: strong pulses naturally involve many electronic levels, and normally perturbative treatments are not useful. Nonlinear laser-matter interactions must sometimes be described *ab initio*.

In this Letter, we are concerned with many-electron systems irradiated with femtosecond pulses, with intensities typically ranging from 10^{11} to 10^{15} $\mathrm{W\,cm^{-2}}$—a nonlinear regime that nevertheless allows for a nonrelativistic treatment. This may lead to a number of interesting phenomena, e.g., above-threshold or tunnel ionization, bond hardening or softening, high harmonic generation, photoisomerization, photofragmentation, Coulomb explosion, etc., [6]. The control of these processes should be treated with an electronic first principles theory; some possibilities are, for example, the time-dependent configuration interaction or time-dependent multiconfiguration Hartree-Fock [7,8] theories. However, the time-dependent density-functional theory [9] (TDDFT) has emerged as a viable alternative to more computationally expensive approaches based on the wave function.

In TDDFT, the system of interacting electrons is substituted by a proxy system of noninteracting electrons—the "Kohn-Sham" system, which is computationally much less demanding. The theory guarantees the identity of the electronic densities of the two systems and existence of a density functional for each possible observable, thus allowing the computation of any property without having to deal with the many-body wave function. The theory is however hindered by the lack of knowledge of the precise external potential seen by the auxiliary noninteracting system. Fortunately, a number of valid approximations have been developed over the years, which have made of the TDDFT a computationally efficient possibility to describe many processes.

We are thus led to the necessity of inscribing the TDDFT into the general QOCT framework. We will lay down and discuss the equations that result when TDDFT is used to model the system. Then, in order to demonstrate its computational feasibility, we present one sample calculation: a 2D two-electron system optimally driven between two potential wells.

In the spirit of TDDFT, we substitute the problem of formulating QOCT in terms of a real interacting system by formulating the optimization problem for the noninteracting system of electrons. The equations of motion for the single-particle electronic orbitals of this system, also known as the time-dependent Kohn-Sham equations, are

$$i\frac{\partial\varphi_i}{\partial t}(\vec{r},t) = \hat{H}_{\mathrm{KS}}[n(t),u,t]\varphi_i(\vec{r},t) = -\frac{1}{2}\nabla^2\varphi_i(\vec{r},t) + v_0(\vec{r})\varphi_i(\vec{r},t) + v_H[n(t)](\vec{r})\varphi_i(\vec{r},t) + v_{\mathrm{xc}}[n(t)]\varphi_i(\vec{r},t) + v_{\mathrm{ext}}(\vec{r},u,t)\varphi_i(\vec{r},t), \quad (1)$$

$$n(\vec{r},t) = \sum_{i=1}^{N/2} 2\varphi_i^*(\vec{r},t)\varphi_i(\vec{r},t), \quad (2)$$

for $i = 1,\ldots,N/2$ orbitals that accomodate N electrons. For simplicity, we will assume a spin-restricted or spin-compensated situation, in which spin-up and spin-down electrons are paired, occupying equal orbitals [10]. The density is, by construction, equal to that of the real, interacting system of electrons; v_0 contains the internal, time-independent fields—usually a nuclear Coulomb potential determined by the charges Z_α and positions $\vec{R}_\alpha$ of a set of nuclei. To improve readability, we omit these parameters in the notation. The term $v_H[n(t)](\vec{r}) = \int d^3r' \frac{n(\vec{r}',t)}{|\vec{r}-\vec{r}'|}$ is the Hartree potential, and $v_{\mathrm{xc}}[n]$ is the exchange and correlation potential operator. We assume here an adiabatic approximation; i.e., v_{xc} at each time t is a functional of the density at that time, $n(t)$. This restriction is nonessential for the derivations that follow, but the use of nonadiabatic functionals is very scarce, and adiabatic approximations will result in simpler equations.

The last potential term, v_{ext}, is the external time-dependent potential, which is determined by a "control" u. In a typical case, this external potential is the electric pulse created by a laser source in the dipole approximation and u is the real time-dependent function that determines its temporal shape [in this case, $v_{\mathrm{ext}}(\vec{r},u,t) = u(t)\vec{r}\cdot\vec{p}$, where $\vec{p}$ is the polarization vector of the pulse].

