Analysis of Core Level Spectra

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Workshop on
Theory and Computation for Interface Science and Catalysis: Fundamentals, Research and Hands on Engagement using VASP
Brookhaven National Laboratories, November 3-7, 2014

How Do We Characterize & Understand a Material ?

How are the atoms organized ?

- Do they form a crystal ?
- If so, what is the lattice ?
- …

Is it metallic or insulating ?

- What is the conductivity ?
- Is there an energy band gap ?
- If so, how big is it ?
- …

Does it reflect and/or absorb light ?

…

Single crystal of silicon, Czochralski process
Deutsches Museum, Munich, 17 March 2008
Massimiliano Lincetto
Commons.wikimedia.org

Materials Characteristics: All About Excitations

Experiments probe materials by forcing them out of equilibrium & monitoring the response …

… Heat, beat, irradiate, …

Theory:

Predict fundamental excitations of materials

Focus Today:
Core electrons excited by X-rays

Outline

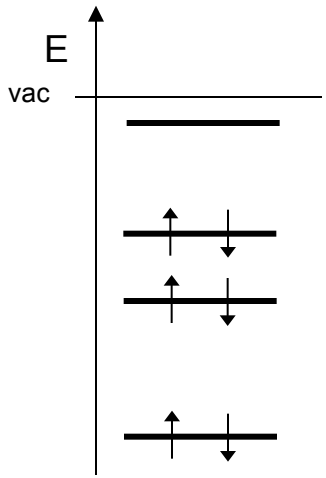
Excited States: Whither-whence with DFT & post-DFT Methods

Introduction to X-ray probes & Core-level excitations

DFT-based approach to chemical shifts

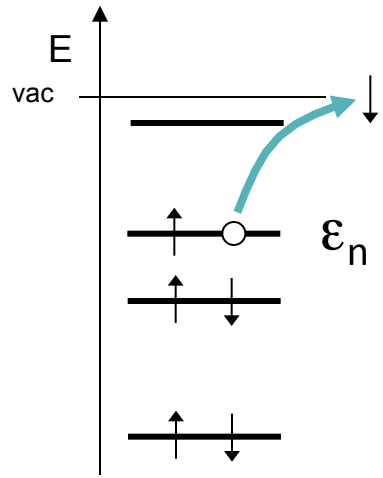
Independent Electron Model

Ground State



N electrons

Ionization: charged excited state

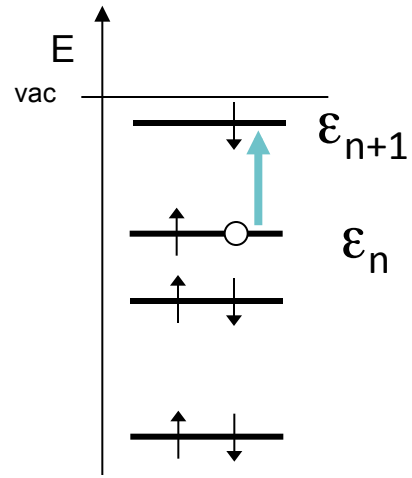


N-1 electrons

Excitation energy:

$$\mathbf{IP} = -\,\varepsilon_n$$

Internal excitation: neutral excited state

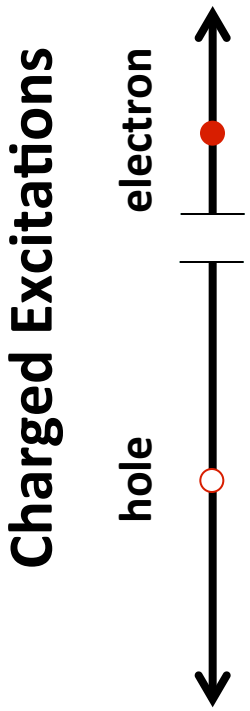


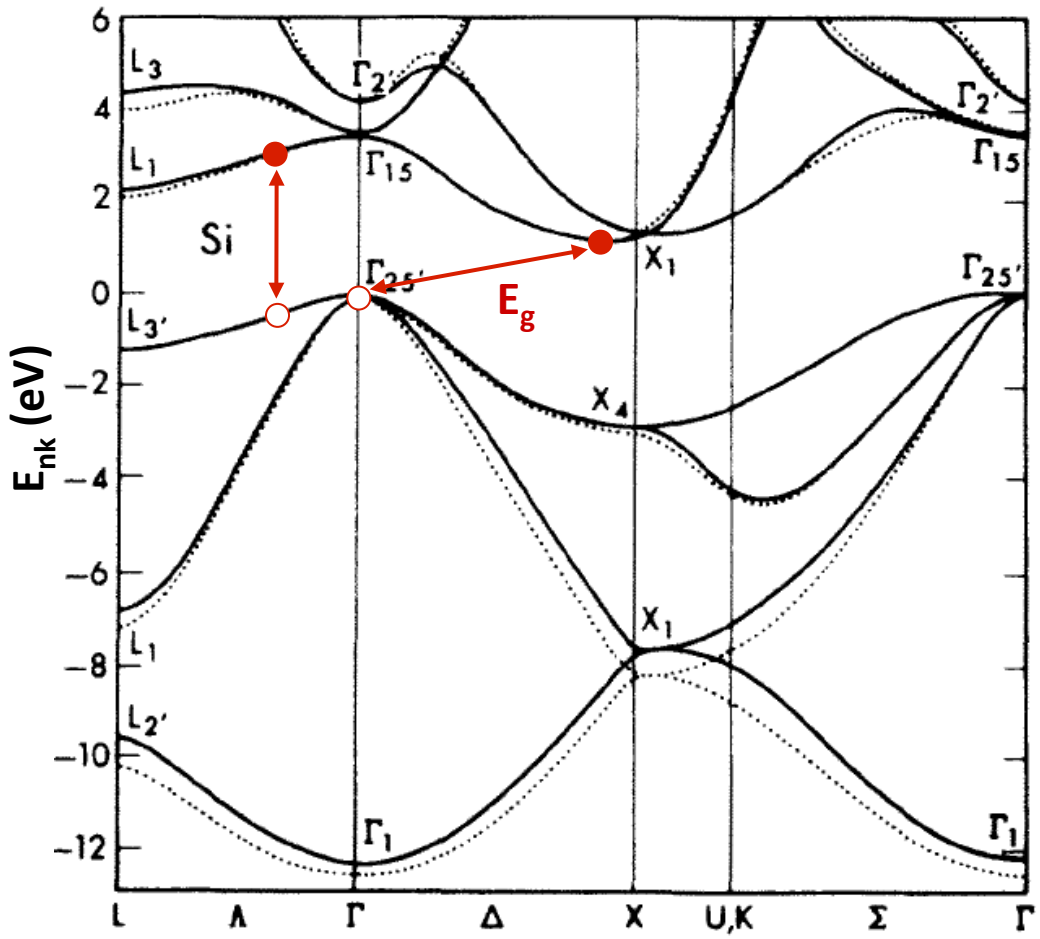
N electrons

Excitation energy:

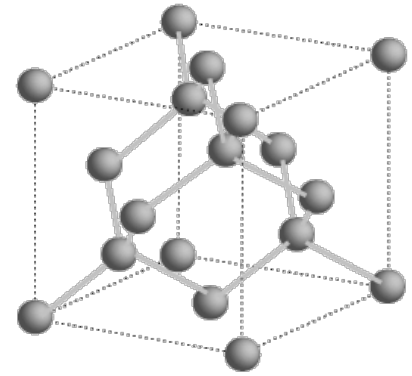
$$\Delta\mathbf{E} = \varepsilon_{n+1} - \varepsilon_n$$

