

Nonequilibrium solvent effects in Born-Oppenheimer molecular dynamics for ground and excited electronic states

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The effects of solvent on molecular processes such as excited state relaxation and photochemical reaction often occurs in a nonequilibrium regime. Dynamic processes such as these can be simulated using excited state molecular dynamics. In this work, we describe methods of simulating nonequilibrium solvent effects in excited state molecular dynamics using linear-response time-dependent density functional theory and apparent surface charge methods. These developments include a propagation method for solvent degrees of freedom and analytical energy gradients for the calculation of forces. Molecular dynamics of acetaldehyde in water or acetonitrile are demonstrated where the solute-solvent system is out of equilibrium due to photoexcitation and emission. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4946009>]

I. INTRODUCTION

Determining the effects of solvent on the electronic and/or vibrational dynamics of chemical species has been a challenge for many years.¹⁻⁷ Important developments regarding nonequilibrium dynamics for excited electronic states have been made in recent years.⁸⁻¹⁵ The most popular method of simulating large molecular systems is currently the density functional theory (DFT).¹⁶ The standard for molecular systems, Kohn-Sham DFT, is most often applied to the ground electronic state. Excited electronic states of molecular systems can be efficiently simulated using the related linear-response time-dependent density functional theory (LR-TD-DFT).¹⁷ Both DFT and LR-TD-DFT can be used to perform Born-Oppenheimer molecular dynamics (BOMD).¹⁸⁻²¹ Although relatively efficient in comparison to other *ab initio* methods, using DFT or TD-DFT to simulate the combined solvent and solute system (wherein both solvent and solute are treated at the same level of theory) is often intractable because the number of solvent degrees of freedom often surpasses the limits of tractable system size. Thus, approximations of solvent effects are necessary.

The interaction between the solute and solvent can involve charge transfer, dispersion, polarization, and Coulombic interactions.²² In most cases, charge transfer and dispersion can be neglected, while notable exceptions to this approximation include hydrogen bonding and ionic solvents.²² For most polar solvents where only polarization and Coulombic interactions are important, a dielectric continuum model for the solvent is often used. The dielectric continuum model has the added advantage of being an effective average over

solvent configurations. This averaging is reflective of most experimental measurements and would otherwise need to be performed explicitly by simulating multiple molecular configurations.²³

When a fast process occurs in a solute, such as electronic excitation, a polar solvent will usually not reach an equilibrium with the solute on the same fast time scale. The solute-solvent system is thus put into a nonequilibrium state.^{2,3,24,25} The nonequilibrium response of the solvent to the electrostatic effects of the solute can be described by the solvent's complex dielectric permittivity.⁸ Sometimes the complex permittivity is approximated using a combination of fast and slow time scale limits, where optical and static dielectric constants describe the magnitude of the solvent response to oscillating electric fields of infinite and zero frequency.²⁶⁻²⁹ This type of approximation is only suitable for step changes in the solute charge density and inappropriate for dynamics simulations where memory effects in the dynamic responses are present and can be important. In dynamics simulations the evolution of both solute and solvent subsystems occurs on a range of time scales. At finite temperature, the molecular motion of the solute causes dynamic solvation effects to persist when the solvent relaxation rate is slower than some time scale of molecular motion of the solute.

Many experimental measurements of molecular systems are performed in solution.⁵ It is no surprise that nonequilibrium solvent effects are well known in the literature. For example, intramolecular charge-transfer rates have been well correlated with the longitudinal solvent relaxation rate τ_L^{-1} .³⁰ In experiment, the nonequilibrium effects are often referred to as dielectric friction and discussed in terms of dipolar orientation relaxation of the solvent molecules. This has strong effects on charge redistribution processes, such as those which happen in many chemical reactions. Examples of measurements of

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the effect of polar solvents on the dynamics of chemical systems include photoisomerization and dynamic Stokes shift in solution.^{4,5}

The methods developed here follow some previous studies. The exploration of nonequilibrium solvent effects in *ab initio* simulations was initiated by Bagchi, Oxtoby, and Fleming by introducing the dynamic solvation effects on a dipolar molecule in a cavity according to a linear response function.²⁴ Following this, dynamic solvation effects were included in calculations of excited electronic states of frozen nuclei (frozen such that there was no motion of the nuclei) within an Onsager formalism by Hsu, Song, and Marcus.⁷ Ingrosso, Mennucci, and Tomasi extended these methods to a more realistic model of the solute cavity with the integral equation formalism of the polarizable continuum model in LR-TD-DFT.³¹ Following this, Caricato *et al.* presented a multistep integration procedure for the same model, again with frozen nuclei.⁸ Most recently, Ding, Lingerfelt, Mennucci, and Li extended these methods to real-time time-dependent density functional theory (RT-TD-DFT) simulations of electronic dynamics with the conductor-like polarizable continuum model CPCM¹⁵ while Corni, Pipolo, and Cammi formulated time-dependent solvent effects for several versions of the polarizable continuum model (PCM) including CPCM and applied them to RT-TD-DFT.³⁷ The study presented here adds to these previous studies by formulating energy gradients and forces for the nonequilibrium solvent effect. The nonequilibrium solvent effects are formulated for propagation in excited state BOMD simulations.

