Core level spectroscopy

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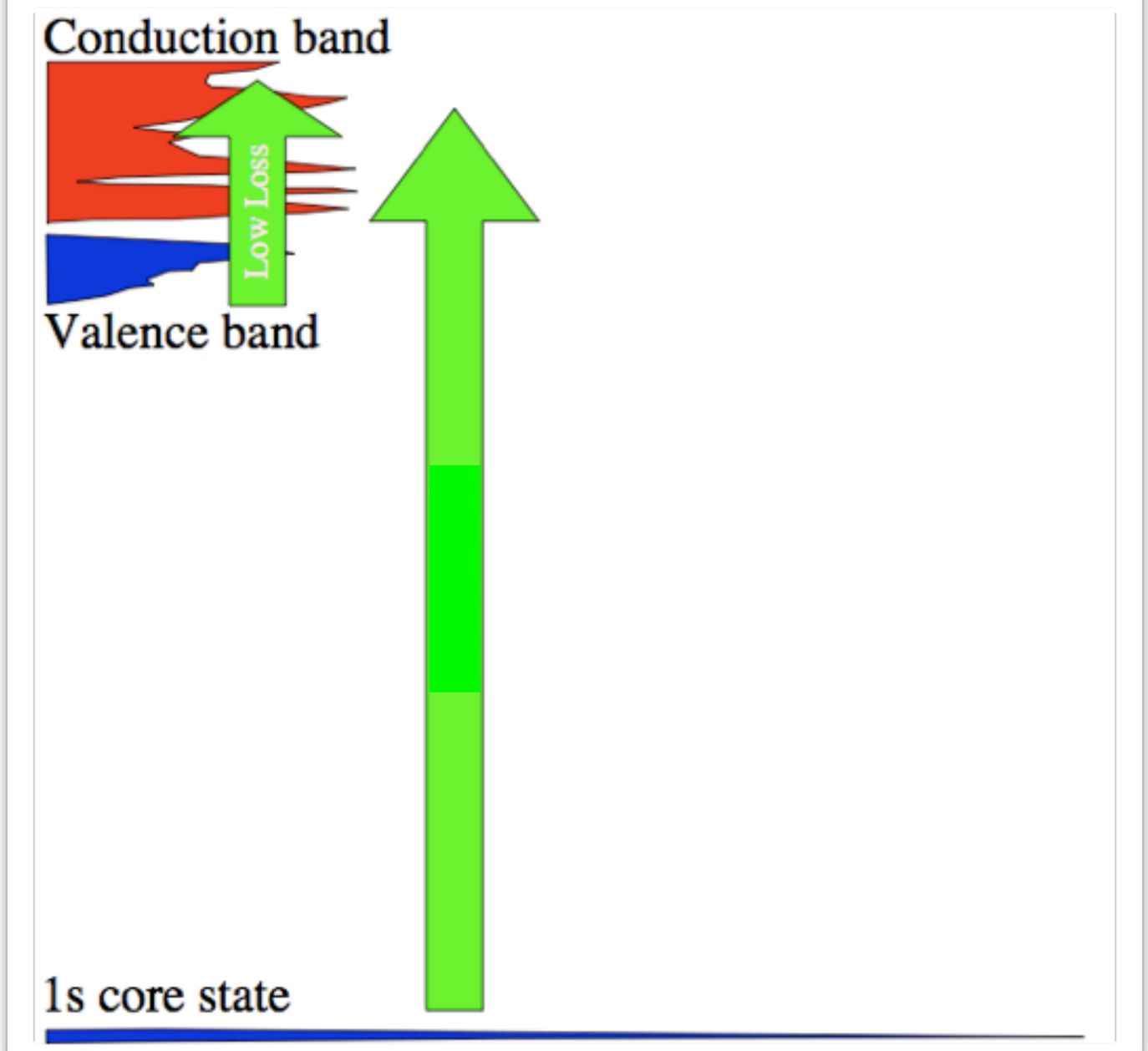
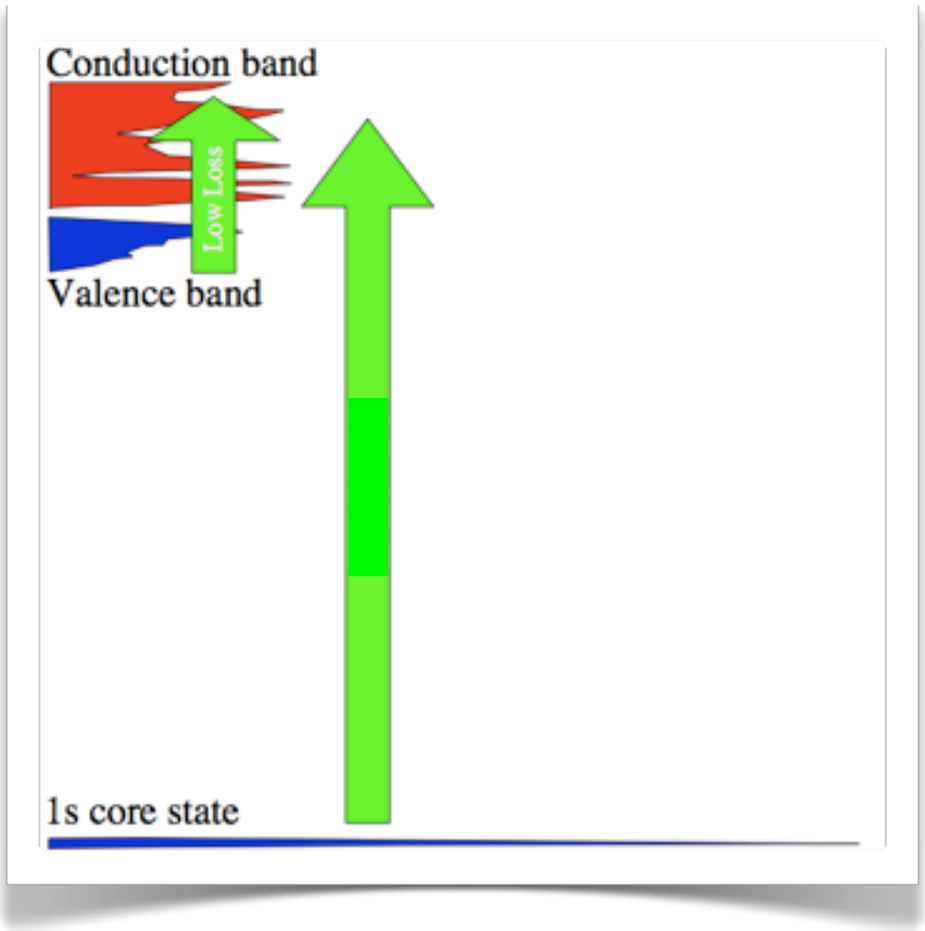


