Tutorial 7: VASP Calculations With Model Solvation

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Worhshop on "Theory and Computation for Interface Science and Catalysis: Fundamentals, Research and Hands on Engagement using VASP"
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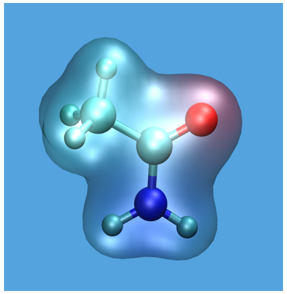
Outline

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

Solvated Systems

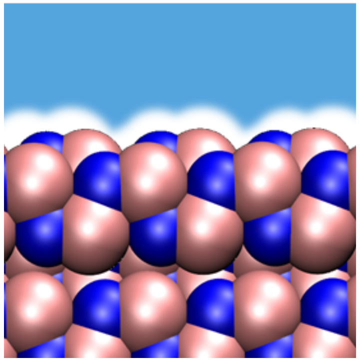
Finite systems

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



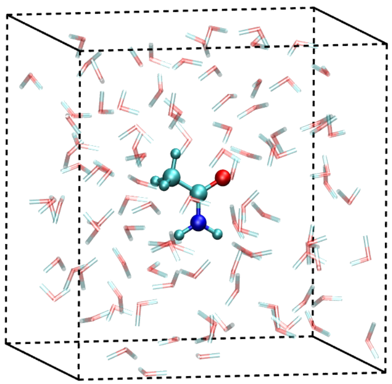
Extended systems

- 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***



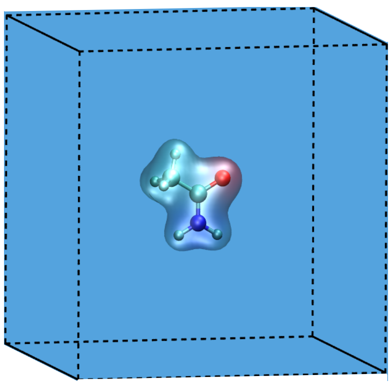
Explicit vs. Implicit Solvent Models

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***

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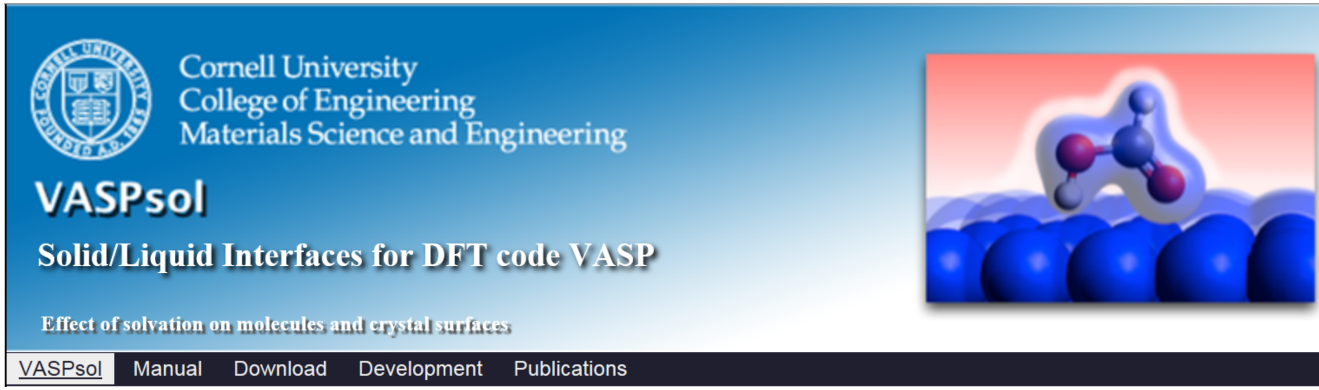
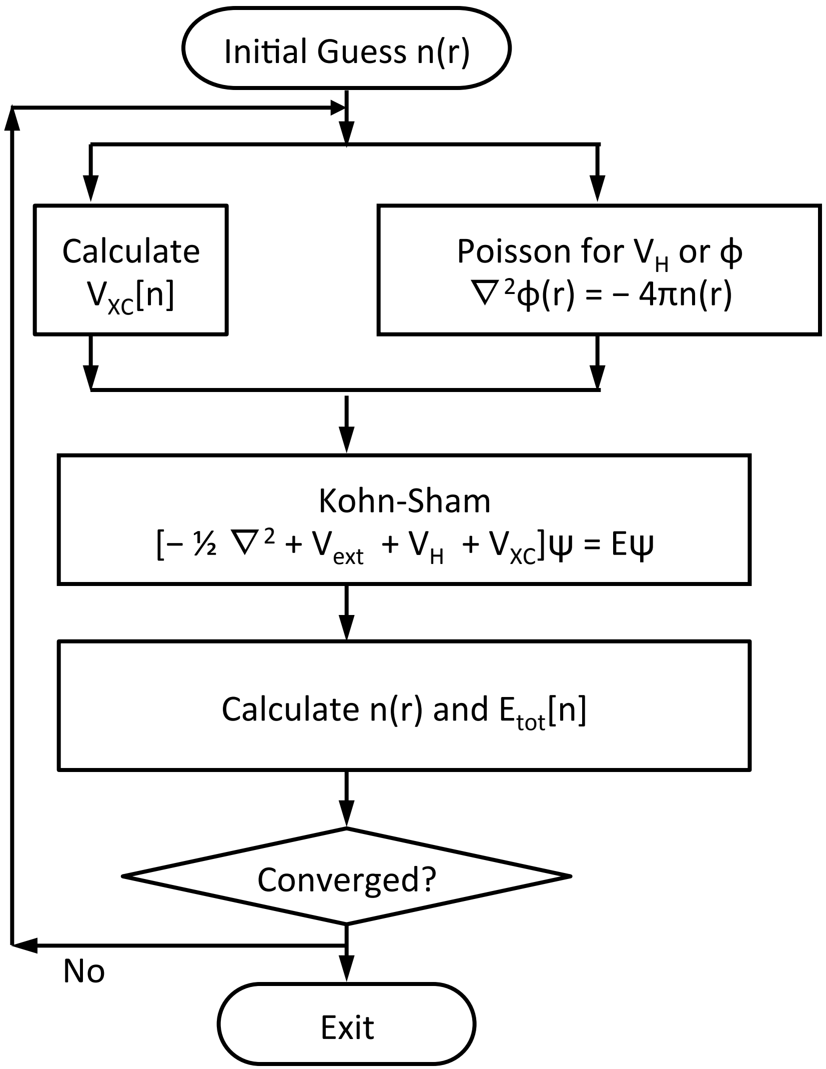
Solvation Code VASPsol



