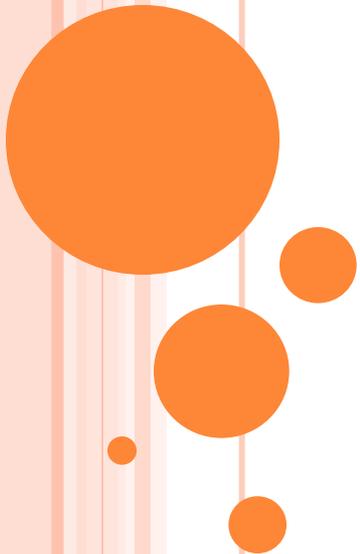


# **ELECTRONIC STRUCTURE: COMPUTATIONAL METHODS**

**Jorge Kohanoff  
Queen's University Belfast  
United Kingdom**

**[j.kohanoff@qub.ac.uk](mailto:j.kohanoff@qub.ac.uk)**



# THE PROBLEM: SOLVING KOHN-SHAM EQUATIONS

- Kohn-Sham equations:

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{ext}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \mu_{XC}[\rho](\mathbf{r}) \right] \varphi_n^{KS}(\mathbf{r}) = \varepsilon_n \varphi_n^{KS}(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_{n=1}^N f_n |\varphi_n^{KS}(\mathbf{r})|^2$$

*Density constructed with KS orbitals*  
 *$f_n$  = occupation numbers*

$$\int \varphi_n^{KS*}(\mathbf{r}) \varphi_m^{KS}(\mathbf{r}) d\mathbf{r} = \delta_{nm}$$

*KS orbitals must be orthogonal*

- to be solved **self-consistently** (Hartree-Fock very similar)

## Nuclear-electron interactions

All-electron

Pseudopotentials

## Basis sets

Basis functions ( $\phi$ ), Size (M)

$$\varphi_n^{KS}(\mathbf{r}) = \sum_{\alpha=1}^M c_{n\alpha} \phi_{\alpha}(\mathbf{r})$$



# NUCLEAR-ELECTRON INTERACTION

## ALL-ELECTRON METHODS

### ○ All-electron methods:

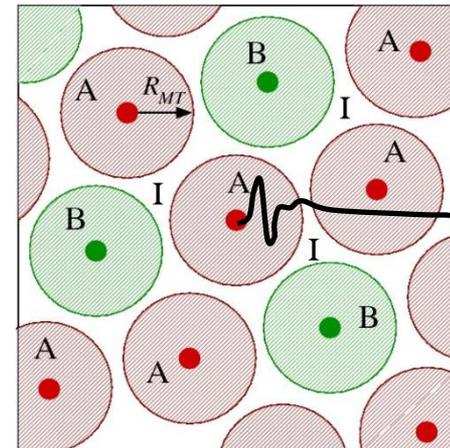
- Core, semi-core and valence electrons treated on same footing
- Bare Coulomb interaction used

### ○ **Muffin-tin orbitals** (solid-state): divide space into atomic spheres and interstitial regions. Atomic problem solved in the spheres, and matched to interstitial solutions.

- **KKR – LMTO (Hankel functions)**
- **APW – LAPW (Plane waves)**
- **ASW (Spherical waves)**

### ○ **Localized basis sets** (quantum chemistry):

- **Gaussian-type orbitals (GTO)**
- **Slater-type orbitals (STO)**
- **Linear combination of atomic orbitals (LCAO)**



# NUCLEAR-ELECTRON INTERACTION

## PSEUDOPOTENTIALS

- **Constructing pseudopotential theories:**
  - Core electrons do not participate in bonding. Consider explicitly only valence electrons
  - Replace nucleus and core electrons with an ionic core or **ion**
  - Replace bare Coulomb interaction with **screened Coulomb**
  - Valence orbitals have many oscillations in the core region ( $r < r_c$ ). This is expensive computationally for certain popular basis sets (PW). However, this region is not relevant for the chemistry. Hence, **replace the screened potential  $v_{sc}^l(r)$  with a nodeless, smooth pseudopotential  $v_{ps}^l(r)$  for  $r < r_c$**
  - For each angular momentum  $l$ , the valence pseudo-wave function should be the ground state of  $v_{ps}^l(r)$ .
  - Be careful that the **atomic scattering properties** (phase shifts) are not effected by pseudization.
- **Caution:** swift projectiles can probe the core region, where pseudization took place. This has to be monitored carefully



# PSEUDOPOTENTIALS: NON-LOCALITY AND NORM-CONSERVATION

- Valence orbitals must be orthogonal to core orbitals of the same angular quantum number. It is convenient (flexibility) to have an ***l*-dependent pseudopotential**:

$$v_{ps}(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^l |lm\rangle v_{ps}^l(r) \langle lm| = v_{loc}(r) + \sum_{l=0}^{l_{\max}} \Delta v_{ps}^l(r) P_l$$

