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Matthias Krack :: Paul Scherrer Institute

Implicit Solvent Methods and DFT+U

CP2K User Tutorial: "Computational Spectroscopy“, Uni Paderborn, 28 August 2018

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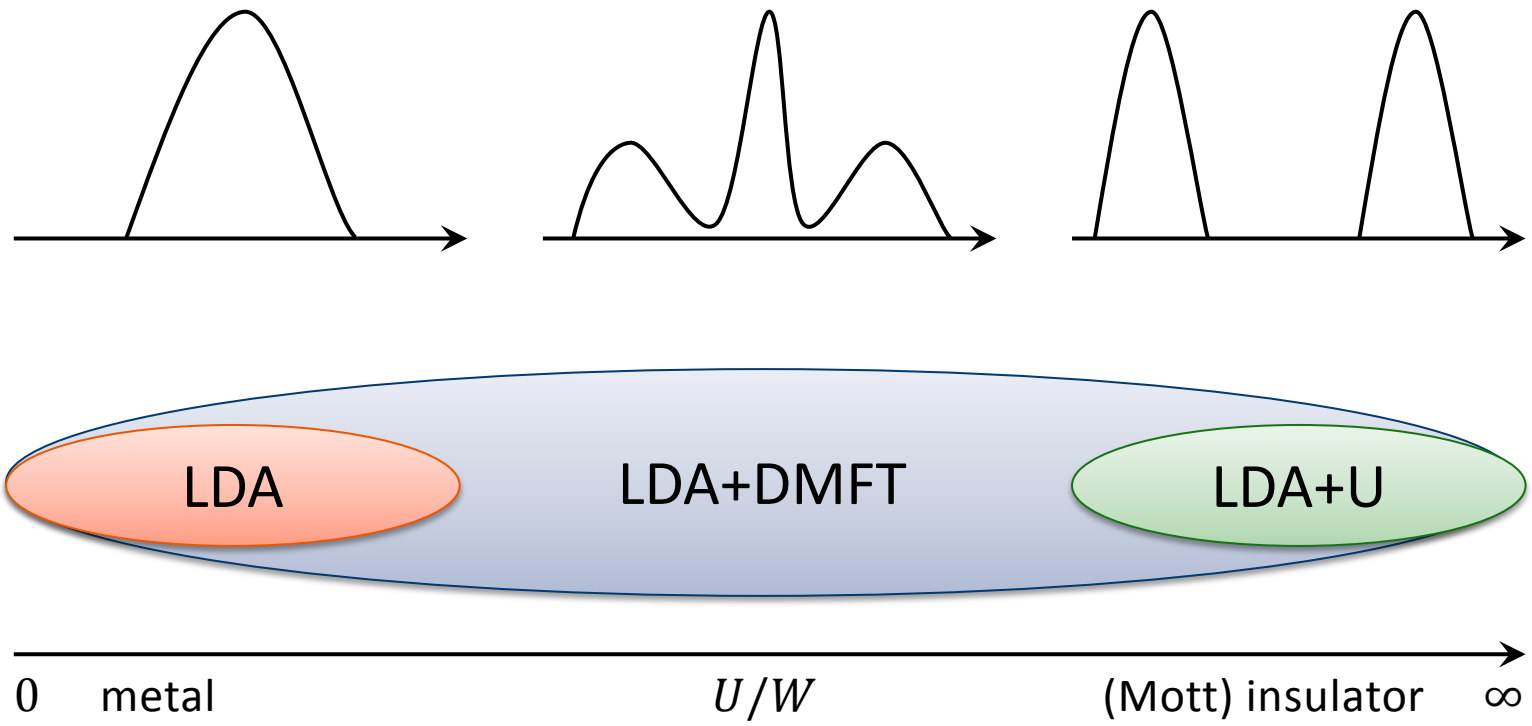
DFT+U

Local density approximation (LDA)

- Plain DFT (LDA, GGA) performs unexpectedly well for many solid state systems
- But:
  - LDA provides a poor description of the Coulomb interaction
  - The LDA functional is derived from a weakly correlated reference system, the jellium model (uniform or homogeneous electron gas)
  - Generalised Gradient Approximation (GGA) does not overcome these shortcomings as it is still a “local” approximation by adding only gradient information
  - Fortuitous error cancellation obscures the deficiencies
  - LDA fails badly for *strongly correlated systems* like transition metal (TM) oxides and heavy fermion materials with partially filled 4f and 5f orbitals

Mott insulator

- Hubbard bands form as an effect of the electronic correlation:
  - LDA bands split into two sets of bands separated by a local Coulomb repulsion U and band width W → Mott insulator



Strongly correlated systems

- Though it is possible to calculate the Hubbard parameter U using linear response theory*, it is usually treated as an empirical fitting parameter
- Fixed U parameter does not adapt to the chemical environment (e.g. change of oxidation state)
- Occurrence of meta-stable states for heavy fermion materials like CeO_2, UO_2 etc. ⇒ major obstacle technically
- On-going development, e.g. dynamical mean field theory (LDA+DMFT)
  - However, such methods are computationally very expensive
  - Accessible model system sizes are quite limited currently (≈ 30 atoms per cell)
  - Analytical energy gradients, i.e. atomic forces, are not straightforwardly available

