

Real-time linear response for time-dependent density-functional theory

Roi Baer

Department of Physical Chemistry and the Lise Meitner Minerva-Center for Quantum Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

Daniel Neuhauser

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095

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We present a linear-response approach for time-dependent density-functional theories using time-adiabatic functionals. The resulting theory can be performed both in the time and in the frequency domain. The derivation considers an impulsive perturbation after which the Kohn–Sham orbitals develop in time autonomously. The equation describing the evolution is not strictly linear in the wave function representation. Only after going into a symplectic real-spinor representation does the linearity make itself explicit. For performing the numerical integration of the resulting equations, yielding the linear response in time, we develop a modified Chebyshev expansion approach. The frequency domain is easily accessible as well by changing the coefficients of the Chebyshev polynomial, yielding the expansion of a formal symplectic Green’s operator. © 2004 American Institute of Physics. [DOI: 10.1063/1.1808412]

I. INTRODUCTION

The use of time-dependent density-functional theory (TDDFT) within linear response (LR) theory is one of the most robust and accurate methods for determining excitation energies and properties of molecules.^{1–14} The application of LR within TDDFT is usually based on a frequency domain framework, similar to the random-phase approximation, and is considered the method of choice. There has not been a time-dependent alternative suggested, as far as we know, except for a solution of the exact time-dependent density-functional equations with a weak perturbation.^{12,15–17} The latter method is very slow as the equations are nonlinear. Linear equation formulation benefits from the availability of efficient Chebyshev methods developed for molecular quantum dynamics,^{18,19} which does not work well for nonlinear problem.

In this paper we develop a time-dependent approach for linear response. Instead of the sinusoidal perturbation used for the frequency LR, we use an impulsive (δ -function) perturbation. The resulting equations assume the form of linear Schrödinger-like equations for the *perturbed orbitals*. All the LR information about system is obtained from the time-dependent propagation. The spectrum, if needed, can be obtained directly; for example, by Fourier transforming. The linearization in time potentially allows us to “watch” the processes, obtaining useful insight, not available in the frequency domain. It has an additional advantage by allowing a host of methods developed originally for the usual linear Schrödinger equation, including approaches for obtaining very efficiently spectra from short-time propagation^{20,21} (filter diagonalization). In this paper we first derive the methodology and then exemplify for clamped (frozen) nuclei.

II. THEORY

A. Generalities

Consider $2N$ electrons in their singlet ground state. This ground state can be treated using density-functional theory, where the density $n_0(\mathbf{r}) = 2\sum_{k=1}^N |\phi_k(\mathbf{r})|^2$ is written in terms of the N normalized Kohn–Sham orbitals which are solutions of the Kohn–Sham equations:

$$H_0 \phi_k(\mathbf{r}) = \varepsilon_k \phi_k(\mathbf{r}), \quad (1)$$

where $H_0 = K + v[n_0](\mathbf{r})$ is the Kohn–Sham Hamiltonian. Here $v[n](\mathbf{r}) = v_{ext}(\mathbf{r}) + v_H[n](\mathbf{r}) + v_{xc}[n](\mathbf{r})$ is the Kohn–Sham potential composed of the external, Hartree, and exchange–correlation potentials. (We often suppress the reference to the n dependence of the potential.) Suppose that at time $t=0$ the external potential is subject to a impulsive time-dependent perturbation (with $\hbar = 1$):

$$V(\mathbf{r}, t) = v(\mathbf{r}) + \eta \lambda(\mathbf{r}) \delta(t), \quad (2)$$

where η is a small parameter and $\lambda(\mathbf{r})$ is a spatial function (referred to below as the dipole function, although it could be quite general). The Runge–Gross theory assumes that there exists (and proves uniqueness of) a time-dependent exchange correlation potential $v_{xc}[n](\mathbf{r}, t)$ with which the time-dependent density can be expressed as $n(\mathbf{r}, t) = 2\sum_{k=1}^N |\psi_k(\mathbf{r}, t)|^2$, where

