

Joint time-dependent density-functional theory for excited states of electronic systems in solution

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We present a joint time-dependent density-functional theory for the description of solute-solvent systems in time-dependent external potentials. Starting with the exact quantum-mechanical action functional for both electrons and nuclei, we systematically eliminate solvent degrees of freedom and thus arrive at coarse-grained action functionals that retain the highly accurate *ab initio* description for the solute and are, in principle, exact. This procedure allows us to examine approximations underlying popular embedding theories for excited states. Finally, we introduce an approximate action functional for the solute-water system and compute the solvatochromic shift of the lowest singlet excited state of formaldehyde in aqueous solution, which is in good agreement with experimental findings.

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I. INTRODUCTION

Electronic excited states are important in many areas of physics, chemistry, and biology. They are probed in spectroscopic experiments, such as absorption, reflectivity, or photoluminescence measurements. In addition, they are important in many technical applications, such as photovoltaics,^{1,2} laser technology,³ and light-emitting diodes.^{4,5} However, in most situations the excited system is not in isolation but in contact with an environment. For example, dyes in Grätzel cells^{6,7} are in contact with an electrolyte and spectra of DNA molecules are typically obtained in an aqueous solution.^{8,9}

Various methods for the theoretical modeling of electronic excited states have been developed. For extended systems, such as periodic solids or surfaces, excitation energies are typically extracted from the single-particle and two-particle Green's functions by solving the quasiparticle¹⁰ and the Bethe-Salpeter equation¹¹ in the GW approximation. Quantum chemistry methods, such as configuration interaction¹² or coupled cluster theory,¹³ yield highly accurate excitation energies for atoms and small molecules. In contrast to the aforementioned methods, which scale unfavorably with the system size, in recent years time-dependent density-functional theory^{14,15} emerged as an economical yet accurate theory for larger molecules and clusters.^{6,16,17}

However, despite its good scaling properties, the application of time-dependent density-functional theory to electronic systems, which are not in isolation, but in contact with an environment, remains numerically challenging. To capture solvent effects on excited states, a number of embedding approaches have been developed.^{18–25} These methods model the solvent atomistically, for example, by using the molecular dynamics technique^{19,21,24} or via a continuum approach.^{18,20,22} Due to its simplicity, the latter approach has enjoyed great popularity. In particular, many calculations employed time-dependent density-functional theory in conjunction with the “polarizable continuum model,”^{6,7,18,26} where the molecule is placed inside a cavity in a linear dielectric medium. The solute-solvent interactions are then separated into equilibrium and nonequilibrium contributions, accounting for the fact that

the electronic excitations on the molecule are screened by the high-frequency dielectric constant, which in many systems is much smaller than the static dielectric constant.

Despite the success of these continuum models, it is important to recall that their construction is purely phenomenological. To improve on these theories and understand their limitations, it is necessary to understand their origin from first principles. In this paper, we derive different levels of continuum embedding theory starting from the exact quantum-mechanical action functional for the full solute-solvent system (Sec. II). Next, as a demonstration that the approach can lead to practical calculations, we introduce a time-dependent continuum model (Sec. III), which takes into account the deviation from bulk behavior of the solvent response in the first solvation shells and also retains the full frequency dependence of the dielectric response and then apply this functional to the excitations of a formaldehyde molecule in aqueous solution (Sec. IV). Finally, in Sec. V we discuss our conclusions and describe possible future developments and applications.

II. JOINT TIME-DEPENDENT DENSITY-FUNCTIONAL THEORY

In this section, we consider a physical system composed of an explicit subsystem (solute) in contact with an environment (solvent). Both solute and solvent consist of electrons and nuclei of various species. Examples of such solute-solvent systems are a molecule dissolved in water or a defect in a host crystal. To investigate the behavior of a solute-solvent system in a time-dependent external potential, we employ time-dependent density-functional theory.¹⁴ Here, we begin with the straightforward generalization of the standard, fully causal expression for the action of a single-component system at zero temperature²⁷ to multicomponent systems at finite temperature. This generalization is similar to the theory of Li and Tong.²⁸ Those authors, however, worked only at zero temperature and employed the Frenkel-Dirac action functional, which violates the causality requirement of van Leeuwen.²⁷ Generalizing the approach of van Leeuwen to the

present situation yields for the action functional S of the full solute-solvent system,

$$S[n, \{N_\alpha\}] = A[n, \{N_\alpha\}] - \int_{\Omega} d\mathbf{r} \int_C d\tau n(\mathbf{r}, \tau) v(\mathbf{r}, \tau) - \sum_{\alpha} \int_{\Omega} d\mathbf{r} \int_C d\tau N_{\alpha}(\mathbf{r}, \tau) V_{\alpha}(\mathbf{r}, \tau), \quad (1)$$

where $n(\mathbf{r})$ and $N_{\alpha}(\mathbf{r})$ denote the density of electrons and the various nuclear species, while $v(\mathbf{r})$ and $V_{\alpha}(\mathbf{r})$ denote the respective external potentials. Also, Ω denotes an open volume as required when working in the grand canonical ensemble and τ denotes the Keldysh time,²⁹ which is defined on the contour C ranging from 0 to ∞ just above the real time axis and then back from ∞ to 0 just under the real time axis and, finally, from 0 to $-i\beta$ on the imaginary time axis, with $\beta = 1/(k_B T)$ being the inverse thermal energy. Finally, in Eq. (1), the intrinsic action A is the Legendre transform, with respect to the potentials v and V_{α} ,²⁷ of

$$\begin{aligned} & \tilde{A}[v, \{V_{\alpha}\}] \\ &= i \log \text{Tr} \left\{ \exp \left[\beta \left(\mu_{\text{el}} \hat{N}_{\text{el}} + \sum_{\alpha} \mu_{\alpha} \hat{N}_{\alpha} \right) \right] \hat{U}(-i\beta; 0) \right\}, \end{aligned} \quad (2)$$

where μ_{el} and μ_{α} are the chemical potentials of the electrons and nuclei, while \hat{N}_{el} and \hat{N}_{α} denote the respective particle number operators. In the above, $\hat{U} = T_C \exp[-i \int d\tau \hat{H}(\tau)]$ denotes the quantum-mechanical evolution operator²⁷ with T_C being the Keldysh time-ordering operator and $\hat{H}(\tau)$ denotes the standard many-body Hamiltonian for the electrons and nuclei of the solute-solvent system.

