Excited state gradients within a polarizable QM/MM formulation

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Abstract—Multiscale approaches that partition the system into an active site (where the electronic process under study occurs) and a remaining region, the environment, have proven to be good strategies for the computation of electronic excitations in complex systems. In this work the implementation of a polarizable QM/MM scheme for the computation of excited state gradients is presented and are applied to a test case.

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1 INTRODUCTION

In standard QM/MM models, the environment is described in terms of fixed charges (or multipoles), that remain unchanged during the calculation. In our polarizable QM/MM approach (QM/MMPol), on the other hand, polarizablities on the MM sites are included additionally (see Fig. 1). Therefore the environment is allowed to respond to the electron density of the QM subsystem or its changes upon excitation by polarizing. The polarization of the environment is represented in terms of classical dipoles, induced by the QM electric field F_p. The dipoles are obtained by

$$\mathbf{F}_p = (\mathbf{D}\boldsymbol{\mu})_p$$

where $\mathbf{D}$ is the MMPol matrix, that only depends on the geometrical parameters of the MM sites and the atomic polarizabilities.

The effective interaction energy between QM and MM region of the system is given by:

$$\begin{aligned} E^{es} &= U_q^{es} + U_n^{es} + U_e^{es} \\ E^{pol} &= \frac{1}{2}\left[U_{en}^{pol} + U_{ne}^{pol} + U_{ee}^{pol} + U_{nn}^{pol}\right] \end{aligned}$$

Hereby is U_i^{es} the electrostatic interaction energy between MM charges and the potential by the other MM charges ($i = q$), the nuclei ($i = n$) and the electron density ($i = e$). E^{pol} denotes the interaction energy between the induced dipoles and the electric fields generated by charges, nuclei, electrons and the other dipoles.

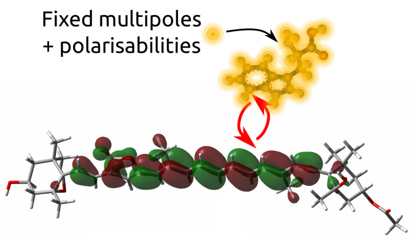

Fig. 1. Schematic representation of the polarizable QM/MM approach.

2 POLARIZABLE TDDFT/MM GRADIENTS

The energy derivative of a system represented by its wavefunction Ψ and its corresponding Hamiltonian $\mathbf{H}$ with respect to a generic parameter λ can in general be written as:

$$E^\lambda = \left\langle \Psi \left| \frac{\partial \mathbf{H}}{\partial \lambda} \right| \Psi \right\rangle + 2\left\langle \frac{\partial \Psi}{\partial \lambda} \left| \mathbf{H} \right| \Psi \right\rangle \tag{1}$$

The first term is the so-called Hellmann Feynman force, while the second term is the Pulay force. In the case of a purely variational energy functional the Pulay force vanishes. This is also desirable in the case for non variational energy functionals, as the computation of the molecular orbital response with respect to the perturbation is very costly. A better ansatz is to introduce a so-called relaxed density to account for the wavefunction response. This avoids the computation of the perturbed basis.

In our approach for the analytic gradients of the polarizable TDDFT/MM approach, we use an ansatz that was already applied by Furche and Ahlrichs [1] to pure TDDFT and later expanded by Scalmani et al. [2] on TDDFT gradients in combination with the polarizable continuum model [3] (PCM). The starting point for this approach is a fully variational Lagrangian $\mathbf{L}$, defined as following:

$$\begin{aligned} \mathbf{L}[\mathbf{X},\mathbf{Y},\Omega,\mathbf{C},\mathbf{Z},\mathbf{W}] &= G[\mathbf{X},\mathbf{Y},\Omega] + \sum_{ia} \mathbf{Z}_{ia}\mathbf{F}_{ia} \\ &\quad - \sum_{pq,p\leq q} \mathbf{W}_{pq}(\mathbf{S}_{pq} - \delta_{pq}) \end{aligned}$$

The derivation of analytic gradients from $\mathbf{L}$ is straightforward and the resulting Z-Vector method is computational advantageous with respect to others.