In a recent study,¹² the authors of this paper described excited state BOMD using a continuum solvent model under the assumption that the solvent and solute remained in equilibrium at all times. The purpose of the current study is to lift both the approximation of frozen nuclei and of equilibrium between solute and solvent, i.e., to simulate the molecular dynamics of the solute with dynamic solvation effects. These simulation methods are applied to BOMD in either ground or excited electronic states of the solute using molecular forces determined from DFT and LR-TD-DFT. The method described here can be considered state specific because the simulated solvent is polarized by the solute charge density in the specific electronic state in which the solute dynamics are propagated.²⁹ Until the methods described here were developed, a state specific solvent model in molecular dynamics was not computationally feasible due to the fact that analytical energy gradients in LR-TD-DFT were not possible without separating ground and excited state polarization effects.¹⁴

This paper is outlined as follows. In Sec. II we discuss the inclusion of nonequilibrium solvent effects for *ab initio* simulations and apply them to molecular dynamics. In Sec. III the calculation of molecular forces in a nonequilibrium solvent for DFT and LR-TD-DFT is described. Sec. IV gives the specific computational methods used to demonstrate the dynamics simulations. In Sec. V, model results are shown describing the nonequilibrium solvent effects on molecular dynamics after photoexcitation or emission. The paper is concluded in Sec. VI.

II. NONEQUILIBRIUM SOLVATION MODEL

As in the other studies mentioned above, we begin by writing the energy of interaction of a molecular charge density with a solvent at time t ,

$$U_{\text{solv}}(t) = \int_0^{r_c} dr \mathcal{R}(r,t) P(r,t), \quad (1)$$

where $P(r,t)$ is the molecular charge density including nuclear charge and r_c is some cavity radius in which the molecular charge density is contained. $\mathcal{R}(r,t)$ is the solvent reaction potential induced by the molecular charge density and could have complicated dependence on $P(r,t)$.^{1,7,32} In a Taylor expansion of $\mathcal{R}(r,t)$, the zeroth order term describes static charges and vanishes when no net charge is apparent on the cavity surface. This is not the case when, e.g., a dissolved ion is present in the molecule's solvation shell. Nonlinear terms can be neglected most accurately for solutes with small dipole moments. However, it has been found to be a good approximation for polar solvents in experiments³³ and seen broad success for the calculation of solvent effects in molecular systems.²³

We are thus able to use a linear response approximation for the solvent. Others have implemented a linear response approximation for $\mathcal{R}(r,t)$ in DFT and LR-TD-DFT where the solvent reaction potential can be determined to first order in $P(t,r)$ as

$$\mathcal{R}(t,r) = \int_0^{r_c} dr' \int_{-\infty}^t dt' \mathcal{V}(t,t',r,r') P(t',r'), \quad (2)$$

where $\mathcal{V}(t,t',r,r')$ is like a linear response function for relating the time dependent molecular charge density to the solvent reaction potential.

A. Nonequilibrium reaction potential

Thus far, we have not defined an approximation for describing the solvent reaction potential. Others have used the Onsager model or Integral Equation Formalism (IEF)-PCM.^{7,31} In general, the kernel of Eq. (2) can be described using apparent surface charge (ASC) methods. Using ASC methods, the molecular charge density is contained in a polarizable cavity of arbitrary shape. The problem is solved electrostatically using boundary values for the frequency dependent dielectric constant $\epsilon(\omega)$. Inside of the cavity $\epsilon(\omega) = 0$ while outside of the cavity $\epsilon(\omega)$ has finite value.³⁴ Upon solution of the Poisson equation, $\mathcal{V}(t,t',r,r')$ can have complicated dependence on $\epsilon(\omega)$ which makes obtaining a simple analytical expressions difficult to be derived for time propagation of $\mathcal{R}(t,r)$. Others have derived expressions based on a specific type of ASC method with an initial condition based on a step change in the molecular charge density. This step change, signifying photoexcitation, leads to the nonequilibrium solvent response. In this case, integration of Eq. (2) has been performed using the methods of Hsu, Song, and Marcus.⁷

In developing nonequilibrium solvent effects for BOMD, we allow for an initial condition based on the memory of past solute charge density fluctuations. This is different from previous formulations which used a step change in charge

density to form a nonequilibrium solute-solvent interaction. To do so, we first make the factorization approximation for $\mathcal{V}(t, t', r, r')$ discussed in detail by Fried and Mukamel.³² This approximation is closely related to CPCM. In CPCM Eq. (2) is solved in the limit of $\epsilon(\omega) \rightarrow \infty$. Then, a function of the dielectric constant $f(\epsilon(\omega))$ is inserted for finite $\epsilon(\omega)$ in the resulting reaction potential.³⁴ In this case, $\mathcal{R}(\omega, r)$ can be written as a product of $f(\epsilon(\omega))$ and a function describing the unscaled potential associated with the distribution of apparent surface charge, $\bar{\mathcal{R}}(\omega, r)$. Here, frequency and time dependent variables are straightforwardly related by the Fourier transform,

$$\begin{aligned} \mathcal{R}(\omega, r) &= f(\epsilon(\omega))\bar{\mathcal{R}}(\omega, r, r') \\ &= f(\epsilon(\omega)) \int_0^{r_c} dr' \bar{\mathcal{V}}(\omega, r, r') P(\omega, r'), \end{aligned} \quad (3)$$

where $f(\epsilon(\omega))$ acts as a scaling function and $\bar{\mathcal{V}}(\omega, r, r')$ is the possibly time-dependent factor of the solvent reaction potential involving the spatial structure of the cavity. This factorization later allows analytical energy gradients to be formulated.

