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Generalized time-dependent density-functional-theory response functions for spontaneous density fluctuations and nonlinear response: Resolving the causality paradox in real time

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Time-ordered superoperators are used to develop a unified description of nonlinear density response and spontaneous fluctuations of many-electron systems. The pth-order density response functions are decomposed into 2^{p+1} non-causal *Liouville space pathways*. Individual pathways are symmetric to the interchange of their space, time, and superoperator indices and can thus be calculated as functional derivatives. Other combinations of these pathways represent spontaneous density fluctuations and the response of such fluctuations to an external field. The resolution of the causality paradox of time-dependent density-functional theory (TDDFT) is shown to be intimately connected with the nonretarded nature of fluctuations.

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Time-dependent density-functional theory (TDDFT) is based on the theorem of Runge and Gross [1] that maps the interacting many-electron system onto a noninteracting system which has the same time-dependent charge-density profile $n(\mathbf{r}t)$, and is driven by an effective potential that includes an exchange-correlation contribution $v_{\rm xc}(n)$. The theorem has had remarkable successes in predicting electronic excitations and currents of molecules and materials [2–7]. It is desirable to base the theory on a time-dependent action principle which, in analogy with ordinary DFT, should allow us to obtain the density as a functional derivative of an action $\widetilde{A}(v(\mathbf{r}t))$ with respect to the external potential $v(\mathbf{r}t)$

$$n(\mathbf{r}t) = \frac{\delta\widetilde{A}}{\delta v(\mathbf{r}t)}. \tag{1}$$

Such action-principle could allow us to construct functionals variationally. However, such an action does not exist. To see the problem, consider the second derivative

$$\frac{\delta^2\widetilde{A}(v(\mathbf{r}t))}{\delta v(\mathbf{r}t)\,\delta v(\mathbf{r}'t')} = \frac{\delta n(\mathbf{r}t)}{\delta v(\mathbf{r}'t')} \equiv \chi(\mathbf{r}t,\mathbf{r}'t'). \tag{2}$$

Permutation of the space/time arguments of both sides leads to a paradox [3]: The right-hand side is the density response function which must be causal, i.e., vanish for $t' > t$, whereas the left-hand side is symmetric to the interchange of its space and time arguments. van Leeuwen [8,9] has recently shown how to construct such an action on the Keldysh loop [10–12]whereby an artificial pseudotime τ goes forward in one part of the loop and then backward. The actual response can then be obtained by a transformation to real (physical) time. The time-dependent Kohn-Sham equations and the time-dependent optimized potential method TDOPM were obtained using this technique.

In this paper we provide different insight into this issue by introducing *generalized response functions* which describe both spontaneous density fluctuations and nonlinear response along the same footing. DFT had shifted the focus of electronic structure theory from the many-body wave function to the charge density. TDDFT had extended these ideas to the time-dependent charge density created in response to an external potential. However, neither theory had paid much attention to *spontaneous* density fluctuations which constitute another important aspect of the charge density, perhaps since they do not show up naturally in the standard derivations. Such fluctuations may be observed by ultrafast x-ray diffraction [13–15]. They also play an important role in intermolecular forces [16,17].

Small fluctuations are related to the linear response by the fluctuation dissipation theorem and are not independent. Therefore they are automatically built into the theory in this regime and need not be addressed explicitly. This is no longer the case for nonlinear fluctuations and response which do not have a unique simple relation [18].

We employ superoperator techniques in Liouville space [19–22] to construct a generalized action directly in real time. TDDFT is extended towards the computation of a generating function for multipoint correlation functions representing spontaneous fluctuations. van Leeuwen's results are recovered since the Keldysh and the superoperator formalisms can be uniquely mapped [19,23]. Denoting the space-time coordinates as $\mathbf{x}_j \equiv \mathbf{r}_j t_j$, the pth-order ordinary response function is given by [3,24]

$$\begin{aligned}\chi^{(p)}(\mathbf{x}_{p+1}\cdots\mathbf{x}_1) &= (-i)^p \sum_{\rm perm} \theta(t_{p+1}-t_p)\,\theta(t_p-t_{p-1})\cdots\theta(t_2-t_1)\\ &\quad\times\langle[\cdots[[\hat{n}(\mathbf{x}_{p+1}),\hat{n}(\mathbf{x}_p)],\hat{n}(\mathbf{x}_{p-1})]\cdots,\hat{n}(\mathbf{x}_1)]\rangle. \end{aligned}\tag{3}$$