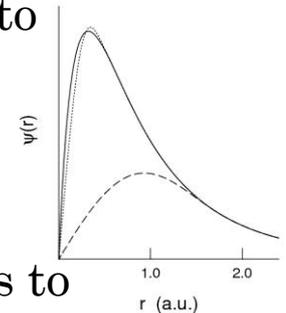
- Norm-conserving pseudopotentials (Hamann, Schlüter and Chiang 1979):
  - If all-electron and pseudo wave functions coincide for  $r > r_c$ , the atomic **scattering properties are preserved**.
  - If the norm of all-electron and pseudo wave functions inside the core is preserved, the true potential and the pseudopotential have the same first order variation in energy around the pseudization energy (generally the neutral atom eigenvalue):  
**transferability**

$$\int_0^{r_c} |r\phi_{ps}(r)|^2 dr = \int_0^{r_c} |r\phi_{ae}(r)|^2 dr$$

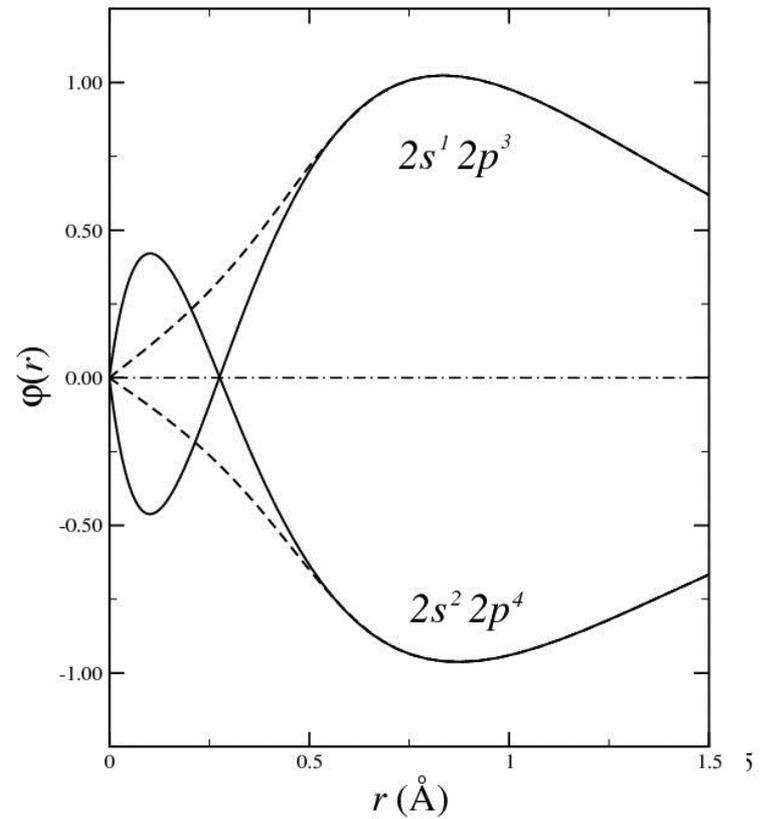
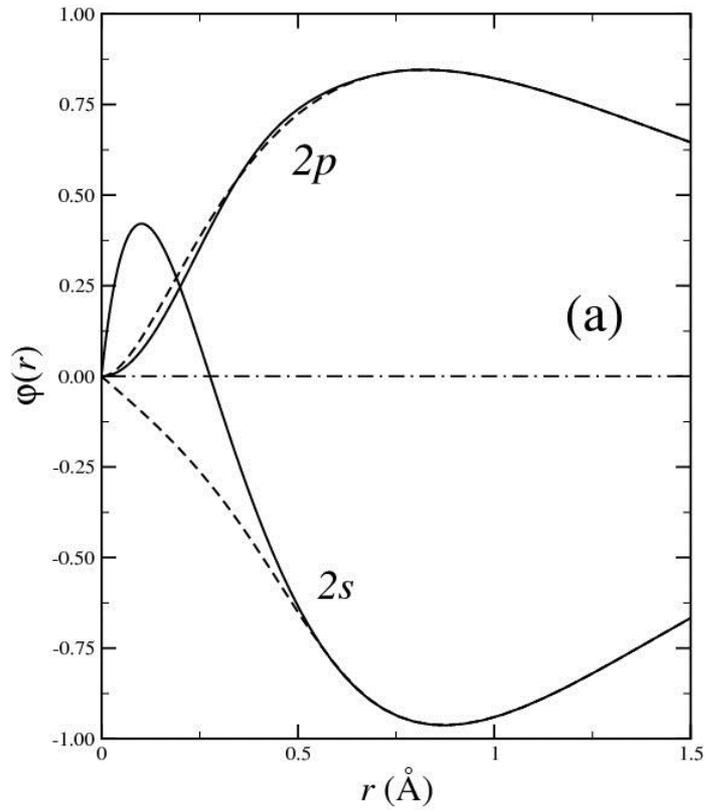