As in CPCM, $f(\epsilon(\omega))$ is given here by

$$f(\epsilon(\omega)) = \frac{\epsilon(\omega) - 1}{\epsilon(\omega)}. \quad (4)$$

Several models exist to describe $\epsilon(\omega)$. The Debye model is the simplest and most widely known, being described by a single exponential function.³⁵ Other models generalize the solvent response to multiexponential or nonexponential behaviour such as in the Cole-Davidson model.³⁶ In several studies of nonequilibrium solvent response, experimental data have been used for this quantity, either for the entire solvent response or for only the high frequency portion of the response when combined with a model for the lower frequency region.^{8,31,32} In the Debye model, $\epsilon(\omega)$ is given by

$$\epsilon(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + i\omega\tau_D}. \quad (5)$$

The static and optical dielectric constants are ϵ_0 and ϵ_∞ , respectively, and τ_D is the Debye relaxation time for a given solvent. The Debye model describes the solvent polarization due only to solvent dipole orientation and neglects the induced polarization of the solvent. This causes the instantaneous polarization to be neglected. The instantaneous polarization is mostly relevant for fast processes such as when a molecule is photoexcited. The molecular motion occurs on a longer time scale and is mainly affected by the slower relaxation of the solvent, as it is on a longer time scale. The neglect of the high frequency response of the solvent present in the Debye model is thus a good approximation for molecular dynamics.

It is required that the solvent response to the molecular charge density at times infinitely in the past is zero such that

$$\lim_{t_0 \rightarrow -\infty} f(t - t_0) = 0. \quad (6)$$

Using the Debye model and enforcing this limit gives

$$f(t) = \tau_D^{-1} \frac{\epsilon_0 - \epsilon_\infty}{\epsilon_0 \epsilon_\infty} e^{-\frac{t}{\tau_D}} \quad (7)$$

in the time domain where $\tau_L = \tau_D \epsilon_0 / \epsilon_\infty$ is called the longitudinal relaxation time. This equation departs from the previous works which follow Hsu, Song, and Marcus where the molecular charge density at times infinitely in the past is constant.³⁷ In some previous studies, the electrostatic potential of the cavity surface is separated into a static partition due to the ground state charge density and a partition due to the difference in charge density between the ground and excited state. This difference in charge density has been based on an instantaneous change due to photoexcitation and is introduced using the unit step function. In the following, we have instead formulated the problem such that a step change in the charge density is not necessary for nonequilibrium effects. For example, one could use the reaction potential corresponding to the ground state charge density and then propagate on the ground state potential energy surface with nonequilibrium solvent effects.

If it is assumed that the solute and solvent are at equilibrium before some time t_0 such that the equilibrium solvent potential $\mathcal{R}(-\infty)$ is static, we can write $\mathcal{R}(t; t \leq t_0) = \mathcal{R}(-\infty)$. Then, the time integral related to Eq. (2) is

$$\bar{\mathcal{R}}(-\infty) \int_{-\infty}^{t_0} dt' f(t_0 - t') = \frac{\epsilon_0 - \epsilon_\infty}{\epsilon_0 \epsilon_\infty} \bar{\mathcal{R}}(-\infty). \quad (8)$$

For brevity, here and in the remainder of this section, the spatial dependence of quantities is not written unless necessary, e.g., $\bar{\mathcal{R}}(\omega)$ is equivalent to $\bar{\mathcal{R}}(\omega, r)$. Eq. (8) provides the initial conditions of a solute-solvent equilibrium. It has a different form from the static PCM equations due to the integration over $f(t_0 - t')$. The magnitude of the total solvent effect at this initial condition is controlled only by the dielectric constants. For photoexcitation or propagation on the ground state potential energy surface with nonequilibrium solvent effects, one would choose the initial reaction potential $\mathcal{R}(t_0)$ according to the ground state charge density self-consistently optimized in the reaction potential given by Eq. (8). For photoemission a similar procedure is performed with the excited state charge density.

B. Integration scheme for the reaction potential in BOMD

In BOMD, each time step involves a self-consistent potential calculation, calculation of molecular forces, and classical propagation of nuclei. At time t , $\mathcal{R}(t)$ can be included in the electronic Fock or Kohn-Sham operator $F(t)$ according to

$$F(t) = h(t) + U(t) + \mathcal{R}(t), \quad (9)$$

where $h(t)$ is the one electron operator, $U(t)$ is the Coulomb-exchange operator for Hartree-Fock³⁸ or the Coulomb, exchange and/or exchange-correlation operators for Kohn-Sham and hybrid DFT.^{39,40} Both $U(t)$ and $\mathcal{R}(t)$ depend on the density matrix $P(t)$, but only $\mathcal{R}(t)$ involves memory effects from nonequilibrium solvation, i.e., it depends on the density matrices calculated in previous time steps. To calculate the effective solvent potential for each subsequent time step beginning from the initial condition of Eq. (8), we write

$$\mathcal{R}(t + \Delta t) = \int_{-\infty}^{t+\Delta t} dt' f(t + \Delta t - t') \bar{\mathcal{R}}(t + \Delta t, t'), \quad (10)$$

where $\bar{R}(t, t') = \bar{V}(t, t')P(t')$ and Δt is the time step used in the time integration of the molecular dynamics simulation. For later calculation of forces, the part of this integral related to the next time step, called the instantaneous part $\mathcal{R}_I(t)$, must be treated differently from the part related to previous time steps, called the memory part, $\mathcal{R}_M(t)$,

$$\mathcal{R}(t + \Delta t) = \mathcal{R}_I(t + \Delta t) + \mathcal{R}_M(t + \Delta t), \quad (11)$$

where $\mathcal{R}_I(t + \Delta t)$ and $\mathcal{R}_M(t + \Delta t)$ are given by

$$\begin{aligned} \mathcal{R}_I(t + \Delta t) &= \int_t^{t+\Delta t} dt' f(t + \Delta t - t') \bar{R}(t + \Delta t, t'), \\ \mathcal{R}_M(t + \Delta t) &= \int_{-\infty}^t dt' f(t + \Delta t - t') \bar{R}(t + \Delta t, t'). \end{aligned} \quad (12)$$

Using the Debye type model for $f(t)$, these integrals are readily transformed into equations which are tractable for use in BOMD simulations.