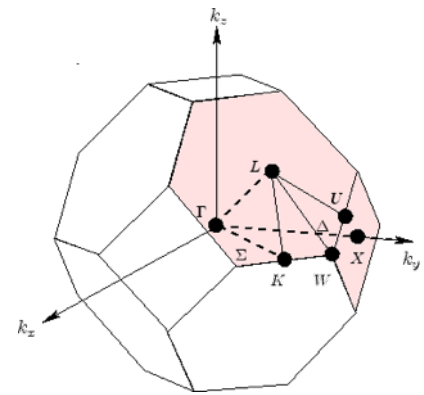
Independent Electron Model: Silicon





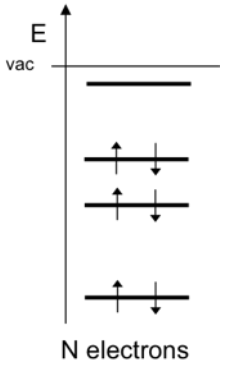
Chelikowsky & Cohen PRB, 1976





Gold standard for semiconductor band structures

Coulomb Interactions: DFT & Beyond



Ground State: Density Functional Theory – Total Energy

$$E[n] = T_0[n] + \int dr V_{ext}(r) n(r) + \frac{1}{2} \iint dr dr' n(r) v(r,r') n(r') + E_{xc}[n]$$

Powerful tool giving access to a broad array of phenomena:

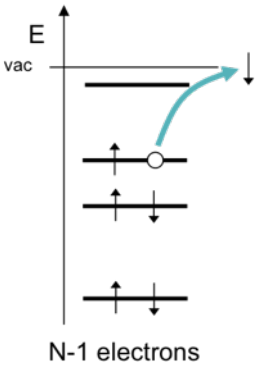
- **Equilibrium structure**
- **Stress-strain, vibrations, …, Free energy**
- **Electronic screening**
- **Ab initio molecular dynamics, e.g., liquids**
- **Other response functions, e.g., non-resonant Raman**

Clever use of energy differences (derivatives)

Coulomb Interactions: DFT & Beyond

Charged excited states: Selected cases –
Ground state total energy difference

$$IP = E(N-1) - E(N)$$



Charged excited states: General cases –
Many-body theory, e.g., GW approach

Non-local
E-dependent

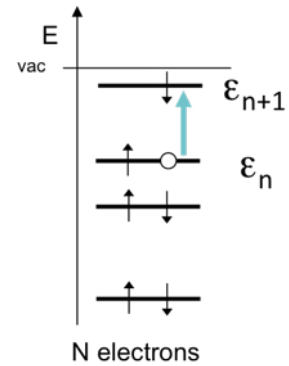
$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{ext}(r) + V_H(r)\right)\phi_k(r) + \int dr'\Sigma(r,r';E_k)\phi_k(r') = E_k\phi_k(r)$$

Charged excited states: Approximate via Kohn-Sham equations –
Impact of hybrid functionals

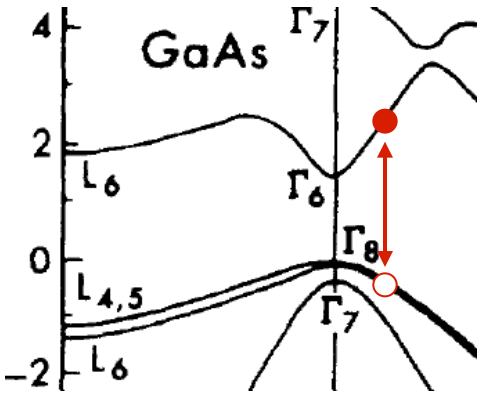
Theory justification non-rigorous: Empirical approach

Useful as an intermediate-cost empirical approximation:
Eigenvalues → excitation energies

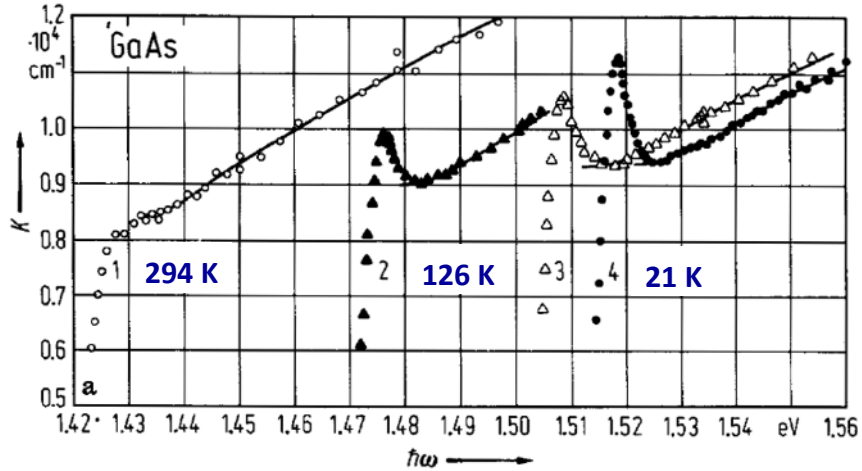
Coulomb Interactions: DFT & Beyond



Neutral excited states: Example optical absorption –



Chelikowsky & Cohen PRB, 1976



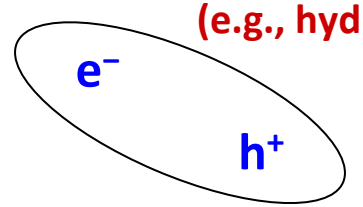
LB Database: Sturge, Phys Rev 127, 768, 1962

Modern Approach:

Bethe-Salpeter Equation

(Many-body perturbation theory)

e-h interactions
(e.g., hydrogenic)



