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The Second-Order Polarization Propagator Approximation (SOPPA) method coupled to the polarizable continuum model

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ABSTRACT

We present an implementation of the Polarizable Continuum Model (PCM) in combination with the Second-Order Polarization Propagator Approximation (SOPPA) electronic structure method. In analogy with the most common way of designing ground state calculations based on a Second-Order Møller–Plesset (MP2) wave function coupled to PCM, we introduce dynamical PCM solvent effects only in the Random Phase Approximation (RPA) part of the SOPPA response equations while the static solvent contribution is kept in both the RPA terms as well as in the higher order correlation matrix components of the SOPPA response equations. By dynamic terms, we refer to contributions that describe a change in environmental polarization which, in turn, reflects a change in the core molecular charge distribution upon an electronic excitation. This new combination of methods is termed PCM–SOPPA/RPA. We apply this newly defined method to the challenging cases of solvent effects on the lowest and intense electronic transitions in *o*-, *m*- and *p*-nitroaniline and *o*-, *m*- and *p*-nitrophenol and compare the performance of PCM–SOPPA/RPA with more conventional approaches. Compared to calculations based on time-dependent density functional theory employing a range-separated exchange–correlation functional, we find the PCM–SOPPA/RPA approach to be slightly superior with respect to systematicity. On the other hand, the absolute values of the predicted excitation energies are largely underestimated. This – however – is a well-known feature of the SOPPA model itself and is not connected to its combination with the PCM.

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1. Introduction

Development of models for calculations of medium effects on confined molecules is a long-standing challenge in computational quantum chemistry. It is well-known that a medium, e.g., a solvent, can have a strong influence on the electronic structure of a molecule, e.g., a solute, and as a consequence the environment may significantly perturb both structure, reactivity, and molecular properties of the confined molecule, thereby leading to large changes in, e.g., its spectroscopic properties. Since various spectroscopic properties can be considered as fingerprints of a molecule, it is of great importance to be able to both predict and rationalize the effects a medium exerts on a specific molecule. The difficulties one encounters when introducing an environment in quantum

chemical calculations are manifold. First of all, the size of the system increases significantly, for instance in the case of a solute surrounded by a solvent. In case of the solvent being water, the most common solvent of them all, its fairly large dipole moment as well as its relatively high polarizability imply that in order to consider converged electrostatic solute–solvent interactions, a water shell radius of approximately 12 Å is needed [1]. This amounts to around 240 water molecules, thus increasing the size of the system – as compared to the isolated solute molecule – by around 720 atoms. Thus, even though the interest is usually not on the details of the electronic structure of the solvent, almost all the computational time will inevitably be spent on evaluating these. Secondly, a solvent is by nature dynamical in the sense that conformational sampling gains importance even if the solute molecule itself is fairly rigid. As compared to the case of the isolated solute molecule, there will be a need for repeating these expensive quantum chemical calculations a sufficient number of times in order to sample different solvent configurations and obtain averaged results for,

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e.g., spectroscopic parameters. From this example, it is clear that effective ways of introducing the effect of the solvent into quantum chemical calculations, thereby avoiding explicit consideration of the electronic structure of the solvent molecules, are highly needed. Indeed, brute-force methods will quickly become both too expensive and practically unnecessary.

A popular approach for circumventing some of the problems described above is to rely on hybrid methods, i.e., methods in which the confined molecule is treated by means of quantum mechanics and the environment is given a classical description using molecular mechanics [2–4]. In recent years, we have developed such an approach and applied it in the prediction and rationalization of various spectroscopic parameters. This method is termed Polarizable Embedding (PE) [5,6]. In contrast to most other hybrid methods, the PE method accounts explicitly for the environment polarization that reflects the electronic degrees of freedom which are important when considering, e.g., the prediction of electronic excitation energies. This is so, as a change in the solute electronic structure upon electronic excitation may potentially lead to large changes in the environment polarization. However, in the class of hybrid methods where the solvent is treated explicitly, sufficient samplings over solute–solvent configurations are still needed, meaning that molecular simulations need to be invoked [7]. Thus, even though the cost of performing these quantum chemical calculations has been reduced significantly, as compared to a full quantum chemical calculation on the entire system, many of these quantum chemical calculations still need to be performed and indeed it would be desirable to reduce this number to one, i.e., mimicking what is needed in the case of the isolated molecule. A route to achieve this goal is to consider the environment implicitly, i.e., by describing this as a dielectric continuum [8]. By defining the solvent implicitly, both the explicit cost of performing a solute–solvent calculation as well as the number of such calculations become significantly reduced. For example, the Generalized Born solvation model has been successfully implemented into molecular dynamics (and Monte Carlo) codes resulting in tremendous savings in computational time [9].

