A Short Lecture on Electronic Structure Theory for Experimental Condensed Matter Physicists

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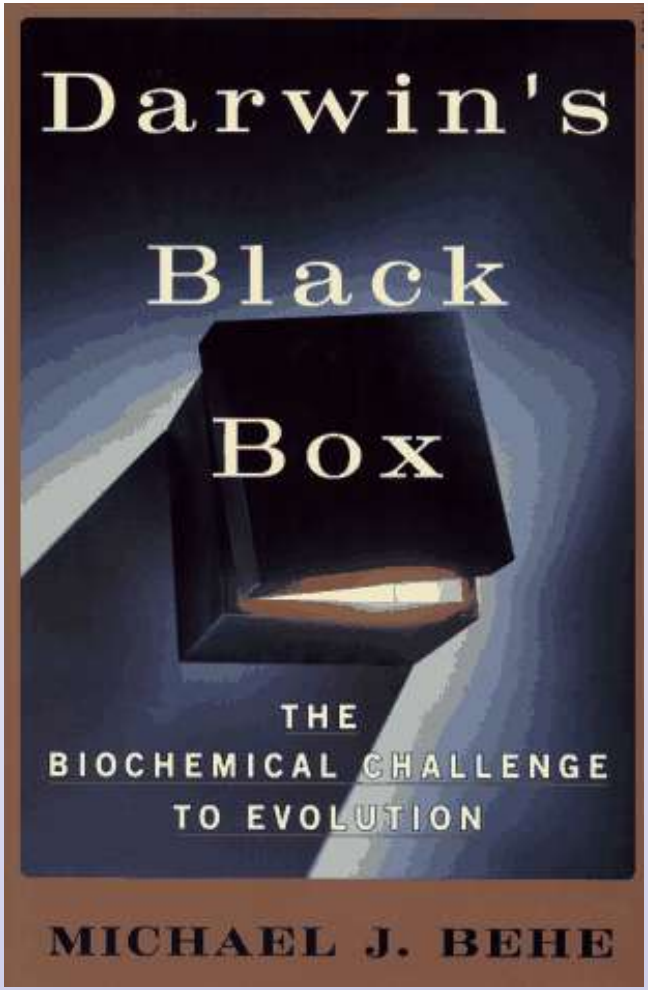
Frequently Asked Questions

1. First-principles? *What the heck is it?*
2. What is "density functional theory" for?
3. What can we learn from "total energies"?
4. When does it works or when does not?
5. LDA, GGA, GW, LDA+U, screened-X;
   What do they mean by these acronyms?
6. Does "pseudo-potential" make a sense to you?
7. Band structure? What is it for?
8. Computational materials physics:
   a new paradigm in material sciences

First-principles? What the heck is it?

- *"Ab initio"* or *"first principles"* means "starting from the self-consistent electronic structure based on the *density functional theory*.
- Approximations:
  - Born-Oppenheimer (with fixed ionic positions)
  - LDA (local-density approximation) or GGA (generalized gradient approximation)
  - and some technical (controlled) approximations

Is it like something "a black box"?



A microscopic
picture
provided by
...
"computations"
based on
first-principles.

What is "density functional theory" for?

- Hohenberg-Kohn theorem (1964):
- The total energy of the ground state of a many-electron system:

$$E(\{\boldsymbol{R}_i\}) = \langle \Psi | \hat{H}(\{\boldsymbol{R}_i\}) | \Psi \rangle$$

- a unique density function $n(\boldsymbol{r})$ for a given external potential $v(\boldsymbol{r}) = v(\boldsymbol{r}, \{\boldsymbol{R}_i\})$:

$$n(\boldsymbol{r}) = n(\Psi_v) = \langle \Psi | \hat{\psi}^{+}(\boldsymbol{r}) \hat{\psi}(\boldsymbol{r}) | \Psi \rangle$$

- The ground state and its properties can be determined by the density $n(\boldsymbol{r})$:

$$E_0(\{\boldsymbol{R}_i\}) = min_{n(\boldsymbol{r})} E_{v(\{\boldsymbol{R}_i\})}[n]$$

$$\Psi_v(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N) = \Psi[n(\boldsymbol{r})]$$

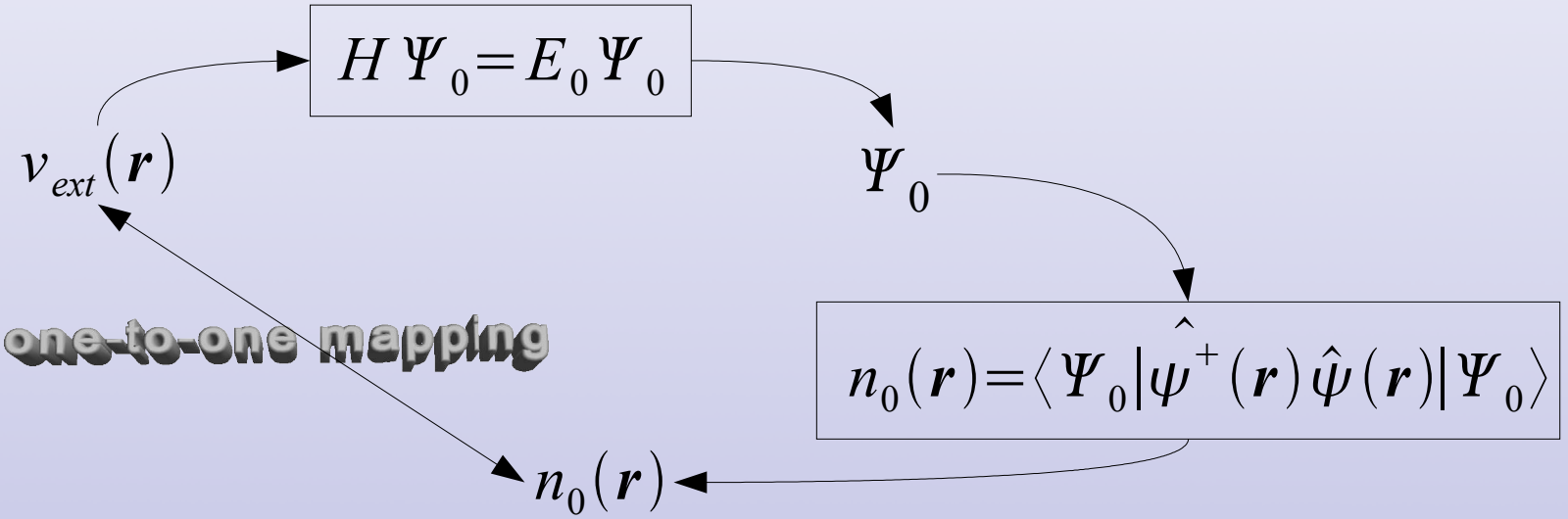
The Hohenberg-Kohn Theorem

- Interacting many-electron Hamiltonian:

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i<j}\frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} + \sum_{i=1}^{N} v_{ext}(\boldsymbol{r}_i)$$

