Institut Néel
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Introduction to electronic structure calculations

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Ecole GdR Matériaux et Interactions en COmpétitions
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The Born-Oppenheimer approximation

System : *No* nucleus and *N* electrons

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$$\hat{H} = \overbrace{\hat{T}_n}^{\text{Nucl. kin. energy}} + \overbrace{\hat{T}_e}^{\text{Elec. kin. energy}} + \overbrace{\hat{v}_{ne}}^{\text{Elec.-nucl. attraction}} + \overbrace{\hat{v}_{ee}}^{\text{Elec.-elec repulsion}} + \overbrace{\hat{v}_{nn}}^{\text{Nucl.-nucl repulsion}}$$

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$$\hat{T}_n = -\sum_{a=1}^{No} \frac{\hbar^2}{2\,\mathbf{M_a}} \vec{\nabla}^2_{\vec{R}_a}$$

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$$\hat{T}_n = -\sum_{a=1}^{No} \frac{\hbar^2}{2\,\mathbf{M_a}} \vec{\nabla}^2_{\vec{R}_a} \qquad \hat{T}_e = -\sum_{i=1}^{N} \frac{\hbar^2}{2\,\mathbf{m_e}} \vec{\nabla}^2_{\vec{r}_i}$$

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$$\hat{v}_{ne} = -\frac{e^2}{4\pi\epsilon_0} \sum_{a=1}^{No} \sum_{i=1}^{N} \frac{Z_a}{|\vec{R}_a - \vec{r}_i|}$$

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$$\hat{v}_{ee} = \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^{N} \sum_{j=1}^{i-1} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

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$$\begin{aligned} \text{Electron mass} \quad m_{\bar{e}} &= 9,109\,53 \times 10^{-31}\ \text{kg} \\ \text{Proton mass} \quad m_p &= 1,672\,65 \times 10^{-27}\ \text{kg} \\ \text{Neutron mass} \quad m_n &= 1,674\,95 \times 10^{-27}\ \text{kg} \end{aligned}$$

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Approximation :

- Mobile electrons
- Fixed nucleus

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First step :

$$\hat{H}_e = \hat{T}_e + \hat{v}_{ne} + \hat{v}_{ee} + K$$

with $K = v_{nn}$

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$$\hat{H}_e \, |\Psi - e\rangle = E_e \, |\Psi_e\rangle$$

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$$\hat{H}_n = \hat{T}_n + E_e$$

$$\hat{H}_n \, |\xi_\nu\rangle = (\mathcal{E}_\nu + E_e) \, |\xi_\nu\rangle$$

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$$\hat{H}_n = \hat{T}_n + E_e$$
$$\hat{H}_n |\xi_\nu\rangle = (\mathcal{E}_\nu + E_e) |\xi_\nu\rangle$$

$$E = E_e + \mathcal{E}_\nu \qquad |\Psi\rangle = |\Psi_e\rangle \otimes |\xi_\nu\rangle$$

What type of information can we get ?

The electronic part

- The ground state energy ($E_e(\vec{R}_a)$)
- The ground state wave-function (charge, orders, etc...)
- Structural optimization ($\min_{\vec{R}_a} E_e(\vec{R}_a)$)
- The electronic excitation spectrum ($E_e^{(k)}(\vec{R}_a)$)
- dots

The nuclear part

- Phonons spectrum ($\mathcal{E}_\nu$)
- Dynamics
- Diffusion processes (impurity, vacancies etc...)
- dots

Solving the electronic problem

$$
\begin{aligned}
\hat{H}_e &= \hat{T}_e + \hat{v}_{ne} + \hat{v}_{ee} + v_{nn} \\
&= \sum_{i=1}^{N} \left[-\frac{\hbar^2}{2\,m_e} \vec{\nabla}^2_{\vec{r}_i} - \frac{e^2}{4\pi\epsilon_0} \sum_{a=1}^{No} \frac{Z_a}{|\vec{R}_a - \vec{r}_i|} \right] + \sum_{i=1}^{N} \sum_{j=1}^{i-1} \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_i - \vec{r}_j|} + v_{nn} \\
&= \underbrace{\sum_{i=1}^{N} \hat{h}_1(\vec{r}_i)}_{\text{simple}} + \underbrace{\sum_{i=1}^{N} \sum_{j=1}^{i-1} \hat{h}_2(\vec{r}_i, \vec{r}_j)}_{\text{difficult}} + v_{nn}
\end{aligned}
$$