Example: Optical Absorption in Bulk Silicon

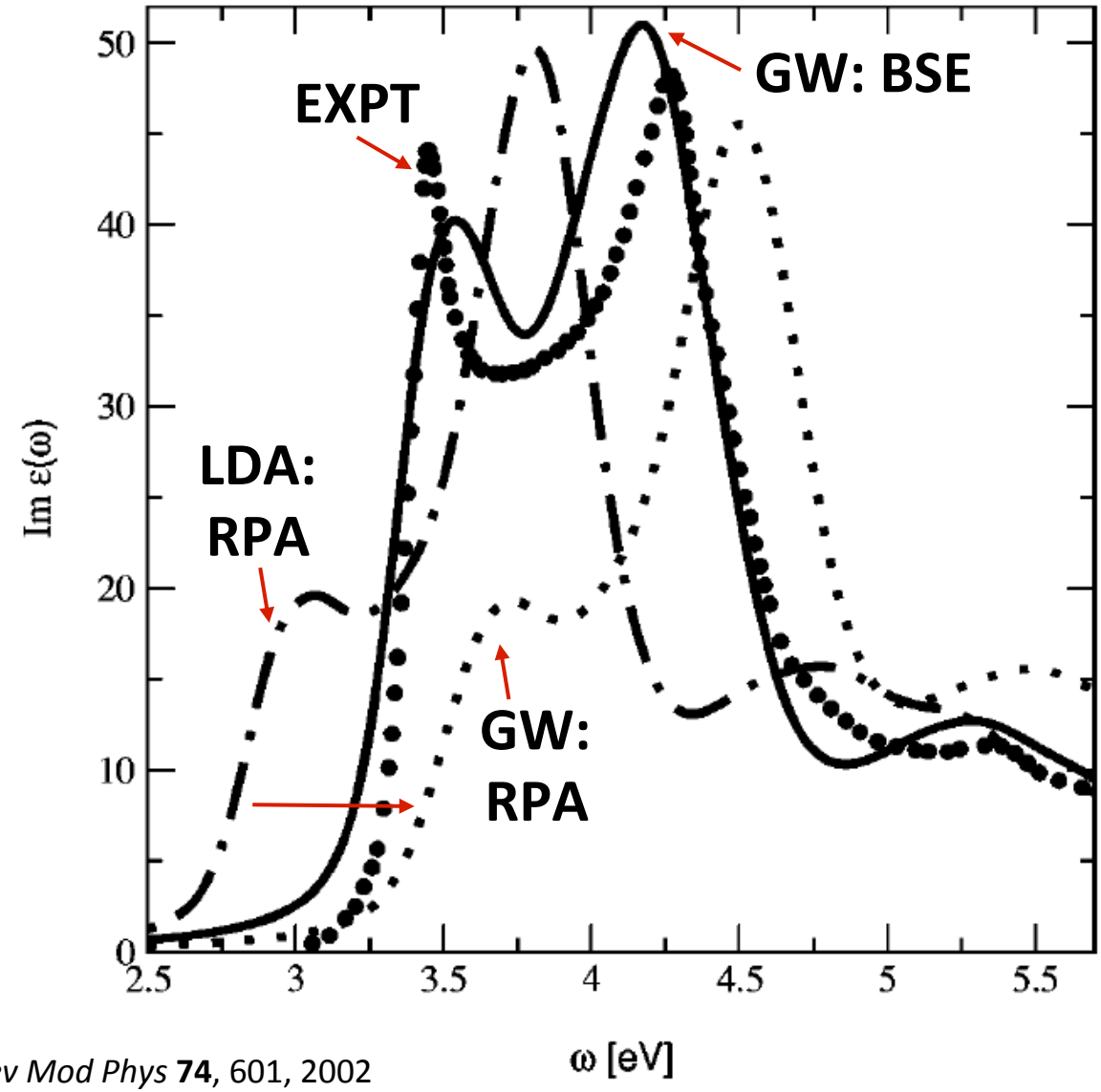
METHODS

LDA: DFT eigenvalues

GW: Include GW approach

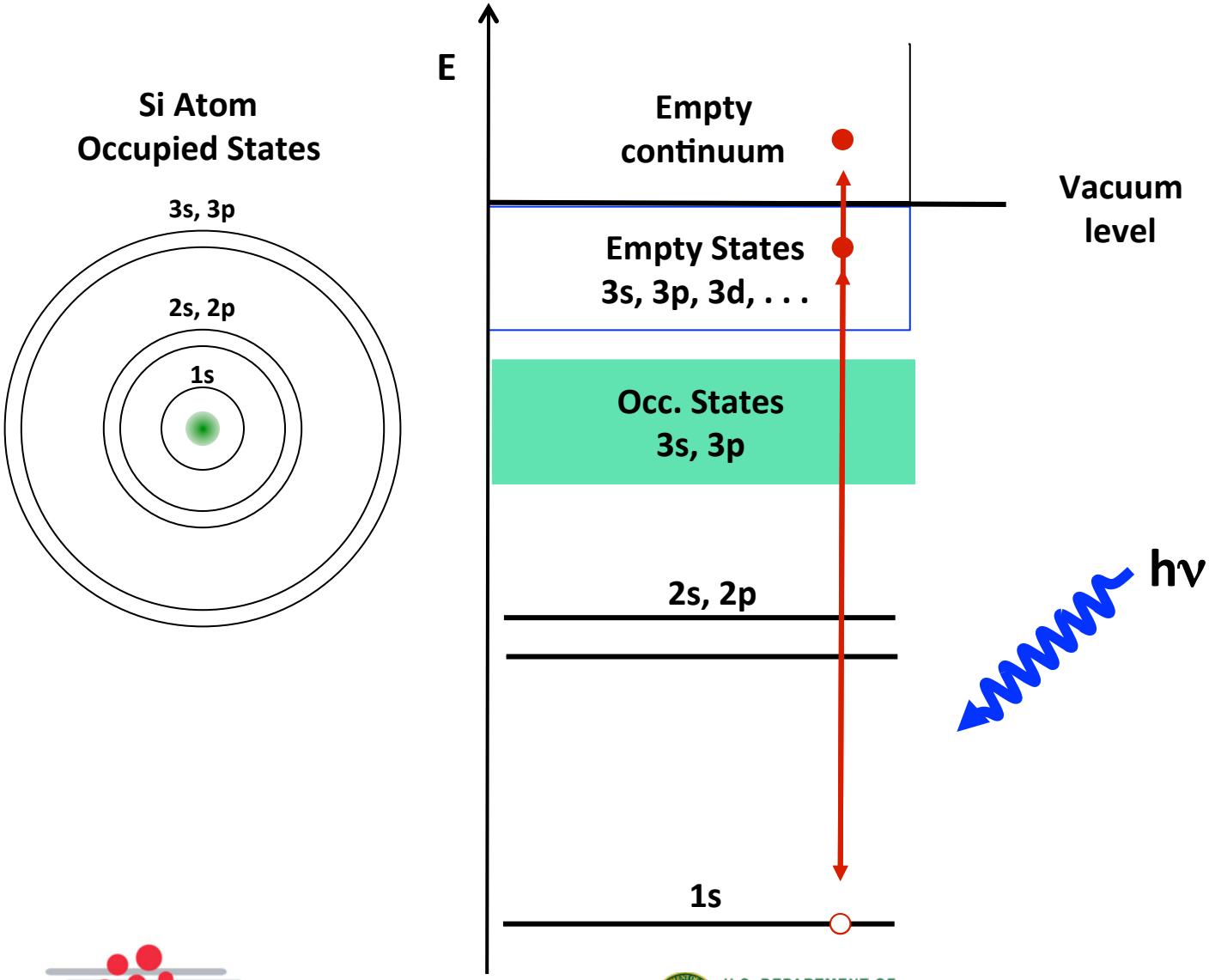
RPA: Independent particle for excitation amplitude