- External potential:

$$v_{ext}(\boldsymbol{r}) = v(\boldsymbol{r}, \{\boldsymbol{R}_i\}; \boldsymbol{B}; \boldsymbol{E}; \cdots)$$



Density: a basic variable for the interacting electrons

- Ground state properties depends on $n_0(\boldsymbol{r})$

$$\langle \hat{O} \rangle = \langle \Psi_0[n_0] | \hat{O} | \Psi_0[n_0] \rangle$$

- $n_0(\boldsymbol{r})$: a basic variable

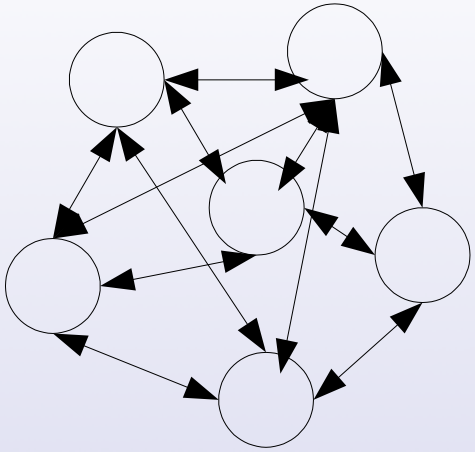
- Variational determination of $n_0(\boldsymbol{r})$ and $E_0[n_0]$ with the constraint $\int_V n(\boldsymbol{r})\, d\boldsymbol{r} = N$

$$\delta\left(E_v[n] - \mu\left(N - \int_V n(\boldsymbol{r})\, d\boldsymbol{r} \right) \right) = 0$$

- Now how do we evaluate this? There still remain many-body interactions ...

The "Kohn-Sham" Way …

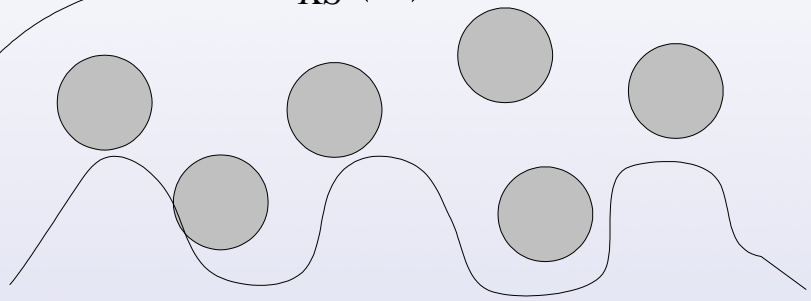
- Mapping the $n_0(\boldsymbol{r})$ of "interaction *N*-electrons" into that of fictitious particle moving under an effective potential:



interacting electrons

$n_0(\boldsymbol{r})$

$n_{KS}(\boldsymbol{r})$



non-interacting electrons
under an effective potential

$$n_{KS}(\boldsymbol{r}) = \sum_n |\phi_n(\boldsymbol{r})|^2 f(\epsilon_n)$$

$$\left[-\frac{1}{2}\nabla^2 + V_{eff}(\boldsymbol{r};n_0) + v_{ext}(\boldsymbol{r};n_0;\{\boldsymbol{R_i}\})\right]\phi_n(\boldsymbol{r}) = \epsilon_n^{KS}\phi_n(\boldsymbol{r})$$

Total energy of the interacting electron system

- Total energy functional:

$$E_{v(\{\boldsymbol{R}_i\})}[n(\boldsymbol{r})] = \int d^3\boldsymbol{r}\, v(\boldsymbol{r};\{\boldsymbol{R}_i\})\, n(\boldsymbol{r}) + T_s[n] + \frac{1}{2}\int\int d^3\boldsymbol{r}\, d^3\boldsymbol{r}'\, \frac{n(\boldsymbol{r})\, n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + E_{xc}[n]$$

- Approximations to the exchange-correlation functional:
  - LDA (local density approximation)
  - GGA (generalized gradient approximation)
  - Screened-exchange functional
  - GW
  - LDA+U
  - ...
- Accurate estimation of the total energy for a given configuration of $\{\boldsymbol{R}_i\}$

Exchange-Correlation Potential

- Effective potential in a KS formalism

$$V_{eff}(\boldsymbol{r};n_0)=\int d\boldsymbol{r}'\frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}+V_{xc}(\boldsymbol{r})$$

$$V_{xc}(\boldsymbol{r};n_0)=\frac{\delta E_{xc}[n]}{\delta n(\boldsymbol{r})}_{n=n_0}$$

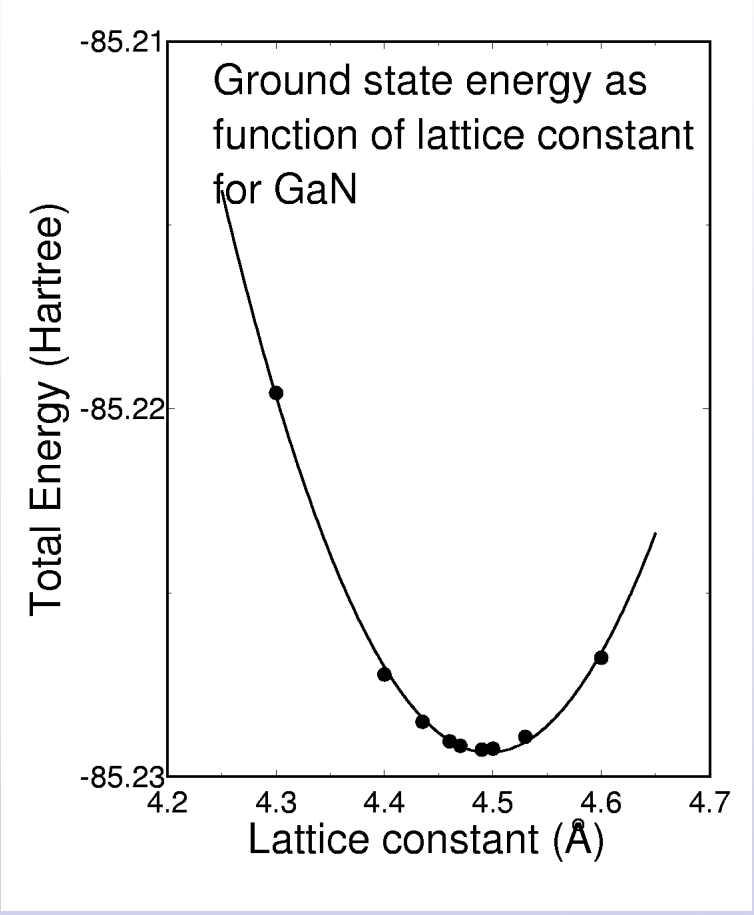
- Local density approximation for
  - Exchange-correlation potential of the homogeneous electron gas as a function of density, not as a functional!
  - For the slowly varying density,