We note that, relatively recently, Butriy *et al.* have also considered multicomponent time-dependent density-functional theory³⁰ but chose as the variational variables the electron density in body-fixed coordinates and the diagonal of the nuclear N-body density matrix, whereas we here employ as the variables the much more tractable densities $n(\mathbf{r}, \tau)$ and $N_{\alpha}(\mathbf{r}, \tau)$. Butriy *et al.* employed their formalism to study correlated electron-nuclear excitations in isolated molecules. By contrast, we here are interested in electronic excitations of the system while treating the solute nuclei in the Born-Oppenheimer approximation, holding them fixed in place, so they present a simple fixed external potential in which the electrons and solvent nuclei evolve. With the solute nuclear coordinates fixed, there is no need to work in body-fixed coordinates and a simple density description is sufficient for us to extract the density fluctuations of interest.

We do, however, find it mathematically convenient as a matter of bookkeeping to treat the solute and environment nuclear densities on an equal footing for as long as possible; therefore, we treat the solute nuclear densities as time dependent in our derivation and fix only the locations of the solute nuclei in the final step. Consequently, the index α in Eqs. (1) and (2) ranges over all nuclear species in both the solvent and the solute.

Because of the many environment degrees of freedom, finding the time-dependent densities that make the action in Eq. (1) stationary is numerically challenging. Moreover, the explicit details of the density fields describing the solvent are often irrelevant, because one is typically interested in properties of

the solute. We, therefore, seek a fundamental description which treats the solute explicitly and the solvent either at a simplified level or implicitly. Petrosyan and coworkers^{31,32} have developed just such a rigorous “joint” density-functional theory for the static, equilibrium case. Specifically, Petrosyan *et al.* first minimize the full solute-solvent free-energy functional over the solvent electron density to arrive at a free-energy functional in terms of the solute electron and the solvent nuclear densities. The resulting theory treats both solute and solvent explicitly, but the solvent at a more coarse-grained level. Ultimately, for specific solute-solvent systems the coarse-grained free-energy functional is minimized over all solute electron and solvent nuclear densities to obtain the free energy of the overall system and its equilibrium properties. Petrosyan *et al.* developed accurate and numerically tractable approximations to the coarse-grained functional and employed them to study surfaces and small molecules in aqueous solution with encouraging results.^{31,32} We note that Fattbert and Gygi³³ have developed a computationally similar approach for carrying out electronic structure calculations in aqueous environments but without the underlying exact framework of joint density-functional theory.

To generalize the theory of Petrosyan and coworkers to the present nonequilibrium context, we split the total electron density in Eq. (1) into solute (n_s) and environment (n_e) contributions, $n(\mathbf{r}, \tau) = n_s(\mathbf{r}, \tau) + n_e(\mathbf{r}, \tau)$. Fundamentally, a rigorous partitioning of electrons into solute and environment electrons is, of course, impossible because of their quantum-mechanical indistinguishability. Nonetheless, making S stationary with respect to all physically allowed environment electron densities and, subsequently, with respect to all physically allowed solute electron densities is guaranteed to recover the correct total electron density. There are, of course, many ways to express the total electron density as a sum of two subsystem densities. Thus, instead of a unique solution, there exists, in principle, a vast degenerate set of solutions in joint time-dependent density-functional theory consisting of all solute and environment electron densities that sum up to the correct total electron density. In practice, however, we find that practical approximations break this degeneracy and pick out a sensible particular solution. This is reminiscent of the equilibrium case, where Petrosyan *et al.*³² observed that the use of molecular pseudopotentials³⁴ leads to sensible nondegenerate solutions.

A. Explicit solvent functionals

Making the action stationary with respect to the environment electron density while holding the solute electron and environment nuclear densities fixed, we obtain the coarse-grained explicit-solvent functional S_{ex} ,

$$\begin{aligned} & S_{\text{ex}}[n_s, \{N_{\alpha}\}] \\ &= \text{stat}_{n_e} \left\{ A[n_s + n_e, \{N_{\alpha}\}] - \int_{\Omega} d\mathbf{r} \int_C d\tau \left[n_e(\mathbf{r}, \tau) v(\mathbf{r}, \tau) + \sum_{\alpha} N_{\alpha}(\mathbf{r}, \tau) V_{\alpha}(\mathbf{r}, \tau) \right] \right\} - \int_{\Omega} d\mathbf{r} \int_C d\tau n_s(\mathbf{r}, \tau) v(\mathbf{r}, \tau) \\ &\equiv \mathcal{A}^{(v, \{V_{\alpha}\})}[n_s, \{N_{\alpha}\}] - \int_{\Omega} d\mathbf{r} \int_C d\tau n_s(\mathbf{r}, \tau) v(\mathbf{r}, \tau), \end{aligned} \quad (3)$$

where stat_{n_e} indicates that the expression in curly brackets is made stationary with respect to variations of n_e and the

superscript of \mathcal{A} makes explicit the additional dependence of this functional on the external potentials. Note that we include the coupling term for the nuclear densities ($\sum N_\alpha V_\alpha$) in \mathcal{A} : This partitioning is not functionally necessary, because the coupling term does not depend on n_e and therefore maintains its simple form. This choice, however, ensures that \mathcal{A} describes a neutral system: Maintaining charge neutrality is important both formally to ensure the existence of the thermodynamic limit³⁵ and practically to mitigate the need to capture long-range couplings within an approximate functional. We stress that our partitioning does not fundamentally complicate the functional dependence of the new functional \mathcal{A} because the coupling to V_α will retain its simple form in terms of N_α .

To find practical approximations, we partition \mathcal{A} into various physically meaningful contributions according to

$$\begin{aligned} \mathcal{A} = & A_{\text{el},s}[n_s] + A_{\text{nuc},s}[\{N_{s,\alpha}\}] - A_{\text{nuc/ext},s}^{(V_s,\alpha)}[\{N_{s,\alpha}\}] \\ & - A_{\text{nuc/el},s}[n_s, \{N_{s,\alpha}\}] + A_e[\{N_{e,\alpha}\}] - \Delta\mathcal{A}_{\text{ext},e}^{(v_s, \{V_{e,\alpha}\})}[\{N_{e,\alpha}\}] \\ & - \Delta\mathcal{A}_{s,e}^{(v_s, \{V_{e,\alpha}\}, \{V_{s,\alpha}\})}[n_s, \{N_{s,\alpha}\}, \{N_{e,\alpha}\}], \end{aligned} \quad (4)$$

where the first four terms describe the solute: The first term, $A_{\text{el},s}$, denotes the intrinsic action of the solute electrons and is typically²⁷ written as