BSE: Include e-h interaction for excitation amplitude

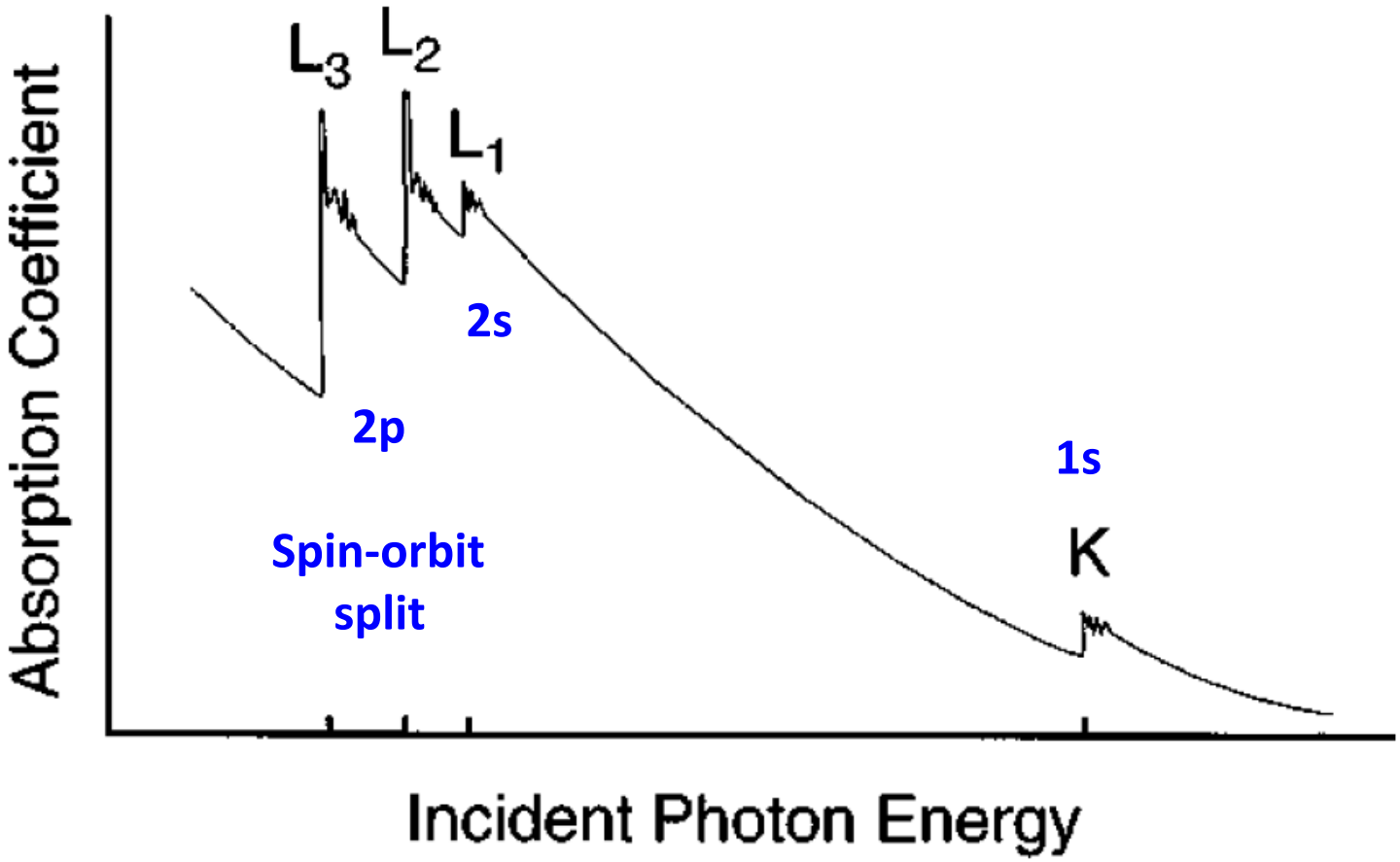


Onida, Rubio & Reining, *Rev Mod Phys* **74**, 601, 2002

Basic Picture: X-Ray Absorption

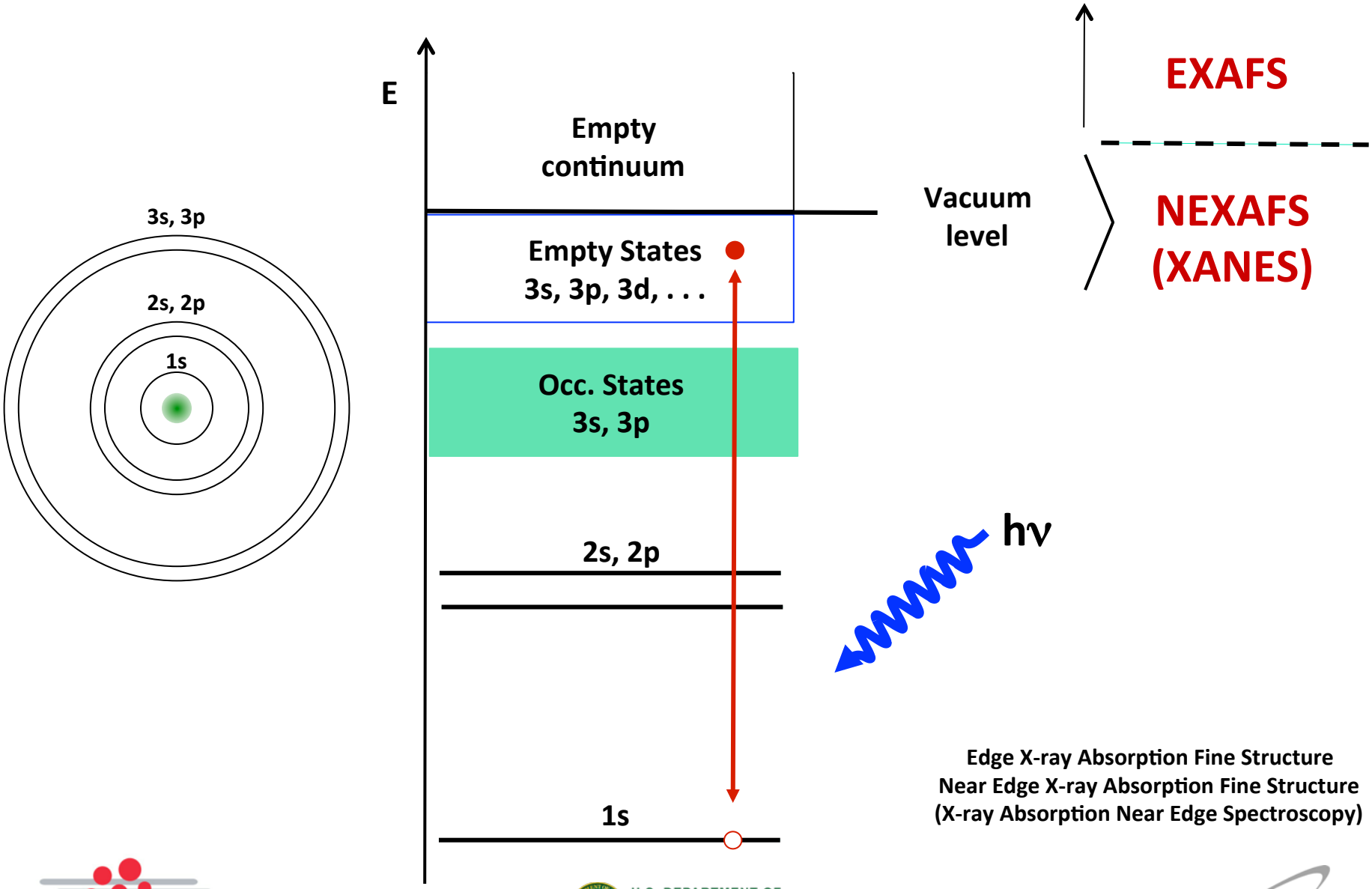


General Picture