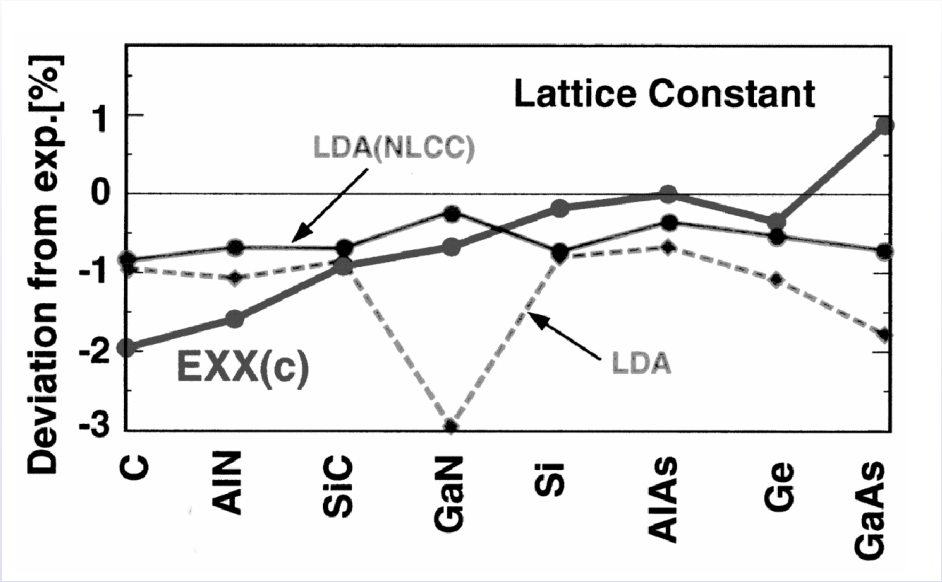
$$E_{xc}^{inhomo}[n]\approx\int n(\boldsymbol{r})\epsilon_{xc}^{homo}(n(\boldsymbol{r}))d\boldsymbol{r}$$

$$V_{xc}^{LDA}(\boldsymbol{r})\approx\frac{\delta E_{xc}^{homo}[n(\boldsymbol{r})]}{\delta n(\boldsymbol{r})}$$

What can we learn from "total energies"?

- LDA works for the most cases

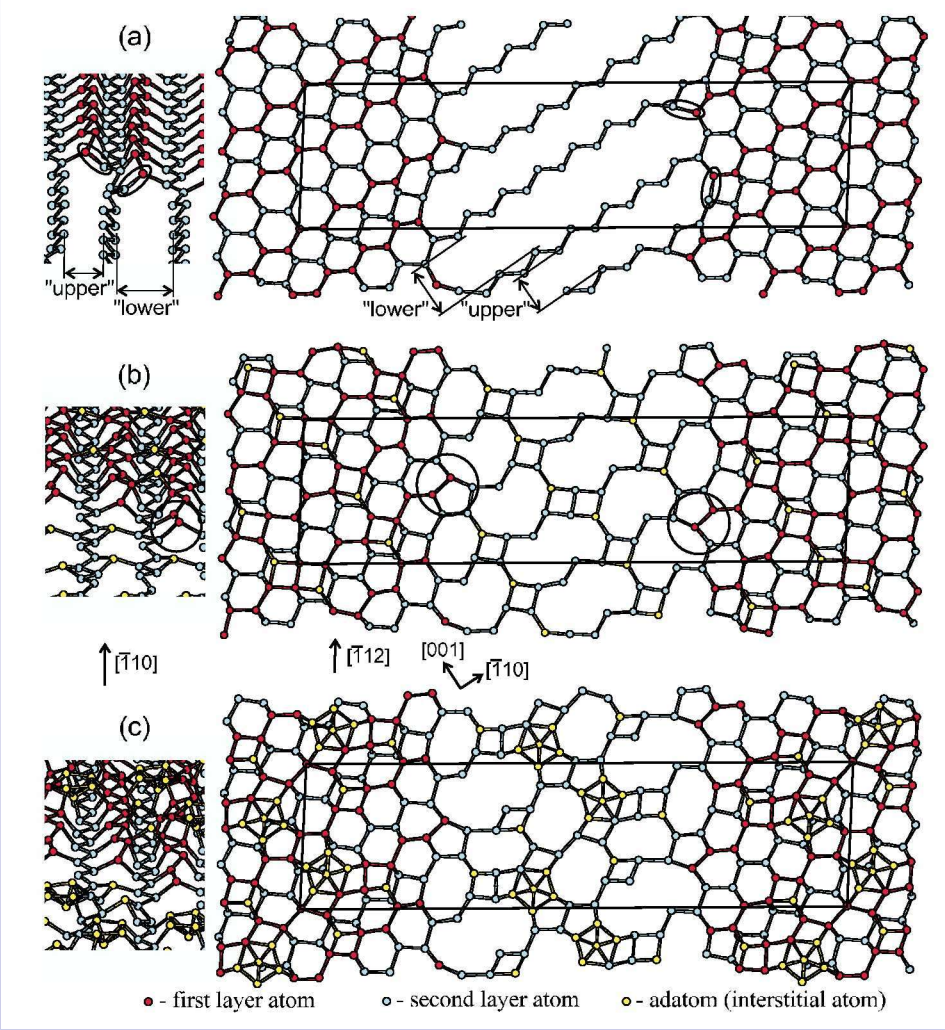


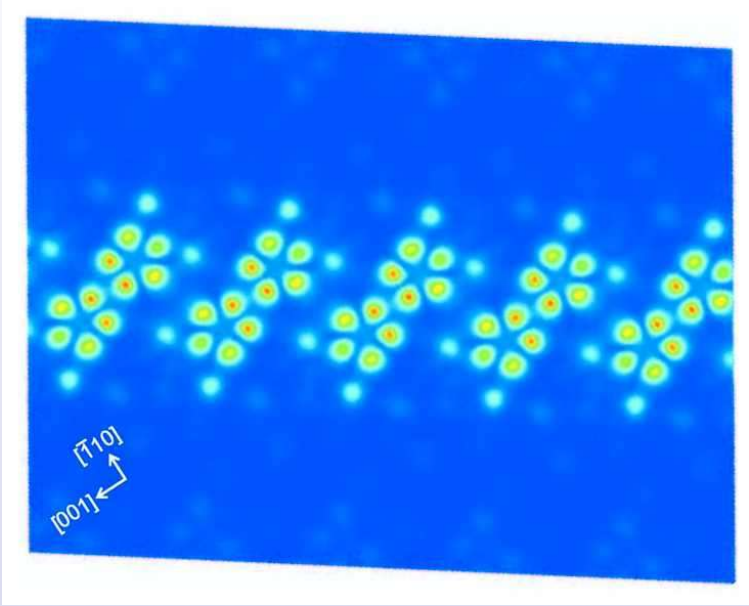


- Total energy results predicts the lattice constants within ~2%

Example:
Long Range Surface Reconstruction: Si(110) - (16x2)

