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

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We present a novel 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 which retain the highly accurate \textit{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 a novel approximate action functional for the solute-water system and compute the solvato-chromic 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 \cite{1,2}, laser technology \cite{3} or light-emitting diodes \cite{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 \cite{6,7} are in contact with an electrolyte and spectra of DNA molecules are typically obtained in an aqueous solution \cite{8,9}.

Various methods for the theoretical modelling 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 quasi-particle \cite{10} and the Bethe-Salpeter equation \cite{11} in the GW approximation. Quantum chemistry methods, such as configuration interaction \cite{12} or coupled cluster theory \cite{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 \cite{14,15} emerged as an economical yet accurate theory for larger molecules and clusters \cite{7,16,17}.

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 \cite{18,20,22}. These methods either model the solvent atomistically, for example by using the classical molecular dynamics technique \cite{19,21}, or via a continuum approach \cite{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” \cite{6,7,18,23}, where the molecule is placed inside a cavity in a linear dielectric medium. The solute-solvent interactions are then separated into equilibrium and non-equilibrium 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 upon these theories and understand their limitations, it is necessary to understand their origin \textit{from first principles}. In this paper, we derive different levels of continuum embedding theory starting from the \textit{exact} quantum-mechanical action functional for the full solute-solvent system (Sections II). Next, as a demonstration that the approach can lead to practical calculations, we introduce a novel time-dependent continuum model (Section 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 (Section IV). Finally, in Section 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 temperature \[24\] to multi-component systems at finite temperature. This generalization is similar to the theory of Li and Tong \[25\]. Those authors, however, worked only at zero temperature and employed the Frenkel-Dirac action functional, which violates the causality requirement of van Leeuwen \[24\]. Generalizing the approach of van Leeuwen to the present situation yields for the action functional of the full solute-solvent system,

\[
S[n, \{N_\alpha\}] = A[n, \{N_\alpha\}] - \int d\tau \int_C d\tau n(r, \tau) v(r, \tau) \]

\[
- \sum_\alpha \int d\tau \int_C d\tau N_\alpha(r, \tau) V_\alpha(r, \tau), \tag{1}
\]

where \(n(r)\) and \(N_\alpha(r)\) denote the density of electrons and the various nuclear species, while \(v(r)\) and \(V_\alpha(r)\) denote the respective external potentials. Also, \(\Omega\) denotes an open volume as required when working in the grand canonical ensemble and \(\tau\) denotes the Keldysh time \[24\], which is defined on the contour \(C\) ranging from \(0\) to \(\infty\) just above the real time axis and then back from \(\infty\) 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 (1), the intrinsic action \(A\) is the Legendre transform, with respect to the potentials \(v\) and \(V_\alpha\) \[24\], of

\[
\tilde{A}[v, \{V_\alpha\}] =
\]

\[
i \log \text{Tr} \left\{ \exp \left( \beta \left[ \mu_\text{el} \hat{N}_\text{el} + \sum_\alpha \mu_\alpha \hat{N}_\alpha \right] \right) \right\}, \tag{2}
\]

where \(\mu_\text{el}\) and \(\mu_\alpha\) are the chemical potentials of the electrons and nuclei, while \(\hat{N}_\text{el}\) and \(\hat{N}_\alpha\) denote the respective particle number operators. In the above, \(U = T_C \exp(-i \int d\tau \hat{H}(\tau))\) denotes the quantum-mechanical evolution operator \[24\] 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 multi-component time-dependent density-functional theory \[25\], 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 \(n(r, \tau)\) and \(N_\alpha(r, \tau)\). 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 that 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 only fix the locations of the solute nuclei in the final step. Consequently, the index \(\alpha\) in (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 which make the action in (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 \[28\] 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 \[28\].

To generalize the theory of Petrosyan and coworkers to the present non-equilibrium context, we split the total electron density in (1) into solute \(n_s\) and environment \(n_e\) contributions, \(n(r, \tau) = n_s(r, \tau) + n_e(r, \tau)\). Fundamentally, a rigorous partitioning of electrons into solute and environment electrons is, of course, impossible because of the 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 which 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. [29] observed that the use of molecular pseudopotentials [30] leads to sensible non-degenerate 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 $S_{\text{ex}}$.