In this paper, we present a new combination of methods with the aim of performing calculations of spectroscopic parameters, here mainly in the context of solute molecules subjected to a solvent. The solvent model explored here is the Polarizable Dielectric Continuum Model (PCM) [8] and in the following sections we will investigate the coupling of this model to the Second-Order Polarization Propagator Approximation (SOPPA) [10–14]. The aim is to develop a fairly simple, yet reasonably accurate way of introducing solvent effects into an electronic correlated description of the solute. As discussed below, SOPPA parallels the well-known second-order Møller–Plesset (MP2) method, but whereas MP2 is designed for molecular electronic ground states, SOPPA is designed for calculations of excited states and general response properties.

2. Theory

In the present section, we give a brief description of the basics of the PCM. Next, we summarize SOPPA and end by describing how these two approaches can be combined in an effective way.

2.1. PCM

The Polarizable Continuum Model [8] (PCM) represents one of the most powerful and effective approaches developed for introducing medium effects in an electronic structure calculation. Here, we will only be interested in describing effects from simple solvents although the PCM model may also be applied to more complex environments. In addition, we will only consider environmental

effects of electrostatic nature. In the PCM, the solvent is represented as a homogeneous dielectric continuum that becomes polarized by the solute, which is placed within a molecular shaped cavity embedded by said dielectric continuum. The cavity is defined by assigning spheres to each atom (or a group of atoms) forming the solute and considering the final envelope of these interlocking spheres. The radii used to define these spheres enter into the model as empirical parameters. Once the cavity has been defined, the procedure is to solve the Poisson equation, i.e., to derive the (electric) potential which characterizes the electrostatics. The formalism used to solve the Poisson equation is here the Integral Equation Formalism [15] (IEF) version of PCM. In this model, the potential has two contributions: one from a potential produced by the solute charge distribution and another from a potential that is due to an apparent surface charge (ASC) distribution, which arises due to polarization of the dielectric medium by the quantum mechanically treated system. The latter charge distribution gives rise to what is termed the reaction-field, i.e., the potential used to perturb the electronic structure of the solute. In order to solve for the ASC distribution, a partitioning of the cavity surface into N finite elements, known as tesserae, is invoked. Each tessera contains a point charge (q_k), and the potential due to the polarization of the dielectric medium is then discretized according to

$$\phi(r) = \sum_{k=1}^N \frac{q_k}{|r - r_k|} \quad (1)$$

where r_k is the position of tessera k and q_k the corresponding charge. These charges – used to define the ASC distribution – may be obtained as the solution to the linear set of equations

$$\mathbf{B}\mathbf{q} = -\mathbf{V} \quad (2)$$

where \mathbf{V} is a vector of dimension N , which collects the solute electric potential at each tessera, \mathbf{q} is similarly a vector of dimension N holding the induced charges, and the matrix \mathbf{B}^{-1} is referred to as the solvent response matrix, i.e., it may be considered as a matrix representation of a classical response function that connects the perturbation (the solute electric potential) with the response (the induced charges). Once the ASC distribution has been obtained, the resulting point charges may be included into the solute Hamiltonian, in return giving rise to an effective solute Hamiltonian

$$\hat{H}_{\text{eff}}|\Psi_0\rangle = (\hat{H}_0 + \hat{\phi})|\Psi_0\rangle \quad (3)$$

where $|\Psi_0\rangle$ represents the ground state wave function, \hat{H}_0 is the Hamiltonian for the isolated (solute) molecule, and $\hat{\phi}$ represents an operator corresponding to the electrostatic potential. We note that since the induced charges depend on the solute charge distribution, so does the potential created by these charges and, in effect, the perturbation. Thus, we are left with a density-dependent perturbation, implying that the electronic structure and solvent polarization problems need to be determined using a double self-consistent-field approach.

Considering now calculations of excited states, two different approaches can generally be followed: the state specific or response based methods [8]. Here, we will exclusively be concerned with the linear response formulation. As shown in Refs. [16,17], contributions to the linear response function due to the polarizable continuum may be classified as either static or dynamic. The static contributions describe the excitation process within the solute in a frozen environment and are included in the response functions through the use of orbital energies and coefficients that contain the effect of the medium. Relaxation – or differential polarization between the ground and excited states – is introduced through explicit terms in the linear response functions, see e.g. Refs. [16,17] for a detailed derivation. These explicit contributions

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