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&= \underbrace{\sum_{i=1}^{N} \hat{h}_1(\vec{r}_i)}_{\text{dominant}} + \underbrace{\sum_{i=1}^{N} \sum_{j=1}^{i-1} \hat{h}_2(\vec{r}_i, \vec{r}_j)}_{\text{dominated by average}} + v_{nn}
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$$

$$
\sum_{i=1}^{N} \sum_{j=1}^{i-1} \hat{h}_2(\vec{r}_i, \vec{r}_j) \longrightarrow \sum_{i=1}^{N} \delta\hat{h}_1(\vec{r}_i)
$$

Solving the electronic problem

The one-particle approximation

$$\sum_{i=1}^{N} \hat{h}_1(\vec{r}_i) + \sum_{i=1}^{N} \sum_{j=1}^{i-1} \hat{h}_2(\vec{r}_i, \vec{r}_j) \longrightarrow \sum_{i=1}^{N} \left[\hat{h}_1(\vec{r}_i) + \delta\hat{h}_1(\vec{r}_i) \right]$$

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From a N electrons problem to a 1 electron problem

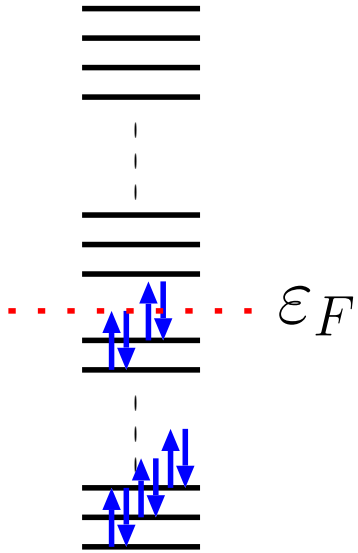
$$\begin{aligned} \text{From} \quad & \hat{H}_e \, |\Psi_e(\vec{r}_1, \ldots, \vec{r}_N)\rangle = E_e \, |\Psi_e(\vec{r}_1, \ldots, \vec{r}_N)\rangle \\ \text{to} \quad & \left(\hat{h}_1 + \delta\hat{h}_1\right) \varphi_k(\vec{r}) = \varepsilon_k \, \varphi_k(\vec{r}) \end{aligned}$$

Solving the electronic problem

The one-particle approximation

$$\sum_{i=1}^{N} \hat{h}_1(\vec{r}_i) + \sum_{i=1}^{N}\sum_{j=1}^{i-1} \hat{h}_2(\vec{r}_i,\vec{r}_j) \longrightarrow \sum_{i=1}^{N} \left[\hat{h}_1(\vec{r}_i) + \delta\hat{h}_1(\vec{r}_i)\right]$$

From the 1 electron system to the N electrons one



Filling following Hund's rules

$$|\Psi_e(\vec{r}_1,\ldots,\vec{r}_N)\rangle = |\varphi_1(\vec{r}_1)\ldots\varphi_N(\vec{r}_N)\rangle$$

$$E_e = \sum_{i=1}^{n} \varepsilon_i + v_{nn}$$

Mean-field approximation on electron positions

$$\sum_{i=1}^{N} \sum_{j=1}^{i-1} \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_i - \vec{r}_j|} \longrightarrow \sum_{i=1}^{N} \frac{e^2}{4\pi\epsilon_0} \left\langle \frac{1}{|\vec{r}_i - \vec{r}_j|} \right\rangle_{\vec{r}_j}$$

- The average is taken over the ground-state wave-function

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- The average is taken over the ground-state wave-function
- Fock operator $\hat{F} = \hat{h}_1 + \delta\hat{h}_1$ depends on its solution
- Lowest energy Slater determinant
- $\hat{F}$ treats exactly
  - Kinetic energy
  - Nuclear attraction
  - Coulomb repulsion energy
  - Exchange energy

$\hat{F}$ does not contain

- Correlation energy (correlation between electrons positions)

Solving the electronic problem for the ground state

The Hartree-Fock approximation

Advantages

- Well defined method
- Much less costly than N-body methods
- Easy to improve on it (perturbation theory etc. . .)