$$S_{\text{ex}}[n_s, \{N_\alpha\}] = \text{stat}_{n_s} \left\{ A[n_s + n_e, \{N_\alpha\}] - \int d\tau \int d\Omega \left[ n_e(r, \tau)v(r, \tau) + \sum_\alpha N_\alpha(r, \tau)V_\alpha(r, \tau) \right] \right\}$$

$$- \int d\tau \int d\Omega n_s(r, \tau)v(r, \tau)$$

$$\equiv A^{(v,\{V_\alpha\})}[n_s, \{N_\alpha\}] - \int d\tau \int d\Omega n_s(r, \tau)v(r, \tau),$$

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 $A$ 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 $A$: 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 $A$ describes a neutral system: Maintaining charge neutrality is important both formally to ensure the existence of the thermodynamic limit [31] and also 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 $A$ because the coupling to $V_\alpha$ will retain its simple form in terms of $N_\alpha$.

To find practical approximations, we partition $A$ into various physically meaningful contributions according to

$$A = A_{\text{el},s}[n_s] + A_{\text{nuc},e}[\{N_{s,\alpha}\}] - A_{\text{nuc/ele},s}[\{N_{s,\alpha}\}] - A_{\text{nuc/el},s}[n_s, \{N_{s,\alpha}\}]$$

$$+ A_{e}[\{N_{e,\alpha}\}] - \Delta A_{\text{ext/e}}[\{N_{e,\alpha}\}] - \Delta A_{\text{ext/e}}^{(v,\{V_\alpha\})}[n_s, \{N_{s,\alpha}\}, \{N_{e,\alpha}\}],$$

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 typically [24] written as

$$A_{\text{el},s} = A_{\text{KS}} - A_H - A_{\text{XC}},$$

where $A_{\text{KS}}$ denotes the action of non-interacting electrons, $A_H = 1/2 \int d\tau \int d\Omega n_s(r, \tau)n_s(r', \tau)/|r-r'|$ is the Hartree contribution and $A_{\text{XC}}$ the exchange-correlation term. The second and third terms in (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 $A_{\text{nuc/ele},s} = \int d\tau \int d\Omega n_s(r, \tau)v_{\text{ex}}(r)$, with $v_{\text{ex}}$ being the static potential created by the solute nuclei. Under these conditions, the second and third term in (4) become independent of all time-dependent degrees of freedom (though, not of time-dependent potentials) and can be dropped for the purpose of the variational calculations. However, for later convenience we retain $A_{\text{nuc/el},s} = \int d\tau \sum_{I<J} Z_I Z_J |R_I - R_J|$ with $R_I$ and $Z_I$ denoting the positions and charges of the solute nuclei.

The fifth term in (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 [32, 33], 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 [41] to be relatively small. The sixth term, $\Delta A_{\text{ext,e}}$, describes the interaction between the neutral solvent and the external potentials. The final, seventh term, $\Delta A_{s,e}$, 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 $\Delta A_{\text{ext,e}}$, 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 $\bar{Z}_\alpha$, the corresponding action would be $\sum_\alpha \int d\tau \int d\tau' [N_{e,\alpha} V_\alpha + (Z_\alpha - \bar{Z}_\alpha) N_{e,\alpha} v]$ with $Z_\alpha$ 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 $q_\alpha$ and all partial charges in a molecule add up to zero, one should replace $\bar{Z}_\alpha$ in the above expression by $q_\alpha$. Finally, if the solvent consists of apolar molecules or neutral atoms, we can approximate the coupling by $\sum_\alpha \int d\tau \int d\tau' \pi_{N,e,\alpha} |V|^2$ with $\pi_\alpha$ being the polarizability of the “effective” nucleus $\alpha$.

The final term, $\Delta A_{s,e}$, 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 $\Delta A_{s,e}$ as a Taylor series in the various densities, keeping only the lowest-order coupling terms,

$$
\Delta A_{s,e} = \int_\Omega dr \int_\Omega dr' \int_C d\tau \int_C d\tau' \sum_\alpha N_{e,\alpha}(r', \tau') \left[ w_\alpha(r, r', \tau, \tau') n_s(r, \tau) + \sum_\beta w_{\alpha\beta}(r, r', \tau, \tau') N_{s,\beta}(r', \tau') \right],
$$

where $w_\alpha(r, r', \tau, \tau') = \delta^2 \Delta A_{s,e}/\delta n_s(r, \tau) \delta N_{e,\alpha}(r', \tau')$ and $w_{\alpha\beta}(r, r', \tau, \tau') = \delta^2 \Delta A_{s,e}/\delta N_{e,\alpha}(r, \tau) \delta N_{s,\beta}(r', \tau')$ 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 $A_{el,s}$ and is therefore neglected in [41].