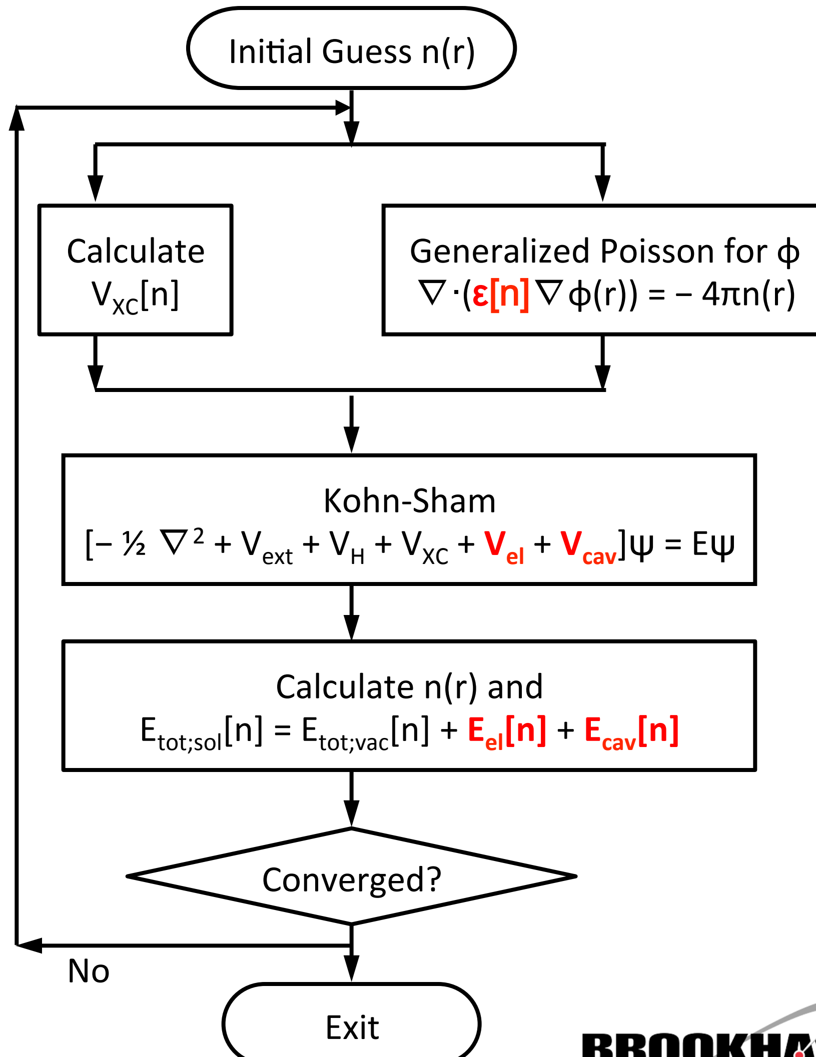
- Developed by Henning and Arias research groups at Cornell University
- Available as a patch to the original VASP source code
- Precompiled executables **vaspP_vaspsol** and **vaspPG_vaspsol** available on CFN cluster in directories
  - ***/software/Workshop14/bin and***
  - ***/software/vasp/Vasp.5.3.3/bin***
- More info.