If we group the $N/2$ single particle states into a vector $\underline{\varphi}(t)$, we can rewrite the time-dependent Kohn-Sham equations in a matrix form:

$$i\dot{\underline{\varphi}}(t) = \underline{\hat{H}}[n(t),u,t]\underline{\varphi}(t), \quad (3)$$

where $\underline{\hat{H}}[n(t),u,t] = \hat{H}_{\mathrm{KS}}[n(t),u,t]\underline{I}$ and $\underline{I}$ is the $N/2$-dimensional unit matrix. With this notation, we stress the fact that we have only one dynamical system, and not $N/2$ independent ones, since all φ_i are coupled. This coupling, however, comes solely through the density, since the Hamilton matrix is diagonal.

The specification of the value of the control u, together with the initial conditions, determines the solution orbitals: $u \rightarrow \underline{\varphi}[u]$. Our task is now the following: we have to find an external field—in the language of the OCT, a control u—that induces some given behavior of the system, which can be mathematically formulated by stating that the induced dynamics maximizes some target functional F. Since we are using TDDFT, this functional will be defined in terms of the Kohn-Sham orbitals, and will possibly depend explicitly on the control u:

$$F = F[\underline{\varphi},u]. \quad (4)$$

In the most general case, the functional F depends on $\underline{\varphi}$ at all times during the process (we have a "time-dependent target"). In many cases, however, the goal is the achievement of some target at a given time T that determines the end of the propagation interval (we then have a "static" or "terminal" target). In order to accommodate both possibilities, we may split F into two parts, one terminal target F^{term}, and one time-dependent target F^{td}:

$$F[\underline{\varphi},u] = F^{\mathrm{td}}[\underline{\varphi},u] + F^{\mathrm{term}}[\underline{\varphi}(T),u]. \quad (5)$$

Note that the argument of F^{term} is not the full evolution of the Kohn-Sham system, but only its state at the end of the propagation.

Since the orbitals depend on u as well, the goal of QOCT can be formulated as finding the maximum of the function:

$$G[u] = F[\underline{\varphi}[u],u]. \quad (6)$$

There are many optimization algorithms capable of maximizing the functions by utilizing solely the knowledge of the function values ("gradient-free algorithms"). We have recently employed one of such algorithm in this context [11]. However, QOCT provides the solution to the problem of computing the gradient of G—or, properly speaking, the functional derivative, if u is a function. The nonlinear dependence of the Hamiltonian on the density slightly complicates the derivation in comparison to the common derivation for standard linear Schrödinger systems [12], but we sketch the key steps. First, we must note that searching for a maximum of G is equivalent to a constrained search for F—constrained by the fact that the $\underline{\varphi}$ orbitals must fulfill the time-dependent Kohn-Sham equations. In order to do so, we introduce a new set of orbitals $\underline{\chi}$ that act as Lagrange multipliers, and define a new functional J by adding a Lagrangian term L to F:

$$J[\underline{\varphi},\underline{\chi},u] = F[\underline{\varphi},u] + L[\underline{\varphi},\underline{\chi},u], \quad (7)$$

$$L[\underline{\varphi},\underline{\chi},u] = -2\sum_{j=1}^{N/2}\mathrm{Re}\left[\int_0^T dt\langle\chi_j(t)\left|\frac{d}{dt} + i\hat{H}_{\mathrm{KS}}[n(t),u,t]\right|\varphi_j(t)\rangle\right]. \quad (8)$$

Setting the functional derivatives of J with respect to the χ orbitals to zero, we retrieve the time-dependent Kohn-Sham equations. In an analogous manner, we obtain a set of solution $\underline{\chi}[u]$ orbitals by taking functional derivatives with respect to $\underline{\varphi}$:

$$\frac{\delta J}{\delta\underline{\varphi}^*} = 0 \Rightarrow$$

$$i\dot{\chi}(t) = [\hat{H}_{\mathrm{KS}}[n[u](t), u, t] + \hat{K}[\underline{\varphi}[u](t)]]\underline{\chi}(t) - i\frac{\delta F^{\mathrm{td}}}{\delta \underline{\varphi}^*}, \tag{9}$$

$$\underline{\chi}(T) = \frac{\delta F^{\mathrm{term}}}{\delta \underline{\varphi}^*(T)}. \tag{10}$$

