Ensemble time-dependent density functional theory

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Time-dependent density functional theory (TDDFT) is a standard approach for calculating optical excitations of molecules and solids, while ensemble DFT (EDFT) is a promising alternative under development. We introduce ensemble TDDFT (ETDDFT), a practical theory that combines the two, generalizing both; we ensemble-generalize the Gross-Kohn equation and the exchange-correlation kernel of TDDFT, and generalize EDFT to time-dependent problems. We relate coordinate scaling to the adiabatic connection. The new theory provides multiple avenues for constructing and using approximations. We illustrate these on the 2-site Hubbard model. We connect our results to the more general case of non-perturbative time-dependence.

Ground-state density functional theory (GS-DFT) in its Kohn-Sham formulation [1, 2] has been remarkably successful in both materials and chemistry [3–7]. But, by construction, it is designed to yield only ground-state energies and densities and possibly any excitation energy that can deduced therefrom. Time-dependent density functional theory (TDDFT) is the standard generalization to time-dependent fields [8–10]. The most common application is in the linear optical response regime, yielding the absorption spectrum (both transition frequencies and oscillator strengths) [11–14]. While successful for many routine applications, such as low-lying excitations of large molecules, its limitations with standard approximations are well documented [15, 16]. Real-time TDDFT yields the same results [17], but can also handle non-perturbative time-dependent external fields. [18]

A promising alternative to TDDFT for extracting excitations is provided by ensemble DFT [19–27]. This theory is formulated in close analogy with ground-state DFT [24, 25, 28, 29]. The HK theorem [1] was generalized to weighted ensembles of low-lying states, and corresponding Kohn-Sham equations for the ensemble energy and density can be defined [24, 29, 30] and solved with some approximate ensemble (exchange correlation) XC energy [25]. There has been a recent explosion of interest in finding usefully accurate approximations using EDFT [26, 31–33], which is now available in some quantum chemical codes [34–36]. However, such calculations have not yet become widespread. While EDFT can overcome some limitations of standard TDDFT, it has some of its own, such as not predicting oscillator strengths.

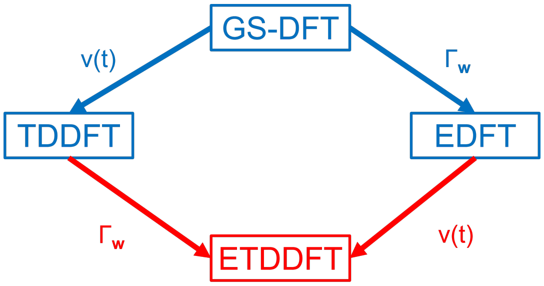

FIG. 1: Logical relation between ETDDFT and other versions of DFT.

The current work generalizes the proof of TDDFT [37] to initial states that begin from an ensemble, rather than from a non-degenerate ground state. Its logical relation to other forms of DFT is shown in Fig 1, and ETDDFT can be considered either as a generalization of linear-response TDDFT to initial ensembles instead of pure non-degenerate ground states or a generalization of (static) ensemble DFT to time-dependent response but with time-independent weights. The one-body potential is allowed to vary in time, but the weights remain fixed. To establish its validity, we first generalize the linear response proof of van Leeuwen for the ground state [38, 39] using modified techniques developed by Pribram-Jones et al. [40] for thermal DFT. The standard theorems of EDFT apply only when weights are non-increasing with excitation level, and our proof fails explicitly if these conditions are violated. The linear response proof immediately allows the generalization of the XC kernel of TDDFT to an ensemble XC kernel, which appears in a generalized Gross-Kohn formula. We establish the connection between coordinate scaling and the coupling constant, reproducing the adiabatic-connection formula for the ensemble energy [41]. We also derive various properties of the XC kernel and suggest several approximations. All results are illustrated on the two-site Hubbard model. We end by discussing the more general case of arbitrarily strong time-dependent fields [37], and explain how our work is an application of an early generalization [42, 43] of the RG proof to initial-state ensembles.