$\chi^{(p)}$ describes the response generated at point $\mathbf{r}_{p+1}t_{p+1}$ to p fields interacting with the system at points $\mathbf{r}_1t_1\cdots\mathbf{r}_pt_p$ and $\hat{n}$ is the charge-density operator. The step functions $\theta(t)$ which guarantee causality $t_1\cdots t_p < t_{p+1}$ and also keep track of time ordering make it impossible to recast the response function as a functional derivative. $\Sigma_{\rm perm}$ is a sum over the $p!$ permutations of $\mathbf{x}_1\cdots\mathbf{x}_p$. Without these permutations $t_1\cdots t_p$ are chronologically ordered: t_1 is the time of the first interaction, etc. With these permutations, $\chi^{(p)}$ is symmetrized. t_1 is then the interaction at point $\mathbf{r}_1$, but not necessarily the first. The frequency-domain susceptibility is given by the p-fold Fourier transform of $\chi^{(p)}$.

The connection between the response and spontaneous fluctuations is most clearly and naturally established by introducing a superoperator notation [19–22]. With every ordinary operator B we associate two superoperators B^L and B^R which act on any other operator X from the left and the right, respectively, $B^L X \equiv BX, B^R X \equiv XB$. We further introduce their symmetric and antisymmetric combinations $B^+ \equiv \frac{1}{2}(B^L + B^R), B^- \equiv B^L - B^R$. We then have $B^+ X \equiv \frac{1}{2}[BX + XB], B^- X \equiv BX - XB$. Another important operation is the time ordering operator of superoperators T: when acting on any product of superoperators it rearranges them so that time increases from right to left. T is the key for the following derivations: it allows us to remain in real time and avoid the Keldysh forward/backward time loop. Using this notation we can recast $\chi^{(p)}$ in the compact form

$$\chi^{(p)}(\mathbf{x}_{p+1}\cdots\mathbf{x}_p) = (-i)^p \left\langle T\hat{n}^+(\mathbf{x}_{p+1})\hat{n}^-(\mathbf{x}_p)\hat{n}^-(\mathbf{x}_{p-1})\cdots\hat{n}^-(\mathbf{x}_1)\right\rangle, \tag{4}$$

where $\hat{n}^+$ and $\hat{n}^-$ are the superoperators corresponding to the charge density. The entire bookkeeping of time ordering and all the step functions and permutations in Eq. (3) now follow naturally from the superoperator time ordering operator T. Causality enters in Liouville space in an interesting way: since the trace of a commutator is zero, the last superoperator to the far left must be a "+." This guarantees that $t_1 \cdots t_p \leqslant t_{p+1}$. Since each superoperator (+ or −) is a combination of two superoperators (L and R), the response function $\chi^{(p)}$, Eq. (4), can be decomposed into a sum of 2^{p+1} more elementary objects called *Liouville space pathways* (LSPs),

$$\chi^{(p)}(\mathbf{x}_{p+1}\cdots\mathbf{x}_1) = (-i)^p \sum_{\{\nu_j\}=L,R} (-1)^{\xi} \chi^{\nu_{p+1}\cdots\nu_1}(\mathbf{x}_{p+1}\cdots\mathbf{x}_1), \tag{5}$$

where

$$\chi^{\nu_{p+1}\cdots\nu_1}(\mathbf{x}_{p+1}\cdots\mathbf{x}_1) \equiv \left\langle T\hat{n}^{\nu_{p+1}}(\mathbf{x}_{p+1})\cdots\hat{n}^{\nu_1}(\mathbf{x}_1)\right\rangle. \tag{6}$$

The indices ν_j assume the values L or R, and ξ is the number of "right" indices associated with $\hat{n}^-$ operators. Equation (3) has 2^p terms (p nested commutators) whereas Eq. (4) has 2^{p+1} terms. Nevertheless, the two are identical by virtue of the cyclic invariance of the trace [$\hat{n}^+(\mathbf{x}_{p+1})$ can be replaced by either $\hat{n}^L(\mathbf{x}_{p+1})$ or $\hat{n}^R(\mathbf{x}_{p+1})$ without affecting the trace]. The extra permutation provides for a more symmetric representation. It should be emphasized that individual LSPs are noncausal. In fact they are *symmetric* with respect to the permutation of any pair of their space/time and ν indices $\mathbf{x}_j\nu_j \leftrightarrow \mathbf{x}_{j'}\nu_{j'}$. It is this superoperator symmetry that makes it possible to work in real (physical) time and will allow us to recast the response in terms of functional derivatives. To illustrate this supersymmetry and how the time ordering prescription for superoperators works, let us consider the four pathways contributing to the linear ($p=1$) response,