Drawbacks

- A tendency to pair localize the electrons
- Over-estimate the gaps
- Still too costly for very large systems

The fundamental theorems

- There is a one to one correspondence between nuclear positions and GS electronic density

$$\hat{v}_{ne} \leftrightarrow n(\vec{r})$$

- The GS density is the N-representable density associated with the lowest energy

$$Min_{n(\vec{r}),\, N-rep.}\, E[n(\vec{r})]$$

Solving the electronic problem for the ground state

The Density Functional Theory

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A major problem

Nobody knows how to get

- An exact functional for $E[n(\vec{r})]$
- Even for the kinetic energy part

Back to a one-electron pb : the Kohn-Sham approximation

A N-electron pb :		An effective 1-electron pb :
$\hat{H}(\vec{r}_1 \dots \vec{r}_N)$	$\longrightarrow$	$\hat{H}_{\text{eff}} = \sum_{i=1}^{N} \hat{h}_{\text{KS}}(\vec{r}_i)$
$\lvert\Psi(\vec{r}_1 \dots \vec{r}_N)\rangle$	$\longrightarrow$	$\lvert\varphi_1(\vec{r}_1) \dots \varphi_N(\vec{r}_N)\rangle$
Density $n(\vec{r})$	$\longrightarrow$	Density $n_{\text{KS}}(\vec{r}) = n(\vec{r})$

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Kinetic energy $\hat{T}_e$	$\longrightarrow$	Kinetic ener. of $1\bar{e}$ pb : $\hat{T}_{\text{KS}}$

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$\hat{v}_{ee}$	$\longrightarrow$	$\hat{v}_{\text{Hartree}}[n] + \hat{v}_{\text{xc}}[n]$ $\hat{v}_{\text{Hartree}}[n] = \frac{e^2}{4\pi\epsilon_0} \int \frac{n(\vec{r}')}{\lvert\vec{r}' - \vec{r}\rvert} d\vec{r}'\, n(\vec{r})$ $\hat{v}_{\text{xc}}[n] = ??$

The $\hat{v}_{\mathbf{xc}}[n]$ functionals

- **LDA/LSDA** Local Density Approximation
  $\hat{v}_{\mathrm{xc}}[n] =$ homogeneous $\bar{e}$ gas
  Perdew et Zunger (PZ), Vosko Wilkes and Nusiar (VWN)

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- **LDA/LSDA** Local Density Approximation
  $\hat{v}_{xc}[n] =$ homogeneous $\bar{e}$ gas
  Perdew et Zunger (PZ), Vosko Wilkes and Nusiar (VWN)

  - Easy, fast
  - OK for Fermi $\bar{e}$ of metals
  - Bad for core $\bar{e}$
  - Only local $f(n(\vec{r}))$
    exch.-corr. : non local $f(\vec{r}, \vec{r}')$
  - Self-inter. pb
  - Overdelocalize
  - Underestimates gaps
  - No dispersion forces

The $\hat{v}_{xc}[n]$ functionals

- **GGA** Generalized Gradient Approximation
  Add semi-local terms : $f(n(\vec{r}), \vec{\nabla}_{\vec{r}}(n(\vec{r}))$
  Perdew-Burke-Ernzerhof (PBE, PBESOL), Perdew-Wang 91 (PW91), BLYP, second order (SOGGA), Perdew-Wang (PW), Wu-Cohen (WC)
  - A little better than LDA
  - Still same pb

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The $\hat{v}_{xc}[n]$ functionals

- **Hybrids functionals**
  Mix of LDA - GGA - HF exact exchange
  B3LYP, B3PW, PBE0 and PBESOL0, B1PW, B1WC