*Cococcioni and Gironcoli, Phys. Rev. B **71**, 035105

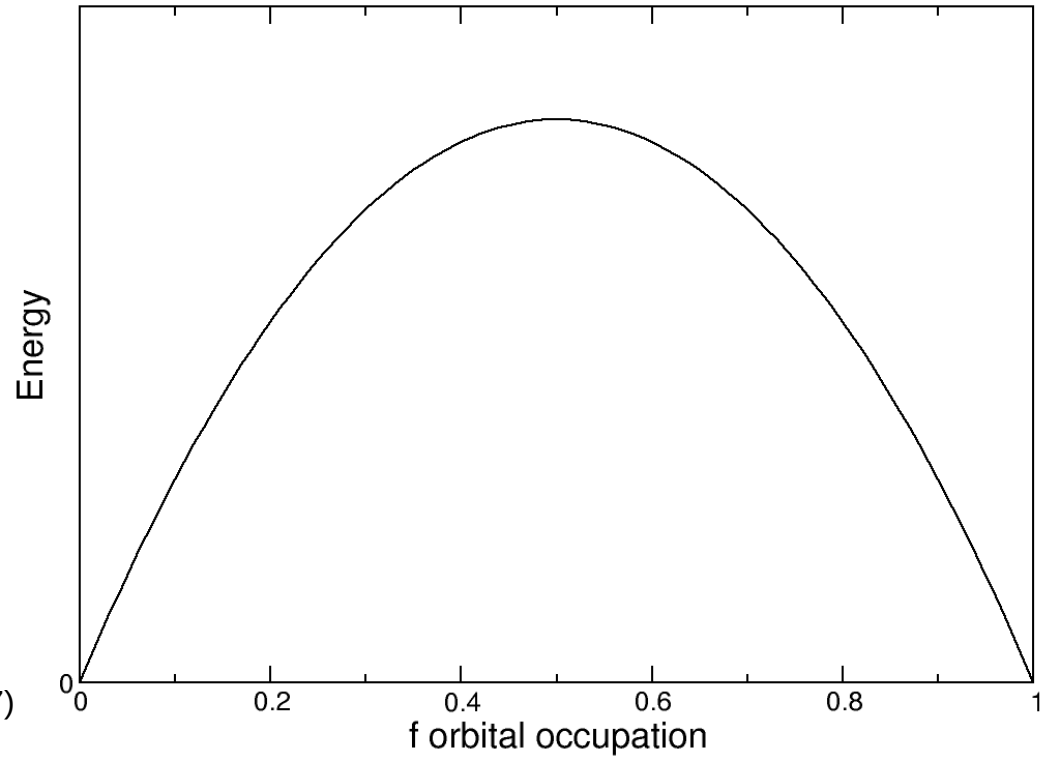
DFT+U method

- Hubbard correction term is added to the DFT energy functional as an atomic on-site term (V. I. Anisimov et al., Phys. Rev. B **44**, 943 (1991))

- Explicit correction that acts as an energy penalty function, e.g. Dudarev*:

$$E_{\mathrm{U}} = \frac{U_{\mathrm{eff}}}{2} \sum_{\sigma,I} \mathrm{Tr}[\boldsymbol{n}^{\sigma,I}(\mathbf{1} - \boldsymbol{n}^{\sigma,I})] \quad \text{with atom } I \text{ and spin } \sigma$$

- Computationally cheap
- Right physical effect
- Rotationally invariant
- Effective U parameter:
- $U_{\mathrm{eff}} = U - J$



*Dudarev et al., Phil. Mag. B **75**, 613 (1997)

Population analyses

- Orbital based methods:
  - Chirgwin and Coulson: $\boldsymbol{P} = \frac{1}{2}(\boldsymbol{DS} + \boldsymbol{SD})$
  - Mulliken: $\boldsymbol{P} = \boldsymbol{D}\,\boldsymbol{S}$
  - Löwdin: $\boldsymbol{P} = \boldsymbol{S}^{1/2}\boldsymbol{D}\,\boldsymbol{S}^{1/2}$

  with density matrix $\boldsymbol{D}$, overlap matrix $\boldsymbol{S}$, and occupation matrix $\boldsymbol{P}$

- Partitioning of the electronic density:
  - Bader charges: Gradient of the electronic charge density (zero-flux surface)
  - Hirshfeld charges: Difference to unrelaxed atomic densities (pro-density)