# PSEUDOPOTENTIALS: SOME DETAILS

- **Electronic configuration:** the all-electron reference calculation is done for a particular electronic configuration. Transferability should be such that this choice is not terribly important.
- **Norm-conserving:**
  - Bachelet-Hamann-Schlüter (1982)
  - Troullier-Martins (1991)
- **Ultrasoft:** Norm-conservation leads to “hard” pseudopotentials. Wave functions very peaked, require many PW to represent them. Relaxing the norm-conservation condition for the matching at the core radius, but retaining the norm for transferability leads to “softer” pseudopotentials.
  - RKKJ
  - Vanderbilt
  - PAW (Projected Augmented Waves, is practically all-electron)
- **Multiple panels:** pseudize at two or three different energies to improve transferability
- **Nonlinear core corrections:** take into account non-linearity of XC in the region where core and valence densities overlap



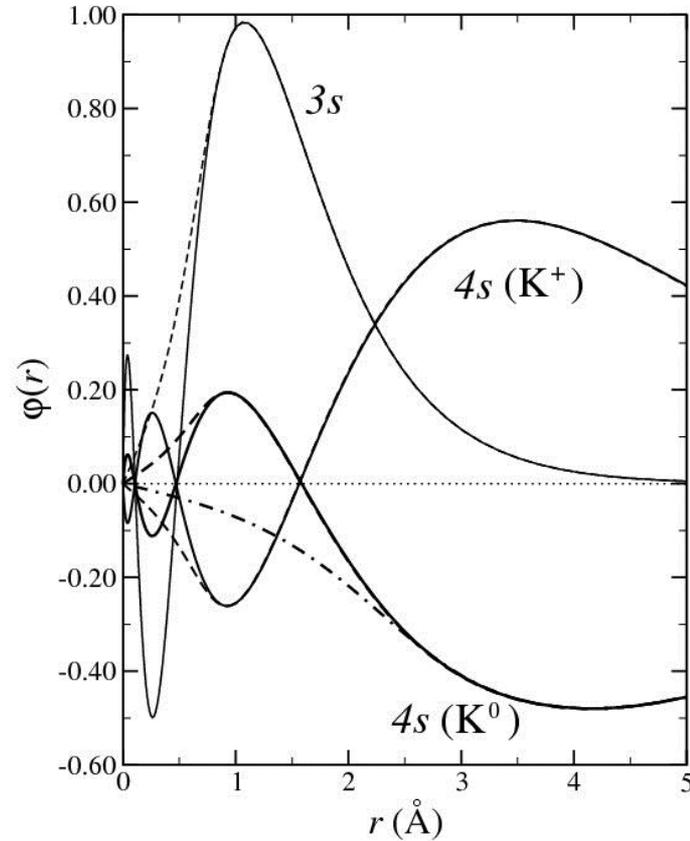
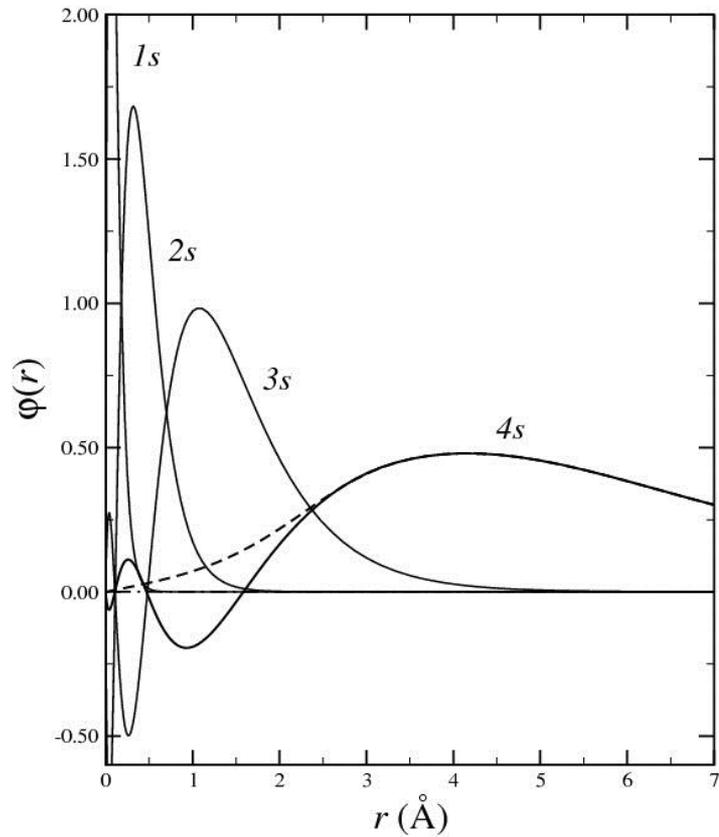
# PSEUDOPOTENTIALS: OXYGEN