Absorption and Fermi's Golden Rule

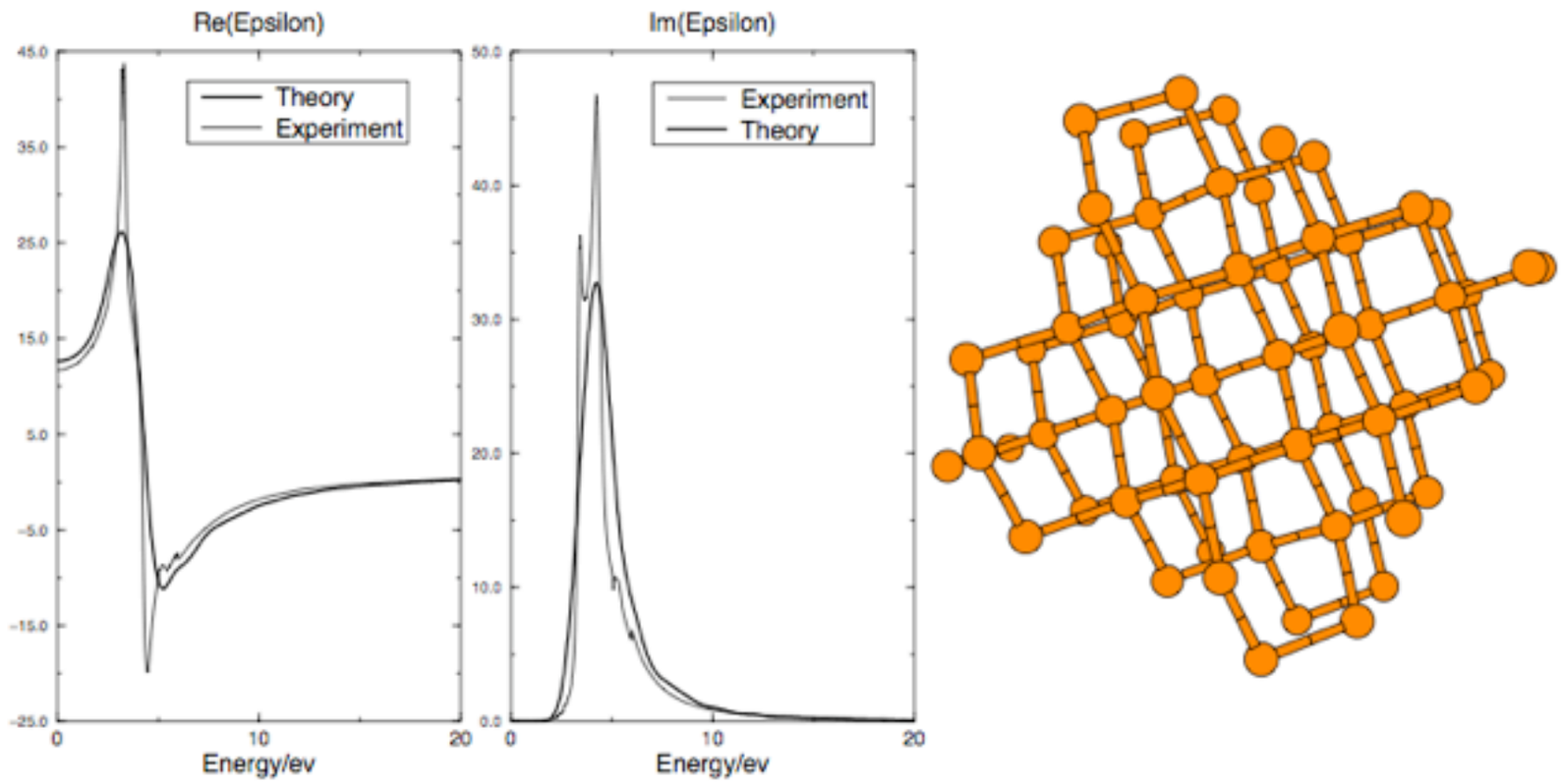
f



i

$$T_{i\to f} = \frac{2\pi}{\hbar} \left|\langle f \left| H \right| i \rangle\right|^2 \rho$$

Dielectric function



$$\varepsilon(\omega, \mathbf{q}) = \varepsilon_1(\omega, \mathbf{q}) + i\varepsilon_2(\omega, \mathbf{q})$$

Loss function:

$$\mathrm{Im}\left\{\frac{-1}{\varepsilon(\omega, \mathbf{q})}\right\}$$

Kramers-Kronig:

$$\varepsilon_1 \leftrightarrow \varepsilon_2$$

