

# The density of electronic states in a solid

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# Density of states

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- ❖ **Density of states (DOS):** the number of states per interval of energy at each energy level that are available to be occupied.
- ✓ High DOS at a specific energy level means that there are many states available for occupation.
- ✓ A DOS of zero means that no states can be occupied at that energy level.
- ✓ In general a DOS is an average over the space and time domains occupied by the system.
- ❖ Local variations, most often due to distortions of the original system, are often called **local density of states (LDOS)**. If the DOS of an undisturbed system is zero, the LDOS can locally be non-zero due to the presence of a local potential.



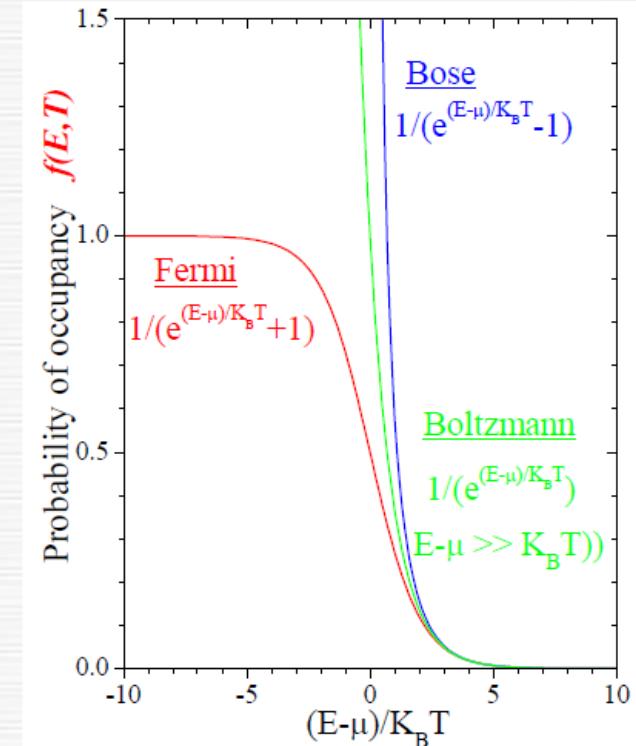
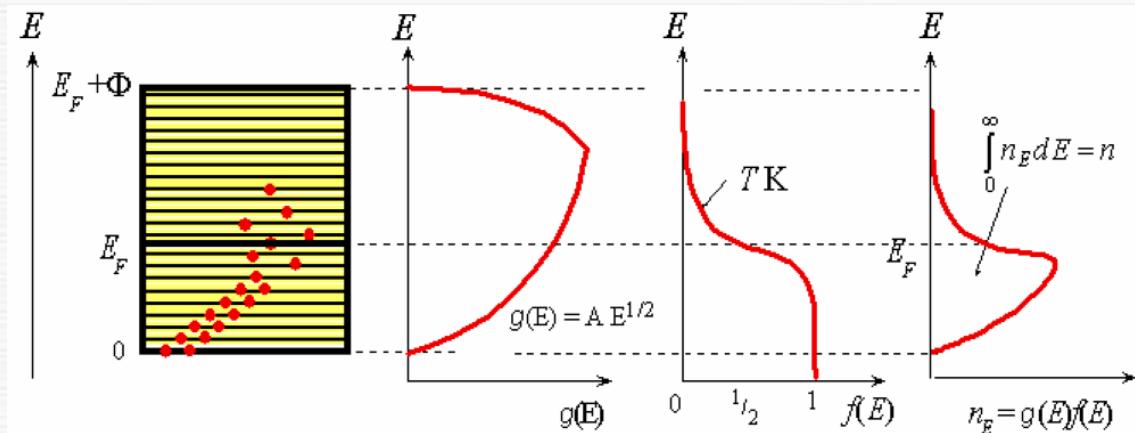
# Why?

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- ❖ The density of states for electrons in a semiconductor
- ✓ For electrons at the conduction band edge, **very few states are available** for the electron to occupy.
- ✓ As the electron increases in energy, the electron density of states increases and more states become available for occupation. However, because there are no states available for electrons to occupy within the band gap, electrons at the conduction band edge must lose at least the energy ( $E_g$ ) in order to transition to another available mode.
- ❖ Fairly small number electrons in an atom but how can one deal with electrons in a solid ( $\approx 10^{23}$  atoms)?
- ✓ Solution: instead of number of electrons consider the density of electronic states.

