Implicit Solvent Methods and DFT+U

CP2K User Tutorial: "Computational Spectroscopy“, Uni Paderborn, 28 August 2018
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
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 $W \rightarrow$ Mott insulator

![Diagram showing the transition from metal to (Mott) insulator with $U/W$ ratio.

0 metal $U/W$ (Mott) insulator $\infty$]
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 ($\approx$ 30 atoms per cell).

– Analytical energy gradients, i.e. atomic forces, are not straightforwardly available.

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

\[ E_U = \frac{U_{\text{eff}}}{2} \sum_{\sigma,I} \text{Tr}[n^{\sigma,I}(1 - n^{\sigma,I})] \] with atom \( I \) and spin \( \sigma \)

• Computationally cheap

• Right physical effect

• Rotationally invariant

• Effective \( U \) parameter:

\[ U_{\text{eff}} = U - J \]

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

• Orbital based methods:
  – Chirgwin and Coulson: \( P = \frac{1}{2}(DS + SD) \)
  – Mulliken: \( P = DS \)
  – Löwdin: \( P = S^{1/2}DS^{1/2} \)

  with density matrix \( D \), overlap matrix \( S \), and occupation matrix \( P \)

• 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)**

- **U ramping method**

- **Quasi-annealing (QA) method**

- **Controlled symmetry reduction (CSR) method**

- **f occupation smearing and U ramping (FOUR)**

- **Local electronic minima inhibition by averaging occupations (LEMIAO)**
Example: Uranium dioxide (UO$_2$)
• Antiferromagnetic ground state below 30.4 K:

```plaintext
&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 ($\text{UO}_2$)

- 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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• 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:
\[ 5f^3 \ 6d^1 \ 7s^2 \]
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$_2$)

- 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$_2$)

- 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$_2$)

- All-electron configuration of oxygen: 8 electrons
  \[ 1s^2 \ 2s^2 \ 2p^4 \]

- Pseudo atom configuration of oxygen: 2 + 6 electrons
  \[ \text{[He]} \ 2s^2 \ 2p^4 \]
Example: Uranium dioxide ($\text{UO}_2$)

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

- Medium-core pseudo atom configuration of uranium: 78 + 14 electrons
  
  \[\text{[Xe]} \ 4f^{14} \ 5d^{10} \] \ 6s^2 \ 6p^6 \ 7s^2 \ 5f^3 \ 6d^1

- Small-core pseudo atom configuration of uranium: 60 + 32 electrons
  
  \[\text{[Kr]} \ 4d^{10} \ 4f^{14} \] \ 5s^2 \ 5p^6 \ 5d^{10} \ 6s^2 \ 6p^6 \ 7s^2 \ 5f^3 \ 6d^1

Example: Uranium dioxide ($\text{UO}_2$)
DFT+U section in the atomic kind section

&KIND 0
   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$^{4+}$:
  
  $[\text{Xe} \, 4f^{14} \, 5d^{10}] \, 6s^2 \, 6p^6 \, 5f^2$

- Electronic configuration of O$^{2-}$:
  
  $1s^2 \, 2s^2 \, 2p^6$

- Pseudo atom configuration of O$^{2-}$:
  
  $[\text{He}] \, 2s^2 \, 2p^6$
• Set up the (on-site) atomic orbital occupations for $O^{2-}$:

\[
O^+ \rightarrow O^{2-} \\
2p^4 \rightarrow 2p^6
\]

• BS section input is not processed quite intuitively:

```plaintext
&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 $U^{4+}$:

$$U \rightarrow U^{4+}$$

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

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

```shell
&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

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<th>$f_{-3}$</th>
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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
• 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
```
• 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
Implicit Solvent Methods
Modelling of solvation effects

- Vacuum
- Gas phase
- Explicit solvent with solute
Modelling of solvation effects

- Vacuum
- Gas phase
- Explicit solvent with solute
- Implicit solvent with solute
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
Smoothened dielectric function