$$\psi_k(\mathbf{r}, 0) = \phi_k(\mathbf{r}), \quad (3)$$

and the time-dependent orbitals obey the following equations of motion:

$$i \dot{\psi}_k(\mathbf{r}, t) = H \psi_k(\mathbf{r}, t) \equiv [K + V(\mathbf{r}, t)] \psi_k(\mathbf{r}, t), \quad (4)$$

where we introduce the Hamiltonian, which, we recall, depends on the wave function through its dependence on the Kohn–Sham potential (so $v = v[n], H = H[n]$). Note that there is no problem with the use of a δ -function pulse even if

the functional is adiabatic, so that formally it requires smooth time variation in the system. The reason is the use of a linear response, which makes the system linear. Essentially, by applying a weak δ -function pulse and then Fourier transforming the results, we get exactly the same results (up to a trivial frequency-dependent normalization constant) that would have been obtained if we were to apply a pulse made of a smooth envelope function. If we were to derive the formalism more strictly, we would need to apply a smooth pulse of an arbitrary center frequency and then linearize the evolution, but the results would be the same (for linear response only) as those from a weak δ -function pulse.

Linear-response theory can be obtained by considering only the first-order changes in the orbitals:

$$\psi_k(\mathbf{r}, t) = e^{-i\varepsilon_k t} [\phi_k(\mathbf{r}) + \eta v_k(\mathbf{r}, t)]. \quad (5)$$

The parameter η is the same as that in Eq. (2). The normalized response of the orbital is $v_k(\mathbf{r}, t)$ and the linear response density is

$$\eta n_1(\mathbf{r}, t) = 2\eta \sum_{k=1}^N \phi_k(\mathbf{r}) \{v_k(\mathbf{r}, t) + v_k(\mathbf{r}, t)^*\}, \quad (6)$$

where

$$\begin{aligned} \eta n_1 &= n - n_0, \\ n_0 &= 2 \sum_k |\phi_k|^2. \end{aligned} \quad (7)$$

The equation of motion for $v_k(\mathbf{r}, t)$ at $t > 0$ is derived by using Eq. (5) in Eq. (4). The existence of the perturbation is manifest in noting that immediately after the perturbation (formally at “ $t = 0^+$ ”) $\psi_k(0^+) = [1 - i\eta\lambda(\mathbf{r})]\phi_k$, or

$$v_k(\mathbf{r}, t = 0) = -i\lambda(\mathbf{r})\phi_k(\mathbf{r}). \quad (8)$$

The equations obeyed by v are obtained by plugging Eq. (5) into Eq. (4) and keeping only first order in η :

$$\begin{aligned} i\dot{v}_k(\mathbf{r}, t) &= (H_0 - \varepsilon_k)v_k(\mathbf{r}, t) \\ &+ \eta^{-1} \{v[n_0 + \eta n_1](\mathbf{r}, t) - v_0(\mathbf{r})\} \phi_k(\mathbf{r}), \end{aligned} \quad (9)$$

where $v_0(\mathbf{r}) \equiv v[n_0](\mathbf{r})$, $H_0 \equiv H[n_0]$. We now show how the last (nonhomogeneous) term can be represented as a linear operator acting on the unknown v . A shorthand notation is

$$i\dot{v}_k(\mathbf{r}, t) = (H_0 - \varepsilon_k)v_k(\mathbf{r}, t) + [L\nu]_k(\mathbf{r}, t), \quad (10)$$

where $\varepsilon = \text{diag}\{\varepsilon_1, \varepsilon_2, \dots\}$. The operator L operates on the vector of functions $\{v_k\}_{k=1}^N$ in the following form:

$$\begin{aligned} [L\nu(\mathbf{r}, t)]_k &= \eta^{-1} \{v[n_0 + \eta n_1](\mathbf{r}, t) - v_0(\mathbf{r})\} \phi_k(\mathbf{r}) \\ &= \phi_k(\mathbf{r}) \int \frac{\delta v[n](\mathbf{r}, t)}{\delta n(\mathbf{r}', t)} n_1(\mathbf{r}', t) d\mathbf{r}' \\ &= 4 \sum_{k'=1}^N \int L_{kk'}(\mathbf{r}, \mathbf{r}') v'_{k'}(\mathbf{r}', t) d\mathbf{r}', \end{aligned} \quad (11)$$

where

$$L_{kk'}(\mathbf{r}, \mathbf{r}') = \phi_k(\mathbf{r}) \frac{\delta v[n](\mathbf{r})}{\delta n(\mathbf{r}')} \phi_{k'}(\mathbf{r}'). \quad (12)$$

