Molecular Properties through Polarizable Embedding

Jógvan Magnus Haugaard Olsen[1], Arnfinn Hykkerud Steindal[2], Kestutis Aidas[3] and Jacob Kongsted[1]

[1]Department of Physics and Chemistry, University of Southern Denmark, Campusvej 55, DK-5230 Odense M, Denmark
[2]Centre of Theoretical and Computational Chemistry, Department of Chemistry, University of Tromsø, N-9037 Tromsø, Norway
[3]Department of Theoretical Chemistry, School of Biotechnology, Royal Institute of Technology, SE-10691 Stockholm, Sweden

Introduction

We present a multilevel model which we denote the polarizable embedding (PE) method(1) and is implemented in the DALTON program(2).

- Layered model designed for effective inclusion of an anisotropic environment in a QM calculation
- Atomistic representation including terms up to localized octupoles and anisotropic dipole polarizabilities
- Fully self-consistent nonequilibrium formulation of the environmental response
- Combined with TDQM linear and nonlinear response
- Parallelized for large scale calculations

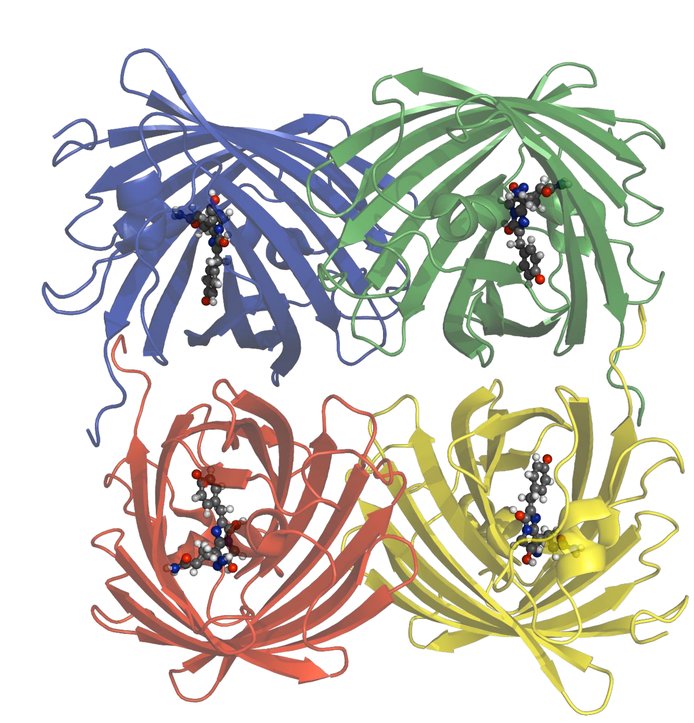

Figure 1: The DsRed protein tetramer: the chromophore subsystem is treated using QM while the protein environment is represented by a classical potential

Theory

The PE method accurately models the effects from the environment surrounding a central core subsystem by including the effects directly in the density/wavefunction of the core. Here we outline the PE-DFT method:

- Effective Kohn-Sham operator

$$\hat{f}_{\text{eff}} = \hat{f}_{\text{KS}} + \hat{v}_{\text{PE}}$$

- Polarizable Embedding operator

$$\hat{v}_{\text{PE}} = \hat{v}^{\text{es}}_{\text{PE}} + \hat{v}^{\text{ind}}_{\text{PE}}$$

- Electrostatic contribution

$$\hat{v}^{\text{es}}_{\text{PE}} = \sum_s \sum_k \frac{(-1)^{(k+1)}}{k!} \mathbf{Q}_s^{(k)} \sum_{pq} \mathbf{T}^{(k)}_{s,pq} \hat{E}_{pq}$$

  - $\mathbf{Q}_s^{(k)}$ are kth order multipole moments

$$\mathbf{Q}_s^{(0)} = q_s, \mathbf{Q}_s^{(1)} = \boldsymbol{\mu}_s, \mathbf{Q}_s^{(2)} = \boldsymbol{\Theta}_s, \cdots$$