We first note that when using the Debye model, the memory effects can be exactly propagated from the previous time step according to

$$\mathcal{R}_M(t + \Delta t) = e^{-\Delta t/\tau_L} \mathcal{R}(t). \quad (13)$$

On the other hand, the instantaneous effects require further approximation. One method of calculating $\mathcal{R}_I(t + \Delta t)$ is to assume constant $\bar{R}(t + \Delta t, t')$ between $t' = t$ and $t' = t + \Delta t$. The result is

$$\mathcal{R}_I(t + \Delta t) = \frac{\epsilon_0 - \epsilon_\infty}{\epsilon_0 \epsilon_\infty} (1 - e^{-\frac{\Delta t}{\tau_L}}) \bar{R}(t + \Delta t, t). \quad (14)$$

One could also linearly interpolate between the current and previous time step. However, this would not provide analytic excited state energy gradients due to issues with the ground state variational principle described in Sec. III.

Caricato *et al.* developed a multistep integration procedure for use with similar nonequilibrium solvent models in TD-DFT which was used by Ding *et al.* to propagate the solvent reaction potential in RT-TD-DFT electronic dynamics. This procedure is more general than the one presented here in that it allows for use of an experimental dielectric function to be used. It is therein necessary to store information about the reaction potential at each time step. This could quickly become cumbersome for a long time scale or large BOMD simulation. Thus, we have opted to use the alternative approach described above for propagation of the solvent since it requires storage of the information from only the previous time step.

The Debye model of dielectric relaxation is based on the rotational diffusion of static solvent dipoles. It does not include the effects of electronic polarization of the solvent, which is often the main source of instantaneous solvent effects. Although this provides justification for the approximation of Eq. (14), it neglects some aspects of the physical picture. It may be possible to include instantaneous polarization effects in these simulations by using a different form of $\epsilon(\omega)$.

By combining the approximate $\mathcal{R}_I(t)$ given by Eq. (14) with Eqs. (13) and (11), it is now possible to efficiently propagate nonequilibrium dynamic solvation effects according to the Debye model and calculate forces as described in Sec. III.

III. MOLECULAR ENERGY GRADIENT AND FORCES

We now describe the main result of this paper, the molecular energy gradients and forces. These allow BOMD to be performed with nonequilibrium solvent effects. The ground state energy is the sum of components without solvent effects and $E_{solv}(t)$

$$E_{gs}(t) = \bar{E}_{gs}(t) + E_{solv}(t), \quad (15)$$

where the part of the energy without solvent effect and its gradient are given elsewhere.^{14,21}

In the following, the gradient of E_{solv} with respect to nuclear coordinate Q is formulated. When using the static instantaneous potential approximation, $\mathcal{R}(t, r')$ does not depend on $P(t, r)$. The energy gradient is

$$\begin{aligned} E_{solv}^{(Q)}(t) &= \int_0^{r_c} dr P_0(t, r) \int_0^{r_c} dr' \\ &\times \int_{-\infty}^t dt' f(t - t') \bar{V}^{(Q)}(t, t', r, r') P(t', r'). \end{aligned} \quad (16)$$

Since $P_0(t, r)$ is the ground state charge density, $E^{(Q)}$ is stationary with respect to variation of $P_0(t, r)$ so that the only factor involving a gradient on the left hand side of Eq. (16) is $\bar{V}^{(Q)}(t, t', r, r')$. This allows the analytical gradient to be formulated for a specific PCM type model of the solvent potential according to previously developed methods.^{41,42}

The charge density polarizing the solvent when performing excited state BOMD is $P(t, r) = P_0(t, r) + P_\Delta(r, t)$ where $P_\Delta(r, t)$ is the so-called relaxed difference in density between the ground and excited state.^{14,21,43} When the static instantaneous potential approximation is used, $\mathcal{R}(t, r)$ has no dependence on $P(t, r)$ at the current time step. If it did, the variational principle for $P_0(t, r)$ would not hold as described in detail in Ref. 14. When performing ground state BOMD, $P_\Delta(r, t) = 0$. Then, it is not necessary to resort to the static instantaneous potential approximation for analytical gradients. However, the *ab initio* calculation at each time step would require a self-consistent calculation between the reaction potential and molecular charge density. This is not necessary for the methodology outlined herein.

This property of $\mathcal{R}(t, r)$ when using the static instantaneous potential approximation is important for excited state energy gradients. It eliminates breaking of a variational principle for quantities calculated in the DFT or LR-TD-DFT equations with a state-specific equilibrium formulation.¹⁴ There, the inclusion of instantaneous polarization effects could not be avoided such that a stationary excited state charge density could not be found. Due to the stationarity of $P(r, t)$ described above for the nonequilibrium formulation described here, the following equations are sufficient for a description of the gradient of the solvent effects in the excited state energy.¹⁴

The excited state energy at time t is the sum of the ground state and excitation energy $\Omega(t)$,

$$E_{es}(t) = E_{gs}(t) + \Omega(t). \quad (17)$$

The excitation energy is separated into portions with solvent effects, $\Omega_{solv}(t)$, and without, $\bar{\Omega}(t)$,

$$\Omega(t) = \bar{\Omega}(t) + \Omega_{solv}(t). \quad (18)$$

Similarly to Eq. (15), the gradient of $\Omega_{\text{solv}}(t)$ can be written as

$$\begin{aligned} \Omega_{\text{solv}}^{(Q)}(t) &= \int_0^{r_c} dr P_{\Delta}(t, r) \int_0^{r_c} dr' \\ &\times \int_{-\infty}^t dt' f(t-t') \bar{\mathcal{V}}^{(Q)}(t, t', r, r') P(t', r'), \end{aligned} \quad (19)$$

where $\mathcal{R}(t, r)$ does not depend on $P_{\Delta}(t, r)$ at the current time step. When the methods of calculating the excited state energy gradient in the gas phase are followed, namely, using the so called Z-vector equation,²¹ $\Omega(t)$ is stationary with respect to variation of $P_{\Delta}(t, r)$ and Eq. (19) holds.

