Core-level energies

On how to model XPS energies

Questions

- How to model core-level binding energies in VASP?
  - Relationship to XPS?
- How to extract core-level binding energies?

- Timeline: ~~VASP 3~~ > VASP 4: unofficial > VASP 5: more official > VASP 6: new features

Physical models

X-ray Photo-emission Spectroscopy

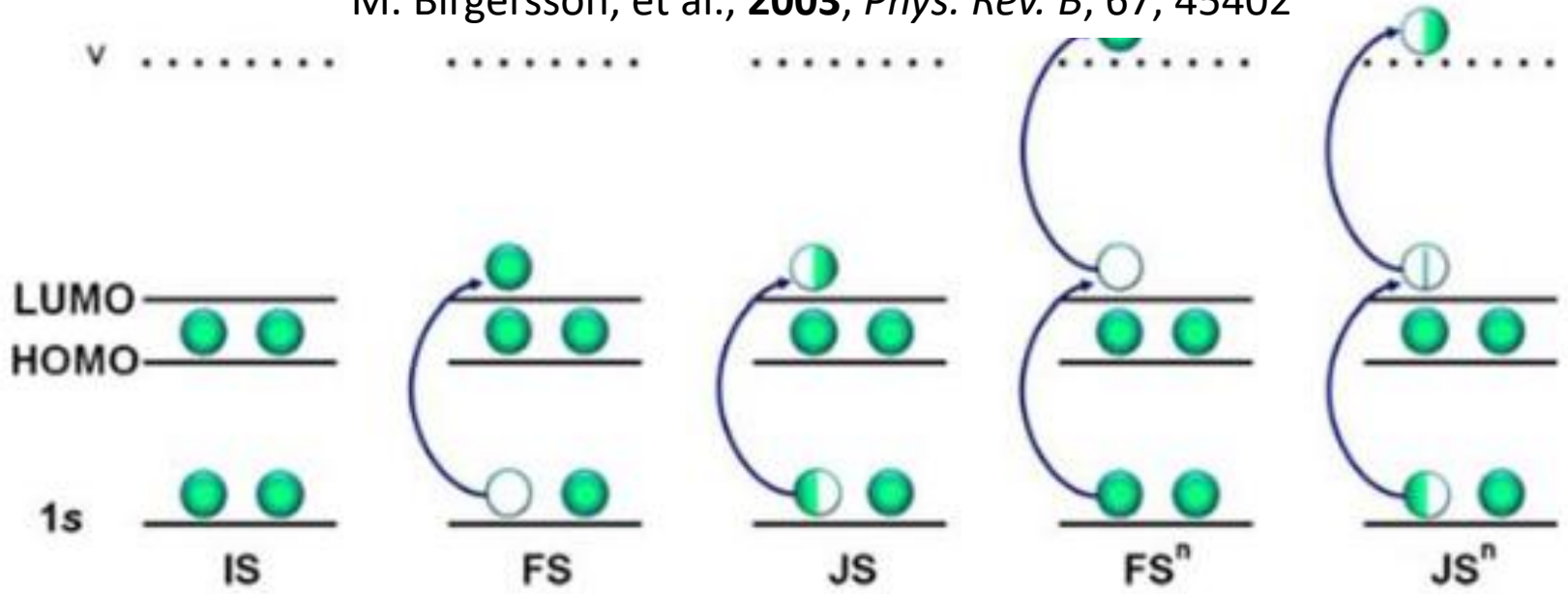
In core-level photoemission a core electron is removed from the system by a photon (usually in the x-ray regime) and leaves the solid to get its kinetic energy and possibly its momentum measured in a detector. The difference between

M. Birgersson, et al., **2003**, *Phys. Rev. B*, 67, 45402

off
IS
FS

Main tags:

- ICORELEVEL = 0/1/**2**
- (ISPIN = 2)
- CLNT = atom type
- CLN = N quantum number
- CLL = L quantum number



Files:

- core_rel.F
- cl_shift.F

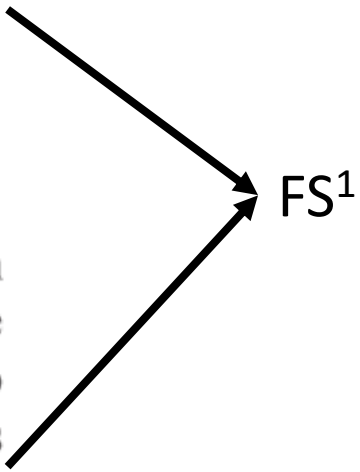
NELECT =	-	N + 1	N + 1	N	N
CLZ =	-	1.0	0.5	1.0	0.5

Physical models in VASP

- L. Kohler, G. Kresse, **2004**, *Phys. Rev. B*, 70, 165405

In the second calculation one electron is removed from the core of one particular atom and added to the valence or conduction band $[E(n_c-1)]$. The energy difference is a measure for the experimentally determined core-level binding energy

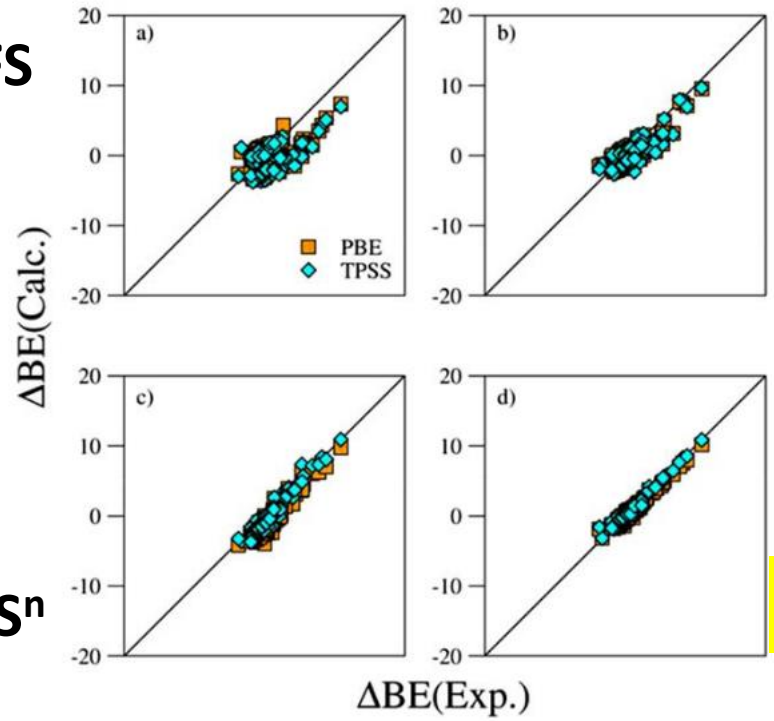
with an accuracy of about 20–50 meV. This correlates with the observation that core electron binding energies of one kind of atom in different environments are not sensitive to the precise configuration of the other core electrons, which is underlined by the success of the $Z+1$ approximation, in which the core hole is modeled by increasing the nuclear charge of the core ionized atom by one and adding an extra valence electron.[22] A detailed account of the present PAW



Physical models in VASP

FS

JS



FS^n

JS^n

MOLECULES

Reducible Metaloxides: FS or JS reduce a metal-ion > FS^n or JS^n

Energy extraction

- Various models encountered:
  - Using Core States

```
the core state eigenenergies are
  1-  1s -40257.4939  2s  -6444.1802  2p  -5770.4054  3s  -1386.7985  3p  -1172.6336
      3d   -868.7367  4s   -278.6090  4p   -208.5615  4d   -107.7663

109-  1s -78415.1004  2s -13784.9571  2p -11945.1921  3s  -3248.6737  3p  -2713.1295
      3d  -2133.6280  4s   -704.6359  4p   -528.4672  4d   -314.9971  5s   -102.7500
      4f    -77.7993  5p    -55.5722

E-fermi :  -1.4861     XC(G=0):  -5.4205     alpha+bet : -6.7307
```

  - Using Energy

```
FREE ENERGIE OF THE ION-ELECTRON SYSTEM (eV)
---------------------------------------------------
free  energy   TOTEN  =      -912.98770933 eV

energy  without entropy=     -912.95965704  energy(sigma->0) =     -912.97368319
```

  - Role of E_{Fermi} and E_{vacuum}?