[Ref] A.A. Stekolnikov et al., Phys. Rev. Lett. 93 (2004)

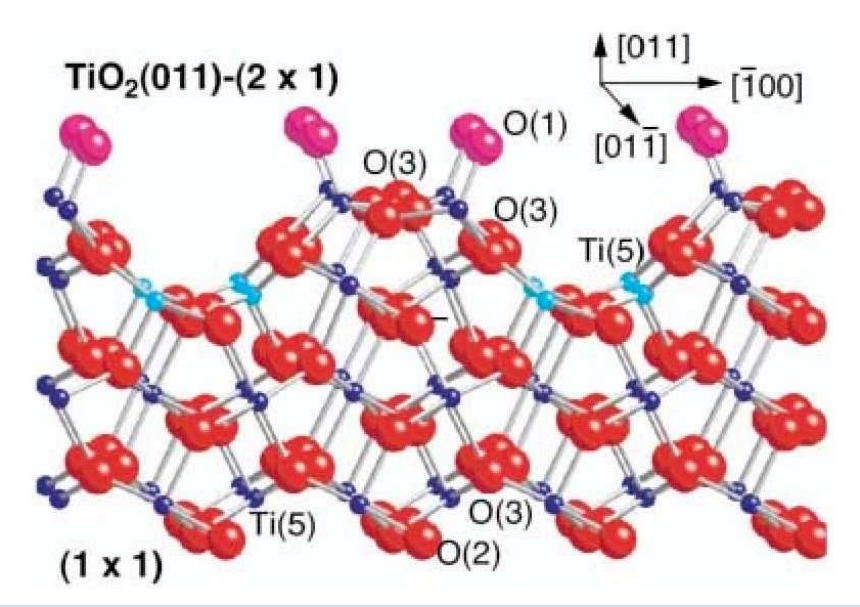


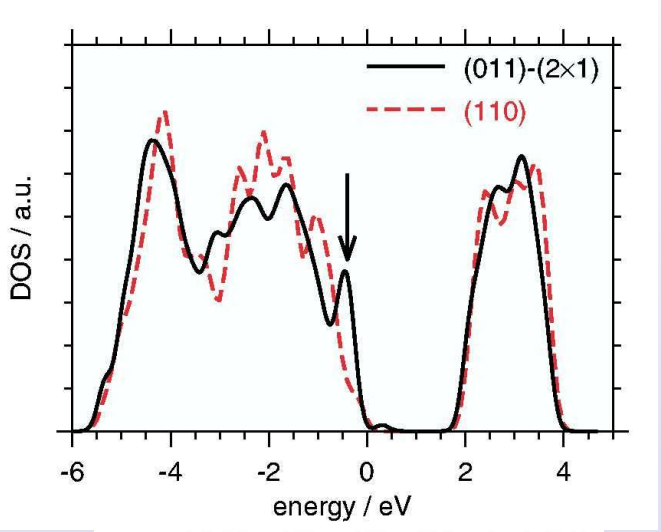


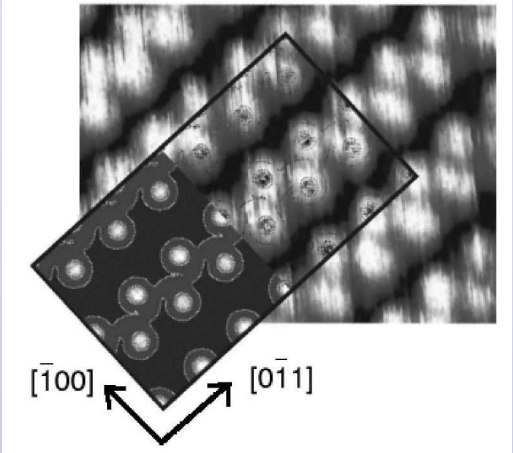
Simulated STM Image

Example:
Surface Structure of TiO_2(011)-(2x1)

[Ref] T.J. Beck et al., Phys. Rev. Lett. 93 (2004)





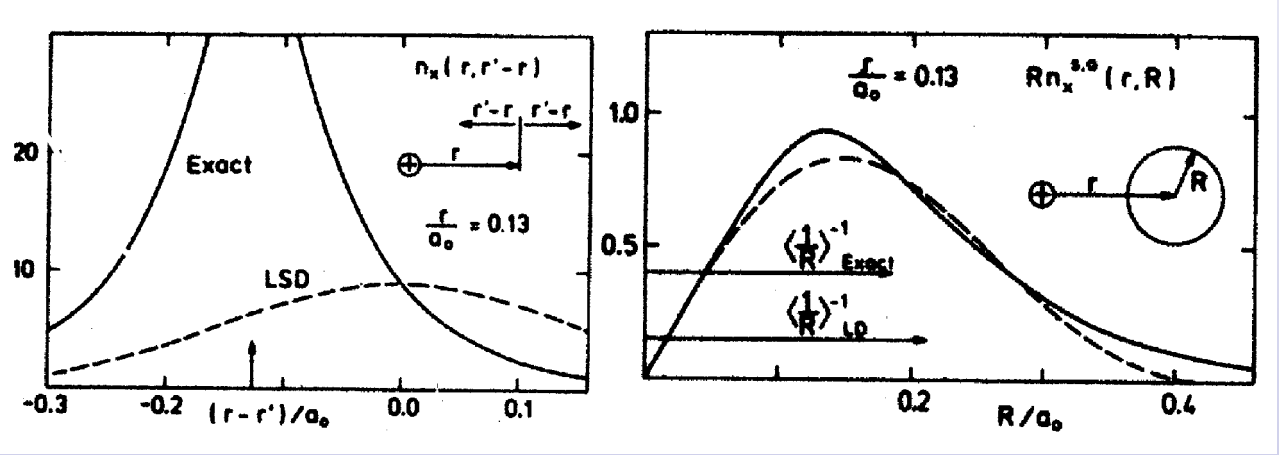


When does it works or when does not?