Forces are calculated directly from these potential energy gradients. For microcanonical dynamics performed here, the force is equivalent to $-E_{gs}^{(Q)}(t)$ or $-E_{es}^{(Q)}(t)$ for the ground state or excited state at each time step. Here we note that the solvent effects on the forces described in this study are affected only by the screening effects of the solvent on the coulombic interactions in the solute. They do not include the effects of coupling between solvent and solute vibrational modes, commonly discussed in terms of fluctuations and dissipation. These effects can be included, for example, using a Langevin type equation of motion in BOMD. Further details of model computations for testing the described nonequilibrium effects are given below.

IV. COMPUTATIONAL METHODS

The microcanonical BOMD performed here follow the methodology detailed in several prior publications.^{12,19,44–48} Nuclear degrees of freedom are propagated using Verlet integration in a microcanonical scheme. The electronic structure is calculated using semiempirical AM1 model chemistry.^{18,49}

For testing purposes, an Onsager type solute-solvent interaction, i.e., dipole in a spherical conducting cavity, is used for the effective solvent potential. The radius of the sphere is held constant during the dynamics simulation at 5 Å. This type of model potential avoids possible issues related to the movement of an explicit cavity, e.g., a superposition of atom centered spheres, which could arise in these dynamics due to the need to store the solvent cavity charges from the previous time step and the number of charges being recalculated at each subsequent time step. This issue can be solved using the variational PCM method of Lipparini and colleagues.⁵⁰ Here, we intend to test the propagation of the nonequilibrium solvent reaction potential in BOMD and use an Onsager-like effective potential which avoids this issue. The model solvent effective potential operator can be written explicitly as

$$\bar{\mathcal{V}}(t, t', r, r') = R_c(t)^{-3} \hat{\mu}(0, r) \cdot \hat{\mu}(t - t', r'), \quad (20)$$

where $\hat{\mu}(t, r)$ is the dipole operator and $R_c(t)$ is a (possibly) time-dependent cavity radius. The gradient of this potential with respect to nuclear coordinate Q is straightforwardly given by

$$\bar{\mathcal{V}}^{(Q)}(t - t', r, r') = -R_c(t)^{-3} \hat{\mu}^{(Q)}(0, r) \cdot \hat{\mu}(t - t', r'), \quad (21)$$

where we assume a constant cavity radius $R_c(t)$. The cavity radius need not be kept constant and may depend on the molecular configuration, but the gradient then depends on

TABLE I. Parameters for the solvents water and acetonitrile used in simulations.

	ϵ_0	ϵ_{∞}	τ_D (ps)	τ_L (ps)
Water	78.36	1.78	8.2	0.32
Acetonitrile	35.95	2.00	3.9	0.21

the method by which the radius is determined. We note that the derivative of $\hat{\mu}(t - t', r)$ is zero if $t - t' < 0$. Practically, calculation of $\mathcal{R}(t)$ at each time step under the approximations outlined above involves calculation of the molecular dipole in the ground or excited state, updating R_M according to Eq. (13), and calculation of R_I according to Eq. (14). The energy gradient is then straightforwardly calculated according to Eq. (21).

Simulations are performed on acetaldehyde as a test system for the solute. Solvent effects are parameterized for the solvents acetonitrile and water using the values given in Table I.⁸ All simulations are performed using initial conditions corresponding to the optimized ground state geometry with solvent effective potential operator corresponding to Eq. (20) and a dielectric scaling factor corresponding to Eq. (8). As described above, simulations of dynamics after photoexcitation use the ground state molecular charge density for the initial condition in Eq. (8). For simulations of dynamics after photoemission, the so called relaxed excited state charge density corresponding to the first excited state is used.^{14,21} The initial velocities for Verlet integration are set to zero and dynamics performed with a time step of 0.1 fs. Simulations are performed for 1 ps. For comparison, simulations are also carried out with frozen nuclei, where at each time step a new electronic structure calculation is carried out with updated solvent effects and constant nuclear configuration.

V. RESULTS AND DISCUSSION

The total potential energy is given in Fig. 1 for simulations of dynamics after photoabsorption or emission, corresponding to either the excited state energy E_{es} or ground state energy E_{gs} . For static simulations, the potential energy reaches an equilibrium after a time scale associated with τ_L . A similar trend is seen in simulations with moving nuclei, although fluctuations corresponding to the classical motion of the nuclei are still present.

The initial condition for atomic coordinates is the optimized ground state geometry for both simulations of dynamics after photoabsorption and emission. As expected, the changes in energy for static nuclei are then mirror images. It is also observed that the effect of nonequilibrium solvation is stabilizing for dynamics after photoabsorption and destabilizing for dynamics after photoemission. This is due to a decrease in the dipole moment of the first excited state relative to the ground state as shown in Fig. 2. Here, the evolution of the dipole moment of the solvent, $\|\bar{\mu}_S\|$ is shown. As the nonequilibrium solvent effects evolve, the solvent dipole tends toward a scaled ground state dipole moment for post-photoemission dynamics and scaled excited state dipole moment for post-photoabsorption dynamics.