X-rays vs electrons

Identical theory to the first approximation

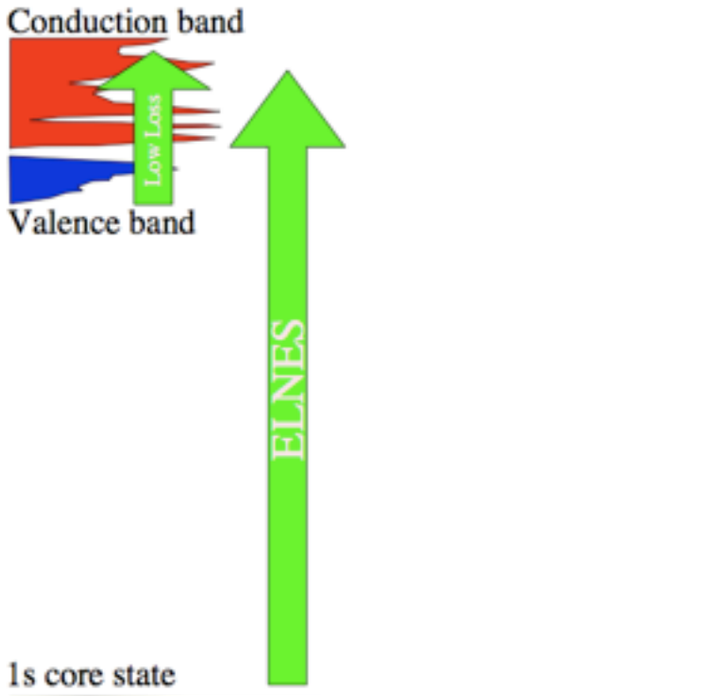
BUT

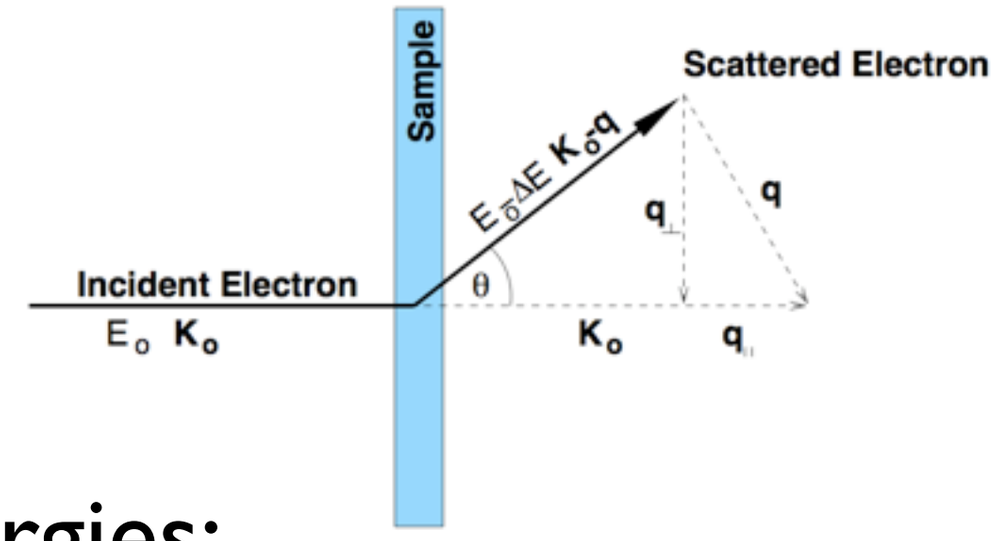
Electrons:

- Carry much more momentum
- Can be focussed into probes
- Can interact with ejected electrons

Core level spectroscopy

$$\frac{d^2\sigma}{d\Omega dE} = \frac{1}{(\pi e a_o)^2}\frac{1}{q^2} Im\left\{\frac{-1}{\varepsilon_M(\mathbf{q},\omega)}\right\}$$