# Definitions

- Density of states  $g(E)$  gives the number of energy states per energy interval.
- Probability that state of energy  $E$  is occupied is  $f(E)$
- Number of particles per energy interval  
 $n_E = D(E) \cdot f(E, T)$
- Chemical potential  $\mu(E_F)$



# Different mechanisms for transitions involving “free” electrons



- Inter-band transitions (direct and indirect):  $\approx$  few eV

$\text{VB} \rightarrow \text{CB}$  : Transitions between all states are possible but:

- direct transitions are much more likely
- Obey selection rules for symmetry of involved bands.

If there is no band gap (metal) the absorption is continuous and no absorption edge in this energy range occurs.

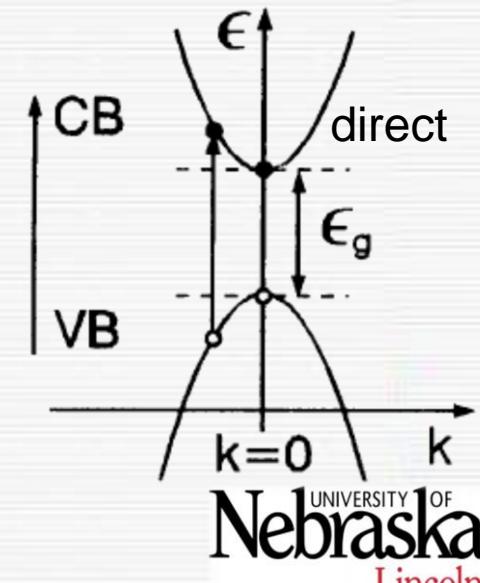
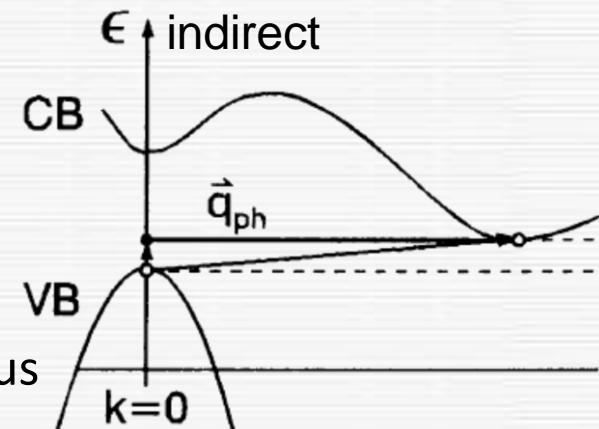
- Single electron oscillations: below  $\text{IR} \leq 0.5 \text{ meV}$

Described by dielectric function  $\epsilon(\omega, k)$ .

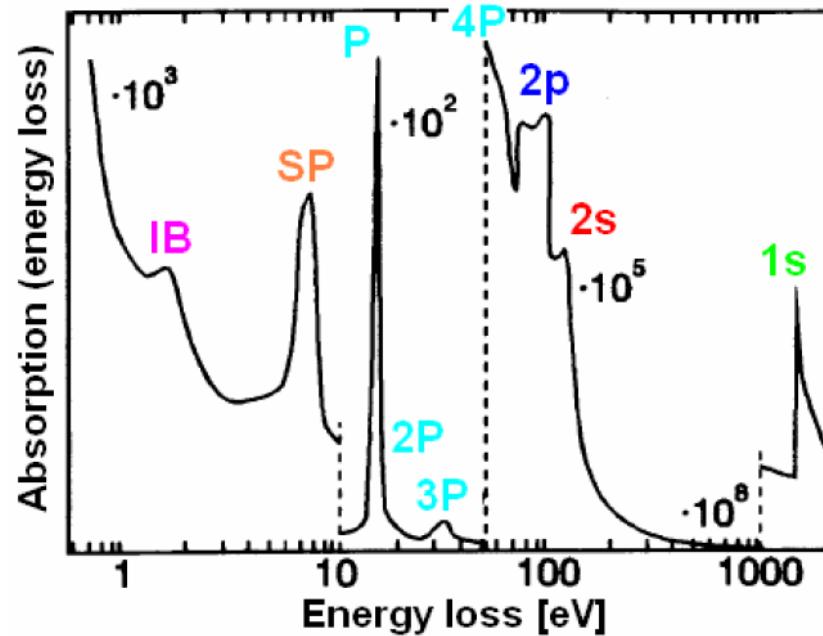
- Collective electron oscillations (Plasmons):  $2 \sim 17 \text{ eV}$

In metals the free electrons collectively oscillate (longitudinal).