  - Best GS energies
  - Good structures
  - Part self-inter. pb
  - Gaps

  - Bad for core $\bar{e}$
  - No dispersion forces
  - More costly
  - Cooking recipe

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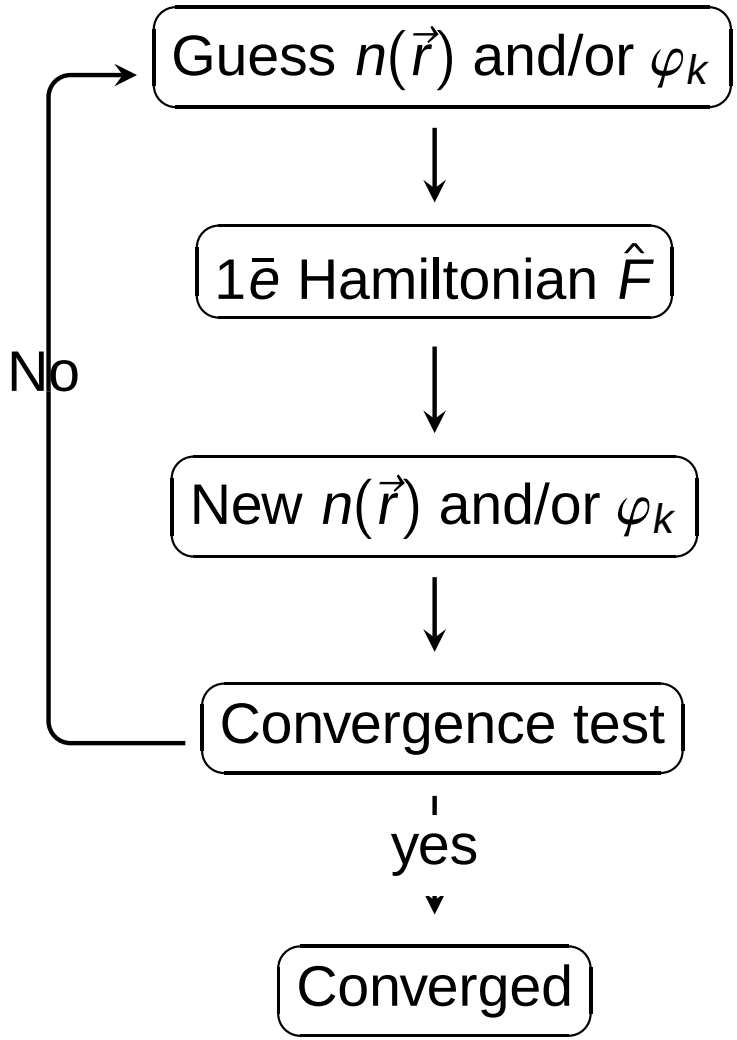
- **Double Hybrid functionals** Dispersion forces
  Mix LDA - GGA - HF exchange - 2^{nd} order pert. (Grimme)

Solving the electronic problem for the ground state

The SCF procedure

1$\bar{e}$ Hamiltonian $\hat{F}$ depends on its solution $\Rightarrow$ SCF



$1\bar{e}$ Hamiltonian projected on a finite basis set

- Plane waves (CASTEP, AbInit. . .)
- Atom centered gaussians (radial) + Y_{lm} (angular) CRYSTAL
- Atom centered staler (radial) + Y_{lm} (angular) SIESTA
- Atom centered numerical basis sets SIESTA, AdfBand
- Numerical grids
- Wavelets on grids BigDFT