  - ***http://vaspsol.mse.cornell.edu***
  - ***Mathew, Sundararaman, Letchworth-Weaver, Arias, Hennig, J Chem Phys 140, 084106 (2014)***

Self-Consistency Cycles

Vacuum calculation



Solvent calculation



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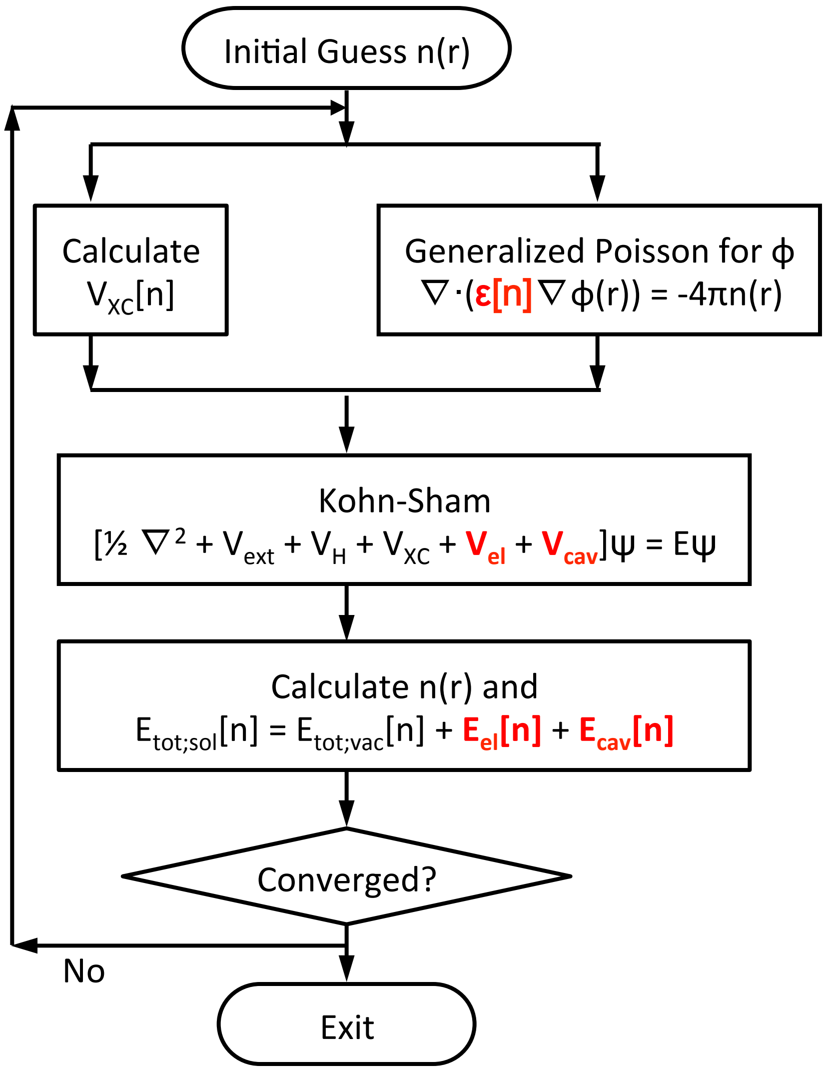
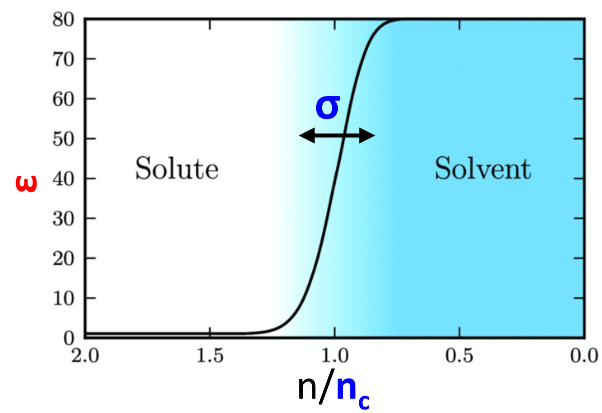
Dielectric Function