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

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

• Adding a dielectric medium to the system

\[ \epsilon(\mathbf{r}) \equiv \epsilon[\rho^{\text{elec}}(\mathbf{r})] \]

\[ \nabla^2 \phi^{\text{tot}}(\mathbf{r}) = -4\pi \rho^{\text{solute}}(\mathbf{r}) \quad \text{with} \quad \rho^{\text{solute}}(\mathbf{r}) = \rho^{\text{ions}}(\mathbf{r}) + \rho^{\text{elec}}(\mathbf{r}) \]

\[ \nabla \cdot \epsilon[\rho^{\text{elec}}(\mathbf{r})] \phi^{\text{tot}}(\mathbf{r}) = -4\pi \rho^{\text{solute}}(\mathbf{r}) \]

\[ \nabla \cdot \mathbf{E}(\mathbf{r}) = 4\pi \rho^{\text{solute}}(\mathbf{r}) - 4\pi \cdot \mathbf{P}(\mathbf{r}) \]

\[ \rho^{\text{pol}}(\mathbf{r}) = -\nabla \cdot \mathbf{P}(\mathbf{r}) = \nabla \cdot \left( \frac{\epsilon(\rho^{\text{elec}}(\mathbf{r})) - 1}{4\pi} \nabla \phi^{\text{tot}}(\mathbf{r}) \right) \]

• Finally a vacuum-like Poisson problem is recovered

\[ \nabla^2 \phi^{\text{tot}}(\mathbf{r}) = -4\pi \left( \rho^{\text{solute}}(\mathbf{r}) + \rho^{\text{pol}}(\mathbf{r}) \right) \]
• Vacuum-like Poisson problem is recovered

\[ \nabla^2 \phi^{\text{tot}}(r) = -4\pi (\rho^{\text{solute}}(r) + \rho^{\text{pol}}(r)) \]

• Energy term

\[ E^{\text{el}} = E^{\text{solute}} + E^{\text{pol}} \]
Solvation free energy

\[ \Delta G_{\text{sol}} = \Delta G_{\text{el}} + G_{\text{rep}} + G_{\text{dis}} + G_{\text{cav}} + \Delta G_{\text{tm}} + P\Delta V \]

- Electrostatic contribution:
  \[ \Delta G_{\text{el}} = G_{\text{el}} - G^0 \]
  with the energy \( G^0 \) of the solute in vacuum

- Repulsion term*:
  \[ G_{\text{rep}} = \alpha S \]
  where \( S \) is the (quantum) surface of the cavity

- Dispersion term*:
  \[ G_{\text{dis}} = \beta V \]
  where \( V \) is the (quantum) volume of the cavity

• Cavitation term*:

\[ G^{\text{cav}} = \gamma S \]

where \( S \) is the (quantum) surface of the cavity

• Thermal motion term \( G^{\text{tm}} \) and the volume change term \( P\Delta V \) are often ignored

• Collecting all terms results in an approximation for the solvation free energy

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

• Quantum volume \( V \) and surface \( S \):


&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

$$\varepsilon[\rho^{\text{elec}}(\mathbf{r})] = 1 + \frac{\varepsilon_0 - 1}{2} \left( 1 + \frac{1 - (\rho^{\text{elec}}/\rho_0)^{2\beta}}{1 + (\rho^{\text{elec}}/\rho_0)^{2\beta}} \right)$$

• Andreussi et al.

$$\varepsilon[\rho^{\text{elec}}(\mathbf{r})] = \begin{cases} 1 & \rho^{\text{elec}} > \rho_{\text{max}} \\ \exp\left(t(\ln \rho^{\text{elec}})\right) & \rho_{\text{min}} < \rho^{\text{elec}} < \rho_{\text{max}} \\ \varepsilon_0 & \rho^{\text{elec}} < \rho_{\text{min}} \end{cases}$$

$$t(x) = \frac{\ln \varepsilon_0}{2\pi} \left[ 2\pi \frac{\ln \rho_{\text{max}} - x}{\ln \rho_{\text{max}} - \ln \rho_{\text{min}}} - \sin \left( 2\pi \frac{\ln \rho_{\text{max}} - x}{\ln \rho_{\text{max}} - \ln \rho_{\text{min}}} \right) \right]$$
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
Questions or comments?