Solving the electronic problem for the ground state

The basis sets

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Inner electrons

- All electrons
- Pseudopotentials
- Atomic functions within muffin-tin spheres

Solving the electronic problem for the ground state

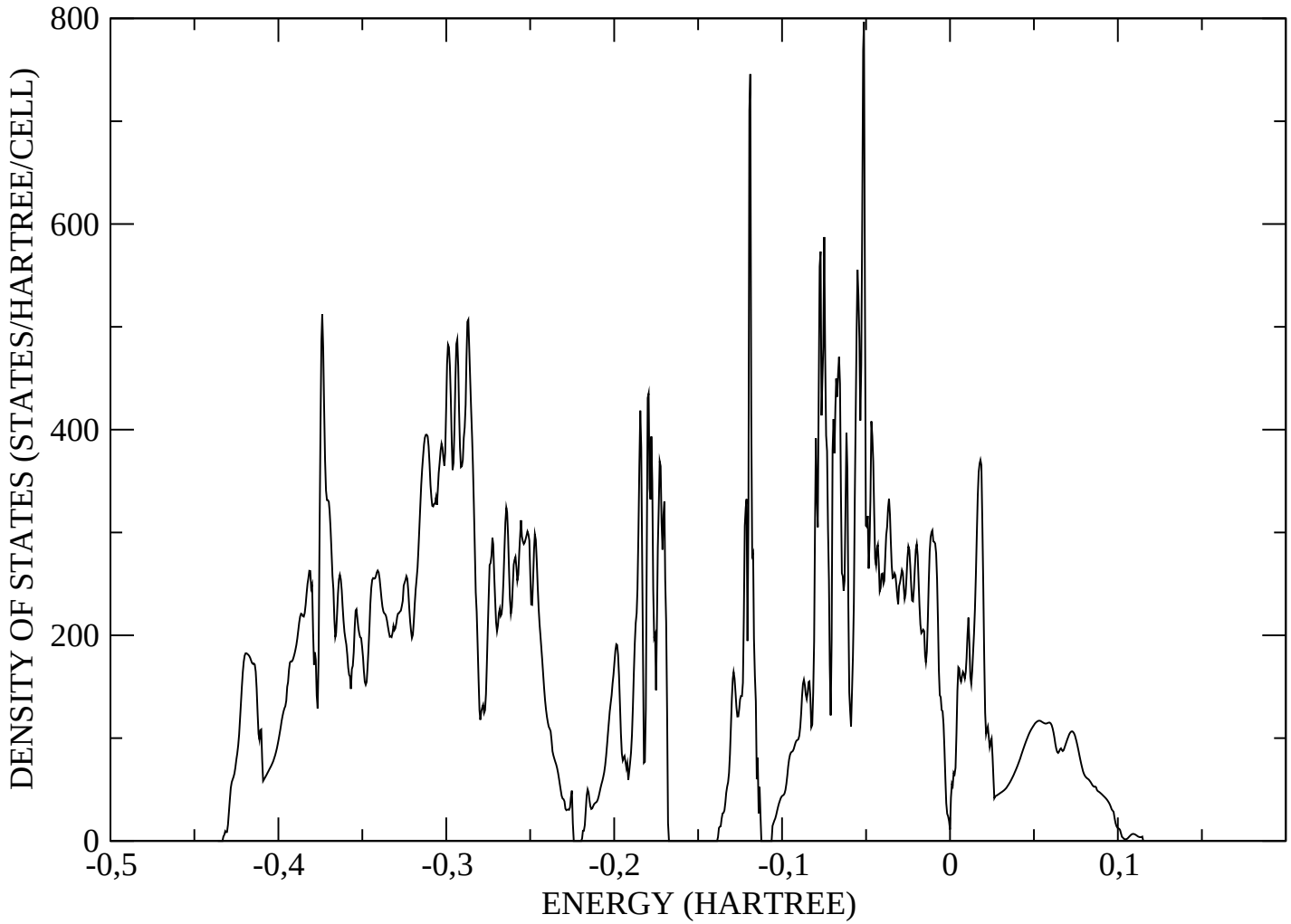
Do not forget

Test numerical parameters

- Type of pseudopotential
- Heavy elements : relativistic corrections
- Plane waves : energy cutoff
- Atomic basis sets : basis set quality
- $\vec{k}$ points convergence
- Metals : smearing temperature
- Phonons : geom. opt. convergence (negative phonons)