Table I summarizes all of the above considerations, listing all of the various contributions to $S_{ax}$ and the terms which capture them.

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

$$
S_{im}[n_s, \{N_{s,\alpha}\}] = \text{stat}_{\{N_{e,\alpha}\}} \mathcal{A}^{(v, \{V_\alpha\})}[n_s, \{N_{s,\alpha}\}] - \int_\Omega dr \int_C d\tau n_s(r, \tau) v(r, \tau)
$$

$$
\equiv \mathcal{G}^{(v, \{V_\alpha\})}[n_s, \{N_{s,\alpha}\}] - \int_\Omega dr \int_C d\tau n_s(r, \tau) v(r, \tau).
$$

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

$$
\mathcal{G} = A_{el,s}[n_s] + A_{\text{nuc,s}}[\{N_{s,\alpha}\}] - A_{\text{nuc/ext,s}}[\{N_{e,\alpha}\}],
$$

$$
- A_{\text{nuc/el,s}}[n_s, \{N_{s,\alpha}\}] - \Delta \mathcal{G}^{(v, \{V_\alpha\})}[n_s, \{N_{s,\alpha}\}]
$$

with $\Delta \mathcal{G} = -\text{stat}_{\{N_{s,\alpha}\}}[A_e - \Delta A_{\text{ext,e}} - \Delta A_{s,e}]$ and $A_{el,s}$ is given by [41]. 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, $\delta S_{im} = 0$, which implies $\delta \mathcal{G}/\delta n_s = v$. Using [41] we thus have (assuming fixed solute nuclei)

$$
v(r, \tau) = v_{KS}(r, \tau) - v_H(r, \tau) - v_{XC}(r, \tau) - v_{st}(r) - v_{e}^{(v, \{V_\alpha\})}(r, \tau),
$$
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 |
|--------------|--------------|
| $N_s/N_s$    | $A_{nuc,s}$  |
| $N_s/n_e$    | $A_{nuc/el,s}$ |
| $N_s/N_e$    | $\Delta A_{s,e}$ |
| $N_s/n_e$    | $\Delta A_{s,e}$ |
| $NS/V$       | $A_{nuc/ext,s}$ |
| $n_s/n_s$    | $A_{el,s}$ |
| $n_s/n_e$    | $\Delta A_{s,e}$ |
| $n_s/n_e$    | $\Delta A_{s,e}$ |
| $n_s/v$      | last term in Eq. (10) |
| $N_e/N_e$    | $A_{el}$ |
| $N_e/n_e$    | $\Delta A_{ext,e}$ |
| $N_e/V$      | $\Delta A_{ext,e}$ |
| $n_e/n_e$    | $\Delta A_{ext,e}$ |
| $n_e/v$      | $\Delta A_{ext,e}$ |

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

A small change $\delta v$ in the external potential causes a change $\delta n_s$ in the solute electron density. In the linear response regime, these quantities are related via the response function $\chi$

$$\delta n_s(r, \tau) = \int_\Omega d\tau' \int_C d\tau' \chi(r, r', \tau, \tau') \delta v(r', \tau').$$

To compute $\chi$, which is the observable in spectroscopic experiments on the solute-solvent system, we first determine the change in the Kohn-Sham potential $\delta v_{KS}$ corresponding to $\delta v$. (Strictly speaking, only the total response function $\chi_{tot} = \delta n/\delta v = \delta n_s/\delta v + \delta n_e/\delta v$ is measured. However, for solute-solvent systems where the response of the solute occurs in a different frequency range than the response of the solvent one can determine experimentally the solute response function $\chi$. This is the case for the lowest singlet excitation of formaldehyde in water, which we study in the Section IV.) Using (7), we find

$$\delta v_{KS}(r, \tau) = \delta v(r, \tau) + \int_\Omega d\tau' \frac{\delta n_s(r', \tau)}{|r - r'|} + \int_\Omega \int_C d\tau' d\tau' f_{XC}(r, r', \tau, \tau') \delta n_s(r', \tau')$$

$$+ \int_\Omega \int_C d\tau' d\tau' f^A_e(r, r', \tau, \tau') \delta n_s(r', \tau')$$

$$+ \int_\Omega \int_C d\tau' d\tau' f^B_e(r, r', \tau, \tau') \delta v(r', \tau')$$

$$+ \sum_\alpha \int d\tau' \int d\tau' f^C_{e,\alpha}(r, r', \tau, \tau') \delta V_{e,\alpha}(r', \tau'),$$

where $f^A_e = \delta v_e/\delta n_s$, $f^B_e = \delta v_e/\delta v$ and $f^C_{e,\alpha} = \delta v_e/\delta V_{e,\alpha}$ denote additional contributions to $\delta v_{KS}$ 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 $\delta v$. In this case, we can express the last term in (11) as $f^D_e \delta v$ with $f^D_e = \sum_\alpha f^C_{e,\alpha} \delta V_{e,\alpha}/\delta v$.