The quant of this excitation is the *Plasmon*.



# Overview: putting the fundamental processes together for Al

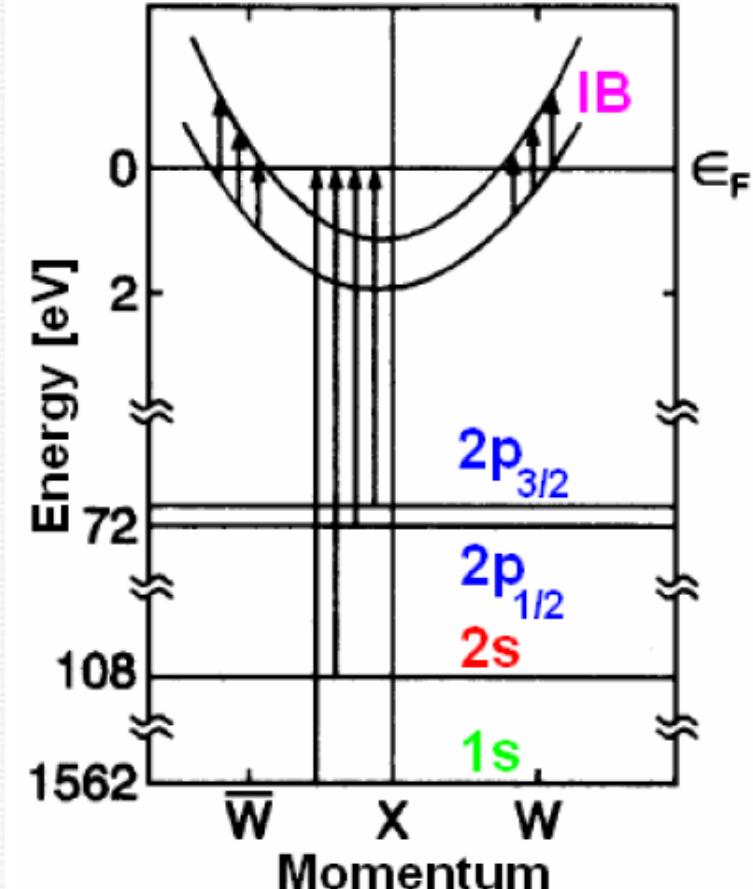


Excitation of core electron (1s)

Excitation of valence band electrons (2s, 2p)

Plasmons: Surface plasmons (SP), volume plasmons P, 2P, 3P, 4P

Intra-band transitions (IB)





# Fundamental excitations and energy scales in solids

## Due to “free” (VB) electrons:

- Intra-band transitions:  $\leq E_{\text{band width}}$  (few eV)
- Single electron oscillations (Plasmaoptic):  $\leq 0.5 \text{ meV}$
- Collective electron oscillations (Plasmons):  $\approx 2 - 17 \text{ eV}$