*Effect of electronic configuration*



# PSEUDOPOTENTIALS: POTASSIUM



***Neutral vs charged reference  
electronic configuration***



# BASIS SETS

- Basis set representation of KS orbitals:

$$\varphi_n^{KS}(\mathbf{r}) = \sum_{\alpha=1}^M c_{n\alpha} \phi_{\alpha}(\mathbf{r})$$

- $\phi_{\alpha}(\mathbf{r})$  can depend on energy (eigenvalue). In that case one has to solve a complex non-linear secular equation (e.g. KKR)
- If they are energy-independent, the KS equations become a generalized eigenvalue problem:

$$H_{\alpha\beta} = \int \phi_{\alpha}^*(\mathbf{r}) H \phi_{\beta}(\mathbf{r}) d\mathbf{r}$$

$$S_{\alpha\beta} = \int \phi_{\alpha}^*(\mathbf{r}) \phi_{\beta}(\mathbf{r}) d\mathbf{r}$$

$$\sum_{\beta=1}^M (H_{\alpha\beta} - \varepsilon_n S_{\alpha\beta}) c_{n\beta} = 0$$

*Hamiltonian*

*Overlap*

- The same can be done for Hartree-Fock (Roothaan-Hall eq.)



# BASIS SETS

## PERIODIC SYSTEMS

- Basis set representation of KS orbitals:

$$\varphi_n^{(\mathbf{k})}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}) \sum_{\alpha=1}^M c_{n\alpha}^{(\mathbf{k})} \phi_{\alpha}(\mathbf{r})$$

*if basis functions respect PBC (PW)*

$$\varphi_n^{KS}(\mathbf{r}) = \sum_{\alpha=1}^M c_{n\alpha}^{(\mathbf{k})} \left( \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{T}} \exp(i\mathbf{k} \cdot \mathbf{T}) \phi_{\alpha}(\mathbf{r} - \mathbf{T}) \right)$$

*if basis functions are not periodic (local)*

- KS equations:

$$\sum_{\beta=1}^M \left( H_{\alpha\beta}^{(\mathbf{k})} - \varepsilon_n^{(\mathbf{k})} S_{\alpha\beta}^{(\mathbf{k})} \right) c_{n\beta}^{(\mathbf{k})} = 0$$

- Density:

$$\rho(\mathbf{r}) = \sum_{\mathbf{k}} \omega_{\mathbf{k}} \sum_{n=1}^{N_{\mathbf{k}}} f_n^{\mathbf{k}} |\varphi_n^{(\mathbf{k})}(\mathbf{r})|^2$$

*k*-points

weights

occupations

- *Baldereschi*
- *Chadi-Cohen*
- *Monkorst-Pack*
- *Moreno-Soler*

- *Fermi-Dirac*
- *Methfessel-Paxton*
- *Marzari-Vanderbilt*
- *Tetrahedron*

# BASIS FUNCTIONS

- **Floating**: do not move with the atoms
  1. Plane waves (PW)
  2. Real space grids (fixed and adaptive)
  3. Wavelets
  4. B-splines
  5. Lagrange polynomials
  6. Psinc
- **Local orbitals**: move with atoms
  1. Atomic orbitals (LCAO)
  2. Numerical
  3. Hydrogenic
  4. Slater-type orbitals (STO)
  5. Gaussian-type orbitals (GTO)
- **Mixed**:
  1. PW + GTO
- **Augmented**:
  1. APW, ASW, MTO

*Completeness*  
*BSSE*



# CODES AVAILABLE

## ○ All-electron

### 1. LAPW

1. Wien2k (Vienna)

### 2. LMTO

1. Stuttgart (Andersen, Jepsen)
2. Methfessel-van Schilfgaarde-Paxton
3. Savrasov

### 3. Local orbitals

1. Crystal (Torino, Gaussians)
2. Dmol (PSI, Gaussians)
3. FHI-AIMS (Berlin, Numerical)
4. Gaussian, Gamess, NWChem, Dgauss, etc (Gaussians, Quantum Chemistry)