  - $\mathbf{T}^{(k)}_{s,pq}$ are integrals over the interaction tensors

$$\mathbf{T}_s^{(k)} = \left(\frac{\partial}{\partial r_x}\right)^{k_x} \left(\frac{\partial}{\partial r_y}\right)^{k_y} \left(\frac{\partial}{\partial r_z}\right)^{k_z} \frac{1}{|\mathbf{r} - \mathbf{r}_s|}$$

- Polarization/induction contribution

$$\hat{v}^{\text{ind}}_{\text{PE}} = -\sum_s \boldsymbol{\mu}_s^{\text{ind}} \sum_{pq} \mathbf{T}^{(1)}_{s,pq} \hat{E}_{pq}$$

  - induced dipoles obtained as classical linear response

$$\boldsymbol{\mu}_s^{\text{ind}} = \boldsymbol{\alpha}_s \left(\mathbf{F}_{\text{el}}(\mathbf{r}_s) + \mathbf{F}_{\text{nuc}}(\mathbf{r}_s) + \mathbf{F}_{\text{mul}}(\mathbf{r}_s) + \mathbf{F}_{\text{ind}}(\mathbf{r}_s)\right)$$

Theory (continued)

The PE method is combined with linear, quadratic and cubic response in a fully self-consistent formalism. Here we show the linear response PE-TDDFT formalism:

- Linear response function

$$\langle\langle \hat{A}; \hat{B} \rangle\rangle_\omega = -\mathbf{A}^\dagger \left(\mathbf{E} - \omega \mathbf{S}\right)^{-1} \mathbf{B}$$

- Polarizable Embedding contribution

$$\mathbf{E}_{\text{PE}} \boldsymbol{\kappa}^\omega = -\langle 0 | [\hat{\mathbf{q}}, \hat{Q}_1^\omega + \hat{Q}_2^\omega | 0 \rangle$$

  - response from static environment

$$\hat{Q}_1^\omega = [\hat{\kappa}^\omega, \hat{v}^0_{\text{PE}}] = \hat{v}^0_{\text{PE}}(\kappa^\omega)$$

  - dynamical response from the environment

$$\hat{Q}_2^\omega = \hat{v}^\omega_{\text{PE}} = \sum_s \boldsymbol{\mu}_s^{\text{ind}}(\tilde{\mathbf{F}}^\omega) \hat{\mathbf{T}}_s^{(1)}$$

  - transformed electric field

$$\tilde{\mathbf{F}}^\omega = \langle 0 | [\hat{\kappa}^\omega, \hat{\mathbf{T}}_s^{(1)}] | 0 \rangle = \langle 0 | \hat{\mathbf{T}}_s^{(1)}(\kappa^\omega) | 0 \rangle$$

The contributions to the quadratic and cubic response are obtained in a similar manner.

Typical Workflow

- Obtain structures
  - MD snapshots
  - crystal structure
  - geometry optimization
- Fragment environment (see Fig. 5)
  - amino acid residues
  - nucleotide fragments
  - solvent molecules
- Calculate localized properties of fragments
  - multipole moments upto octopoles
  - anisotropic dipole polarizabilities
- Merge fragments to create the polarizable embedding potential
- Calculate property of interest using PE-DFT
  - excitation energies with OPA, TPA and 3PA
  - (hyper)polarizabilities: α, β and γ
  - excited state dipole moment and polarizability
  - magnetic properties using GIAOs/LAOs
  - ...

Acetone in Water Solution

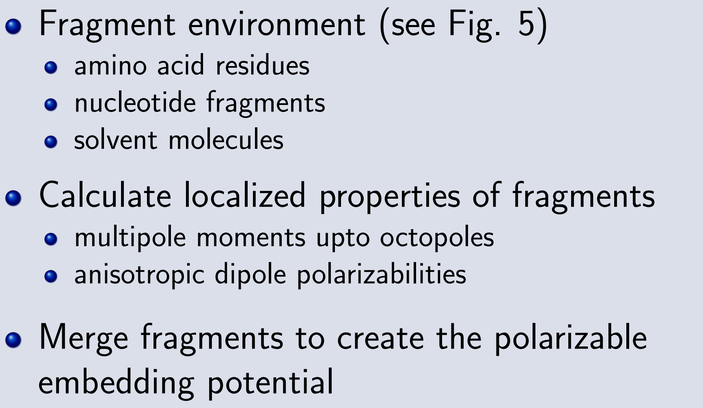

Figure 2: Solvent shift of the $n \longrightarrow \pi^*$ excitation in acetone compared to experiment