$$A_{\text{el},s} = A_{\text{KS}} - A_H - A_{\text{XC}}, \quad (5)$$

where A_{KS} denotes the action of noninteracting electrons, $A_H = 1/2 \int d\mathbf{r} \int d\mathbf{r}' \int d\tau n_s(\mathbf{r}, \tau) n_s(\mathbf{r}', \tau) / |\mathbf{r} - \mathbf{r}'|$ is the Hartree contribution, and A_{XC} the exchange-correlation term. The second and third terms in Eq. (4), respectively, are the intrinsic action of the solute nuclei (with densities $N_{s,\alpha}$) and their coupling to the external potentials. The fourth term captures the interaction between solute electrons and solute nuclei. In our actual calculations, we hold the solute nuclei fixed in space, finding $A_{\text{nuc/el},s} = \int d\mathbf{r} \int d\tau n_s(\mathbf{r}, \tau) v_{\text{st}}(\mathbf{r})$, with v_{st} being the static potential created by the solute nuclei. Under these conditions, the second and third terms in Eq. (4) become independent of all time-dependent degrees of freedom (although not of time-dependent potentials) and can be dropped for the purpose of the variational calculations. However, for later convenience we retain $A_{\text{nuc},s} = \int d\tau \sum_{I < J} Z_I Z_J / |\mathbf{R}_I - \mathbf{R}_J|$ with \mathbf{R}_I and Z_I denoting the positions and charges of the solute nuclei.

The fifth term in Eq. (4) describes the isolated neutral environment in terms of its nuclear densities, $N_{e,\alpha}$. Accurate approximations for this action functional are less well known than for electrons. However, there has been much progress recently in the construction of such action functionals for classical liquids,^{36,37} which constitute an important and technologically relevant class of solvents.

Finally, having identified all interactions between charged species, we expect the remaining two contributions in Eq. (4) to be relatively small. The sixth term, $\Delta\mathcal{A}_{\text{ext},e}$, describes the interaction between the neutral solvent and the external potentials. The final, seventh term, $\Delta\mathcal{A}_{s,e}$, maintains the full functional dependence and captures by definition all remaining interactions. We find that the coupling between the neutral solute and the neutral solvent constitutes the most important contribution to this term.

To find approximations to $\Delta\mathcal{A}_{\text{ext},e}$, we observe that the best form for this term depends on the physical system under consideration, because the solvent electrons screen the bare

nuclear charges in qualitatively different ways depending on the physical nature of the solvent. If the solvent consists of ions of charge \bar{Z}_α , the corresponding action would be $\sum_\alpha \int d\tau \int d\mathbf{r} [N_{e,\alpha} V_\alpha + (Z_\alpha - \bar{Z}_\alpha) N_{e,\alpha} v]$, with Z_α being the true charge of the nucleus. If, however, the solvent is composed of neutral polar molecules, where each “effective” nucleus carries a partial charge q_α and all partial charges in a molecule add up to zero, one should replace \bar{Z}_α in the above expression by q_α . Finally, if the solvent consists of apolar molecules or neutral atoms, we can approximate the coupling by $\sum_\alpha \int d\tau \int d\mathbf{r} \pi_\alpha N_{e,\alpha} |\nabla v|^2$ with π_α being the polarizability of the “effective” nucleus α .

The final term, $\Delta\mathcal{A}_{s,e}$, has the full functional dependence and thus can capture all remaining interactions. In typical density-functional theory fashion, because we have separated out by various approximations all other possible interactions and ensured that this term represents a charge-neutral interaction, we expect this term to be relatively small with mild functional dependencies and thus amenable to simple approximations. Accordingly, we expand $\Delta\mathcal{A}_{s,e}$ as a Taylor series in the various densities, keeping only the lowest-order coupling terms,

$$\begin{aligned} \Delta\mathcal{A}_{s,e} &= \int_\Omega d\mathbf{r} \int_\Omega d\mathbf{r}' \int_C d\tau \int_C d\tau' \sum_\alpha N_{e,\alpha}(\mathbf{r}', \tau') \\ &\times \left[w_\alpha(\mathbf{r}, \mathbf{r}', \tau, \tau') n_s(\mathbf{r}, \tau) + \sum_\beta w_{\alpha\beta}(\mathbf{r}, \mathbf{r}', \tau, \tau') N_{s,\beta}(\mathbf{r}', \tau') \right], \end{aligned} \quad (6)$$

where $w_\alpha(\mathbf{r}, \mathbf{r}', \tau, \tau') = \delta^2 \Delta\mathcal{A}_{s,e} / \delta n_s(\mathbf{r}, \tau) \delta N_{e,\alpha}(\mathbf{r}', \tau')$ and $w_{\alpha\beta}(\mathbf{r}, \mathbf{r}', \tau, \tau') = \delta^2 \Delta\mathcal{A}_{s,e} / \delta N_{e,\alpha}(\mathbf{r}, \tau) \delta N_{s,\beta}(\mathbf{r}', \tau')$ denote effective time-dependent interaction potentials between solvent nuclei and solute electrons or solute nuclei. Note that, in principle, the Taylor series contains various other coupling terms: for example, a term quadratic in the solute electron density can occur. However, such a term only renormalizes the Hartree contribution in $\mathcal{A}_{\text{el},s}$ and is therefore neglected in Eq. (6). Table I summarizes all of the above considerations, listing all of the various contributions to S_{ex} and the terms which capture them.

Recently, Kaminski and coworkers²⁵ have constructed a time-dependent embedding theory similar to the explicit solvent approach described in this section. In particular, these authors first use the theory of classical molecular liquids²⁵ to obtain averaged nuclear solvent densities which they then “dress up” with electrons to obtain the total equilibrium potential created by the solvent. Next, they compute orbital wave functions and energies of the embedded solute which are used as input into time-dependent density-functional theory calculations. This approach is very promising and may be viewed as an approximate implementation of the formally exact explicit solvent approach presented in this section.

B. Implicit solvent functionals

1. General considerations

Rather than follow the above route of dealing explicitly with the solvent nuclei, for this initial work, we take a simpler

TABLE I. The table shows the various contributions to S_{ex} due to interactions between solute nuclei (N_s), solute electrons (n_s), solvent nuclei (N_e), solvent electrons (n_e), and the external potentials (v and V). Note that in S_{ex} the solvent electrons are treated implicitly.