This form, where $L_{kk'}(\mathbf{r}, \mathbf{r}')$ is time independent, is strictly correct only when the functional is adiabatic, i.e., $v[n] \times(\mathbf{r}, t) = v[n(t)](\mathbf{r})$, depending only on the present density and not on its history. This is the case with most potentials employed nowadays in TDDFT, and should carry over to current-dependent functionals.

B. Practical evolution

Despite the existence of an explicit definition of L in Eq. (12), this equation should not be used in practical calculations as it is extremely expensive numerically. We derive the practical equations in two stages, the first employing separately the real and imaginary parts, and then an even simpler version, which employs complex algebra.

The starting point is to note that we can define directly

$$[L\nu]_k(\mathbf{r}, t) = l(\mathbf{r}, t) \phi_k(\mathbf{r}), \quad (13)$$

where

$$l(\mathbf{r}, t) = \lim_{\beta \rightarrow 0} \frac{1}{\eta} [v[n + \eta n_1](\mathbf{r}, t) - v[n](\mathbf{r}, t)]. \quad (14)$$

From Eq. (11) it is immediately evident that when operating on a vector of real-valued functions *this operator is linear*. (It turns out, as we will show in a future publication, that this is also *positive definite*.) However, when operating on *complex* valued functions this operator is not linear because evidently, for ν real, $L(i\nu) \neq iL\nu$. There is a very clear reason for that. In essence, a purely imaginary ν does not change the density (to the first order, which we consider), just like an addition of a small imaginary part to a real number does not change, to first order, its amplitude. However, a real ν does change the density.

Yet, we can go to a representation in which everything is *linear*, by working with purely real functions, the real and imaginary part of the wave function (remember that the imaginary part of a function is real). Formally, this separation into real and imaginary parts, $\nu = \nu' + i\nu''$, is a “symplectic representation of quantum mechanics.”²² From Eq. (10),

$$\begin{aligned} \dot{v}'_k(\mathbf{r}, t) &= (H_0 - \varepsilon_k)v''_k(\mathbf{r}, t), \\ \dot{v}''_k(\mathbf{r}, t) &= -(H_0 - \varepsilon_k)v'_k(\mathbf{r}, t) - (L\nu')_k(\mathbf{r}, t), \end{aligned} \quad (15)$$

or, ignoring the indices,

$$\frac{d}{dt} \begin{pmatrix} \nu' \\ \nu'' \end{pmatrix}_t = \mathbf{A} \begin{pmatrix} \nu' \\ \nu'' \end{pmatrix}, \quad (16)$$

where

$$\mathbf{A} = \begin{pmatrix} 0 & H_0 - \varepsilon \\ -(H_0 - \varepsilon) - L & 0 \end{pmatrix}. \quad (17)$$

The operator \mathbf{A} is linear on the space of real vector functions. Evidently, it is nonsymmetric, but this by itself does not preclude using any of the standard computational approaches of quantum mechanics.

Equations (16) and (17), together with the definitions of L [Eqs. (13) and (14)] are sufficient to calculate the action of \mathbf{A} . However, it is interesting that there is an even simpler shortcut,

$$\mathbf{A} \begin{pmatrix} \nu' \\ \nu'' \end{pmatrix} = \begin{pmatrix} \text{Re } \gamma \\ \text{Im } \gamma \end{pmatrix}, \quad (18)$$

where

$$\gamma = \frac{1}{i\eta} [H[n_0 + \eta n_1(\nu')] [\phi + \eta(\nu' + i\nu'')] - H_0 \phi], \quad (19)$$

and where the calculation is taken in the limit of weak perturbation ($\eta \rightarrow 0$). This is the form we used in practice. (It may seem that this equation can be derived immediately, by simply writing H as a complex function of $\phi + \eta\nu$; however, there are complications associated with the fact that H is also a function of ν^* , so that the longer derivation is necessary.)