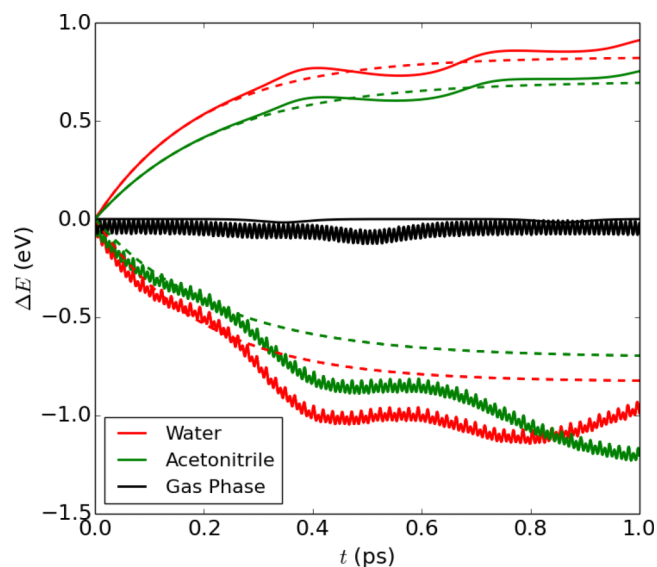


FIG. 1. Change in the potential energy ΔE of acetaldehyde during excited state dynamics. Solvent parameters for acetonitrile and water are used. Dashed lines correspond to frozen nuclei. Smoother, initially increasing lines correspond to post-photoemission simulations and initially decreasing lines represent post-photoabsorption simulations. For post-photoabsorption simulations $\Delta E = \Delta E_{es}$, while for post-photoemission simulations $\Delta E = \Delta E_{gs}$.

In simulations with moving nuclei, similar trends are seen in the evolution of ΔE as in the case of frozen nuclei. However, fast oscillations are present in post-photoabsorption dynamics induced by excitation to the first singlet excited state surface in the optimized ground state geometry. These fast oscillations are not present in the evolution on the ground state potential energy surface for post-photoemission dynamics. Simulations of photoabsorption in molecular dynamics also show an increased stabilization compared to static simulations due to relaxation of the molecular structure. This is not seen

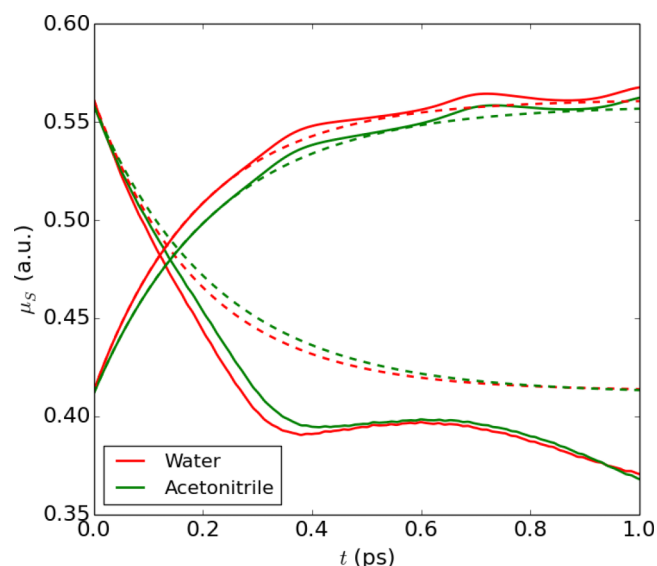


FIG. 2. Solvent dipole moment during excited state dynamics of acetaldehyde. Solvent parameters for acetonitrile and water are used. Dashed lines correspond to frozen nuclei. Initially increasing dipole moments correspond to post-photoabsorption simulations, while initially decreasing dipole moments correspond to post-photoemission simulations.

in post-photoemission dynamics since the geometry is already relaxed on the ground state potential energy surface.

For post-photoemission dynamics, a more realistic choice of initial conditions would involve optimization of the molecular geometry on the excited state potential energy surface. Efficient use of common optimization tools such as the conjugate gradient method would require analytical gradients to be formulated for a state specific solvent model. This is not possible due to the lack of available variational formulations of the excited state energy when a state specific solvent model is used.¹⁴ However, optimization of the molecular geometry for a state-specific solvent model in LR-TD-DFT could be performed by combining the methods described here with simulated annealing methods in molecular dynamics. This is currently under development and will be described in a future publication. We also intend to explore nonequilibrium solvent effects for nonadiabatic excited state molecular dynamics.

VI. CONCLUSION

In this study, analytical energy gradients and forces were formulated for nonequilibrium solvent effects in Born-Oppenheimer molecular dynamics using linear-response time-dependent density functional theory and apparent surface charge methods. A method of propagating the solvent degrees of freedom in excited state molecular dynamics was described in a factorization approximation that is identical to the conductor-like polarizable continuum model. Analytical gradients for the excited state energy with nonequilibrium solvent effects were then easily formulated. The nonequilibrium solvent effects were demonstrated in dynamics after photoabsorption and emission.