- LDA works well ...
  - ✔ Errors in the approximation E_x and E_c cancels each other.
  - ✔ LDA satisfies the sum rule for the exchange-correlation hole:

$$\int d\boldsymbol{r}'\, n_{xc}(\boldsymbol{r}, \boldsymbol{r}'-\boldsymbol{r}) = -1$$

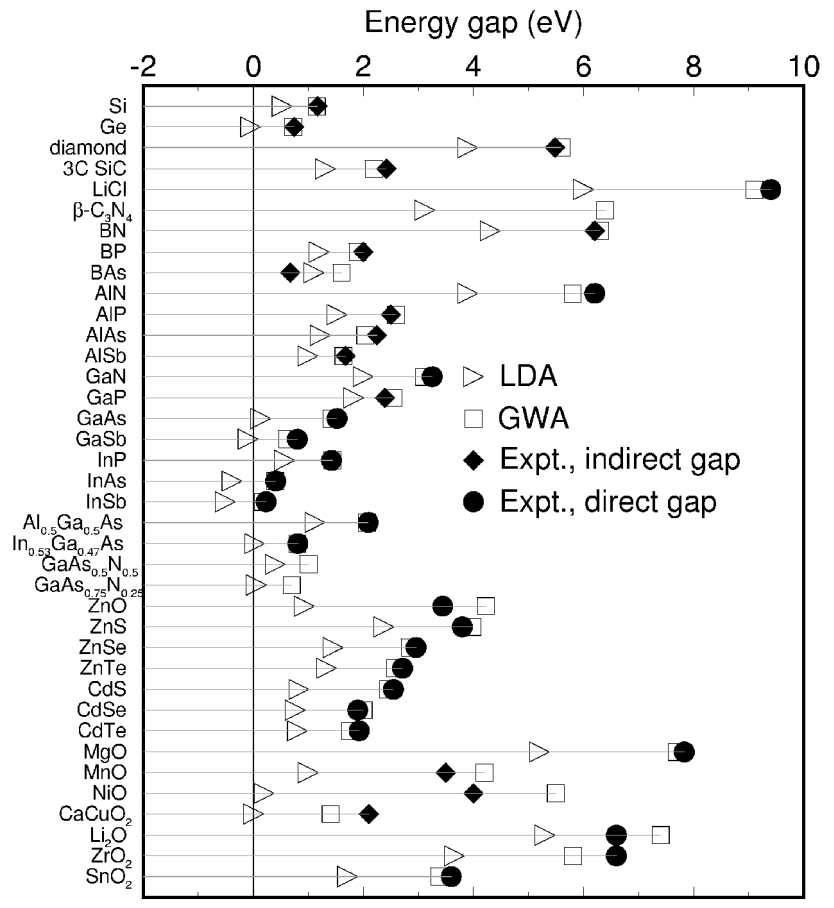
$$n_{xc}(\boldsymbol{r}, \boldsymbol{r}') = n(\boldsymbol{r}')[g(\boldsymbol{r}, \boldsymbol{r}')-1]$$



When does it works or when does not?

- But, it fails ...
- when it deals with the excited state properties

  - ✔ Band-gap problems
  - ✔ Self-interaction problems
  - ✔ Mirror image charges
  - ✔ Two-body correlations
  - ✔ ...



LDA, GGA, GW, LDA+U, screened-X;

What do they mean by these acronyms?

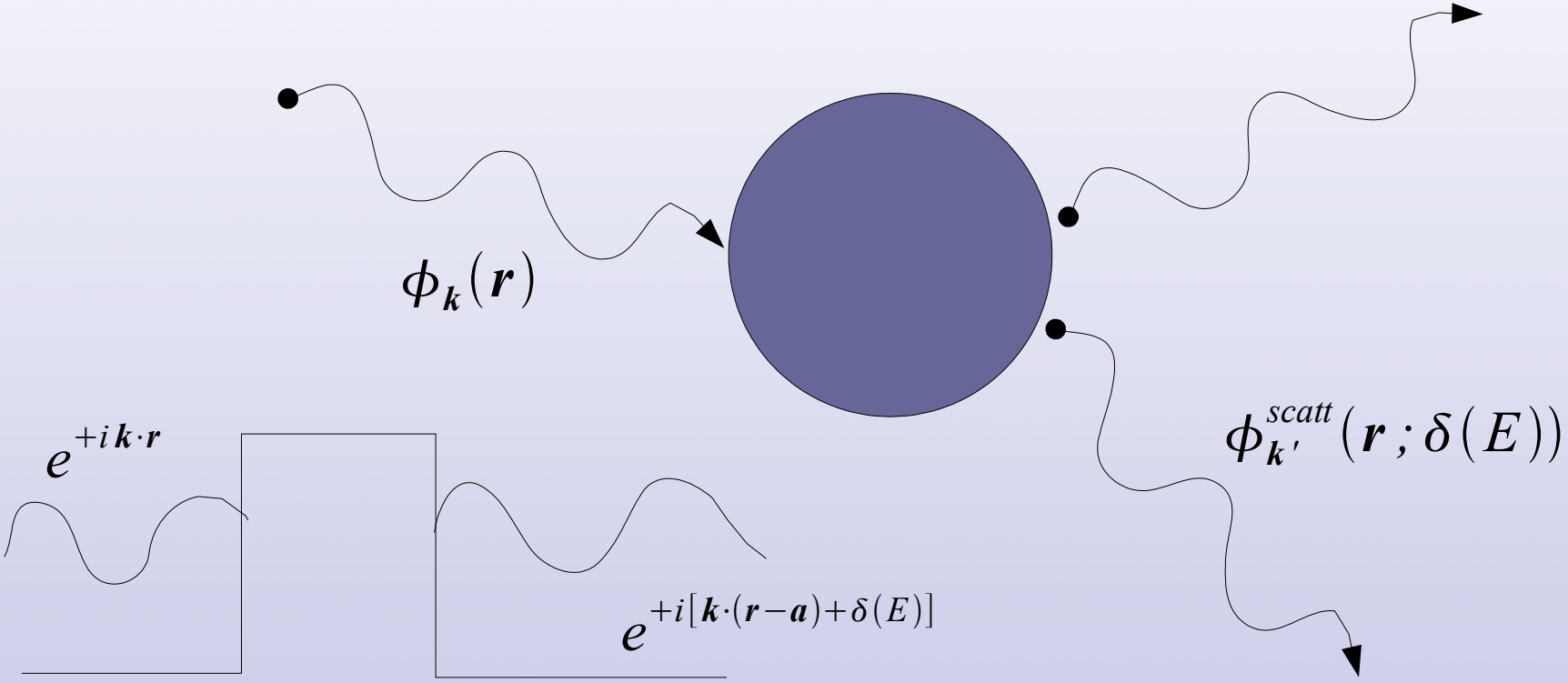
- LDA = local density approximation
- GGA = generalized gradient approximation
  - Include the density gradient for the higher order correction
  - preserving the sum rule for the exchage-correlation hole
- GW = Green's function + screened interaction potential
  - Self-energy correction by

$$\Sigma(\boldsymbol{r},\boldsymbol{r}';\omega)\approx G(\boldsymbol{r},\boldsymbol{r}';\omega)\epsilon^{-1}(\boldsymbol{r},\boldsymbol{r}';\omega)V_C(\boldsymbol{r},\boldsymbol{r}')$$

- LDA+U
  - Unrestricted Hartree-Fock treatments for the localized orbital states
- Screened-X
  - A linear combination of LDA and an exact exchange interaction term

