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A harmonic approximation of intramolecular vibrations in a mixed quantum–classical methodology: Linear absorbance of a dissolved Pheophorbid-*a* molecule as an example

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ABSTRACT

Linear absorption spectra of a single Pheophorbid-*a* molecule (Pheo) dissolved in ethanol are calculated in a mixed quantum–classical approach. In this computational scheme the absorbance is mainly determined by the time-dependent fluctuations of the energy gap between the Pheo ground and excited electronic state. The actual magnitude of the energy gap is caused by the electrostatic solvent solute coupling as well as by contributions due to intra Pheo vibrations. For the latter a new approach is proposed which is based on precalculated potential energy surfaces (PES) described in a harmonic approximation. To get the respective nuclear equilibrium configurations and Hessian matrices of the two involved electronic states we carried out the necessary electronic structure calculations in a DFT-framework. Since the Pheo changes its spatial orientation in the course of a MD run, the nuclear equilibrium configurations change their spatial position, too. Introducing a particular averaging procedure, these configurations are determined from the actual MD trajectories. The usability of the approach is underlined by a perfect reproduction of experimental data. This also demonstrates that our proposed method is suitable for the description of more complex systems in future investigations.

1. Introduction

It is of increasing interest to achieve a detailed understanding of photo absorption and excitation energy transfer (EET) dynamics in large chromophore complexes. Respective studies concentrated on helical polyisocyanides with regularly arranged porphyrin pendants [1]. Moreover, details of EET in covalently linked multiporphyrin arrays have been reported in [2]. EET in dendrimeric structures was investigated using either single molecule spectroscopy [3] or ensemble measurements [4]. Recent experiments uncover EET details in huge chromophore assemblies templated by the tobacco mosaic virus coat protein [5]. Of particular interest for the following are the different types of Pheo complexes studied in [6,7] with the focus here on those systems built up by butanediamine dendrimers to which Pheo molecules are covalently linked [6] (cf. Fig. 1).

Related simulations of EET and optical spectra require the treatment of systems with some hundreds of atoms excluding an exact quantum simulation but indicating the need to utilize mixed quantum–classical methodologies. Different variants have been described in literature (see Ref. [8]). For the systems we are interested in only the ground-state classical path approximation offers a reliable scheme since it can be based on precalculated electronic structure data. Up to now these precalculated data concern the permanent Pheo charge distributions of the electronic ground-state and the first excited state to account for intermolecular electrostatic couplings as well as the so-called transition charge densities which determine the strength of the excitonic coupling (cf. [8–12]).

The present letter starts to extend this work by an incorporation of intra-Pheo vibrational dynamics based on precalculated PES. Of course, such an inclusion can only be achieved approximately, here, by introducing a harmonic description of the PES. This requires the computation of the Hessian matrix and the nuclear equilibrium configuration (coordinate values at the minimum of the PES), both for the two involved electronic states. The necessary electronic structure calculations have been carried out in a DFT/TD–DFT scheme. The nuclear trajectories are determined by MD simulations. Their difference to the respective equilibrium values (of the chosen electronic state) determines the extent of intramolecular vibrational excitation. In the present case of a solvent solute system at room temperature conditions the

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solute nuclear equilibrium configurations (defining a rigid frame of the molecule) also change their spatial position and orientation. Thus, the computation of intramolecular energy fluctuations requires a determination of these *time-dependent* equilibrium configurations. The approach allows to separate translational, rotational and low frequency bending motion from the atomic intra-molecular vibrations, thus guaranteeing for the latter the validity of the harmonic approximation.

Such a harmonic description of the PES necessary here can be circumvented by calculating the vertical transition energies (energy gap function) on the fly, i.e. for every molecular conformation realized in the MD run. This would be possible if the molecular system is small enough or if semi-empirical electronic structure methods are applied (usually it is connected with a cumulant approximation ending up with a double time-integral of the energy gap correlation function; see [13] and for a recent application [14]). For the large chromophore complexes we are interested in such types of calculations done on the fly might be less precise than our DFT/TD–DFT schemes and also numerically too expensive. Although devoted to Pheo complexes with up to 32 single molecules, here the described concept is applied to the computation of the linear absorbance of a single Pheo dissolved in ethanol, thus avoiding effects of excitonic coupling typical for complexes [8–12]. Therefore, we can concentrate on the absorption line broadening due to intra-Pheo vibrations and the solvent solute coupling.

The methods to describe intra molecular vibrations and the solvent solute coupling are shortly introduced in the subsequent section together with some details on our DFT/TD–DFT computations. Section 3 reminds on the computation of linear absorption spectra in a mixed quantum–classical frame. Our MD simulations are characterized in Section 4 in some more detail. The obtained data for Pheo absorbance are also discussed there together with the way to get the time-dependent equilibrium configurations introduced above (some more involved details can be found in Appendix A). The paper ends with some concluding remarks in Section 5.