At high energies:

$$Im\left\{\frac{-1}{\varepsilon(\mathbf{q},\omega)}\right\} = \varepsilon_2(\mathbf{q},\mathbf{q};\omega)$$

$$\varepsilon_2(\mathbf{q},E) = \frac{4\pi e^2}{\Omega q^2}\sum_{n,\mathbf{k}} |\langle\psi^n_{\mathbf{k}}|e^{i\mathbf{q}.\mathbf{r}}|\mathrm{c}\rangle|^2 \delta(E^c_{\mathbf{k}} - E_{1\mathrm{s}} - E)$$

Dipole approximation

$$\langle f|e^{i\mathbf{q}.\mathbf{r}}|i\rangle = \langle f|i\rangle + i\langle f|\mathbf{q}.\mathbf{r}|i\rangle + \frac{1}{2}\langle f|(\mathbf{q}.\mathbf{r})^2|i\rangle - \frac{i}{6}\langle f|(\mathbf{q}.\mathbf{r})^3|i\rangle + \frac{1}{24}\langle f|(\mathbf{q}.\mathbf{r})^4|i\rangle + \cdots$$

Dipole term

$$\langle f\,|x|\,1s\rangle \approx \langle f|P_x\rangle$$

Core level spectra can be thought of as angular momentum projected density of states

General strategy

Structural optimisation

Calculate self consistent ground state density

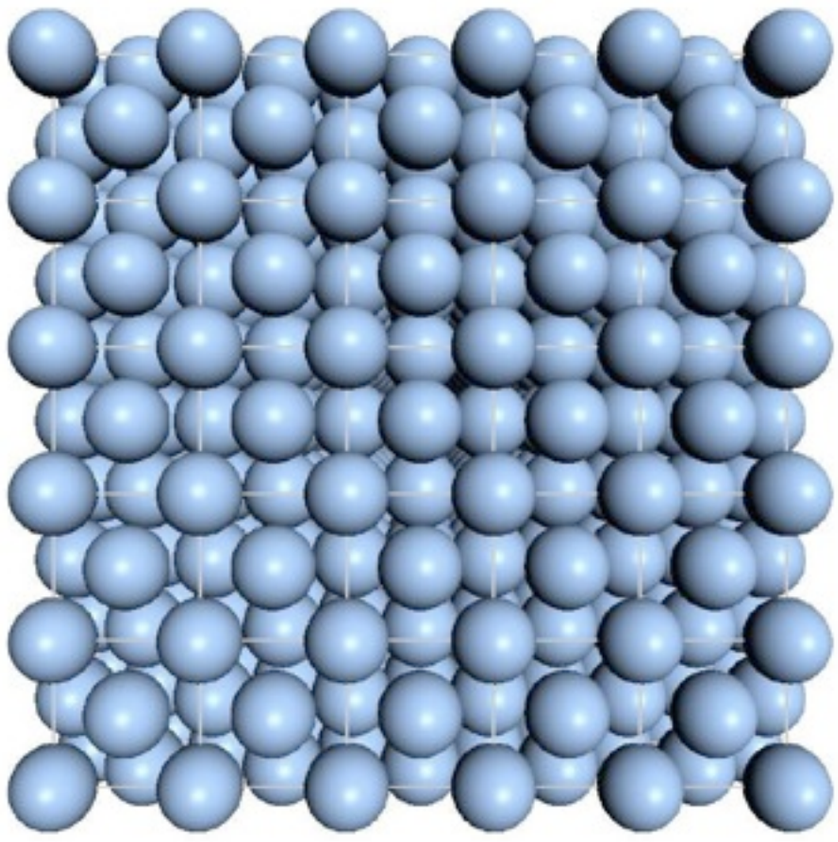
Calculate KS wavefunctions and eigenvalues