$$\begin{aligned}\chi^{LL}(\mathbf{x}_2,\mathbf{x}_1) &= \left\langle T\hat{n}^L(\mathbf{x}_1)\hat{n}^L(\mathbf{x}_2)\right\rangle \\ &= \theta(t_1 - t_2)\left\langle \hat{n}(\mathbf{x}_1)\hat{n}(\mathbf{x}_2)\right\rangle + \theta(t_2 - t_1)\left\langle \hat{n}(\mathbf{x}_2)\hat{n}(\mathbf{x}_1)\right\rangle,\end{aligned} \tag{7}$$

$$\begin{aligned}\chi^{RR}(\mathbf{x}_2,\mathbf{x}_1) &= \left\langle T\hat{n}^R(\mathbf{x}_1)\hat{n}^R(\mathbf{x}_2)\right\rangle \\ &= \theta(t_1 - t_2)\left\langle \hat{n}(\mathbf{x}_2)\hat{n}(\mathbf{x}_1)\right\rangle + \theta(t_2 - t_1)\left\langle \hat{n}(\mathbf{x}_1)\hat{n}(\mathbf{x}_2)\right\rangle,\end{aligned} \tag{8}$$

$$\chi^{RL}(\mathbf{x}_2,\mathbf{x}_1) = \left\langle T\hat{n}^R(\mathbf{x}_1)\hat{n}^L(\mathbf{x}_2)\right\rangle = \left\langle \hat{n}(\mathbf{x}_1)\hat{n}(\mathbf{x}_2)\right\rangle, \tag{9}$$

$$\chi^{LR}(\mathbf{x}_2,\mathbf{x}_1) = \left\langle T\hat{n}^L(\mathbf{x}_1)\hat{n}^R(\mathbf{x}_2)\right\rangle = \left\langle \hat{n}(\mathbf{x}_2)\hat{n}(\mathbf{x}_1)\right\rangle. \tag{10}$$

Combining all four terms yields the linear-response function

$$\begin{aligned}\chi^{(1)}(\mathbf{x}_2,\mathbf{x}_1) &\equiv \chi^{+-}(\mathbf{x}_2,\mathbf{x}_1) \\ &= \tfrac{1}{2}(\chi^{LL} - \chi^{RR} + \chi^{RL} - \chi^{LR}) \\ &= -i\theta(t_1 - t_2)\left\langle\left[\hat{n}(\mathbf{x}_1),\hat{n}(\mathbf{x}_2)\right]\right\rangle.\end{aligned} \tag{11}$$

For completeness we also give the other combination representing spontaneous fluctuations,

$$\begin{aligned}\chi^{++}(\mathbf{x}_2,\mathbf{x}_1) &= \tfrac{1}{4}(\chi^{LL} + \chi^{RR} + \chi^{LR} + \chi^{RL}) \\ &= \tfrac{1}{2}\left[\left\langle \hat{n}(\mathbf{x}_1)\hat{n}(\mathbf{x}_2)\right\rangle + \left\langle \hat{n}(\mathbf{x}_2)\hat{n}(\mathbf{x}_1)\right\rangle\right].\end{aligned} \tag{12}$$

Note that the four LSPs [Eqs. (7)–(10)] are not symmetric with respect to the space/time ($\mathbf{x}_j$) permutation alone. However, they are symmetric when permuting the superoperator index as well ($\mathbf{x}_j\nu_j$). The entire response function given by the combination of LSPs is causal. The same symmetries hold for higher-order response functions: superoperator time ordering thus allows us to recast the pth-order response as a combination of 2^{p+1} symmetric terms. LPSs have proven very useful in nonlinear spectroscopy [24,25]. Individual pathways can now be obtained naturally as functional derivatives which can be combined at the end to yield the response functions. The LSPs are not merely artificial constructs but offer a physical picture of the density response based on the single electron density matrix rather than the Kohn-Sham orbitals. In fact, it is possible to design resonant nonlinear optical measurements that could select individual pathways out of the entire response through phase matching (selection of wave vectors) [24].

