Tutorial 7: VASP Calculations With Model Solvation

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Outline

- Solvated systems
- Explicit vs. implicit solvent models
- VASP implicit solvent model
- Hands-on examples
  - $H_2O$ molecule
  - Acetamide molecule
  - GaN surface
Solvated Systems

Finite systems

- Solvated molecules
- Homogeneous catalysis, biological systems, etc.
- Quantum chemistry codes
  - Gaussian, Q-Chem, GAMESS, etc.
  - Solvation studies routinely done for finite molecular systems

Extended systems

- Solid-liquid interfaces
- Heterogeneous catalysis
- Batteries, fuel cells, photoelectrochemical cells, etc.
- Periodic DFT codes
  - VASP, Quantum ESPRESSO
  - Solvation models only recently developed for periodic systems
  - Finite systems can be modeled as well
Explicit vs. Implicit Solvent Models

**Explicit**
- Fully ab initio approach
- Most detailed representation of system
- Requires averaging over solvent molecular configurations
- Computationally very expensive

**Implicit**
- Parameterized approach
- Replace solvent molecules with continuum dielectric
- Average over molecular configurations embedded in solvent model parameters
- Computationally tractable
- Use with care
  - Some cases may require including first few solvation shells explicitly
Solvation Code VASPsol

- Developed by Henning and Arias research groups at Cornell University
- Available as a patch to the original VASP source code
- Precompiled executables `vaspP_vaspsol` and `vaspPG_vaspsol` available on CFN cluster in directories
  - `/software/Workshop14/bin` and
  - `/software/vasp/Vasp.5.3.3/bin`
- More info.
  - [http://vaspsol.mse.cornell.edu](http://vaspsol.mse.cornell.edu)
Self-Consistency Cycles

Vacuum calculation

- Initial Guess \( n(r) \)
- Calculate \( V_{XC}[n] \)
- Poisson for \( V_H \) or \( \phi \)
  \[ \nabla^2 \phi(r) = -4\pi n(r) \]
- Kohn-Sham
  \[ [-\frac{1}{2} \nabla^2 + V_{ext} + V_H + V_{XC}]\psi = E\psi \]
- Calculate \( n(r) \) and \( E_{tot}[n] \)
- Converged?
- No: Exit
- Yes: Exit

Solvent calculation

- Initial Guess \( n(r) \)
- Calculate \( V_{XC}[n] \)
- Generalized Poisson for \( \phi \)
  \[ \nabla \cdot (\epsilon[n] \nabla \phi(r)) = -4\pi n(r) \]
- Kohn-Sham
  \[ [-\frac{1}{2} \nabla^2 + V_{ext} + V_H + V_{XC} + V_{el} + V_{cav}]\psi = E\psi \]
- Calculate \( n(r) \) and \( E_{tot;sol}[n] \)
  \[ E_{tot;sol}[n] = E_{tot;vac}[n] + E_{el}[n] + E_{cav}[n] \]
- Converged?
- No: Exit
- Yes: Exit
Dielectric Function

Smoothly varying dielectric function

\[ \varepsilon(n(r)) = 1 + (\varepsilon_b - 1)S(n(r)) \]

\[ S(n(r)) = \frac{1}{2} \text{erfc} \left( \frac{\ln \left( \frac{n(r)}{n_c} \right)}{\sigma \sqrt{2}} \right) \]

**VASP input parameters**

- Set from INCAR file
- \( EB_k \): Solvent dielectric constant
- \( SIGMA_K \): Width of dielectric cavity
- \( NC_K \): Cutoff charge density
**Additional Terms in K-S Energy and Potential**

**VASP input parameters**
- $EB_k$, $SIGMA_K$, $NC_K$
- $TAU$: Effective cavity surface tension

**Electrostatic**

$$ E_{el} = -\frac{1}{8\pi} \int d^3r \varepsilon[n] |\nabla \phi|^2 $$

$$ V_{el} = -\frac{d\varepsilon(n)}{dn} \frac{|
abla \phi|^2}{8\pi} $$

**Cavitation**

$$ E_{cav} = \tau \int d^3r |\nabla S| $$

$$ V_{cav} = \tau \frac{d|\nabla S|}{dn} $$

**Flowchart:**
1. Initial Guess $n(r)$
2. Calculate $V_{xc}[n]$
3. Generalized Poisson for $\phi$
   $$ \nabla \cdot (\varepsilon[n] \nabla \phi(r)) = -4\pi n(r) $$
4. Kohn-Sham
   $$ \left[ \frac{1}{2} \nabla^2 + V_{ext} + V_H + V_{xc} + V_{el} + V_{cav} \right] \psi = E\psi $$
5. Calculate $n(r)$ and $E_{tot;sol}[n] = E_{tot;vac}[n] + E_{el}[n] + E_{cav}[n]$
6. Converged?
   - Yes
   - No
     - Exit
     - Calculate $\psi = E\psi$
     - Converged?
       - Yes
       - No
         - Exit
VASP Solvation Model Results