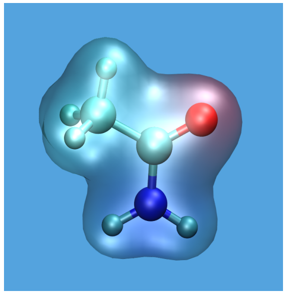


Smoothly varying dielectric function

$$\varepsilon(n(r)) = 1 + (\boldsymbol{\varepsilon_b} - 1)S(n(r))$$

$$S(n(r)) = \frac{1}{2} erfc\left(\frac{\ln (n(r)/\boldsymbol{n_c})}{\boldsymbol{\sigma}\sqrt{2}}\right)$$





VASP input parameters

- Set from INCAR file
- EB_k: Solvent dielectric constant
- SIGMA_K: Width of dielectric cavity
- NC_K: Cutoff charge density

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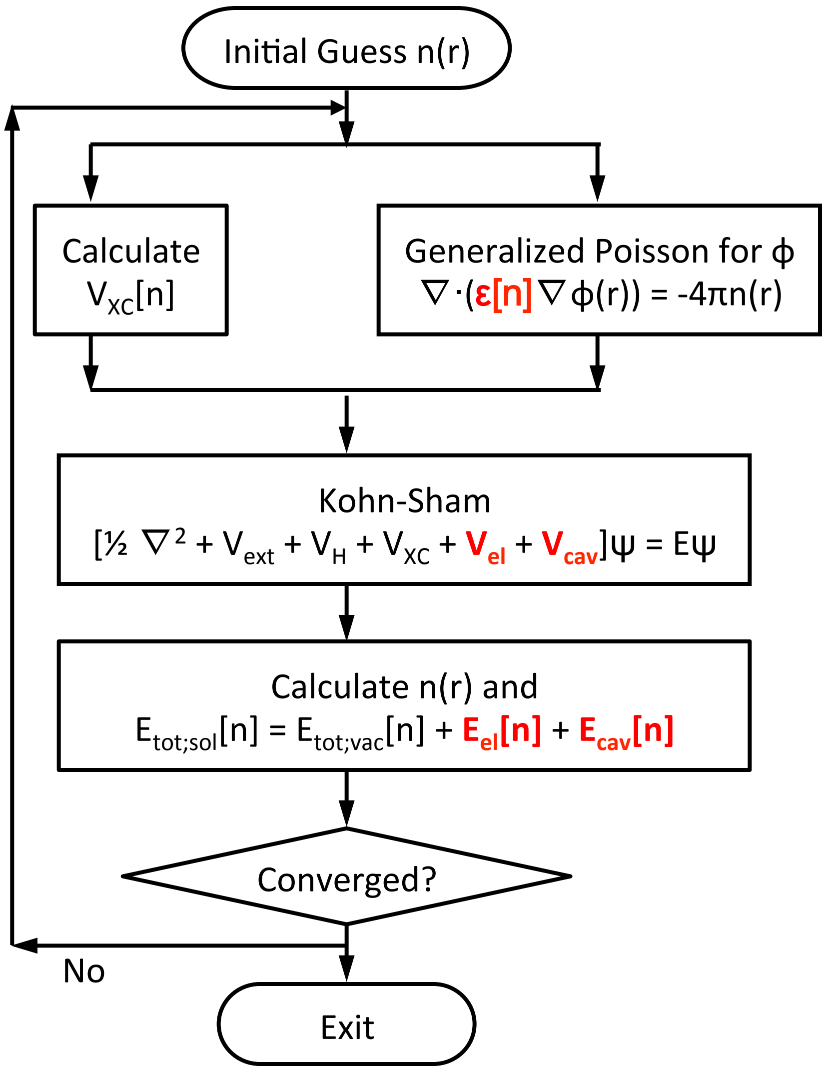
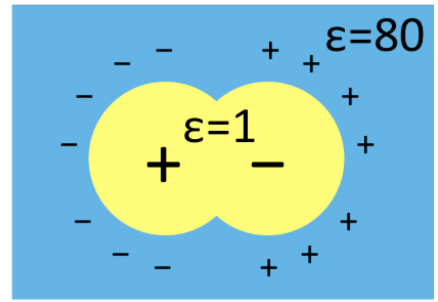