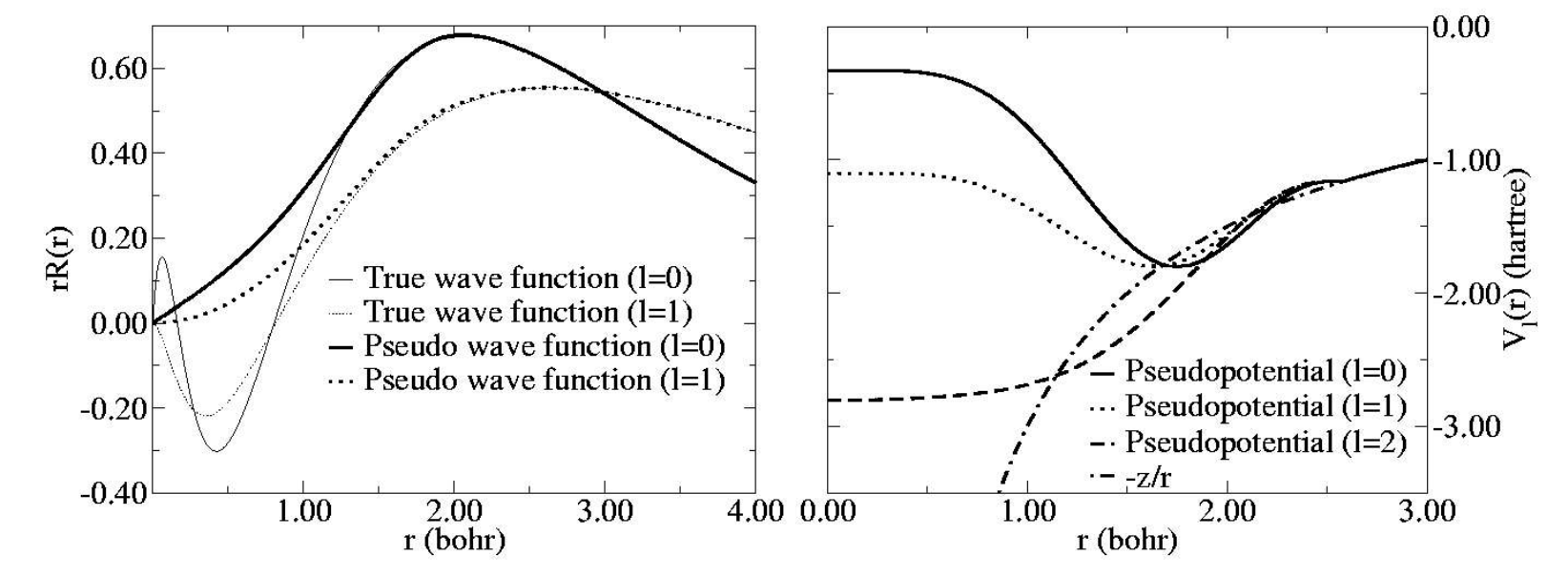
Does "pseudo-potential" make a sense to you?

- Interactions between valence electrons and core states can be replaced by a "pseudo-potential", which provides exactly the same scattering properties mimicking the role of core states.



Pseudo-potential: matching the boundary conditions

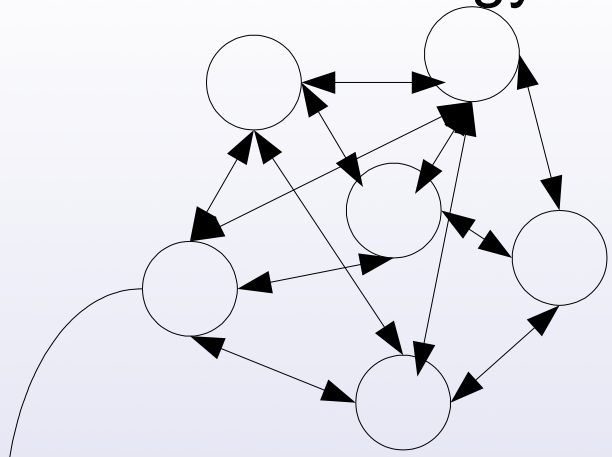
- Pseudo-potential for Al



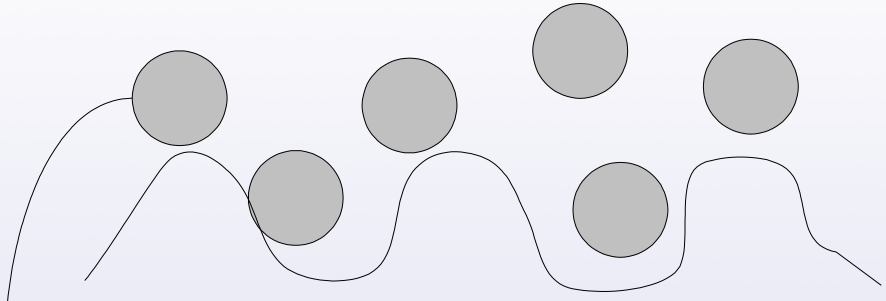
$$\frac{d}{dr}\ln\left[rR_{nl}^{AE}(r)\right]_{r=r_c-0}=\frac{d}{dr}\ln\left[r\,\bar{R}_{nl}(r)\right]_{r=r_c+0}$$

Band structure? What is it for?

- Is it the energy of a real electron which we measure?

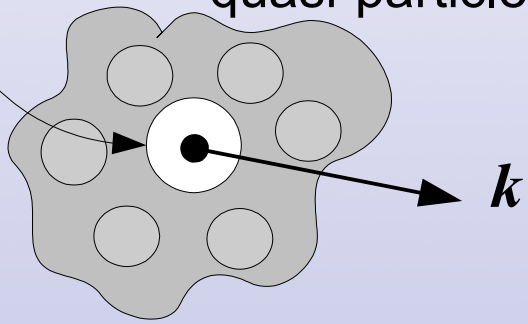


interacting electrons



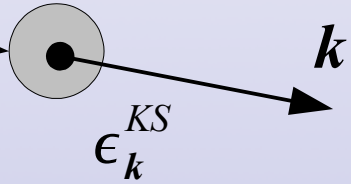
non-interacting electrons
under an effective potential

quasi-particle



$$E_{\boldsymbol{k}}^{qp} = \epsilon_{\boldsymbol{k}}^{KS} + \Sigma_{\boldsymbol{k}}\left(E_{\boldsymbol{k}}^{qp}\right)$$