The presence of the nondiagonal operator matrix $\hat{K}[\underline{\varphi}[u](t)]$ is the main difference with respect to the normal QOCT equations for a linear quantum system. Its origin is the nonlinear dependence of the Kohn-Sham Hamiltonian with respect to the propagating orbitals. Indeed, we can see in Eq. (8) how the Kohn-Sham orbitals $\underline{\varphi}$ appear not only explicitly at the right-hand side of the Dirac bracket expression inside the integral, but also implicitly through the density $n(t)$ that determines the Kohn-Sham Hamiltonian $\hat{H}_{\mathrm{KS}}[n(t), u.t]$. This fact must be considered when taking the functional derivative, and leads to the appearance of the matrix $\hat{K}$. This is given by

$$\langle\vec{r}|\hat{K}_{ij}[\underline{\varphi}[u](t)]|\psi\rangle = -4i\varphi_i[u](\vec{r}, t)\,\mathrm{Im}\Big[\int d^3r'\,\psi^*(\vec{r}') \times f_{H\mathrm{xc}}[n[u](t)](\vec{r}, \vec{r}')\varphi_j[u](\vec{r}', t)\Big], \tag{11}$$

where f_{Hxc} is the kernel of the Kohn-Sham Hamiltonian, defined as

$$f_{\mathrm{Hxc}}[n](\vec{r}, \vec{r}') = \frac{1}{|\vec{r} - \vec{r}'|} + \frac{\delta v_{\mathrm{xc}}[n](\vec{r})}{\delta n(\vec{r}')}. \tag{12}$$

If we now note that $G[u] = J[\underline{\varphi}[u], \underline{\chi}[u], u]$, we arrive at

$$\nabla_u G[u] = \nabla_u F[\underline{\varphi}, u]|_{\underline{\varphi}=\underline{\varphi}[u]} + 2\mathrm{Im}\Bigg[\sum_{j=1}^{N/2}\int_0^T dt\langle\chi_j[u](t)|\nabla_u\hat{V}_{\mathrm{ext}}[u](t)|\varphi_j[u](t)\rangle\Bigg]. \tag{13}$$

Several aspects of these equations deserve further discussion:

(1) Equations (9) and (10) are a set of first-order differential equations, whose solution must be obtained by backward propagation, since the boundary condition Eq. (10) is given at the end of the propagating interval T. Note that this propagation depends on the Kohn-Sham orbitals $\underline{\varphi}[u]$. Therefore, the numerical procedure consists of a forward propagation to obtain $\underline{\varphi}[u]$, followed by a backward propagation to obtain $\underline{\chi}[u]$.

(2) These backward equations are nonhomogeneous owing to the presence of the last term in Eq. (9), the functional derivative of F with respect to $\underline{\varphi}$.

(3) Often, the control target functional F is split like

$$F[\underline{\varphi}, u] = J_1[\underline{\varphi}] + J_2[u]. \tag{14}$$

Here, J_1 codifies the actual purpose of the optimization, whereas J_2 imposes a penalty on the control function in order to avoid, for example, the solution field to have unreasonable amplitudes. In the following, we will assume this division.

(4) Equation (13) shown above assumes that u is a set of M parameters, $u \in \mathbb{R}^M$, that determines the control function. If u is directly the control function, the gradient has to be substituted by a functional derivative, and the result will be

$$\frac{\delta G}{\delta u(t)} = \frac{\delta F[\underline{\varphi}, u]}{\delta u(t)}\Big|_{\underline{\varphi}=\underline{\varphi}[u]} + 2\mathrm{Im}\Bigg[\sum_{j=1}^{N}\langle\chi_j[u](t)|\hat{D}|\varphi_j[u](t)\rangle\Bigg]. \tag{15}$$

We have assumed here that the external potential operator $\hat{v}_{\mathrm{ext}}$ is determined by the function u by a linear relationship,

$$\hat{v}_{\mathrm{ext}}[u](t) = u(t)\hat{D}. \tag{16}$$

This is the most usual case [$\hat{D}$ would be the dipole operator, and $u(t)$ the amplitude of an electric field], but of course it would be trivial to generalize this to other possibilities.