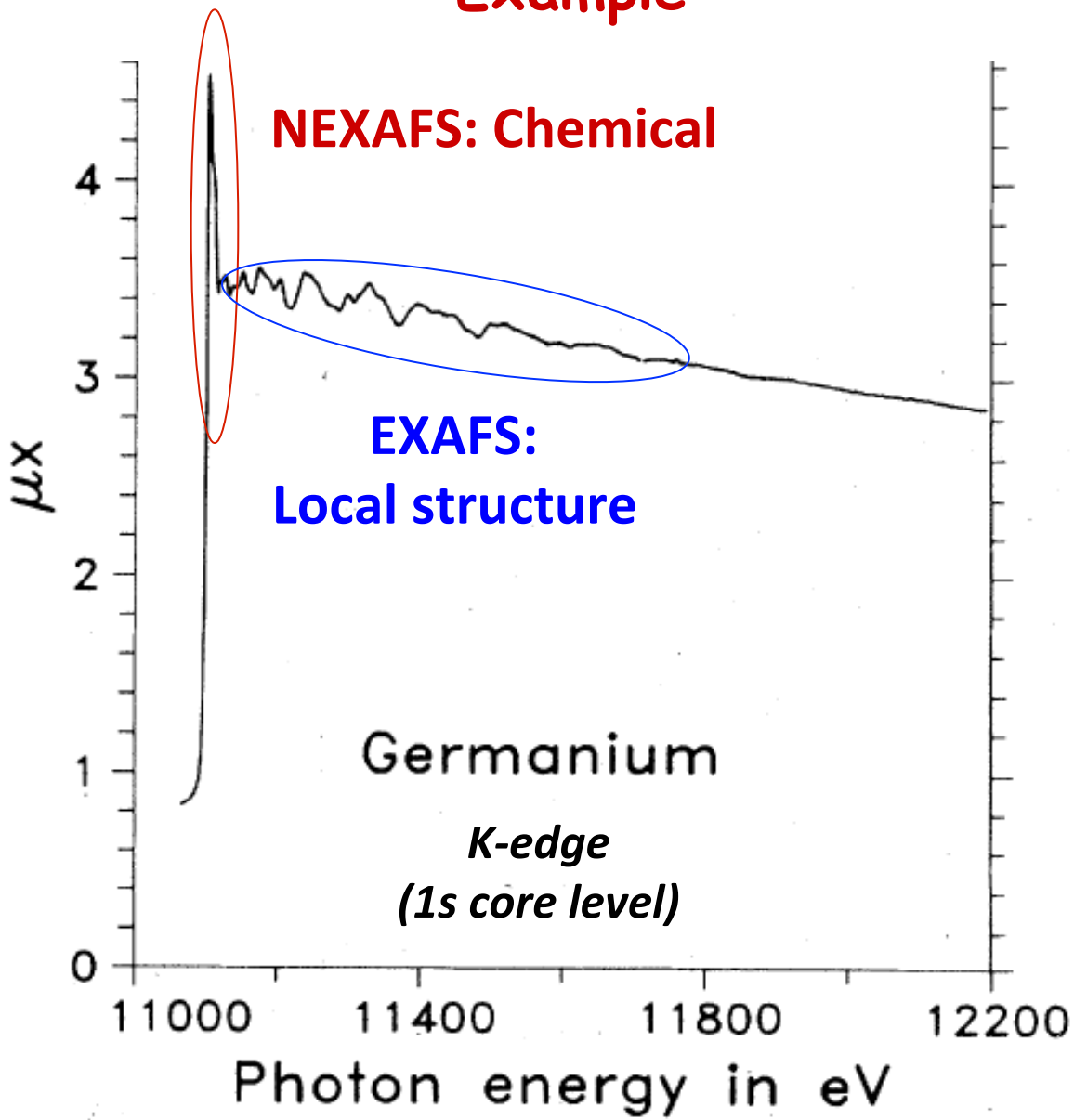
Rehr & Albers, RMP, 2000

Basic Picture: X-Ray Absorption



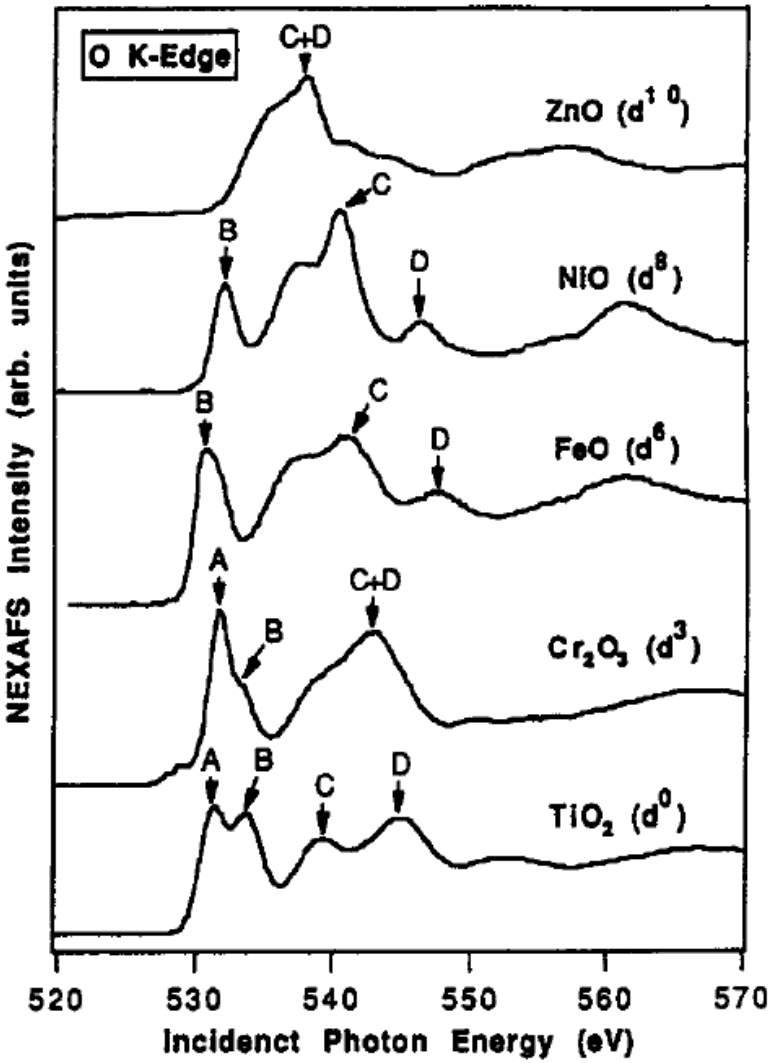
Edge X-ray Absorption Fine Structure
Near Edge X-ray Absorption Fine Structure
(X-ray Absorption Near Edge Spectroscopy)