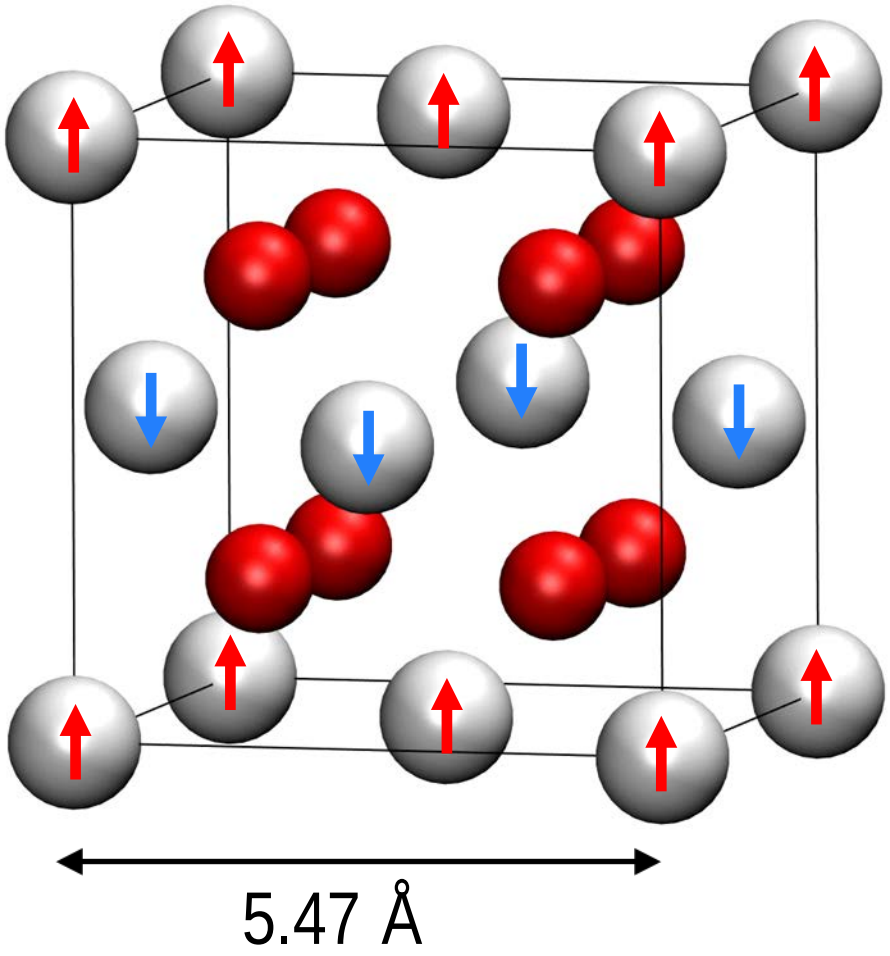
- Potential derived charges methods

- Moment derived charges

Tackling the meta-stable state problem

- Occupation matrix control (OMC)
  B. Dorado et al., Phys. Rev. B **79**, 235125 (2009)
- U ramping method
  B. Meredig et al., Phys. Rev. B **82**, 195128 (2010)
- Quasi-annealing (QA) method
  H. Y. Geng et al., Phys. Rev. B **82**, 094106 (2010)
- Controlled symmetry reduction (CSR) method
  D. Gryaznov et al., Phys. Chem. Chem. Phys. **14**, 4482 (2012)
- f occupation smearing and U ramping (FOUR)
  J. Rabone and M. Krack, Comput. Mat. Sci. **71**, 157 (2013)
- Local electronic minima inhibition by averaging occupations (LEMIAO)
  J. Rabone and M. Krack, Comput. Mat. Sci. **71**, 157 (2013)

Example: Uranium dioxide (UO_2)



Force evaluation section

- Antiferromagnetic ground state below 30.4 K:

```
&FORCE_EVAL
 METHOD Quickstep
 STRESS_TENSOR analytical
 &DFT
  CHARGE 0
  LSD
  MULTIPLICITY 1
  PLUS_U_METHOD Mulliken
  . . .
 &END DFT
 . . .
&END FORCE_EVAL
```

Example: Uranium dioxide (UO_2)

- All-electron configuration of uranium: 92 electrons

  $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^{10}\ 6s^2\ 6p^6\ 5f^3\ 6d^1\ 7s^2$

- 86 core electrons:

  $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^{10}\ 6s^2\ 6p^6$

- 6 valence electrons:

  $5f^3\ 6d^1\ 7s^2$

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- 6 valence electrons:

  $5f^3\ 6d^1\ 7s^2$

Example: Uranium dioxide (UO_2)

- All-electron configuration of oxygen: 8 electrons

$$1s^2\ 2s^2\ 2p^4$$

- 2 core electrons:

$$1s^2$$

- 6 valence electrons:

$$2s^2\ 2p^4$$

Example: Uranium dioxide (UO_2)

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Example: Uranium dioxide (UO_2)

- All-electron configuration of oxygen: 8 electrons

$$1s^2\ 2s^2\ 2p^4$$

- Pseudo atom configuration of oxygen: 2 + 6 electrons

$$[\mathrm{He}]\ 2s^2\ 2p^4$$

Example: Uranium dioxide (UO_2)

- All-electron configuration of uranium: 92 electrons

  $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^{10}\ 6s^2\ 6p^6\ 7s^2\ 5f^3\ 6d^1$

- Large-core pseudo atom configuration of uranium: 86 + 6 electrons

  $[\mathrm{Rn}]\ 7s^2\ 5f^3\ 6d^1$

- Medium-core pseudo atom configuration of uranium: 78 + 14 electrons

  $[\mathrm{Xe}\ 4f^{14}\ 5d^{10}]\ 6s^2\ 6p^6\ 7s^2\ 5f^3\ 6d^1$

- Small-core pseudo atom configuration of uranium: 60 + 32 electrons

  $[\mathrm{Kr}\ 4d^{10}\ 4f^{14}]\ 5s^2\ 5p^6\ 5d^{10}\ 6s^2\ 6p^6\ 7s^2\ 5f^3\ 6d^1$

DFT+U section in the atomic kind section

```
&KIND O
 BASIS_SET DZVP-MOLOPT-SR-GTH-q6
 POTENTIAL GTH-PBE-q6
 &BS
  . . .
 &END BS
 ! Not needed for O
&END KIND
```

DFT+U section in the atomic kind section

```
&KIND Ua
 BASIS_SET DZVP-MOLOPT-GTH-q14
 ELEMENT U
 POTENTIAL GTH-PBE-q14
 &BS
  . . .
 &END BS
 &DFT_PLUS_U on
  L 3
  U_MINUS_J [eV] 2.00
  &ENFORCE_OCCUPATION on/off
   . . .
  &END ENFORCE_OCCUPATION
 &END DFT_PLUS_U
&END KIND
```

Example: Uranium dioxide (UO_2)

- Electronic configuration of U^{4+}:

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^{10}\ 6s^2\ 6p^6\ 5f^2$$

- Medium-core pseudo atom configuration of U^{4+}:

$$[\mathrm{Xe}\ 4f^{14}\ 5d^{10}]\ 6s^2\ 6p^6\ 5f^2$$

- Electronic configuration of O^{2-}:

$$1s^2\ 2s^2\ 2p^6$$

- Pseudo atom configuration of O^{2-}:

$$[\mathrm{He}]\ 2s^2\ 2p^6$$

BS section: Initial atomic orbital occupations

- Set up the (on-site) atomic orbital occupations for O^{2-}:

$$O \xrightarrow{+2e} O^{2-}$$
$$2p^4 \xrightarrow{+2e} 2p^6$$

- BS section input is not processed quite intuitively:

```
&BS
 &ALPHA
  N    2 ! 2
  L    1 ! p
  NEL +2 ! (4 + 2)/2 = 3 alpha 2p electrons
 &END ALPHA
 &BETA
  N    2 ! 2
  L    1 ! p
  NEL +2 ! (4 + 2)/2 = 3 beta 2p electrons
 &END BETA
&END BS
```

BS section: Initial atomic orbital occupations

- Set up the (on-site) atomic orbital occupations for U^{4+}:

$$\mathrm{U} \xrightarrow{-4e} \mathrm{U}^{4+}$$

$$5f_\alpha^3\ 6d_\alpha^1\ 7s^2 \xrightarrow{-4e} 5f_\alpha^2$$

- On-site triplet state for U^{4+} for the spin-up (alpha) uranium atoms Ua and swap &ALPHA and &BETA sections for the spin-down (beta) Ub kind (not shown):

```
&BS
&ALPHA

  N      5    6    7
  L      3    2    0
  NEL   +1   -1   -2 ! (3 + 1)/2 = 2 alpha 5f electrons
 &END ALPHA
 &BETA
  N      5    6    7
  L      3    2    0
  NEL   -3   -1   -2 ! remove all beta valence electrons
 &END BETA
&END BS
```

Example: Uranium dioxide (UO_2)

- Two alpha electrons in seven 5f orbitals: $\binom{7}{2} = 21$ combinations

	f_{-3}	f_{-2}	f_{-1}	f_0	f_{+1}	f_{+2}	f_{+3}
1	↑	↑					
2	↑		↑				
3	↑			↑			
4	↑				↑		
5	↑					↑	
6							↑
7		↑	↑				
8		↑		↑			
9		↑			↑		
10		↑				↑	

	f_{-3}	f_{-2}	f_{-1}	f_0	f_{+1}	f_{+2}	f_{+3}
11		↑					↑
12			↑	↑			
13			↑		↑		
14			↑			↑	
15			↑				↑
16				↑	↑		
17				↑		↑	
18				↑			↑
19					↑	↑	
20					↑		↑
21						↑	↑

Print DFT+U specific information

- Print occupation of each atom with a U value greater zero:

```
&GLOBAL
 PRINT_LEVEL medium
 . . .
&END GLOBAL

&FORCE_EVAL
 . . .
 &DFT
  . . .
  &PRINT
   &PLUS_U on
    &EACH
     QS_SCF 1
    &END EACH
   &END PLUS_U
  &END PRINT
  . . .
 &END DFT
 . . .
&END FORCE_EVAL
```

Print DFT+U specific information

- Use a tiny U value to trigger printout for the $U = 0$ case:

```
&DFT_PLUS_U
  . . .
 U_MINUS_J [eV] 2.00E-20
  . . .
&END DFT_PLUS_U
```

Occupation control

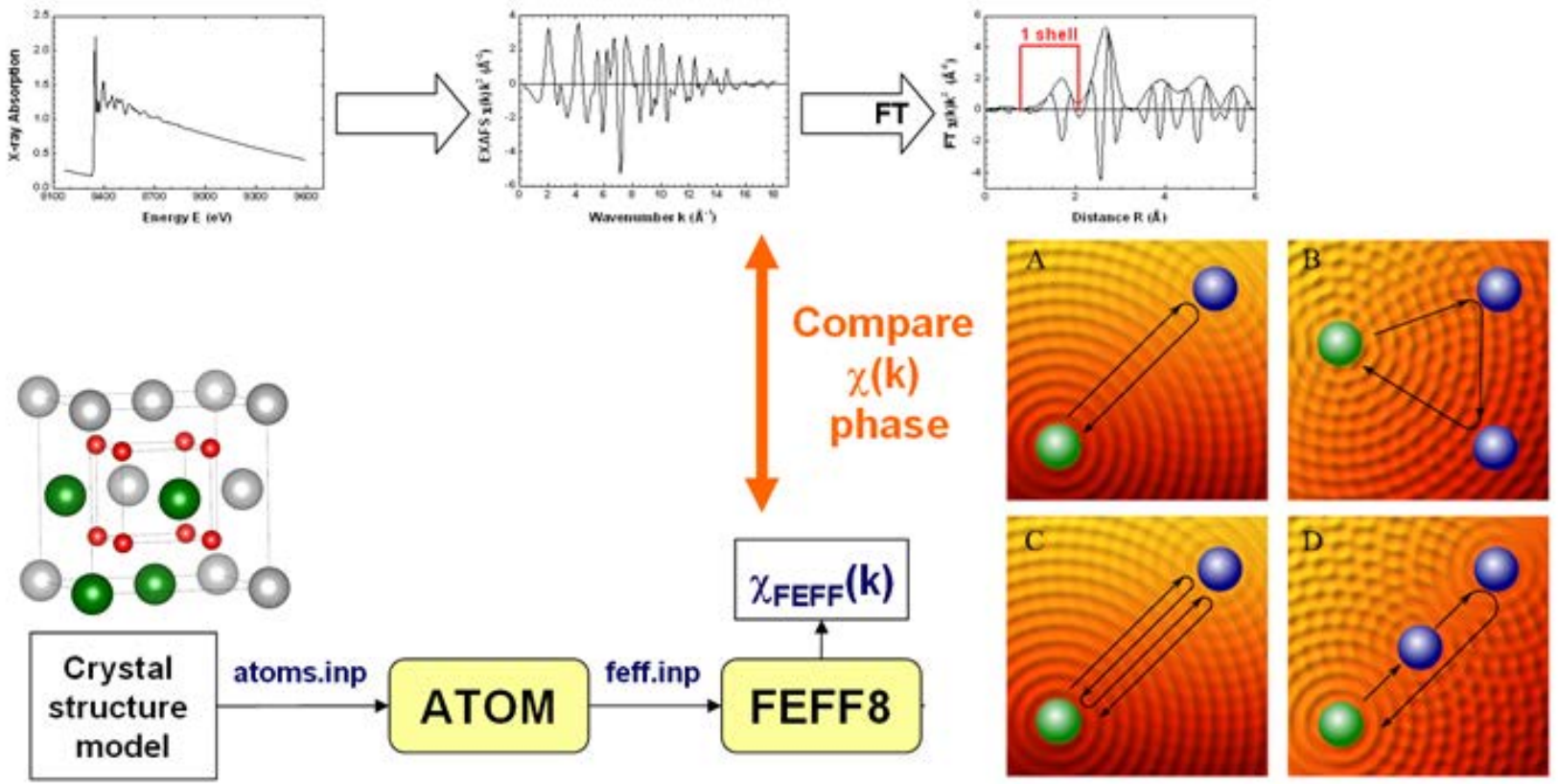
- A specific (initial) orbital occupation can be enforced:

```
&DFT_PLUS_U
 . . .
 &ENFORCE_OCCUPATION on/off
  EPS_SCF 1.0E-5 ! Enforce until a certain SCF convergence is reached
  MAX_SCF 20     ! Enforce occupation for first 20 SCF iterations
  ORBITALS -3 -2 -1 +0 +1 +2 +3 ! Smear f electrons over all f orbitals
SMEAR on
 &END ENFORCE_OCCUPATION
 . . .
&END DFT_PLUS_U
```