Background and notation: TDDFT in general allows inexpensive simulation of electronic systems (both molecules and materials) in time-dependent external fields [8, 9, 44, 45]. In linear response (LR) [15], weak electric fields are a small perturbation on the ground state KS potential, creating a proportionate time-dependent density. The central quantity is the density-density response function for the ground state $m = 0$. For the mth state:

$$\chi_m(\mathbf{r}, \mathbf{r}', \omega) = \sum_{k \neq m} \frac{n^*_{mk}(\mathbf{r}) n_{mk}(\mathbf{r}')}{\omega - \Omega_{km} + i\eta} - \text{c.c.} \tag{1}$$

with $n_{mk}(\mathbf{r}) = \langle m|\hat{n}(\mathbf{r})|k\rangle$ and $\hat{n}(\mathbf{r})$ being the density operator, and Ω_{km} the transition frequencies between states k and m. The sums are over many-body states of the system. This has a KS analog, i.e., the response function of the ground-state KS electrons in their single Slater determinant. The full many-body χ can be found from its KS analog via the Gross-Kohn equation and the exact time-dependent XC kernel [46].

In practice, most quantum chemical codes rewrite this expression as a matrix equation [11, 12], which has become standard. Almost all TDDFT calculations use the *adiabatic* approximation [13, 14], ignoring the time dependence of the XC kernel, which is then just the second functional derivative of the GS XC energy. Even without this approximation, this scheme does not predict all desired properties [3, 47]. In particular, the transition matrix elements between excited states are not accessed [48–50]. These are needed for beyond-TDDFT treatments, but require higher-order response properties [50, 51].

In an unrelated theoretical development, the ensemble DFT (EDFT) also predicts excitation energies [24, 25, 29], but using a variational principle analogous to the ground state case. Consider an ensemble of the ground and the first M excited states (m), with density matrix,

$$\Gamma_{\mathbf{w}} = \sum_{m=0}^{M} w_m \left|\Psi_m\right\rangle \left\langle\Psi_m\right|, \quad \mathbf{w} = (w_1, \ldots, w_M), \tag{2}$$

whose weights (w_m) are monotonically non-increasing and normalized ($\sum_{m=0}^{M} w_m = 1$). This satisfies Hohenberg-Kohn theorems of one-to-one correspondence between potentials and ensemble densities ($n_{\mathbf{w}}(\mathbf{r}) = \sum_{m=0}^{M} w_m n_m(\mathbf{r})$ with excited-state density $n_m(\mathbf{r})$). A constrained search gives the energy as a density functional:

$$E_{\mathbf{w}} = \min_n \left\{ F_{\mathbf{w}}[n] + \int d^3r\, n(\mathbf{r})\, v(\mathbf{r}) \right\} \tag{3}$$

with $F_{\mathbf{w}}[n] = \min_{\Gamma_{\mathbf{w}} \to n} \mathrm{Tr}\{\hat{\Gamma}_{\mathbf{w}}(\hat{T} + \hat{V}_{\rm ee})\}$ and $n_{\mathbf{w}}(\mathbf{r})$ being the minimizing density. One constructs a non-interacting KS system with the same density and weights and defines a corresponding ensemble-dependent XC functional,

$$E_{\mathbf{w}} = \min_n \left\{ T_{\rm S,\mathbf{w}}[n] + \int d\mathbf{r}\, n(\mathbf{r})\, v(\mathbf{r}) + E_{\rm HXC,\mathbf{w}}[n] \right\}. \tag{4}$$

Here the Hartree energy has been folded in with the XC contribution, as the separation of Hartree and exchange is subtle in EDFT [31]. The user chooses how many states to include and the weights. Unlike thermal DFT, the weights of the KS systems are identical to the true systems, by construction. Transition frequencies are deduced from one or more ensemble calculations. Not only can one use ensemble energy values to extract the transition frequencies [52], one is also able to obtain the double transitions that adiabatic KS-TDDFT is unable to approximate [53]. There are many excellent suggested approximations [26, 30–32, 41, 52], which can overcome some limitations of standard TDDFT approaches. Recently, focus has shifted towards state specific EDFT [34] to study individual excited-states, including an investigation into static linear response EDFT [54, 55]. This shows the need for a time dependent extension to EDFT.

A downside of EDFT is that there are so many possible choices of weights and any $\mathbf{w}$-dependent HXC approximation is likely to yield weight-dependent transition frequencies. The two most common choices of ensemble are the original Gross-Olivera-Kohn definition (GOK) [24], where all weights are the same except for the highest, or GOKII, where only the ground-state has a different weight [24, 56].