The change in the Kohn-Sham potential is related to $\delta n_s$ via

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

where $\chi_{KS}$ denotes the response function of non-interacting electrons. Combining (12), (11) and (10) and adopting a matrix formulation for the space and Keldysh-time variables then yields

$$\chi^{-1} = [1 + f^B_e + f^D_e]^{-1} \{ \chi_{KS}^{-1} - [K + f_{XC} + f^A_e] \},$$

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

Compared to the familiar equation for $\chi$ without solvent, given by $\chi^{-1} = \chi_{KS}^{-1} - [K + f_{XC}]$, we find that (13) contains three extra terms due to the presence of the solvent: $f^A_e$ describes the change of the solvent potential due to a change in the solute electron density, while $f^B_e$ and $f^D_e$ describe changes induced by a variation in the external potential. Without justification, “polarizable continuum model” approaches typically (8) approximate the potential due to the solvent as a functional of the solute density only, which means they only include $f^A_e$ and neglect $f^B_e$ and $f^D_e$. This insight into the assumptions underlying popular embedding approaches underscores the value of following the density-functional approach rigorously, so as to identify all potentially relevant functional dependencies.
2. Practical approximations

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

$$\Delta G_{s,e} = \int_\Omega dr \int_\Omega dr' \int_C d\tau \int_C d\tau' \left[ \frac{1}{2} n_s(r, \tau) W(r, r', \tau, \tau') n_s(r', \tau') \right]$$

$$+ \sum_\alpha N_{s,\alpha}(r, \tau) \left( W_\alpha(r, r', \tau, \tau') n_s(r, \tau') + \frac{1}{2} \sum_\beta W_{\alpha\beta}(r, r', \tau, \tau') N_{s,\beta}(r', \tau') \right), \tag{14}$$

where $W(r, r', \tau, \tau')$, $W_\alpha(r, r', \tau, \tau')$ and $W_{\alpha\beta}(r, r', \tau, \tau')$ 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 $\Delta G_{\text{ext}}$ is more difficult: a possible route to finding explicit functionals is to express the environment nuclear densities in terms of solute densities according to $N_{\alpha,\alpha}(r) = g_\alpha[n_s, \{N_{s,\alpha}\}](r)$ and insert this relation into the various forms for $\Delta A_{\text{ext}}$ discussed in the last section. We expect that $g_\alpha$ has a similar form as the dielectric function employed in the next section [Equation (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 $\Delta G_{\text{ext}}$. We expect, however, that the additional solvent response due to this term can be included by "renormalizing" the dielectric function describing the environment (see Section 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 \cite{18,34}, 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 \cite{12} 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

$$\mathcal{G} = A_{KS} - A_{XC} - \Delta V_{ps} - \frac{1}{2} \int_\Omega dr \int_\Omega dr' \int_C d\tau \int_C d\tau' \rho_s(r, \tau) \tilde{K}(r, r', \tau, \tau') \rho_s(r', \tau'), \tag{15}$$

with $\rho_s(r, \tau) = -n_s(r, \tau) + \sum_l Z_l \delta(r - R_l)$ denoting the solute charge density and $\tilde{K} = K + \tilde{W}$, where $K$ is the bare Coulomb interaction defined as above. Also, $\Delta V_{ps}$ reflects the fact that, in practical calculations, we employ the pseudopotential approximation \cite{35}, in which the nuclei are replaced with ionic cores of charge $Z_l$, whose
The screened potential corresponding to a physical charge density \( \rho_s(r, t) \), which is equal on both vertical branches of the Keldysh contour, is given by \( \dot{\phi}_s = \tilde{K}^R \rho_s \), where \( \tilde{K}^R \) denotes the retarded interaction \([24]\). In actual calculations, we obtain \( \dot{\phi}_s \) by solving the screened Poisson equation

\[
\nabla \cdot \epsilon(r, \omega) \nabla \tilde{\phi}(r, \omega) = -4\pi \rho_s(r, \omega).
\]