Additional Terms in K-S Energy and Potential



Electrostatic



Cavitation

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

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

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

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

VASP input parameters

- EB_k, SIGMA_K, NC_K
- TAU: Effective cavity surface tension

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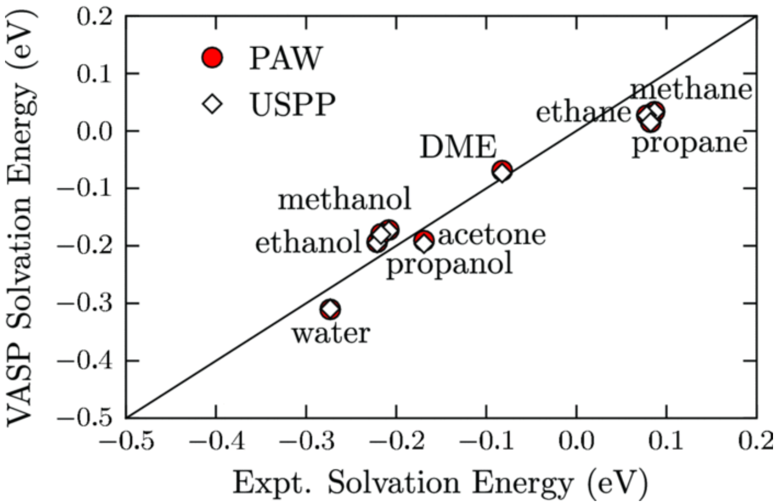
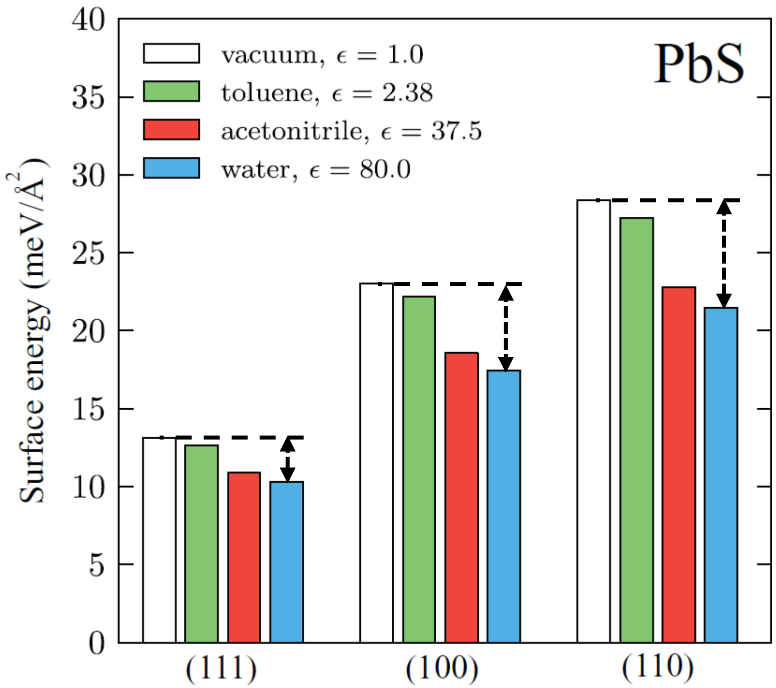
VASP Solvation Model Results