The equation for the analytic derivatives can be written in a compact form, by expressing it in the AO basis:

$$\begin{aligned} \Omega^\xi &= \sum_{\mu\nu} h_{\mu\nu}^\xi P_{\mu\nu}^\Delta + \sum_{\mu\nu} S_{\mu\nu}^\xi W_{\mu\nu} + \sum_{\mu\nu\kappa\lambda} \langle \mu\nu|\kappa\lambda\rangle^\xi \Gamma_{\mu\nu\kappa\lambda} \\ &\quad + \omega^{xc,\xi} + \omega^{MMPol,\xi} \end{aligned}$$

The exponent ξ denotes derivatives with respect to a general variable. P^Δ and Γ are the one- and two-particle density matrices. $\omega^{xc,\xi}$ is the derivative of the DFT exchangecorrelation energy and $\omega^{MMPol,\xi}$ of the QM-MMPol interaction energy. The exact expressions and a detailed discussion can be found in the articles of Furche [1] and Scalmani [2] for the case of pure DFT and DFT/PCM.

3 IMPLEMENTATION AND APPLICATION

3.1 Implementation

The analytic gradients are implemented in a local modified version of Gaussian 09 [4]. Analytical Forces for QM and MM sites in excited state calculations at (TDA)-TDDFT/TDHF level of theory for a polarizable embedding are available within the ONIOM scheme. The implementation is an extension of the work of Caprasecca et al. [5], who implemented the corresponding ground state QM/MMPol gradients.

3.2 Application

We applied the model to study the intercalation of the doubly protonated fluorescent stain 4',6-diamidino-2-phenylindole (DAPI, shown in Fig. 2) within two pairs of CG DNA bases. DAPI is a commonly used fluorescent marker that can interact with DNA both by minor groove binding and intercalation. In this test study we will only focus on the latter. The initial structure of the system was taken from the article of Biancardi et al. [6] and the conformer 1 of the intercalated structures was used. Both ground state (GS) and excited state (ES) geometry optimizations were performed and the QM method of choice was DFT/TDA-TDDFT. To assess the effect of polarization on the optimized structures, three different models were introduced: (i) a full-QM model, where both DAPI and DNA are treated at QM level (f-QM); (ii) a non polarizable QM/MM model, where the DAPI is treated at QM level and the DNA is treated at MM level; (iii) a polarizable QM/MM model (QM/MMPol), where the DNA is now represented as a polarizable environment. Computations of the isolated DAPI molecule were performed (g-QM), additionally. In all calculations the DFT functional m06-2X and the 6-31G(d) basis set was used for the DAPI molecule, while 6-31G was used on the DNA in the f-QM calculations. The excited state of interest is the lowest state localized on the DAPI molecule, characterized by a HOMO-LUMO transition in the g-QM model. This state corresponds to the first excited state in the QM/MM and QM/MMPol approaches and the third for f-QM, as two charge transfer state appear at lower energy.

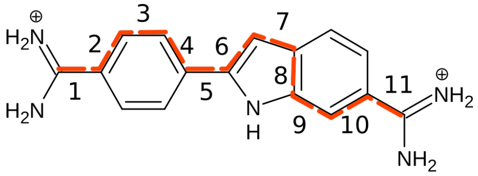

Fig. 2. Structure of the doubly protonated 4',6-diamidino-2-phenylindole (DAPI).

To assess the structural changes induced by the environment on ground and excited state geometries, as well as the structural rearrangement upon excitation, eleven internal bonds (marked in red in Fig. 2) were chosen. From these it is possible to define the bond length alternation (BLA), which is often used as a measure of conjugation. The bond difference between GS and ES calculations are shown in Fig. 3. It is evident from the alternating pattern of the first 8 bond length that, upon excitation, the single (double) bonds tend to become shorter (longer), with an increase in conjugation as consequence. The comparison between different models for the inclusion of the environment do not show significant differences. In several cases, however, the optimization carried out with the newly implemented QM/MMPol model is closer to the more expensive f-QM optimizations than the other models. This seems to point out that the inclusion of the polarisation is particularly useful in describing accurately the environment response to electron density redistribution.

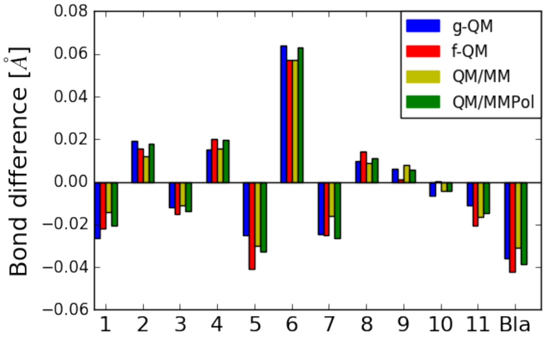

Fig. 3. Difference in bond length of eleven internal bonds and the corresponding BLA in the DAPI molecule (marked in Fig. 2) between ES and GS optimized structures at different levels of theory.

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