Contribution	Contained in
N_s/N_s	$A_{\text{nuc},s}$
N_s/n_s	$A_{\text{nuc/el},s}$
N_s/N_e	$\Delta\mathcal{A}_{s,e}$
N_s/n_e	$\Delta\mathcal{A}_{s,e}$
N_s/V	$A_{\text{nuc/ext},s}$
n_s/n_s	$A_{\text{el},s}$
n_s/N_e	$\Delta\mathcal{A}_{s,e}$
n_s/n_e	$\Delta\mathcal{A}_{s,e}$
n_s/v	Last term in Eq. (3)
N_e/N_e	A_e
N_e/n_e	A_e
N_e/V	$\Delta\mathcal{A}_{\text{ext},e}$
n_e/n_e	A_e
n_e/v	$\Delta\mathcal{A}_{\text{ext},e}$

tack that allows us to make contact with standard continuum solvent models. For this purpose, we eliminate the environment nuclei from S_{ex} and introduce a new action functional S_{im} that depends on the solute densities only and treats the solvent implicitly as follows,

$$\begin{aligned}
S_{\text{im}}[n_s, \{N_{s,\alpha}\}] &= \text{stat}_{\{N_{e,\alpha}\}} \mathcal{A}^{(v, \{V_{e,\alpha}\})}[n_s, \{N_{s,\alpha}\}, \{N_{e,\alpha}\}] \\
&\quad - \int_{\Omega} d\mathbf{r} \int_C d\tau n_s(\mathbf{r}, \tau) v(\mathbf{r}, \tau) \\
&\equiv \mathcal{G}^{(v, \{V_{e,\alpha}\})}[n_s, \{N_{s,\alpha}\}] - \int_{\Omega} d\mathbf{r} \int_C d\tau n_s(\mathbf{r}, \tau) v(\mathbf{r}, \tau).
\end{aligned} \tag{7}$$

Again, we partition \mathcal{G} into meaningful contributions according to

$$\begin{aligned}
\mathcal{G} &= A_{\text{el},s}[n_s] + A_{\text{nuc},s}[\{N_{s,\alpha}\}] - A_{\text{nuc/ext},s}^{(\{V_{e,\alpha}\})}[\{N_{s,\alpha}\}] \\
&\quad - A_{\text{nuc/el},s}[n_s, \{N_{s,\alpha}\}] - \Delta\mathcal{G}^{(v, \{V_{e,\alpha}\})}[n_s, \{N_{s,\alpha}\}]
\end{aligned} \tag{8}$$

where $\Delta\mathcal{G} = -\text{stat}_{\{N_{e,\alpha}\}}[A_e - \Delta\mathcal{A}_{\text{ext},e} - \Delta\mathcal{A}_{s,e}]$ and $\mathcal{A}_{\text{el},f}$ is given by Eq. (5). Note that $\Delta\mathcal{G}$ depends on the solute densities of electrons and nuclei but also on the time-dependent external potential. To understand the consequences of the additional functional dependency, we now investigate the linear response behavior of S_{im} in greater detail (assuming fixed solute nuclei).

The time-dependent solute electron density corresponding to v makes S_{im} stationary, $\delta S_{\text{im}} = 0$, which implies $\delta\mathcal{G}/\delta n_s = v$. Using (8) we thus have (assuming fixed solute nuclei)

$$\begin{aligned}
v(\mathbf{r}, \tau) &= v_{\text{KS}}(\mathbf{r}, \tau) - v_H(\mathbf{r}, \tau) - v_{\text{XC}}(\mathbf{r}, \tau) \\
&\quad - v_{\text{st}}(\mathbf{r}) - v_e^{(v, \{V_{e,\alpha}\})}(\mathbf{r}, \tau),
\end{aligned} \tag{9}$$

where $v_{\text{KS}} = \delta A_{\text{KS}}/\delta n_s$ denotes the Kohn-Sham potential, $v_H = \delta A_H/\delta n_s$, $v_{\text{XC}} = \delta A_{\text{XC}}/\delta n_s$, and v_{st} is the static potential due to the solute nuclei. Also, $v_e = \delta\Delta\mathcal{G}/\delta n_s$ denotes the additional potential due to the presence of the environment. Note that $\Delta\mathcal{G}$ and, therefore, v_e depend on the solute density n_s and the external potential separately.

A small change δv in the external potential causes a change δn_s in the solute electron density. In the linear response regime, these quantities are related via the response function χ

$$\delta n_s(\mathbf{r}, \tau) = \int_{\Omega} d\mathbf{r}' \int_C d\tau' \chi(\mathbf{r}, \mathbf{r}', \tau, \tau') \delta v(\mathbf{r}', \tau'). \tag{10}$$

To compute χ , which is the observable in spectroscopic experiments on the solute-solvent system, we first determine the change in the Kohn-Sham potential δv_{KS} corresponding to δv . (Strictly speaking, only the total response function $\chi_{\text{tot}} = \delta n/\delta v = \delta n_s/\delta v + \delta n_e/\delta v$ is measured. However, for solute-solvent systems where the response of the solute occurs in a frequency range that differs from the response of the solvent can determine experimentally the solute response function χ . This is the case for the lowest singlet excitation of formaldehyde in water, which we study in the Sec. IV.) Using Eq. (9), we find

$$\begin{aligned}
\delta v_{\text{KS}}(\mathbf{r}, \tau) &= \delta v(\mathbf{r}, \tau) + \int_{\Omega} d\mathbf{r}' \frac{\delta n_s(\mathbf{r}', \tau)}{|\mathbf{r} - \mathbf{r}'|} \\
&\quad + \int_{\Omega} d\mathbf{r}' \int_C d\tau' f_{\text{XC}}(\mathbf{r}, \mathbf{r}', \tau, \tau') \delta n_s(\mathbf{r}', \tau') \\
&\quad + \int_{\Omega} d\mathbf{r}' \int_C d\tau' f_e^A(\mathbf{r}, \mathbf{r}', \tau, \tau') \delta n_s(\mathbf{r}', \tau') \\
&\quad + \int_{\Omega} d\mathbf{r}' \int_C d\tau' f_e^B(\mathbf{r}, \mathbf{r}', \tau, \tau') \delta v(\mathbf{r}', \tau') \\
&\quad + \sum_{\alpha} \int_{\Omega} d\mathbf{r}' \int_C d\tau' f_{e,\alpha}^C(\mathbf{r}, \mathbf{r}', \tau, \tau') \delta V_{e,\alpha}(\mathbf{r}', \tau'),
\end{aligned} \tag{11}$$

where $f_e^A = \delta v_e/\delta n_s$, $f_e^B = \delta v_e/\delta v$, and $f_{e,\alpha}^C = \delta v_e/\delta V_{e,\alpha}$ denote additional contributions to δv_{KS} caused by the environment. In an actual experiment, where the whole solute-solvent system is probed, for example, by an electromagnetic wave, we expect $\delta V_{e,\alpha}$ to be related to δv . In this case, we can express the last term in Eq. (11) as $f_e^D \delta v$ with $f_e^D = \sum_{\alpha} f_{e,\alpha}^C \delta V_{e,\alpha}/\delta v$.