Kohn-Sham "fictitious" particle

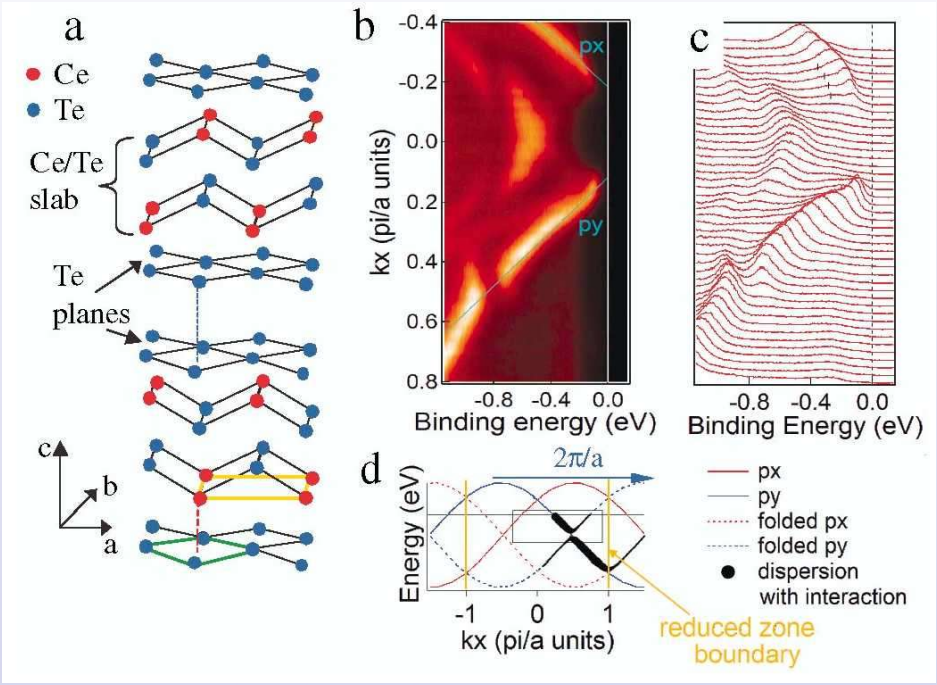


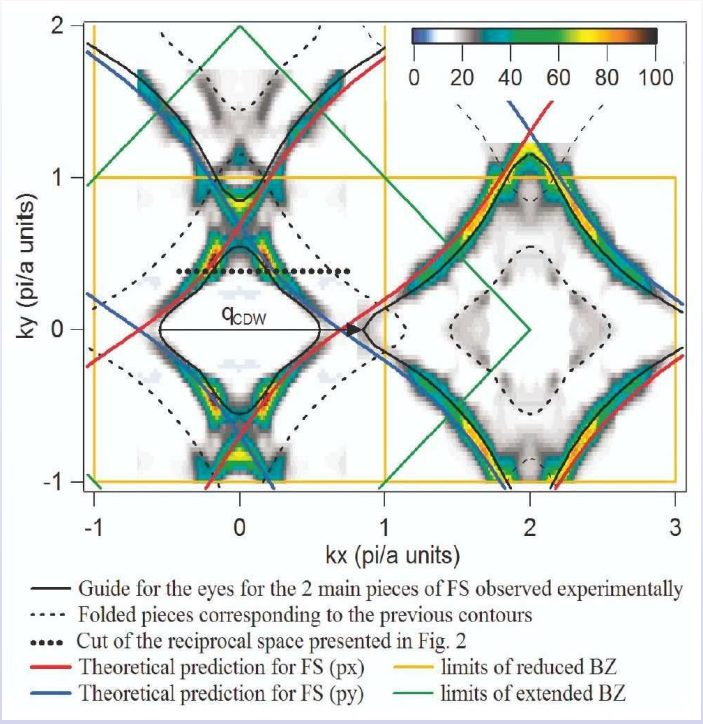
$$\left[-\frac{1}{2}\nabla^2 + V_{eff}(\boldsymbol{r};n_0) + v_{ext}(\boldsymbol{r};n_0;\{\boldsymbol{R_i}\})\right]\phi_{n\boldsymbol{k}}(\boldsymbol{r}) = \epsilon_{n\boldsymbol{k}}^{KS}\phi_{n\boldsymbol{k}}(\boldsymbol{r})$$

Fermi Surface in the CDW State of CeTe3

comparison with photoemission

[Ref] V. Brouet et al., Phys. Rev. Lett. 93 (2004)