## ○ Pseudopotentials

### 1. Plane Waves

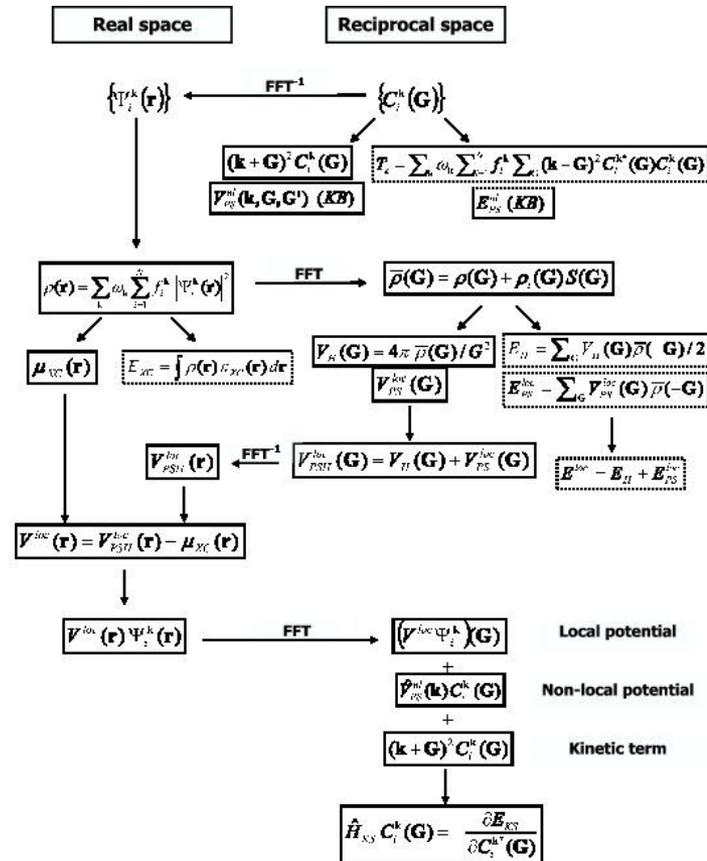
1. VASP (Vienna)
2. Quantum-espresso (Trieste)
3. CPMD (Zurich-Stuttgart)
4. CASTEP (UK)
5. ABINIT (Belgium)
6. FHI (Berlin)

### 2. Local orbitals

1. SIESTA (Spain, LCPAO)
2. QUICKSTEP (Zurich, Gaussians)
3. ONETEP (UK, psinc)
4. CONQUEST (UK, B-splines)



# FLUX DIAGRAM OF A PW CALCULATION



EXAMPLE:  
ELECTRONIC STRUCTURE OF  $\text{UO}_2$

Using the quantum-espresso package  
(<http://www.quantum-espresso.org/>)

- Pseudopotentials
- Plane wave basis set

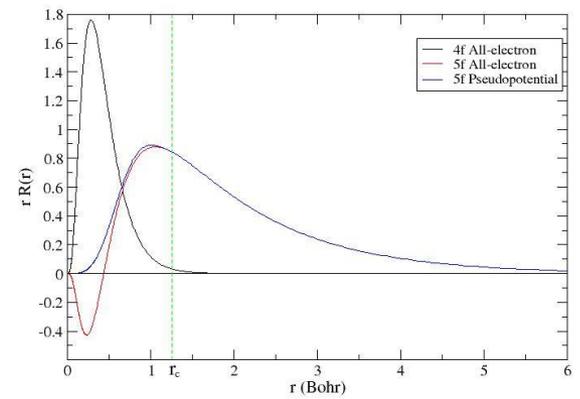
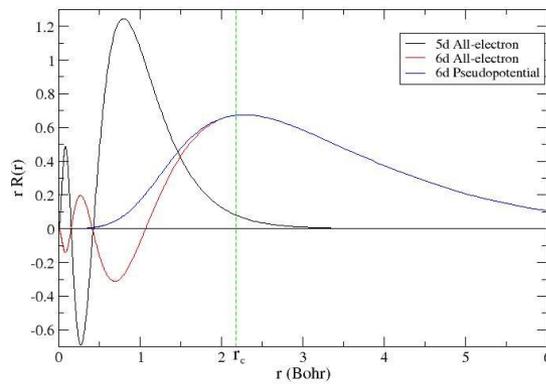
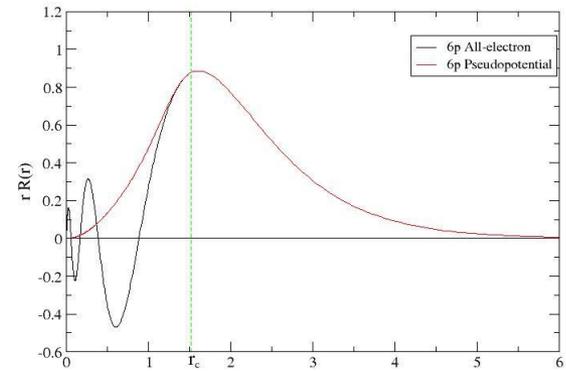
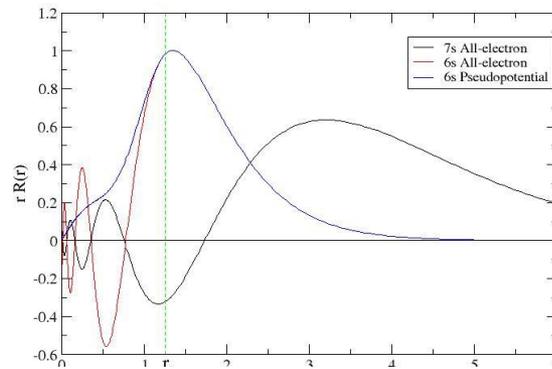