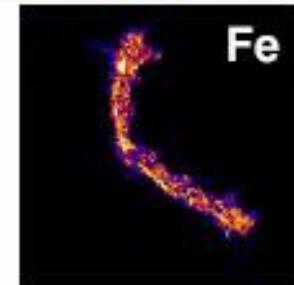
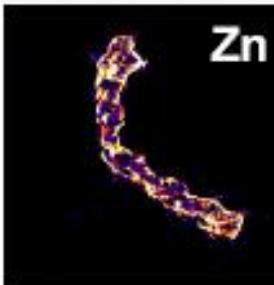
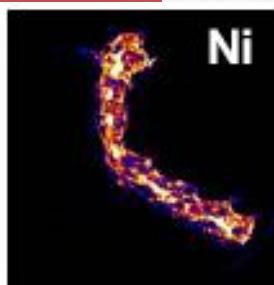
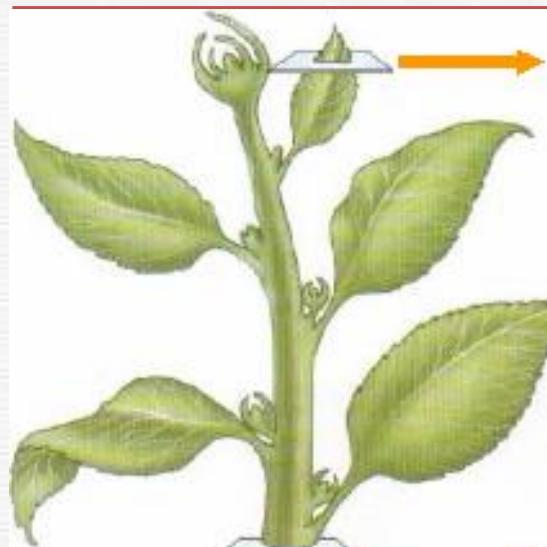
## Due to bound electrons:

- Inner (core & valence) electron shells  $\approx 4 \text{ eV} - 98.5 \text{ keV}$
- Inner-shell excitations (d-d, f-f):  $\approx 100 \text{ meV} - 2 \text{ eV}$
- Inter-band transitions (VB $\rightarrow$ CB):  $\approx 10 \text{ meV} - 11 \text{ eV}$
- Absorption from localized states
  - Excitons:  $\approx E_{\text{Bind}}$  few meV up to few eV
  - Defects (Impurities, vacancies or interstitials):  $\approx 10 - 300 \text{ meV}$
- Spin-orbit splitting:  $\approx \text{few eV (for d and f electr.)}$
- Spin waves (Magnons):  $\approx 10 - 40 \text{ meV}$
- Charge transfer excitations:  $\approx \text{up to several eV}$
- Correlation effects:  $\approx \text{order of eV}$

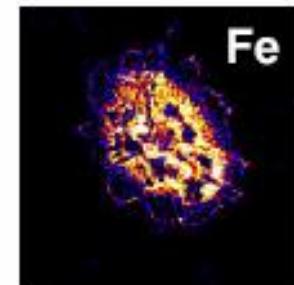
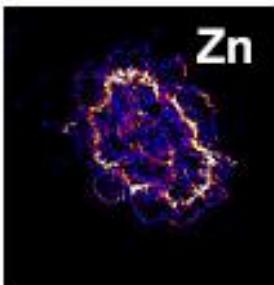
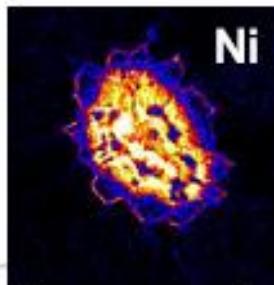
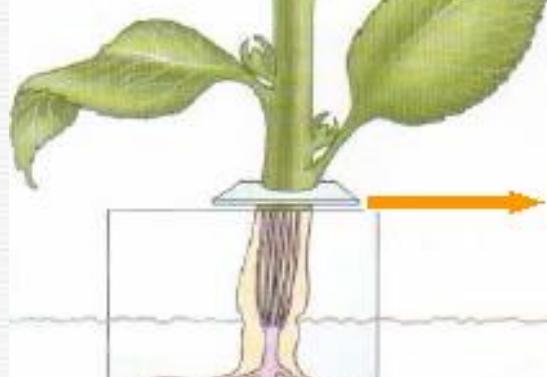
## Due to coupling of photons to Phonons (lattice vibrations):

- Photons – acoustic phonons (Brillouin scatt.)  $\approx 10^{-6} - 0.1 \text{ meV}$
- Photons – optical phonons (Polariton scatt.)  $\approx 40 - 70 \text{ meV}$