Evalulate matrix elements between core and conduction states

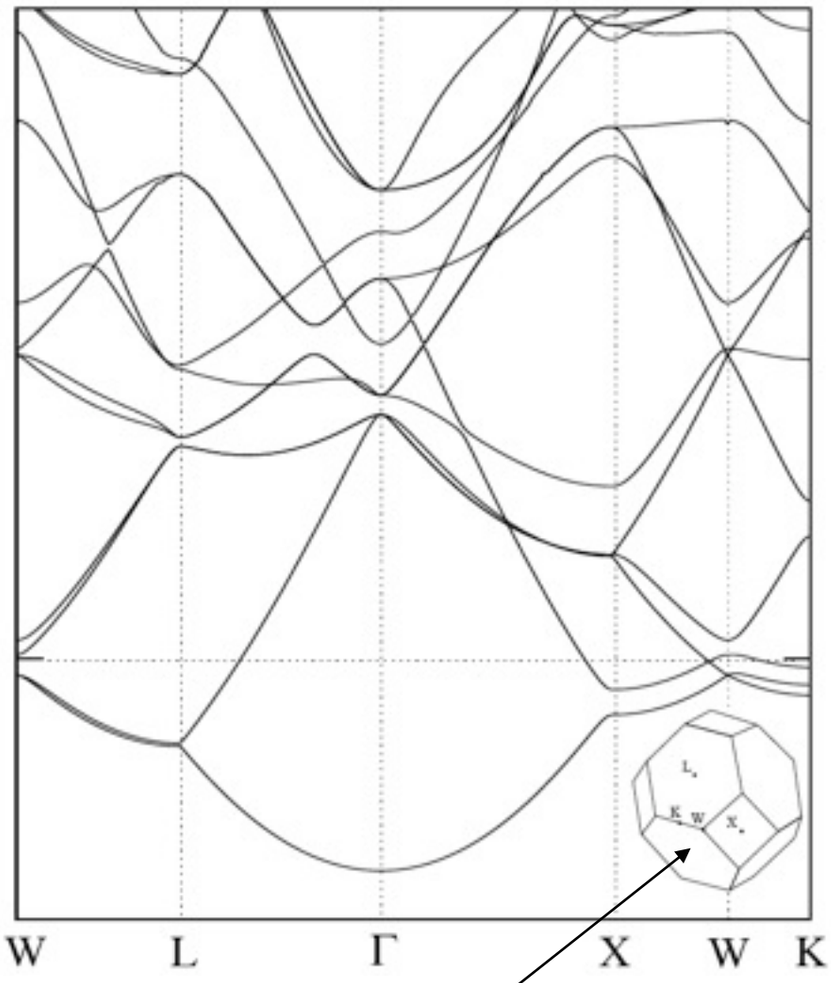
Form a weighted density of states

Periodic boundary conditions

Use the translational symmetry of the crystal



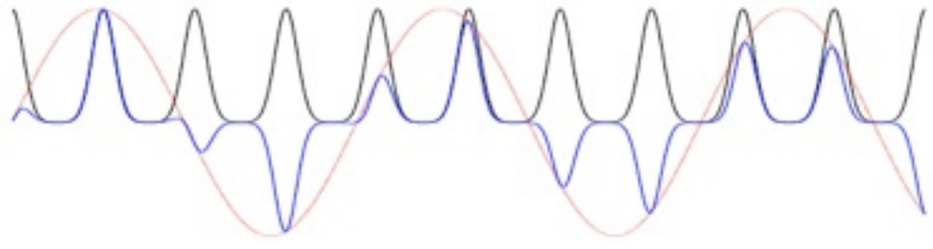
Al Bandstructure



1st Brillouin zone

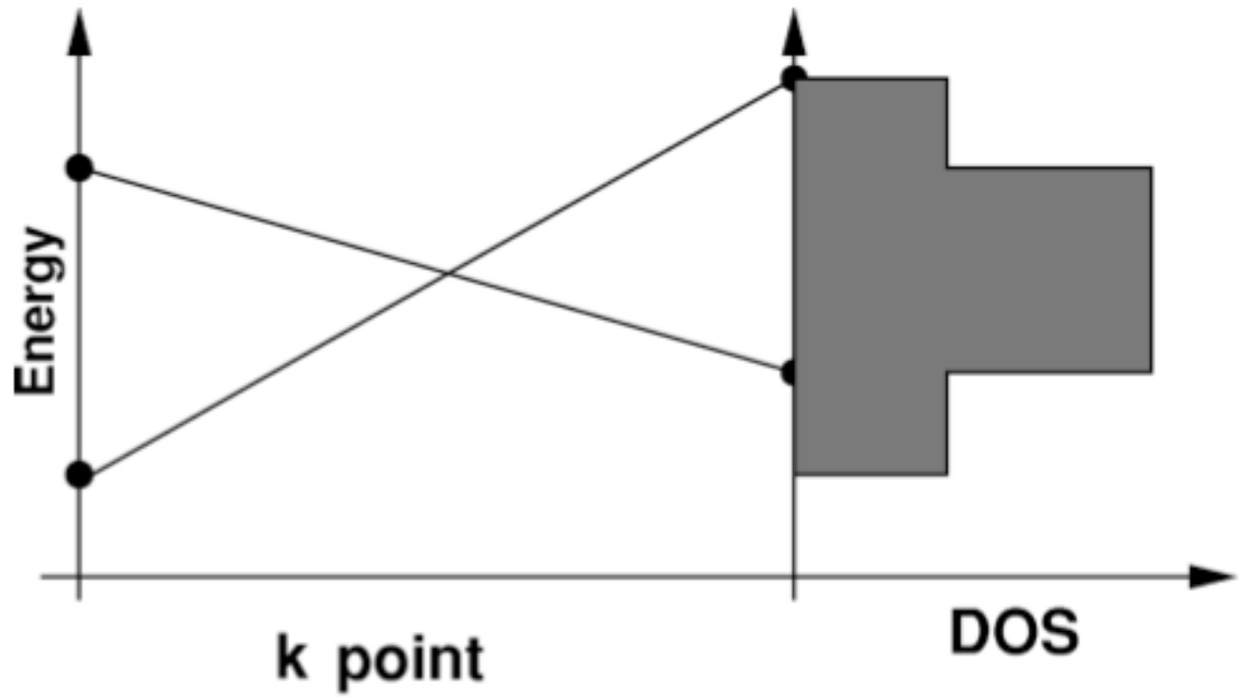
Bloch's theorem

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$$



Density of states

$$D(E) = \sum_i \delta(E - E_i)$$



Gaussian broadening or linear tetrahedron method (extrapolative)