C. Time form

The formal evolution of the perturbation in time is

$$\begin{pmatrix} \nu' \\ \nu'' \end{pmatrix}_t = e^{\mathbf{A}t} \begin{pmatrix} \nu' \\ \nu'' \end{pmatrix}_0, \quad (20)$$

where the initial vector is

$$\begin{pmatrix} \nu' \\ \nu'' \end{pmatrix}_0 = \begin{pmatrix} 0 \\ -\lambda \phi \end{pmatrix}. \quad (21)$$

Interestingly, this leads to the following form for the total dipole, using Eq. (6) and employing an obvious bra-ket notation:

$$\mu \equiv \int n^1(\mathbf{r}, t) \lambda(\mathbf{r}) d\mathbf{r} = 4 \left\langle \lambda \phi \quad 0 \left| e^{\mathbf{A}t} \begin{pmatrix} 0 \\ \lambda \phi \end{pmatrix} \right. \right\rangle, \quad (22)$$

which looks very much like a regular correlation function, except that the order of the zero and nonzero terms in the bra and the ket is switched. Note that this expression involves purely real algebra.

The complex perturbation as a function of time is then, in symbolic notation,

$$\nu_t = \nu' + i\nu'' = (1 \quad i) \begin{pmatrix} \nu' \\ \nu'' \end{pmatrix}_t. \quad (23)$$

The exponential can be evaluated by any standard iterative approach in which one applies \mathbf{A} repeatedly. (Note that it is less suitable to use a split-operator approach²³ since \mathbf{A} is not evaluated here explicitly but is only defined in terms of its action on a vector.) The most common iterative approaches are Chebyshev expansion¹⁸ and Lanczos methods, and we will discuss here the Chebyshev approach (which has here a slightly unfamiliar form since \mathbf{A} replaces the usual $-iH$ term, i.e., has the $-i$ implicitly):

$$e^{\mathbf{A}t} \begin{pmatrix} \nu' \\ \nu'' \end{pmatrix}_0 = \sum_m (2 - \delta_{m0}) J_m(t\Delta) \zeta_m, \quad (24)$$

where ζ_m are vectors that are obtained by a Chebyshev-like iterative operation:

$$\zeta_m \equiv \begin{pmatrix} \zeta'_m \\ \zeta''_m \end{pmatrix} = \tilde{T}_m \left(\frac{\mathbf{A}}{\Delta} \right) \begin{pmatrix} \nu' \\ \nu'' \end{pmatrix}_0, \quad (25)$$

where the action of the quasi-Chebyshev polynomials, $\tilde{T}_m = \cosh[m \cosh^{-1}(\mathbf{A}/\Delta)]$ is defined through

$$\zeta_m = \frac{2}{\Delta} \mathbf{A} \zeta_{m-1} + \zeta_{m-2}, \quad (26)$$

and

$$\begin{aligned} Z_0 &= \zeta_0 = \begin{pmatrix} \nu' \\ \nu'' \end{pmatrix}_0, & \zeta_1 &= \frac{1}{\Delta} \mathbf{A} \zeta_0. \\ Z_1 &= \frac{\mathbf{A}}{\Delta \mathbf{A}}. \end{aligned} \quad (27)$$

Here, Δ is a numerical parameter, conveniently taken to be a typical half-width of the Hamiltonian, as usual in Chebyshev expansion.