The physical reason why the LSPs are nonretarded is that they describe not only the response to external perturbations but also spontaneous charge-density fluctuations which are obviously noncausal. The ordinary response function Eq. (4) is only one possible combination of the 2^{p+1} LSP. Only that particular combination is fully retarded. Other combinations are generalized response functions which describe either spontaneous fluctuations or the effects of external driving on such fluctuations [16]. The "all plus" combination $\langle\hat{n}^+(\mathbf{x}_{p+1})\cdots\hat{n}^+(\mathbf{x}_1)\rangle$ describes pure equilibrium density fluctuations. The "all-minus" combination vanishes identically (being the trace of a commutator). Other combinations may be interpreted as the response of density fluctuations to external fields [21,18]. For example, $\langle\hat{n}^+(\mathbf{x}_3)\hat{n}^+(\mathbf{x}_2)\hat{n}^-(\mathbf{x}_1)\rangle$ represents the linear response of the two time fluctuation $\langle \hat{n}^{+}(\mathbf{x}_3)\hat{n}^{+}(\mathbf{x}_2)\rangle$ to an external potential acting at $\mathbf{x}_1$ [16]. Thus the Liouville space functional also provides a complete characterization of spontaneous fluctuations. The causality paradox originates from focusing solely on the response, which is how TDDFT is traditionally derived. By formulating the problem in Liouville space it becomes evident from the outset that the response and spontaneous fluctuations are inseparable and should be treated along the same footing. Once this is recognized the problem is immediately cured.

Rather than computing directly the density response we should therefore derive a generating functional for the entire family of LSPs. These are the elementary building blocks for both the causal density response and the noncausal density fluctuations, which can be constructed by proper combinations of the LSPs. When the nonlinear response is computed as a sum over the many-electron states we immediately obtain the LSPs [24]. However, such expansion is impractical for complex systems and the standard TDDFT response may not be easily decomposed into LSPs; the bookkeeping is entirely different.

The generating functional may be computed by recasting TDDFT using the density matrix. We start with the Liouville equation for the many electron density matrix ρ, driven by two artificial external potentials v_L for the ket and v_R for the bra,

$$\frac{\partial\rho}{\partial t} = -i[H,\rho] - i\int d\mathbf{r}\, v_L(\mathbf{r},t)\hat{n}^{L}(\mathbf{r})\rho + i\int d\mathbf{r}\,\rho v_R(\mathbf{r},t)\hat{n}^{R}(\mathbf{r}), \tag{13}$$

where H is the material Hamiltonian (including the static potentials). The action is defined as the logarithm of the trace of the formal solution of Eq. (13) in the interaction picture,

$$\tilde{A}(v_L,v_R) = \ln\left\langle T\exp\left(-i\int d\mathbf{x}\, v_L(\mathbf{x})\hat{n}^{L}(\mathbf{x}) + i\int d\mathbf{x}\, v_R(\mathbf{x})\hat{n}^{R}(\mathbf{x})\right)\right\rangle. \tag{14}$$

It follows directly from this definition that $\tilde{A}$ serves as a generating functional for all LSPs,

$$(-i)^{p+1}(-1)^{\xi}\chi_c^{\nu_{p+1}\cdots\nu_1}(\mathbf{x}_{p+1}\cdots\mathbf{x}_1) = \left.\frac{\delta^{p+1}\tilde{A}(v_L,v_R)}{\delta v_{\nu_{p+1}}(\mathbf{x}_{p+1})\cdots\delta v_{\nu_1}(\mathbf{x}_1)}\right|_{v_L=v_R=0}. \tag{15}$$

The subscript c denotes that these are *connected* LSPs: χ_c is equal to χ minus various products of lower-order LSPs. Had we defined the action without the logarithm, Eq. (15) would give directly χ not χ_c. By starting the evolution at $t\to-\infty$ we perform an adiabatic switching of interactions, making sure we have the ground state of the interacting system before the time-dependent interaction is turned on.

The exchange correlation potential can be obtained by using the Legendere transform of Eq. (14),

$$A(n_L,n_R) = -\tilde{A}(v_L,v_R) + \int d\mathbf{x}\, n_L(\mathbf{x})v_L(\mathbf{x}) + \int d\mathbf{x}\, n_R(\mathbf{x})v_R(\mathbf{x}), \tag{16}$$

where $n_L\equiv\langle\hat{n}^{L}\rangle$ and $n_R\equiv\langle\hat{n}^{R}\rangle$. Similarly we define the corresponding Kohn-Sham actions $\tilde{A}_s(v_L,v_R)$ and $A_s(n_L,n_R)$ by replacing the Hamiltonian H in Eq. (13) with the single-particle Kohn-Sham Hamiltonian. The exchange correlation functional A_{xc} is then defined as

$$\begin{aligned} A(n_L,n_R) = A_s(n_L,n_R) &- \frac{1}{2}\int d\mathbf{x}d\mathbf{x}'\, n_L(\mathbf{r}t)n_L(\mathbf{r}'t)W(\mathbf{r}-\mathbf{r}') \\ &- \frac{1}{2}\int d\mathbf{x}d\mathbf{x}'\, n_R(\mathbf{r}t)n_R(\mathbf{r}'t')W(\mathbf{r}-\mathbf{r}') \\ &- A_{\mathrm{xc}}(n_L,n_R). \end{aligned} \tag{17}$$