Plane waves

Basis functions

$$e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

A Fourier series

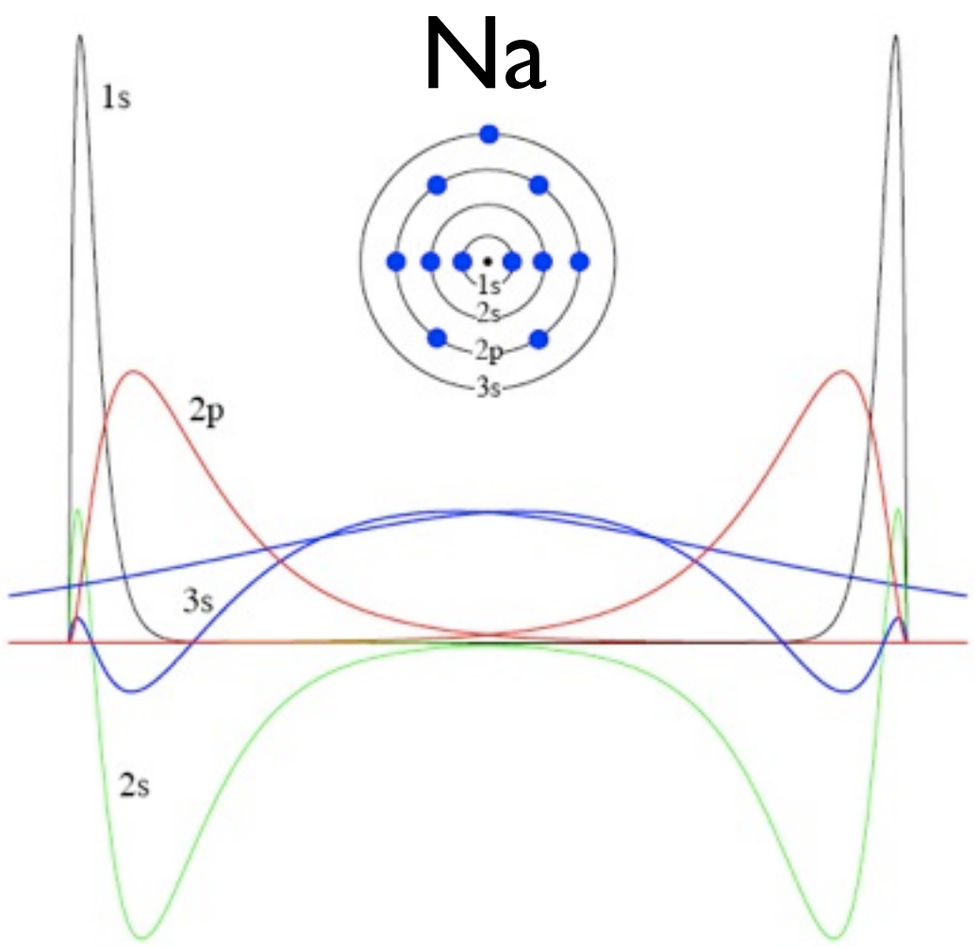
Unlike atom centred atomic orbitals or gaussian functions, there is no "origin" to a plane wave