Although our method was demonstrated with an Onsager-type cavity, it is generally formulated for apparent surface charge methods. Implementation of a variational polarizable continuum model will allow for practical application of more realistic cavity shapes for nonequilibrium solvent effects in excited state Born-Oppenheimer molecular dynamics. We also intend to explore inclusion of the electronic (instantaneous) polarization of the solvent. The solvent effect on the forces described here does not include the direct effects of solvent viscosity as the nuclei move. Only the effects of solvent polarization on the Coulombic interactions in the solute are simulated. We intend to couple a Langevin type equation of motion to the nonequilibrium relaxation of the solvent to capture both concerted effects. Using the methods developed here, it will be possible to use simulated annealing techniques to optimize the molecular geometry in an excited electronic state with state-specific solvent effects. This method solves the issue of optimizing geometry with equilibrium state specific models due to the lack of analytical gradients found in our previous publication. We also intend to explore nonequilibrium solvent effects in nonadiabatic excited state molecular dynamics using the presented and further developments.

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- ¹B. Bagchi, D. W. Oxtoby, and G. R. Fleming, "Theory of the time development of the Stokes shift in polar media," *Chem. Phys.* **86**, 257–267 (1984).
- ²G. Van der Zwan and J. T. Hynes, "Nonequilibrium solvation dynamics in solution reactions," *J. Chem. Phys.* **78**, 4174–4185 (1983).
- ³G. Van der Zwan and J. T. Hynes, "Time-dependent fluorescence solvent shifts, dielectric friction, and nonequilibrium solvation in polar solvents," *J. Phys. Chem.* **89**, 4181–4188 (1985).
- ⁴R. F. Loring and S. Mukamel, "Molecular theory of solvation and dielectric response in polar fluids," *J. Chem. Phys.* **87**, 1272–1283 (1987).
- ⁵J. D. Simon, "Time-resolved studies of solvation in polar media," *Acc. Chem. Res.* **21**, 128–134 (1988).
- ⁶G. J. Moro, P. L. Nordio, and A. Polimeno, "Multivariate diffusion models of dielectric friction and TICT transitions," *Mol. Phys.* **68**, 1131–1141 (1989).
- ⁷C.-P. Hsu, X. Song, and R. A. Marcus, "Time-dependent Stokes shift and its calculation from solvent dielectric dispersion data," *J. Phys. Chem. B* **101**, 2546–2551 (1997).
- ⁸M. Caricato, F. Ingrosso, B. Mennucci, and J. Tomasi, "A time-dependent polarizable continuum model: Theory and application," *J. Chem. Phys.* **122**, 154501 (2005).
- ⁹M. Caricato, B. Mennucci, J. Tomasi, F. Ingrosso, R. Cammi, S. Corni, and G. Scalmani, "Formation and relaxation of excited states in solution: A new time dependent polarizable continuum model based on time dependent density functional theory," *J. Chem. Phys.* **124**, 124520 (2006).
- ¹⁰M. Caricato, "Exploring potential energy surfaces of electronic excited states in solution with the EOM-CCSD-PCM method," *J. Chem. Theory Comput.* **8**, 5081–5091 (2012).
- ¹¹B. Mennucci, G. Scalmani, and D. Jacquemin, "Excited-state vibrations of solvated molecules: Going beyond the linear-response polarizable continuum model," *J. Chem. Theory Comput.* **11**, 847–850 (2015).
- ¹²J. A. Bjorgaard, T. Nelson, K. Kalinin, V. Kuzmenko, K. A. Velizhanin, and S. Tretiak, "Simulations of fluorescence solvatochromism in substituted PPV oligomers from excited state molecular dynamics with implicit solvent," *Chem. Phys. Lett.* **631**, 66–69 (2015).
- ¹³J. A. Bjorgaard, V. Kuzmenko, K. A. Velizhanin, and S. Tretiak, "Solvent effects in time-dependent self-consistent field methods. I. Optical response calculations," *J. Chem. Phys.* **142**, 044103 (2015).
- ¹⁴J. A. Bjorgaard, K. A. Velizhanin, and S. Tretiak, "Solvent effects in time-dependent self-consistent field methods. II. Variational formulations and analytical gradients," *J. Chem. Phys.* **143**, 054305 (2015).
- ¹⁵F. Ding, D. B. Lingerfelt, B. Mennucci, and X. Li, "Time-dependent nonequilibrium dielectric response in QM/continuum approaches," *J. Chem. Phys.* **142**, 034120 (2015).
- ¹⁶J. P. Perdew and K. Schmidt, "Jacob's ladder of density functional approximations for the exchange-correlation energy," *AIP Conf. Proc.* **577**, 1–20 (2001).
- ¹⁷M. E. Casida, in *Recent Advances in Density-Functional Methods*, edited by D. A. Chong (World Scientific, Singapore, 1995), Vol. 3, Part I.
- ¹⁸S. Tretiak, A. Saxena, R. L. Martin, and A. R. Bishop, "CEO/semiempirical calculations of UV-visible spectra in conjugated molecules," *Chem. Phys. Lett.* **331**, 561–568 (2000).
- ¹⁹A. M. Moran, A. M. Kelley, and S. Tretiak, "Excited state molecular dynamics simulations of nonlinear push-pull chromophores," *Chem. Phys. Lett.* **367**, 293–307 (2003).
- ²⁰E. V. Tsiper, V. Chernyak, S. Tretiak, and S. Mukamel, "Density-matrix-spectroscopic algorithm for excited-state adiabatic surfaces and molecular dynamics of a protonated Schiff base," *J. Chem. Phys.* **110**, 8328–8337 (1999).