All information about the environment is contained in the dielectric function \( \epsilon(r, \omega) \). 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 assumption 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 \( n_0(r) \). This suggests the following local ansatz for the dielectric function,

\[
\epsilon(r, \omega) = \epsilon(n_0(r), \omega).
\]

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 \( \epsilon(n_0(r), \omega) \) enters only through the frequency dependence of the bulk dielectric function \( \epsilon_b(\omega) \), we can generalize the form employed by Petrosyan and co-workers \([25]\) to

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

where the parameters \( n_c \) and \( \sigma \) determine the location and width, respectively, of the crossover from the vacuum to the bulk liquid dielectric response. Petrosyan et al. \([25]\) determined the numerical values \( n_c = 4.73 \times 10^{-3} \text{A}^{-3} \) 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 which describes the high-frequency range reliably. For this, we use the Clausius-Mossotti form \([36]\)

\[
\frac{\epsilon_b(\omega) - 1}{\epsilon_b(\omega) + 2} = \frac{4\pi}{3} n_b \tilde{\alpha}(\omega),
\]

where \( n_b \) denotes the bulk molecular particle density of water and \( \tilde{\alpha}(\omega) = \sum_j F_j/(E_j^2 - \omega^2) \) 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 \( \tilde{\alpha}(\omega) \) using time-dependent density-functional theory and demonstrate that \([19]\), 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 \([15]\) resulting in

\[
\chi^{-1} = \chi_{KS}^{-1} - [\tilde{K} + f\tilde{C}],
\]

which lacks the subtleties appearing in Section \([13]\) because the present model lacks any explicit environment dependence on the external potential. Our final working equation is obtained by expressing \([20]\) in transition-space notation \([15]\), where the fused index \( \kappa = (k, j) \) denotes a transition between two equilibrium Kohn-Sham orbitals \( \psi_k(r) \) and \( \psi_j(r) \). We arrive at a self-consistent eigenvalue problem \([15]\) for excitation energies \( E_j \) of the solute,

\[
\sum_\nu \left[ \delta_{\kappa\nu} \Delta \epsilon_{\nu}^2 + 4\sqrt{\Delta \epsilon_{\kappa} \Delta \epsilon_{\nu}} M_{\kappa\nu}(E_j) \right] C_{\nu}^{(j)} = E_j^2 C_{\kappa}^{(j)},
\]

where \( \Delta \epsilon_{\kappa} = \epsilon_j - \epsilon_k \) with \( \epsilon_k \) 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

\[
M_{\kappa\nu}(\omega) =
\int_\Omega d\Omega' \int_\Omega d\Omega' \Phi^{\dagger}_\kappa(r) \left[ \tilde{K}^R(r, r', \omega) + f_{XC}^R(r, r', \omega) \right] \Phi_{\nu}(r'),
\]

with \( \Phi_\kappa(r) = \psi_\kappa^*(r) \psi_j(r) \) 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 \((21)\) 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 solvato-chromatic shifts of formaldehyde in water. 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 formula. 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 last section.

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

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 [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. Then, we employ time-dependent density-functional theory to obtain excitation energies and oscillator strengths using all 4 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 work [44] and also to experiment [44]. 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.

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 calculations [46] and also with experiment [46–48]. We observe that the Clausius-Mossotti formula describes the 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 [49], who also employ the adiabatic local density approximation, and also with experimental findings [18, 49]. 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 II and III 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 only evaluate 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 models.”

| TABLE II: | Comparison of the lowest singlet excitation energies of an isolated water molecule with previous theoretical work by Bernasconi [44] and experiment [44]. All results are given in eV. |
|-----------|------------------------------------------|
| This work | Ref. [44] | Expt. [44] |
| 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 \( \epsilon_{\text{opt}} \equiv \epsilon_0(\omega = 1 \text{ eV}) \) of liquid water with previous theoretical work by Hu et al. [46] and experiment [46–48]. |
|-----------|------------------------------------------|
| Units     | This work | Ref. [46] | Expt. [46–48] |
| \( \alpha(\omega = 0) \) bohr \(^3\) | 10.50 | 10.52 | 9.6–9.9 |
| \( \epsilon_{\text{opt}} \) | 1.83 | — | 1.78 |

| TABLE IV: | Comparison of the three lowest singlet excitation energies of an isolated formaldehyde molecule with previous theoretical work by Bauernschmitt et al. [49] and experiment [18, 49]. All energies are given in eV. |
|-----------|------------------------------------------|
| This work | Ref. [49] | Expt. [18, 49] |
| 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 ($\mu_{\text{vac}}$) and aqueous solution ($\mu_{\text{solv}}$) with experiment [54] and previous theoretical work [38]. Dipole moments are given in bohr.