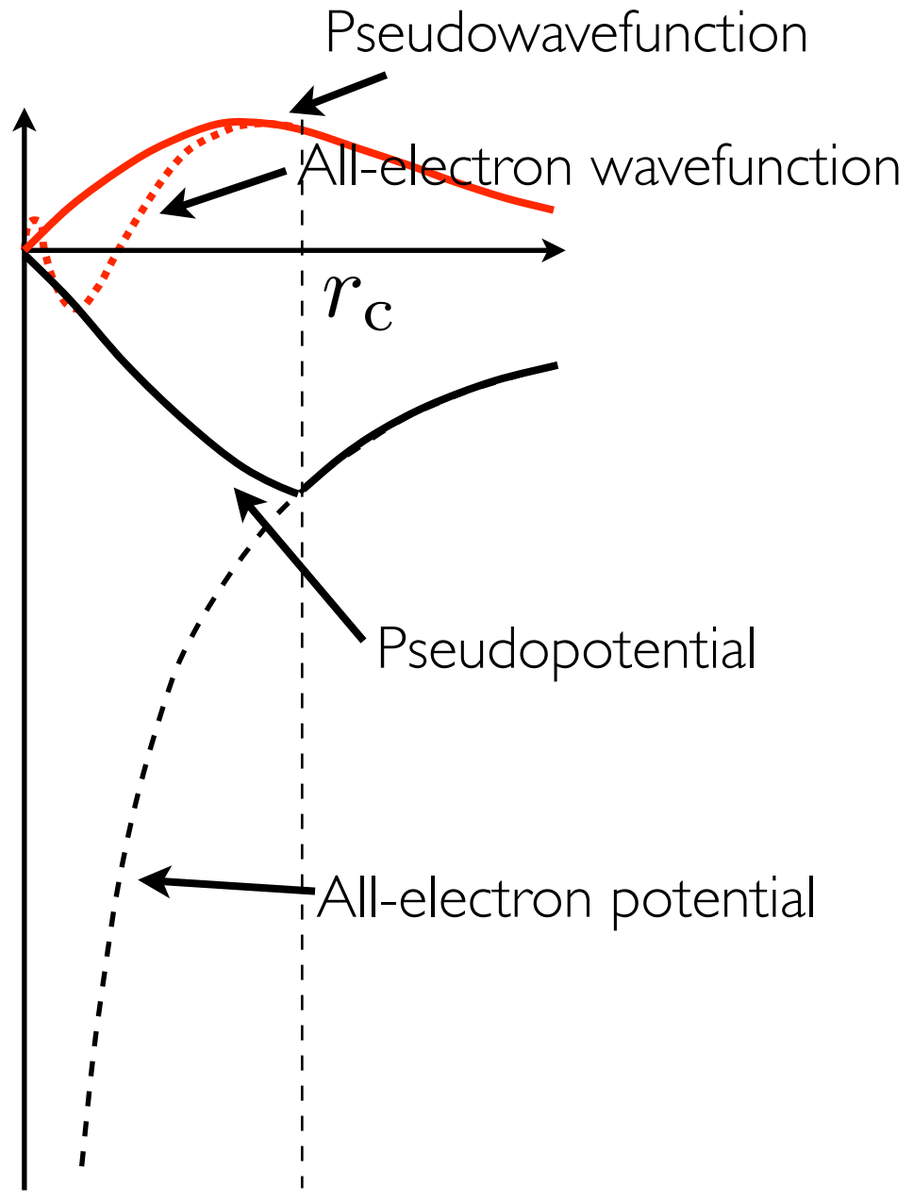
Easy for theory and computation

The quality of the basis is controlled by a single number

$$\frac{1}{2}|\mathbf{k}+\mathbf{G}|^2 \leq E_{\text{cut}}$$

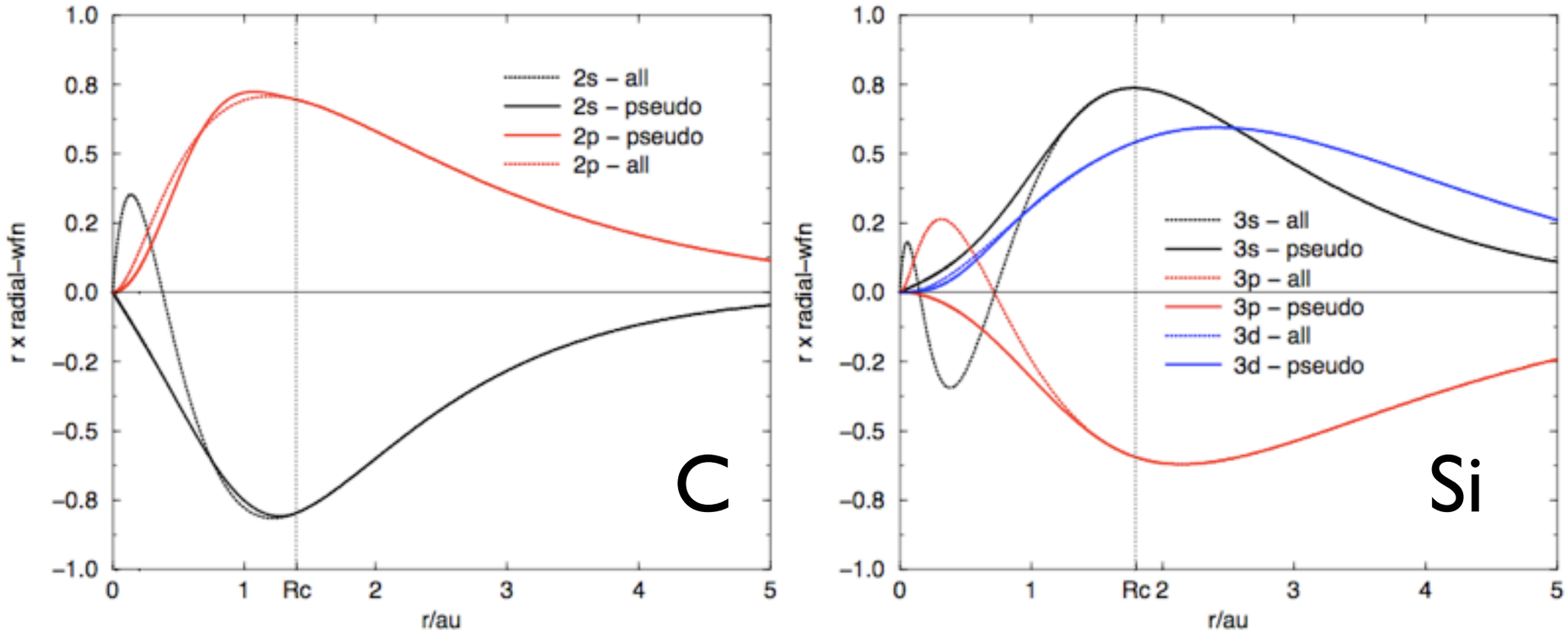
Pseudopotentials





The core electrons are “frozen” and the valence orbitals smoothed within the “core radius”