- Alternatively, define and enforce a specific orbital occupation pattern, e.g.

```
  ORBITALS -3 -1
```

Example: XAFS spectra simulation



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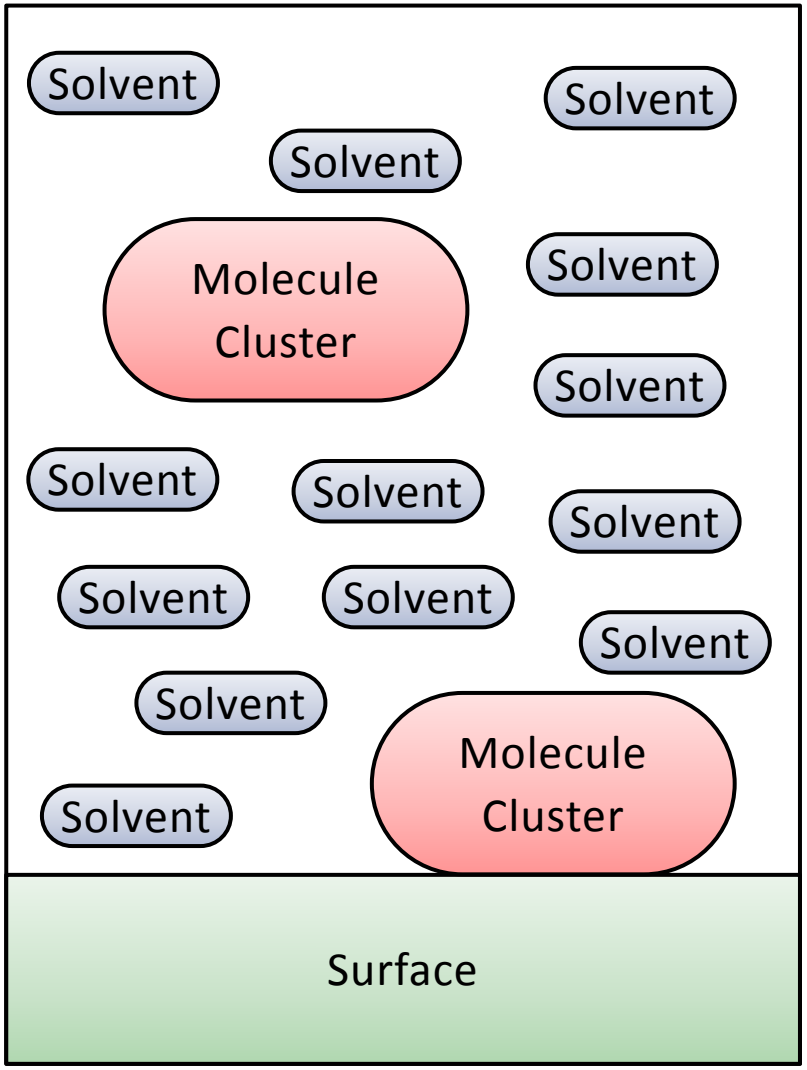
Implicit Solvent Methods