The change in the Kohn-Sham potential is related to δn_s via

$$\delta n_s(\mathbf{r}, \tau) = \int_{\Omega} d\mathbf{r}' \int_C d\tau' \chi_{\text{KS}}(\mathbf{r}, \mathbf{r}', \tau, \tau') \delta v_{\text{KS}}(\mathbf{r}', \tau'), \tag{12}$$

where χ_{KS} denotes the response function of noninteracting electrons. Combining Eqs. (12), (11), and (10) and adopting a matrix formulation for the space and Keldysh time variables then yields

$$\chi^{-1} = [1 + f_e^B + f_e^D]^{-1} \{ \chi_{\text{KS}}^{-1} - [K + f_{\text{XC}} + f_e^A] \}, \tag{13}$$

where K denotes the matrix corresponding to the Coulomb interaction $K(\mathbf{r}, \mathbf{r}', \tau, \tau') = \delta(\tau, \tau')/|\mathbf{r} - \mathbf{r}'|$ with $\delta(\tau, \tau')$ denoting the δ function on the Keldysh contour.

Compared to the familiar equation for χ without solvent, given by $\chi^{-1} = \chi_{\text{KS}}^{-1} - [K + f_{\text{XC}}]$, we find that Eq. (13) contains three extra terms due to the presence of the solvent: f_e^A describes the change of the solvent potential due to a change in the solute electron density, while f_e^B and f_e^D describe changes induced by a variation in the external potential. Without justification, ‘‘polarizable continuum model’’ approaches typically¹⁸ approximate the potential due to the solvent as a functional of the solute density only, which means they only include f_e^A

and neglect f_e^B and f_e^D . This insight into the assumptions underlying popular embedding approaches underscores the value of following the density-functional approach rigorously to identify all potentially relevant functional dependencies.

2. Practical approximations

To develop practical approximations, we separate $\Delta\mathcal{G}$ into a contribution $\Delta\mathcal{G}_{s,e}[n_s, \{N_{s,\alpha}\}]$, which describes the interaction among solute particles mediated by the environment, and a remainder $\Delta\mathcal{G}_{\text{ext}}^{(v, \{V_{e,\alpha}\})}[n_s, \{N_{s,\alpha}\}]$. Taylor expanding $\Delta\mathcal{G}_{s,e}$ yields

$$\begin{aligned} \Delta\mathcal{G}_{s,e} &= \int_{\Omega} d\mathbf{r} \int_{\Omega} d\mathbf{r}' \int_C d\tau \int_C d\tau' \left\{ \frac{1}{2} n_s(\mathbf{r}, \tau) W(\mathbf{r}, \mathbf{r}', \tau, \tau') n_s(\mathbf{r}', \tau') \right. \\ &\quad + \sum_{\alpha} N_{s,\alpha}(\mathbf{r}, \tau) \left[W_{\alpha}(\mathbf{r}, \mathbf{r}', \tau, \tau') n_s(\mathbf{r}', \tau') \right. \\ &\quad \left. \left. + \frac{1}{2} \sum_{\beta} W_{\alpha\beta}(\mathbf{r}, \mathbf{r}', \tau, \tau') N_{s,\beta}(\mathbf{r}', \tau') \right] \right\}, \end{aligned} \quad (14)$$

where $W(\mathbf{r}, \mathbf{r}', \tau, \tau')$, $W_{\alpha}(\mathbf{r}, \mathbf{r}', \tau, \tau')$, and $W_{\alpha\beta}(\mathbf{r}, \mathbf{r}', \tau, \tau')$ denote effective interaction potentials between the various solute particles. In the next section, we approximate these interaction potentials by screened Coulomb interactions, which results in a simple, yet accurate, joint density-functional theory for solute-water systems.

Approximating $\Delta\mathcal{G}_{\text{ext}}$ is more difficult: A possible route to finding explicit functionals is to express the environment nuclear densities in terms of solute densities according to $N_{e,\alpha}(\mathbf{r}) = g_{\alpha}[n_s, \{N_{s,\beta}\}](\mathbf{r})$ and insert this relation into the various forms for $\Delta\mathcal{A}_{\text{ext,e}}$ discussed in the last section. We expect that g_{α} has a similar form as the dielectric function employed in the next section [Eq. (18)], where we employ a local ansatz to describe the crossover from bulk screening to vacuum.

However, for our first implementation of joint time-dependent density-functional theory for solute-water systems presented in the next section we neglect $\Delta\mathcal{G}_{\text{ext}}$. We expect, however, that the additional solvent response due to this term can be included by “renormalizing” the dielectric function describing the environment (see Sec. III). Future work should explore the consequences and importance of this term.

III. AN IMPLICIT ACTION FUNCTIONAL FOR THE WATER-SOLUTE SYSTEM

To allow us to explore and test the potential of the above ideas in an actual application, in this section, we introduce a relatively simple, approximate joint time-dependent density-functional for the solute-water system. In particular, we assume that all solvent effects can be described via a position and frequency-dependent local dielectric function, which depends on the electronic structure of the solute. Inclusion of the spatial dependence of screening effects is crucial, because the dielectric response of water in the first solvation shells differs notably from the bulk response. Also, in contrast to “polarizable continuum model” approaches,^{18,38} where a particular value for the high-frequency dielectric constant is

chosen, we employ the full frequency-dependent dielectric function.

Specifically, the assumption of dielectric screening implies that all effective interactions introduced in Eq. (14) are proportional to the screened interaction \tilde{W} between two unit charges and only rescaled by the charges of the interacting species. In particular, we approximate $W = \tilde{W}$, $W_{\alpha} = -Z_{\alpha}\tilde{W}$, and $W_{\alpha\beta} = Z_{\alpha}Z_{\beta}\tilde{W}$. The resulting action functional for the solute-water system is then given by

$$\begin{aligned} \mathcal{G} &= A_{\text{KS}} - A_{\text{XC}} - \Delta V_{\text{ps}} - \frac{1}{2} \int_{\Omega} d\mathbf{r} \int_{\Omega} d\mathbf{r}' \int_C d\tau \int_C d\tau' \\ &\quad \times \rho_s(\mathbf{r}, \tau) \tilde{K}(\mathbf{r}, \mathbf{r}', \tau, \tau') \rho_s(\mathbf{r}', \tau'), \end{aligned} \quad (15)$$

with $\rho_s(\mathbf{r}, \tau) = -n_s(\mathbf{r}, \tau) + \sum_I Z_I \delta(\mathbf{r} - \mathbf{R}_I)$ denoting the solute charge density and $\tilde{K} = K + \tilde{W}$, where K is the bare Coulomb interaction defined as above. Also, ΔV_{ps} reflects the fact that, in practical calculations, we employ the pseudopotential approximation,³⁹ in which the nuclei are replaced with ionic cores of charge Z_I , whose potentials at large distances (when not screened by the environment) go as $Z_I/|\mathbf{r} - \mathbf{R}_I|$ but which differ from this by a localized function $\Delta V_{\text{ps}}(\mathbf{r} - \mathbf{R}_I)$ within a small “core radius” that represents a distance much smaller than where we would expect screening from the environment to occur. Within our framework, the long-range parts enter through the solution of Eq. (16), and thus are properly screened, and the short-range parts contained in ΔV_{ps} enter directly as they require no such screening.