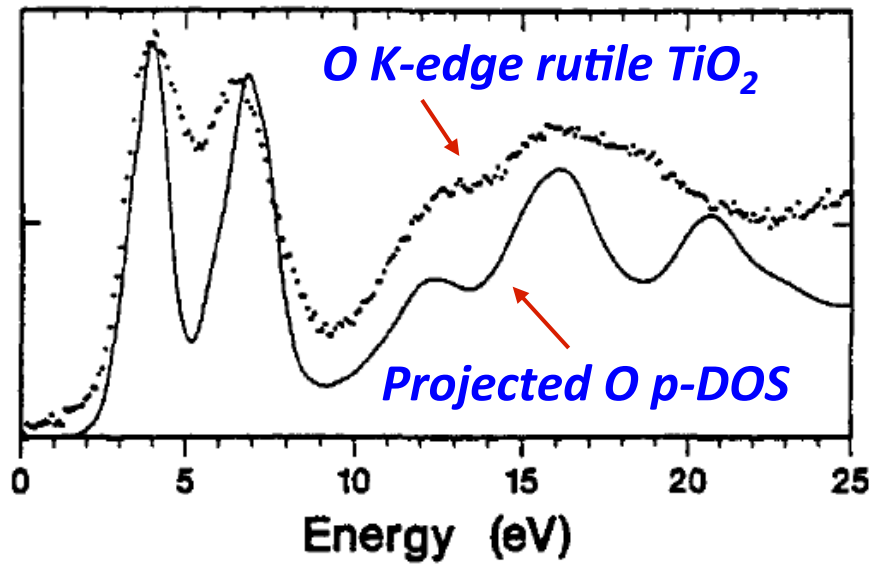
Example



Lee, Citrin, et al., RMP, 1981

NEXAFS: Chemical Information – Finger Print

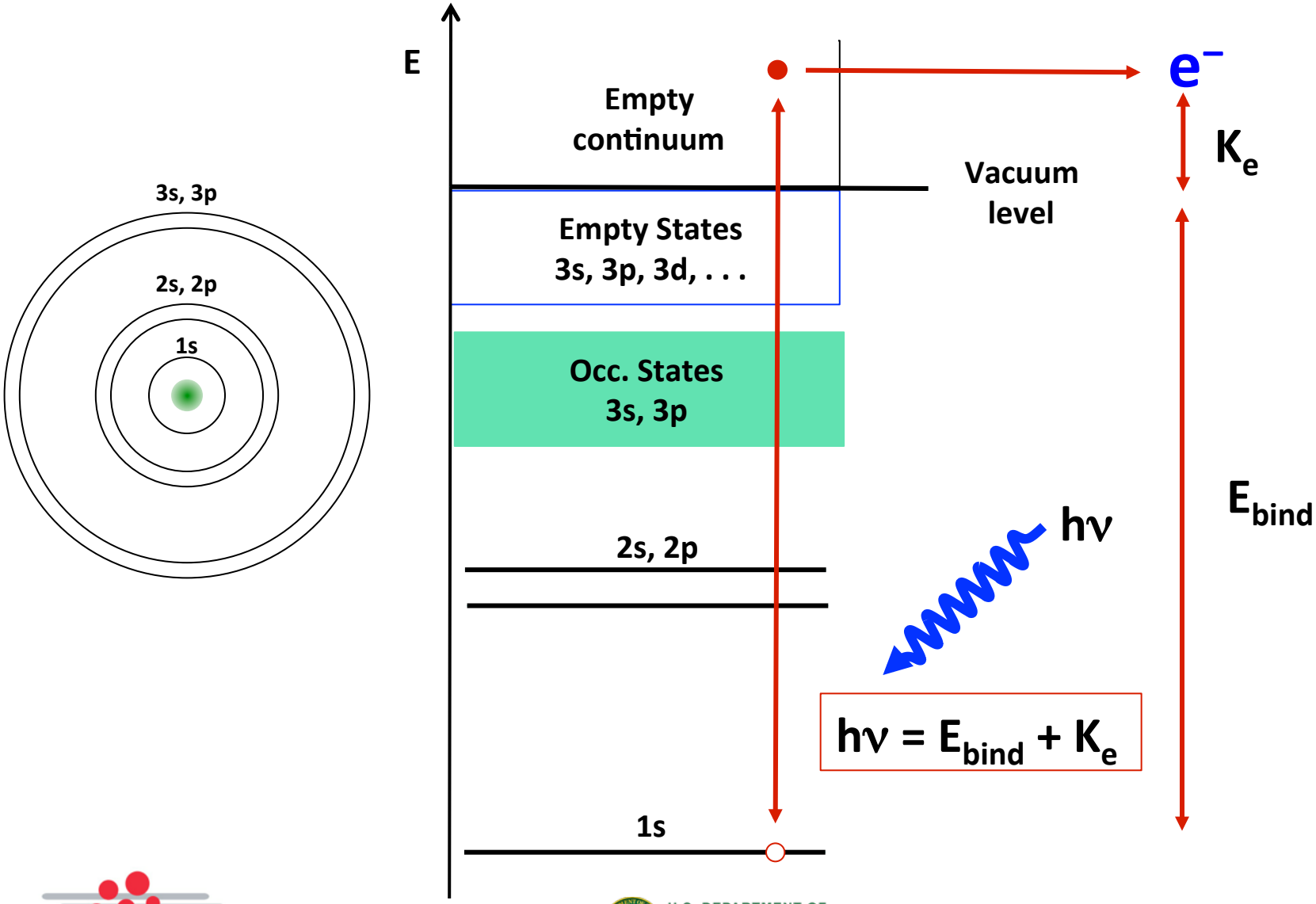




Local probe of empty electronic states dictated by atomic dipole selection rules: e.g. O 1s → 2p

J.G. Chen, Surf Sci Rep, 1997

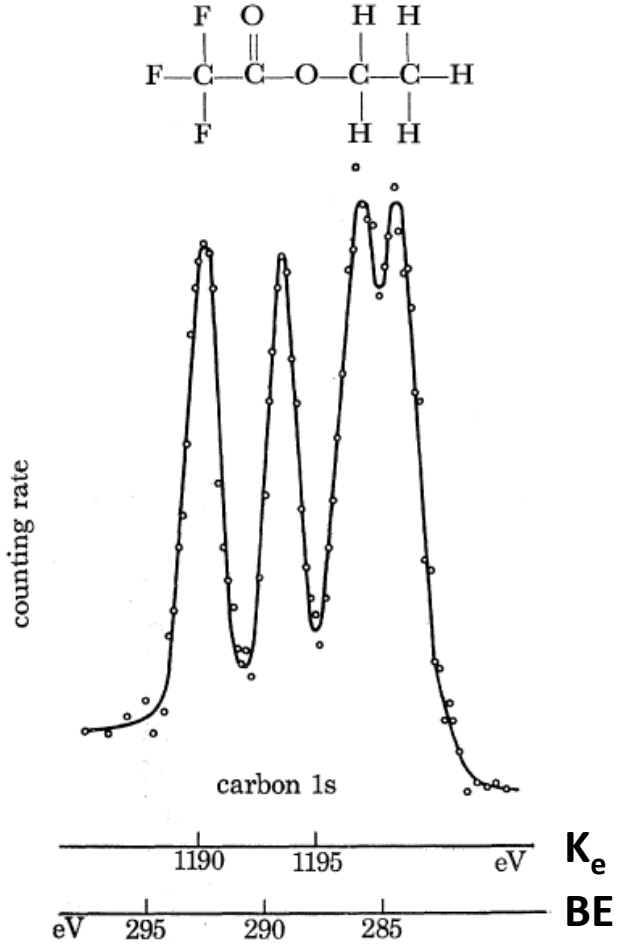
Basic Picture: X-Ray Photoemission



Electron Spectroscopy for Chemical Anaylysis (ESCA)

Chemical Shifts: Fingerprints

Kai M. Siegbahn
Uppsala University, Uppsala, Sweden
1981 Nobel Prize (1/2):
"for his contribution to the development of high-resolution electron spectroscopy"