Computational details:

- Classical MD run using polarizable force field
  - extracted 120 snapshot (every 10th ps)
- Calculated average $n \longrightarrow \pi^*$ excitation energy
  - LoProp(3) force fields
  - CAM-B3LYP/aug-cc-pVDZ

Potential Analysis

Here we present an analysis of the quality of the classical potentials of the H_2O and CCl_4 molecules. The plots show the RMSD, with respect to the distance from the molecular van-der-Waals surface, of the electrostatic potential due the classical potentials compared to a QM reference. K_{vdw} is a factor of the vdw distance. Mx designates a potential with multipole moments upto xth order and M* includes only RESP fitted charges.

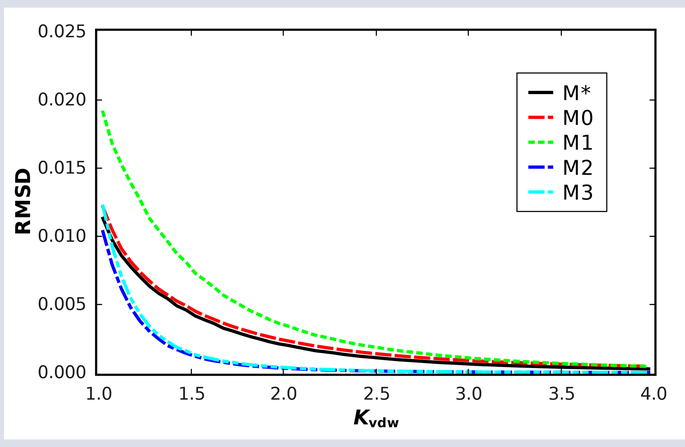

Figure 3: Water

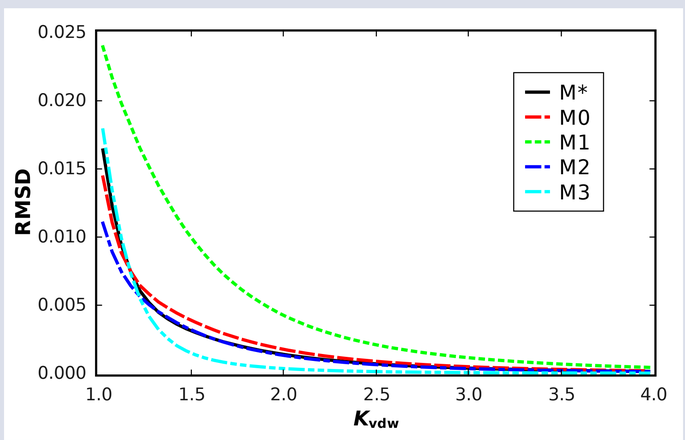

Figure 4: Tetrachloromethane

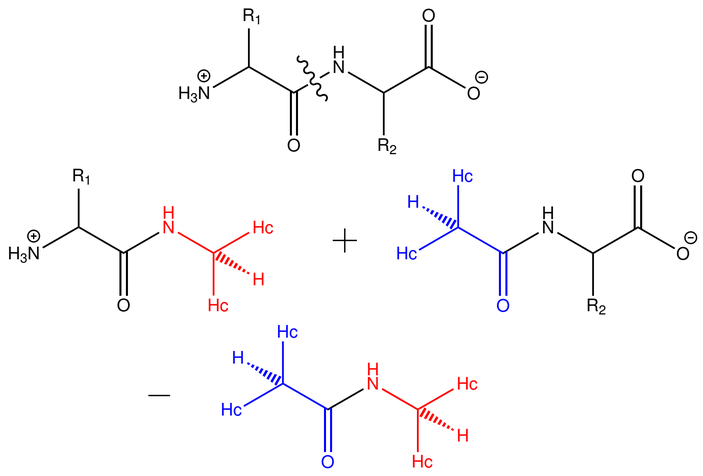

Figure 5: Outline of a fragmentation procedure for proteins

Acknowledgements

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References

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