

Combining Quantum Chemistry and Molecular Simulations

Hybrid
QM-MM
approach

Boundaries
Through
Space

Boundaries
Through
Bonds

Ab-initio and
Car-Parrinello
molecular
dynamics

Course
Summary

- Hybrid QM-MM approach. Approaches for:
 - ① Boundaries through space
 - ② Boundaries through bonds
- Ab-initio and Car-Parrinello molecular dynamics

Outline

- 1 Hybrid QM-MM approach
- 2 Boundaries Through Space
- 3 Boundaries Through Bonds
- 4 Ab-initio and Car-Parrinello molecular dynamics
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- MM methods fast but cannot describe chemical reactions.
 - QM methods can handle reactions but slow.
- ⇒ Divide the system into a classical and quantum parts.

$$H = H_{\text{QM}} + H_{\text{MM}} + H_{\text{QM/MM}}$$

Problem appears when the QM/MM boundary crosses chemical bonds.

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Simplest choice: Polarizable Continuum Model.

- The classical part modelled by polarizable continuum without internal structure.
- Applicable for very weak molecule-solvent interactions.

Models that follow apply to discrete solvent models.

vdW Solvent-Solute Interactions

Sometimes van der Waals interactions cannot be neglected.

- Ordinary Force-Field Solvent Hamiltonian.
- Ordinary QC Solute Hamiltonian.
- The interaction Hamiltonian:

$$H_{\text{QC/MM}} = \sum_j^{\text{solute}} \sum_i^{\text{solvent}} \left[\frac{\alpha q_i q_j}{r_{ij}} + 4\epsilon_{ij} \left(\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right) \right]$$

where usually the vdW parameters taken from the classical FF parameters:

$$\begin{aligned}\sigma_{AB} &= \sigma_A + \sigma_B \\ \epsilon_{AB} &= \sqrt{\epsilon_A \epsilon_B}\end{aligned}$$

Polarized QM/Unpolarized MM

- QM electrons and nuclei interact directly with the MM part.

$$H_{\text{QC/MM}} = \sum_i^{\text{solvent}} \left[\sum_a^{\text{electrons}} \frac{q_i}{r_{ia}} + \sum_j^{\text{solute}} \frac{q_i Z_j}{r_{ij}} \right] + \sum_i^{\text{solvent}} \sum_j^{\text{solute}} \left[+4\epsilon_{ij} \left(\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right) \right]$$

- Extra term to the Fock/KS matrix:

$$F_{pq} = - \sum_m^{\text{solute}} q_m \langle p | r_m | q \rangle$$

Fully Polarized Interactions for QM and MM

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- ① Allow the solvent to respond to QM changes by assigning a polarizability tensor α to each solvent molecule or atom.
- ② This becomes an iterative process as the induced QC charge induces MM charges as well.
- ③ First implementations did not show any difference with respect to unpolarizable MM – probably because the polarization was done on top on conventional force field.
- ④ ... expected to change when polarizable force fields are used.

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Boundaries Through Bonds

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- QM/MM boundary cutting through the bonds complicates the picture.
- The dangling valences from the two separate regions must be joined in a chemically and computationally feasible fashion.
- No “sure-fire” method yet.

Boundaries Through Bonds: Link Atoms

- 1 Cut the bonds and cap them with hydrogen atoms.
- 2 Compute H_{QM} – without the polarization terms to the capping hydrogens.
- 3 Cut-bond stretching energy evaluated using ordinary force field. Additionally, keep the capping hydrogens on the bond line by FF means.
- 4 Bending modes involving two MM atoms and one QM atom evaluated using force field, too. No consensus yet if to treat $1*\text{MM} + 2*\text{QM}$.
- 5 Torsional energies involving two or three MM atoms and two or one QM – computed using force field. No consensus regarding other situations.
- 6 **The MM atom charges near the boundary may affect the calculation stability** considerably – workaround: fix their position in space!

Frozen Density

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- Link atoms have artificial charge instabilities near boundary related to the point charge character of MM charges.
- Add a buffer layer of a frozen density between QM region and MM point charges (auxiliary region).

$$H_{\text{complete}} = H_{\text{QM}} + H_{\text{aux}} + H_{\text{MM}} + H_{\text{QM/aux}} \\ + H_{\text{QM/MM}} + H_{\text{aux/QM}}$$

- **Problem:** QM orbitals must be orthogonal to the Frozen Density orbitals – so that total density fulfills the idempotency condition.

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Ab-initio Molecular Dynamics

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- Traditional approach:
 - ① Converge wave function and compute the gradient (forces).
 - ② Make the Newtonian step $a = F/m$
- Time consuming!
- Instead of converging the wave function at each step, propagate it, too!
- Generally: the forces are quantum but **atoms are still classical**.

Car-Parrinello Molecular dynamics

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- Usually based on:
 - DFT,
 - Effective core potentials,
 - Plane-wave basis functions.
- Treat the density coefficients d_{pq} as dynamical variables; assign fictive mass and propagate them.
- Slower speed.
- Proton transfer processes handled naturally.

Traditional Car-Parrinello formulation

- Use Lagrange formulation:

$$M_a \frac{\partial^2 \vec{R}_a}{\partial t^2} = -\frac{\partial E}{\partial \vec{R}_a} + \sum_{ij} \lambda_{ij} \frac{\partial \sigma_{ij}}{\partial \vec{R}_a}$$

$$\mu_i \frac{\partial c_{i\alpha}}{\partial t^2} = -\frac{\partial E}{\partial c_{i\alpha}} + \sum_{ij}^{N_{\text{orb}}} \frac{\partial \sigma_{ij}}{\partial c_{i\alpha}}$$

$$\sigma_{ij} = \sum_{\alpha\beta}^{N_{\text{basis}}} c_{i\alpha} c_{j\beta} \langle \alpha | \beta \rangle - \delta_{ij} = 0$$

μ_i – fictitious mass. λ_{ij} – “orthonormality-preserving” forces.

“Basic Tools” Course Summary

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Overview course.

- 1 Computers and Programming.
- 2 Algebra.
- 3 Hartree-Fock and Density Functional Theory.
- 4 Basis sets.
- 5 Forces and geometry optimization.
- 6 Wave packets.
- 7 Monte-Carlo and Molecular Dynamics.
- 8 Hybrid QM/MM methods.