(5) Once one has the expression for the gradient [either Eq. (13) or (15)], some algorithm has to be employed in order to obtain the optimized fields. Various OCT-specific choices have been put forward [5], specially when dealing with continuous control parameters [as in Eq. (15)], but for the example shown below, we have simply employed the conjugate gradients scheme.

The previous scheme therefore permits us to control the Kohn-Sham system. However, the goal is to control the real system. In principle, the target is given by some functional $\tilde{J}_1[\Psi]$ that depends on the real many-electron wave function of the interacting system. This object is not provided by TDDFT, which only provides the density n. Therefore, the ideal situation would be one in which $\tilde{J}_1$ depends on Ψ only through the density n, $\tilde{J}_1 = \tilde{J}_1[n]$. In this manner, optimizing the Kohn-Sham system is strictly equivalent to optimizing for the real system [13]. For example, this holds if $\tilde{J}_1$ is given by the expectation value of some one-body local operator $\hat{A}$:

$$\tilde{J}_1[\Psi] = \langle\Psi(T)|\hat{A}|\Psi(T)\rangle = \int d^3r n(\vec{r}, T)a(\vec{r}), \tag{17}$$

where $\hat{A} = \sum_{i=1}^N a(\hat{\vec{r}}_i)$. In this case, Eq. (10) is simply

$$\chi_i[u](\vec{r}, T) = 2a(\vec{r})\varphi_i[u](\vec{r}, T). \tag{18}$$

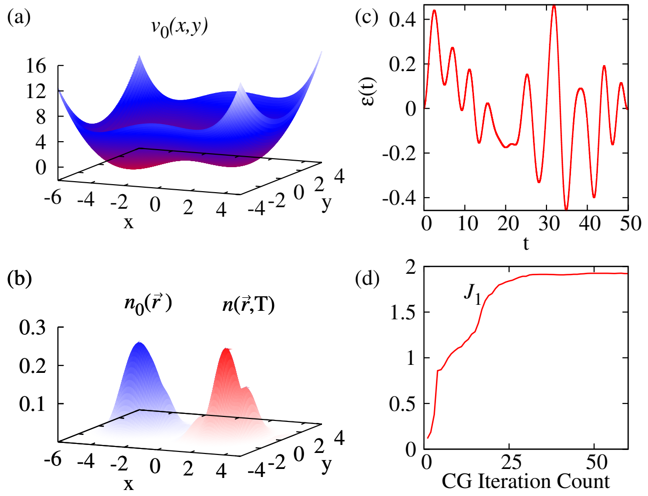

FIG. 1 (color online). (a) External potential defining a model for double quantum dot. (b) Density of the initial ground state [blue, $n_0(\vec{r})$], and final propagated density [red, $n(\vec{r}, T)$]. (c) Optimized electric field for the charge-transfer process described in the text. (d) Convergence history of the conjugate gradient algorithm. All magnitudes are given in effective atomic units.

We have implemented the described TDDFT + QOCT formalisms in the octopus code [14]. In the following, we describe a simple example: the charge transfer between two neighboring potential wells, considered as models for 2D quantum dots, such as the ones created in semiconductor heterostructures. We consider a two-electron system trapped in an asymmetric double quantum dot, well modeled by a potential function, given by (in the following, we consider effective atomic units):

$$v_0(x, y) = \frac{1}{64}x^4 - \frac{1}{4}x^2 + \frac{1}{32}x^3 + \frac{1}{2}y^2. \qquad (19)$$

The potential landscape is depicted in Fig. 1(a). We then solve the ground-state Kohn-Sham equations for this system using local density approximation to the exchange and correlation [15]. The ground-state density will be localized in the left well [see Fig. 1(b)].