# PROPERTIES

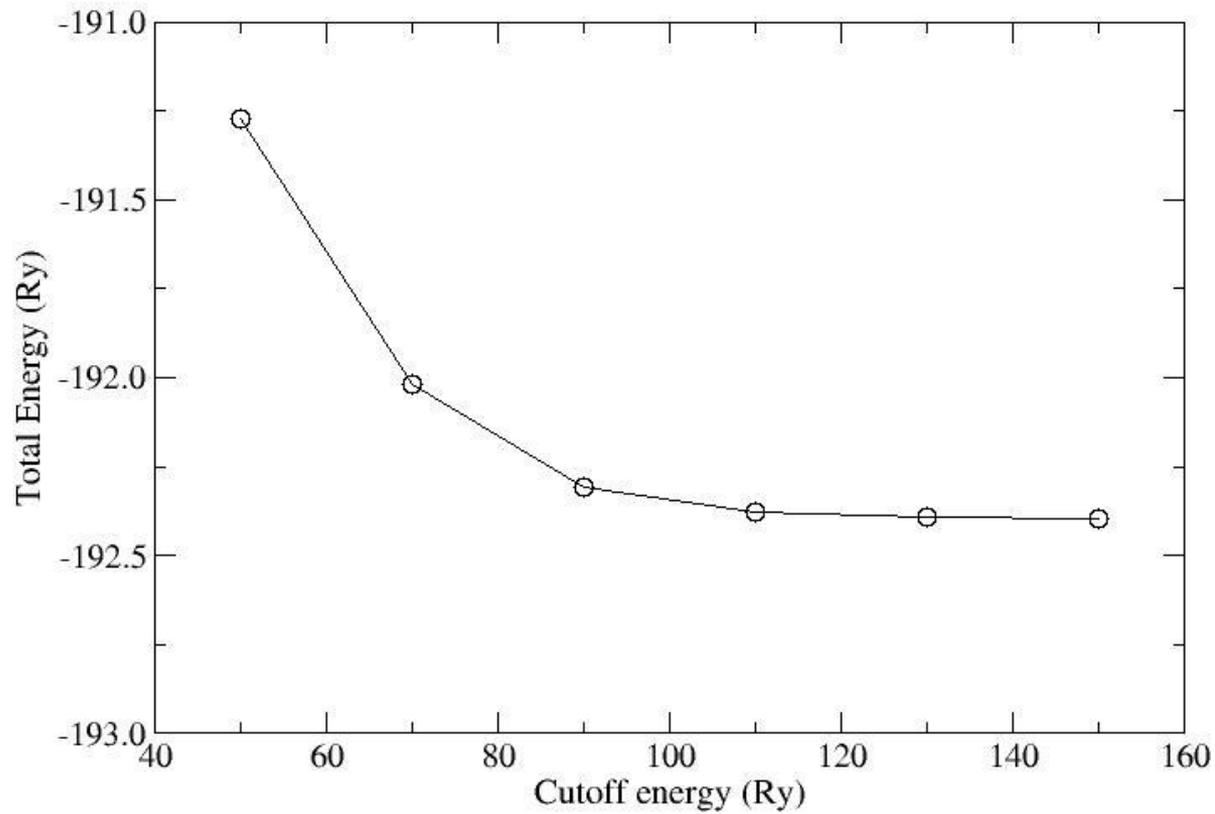
- fluorite structure
- fcc, 3 atoms un unit cell
- Lattice constant = 10.26 Bohr
- Electronic insulator.  $E_g=2.1$  eV
- Electronic configuration of U:  $[\text{Rn}]7s^26d^15f^3$
- $\text{U}^{4+}$ :  $f^2$
- 5f-band partially occupied (2/7)
- $\text{UO}_2$ : splitted by crystal field:  
 $t_{1u}(3)+t_{2u}(3)+a_g(1)$
- Still partially occupied (2/3)
- Jahn-Teller distortion opens gap.