Here $W(\mathbf{r}-\mathbf{r}')=1/|\mathbf{r}-\mathbf{r}'|$ is the two-particle Coulomb potential. Using the chain rule for functional derivatives [3,6] we can then derive Dyson-type equations for LSPs by double differentiation of Eq. (17) with respect to δn. To lowest-order in the fields we obtain

$$\begin{aligned} \chi^{\nu_1\nu_2}(\mathbf{x}_1,\mathbf{x}_2) = \chi_s^{\nu_1\nu_2}(\mathbf{x}_1,\mathbf{x}_2) + \sum_{\nu_3\nu_4}\int\int d\mathbf{x}_3 d\mathbf{x}_4\,\chi_s^{\nu_1\nu_3}(\mathbf{x}_1,\mathbf{x}_3) \\ \times[W(\mathbf{x}_3-\mathbf{x}_4)\delta(t_3-t_4)\delta_{\nu_3\nu_4} \\ + f_{\mathrm{xc}}^{\nu_3\nu_4}(\mathbf{x}_3,\mathbf{x}_4)]\chi^{\nu_4\nu_2}(\mathbf{x}_4,\mathbf{x}_2). \end{aligned} \tag{18}$$

Here $\chi_s^{\nu_1\nu_2}$ is the LSP of the noninteracting (Kohn-Sham) system and

$$f_{\mathrm{xc}}^{\nu_3\nu_4}(\mathbf{x}_3,\mathbf{x}_4) = \frac{\delta^2 A_{\mathrm{xc}}(n_L,n_R)}{\delta n_{\nu_3}(\mathbf{x}_3)\,\delta n_{\nu_4}(\mathbf{x}_4)}. \tag{19}$$

This matrix generalization of the Dyson equation which is normally written for the response [3] couples the contributions of the various LSPs and coincides with the nonequilibrium Green-function formulation of Keldysh [10].

The deeper root of the causality paradox is that response to external fields and spontaneous fluctuations are fundamentally connected and inseparable. In the linear regime this relation is known as the fluctuation dissipation theorem, which using the present notation states that χ^{++} and χ^{+-} are not independent [18]. This is no longer the case in higher order where we have many possible response functions describing various types of spontaneous fluctuations [16,18] and there is no simple relation between fluctuations and response. The two external fields v_L and v_R are needed in order to generate and control both the response and the fluctuations. Constructing a functional which will give the entire response function in “one shot” [Eq. (2)], is prohibited by the causality paradox but there is no difficulty to construct a functional for multipoint equilibrium fluctuations represented by the LSPs. The response is then obtained as a specific combination of these fluctuations. The Keldysh formalism accomplishes the same goal by using an artificial time contour [10,11]. In Liouville space we achieve that through an artificial field v_L-v_R that controls the fluctuations, all elements of the theory thus have a physical significance. Note that since $\langle \hat{n}^- \rangle = 0$ we cannot consider it a dynamical variable conjugate to U_- in the same way that $\langle \hat{n}^+ \rangle$ is conjugate to U_+. However, we can think of $\langle \hat{n}^L \rangle$ as conjugate to v_L and $\langle \hat{n}^R \rangle$ as conjugate to v_R. It is thus better to construct the functional in L/R space. Physical $+/-$ quantities can then be simply obtained as linear combinations. Liouville space provides an intuitive picture since it allows us to stay in real time and its building blocks may be individually measured by carefully designed coherent resonant nonlinear techniques [24,25]. Rather than introducing an artificial pseudotime, we keep track of "left" and "right" labels which control the bra and the ket of the many-electron density matrix. The contour is replaced by a simple time-ordering operation in Liouville space, making it possible to obtain the functional from an ordinary differential equation for the density matrix.

Finally we note that there are $(p+1)!$ multipoint correlation functions of $(p+1)$th order which differ by the permutations of their time/space arguments. The pth order response, Eq. (5), depends on only a subset of 2^{p+1} of these permutations; these are the Liouville space pathways. Since they describe equilibrium fluctuations, they are nonretarded. If we do not keep track of the relative time ordering of the left and right interactions, just follow the number of left and right type, some of the pathways may be combined and the response will only have $p+1$ terms. In the frequency domain we further need to sum over the permutations of the various fields acting from the right and the left. When coupling the electronic system to an external bath (e.g., phonons) a more detailed bookkeeping will result in new contributions to the response functions. Such "dephasing induced" processes are well known in nonlinear spectroscopy [24,26]. The LSP formulation makes it possible to extend the TDDFT expressions of nonlinear response by including additional dephasing mechanisms. These could break the left/right symmetry and give rise to interesting resonances.

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