We apply an electric field $\epsilon(t)$, polarized along the x direction. Its amplitude is parameterized by its Fourier coefficients $\{u_j\}_{j=1}^{N}$ that constitute the control parameters: i.e., $\hat{V}[u](t) = \sum_j u_j g_j(t)\hat{x}$, where $g_j(t)$ are the Fourier basis functions (normalized sines and cosines). The Fourier coefficients are constrained to enforce $\epsilon(0) = \epsilon(T) = 0$. Since our goal is to transfer as much charge as possible from the left well to the right well, we formulate a target in the form

$$F[\underline{\varphi}, u] = \int_{x>0} d^2r\, n(\vec{r}, T) - \alpha \int_0^T dt\, \epsilon^2[u](t). \qquad (20)$$

In other words, we intend to arrive at a state in which all the density is localized in the $x > 0$ region. The last term of Eq. (20) corresponds to the penalty, and it is introduced in order to prevent the solution field from having too much intensity. The equation for the gradient, Eq. (13), reads for this case as follows:

$$\frac{\partial G}{\partial u_j}[u] = -2\alpha u_j + 2\mathrm{Im}\left[\int_0^T dt g_i(t)\langle\chi[u](t)|\hat{x}|\varphi[u](t)\rangle\right]. \qquad (21)$$

The solution field is shown in Fig. 1(c). We have employed a standard conjugate gradients (CG) algorithm to perform the optimization. After around 60 CG iterations [16,17], the control field is converged, and we achieve a value of 1.92 for J_1; the maximum is 2 (see convergence plot in Fig. 1).

In conclusion, we have shown how TDDFT can be combined with QOCT. The computational cost of each optimization amounts to a few tens or hundreds of TDDFT propagations. Therefore, the process is numerically tractable for realistic *ab initio* laser-molecule interactions, thanks to the good scalability of real-time TDDFT [18]. This is proven by the numerous simulations of molecules and clusters in the presence of laser pulses published during the last decade [19].

This provides a scheme to perform QOCT calculations from first principles, in order to obtain tailored function-specific laser pulses capable of controlling the electronic state of atoms, molecules, or quantum dots. Most of the previous applications of QOCT were targeted to control, with femtosecond pulses, the motion of the nuclear wave packet on one or a few potential energy surfaces, which typically happens on a time scale of hundreds of femtoseconds or picoseconds. The approach developed in this Letter, on the other hand, is particularly suited to control the motion of the electronic degrees of freedom, which is governed by the subfemtosecond time scale. The possibilities that are open, thanks to this technique, are numerous: shaping of high harmonic–generation spectra (i.e., quenching or increasing given harmonic orders), selective excitation of electronic excited states that are otherwise difficult to reach with conventional pulses, control of electronic current in molecular junctions, etc. Research along these lines is in progress.

This study was partially supported by the Deutsche Forschungsgemeinschaft within the SFB 762, and by the European Commission within the FP7 CRONOS project (ID 280879). A. C. acknowledges support by the research project FIS2009-13364-C02-01 (MICINN, Spain).

[1] C. M. Tesch, L. Kurtz, and R. de Vivie-Riedle, Chem. Phys. Lett. **343**, 633 (2001); J. P. Palao and R. Kosloff, Phys. Rev. Lett. **89**, 188301 (2002).

[2] T. Laarmann, I. Shchatsinin, P. Singh, N. Zhavoronkov, M. Gerhards, C. P. Schulz, and I. V. Hertel, J. Chem. Phys. **127**, 201101 (2007).

[3] D. Geppert, L. Seyfarth, and R. de Vivie-Riedle, Appl. Phys. B **79**, 987 (2004).

[4] A. M. Weiner, Rev. Sci. Instrum. **71**, 1929 (2000).

[5] M. Shapiro and P. Brumer, *Principles of the Quantum Control of Molecular Processes* (Wiley, New York, 2003); S. A. Rice and M. Zhao, *Optical Control of Molecular Dynamics* (John Wiley & Sons, New York, 2000); J. Werschnik and E. K. U. Gross, J. Phys. B **40**, R175 (2007); J. Werschnik, *Quantum Optimal Control Theory: Filter Techniques, Time-Dependent Targets, and Time-Dependent Density Functional Theory* (Cuvillier Verlag, Göttingen, 2006); G. G. Balint-Kurti, S. Zou, and A. Brown, Adv. Chem. Phys. **138**, 43 (2008); R. Roloff, M. Wenin, and W. Potz, J. Comput. Theor. Nanosci. **6**, 1837 (2009); C. Brif, R. Chakrabarti, and H. Rabitz, New J. Phys. **12**, 075008 (2010); For recent developments, see the dedicated volume edited by H. Rabitz, *ibid.* **11**, 105030 (2009).