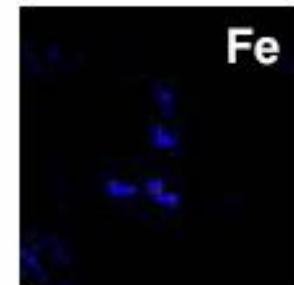
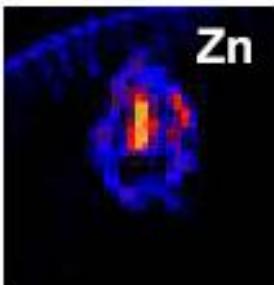
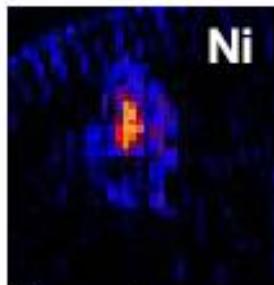
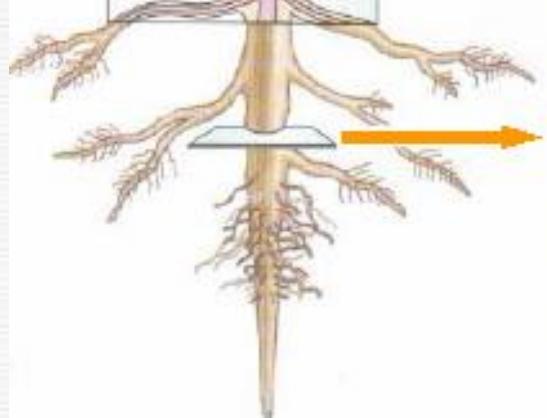
# An example of what you can do with XAS



Leaf cross-section



Stem cross-section



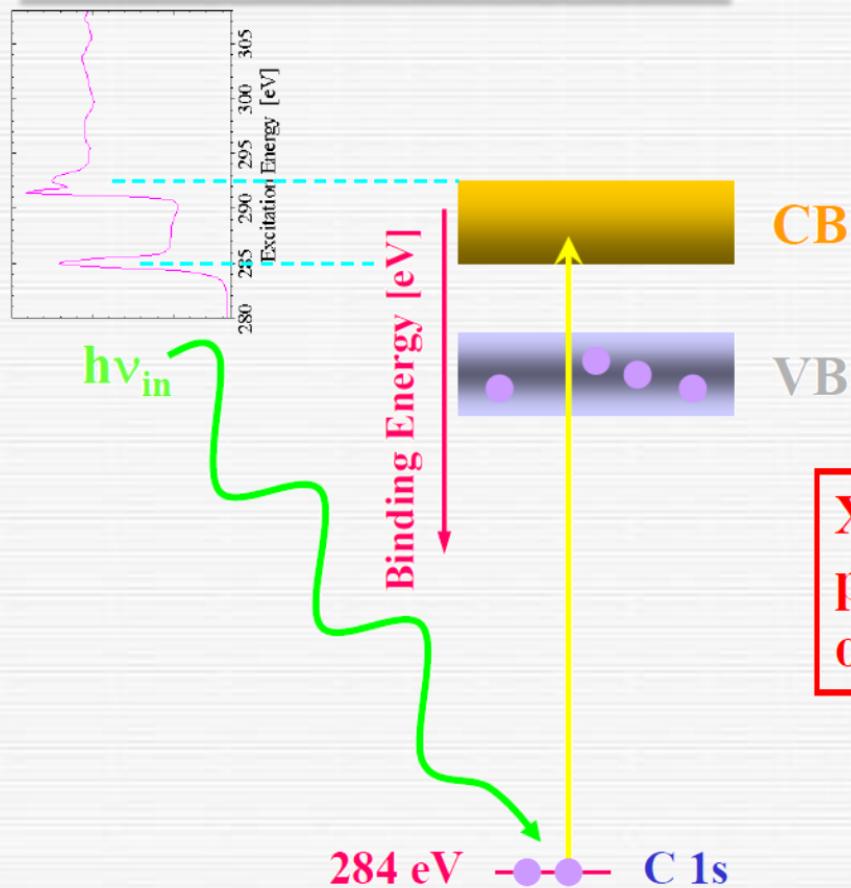
Fine root cross-section

high



low

# Absorption (XAS) Excitation



XAS probes local unoccupied partial density of states (pDOS) or CB states.

The selection rules for XAS and XES ( $\Delta l = \pm 1$ ) only allow for transitions

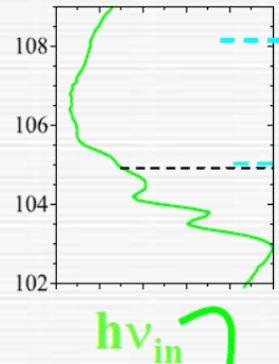
C, N, O :  $2p \rightarrow 1s$ . (Photons carry angular momentum (spin) of  $\hbar$ . It is preserved when photons interact. This gives rise to the selection rule  $\Delta l = \pm 1$ .)