Modelling of solvation effects

- Vacuum
- Gas phase
- Explicit solvent with solute



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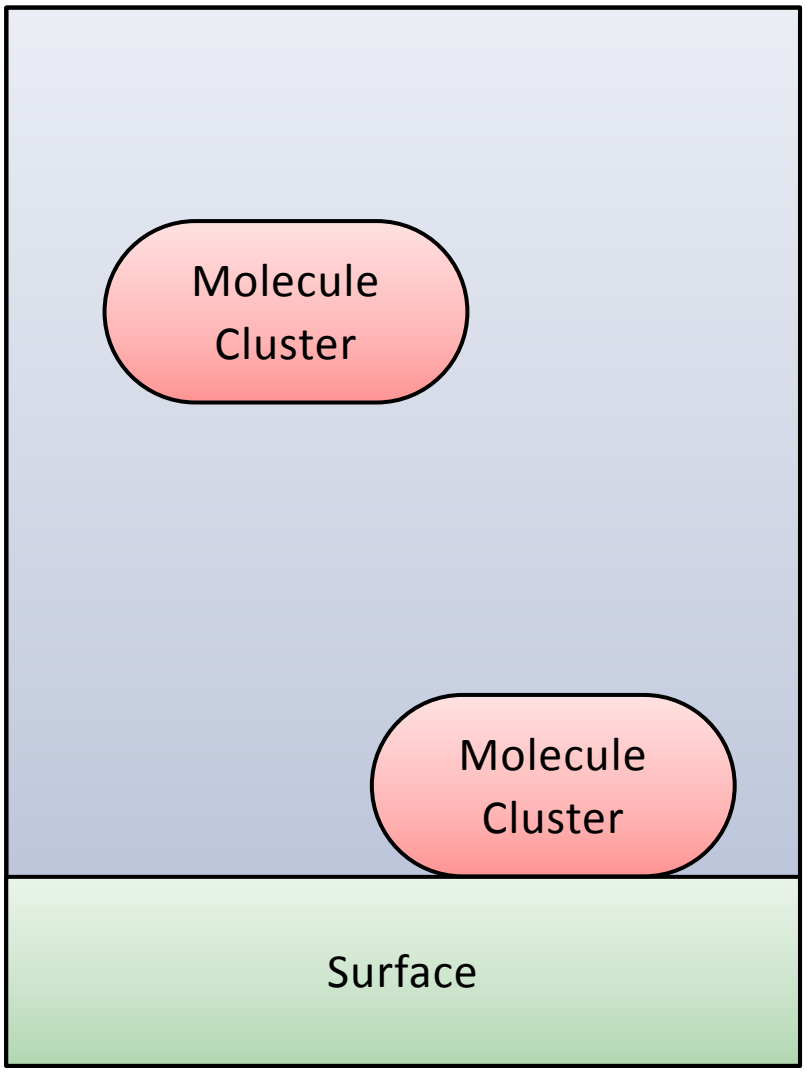
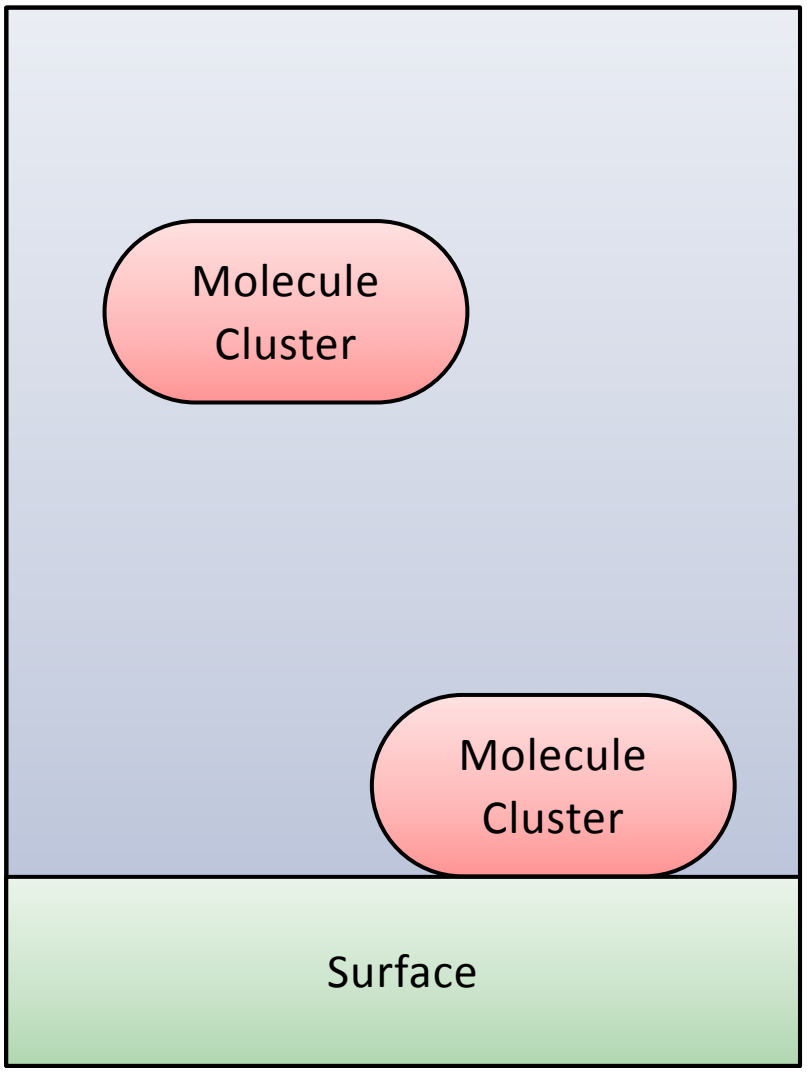


Continuum solvation models

- Polarisable continuum model (PCM, Tomasi et al.)
- Conductor-like screening model (COSMO, Klamt et al.)
- Smooth dielectric models are needed for molecular dynamics (MD) simulations