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

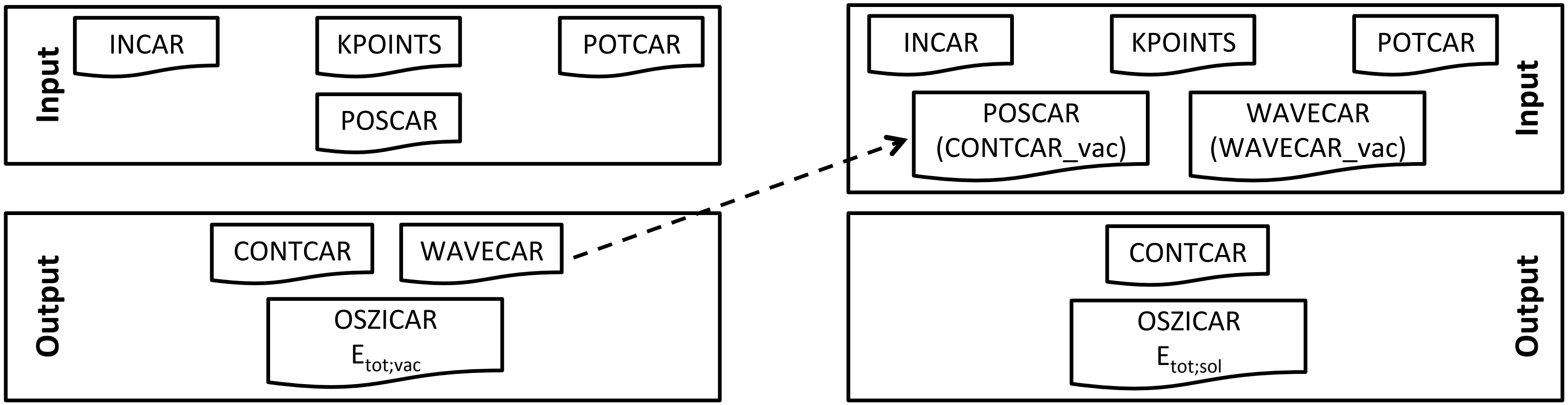


Mathew, Sundararaman, Letchworth-Weaver, Arias, Hennig, J Chem Phys 140, 084106 (2014)