Energy extraction

Core Level Shifts / XPS

by **admin** » Mon Aug 06, 2007 12:22 pm

QUOTE

admin
Administrator

Posts: 2915
Joined: Tue Aug 03, 2004 8:18 am

please have a look at KÃ¶hler and Kresse, PRB 70, 165405 (2004) and the references therein.

As the corelevel shifts are not an officially supported feature of vasp, we do not offer any 'cookbook' how to calculate them.
The atom for which the core level shift has to be calculated has to be given in POSCAR, you are right, otherwise the core electrons of **all** equivalent atoms (as defined in POSCAR) are excited simultaneuosly.
The energy needed to excite a core electron from the core to a conduction band state is TOTEN(2) - TOTEN(1), hence all parameters which are needed to get accurate total energies have to be well-converged.

Last edited by **admin** on Mon Aug 06, 2007 12:22 pm, edited 1 time in total.

The energy needed to excite a core electron from the core to a conduction band state is TOTEN(2) - TOTEN(1),

Energy extraction

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Final State

duction band $[E(n_c-1)]$. The energy difference is a measure for the experimentally determined core-level binding energy

$$E_{CL} = E(n_c - 1) - E(n_c). \quad (1)$$

Initial State

trons) is allowed. Electronic screening is therefore entirely neglected. The core electron binding energy in the initial state approximation can be calculated directly from the Kohn-Sham eigenvalues of the core state of interest ϵ_C and the Fermi level ϵ_F:[21]

$$E_{CL}^{\text{initial}} = \epsilon_C - \epsilon_F. \quad (3)$$

- M. Birgersson, et al., **2003**, *Phys. Rev. B*, 67, 45402

$$\Delta E_{\text{relax}} = \epsilon_c^{\text{solid}} - e_c^{\text{solid}} - [\epsilon_c^{\text{ref.}} - e_c^{\text{ref.}}],$$

Energy extraction

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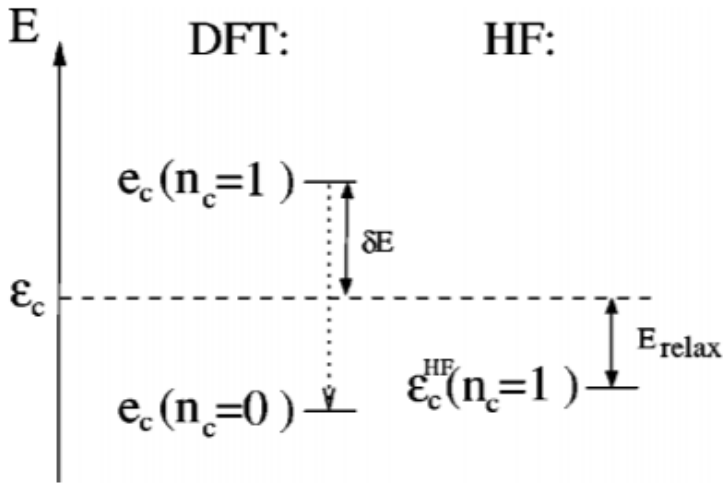

FIG. 1. Relation between HF and DFT eigenvalues and excitation energies for deep core states. The dotted arrow indicates the movement of the DFT eigenvalue as the core state is emptied. The energy difference δE has no physical relevance.

$$\epsilon_c = \epsilon_c^{HF} + \frac{1}{2}\langle c|V_p|c\rangle \qquad (2)$$

in terms of the HF eigenvalue ϵ_c^{HF} with filled core level, and the core-hole induced change V_p in Hartree and exchange potential. (V_p is usually termed 'polarization potential.") The above result is closely related to the results from the dynamically screened exchange or "GW" approximation to the self-energy Σ,[27]

Summary

A new horizon: VASP 6