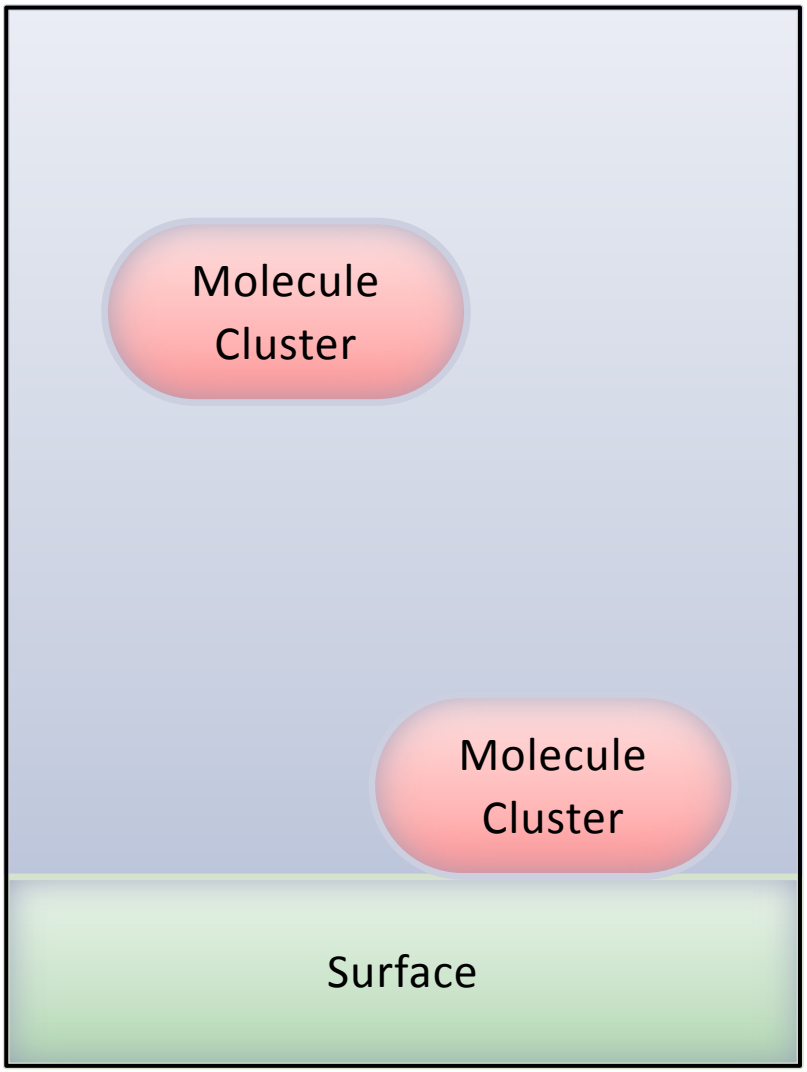
Modelling of solvation effects

- Vacuum
- Gas phase
- Explicit solvent with solute
- Implicit solvent with solute



Modelling of solvation effects

- Vacuum
- Gas phase
- Explicit solvent with solute
- Implicit solvent with solute
- Smoothed solute-solvent transition



Pros and Cons of an implicit solvent approach

- Explicit solute-solvent interactions are missing
  - Pros:
    - Shortcomings of standard DFT in the description of van der Waals and hydrogen bonds w.r.t. the solvent do not matter
    - Shorter sampling times needed to obtain meaningful thermodynamic averages
  - Cons:
    - No detailed description of hydrogen bonds (network)
    - Potential (chemical) reactions between solvent and solute are excluded a priori

- No explicit solvent atoms
  - Pros:
    - Significant reduction in problem size especially for localised basis set methods
    - More efficient sampling
  - Cons:
    - Additional (nested) convergence cycle for polarisation charge required
    - No information about solvation shells (detailed feedback of the solvent)
    - Potentially more noisy forces due to finite differences approach

Smoothed dielectric function

- Dielectric as a smoothed self-consistent function of the electronic density:

$$\epsilon(\boldsymbol{r}) \equiv \epsilon\left[\rho^{\mathrm{elec}}(\boldsymbol{r})\right] = \begin{cases} 1 & \text{large } \rho^{\mathrm{elec}} \\ \epsilon_0 & \rho^{\mathrm{elec}} \to 0 \end{cases}$$

  - J.-L. Fattebert and F. Gygi, J. Comput. Chem. **23**, 662 (2002)
  - J.-L. Fattebert and F. Gygi, Int. J. Quantum Chem. **93**, 139 (2003)
  - O. Andreussi et al., J. Chem. Phys. **136**, 064102 (2012)

Self-consistent Continuum Solvation (SCCS)

- Adding a dielectric medium to the system

$$\epsilon(\boldsymbol{r}) \equiv \epsilon\left[\rho^{\mathrm{elec}}(\boldsymbol{r})\right]$$

$$\nabla^2\phi^{\mathrm{tot}}(\boldsymbol{r}) = -4\pi\rho^{\mathrm{solute}}(\boldsymbol{r}) \quad \text{with } \rho^{\mathrm{solute}}(\boldsymbol{r}) = \rho^{\mathrm{ions}}(\boldsymbol{r}) + \rho^{\mathrm{elec}}(\boldsymbol{r})$$

$$\nabla \cdot \epsilon\left[\rho^{\mathrm{elec}}(\boldsymbol{r})\right]\phi^{\mathrm{tot}}(\boldsymbol{r}) = -4\pi\rho^{\mathrm{solute}}(\boldsymbol{r})$$

$$\nabla \cdot \boldsymbol{E}(\mathrm{r}) = 4\pi\rho^{\mathrm{solute}}(\boldsymbol{r}) - 4\pi \cdot \boldsymbol{P}(\boldsymbol{r})$$

$$\rho^{\mathrm{pol}}(\boldsymbol{r}) = -\nabla \cdot \boldsymbol{P}(\boldsymbol{r}) = \nabla \cdot \left(\frac{\epsilon\left(\rho^{\mathrm{elec}}(\boldsymbol{r})\right) - 1}{4\pi} \nabla\phi^{\mathrm{tot}}(\boldsymbol{r}) \right)$$