|        | This work | Ref. [38] | Expt. [50] |
|--------|-----------|-----------|------------|
| $\mu_{\text{vac}}$ | 0.91      | 0.90      | 0.91       |
| $\mu_{\text{solv}}$ | 1.32      | 1.32      | —          |

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

|        | $E_{\text{vac}}$ | $E_{\text{solv}}$ | Shift | Expt. [19] |
|--------|------------------|------------------|-------|------------|
|        | 3.66             | 3.83             | 0.17  | 0.21       |

model" approaches, which for the non-equilibrium response employ 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 (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 of Petrosyan et al. [28] to determine the equilibrium electronic structure neglecting ionic relaxations induced by the aqueous environment, which as was shown by Kongsted et al. [27] only lead to shifts in the excitation energies of about 0.01 eV [18]. Table V shows that the equilibrium dipole moment obtained in our calculation is in excellent agreement with previous theoretical work [38].

We then solve the linear response equation (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 VII summarizes our results for the excitation energies in vacuum and solution and the resulting solvato-chromic shift, which is in good agreement with the experimental value [19].

To physically understand the observed solvato-chromic blue-shift, we express the excitation energy as

$$E_{\text{vac/solv}} = \Delta\epsilon_{\text{vac/solv}} + \gamma_{\text{vac/solv}},$$

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, $\Delta\epsilon_{\text{vac}} = 3.34$ eV already gives a reasonable approximation to $E_{\text{vac}} = 3.66$ eV with the correction $\gamma_{\text{vac}} = 0.32$ eV being relatively small. In solution, we find $\Delta\epsilon_{\text{solv}} = 3.56$ eV and $\gamma_{\text{solv}} = 0.27$ eV. We conclude that the solvato-chromic shift is determined mostly by the change of the orbital energy differences, $\Delta\epsilon_{\text{vac}} - \Delta\epsilon_{\text{solv}} = 0.22$ eV which is quite close to the total solvato-chromic shift of 0.17 eV, while the correction term changes relatively little (only 0.05 eV).

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

Table VII compares our result for the solvato-chromic shift of the lowest singlet excitation with previous theoretical work [18, 34, 37, 40] and also with experiment [19]. In contrast to 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, 34], while approaches, which treat the solvent atomistically within a supermolecular approach [38, 39], typically overestimate the shift. We point out that both methods suffer from weaknesses which are absent in our approach. In particular, the results of the “polarizable continuum model” approach depend sensitively on the chosen cavity size and shape [51]. 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 which 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. [41], who employ the reference interaction-site model to describe the solute, and Kongsted et al. [37], who combine an atomistic treatment of the first solvation shells with the “polarizable continuum model,” also obtain solvato-chromic 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 mak-
TABLE VII: Comparison of our joint time-dependent density-functional theory results, previous theoretical work \cite{18, 34, 37, 40} and experiment \cite{19} for the solvato-chromic 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. \cite{18} | PCM   | 0.12  |
| Ref. \cite{34} | PCM   | 0.12  |
| Ref. \cite{38} | SM    | 0.33  |
| Ref. \cite{39} | SM    | 0.39  |
| Ref. \cite{40} | RISM  | 0.25  |
| Ref. \cite{37} | SM+PCM| 0.23  |
| This work   | JTDDFT| 0.17  |
| Expt. \cite{19} | —     | 0.21  |

In sum, we describe the construction of a joint time-dependent density-functional theory for the modelling 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 which 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 solvato-chromatic shift of the lowest singlet excited state. The novel implicit functional we introduced can now be applied to more complicated systems, such as dyes in Grätzel cells \cite{2} or solvated DNA molecules \cite{3, 4}.

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 liquids \cite{52} and to generalize time-independent functionals for molecular liquids developed by us \cite{54, 55} 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 which have been measured experimentally \cite{54, 55}.

V. SUMMARY AND CONCLUSIONS

In sum, we describe the construction of a joint time-dependent density-functional theory for the modelling 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 which 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 solvato-chromatic shift of the lowest singlet excited state. The novel implicit functional we introduced can now be applied to more complicated systems, such as dyes in Grätzel cells \cite{2} or solvated DNA molecules \cite{3, 4}.

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