2. Pheo-model and DFT/TD–DFT calculations

The description of a single Pheo (see Fig. 1) can be restricted to the adiabatic electronic states φ_a referring to the ground-state (a = g) and the Q_y excited state (a = e). The related PES are written as

$$U_a(R,Z) = \hbar\omega_a + U_a^{(\mathrm{intra})}(R) + U_a^{(\mathrm{inter})}(R,Z). \tag{1}$$

The set of Pheo nuclear coordinates is abbreviated by $R = \{\mathbf{R}_u\}$, whereas $Z = \{\mathbf{Z}_\xi\}$ represents all solvent nuclear coordinates (u and ξ count the respective atoms). The PES part $U_a^{(\mathrm{inter})}(R,Z)$ describes the Pheo solvent interaction, and $U_a^{(\mathrm{intra})}(R)$ accounts for the intra-Pheo vibrations (the minimum of the particular Pheo PES has been separated and is denoted by $\hbar\omega_a$). The given decomposition of the full PES is not strict but used here, since the Pheo electronic states are only calculated by including the solvent in an averaged description (dielectric screening model, see below). The PES of the solvent molecules are not included since in the considered frequency region (14,500–15,500 cm^{-1}) ethanol only absorbs weakly by high OH overtones ($n \approx 4$–5) [15] and no solvent excitation takes place.

By reducing the solvent–solute coupling to its dominant electrostatic part and using atomic centered partial charges $q_u^{(a)}$ for the Pheo (in electronic state a) and q_ξ for the solvent molecules, we set [9]

$$U_a^{(\mathrm{inter})}(R,Z) = \sum_{u,\xi} \frac{q_u^{(a)} q_\xi}{|\mathbf{R}_u - \mathbf{Z}_\xi|}. \tag{2}$$

The intra-Pheo part of the PES, Eq. (1), is taken in a harmonic approximation

$$U_a^{(\mathrm{intra})}(R) = \frac{1}{2}\sum_{u,v} \kappa_{uv}^{(a)}\left(\mathbf{R}_u - \mathbf{R}_u^{(a)}\right)\left(\mathbf{R}_v - \mathbf{R}_v^{(a)}\right). \tag{3}$$

The $\kappa_{uv}^{(a)}$ define the Hessian matrix of the particular electronic state and $\mathbf{R}_u - \mathbf{R}_u^{(a)}$ are the deviations of the actual nuclear coordinates $\mathbf{R}_u$ from the equilibrium value $\mathbf{R}_u^{(a)}$ (referring to the electronic state a).

The intramolecular part of the Stokes-shift taken in harmonic approximation follows as

$$S_{\mathrm{intra}} = \frac{1}{2}\sum_{u,u'} \left(\kappa_{uv}^{(e)} + \kappa_{uv}^{(g)}\right)\Delta\mathbf{R}_u^{(eg)}\Delta\mathbf{R}_v^{(eg)}, \tag{4}$$

where we introduced the relative displacement upon electronic excitation of Pheo atom u as

$$\Delta\mathbf{R}_u^{(eg)} = \mathbf{R}_u^{(e)} - \mathbf{R}_u^{(g)}. \tag{5}$$

To get the elements of the two types of Hessian matrices (for the Pheo ground and first excited state) and the respective nuclear equilibrium configurations, electronic structure computations have to be utilized. The ground state Pheo structure, Hessian matrix and atomic charges were determined using density functional theory (DFT). The corresponding excited state properties were obtained by employing linear response time-dependent DFT (TD–DFT) as implemented in the Gaussian09 program [16]. Throughout, the hybrid B3LYP functional for exchange and correlation [17–19] was used together with the 6-311(d,p) AO basis sets [20]. This method was proven to give accurate results for organic molecules concerning the heat of formation and isomerization energies [21]. Stationary points were fully optimized and characterized by vibrational frequency calculations to ensure that they represent minima of the potential energy surface. The solvent effect was taken into account for ground and excited state employing the polarizable continuum model (PCM, [22] and References within, [23,24]) with the appropriate choice of dielectric constant for ethanol. The electrostatic potential based atom-centered point charges for the construction of potential parameters of the MD simulation were obtained by the CHelpG [25] method. They reproduce well the experimentally measured molecular dipole moment and were previously validated to be suitable for force-field generation [26,27].

The reliability of the harmonic approximation can be judged in comparing respective reorganization energies (Stokes shifts). The intramolecular part of the Stokes shift following from our electronic structure calculations amounts 90 meV. The respective value obtained in the harmonic approximation, Eq. (4), is 121 meV. This difference may underline a certain importance of unharmonic contributions but is small enough to consider the harmonic approximation as an acceptable approach.

3. The absorption cross section

Within a mixed-quantum classical description the nuclear coordinates R and Z become time-dependent quantities determined by classical mechanics. It is essential to underline that in the present consideration of Pheo dissolved in ethanol at room temperature conditions the nuclear equilibrium configurations $R^{(a)} = \{\mathbf{R}_u^{(a)}\}$ become time dependent, too. This is due to the translational and rotational motion of the Pheo in the solvent and poses the problem not only to determine $R(t)$ and $Z(t)$ but also the time-dependent $R^{(a)}(t)$. Before explaining in detail how to obtain the $R^{(a)}(t)$ we shortly remind on the computation of the linear absorption used in the present case to check the reliability of our approach by comparing with existing experimental data.

In a mixed-quantum classical methodology the frequency resolved absorption cross section can be computed from (see, e.g., [8]):