The time-dependent response of the orbitals is readily then

$$\eta \nu_k(\mathbf{r}, t) = \eta \sum_m J_m(t\Delta) [\zeta'_m(\mathbf{r}, k) + i\zeta''_m(\mathbf{r}, k)], \quad (28)$$

so that the modified density is

$$\begin{aligned} n_1(\mathbf{r}, t) &= \sum_m J_m(t\Delta) n_m(\mathbf{r}), \\ n_m(\mathbf{r}) &= 4 \sum_k \phi_k(\mathbf{r}) \zeta'_m(\mathbf{r}, k), \end{aligned} \quad (29)$$

while for the dipole,

$$\mu(t) = \sum_m J_m(t\Delta) R_m, \quad (30)$$

where the residues are

$$R_m = 4 \left\langle \lambda \phi \quad 0 \left| \begin{pmatrix} \zeta'_m \\ \zeta''_m \end{pmatrix} \right. \right\rangle = 4 \int \sum_k \lambda(\mathbf{r}) \phi_k(\mathbf{r}) \zeta'_m(\mathbf{r}, k) d\mathbf{r}. \quad (31)$$

Similar residues can be defined for expectation values of other operators.

D. Frequency form

The equations can be readily extended to a frequency realm. Formally (ignoring orbital indices),

$$\nu_w = \int e^{(i\omega - \alpha)t} \nu_t dt = \int e^{(i\omega - \alpha)t} (1 \quad i) e^{\mathbf{A}t} \begin{pmatrix} \nu' \\ \nu'' \end{pmatrix}_0 dt, \quad (32)$$

where $e^{-\alpha t}$ is a convergence factor, such that

$$\begin{aligned} \nu_w &= \int (1 \quad i) e^{\mathbf{A}t + (i\omega - \alpha)t} \begin{pmatrix} \nu' \\ \nu'' \end{pmatrix}_0 dt \\ &= (1 \quad i) \frac{1}{\alpha - i\omega - \mathbf{A}} \begin{pmatrix} \nu' \\ \nu'' \end{pmatrix}_0. \end{aligned} \quad (33)$$

The operator $(1 i) [1/(\alpha - i\omega - \mathbf{A})]$ can be identified therefore as a Green's function $G(\omega)$ for the linear-response equations. The relevant equation for the dipole moment is then

$$\mu(\omega) = 4 \left\langle \lambda \phi \quad 0 \left| \frac{1}{\alpha - i\omega - \mathbf{A}} \begin{pmatrix} 0 \\ \lambda \phi \end{pmatrix} \right. \right\rangle. \quad (34)$$

The Chebyshev expansion for the dipole is very simple:

$$\mu(\omega) = 4 \sum_m a_m(\omega) R_m, \quad (35)$$

where^{24,25}

$$\begin{aligned} a_m(\omega) &= (2 - \delta_{m0}) \int e^{(i\omega - \alpha)t} J_m(t\Delta) dt \\ &= \frac{(2 - \delta_{m0}) i^{m-1}}{\sqrt{\Delta^2 - (\omega - i\alpha)^2}} \exp[-im \cos^{-1}(\omega - i\alpha - \Delta)]. \end{aligned} \quad (36)$$

Similarly,

$$\nu_w(\mathbf{r}, k) = \eta \sum_m a_m(\omega) [\zeta'_m(\mathbf{r}, k) + i\zeta''_m(\mathbf{r}, k)]. \quad (37)$$

III. RESULTS

We simulated the dipole response using Eqs. (35), (31), (25), (18), and (19). The system was a jellium (constant positive density) ellipsoid on a grid with $8 \times 8 \times 8$ points. The grid spacing was $2.5a_0$, and the Jellium radii in the x , y , and z directions were 5.88, 6.47, and 7.06 Bohrs, respectively. The jellium density was $0.0088419/a_0^3$, and it was smoothed at the edges using a Fermi-Dirac function with a width of 0.5 Bohr. The total jellium charge was $10.6e$ and a total of eight electrons (four orbitals) were used, so that the overall system is not neutral. The length of each Chebyshev vector was the number of grid points times the number of orbitals, i.e., $8^3 \times 4 = 2048$.

For the simulation we used $\Delta = 3$ a.u. Further savings could have been obtained if we were to use also a shift of the \mathbf{A} operator, but no shift was applied here.