Fundamental proof: Assume a system begins ($t = 0$) in a valid ensemble, and is weakly perturbed by $\delta v(\mathbf{r}, t)$, then

$$\delta n_{\mathbf{w}}(\mathbf{r}, t) = \int d^3r' \int dt'\, \chi_{\mathbf{w}}(\mathbf{r}, \mathbf{r}', t - t')\, \delta v(\mathbf{r}', t') \tag{5}$$

defines the ensemble linear-response $\chi_{\mathbf{w}}(\mathbf{r}, \mathbf{r}', t - t')$ generating the density change $\delta n_{\mathbf{w}}(\mathbf{r}, t)$. Taking Laplace transforms with time-coordinate s:

$$\delta n_{\mathbf{w}}(\mathbf{r}, s) = \int d^3r'\, \tilde{\chi}_{\mathbf{w}}(\mathbf{r}, \mathbf{r}', s)\, \delta v(\mathbf{r}', s), \tag{6}$$

where $\tilde{\chi}_m(\mathbf{r}, \mathbf{r}', s) = \chi_m(\mathbf{r}, \mathbf{r}', -is)$, from Eq. (1). The transformed one-body operator

$$\delta\hat{V}(s) = \int d^3r\, \hat{n}(\mathbf{r})\, \delta v(\mathbf{r}, s) \tag{7}$$

has matrix elements $\delta V_{ij}(s) = \langle\Psi_i|\delta\hat{V}(s)|\Psi_j\rangle$. Consider

$$Y_{\mathbf{w}}(s) = \int d^3r\, \delta n_{\mathbf{w}}(\mathbf{r}, s)\, \delta v(\mathbf{r}, s), \tag{8}$$

where simple manipulations yield

$$Y_{\mathbf{w}}(s) = -2 \sum_{i=0}^{M} \sum_{j=i+1}^{\infty} \frac{(w_i - w_j)\Omega_{ji}}{s^2 + \Omega_{ji}^2} |\delta V_{ij}(s)|^2. \tag{9}$$

As $w_i > w_j$ and $\Omega_{ji} > 0$ (assuming no degeneracies), $Y_{\mathbf{w}}(s)$ vanishes only if every $\delta V_{ij}(s)$ in the sum does. Moreover, we can add a small but infinite set of weights to states above M, and take their weights to zero at the end of the calculation. Then $Y_{\mathbf{w}}(s) = 0$ only if $\delta v(\mathbf{r}, s)$ is uniform, QED. This proof generalizes Ref. [40] to any non-increasing weights and that of Ref. [38] to $\mathbf{w} \neq 0$. Degeneracies couple subspaces to each other, resulting in $\Omega_{km} = 0$ and a non-trivial zero density response [40, 57]. As in Ref. [40], we assume at least Q points outside the nodal hypersurface of the degenerate subspace within the $3N$ dimensional general space, where Q is the number of degeneracies, ensuring that $\delta v(\mathbf{r}, s)$ does not depend on $\mathbf{r}$.

Formalism: From now on, we will switch towards the more common Fourier-transformed version instead of Laplace transformed one, because in practice the differences are not relevant. However, the proof holds only for Laplace transformable potentials. Explicitly

$$\chi_{\mathbf{w}}(\mathbf{r}, \mathbf{r}', \omega) = \sum_{m=0}^{M} w_m \, \chi_m(\mathbf{r}, \mathbf{r}', \omega), \tag{10}$$

is the ensemble version of the density response function from Eq. (1). Its KS analog has the same form, but its many-body states are KS Slater determinants of KS orbitals of the ground-state KS potential. Since both are invertible from our proof, we can define

$$f_{\text{HXC},\mathbf{w}}[n](\mathbf{r}, \mathbf{r}', \omega) = \chi^{-1}_{\text{S},\mathbf{w}}(\mathbf{r}, \mathbf{r}', \omega) - \chi^{-1}_{\mathbf{w}}(\mathbf{r}, \mathbf{r}', \omega) \tag{11}$$

as the ensemble HXC (eHXC) kernel, and the ensemble generalization of the celebrated Gross-Kohn relation [46] is:

$$\chi_{\mathbf{w}}(\mathbf{r}, \mathbf{r}', \omega) = \chi_{\text{S},\mathbf{w}}(\mathbf{r}, \mathbf{r}', \omega) + \int d^3r_1 \int d^3r_2 \, \chi_{\text{S},\mathbf{w}}(\mathbf{r}, \mathbf{r}_1, \omega) \, f_{\text{HXC},\mathbf{w}}[n](\mathbf{r}_1 \mathbf{r}_2, \omega) \, \chi_{\mathbf{w}}(\mathbf{r}_2, \mathbf{r}', \omega). \tag{12}$$

Properties: We generalize our eHXC kernel to be coupling-constant dependent, by simply inserting a λ in front of the electron-electron interaction, while holding the density fixed [58–60] (Sec. S1 of the Supplementary Information). In the linear response case, we start with the scaling of the density response function from Eq (10),

$$\chi^{\lambda}_{\mathbf{w}}[n](\mathbf{r}, \mathbf{r}', \omega) = \lambda^4 \chi_{\mathbf{w}}[n_{t,1/\lambda}](\lambda\mathbf{r}, \lambda\mathbf{r}', \omega/\lambda^2), \tag{13}$$

where $n_\lambda(\mathbf{r}, t) = \lambda^3 n(\lambda\mathbf{r}, \lambda^2 t)$ with $n_t = n(\mathbf{r}, t)$ being the time dependent density, generalizing previous results [21, 40, 61]. With this and Eq. (12), we find

$$f^{\lambda}_{\text{HXC},\mathbf{w}}[n](\mathbf{r}, \mathbf{r}, \omega) = \lambda^2 f_{\text{HXC},\mathbf{w}}[n_{1/\lambda}](\lambda\mathbf{r}, \lambda\mathbf{r}, \omega/\lambda^2). \tag{14}$$

The ACFD theorem for $\chi_{\mathbf{w}}$ is already known from Ref. [26],

$$E_{\text{c},\mathbf{w}}[n] = -\frac{1}{2\pi} \int_0^1 d\lambda \int d^3r \int d^3r' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \int_0^\infty d\omega \, \text{Im} \left[\chi^{\lambda}_{\mathbf{w}}(\mathbf{r}, \mathbf{r}', \omega) - \chi^{0}_{\mathbf{w}}(\mathbf{r}, \mathbf{r}', \omega) \right], \tag{15}$$

and yields the static ensemble $E_{\text{c},\mathbf{w}}[n]$ (the pair density term from Ref. [26] is in the HX energy). This fluctuation dissipation theorem has a long useful history in ground-state DFT, culminating with the recent σ functionals [62–64].

Approximation: We use the ETDDFT formalism to create (perhaps too) many approximations for transition frequencies. In TDDFT, the poles of χ, or equivalently the zeroes of χ^{-1}, yield transition frequencies [11, 12, 37, 46], which remains true for any valid ensemble. Thus any approximate eHXC kernel yields approximate transitions, in exactly the same way as regular TDDFT, but for every valid ensemble. We call these *pole predictions*.

But we can also feed an eHXC kernel into Eq (18) to create a static ensemble correlation functional. This also yields transition frequencies via the methods of EDFT, but only for those transitions extractable from the ensemble. We call these *ensemble predictions*. With the exact kernel, both methods yield identical results. Practical calculations use approximations, which typically yield distinct results. An obvious exact condition is to recover the same result from both procedures, independent of $\mathbf{w}$.

A note on terminology. The adjective *pure* indicates a quantity evaluated with $\mathbf{w} = \mathbf{0}$, but there is an order of limits issue. Any finite weight, no matter how small, generates new poles in $\chi_{\mathbf{w}}$, which yield a zero in $\chi^{-1}_{\mathbf{w}}$ and so a new transition, e.g., between two excited states. The strength of this pole vanishes linearly with $\mathbf{w}$. Any ensemble approximation is *almost pure* if all its excited-state weights are taken as approaching, but not equal to, zero. The adjective *static* indicates a quantity evaluated at $\omega = 0$. For finite systems, static quantities are simply ground-state quantities, and there is no ambiguity.