K. Siegbahn, *Phil. Trans. Roy. Soc. Lond. A* **268**, 33, 1970.

Initial State Picture

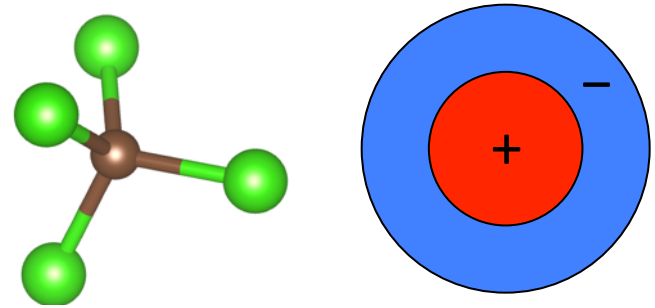
$$E_{Bind} = -\varepsilon_{1s} \qquad \Delta E_{Bind} = -\left(\left\langle \phi_{core} \middle| V_{loc} \middle| \phi_{core} \right\rangle - \left\langle \phi_{core}^{ref} \middle| V_{loc} \middle| \phi_{core}^{ref} \right\rangle\right)$$

Core state: small radius, like a "test charge" probing the changes in electrostatic potential

Atomic Valence:
$M^0 \rightarrow M^+$

Less screening of nucleus → more attractive potential & larger E_{bind}

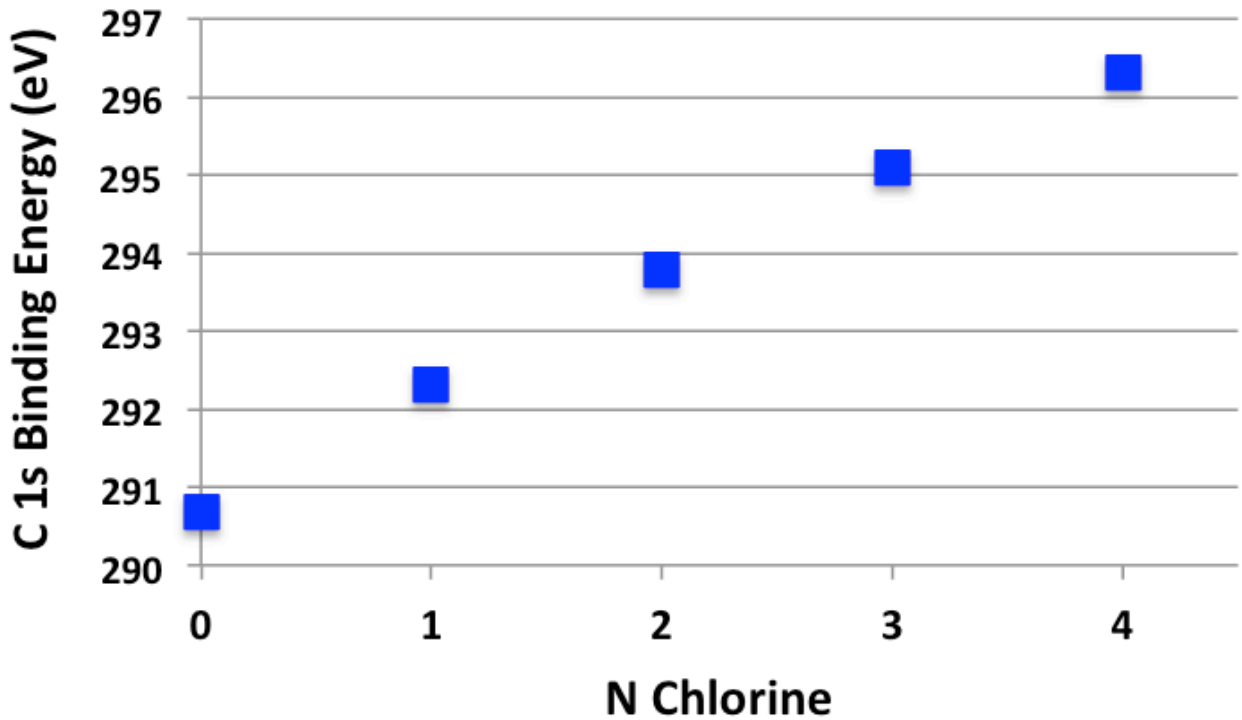
More ionic bond:
$CH_4 \rightarrow CCl_4$



→ Central C 1s larger E_{bind}

Example: CCl_nH_{4-n}

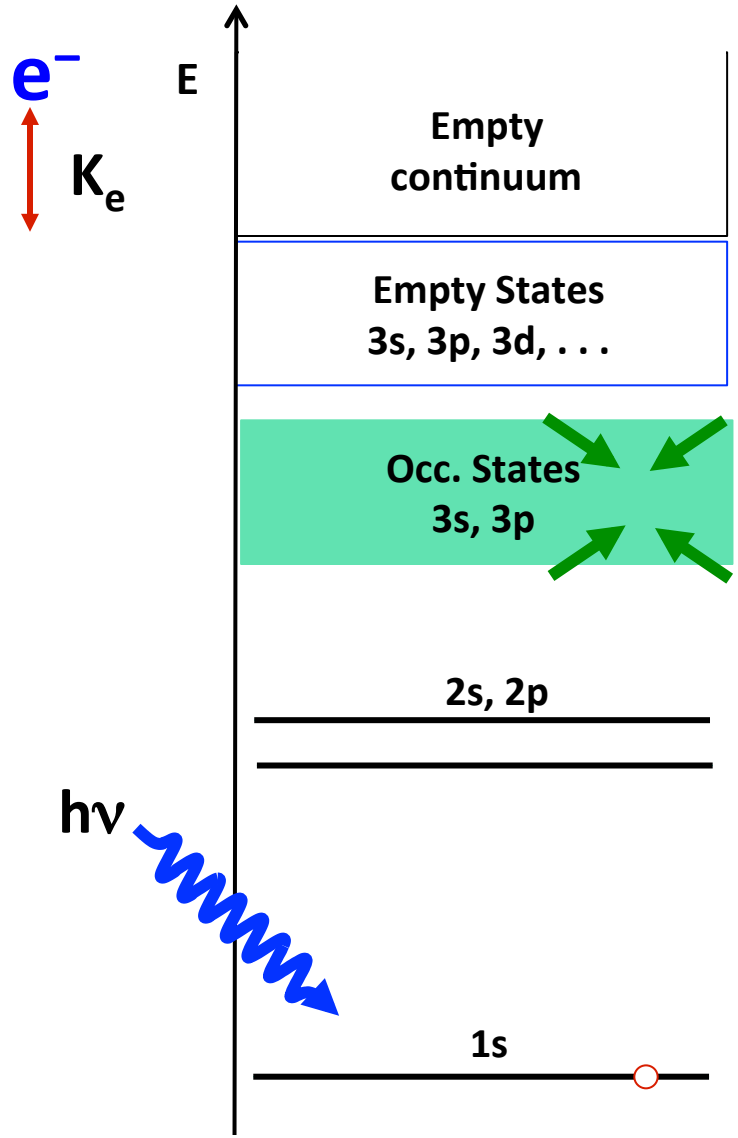
XPS Measurements: C 1s Binding Energy*



***Adiabatic**
(This links to atomic relaxation effects and vibronic structure in the measured spectra – Beyond scope here)