[6] M. Protopapas, C. H. Keitel, and P. L. Knight, Rep. Prog. Phys. **60**, 389 (1997); T. Brabec and F. Krausz, Rev. Mod. Phys. **72**, 545 (2000); A. Scrinzi, M. Y. Ivanov, R. Kienberger, and D. M. Villeneuve, J. Phys. B **39**, R1 (2006).

[7] The use of multiconfiguration time-dependent Hartree Fock in combination with QOCT was proposed by M. Mundt and D. J. Tannor, New J. Phys. **11**, 105038 (2009).

[8] In a different context, another approach to the control of many-body quantum systems has been recently proposed by P. Doria, T. Calarco, and S. Montangero, Phys. Rev. Lett. **106**, 190501 (2011).

[9] E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984); *Time-Dependent Density Functional Theory*, edited by M. A. L. Marques, C. A. Ullrich, F. Nogueira, A. Rubio, K. Burke, and E. K. U. Gross (Springer-Verlag, Berlin, 2006).

[10] A. Castro and E. Gross, in *Fundamentals of Time-Dependent Density Functional Theory*, edited by M. A. Marques, N. T. Maitra, F. M. Nogueira, E. Gross, and A. Rubio Lecture Notes in Physics Vol. 837 (Springer-Verlag, Berlin, 2012), p. 265.

[11] A. Castro, E. Räsanen, A. Rubio, and E. K. U. Gross, Europhys. Lett. **87**, 53001 (2009).

[12] Details on the derivation can be found, for example, in A. P. Peirce, M. A. Dahleh, and H. Rabitz, Phys. Rev. A **37**, 4950 (1988); S. H. Tersigni, P. Gaspard, and S. A. Rice, J. Chem. Phys. **93**, 1670 (1990); I. Serban, J. Werschnik, and E. K. U. Gross, Phys. Rev. A **71**, 053810 (2005).

[13] Although TDDFT ensures that all observables are functionals of the density, in practice we do not know the explicit functional form for many of them (one notable example would be the population of a given excited state). These would have to be approximated, which would introduce additional errors.

[14] M. A. L. Marques, A. Castro, G. F. Bertsch, and A. Rubio, Comput. Phys. Commun. **151**, 60 (2003); A. Castro, H. Appel, M. Oliveira, C. A. Rozzi, X. Andrade, F. Lorenzen, M. A. L. Marques, E. K. U. Gross, and A. Rubio, Phys. Status Solidi B **243**, 2465 (2006).

[15] C. Attacalite, S. Moroni, P. Gori-Giorgi, and G. B. Bachelet, Phys. Rev. Lett. **88**, 256601 (2002).

[16] We are brief on numerical details. The interested reader may find the detailed description of the code used in Ref. [14], and more updated information can be obtained at http://www.tddft.org/programs/octopus/. The code itself is available at that web page.

[17] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.109.153603 for the input and output files of the run.

[18] M. A. L. Marques and E. K. U. Gross, in *Time-Dependent Density Functional Theory*, edited by M. A. L. Marques, C. A. Ullrich, F. Nogueira, A. Rubio, K. Burke, and E. K. U. Gross (Springer Verlag, Berlin, 2006) Chap. 15, p. 227.

[19] F. Calvayrac, P.-G. Reinhard, E. Suraud, and C. Ullrich, Phys. Rep. **337**, 493 (2000); A. Castro, M. Marques, J. Alonso, G. Bertsch, and A. Rubio, Eur. Phys. J. D **28**, 211 (2004); M. Isla and J. A. Alonso, Phys. Rev. A **72**, 023201 (2005); D. Dundas, J. Chem. Phys. **136**, 194303 (2012).