The screened potential corresponding to a physical charge density $\rho_s(\mathbf{r}, t)$, which is equal on both vertical branches of the Keldysh contour, is given by $\tilde{\phi}_s \equiv \tilde{K}^R \rho_s$, where \tilde{K}^R denotes the retarded interaction.²⁷ In actual calculations, we obtain $\tilde{\phi}_s$ by solving the screened Poisson equation

$$\nabla \cdot \epsilon(\mathbf{r}, \omega) \nabla \tilde{\phi}(\mathbf{r}, \omega) = -4\pi \rho_s(\mathbf{r}, \omega). \quad (16)$$

All information about the environment is contained in the dielectric function $\epsilon(\mathbf{r}, \omega)$. In principle, both the ionic and the electronic degrees of freedom of the solvent contribute to the dielectric response. We demonstrate below that for the frequencies of interest, we can safely ignore the motion of the ions and only deal with the electronic response corresponding to a fixed nuclear solvent density. We make the natural assumptions that the system is in equilibrium before the excitation and that the equilibrium nuclear solvent density is determined locally by the equilibrium solute electron density $n_0(\mathbf{r})$. This suggests the following local ansatz for the dielectric function:

$$\epsilon(\mathbf{r}, \omega) = \epsilon(n_0(\mathbf{r}), \omega). \quad (17)$$

This ansatz is physically reasonable in that it interpolates smoothly between the dielectric response of vacuum and the bulk liquid and thus avoids the need to specify a cavity shape. If we further assume that the frequency dependence of $\epsilon(n_0(\mathbf{r}), \omega)$ enters only through the frequency dependence of the bulk dielectric function $\epsilon_b(\omega)$, we can generalize the form employed by Petrosyan and coworkers³¹ to

$$\epsilon(\mathbf{r}, \omega) = 1 + \frac{\epsilon_b(\omega) - 1}{2} \operatorname{erfc} \left\{ \frac{\log[n_0(\mathbf{r})/n_c]}{\sqrt{2}\sigma} \right\}, \quad (18)$$

where the parameters n_c and σ determine the location and width, respectively, of the crossover from the vacuum to the bulk liquid dielectric response. Petrosyan *et al.*³¹ determined the numerical values $n_c = 4.73 \times 10^{-3} \text{ \AA}^{-3}$ and $\sigma = 0.6$ for these parameters by fitting solvation energies of small molecules obtained by their equilibrium joint density-functional theory to experimental data. We choose to work with these values as well.

To complete the theory, we need an expression for the frequency-dependent bulk dielectric constant $\epsilon_b(\omega)$. At frequencies corresponding to electronic excitations, we may ignore the complicated low-frequency dielectric response of water and employ a model that describes the high-frequency range reliably. For this, we use the Clausius-Mossotti form⁴⁰

$$\frac{\epsilon_b(\omega) - 1}{\epsilon_b(\omega) + 2} = \frac{4\pi}{3} n_b \bar{\alpha}(\omega), \quad (19)$$

where n_b denotes the bulk molecular particle density of water and $\bar{\alpha}(\omega) = \sum_j F_j / (E_j^2 - \omega^2)$ denotes the mean polarizability of an isolated water molecule, with F_j and E_j being the oscillator strength and excitation frequencies, respectively, for excited state j . In the next section, we compute $\bar{\alpha}(\omega)$ using time-dependent density-functional theory and demonstrate that Eq. (19), which neglects the contribution from the permanent dipole moments, indeed reliably describes the bulk screening response of water to low-lying electronic excitations. To obtain excitation energies of the solute, we analyze the linear response of Eq. (15), resulting in

$$\chi^{-1} = \chi_{\text{KS}}^{-1} - [\tilde{K} + f_{\text{XC}}], \quad (20)$$

which lacks the subtleties appearing in Sec. II B because the present model lacks any explicit environment dependence on the external potential. Our final working equation is obtained by expressing Eq. (20) in transition-space notation,¹⁵ where the fused index $\kappa = (k, j)$ denotes a transition between two equilibrium Kohn-Sham orbitals $\psi_j(\mathbf{r})$ and $\psi_k(\mathbf{r})$. We arrive at a self-consistent eigenvalue problem¹⁵ for excitation energies E_j of the solute,

$$\sum_{\nu} [\delta_{\kappa\nu} \Delta\epsilon_{\nu}^2 + 4\sqrt{\Delta\epsilon_{\kappa} \Delta\epsilon_{\nu}} \tilde{M}_{\kappa\nu}(E_j)] C_{\nu}^{(j)} = E_j^2 C_{\kappa}^{(j)}, \quad (21)$$

where $\Delta\epsilon_{\kappa} = \epsilon_j - \epsilon_k$ with ϵ_k denoting the equilibrium orbital energies and the eigenvector $C_{\kappa}^{(j)}$ determines the oscillator strength of the transition.¹⁵ The coupling matrix is given by

$$\begin{aligned} \tilde{M}_{\kappa\nu}(\omega) &= \int_{\Omega} d\mathbf{r} \int_{\Omega} d\mathbf{r}' \Phi_{\kappa}^*(\mathbf{r}) [\tilde{K}^R(\mathbf{r}, \mathbf{r}', \omega) + f_{\text{XC}}^R(\mathbf{r}, \mathbf{r}', \omega)] \Phi_{\nu}(\mathbf{r}'), \end{aligned} \quad (22)$$

where $\Phi_{\kappa}(\mathbf{r}) = \psi_k^*(\mathbf{r})\psi_j(\mathbf{r})$ and f_{XC}^R denotes the retarded exchange-correlation kernel. Note that even for a frequency-independent exchange-correlation kernel, the solvent response makes \tilde{M} frequency dependent. Equation (21) is solved iteratively: setting $\tilde{K}^R(E_j) = K$ yields an initial estimate $E_j^{(1)}$ for the excitation energy. Next, we solve Eq. (21) using $\tilde{K}^R(E_j^{(1)})$ and iterate until self-consistency is achieved.