- ²¹F. Furche and R. Ahlrichs, "Adiabatic time-dependent density functional methods for excited state properties," *J. Chem. Phys.* **117**, 7433–7447 (2002).
- ²²V. Luzhkov and A. Warshel, "Microscopic calculations of solvent effects on absorption spectra of conjugated molecules," *J. Am. Chem. Soc.* **113**, 4491–4499 (1991).
- ²³B. Mennucci, "Polarizable continuum model," *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2**, 386–404 (2012).
- ²⁴B. Bagchi, "Dynamics of solvation and charge transfer reactions in dipolar liquids," *Annu. Rev. Phys. Chem.* **40**, 115–141 (1989).
- ²⁵D. F. Calef and P. G. Wolynes, "Classical solvent dynamics and electron transfer. I. Continuum theory," *J. Phys. Chem.* **87**, 3387–3400 (1983).
- ²⁶R. A. Marcus, "Electrostatic free energy and other properties of states having nonequilibrium polarization. I," *J. Chem. Phys.* **24**, 979–989 (1956).
- ²⁷R. Cammi and J. Tomasi, "Nonequilibrium solvation theory for the polarizable continuum model: A new formulation at the SCF level with application to the case of the frequency-dependent linear electric response function," *Int. J. Quantum Chem.* **56**, 465–474 (1995).
- ²⁸O. Christiansen and K. V. Mikkelsen, "Coupled cluster response theory for solvated molecules in equilibrium and nonequilibrium solvation," *J. Chem. Phys.* **110**, 8348–8360 (1999).
- ²⁹R. Improta, V. Barone, G. Scalmani, and M. J. Frisch, "A state-specific polarizable continuum model time dependent density functional theory method for excited state calculations in solution," *J. Chem. Phys.* **125**, 054103 (2006).
- ³⁰E. M. Kosower and D. Huppert, "Excited state electron and proton transfers," *Annu. Rev. Phys. Chem.* **37**, 127–156 (1986).
- ³¹F. Ingrosso, B. Mennucci, and J. Tomasi, "Quantum mechanical calculations coupled with a dynamical continuum model for the description of dielectric relaxation: Time dependent Stokes shift of coumarin C153 in polar solvents," *J. Mol. Liq.* **108**, 21–46 (2003).
- ³²L. E. Fried and S. Mukamel, "Solvation structure and the timeresolved Stokes shift in non-Debye solvents," *J. Chem. Phys.* **93**, 932–946 (1990).
- ³³M. Maroncelli, J. MacInnis, and G. R. Fleming, "Polar solvent dynamics and electron-transfer reactions," *Science* **243**, 1674–1681 (1989).
- ³⁴J. Tomasi, B. Mennucci, and R. Cammi, "Quantum mechanical continuum solvation models," *Chem. Rev.* **105**, 2999–3094 (2005).
- ³⁵B. K. P. Scaife, *Principles of Dielectrics* (Oxford University Press, New York, 1989).
- ³⁶C. J. F. Bottcher, *Theory of Electric Polarization* (Elsevier, Amsterdam, 1973).
- ³⁷S. Corni, S. Pipolo, and R. Cammi, "Equation of motion for the solvent polarization apparent charges in the polarizable continuum model: Application to real-time TDDFT," *J. Phys. Chem. A* **119**, 5405–5416 (2015).
- ³⁸A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory* (McGraw-Hill, New York, 1989).
- ³⁹R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).
- ⁴⁰A. D. Becke, "Density-functional thermochemistry. IV. A new dynamical correlation functional and implications for exactexchange mixing," *J. Chem. Phys.* **104**, 1040 (1996).
- ⁴¹V. Barone and M. Cossi, "Quantum calculation of molecular energies and energy gradients in solution by a conductor solvent model," *J. Phys. Chem. A* **102**, 1995–2001 (1998).
- ⁴²A. Klamt and G. Schramm, "COSMO: A new approach to dielectric screening in solvents with explicit expressions for the screening energy and its gradient," *Perkin Trans.* **2**, 799–805 (1993).
- ⁴³S. Tretiak and V. Chernyak, "Resonant nonlinear polarizabilities in the time-dependent density functional (TDDFT) theory," *J. Chem. Phys.* **119**, 8809–8823 (2003).
- ⁴⁴S. Mukamel, A. Takahashi, H. X. Wang, and G. H. Chen, "Electronic coherence and nonlinear susceptibilities of conjugated polyenes," *Science* **266**, 250–254 (1994).
- ⁴⁵S. Tretiak, V. Chernyak, and S. Mukamel, "Localized electronic excitations in phenylacetylene dendrimers," *J. Phys. Chem. B* **102**, 3310–3315 (1998).
- ⁴⁶S. Tretiak and S. Mukamel, "Density matrix analysis and simulation of electronic excitations in conjugated and aggregated molecules," *Chem. Rev.* **102**, 3171–3212 (2002).
- ⁴⁷S. Tretiak, A. Saxena, R. L. Martin, and A. R. Bishop, "Conformational dynamics of photoexcited conjugated molecules," *Phys. Rev. Lett.* **89**, 097402 (2002).
- ⁴⁸T. Nelson, S. Fernandez-Alberti, A. E. Roitberg, and S. Tretiak, "Nonadiabatic excited-state molecular dynamics: Modeling photophysics in organic conjugated materials," *Acc. Chem. Res.* **47**, 1155–1164 (2014).
- ⁴⁹M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. J. P. Stewart, "AM1: A new general purpose quantum mechanical molecular model," *J. Am. Chem. Soc.* **107**, 3902–3909 (1985).
- ⁵⁰F. Lipparini, G. Scalmani, B. Mennucci, E. Cancs, M. Caricato, and M. J. Frisch, "A variational formulation of the polarizable continuum model," *J. Chem. Phys.* **133**, 014106 (2010).