- Finally a vacuum-like Poisson problem is recovered

$$\nabla^2\phi^{\mathrm{tot}}(\boldsymbol{r}) = -4\pi\left(\rho^{\mathrm{solute}}(\boldsymbol{r}) + \rho^{\mathrm{pol}}(\boldsymbol{r})\right)$$

Self-consistent Continuum Solvation (SCCS)

- Vacuum-like Poisson problem is recovered

$$\nabla^2 \phi^{\mathrm{tot}}(\boldsymbol{r}) = -4\pi\left(\rho^{\mathrm{solute}}(\boldsymbol{r}) + \rho^{\mathrm{pol}}(\boldsymbol{r})\right)$$

- Energy term

$$E^{\mathrm{el}} = E^{\mathrm{solute}} + E^{\mathrm{pol}}$$

Solvation free energy

- Solvation free energy

$$\Delta G^{\mathrm{sol}} = \Delta G^{\mathrm{el}} + G^{\mathrm{rep}} + G^{\mathrm{dis}} + G^{\mathrm{cav}} + \Delta G^{\mathrm{tm}} + P\Delta V$$

- Electrostatic contribution:

$$\Delta G^{\mathrm{el}} = G^{\mathrm{el}} - G^{0}$$

  with the energy G^0 of the solute in vacuum

- Repulsion term*:

$$G^{\mathrm{rep}} = \alpha\, S$$

  where S is the (quantum) surface of the cavity

- Dispersion term*:

$$G^{\mathrm{dis}} = \beta\, V$$

  where V is the (quantum) volume of the cavity

*Scherlis et al., J. Chem. Phys. 124, 074103 (2006)

Solvation free energy

- Cavitation term*:

$$G^{\mathrm{cav}} = \gamma\, S$$

  where S is the (quantum) surface of the cavity

- Thermal motion term G^{tm} and the volume change term $P\Delta V$ are often ignored

- Collecting all terms results in an approximation for the solation free energy

$$\Delta G^{\mathrm{sol}} \approx \Delta G^{\mathrm{el}}(\epsilon_0, \rho_{\mathrm{min}}, \rho_{\mathrm{max}}) + (\alpha + \gamma)\, S + \beta\, V$$

- Quantum volume V and surface S:
  – M. Cococcioni et al., Phys. Rev. Lett. **94**, 145501 (2005)

*Scherlis et al., J. Chem. Phys. 124, 074103 (2006)

SCCS input section

```
&SCCS on/off
 ALPHA [N*m^-1] 0.0
 BETA [kbar] 0.0
 DELTA_RHO 2.0E-5
 DERIVATIVE_METHOD cd3/cd5/cd7/fft
 DIELECTRIC_CONSTANT 78.36
 EPS_SCCS 1.0E-6
 GAMMA [mN/m] 0.0
@IF ${OT}
 EPS_SCF 0.03
@ENDIF
@IF ${TD}
 EPS_SCF 0.3
@ENDIF
 MAX_ITER 100
 METHOD Andreussi/Fattebert-Gygi
 MIXING 0.6
 . . .
&END SCCS
```

Dielectric functions

- Fattebert-Gygi

$$\epsilon\left[\rho^{\mathrm{elec}}(\boldsymbol{r})\right] = 1 + \frac{\epsilon_0 - 1}{2}\left(1 + \frac{1 - \left(\rho^{\mathrm{elec}}/\rho_0\right)^{2\beta}}{1 + \left(\rho^{\mathrm{elec}}/\rho_0\right)^{2\beta}}\right)$$

- Andreussi et al.

$$\epsilon\left[\rho^{\mathrm{elec}}(\boldsymbol{r})\right] = \begin{cases} 1 & \rho^{\mathrm{elec}} > \rho_{\mathrm{max}} \\ \exp\left(t\left(\ln \rho^{\mathrm{elec}}\right)\right) & \rho_{\mathrm{min}} < \rho^{\mathrm{elec}} < \rho_{\mathrm{max}} \\ \epsilon_0 & \rho^{\mathrm{elec}} < \rho_{\mathrm{min}} \end{cases}$$

$$t(x) = \frac{\ln \epsilon_0}{2\pi}\left[2\pi \frac{\ln \rho_{\mathrm{max}} - x}{\ln \rho_{\mathrm{max}} - \ln \rho_{\mathrm{min}}} - \sin\left(2\pi \frac{\ln \rho_{\mathrm{max}} - x}{\ln \rho_{\mathrm{max}} - \ln \rho_{\mathrm{min}}}\right)\right]$$

Smoothing methods for the dielectric function

```
&SCCS on/off
 . . .
 DIELECTRIC_CONSTANT 78.36
 METHOD Andreussi/Fattebert-Gygi
 . . .
 &ANDREUSSI
  RHO_MAX 0.001
  RHO_MIN 0.0001
 &END ANDREUSSI
 . . .
 &FATTEBERT-GYGI
  BETA 1.3
  RHO_ZERO 0.0004
 &END FATTEBERT-GYGI
 . . .
&END SCCS
```

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Questions or comments?