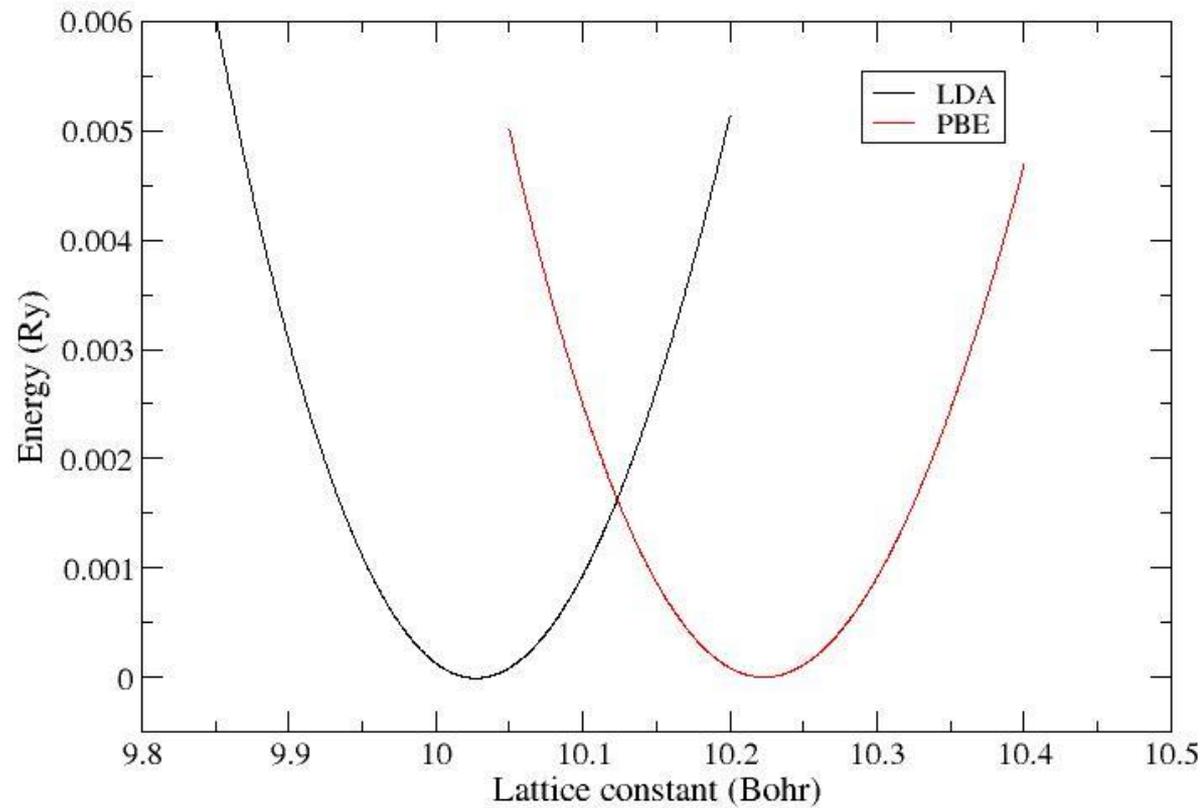
# PSEUDOPOTENTIAL



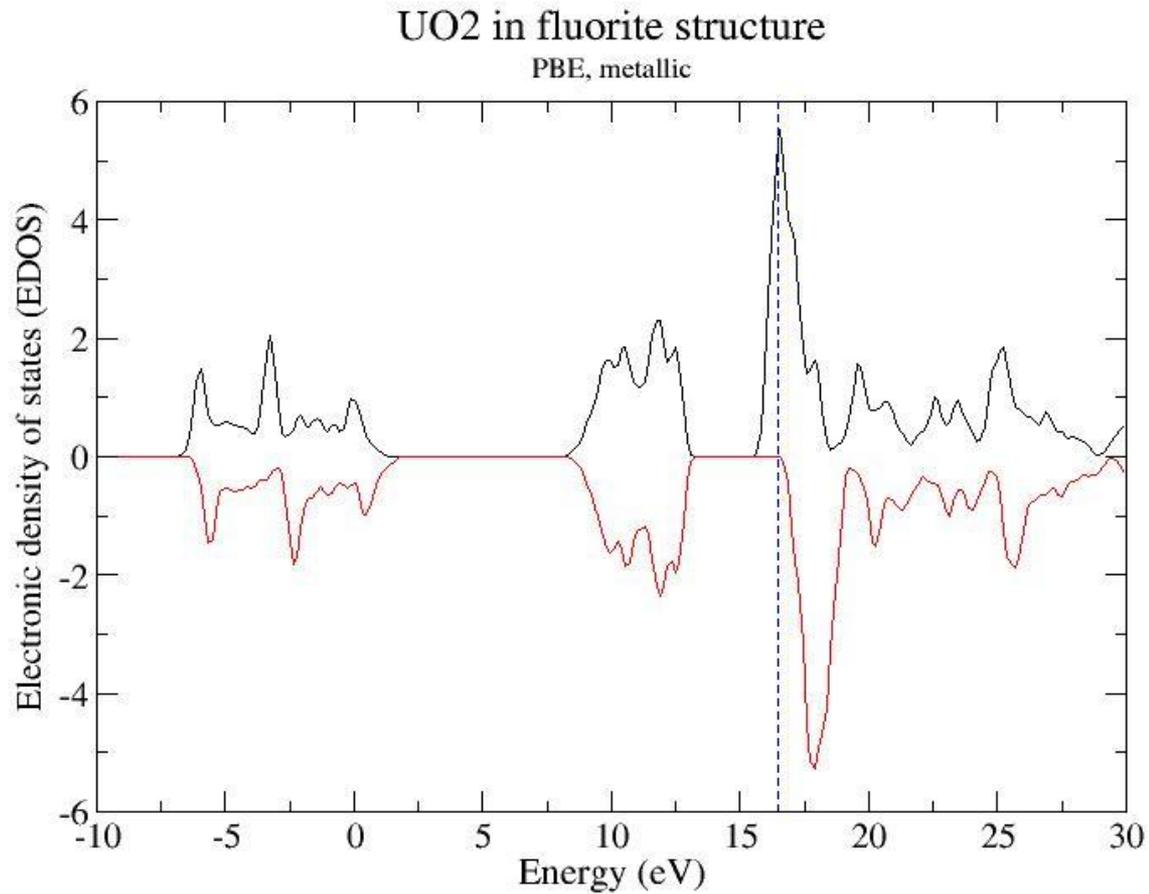
# CONVERGENCE WITH BASIS SET SIZE