IV. APPLICATION TO FORMALDEHYDE IN AQUEOUS SOLUTION

As a test case, we study the lowest singlet excited state of a formaldehyde molecule in aqueous solution. A number of theoretical approaches have been applied to study solvatochromic shifts of formaldehyde in water.^{18,19,38,41-44} However, the agreement with experimental findings has generally been unsatisfactory.

In this section, we first compute the mean polarizability of an isolated water molecule from time-dependent density-functional theory and obtain the frequency-dependent bulk dielectric function of liquid water using the Clausius-Mossotti equation. Next, we explore the excitations of formaldehyde in the gas phase and in solution using the joint time-dependent density-functional theory described in the previous section.

All calculations are carried out in a plane-wave basis with a cutoff of 40 hartree. We use Kleinman-Bylander pseudopotentials⁴⁵ and a cubic supercell of length 20 bohr. For the ground-state calculations we employ the local density approximation^{46,47} and for the excitations the adiabatic local density approximation.¹⁵

A. Dielectric function of liquid water

To compute excitation energies of a formaldehyde molecule in aqueous solution, we need the frequency-dependent dielectric response of water. According to Eq. (19), this requires the mean polarizability of an isolated water molecule. We first carry out ground-state calculations and fully relax the electronic and ionic structure. We then employ time-dependent density-functional theory to obtain excitation energies and oscillator strengths using all four occupied Kohn-Sham orbitals plus an additional 220 unoccupied orbitals. Table II shows our results for the three lowest singlet excitation energies of an isolated water molecule and compares them to previous theoretical work⁴⁸ and to experiment.⁴⁸ The discrepancy between theory and experiment is around 1 eV or larger for all excited states. The poor performance of time-dependent density-functional theory for the water molecule can be traced to the Rydberg character of the excitations, which cannot be described in the adiabatic local density approximation due to the incorrect asymptotic behavior of the exchange-correlation potential at large distances.^{48,49}

Despite these problems, the adiabatic local density approximation gives good results for the static polarizability and for the low-frequency dielectric constant of liquid water: Table III compares our results for these quantities with previous calculations⁵⁰ and also with experiment.⁵⁰⁻⁵² We observe that the Clausius-Mossotti formula (19) describes the

TABLE II. Comparison of the lowest singlet excitation energies of an isolated water molecule with previous theoretical work by Bernasconi⁴⁸ and experiment.⁴⁸ All results are given in eV.

This work	Ref. 48	Expt. ⁴⁸
6.47	6.39	7.4
7.74	7.78	9.1
8.01	8.05	9.7

TABLE III. Comparison of our results for the static mean polarizability of an isolated water molecule and for the optical dielectric constant $\epsilon_{\text{opt}} \equiv \epsilon_b(\omega = 1 \text{ eV})$ of liquid water with previous theoretical work by Hu *et al.*⁵⁰ and experiment.⁵⁰⁻⁵²

	Units	This work	Ref. 50	Expt. ⁵⁰⁻⁵²
$\bar{\alpha}(\omega = 0)$	Bohr ³	10.50	10.52	9.6–9.9
ϵ_{opt}		1.83	—	1.78

dielectric response of liquid water very well in the frequency range corresponding to low-lying electronic excitations.

B. Formaldehyde in the gas phase

Next, we explore the excitations of formaldehyde in the gas phase. Table IV compares our results for the three lowest singlet excited states with a previous calculation by Bauernschmitt and Ahlrich,⁵³ who also employ the adiabatic local density approximation and with experimental findings.^{18,53} We observe that our excitation energy for the lowest state is relatively close to the experimental value, while the higher states deviate more than 1 eV from experiment. Again, the relatively large deviation for the higher excited states is due to the incorrect long-distance behavior of the exchange-correlation potential in the adiabatic local density approximation.

Comparison of Tables IV and II shows that the lowest excitation energy of formaldehyde is several eV smaller than the corresponding value for water. Therefore, in our joint time-dependent density-functional calculations we evaluate only the dielectric function at frequencies smaller than its first pole. In this region, $\epsilon_b(\omega)$ is close to unity and can be approximated by a constant. This is a common approximation in “polarizable continuum model” approaches, which for the nonequilibrium response employs a frequency-independent dielectric function derived from the index of refraction of water.¹⁸

However, this approximation breaks down for solutes with higher-energy excited states that are comparable or larger than the lowest excited state of water. In this case, the full frequency dependence of the dielectric response *must* be retained and a self-consistent solution of Eq. (21) is necessary.

C. Formaldehyde in aqueous solution

We now apply joint time-dependent density-functional theory to calculate excitations of a solvated formaldehyde molecule. We use the static joint density-functional theory

TABLE IV. Comparison of the three lowest singlet excitation energies of an isolated formaldehyde molecule with previous theoretical work by Bauernschmitt *et al.*⁵³ and experiment.^{18,53} All energies are given in eV.

This work	Ref. 53	Expt. ^{18,53}
3.66	3.64	3.8–4.2
5.68	5.93	7.13
6.78	6.79	8.14

TABLE V. Comparison of our results for the equilibrium dipole moment of formaldehyde in vacuum (p_{vac}) and aqueous solution (p_{solv}) with experiment⁵⁴ and previous theoretical work.⁴² Dipole moments are given in bohrs.

	This work	Ref. 42	Expt. ⁵⁴
p_{vac}	0.91	0.90	0.91
p_{solv}	1.32	1.32	—

of Petrosyan *et al.*³¹ to determine the equilibrium electronic structure neglecting ionic relaxations induced by the aqueous environment, which as was shown by Kongsted *et al.* only led to shifts in the excitation energies of about 0.01 eV.¹⁹ Table V shows that the equilibrium dipole moment obtained in our calculation is in excellent agreement with previous theoretical work.⁴²

We then solve the linear response Eq. (21) of joint time-dependent density-functional theory self-consistently, as described in the last section. The lowest excitation energy is converged to within 0.01 eV after two iterations. Table VI summarizes our results for the excitation energies in vacuum and solution and the resulting solvatochromic shift, which is in good agreement with the experimental value.¹⁹

To physically understand the observed solvatochromic blue shift, we express the excitation energy as

$$E_{\text{vac/solv}} = \Delta\epsilon_{\text{vac/solv}} + \gamma_{\text{vac/solv}}, \quad (23)$$

where $\Delta\epsilon_{\text{vac/solv}}$ denotes orbital energy difference in vacuum or solution and $\gamma_{\text{vac/solv}}$ denotes the correction from (joint) time-dependent density-functional theory. For gas-phase formaldehyde, $\Delta\epsilon_{\text{vac}} = 3.34 \text{ eV}$ already gives a reasonable approximation to $E_{\text{vac}} = 3.66 \text{ eV}$ with the correction $\gamma_{\text{vac}} = 0.32 \text{ eV}$ being relatively small. In solution, we find $\Delta\epsilon_{\text{solv}} = 3.56 \text{ eV}$ and $\gamma_{\text{solv}} = 0.27 \text{ eV}$. We conclude that the solvatochromic shift is determined mostly by the change of the orbital energy differences, $\Delta\epsilon_{\text{vac}} - \Delta\epsilon_{\text{solv}} = 0.22 \text{ eV}$, which is quite close to the total solvatochromic shift of 0.17 eV, while the correction term changes relatively little (only 0.05 eV).