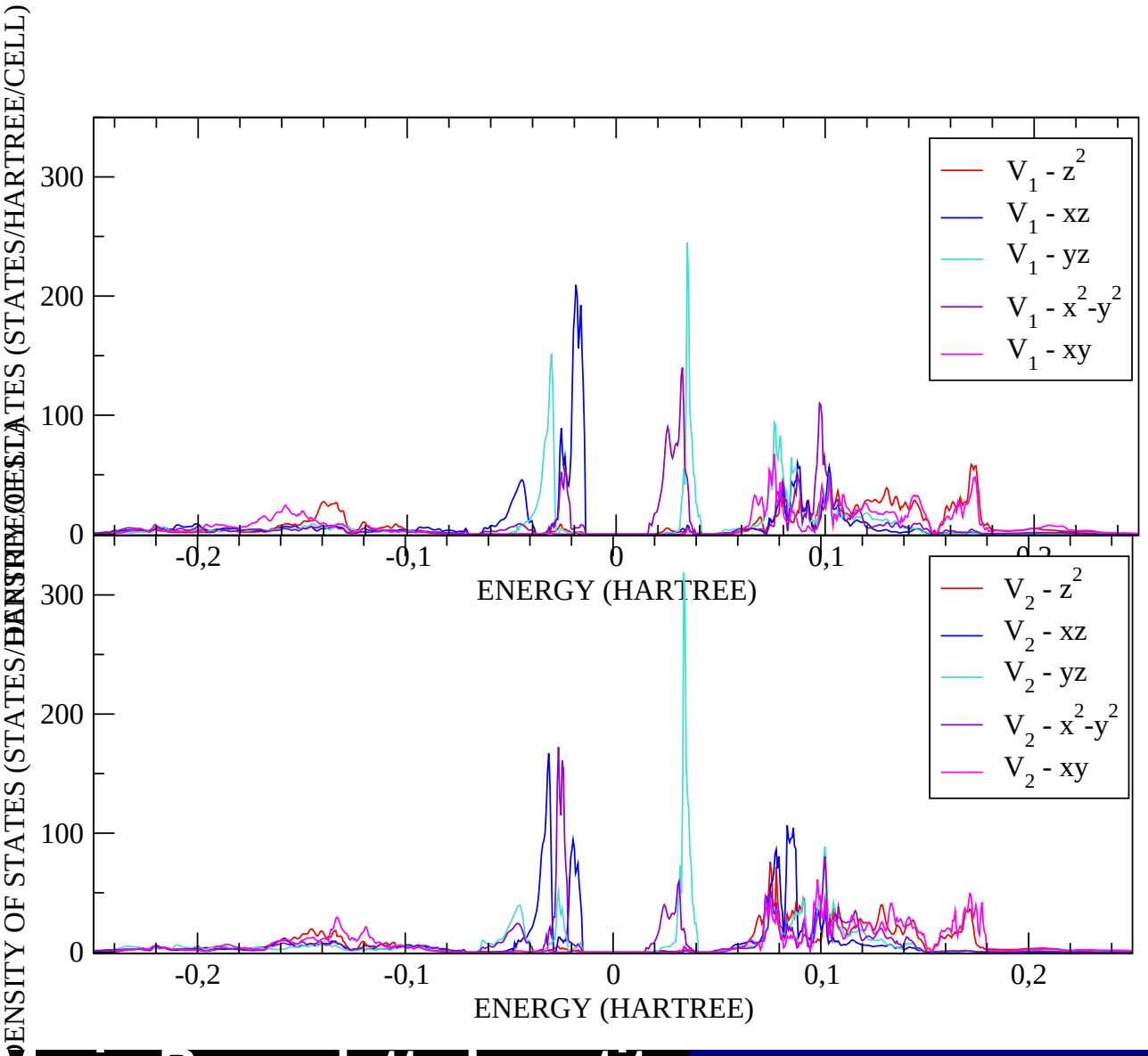
Electronic solution yield many properties

DOSS and PDOSS



Electronic solution yield many properties

DOSS and PDOSS



Conclusion

- Useful methods
- Easy to interpret (1$\bar{e}$ picture)
- Access many properties
- **Do not use as a black box**

- Works well for weakly correlated systems
- Works well for prop. slightly dependent on Fermi level $\bar{e}$
  (geometries, phonons, polarisation, etc . . .)
- **Careful with magnetism**
  (may work reasonably but also be all wrong)

- **Remember to test for validity and computational parameters**