Figure 1 shows the dipole response of this simple system, which is essentially a plasmon resonance, using the linear-response equations enumerated above, and compared with a simple Runge-Kutta calculation of the response. The agreement is excellent.

The results were stable with respect to the numerical parameter η within a more than six orders of magnitude.

IV. SUMMARY AND DISCUSSION

We have presented a formalism of LR within adiabatic TDDFT with which a TD picture of the electronic response can be calculated. This formalism is an efficient alternative for LR calculations in the frequency domain, particularly if the underlying electronic basis is very large, like a plane wave or grid. With the advent of attosecond laser pulses,²⁶⁻²⁸ the TD picture may reveal an interesting wave packet dynamics which is hidden in the frequency regime.

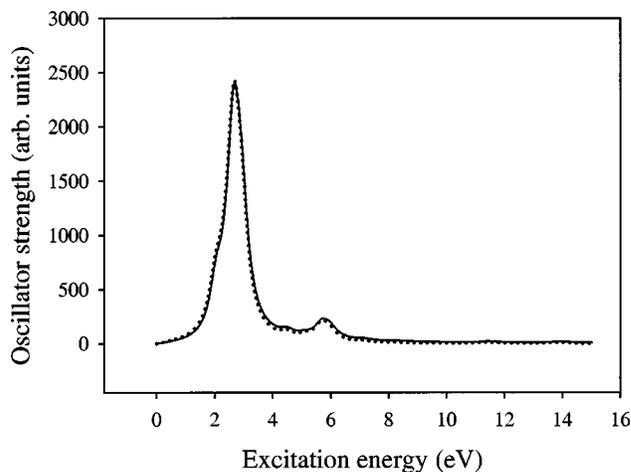


FIG. 1. The dipole spectrum for a metallic (jellium) shell of density $n = 0.0088a_0^{-3}$. The solid line shows the result of the Fourier transformed spectrum directly from the full TD Kohn-Sham equations, and the dotted line shows the results of the linearized Chebyshev propagation.

Performance-wise, the use of a linear propagator (Chebyshev here) makes the approach much more efficient than the original time-dependent propagation; for comparison, for a total time propagation T , we need $T\Delta$ Hamiltonian operations, or one Hamiltonian operation per $1/\Delta \sim 0.3$ a.u.; in a nonoptimized Runge-Kutta we ran, we needed at least 100 times more Hamiltonian operations. As far as the spectrum, the resolution needed to get a width of α is easily shown to be about $(5-10)\Delta/\alpha$, leading to about 3000 Hamiltonian operators in our case.

The numerical effort may be reduced even further once the filter diagonalization or other signal processing approaches are used, as will be studied in a future work.

One drawback of this algorithm which we did not discuss is runoff solutions. Specifically, the time-dependent linear response equation is non-Hermitian, and therefore the eigenvalues may have nonzero imaginary values, leading to damped and run-off solutions. This is an intrinsic problem of linear response; we did not encounter this problem here, but even when it exists the spectra can be still calculated directly using Chebyshev or Lanczos methods.^{24,25}

We note that previous work by Kohn *et al.*¹⁷ have also analyzed the relation between the time-dependent approach and the formal Hamiltonian of the system in the linear response regime, and the use of a weak perturbation to extract the spectra has been done by several groups.^{12,15-17} All those works have used, however, time-dependent methods appropriate for time-dependent Hamiltonians (most usually split-operator methods). The key point distinguishing this paper is that we have shown that it is possible to use methods of time-independent Hamiltonians to extract the time-dependent orbitals. In fact, in an upcoming work we show that with this linear-response reduction we can use the extremely efficient QMR approach to extract spectra with a minimal number of Hamiltonian applications, even though the original functional is nonlinear; this also avoids the problem of run-off solutions.

Finally, note that the formalism was developed for a single determinant. However, it is valid for more general

cases. No matter what the ingredients are—single determinant, multiple determinants, or even a density matrix—the main idea can be used: propagate linearly and add to the zero-order part the propagated linear part at each evolution step.

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