Typical Workflow for Solvation Calculation

Vacuum calculation

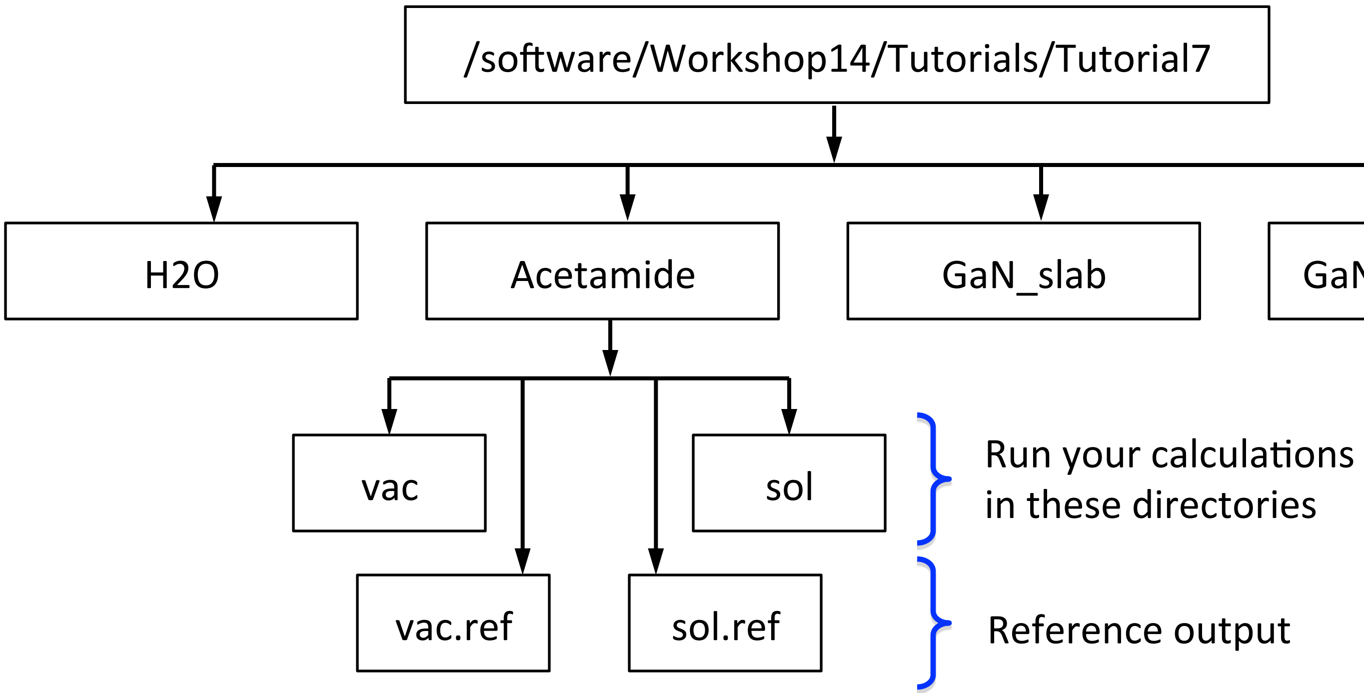
Solvent calculation



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



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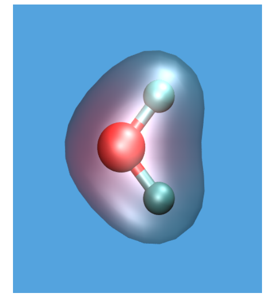
Hands-on Examples

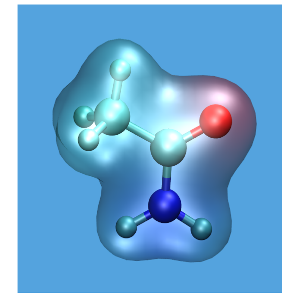
- To save time, we have provided POSCAR files containing relaxed geometries
- How to run solvation examples?
  - `> cd vac && qsub vpbs.com`
  - ***Wait for vacuum calculation to finish***
  - `> cp WAVECAR ../sol`
    `> cd sol && qsub vpbs.com`
- Finally, use total energies from OSZICAR files to calculate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

Finite molecular systems

Water

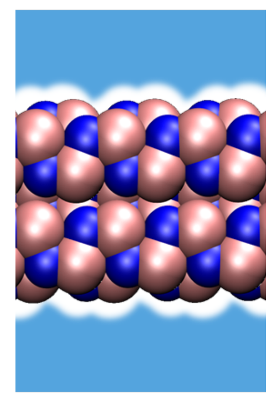


Acetamide



Extended (periodic) system

GaN slab



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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.
```

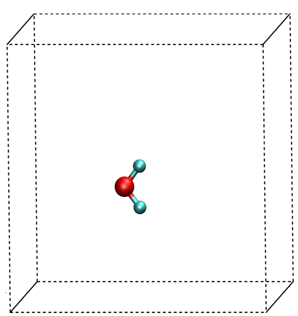
INCAR (Solvent calculation)