To see the myriad ways ETDDFT can be used, begin with the usual approach in TDDFT, namely to use one's favorite ground-state XC functional, producing a static approximation to $f_{\rm XC}$. Pole prediction often yields good approximations to low-lying optical excitations, but misses double excitations, which require frequency dependent kernels [15, 65, 66]. On the other hand, one can also use the adiabatic kernel in the ACFDT formula, to find (typically poor and expensive) approximations for the ground-state $E_{\rm C}$. With ETDDFT, because $\chi_{\rm S}$ depends on $\mathbf{w}$, the pole-predictions now yield approximate transitions for every valid set of ensemble weights, reducing to the TDDFT results when $\mathbf{w}\to 0$. On the other hand, the ensemble predictions from the ACFDT *also* yield transition frequencies among members of the ensemble for every set of valid weights, including transitions between unoccupied states (which can be very useful [48, 49], but usually require higher-order TDDFT response [50, 51]).

Illustrations: We illustrate ETDDFT on the 2-site Hubbard model at half filling, which has proven useful for demonstrating basic principles of DFT [45, 67–69], due to its tiny Hilbert space and analytic solutions. Here we need only the symmetric case to make our points:

$$\hat{H} = -t\sum_{\sigma}(\hat{c}^{\dagger}_{1\sigma}\hat{c}_{2\sigma} + h.c.) + U\sum_{i}\hat{n}_{i\uparrow}\hat{n}_{i\downarrow}, \tag{16}$$

with t the hopping parameter and U the onsite repulsion. Exact expressions for the wavefunctions, eigenvalues and other relations for the asymmetric case are given in Secs. S2-S4 of the SI . As in Ref. [69], we restrict ourselves to the three singlet states: the ground state, the first excitation, which is a singly excited state, and a double excitation. The simplest ensemble is

$$\Gamma_w = \bar{w}\left|\Psi_0\right\rangle\left\langle\Psi_0\right| + w\left|\Psi_1\right\rangle\left\langle\Psi_1\right|, \tag{17}$$

with $\bar{w} = 1 - w$ and $0 \le w < 0.5$. Because of norm conservation, the density can be characterized by a single number (usually $n_2 - n_1$), so $\chi(\omega)$ is just a function. The many-body $\chi_w(\omega)$ is a weighted combination (Eq. (10)) of the ground-state $\chi_0(\omega)$

$$\chi_0(\nu) = \frac{2\nu_1 A_{01}}{\nu_+^2 - \nu_1^2} + \frac{2\nu_2 A_{02}}{\nu_+^2 - \nu_2^2} \tag{18}$$

with $\nu_+ = \omega/(2t) + i\eta$, and of the singly-excited state:

$$\chi_1(\nu) = -\frac{2\nu_1 A_{01}}{\nu_+^2 - \nu_1^2} + \frac{2\Delta\nu_2 A_{12}}{\nu_+^2 - \Delta v_2^2}, \tag{19}$$

which includes the transition back to the ground state and a transition upward to the double excitation at frequency $(\nu_2 - \nu_1)$, where $A_{mk} = \left|\langle m|\,\Delta\hat{n}\,|k\rangle\right|^2$ (see Eq. (S19)). The exact eHXC kernel is given by Eq. (11). Some algebra yields poles at [11, 12, 45],

$$\nu^2 = \nu_s^2 + 2\nu_{\rm S}\left((1-2w)A_{{\rm S},1} + w\,A_{{\rm S},2}\right) f_{{\rm Hxc},w}(\nu)(\nu), \tag{20}$$

and one can also extract oscillator strengths in the usual way (Eq. 30-32 of Ref. [45]), which are generalized in the End Matter, which also contains the derivation of the Small Matrix Approximation (SMA) and Single Pole Approximation (SPA) for the Hubbard model.

Figure 2 shows transition frequencies at $U = 0.5$ found from $(E_w - E_0)/w$ in the ensemble case, and from solving the pole equation, with various approximations. While the exact kernel yields the exact answer for any allowed w, the approximations yield transition frequencies that vary significantly with w. One way out of this maze is to consider only the prediction as $w \to 0$, which can produce lots of other simplifications too [52]. For this simple model and ensemble, solving TDDFT equations is usually more accurate than extracting ensemble energies. However, for the ensemble adiabatic approximation, $f_{{\rm Hxc},w}(0)$, the ensemble prediction is competitive or sometimes better.