The change of $\Delta\epsilon$ on solvation is caused by the different coupling of ground and excited states to the aqueous environment: the ground state has a large dipole moment ($p_{\text{gs}}^{\text{vac}} = 0.91 \text{ bohr}$) and couples strongly to the aqueous environment leading to a large negative solvation energy, while the dipole moment of the excited state ($p_{\text{ex}}^{\text{vac}} = 0.14 \text{ bohr}$) and the resulting solvation energy are much smaller.

Table VII compares our result for the solvatochromic shift of the lowest singlet excitation with previous theoretical work^{18,38,41-44} and also with experiment.¹⁹ In contrast to

TABLE VI. Lowest singlet excitation energy of formaldehyde in vacuum (E_{vac}) and aqueous solution (E_{solv}) obtained from joint time-dependent density-functional theory. The resulting solvatochromic shift ($E_{\text{solv}} - E_{\text{vac}}$) is shown in the third column and compared to experiment.¹⁹ All results are given in eV.

E_{vac}	E_{solv}	Shift	Expt. ¹⁹
3.66	3.83	0.17	0.21

TABLE VII. Comparison of our joint time-dependent density-functional theory results, previous theoretical work^{18,38,41–44} and experiment¹⁹ for the solvatochromic shift of the lowest singlet excited state of formaldehyde in aqueous solution. The second column lists the solvent model: joint time-dependent density-functional theory (JTDDFT), the “polarizable continuum model” (PCM), the supermolecular approach (SM), or the reference interaction-site model (RISM). All results are given in eV.

	Method	Shift
Ref. 18	PCM	0.12
Ref. 38	PCM	0.12
Ref. 42	SM	0.33
Ref. 43	SM	0.39
Ref. 44	RISM	0.25
Ref. 41	SM + PCM	0.23
This work	JTDDFT	0.17
Expt. 19	—	0.21

our calculation, which gives very good agreement with the experimental data, calculations employing the “polarizable continuum model” to describe the solvent underestimate the shift,^{18,38} while approaches that treat the solvent atomistically within a supermolecular approach^{42,43} typically overestimate the shift. We point out that both methods suffer from weaknesses that are absent in our approach. In particular, the results of the “polarizable continuum model” approach depend sensitively on the chosen cavity size and shape.⁵⁵ This indicates that a more realistic description of the solvent response in the vicinity of the solute is of great importance. Atomistic solvent models, on the other hand, offer a reliable description of the solvent structure close to the solute, but to compute converged thermodynamic averages the sampling of many solvent configurations is required. In addition, supermolecular approaches that model the solvent by a finite cluster surrounding the solute do not capture the long-range dielectric response of the solvent.

Our approach includes both long-range screening effects and a reliable description of the solvent response close to the solute. Similarly, Naka *et al.*,⁴⁴ who employ the reference interaction-site model to describe the solute, and Kongsted *et al.*,⁴¹ who combine an atomistic treatment of the first solvation shells with the “polarizable continuum model,” also obtain solvatochromic shifts in good agreement with experiment. However, unlike our action functional, these models are not derived from first principles: Instead, they start out with a partitioning of the action and then approximate each contribution typically with a different level of theory, making it difficult to judge the limits of their applicability *a priori* and to systematically improve on them. For example, Naka *et al.* combine a complete active space self-consistent field treatment of the solute electrons with an electrostatic coupling scheme between solute and solvent and the reference-interaction site model for the solvent structure.⁴⁴

Finally, we discuss the intensity of the transition from the ground state of formaldehyde to the lowest singlet excited state. In our calculations we employ the Franck-Condon approximation,^{56–58} keeping the ions fixed at their equilibrium positions. Within this approximation, we find that the transition

is dipole forbidden both in vacuum and in solution. However, due to vibronic couplings, the transition gains intensity and can be observed in experiments.⁵⁹ In solution, particular solvent configurations can also distort the solute orbitals, making the transition weakly dipole allowed.⁶⁰ The effects of the latter mechanism are contained in the exact implicit functional (7), but the relatively simple dielectric mean-field approximation presented in Sec. III lacks the correlation effects between the solvent and the solute electrons needed to capture the intensity enhancement. Future work should aim at improving the implicit functional and in particular the effective interaction potential $W(\mathbf{r}, \mathbf{r}', \tau, \tau')$ to include the necessary correlations, which would also allow for the study of the inhomogeneous broadening of the absorption lines in solution.⁴⁴ We also plan to study vibronic effects in solution by employing the Herzberg-Teller theory of vibronic transitions.^{61,62}

V. SUMMARY AND CONCLUSIONS

In sum, we describe the construction of a joint time-dependent density-functional theory for the modeling of solute-solvent systems. We derive coarse-grained action functionals by eliminating environment degrees of freedom. This procedure enables us to examine the underlying assumptions and uncover previously ignored functional dependencies in popular approaches, such as the time-dependent “polarizable continuum model,” and to explore their domains of validity. In particular, we find additional contributions to the action functional that are typically neglected in standard approaches. Also, in order to replace the full frequency-dependent solvent response by a high-frequency dielectric constant, as is often done in standard approaches, the excitation energy of the solute has to be far from the poles of the solvent dielectric function. Otherwise, a self-consistent solution of the linear response equation is necessary.

We also introduce an explicit, approximate action functional for the modelling of electronic systems in aqueous solution. Application of this functional to solvated formaldehyde leads to good agreement with experiment for the solvatochromic shift of the lowest singlet excited state. The implicit functional we introduced can now be applied to more complicated systems, such as dyes in Grätzel cells⁷ or solvated DNA molecules.^{8,9}

The framework is now in place for future work to develop approximate forms for the explicit solvent functionals by making use of existing forms of time-dependent functionals for classical liquids³⁷ and to generalize time-independent functionals for molecular liquids developed by us^{63,64} to include time-dependent response of the solvent electrons. The resulting theory would then allow us to describe the nuclear dynamics of the environment during the excitation and to compute solvation relaxation functions that have been measured experimentally.^{65,66}

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