Experimental versus VASP calculated solvation energies for different molecules in water

Surface energies of the (111), (100), and (110) facets of PbS in different solvents

Mathew, Sundararaman, Letchworth-Weaver, Arias, Hennig, J Chem Phys 140, 084106 (2014)
Typical Workflow for Solvation Calculation

**Solvation Energy**

- Electronic contribution
  - $E_{solv} = E_{tot;sol} - E_{tot;vac}$

- For free energy
  - Separate frequency calculations in vacuum and solvent are required
Tutorials: File System

/software/Workshop14/Tutorials/Tutorial7

H2O  Acetamide  GaN_slab  GaN_slab_hydroxylated

vac  vac.ref  sol  sol.ref

Run your calculations in these directories
Reference output
Hands-on Examples

- To save time, we have provided POSCAR files containing relaxed geometries
- How to run solvation examples?
  - `cd vac && qsub vpbs.com`
  - *Wait for vacuum calculation to finish*
  - `cp WAVECAR ../sol`
  - `cd sol && qsub vpbs.com`
- Finally, use total energies from OSZICAR files to calculate solvation energy

Finite molecular systems
- Water
- Acetamide

Extended (periodic) system
- GaN slab
## Water Molecule: Input

### INCAR (Vacuum calculation)
- PREC = Normal  ! standard precision
- ENCUT = 400  ! plane wave cutoff
- ALGO = Fast
- LREAL = Auto
- ISMEAR = 0  ! Gaussian smearing
- SIGMA = 0.05
- ISYM = 0  ! symmetry off

! Write flags
- LWAVE = T  ! write WAVECAR
- LCHARG = F

! Solvation
- LSOL = .FALSE.

### INCAR (Solvent calculation)
- PREC = Normal
- ENCUT = 400
- ALGO = Fast
- LREAL = Auto
- ISMEAR = 0
- SIGMA = 0.05
- ISYM = 0

! Write flags
- LWAVE = F
- LCHARG = F

! Solvation
- LSOL = .TRUE.

- Default solvent is water
- Specify solvent parameters EB_K, SIGMA_K, NC_K, TAU for other solvents e.g. acetonitrile

### KPOINTS (Γ-only)

```
0
Gamma
1 1 1
0 0 0
```
Water Molecule: Output

Total energies from OSZICAR files

- **Vacuum**
  
  \[
  \begin{align*}
  F &= -1.4220343E+02 \\
  E_0 &= -1.4220343E+02 \\
  dE &= -1.55991E-10
  \end{align*}
  \]

- **Solvent**
  
  \[
  \begin{align*}
  F &= -1.4531014E+02 \\
  E_0 &= -1.4531014E+02 \\
  dE &= -2.22468E-10
  \end{align*}
  \]

Solvation energy

- \( E_{sol} = E_{tot;sol} - E_{tot;vac} = -0.31 \text{ eV} \)
- Experimental value: -0.27 eV

For further analysis look for keywords 'Solvation' in OUTCAR and 'SOL' in OSZICAR
Acetamide Molecule

INCAR and KPOINTS files
- Identical to those for H2O

POSCAR
- Acetamide (CH₃CONH₂) in 15 Å box

Total energies from OSZICAR files
- Vacuum
  1\[F= -52062144E+02\] E0= -52062144E+02 d E = -423572E-11
- Solvent
  1\[F= -52498761E+02\] E0= -52498761E+02 d E = -437509E-11

Solvation energy
- \( E_{\text{sol}} = E_{\text{tot:sol}} - E_{\text{tot:vac}} = -0.42 \text{ eV} \)
- Experimental value: -0.42 eV

Acetamide (g) \(-0.42\text{ eV}\)
Acetamide (aq)
**GaN (10-10) Surface**

**INCAR files**
- Identical to those for H2O except DFT+U

**POSCAR**
- GaN slab with 10 Å vacuum

**KPOINTS**
- Γ-centered 6x4x1 grid

**Total energies from OSZICAR files**
- Vacuum
  - \[ E = -9.8475347E+02 \quad E_0 = -9.8475347E+02 \quad dE = -0.500992E-11 \]
- Solvent
  - \[ E = -9.8762773E+02 \quad E_0 = -9.8762773E+02 \quad dE = -0.181161E-10 \]

**Solvation energy**
- \[ E_{\text{sol}} = E_{\text{tot;sol}} - E_{\text{tot;vac}} = -0.29 \text{ eV} \]

**Normalize relative to surface area**
- Surface area: \( A = 3.16 \times 5.14 \text{ Å}^2 \)
- \( E_{\text{sol}}/2A = -8.16 \text{ meV/Å}^2 \)
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