Arbitrary time-dependence: The RG proof of uniqueness allows us to write $v[n,\Psi(0)](\mathbf{r},t)$, i.e., for given statistics (fermions) and electron-electron interaction (Coulomb repulsion), the time-dependent one-body potential is a functional of the time-dependent density and initial wavefunction (compatible with the initial density). [37] In turn, in the TDKS equations, this implies $v_{\rm XC}[n,\Psi(0),\Phi(0)](\mathbf{r},t)$, where $\Phi(0)$ is the initial KS wavefunction. In the special case of an initial non-degenerate ground-state density, the ground-state wavefunction is a functional of that density according to HK, making everything a functional of the time-dependent density alone.

Almost as soon as the RG [37] proof appeared, it was generalized to the case of an initial density matrix, i.e., not just a pure state [42, 43], yielding $v_{\rm XC}[n,\hat{\Gamma}(0),\hat{\Gamma}_s(0)](\mathbf{r},t)$. In fact, applying coordinate scaling to this case, yields

$$v^{\lambda}_{xc}[n_t,\hat{\Gamma}(0),\hat{\Gamma}_{\rm S}](\mathbf{r},t) = \lambda^2 v_{xc}[n_{t,1/\lambda},\hat{\Gamma}_{1/\lambda}(0),\hat{\Gamma}_{{\rm S},1/\lambda}(0)](\lambda\mathbf{r},\lambda^2 t), \tag{21}$$

where we used the scaling of a general density matrix as

$$\hat{\Gamma}^{\lambda}[n_t,\hat{\Gamma}(0)] = \hat{\Gamma}_{\lambda}[n_{t,1/\lambda},\hat{\Gamma}_{1/\lambda}(0)], \tag{22}$$

as shown in Sec. S1.

Restricting ourselves to density matrices with non-increasing weights, we apply the GOK theorem [24, 25, 29]

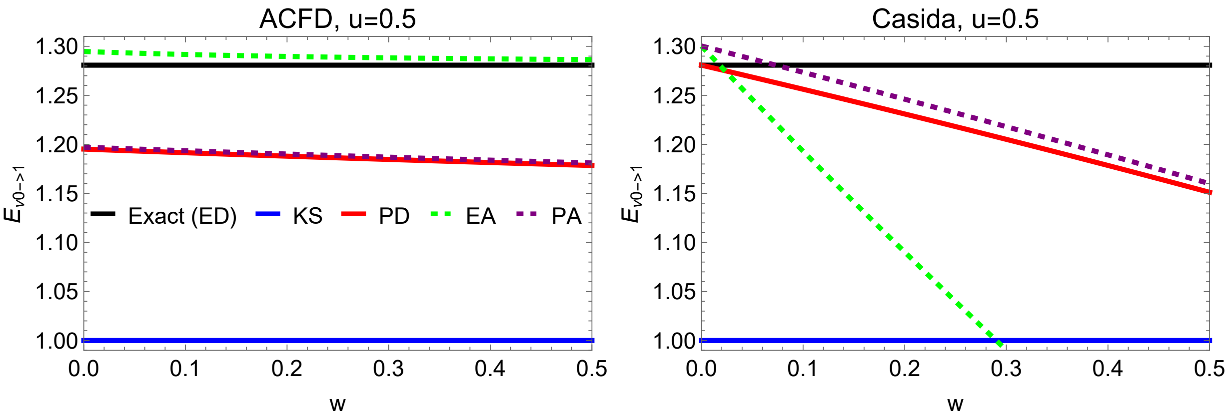

FIG. 2: Weight dependence of the transition from the ground to first excited state for $U = t$ for the exact, KS and 3 approximations (pure dynamic, ensemble adiabatic, and pure adiabatic). More figures in Sec. S5 of the SI.

to eliminate the dependence on the initial density matrices:

$$v_{\text{HXC},\mathbf{w}}[n_t](\mathbf{r},t) = v_{\text{HXC}}[n_t, \hat{\Gamma}_{\mathbf{w}}(0)[n_0], \hat{\Gamma}_{\text{S},\mathbf{w}}(0)[n_0]](\mathbf{r},t) \tag{23}$$

with n_0 being the density at $t = 0$, i.e., a pure weight-dependent functional of the time-dependent density only. Our eHXC kernel Eq. (12) is simply the functional derivative of this $v_{\text{HXC},\mathbf{w}}(\mathbf{r},t)$. On the other hand, our linear response proof used earlier avoids the complications of power series expansions in time [10, 38].