# What do X-ray Absorption & X-ray Emission Spectroscopy probe?



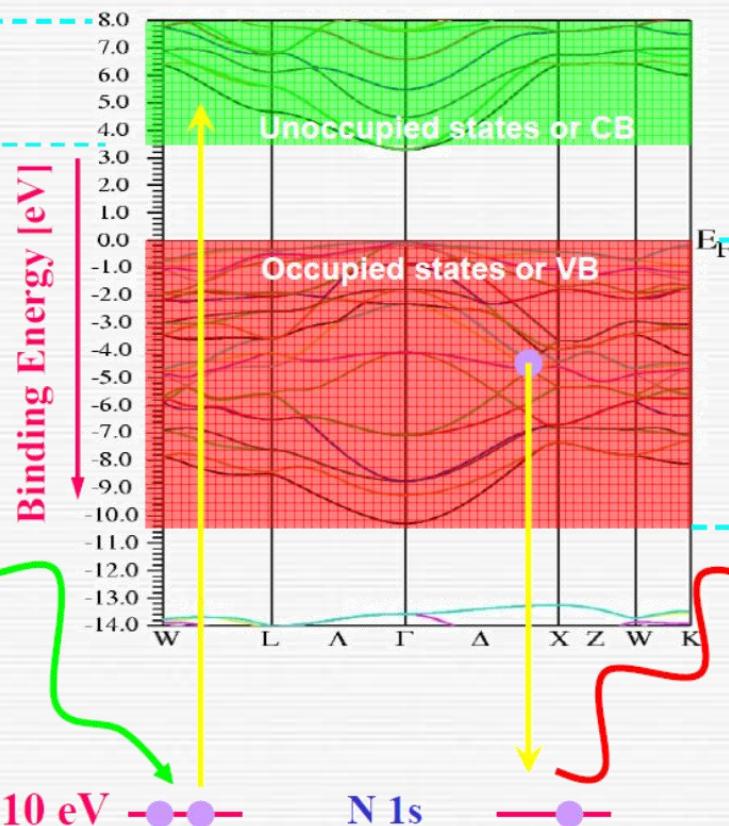
## Excitation

### Absorption (XAS)



XAS probes  
unoccupied  
pDOS (CB)

### Band structure of $\text{Si}_3\text{N}_4$

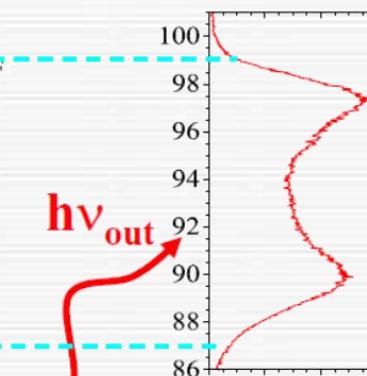


410 eV

N 1s

## Relaxation

### Emission (XES)



XES probes  
occupied  
pDOS (VB)

Note: (Dipole) selection rules for XAS and XES ( $\Delta l = \pm 1$ ) only allow for (dipole) transitions C, N, O :  $2p \rightarrow 1s$



# Summary

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- Distinguish elements distribution
- Study the electronic properties both conductive band and valence band
- ✓ XAS: unoccupied pDOS (CB)
- ✓ XES: occupied pDOS (VB)

A photograph of a modern university building. The left side features a glass and steel structure with large windows. The right side is a red brick building with many windows. A row of small trees lines the sidewalk in front. Several people are walking or standing near the entrance, and a group of bicycles is parked. The sky is clear and blue.

**Thank you for your time!**



# Local density of states and Partial (projected) density of states

- ✓ The LDOS, or local density of states, is the density of state at a particular site of a crystal with some asymmetry. For example: A slab will have a different band structure on the surface than in the bulk region.
- ✓ The PDOS is a projected density of states. This means site-projected DOS, where the information about the different contributions of the different orbitals is computed. You then know **which states (*spd*) contribute at which energy**.