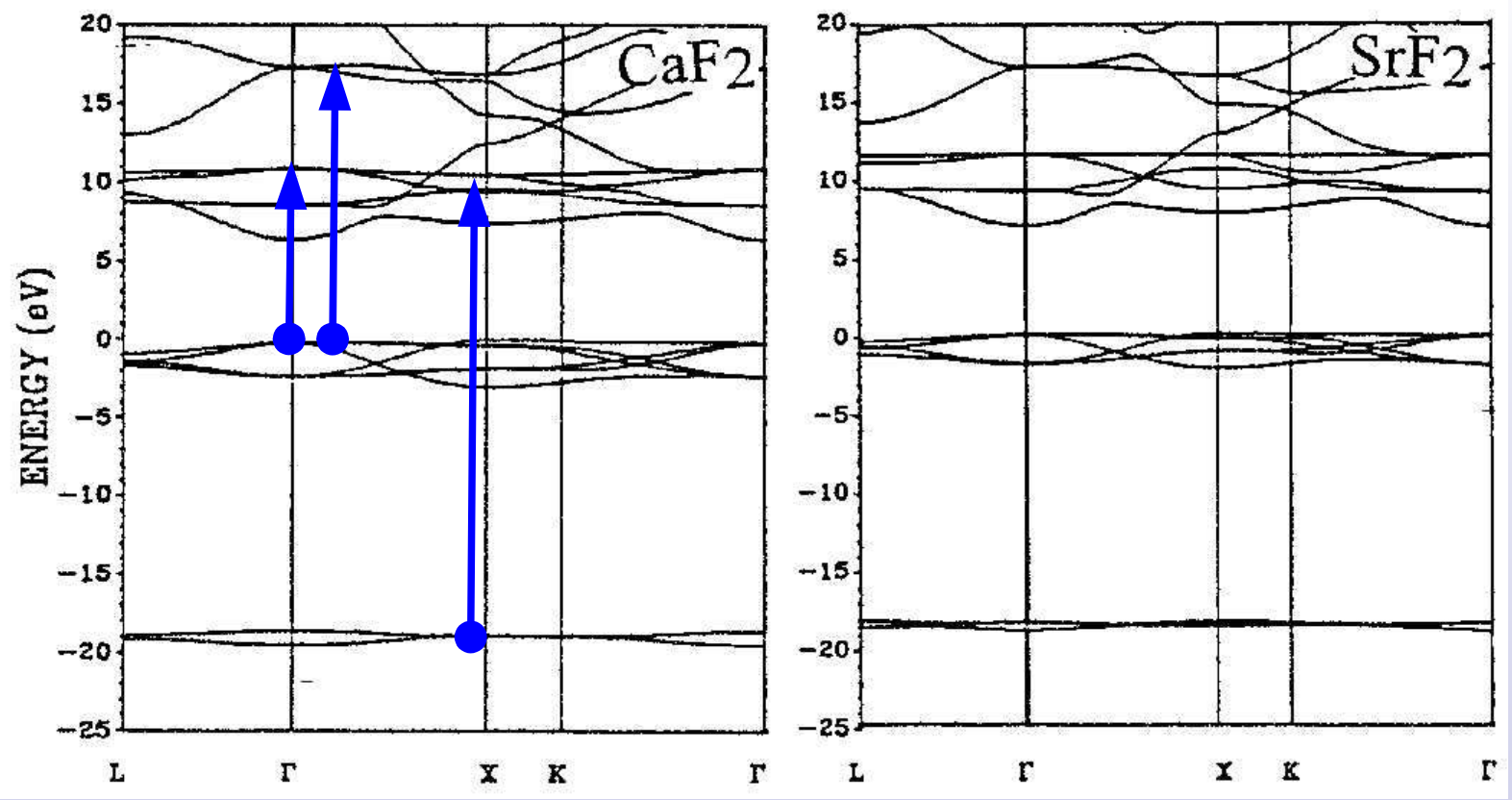




What else other than total energies …

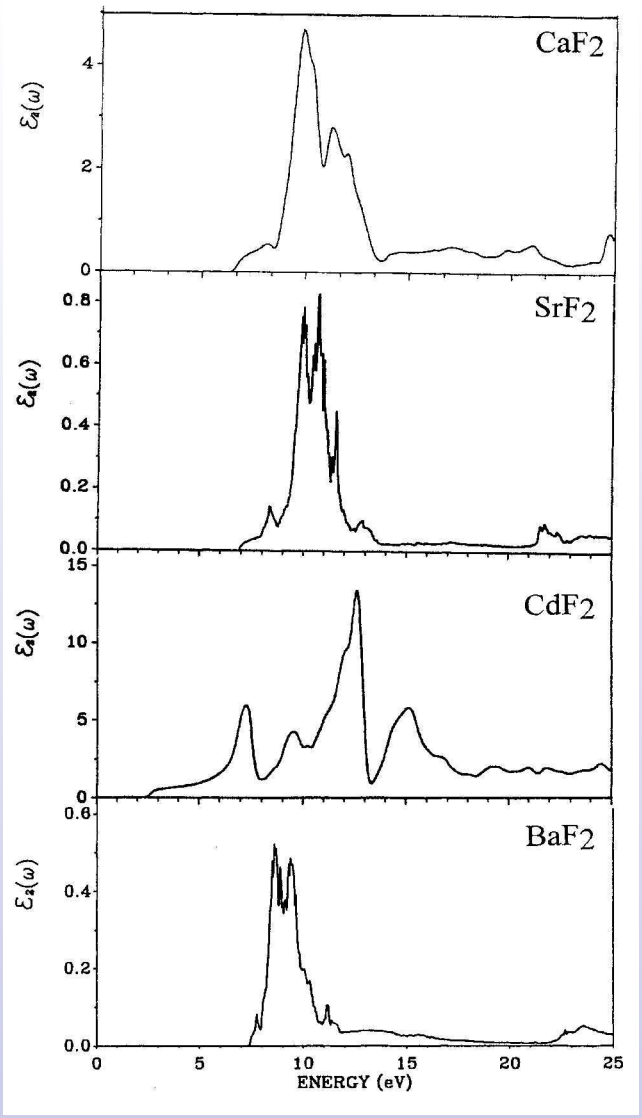
- Structural properties:
  - Structural phase transitions, surface reconstructions
- Elastic properties:
  - Bulk modulus, phonons spectra, lattice dynamics
- Chemical properties:
  - Thermochemical stability, reactivity of surfaces
- Transport properties:
  - effective mass, magnetoresistance
- Optical and spectroscopy properties:
  - Photoemission spectra, light absorption spectra
- And more ...

Band Structure of CaF_2 and SrF_2



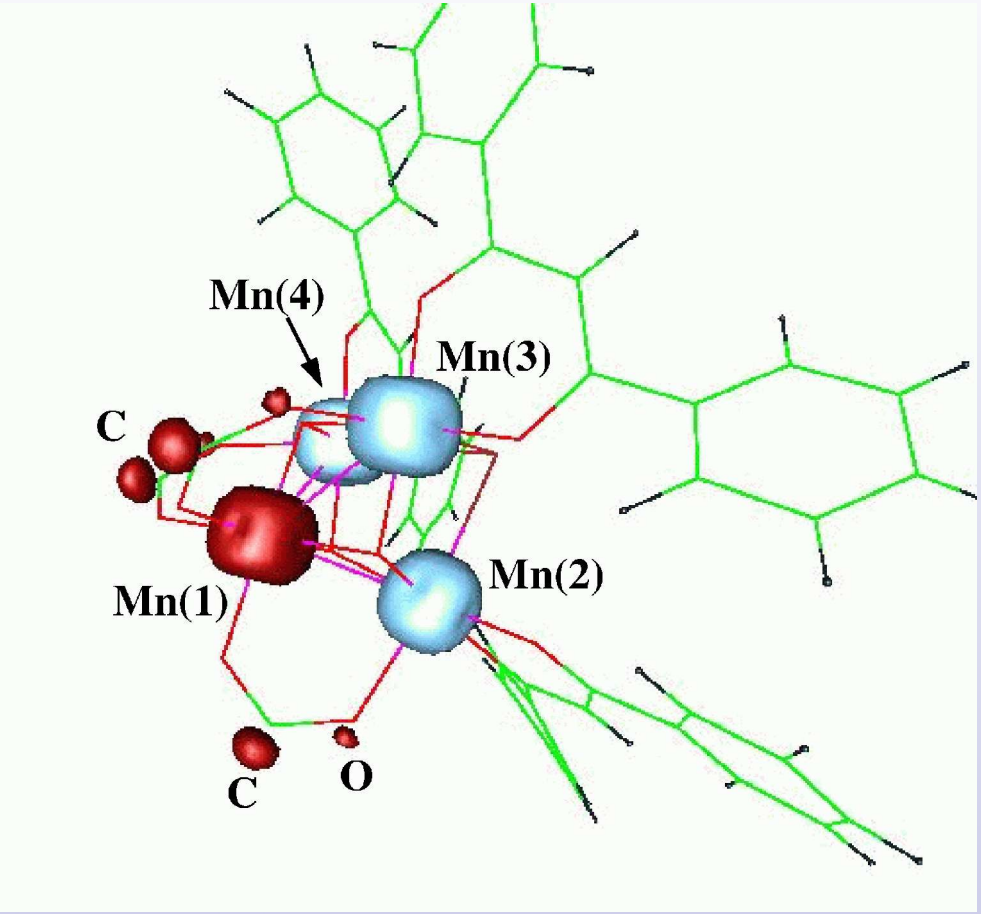
Imaginary Part of Dielectric Constant

for CaF_2, SrF_2, CdF_2, and BaF_2



Spin Density Distribution

incuded by the change of ligands in Mn_{12} Magnetic Molecule



Computational materials physics:

a new paradigm in material sciences

- Density functional theory is one of the most powerful technique in theoretical condensed matter physics
- Major contributions to material science, biological science, ...
- Computational materials design:
  - Predictive power for the structure of a new material
  - Various physical properties
  - Crystal phase transitions in bulk or at surfaces
  - Surfaces structure, chemical reactions, catalysis, thermal desorption
  - Excited states, core-level spectroscopy (many-body effects), photo-chemistry, etc.
  - Crystal growth and self-organization of nano-scale structures