In Ref. [39] it was shown that $\chi_{\mathbf{w}}$ is always invertible if the weights are monotonic, depend only on the energy, and all states are included in the ensemble. The first is required [40, 68, 69], and the second also holds, because the weights are simply constants. To satisfy the last, we can imagine occupying all states higher than M with an infinitesimal weight, and then taking the limit where all those weights vanish.

Summary: In this work, we showed how EDFT can be combined with linear response TDDFT in order to access more information than either of these two approaches. We first generalized linear response regime of TDDFT to general ensembles, under the condition that the weights are monotonically decreasing and time independent. We then derived the exact coupling constant scaling relations of the HXC kernel as well as its potential. With our new insights, we have derived a variety of different flavors of approximations that can be used to calculate the transitions frequencies via the matrix formulation and the ACFD. Indeed, we show that these approximations have widely different $\mathbf{w}$ dependence.

In the future, a more thorough investigation about how well each approximation holds for real chemical and physical systems will be done. This work also extends the applicability of LRTDDFT to more important quantities, such as Rabi oscillations [50], that were assumed to be outside its reach without having to resort to quadratic response formulations. The advantage of this extension is that it is relatively easy to implement in standard quantum chemical packages because it is based on the well established LRTDDFT language that all quantum chemical codes already use [11, 12, 15].

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End Matter

Oscillator Strengths

In this section we generalize the work of Ref. [45] for ensembles. From Eqs. 29 and 30 of Ref. [45], after some simple algebra we find,

$$G_{i,w} = \sqrt{\frac{m_i(w)\nu_i A_i}{(1-2w)\nu_s A_{s,1} + w\Delta v_s A_{s,2}}}, \tag{24}$$

where $i \in [01, 02, 12]$ and $m_i(w) = \{1-2w, 1-w, w\}$. With this the oscillator strengths are given by

$$f_{i,w} = \frac{G_{i,w}^2}{\sum_j G_{j,w}^2} = m_i(w)\nu_i A_i / v_{3,w}, \tag{25}$$

where $\nu_{3,w} = \sum_j m_j(w) v_j A_j$ is chosen so $\sum_i f_{i,w} = 1$. With this auxiliary quantity, we can rewrite the $\chi_w(\omega)$ as,

$$\chi_w(\omega) = 2\nu_{3,w}\left(\frac{f_{1,w}}{\nu_+^2 - \nu_1^2} + \frac{f_{2,w}}{\nu_+^2 - \nu_2^2} + \frac{1 - f_{1,w} - f_{2,w}}{\nu_+^2 - \Delta\nu^2}\right). \tag{26}$$

Small Matrix and Single Pole Approximations

The small matrix approximation (SMA) and single pole approximation (SPA) can be derived in a similar fashion as the general Casida equation [45]. The only difference is that we assume that the poles of $\chi_w(\omega)$ are well separated. To derive the SMA, we assume that instead of looking at all the poles at once, we only look at transitions near a certain many body transition, $\Omega_i \to \nu_i$, which means that only the pole near this transition frequency contributes. After some algebra, we find

$$\nu_i^2 = \nu_{\mathrm{s},i}^2 + 2m_i(w)\nu_{\mathrm{s},i} A_{\mathrm{s},i} f_{\mathrm{HXC,w}}(\nu_{\mathrm{s},i}), \tag{27}$$

with $v_{\mathrm{s},1} = v_\mathrm{s}$ and $v_{\mathrm{s},2} = \Delta v_\mathrm{s}$. We can find the SPA by assuming that there is only a small shift from the KS value, which gives,

$$\nu_i = \nu_{\mathrm{s},i} + 2m_i(w) f_{\mathrm{Hxc,w}}(v_{\mathrm{s},i}). \tag{28}$$

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