Saethre, Borve, and Thomas, *J. Elec. Spec. Rel. Phen.* **183**, 2, 2011

Final State Effects: Core-hole Induced Response



Initial state: Ground state system + photon

$$E_i = E_0 + h\nu$$

Final state: Relaxed system with core-hole + photo-electron

$$E_f = E_0 - \varepsilon_{1s} + E_{relax} + K_e$$

Measured binding energy

$$E_{bind} = h\nu - K_e = -\varepsilon_{1s} + E_{relax}$$

Estimate Coulomb relaxation (dielectric model)

$$E_{relax} = \frac{e^2}{2R}\left(\frac{1}{\varepsilon_0} - 1\right)$$

Example: Silicon vs SiO_2

Compare Si 2p (L edge) in bulk Si vs SiO_2

$$\Delta E_{bind} = E_{bind,Ox} - E_{bind,Si}$$

$$= (-\varepsilon_{2p,\,Ox}) - (-\varepsilon_{2p,\,Si})$$

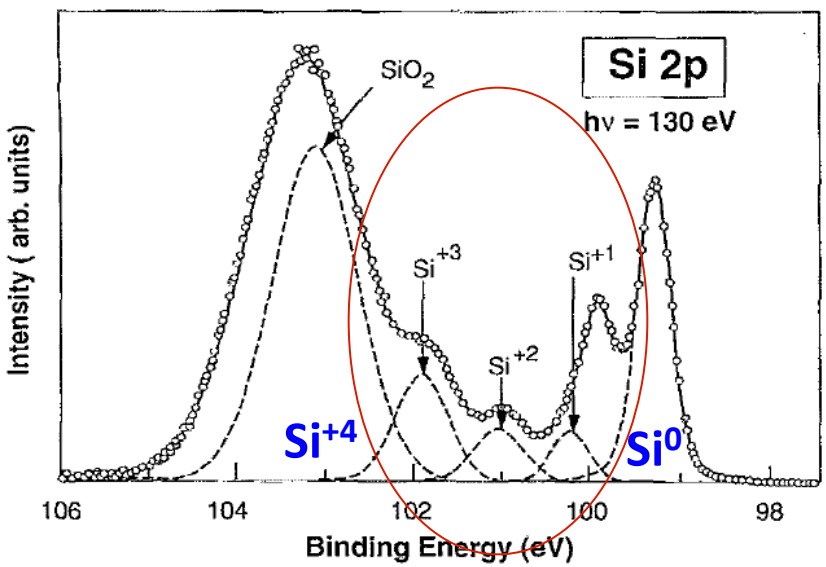
Initial state:
More ionic bond
→ Increase E_{bind}

$$+ (E_{relax,\,Ox} - E_{relax,\,Si})$$

Oxide less polarizable
→ Increase E_{bind}

$$E_{relax} = \frac{e^2}{2R}\left(\frac{1}{\varepsilon_{Ox}} - \frac{1}{\varepsilon_{Si}}\right)$$

Interface: Si(001): SiO_2

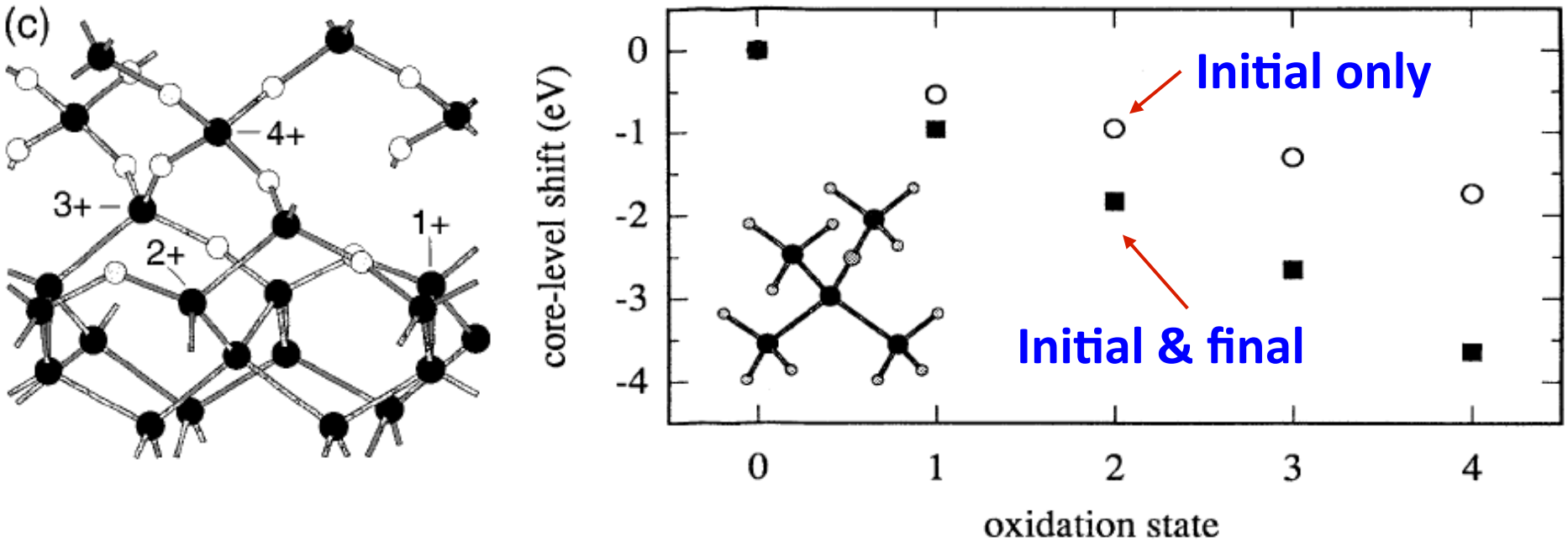


Lu, et al., *Appl. Phys. Lett.* **63**, 2941, 1993

Sub-oxide peaks
→ Interface Structure

Impact Final State Relaxation for Si(100):SiO_2

DFT-based Approach
to include relaxation response to core hole*



***Pseudopotential constructed with a core hole**

Pasquarello, Hybertsen & Car, *Phys. Rev. Lett.* **74**, 1025, 1995;
Phys. Rev. B **53**, 10942,1996.

Concluding Remarks

X-ray absorption and Electron energy loss spectroscopy (similar cross sections) both probe empty electronic states providing chemical fingerprints that probe valence, bonding & phase changes

X-ray photoemission maps local electrostatic potentials with shifts in core-level binding energy that probe valence and bonding

DFT-based approaches can simulate core-level binding energy shifts

Beyond-DFT tools required for the excited state spectra themselves

Resources

Review articles, Many-body Perturbation Theory –

- Hedin and Lundqvist, Solid State Physics, vol. 23, pp. 1-181, 1969
  - ***Strong exposition of fundamentals; no optics / BSE; materials discussion dated & limited***
- Aulbur, Jonsson and Wilkins, Solid State Physics, vol. 54, pp. 1-218, 2000
  - ***Reviews fundamentals; discussion of computational issues c2000; no optics / BSE; diverse materials examples***
- Onida, Reining and Rubio, Rev. Mod. Phys, vol. 74, pp. 601-659, 2002
  - ***Includes both GW and BSE; includes TD-DFT; materials examples and exposition emphasize optics***

Review articles, Core-level studies –

- Nilsson & Pettersson, Surf. Sci. Rep. 55, 49, 2004
  - ***Representative of use of DFT for chemical shifts and to approximate spectra***
- Rehr, et al., Phys Chem Chem Phys 12, 5503, 2010
  - ***Discusses "FEFF", an approach to X-ray spectra; part of a themed issue related to X-ray spectra***

  - ***N.B.: Rehr and Pettersson are senior theorists developing codes and applications for interpreting X-ray spectra***