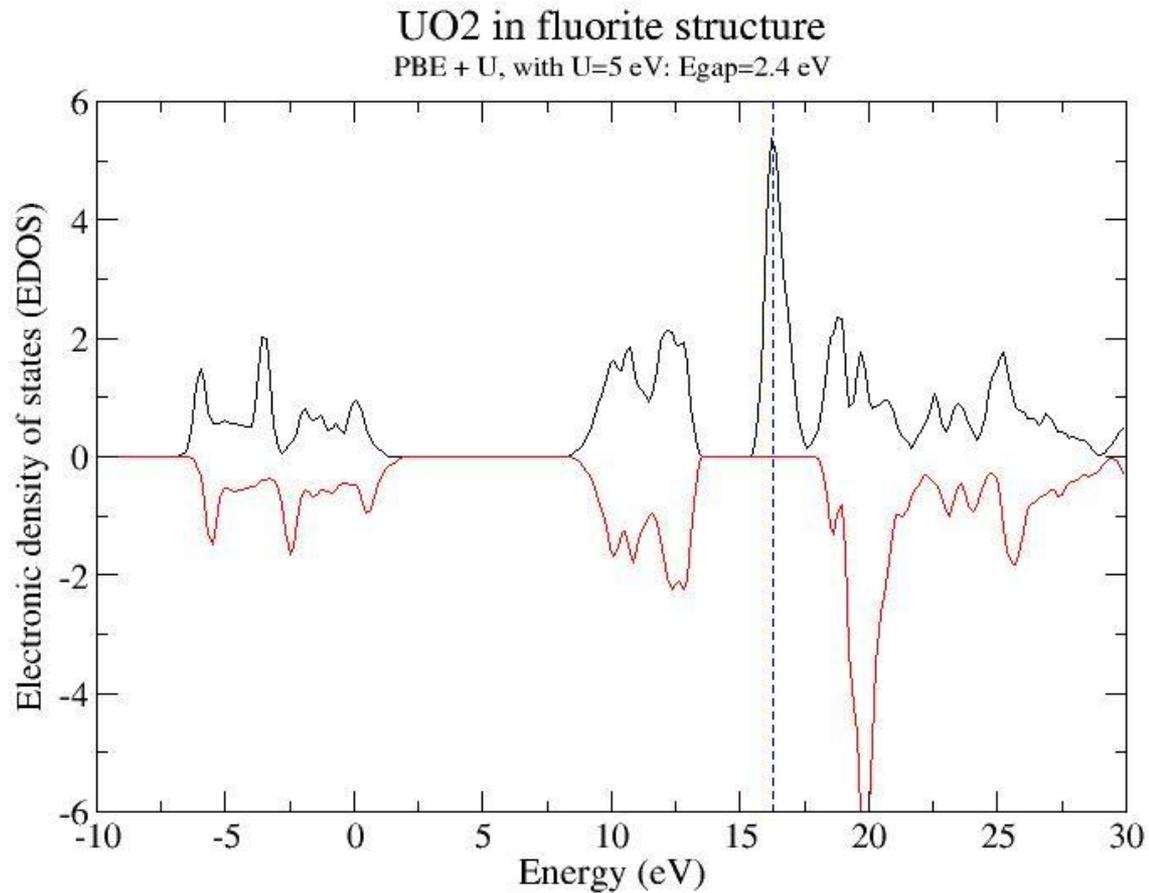
# ENERGY-VOLUME CURVE



# GGA(PBE) DENSITY OF STATES



# GGA+U DENSITY OF STATES



# GGA+U DENSITY OF STATES: DISTORTED