```
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

POSCAR

H_2O in 15 Å box



KPOINTS (Γ-only)

```
0
Gamma
1 1 1
0 0 0
```

Water Molecule: Output

Total energies from OSZICAR files

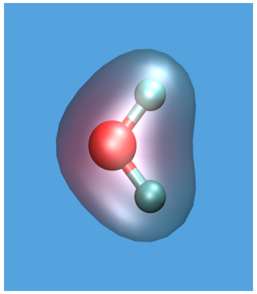
- Vacuum

```
1 F= -.14220343E+02 E0= -.14220343E+02  d E =-.155991E-10
```

- Solvent

```
1 F= -.14531014E+02 E0= -.14531014E+02  d E =-.222468E-10
```

$$H_2O\ (g) \xrightarrow{-0.31\ \text{eV}} H_2O\ (aq)$$



Solvation energy

- $E_{sol} = E_{tot;sol} - E_{tot;vac} = -0.31$ eV
- Experimental value: -0.27 eV

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

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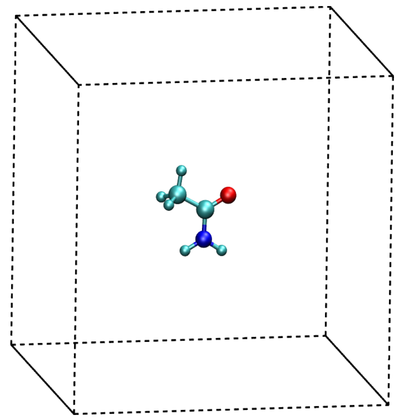
Acetamide Molecule

INCAR and KPOINTS files

- Identical to those for H2O

POSCAR

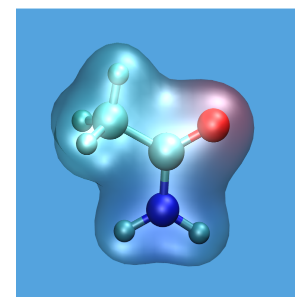
- Acetamide (CH_3CONH_2) in 15 Å box



Acetamide (g)

$\downarrow$ -0.42 eV

Acetamide (aq)



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

- $E_{sol} = E_{tot;sol} - E_{tot;vac} = -0.42$ eV
- Experimental value: -0.42 eV

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GaN (10-10) Surface

INCAR files

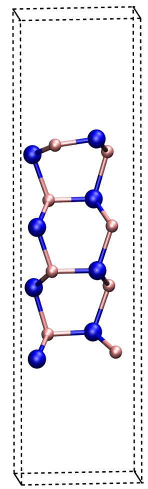
- Identical to those for H2O except DFT+U

POSCAR

- GaN slab with 10 Å vacuum

KPOINTS

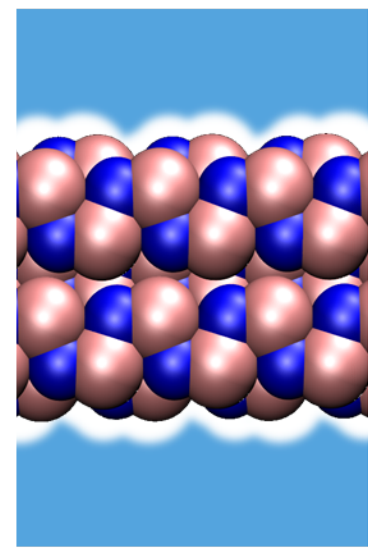
- Γ-centered 6x4x1 grid



GaN (g)

$\downarrow$ -0.29 eV, -8.6 meV/Å^2

GaN (aq)



Total energies from OSZICAR files

- Vacuum

```
1 F= -.98475347E+02 E0= -.98475347E+02  d E =-.500992E-11
```

- Solvent

```
1 F= -.98762773E+02 E0= -.98762773E+02  d E =-.181161E-10
```

Solvation energy

- $E_{sol} = E_{tot;sol} - E_{tot;vac} = -0.29$ eV

Normalize relative to surface area

- Surface area: $A = 3.16 \times 5.14$ Å^2
- $E_{sol}/2A = -8.16$ meV/Å^2

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