A pseudopotential theory



We must fix up the wavefunction near the nucleus

Projector augmented waves

$$|\Phi\rangle = \mathcal{T}|\tilde{\Phi}\rangle \text{ where } \mathcal{T} = 1 + \sum_n (|\phi_n\rangle - |\tilde{\phi}_n\rangle)\langle\beta_n|$$

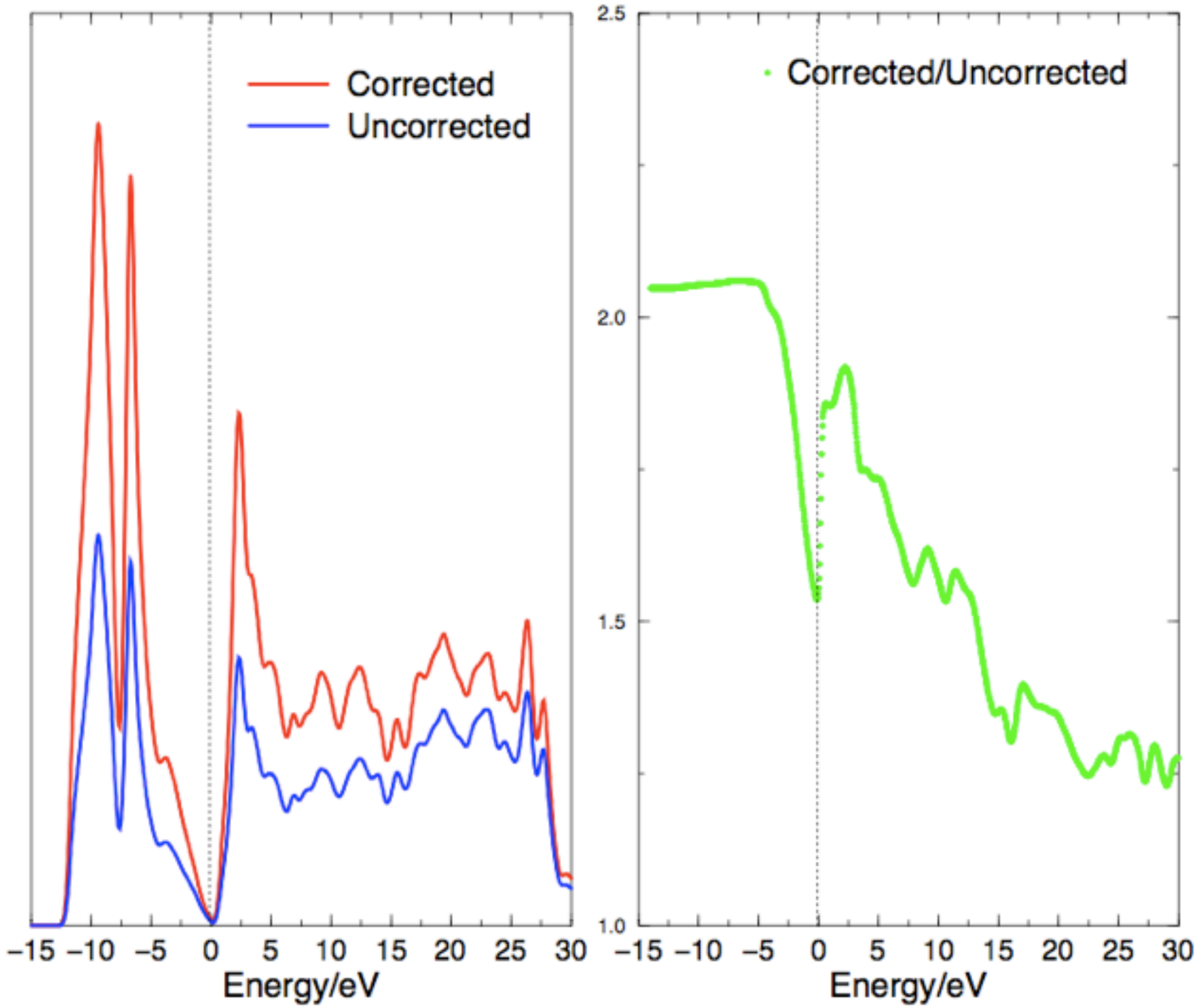
Matrix elements

$$\langle f|e^{i\mathbf{q}.\mathbf{r}}|i\rangle = \langle f|i\rangle + i\langle f|\mathbf{q}.\mathbf{r}|i\rangle - \frac{1}{2}\langle f|(\mathbf{q}.\mathbf{r})^2|i\rangle - \frac{i}{6}\langle f|(\mathbf{q}.\mathbf{r})^3|i\rangle + \frac{1}{24}\langle f|(\mathbf{q}.\mathbf{r})^4|i\rangle + \cdots$$

Dipole

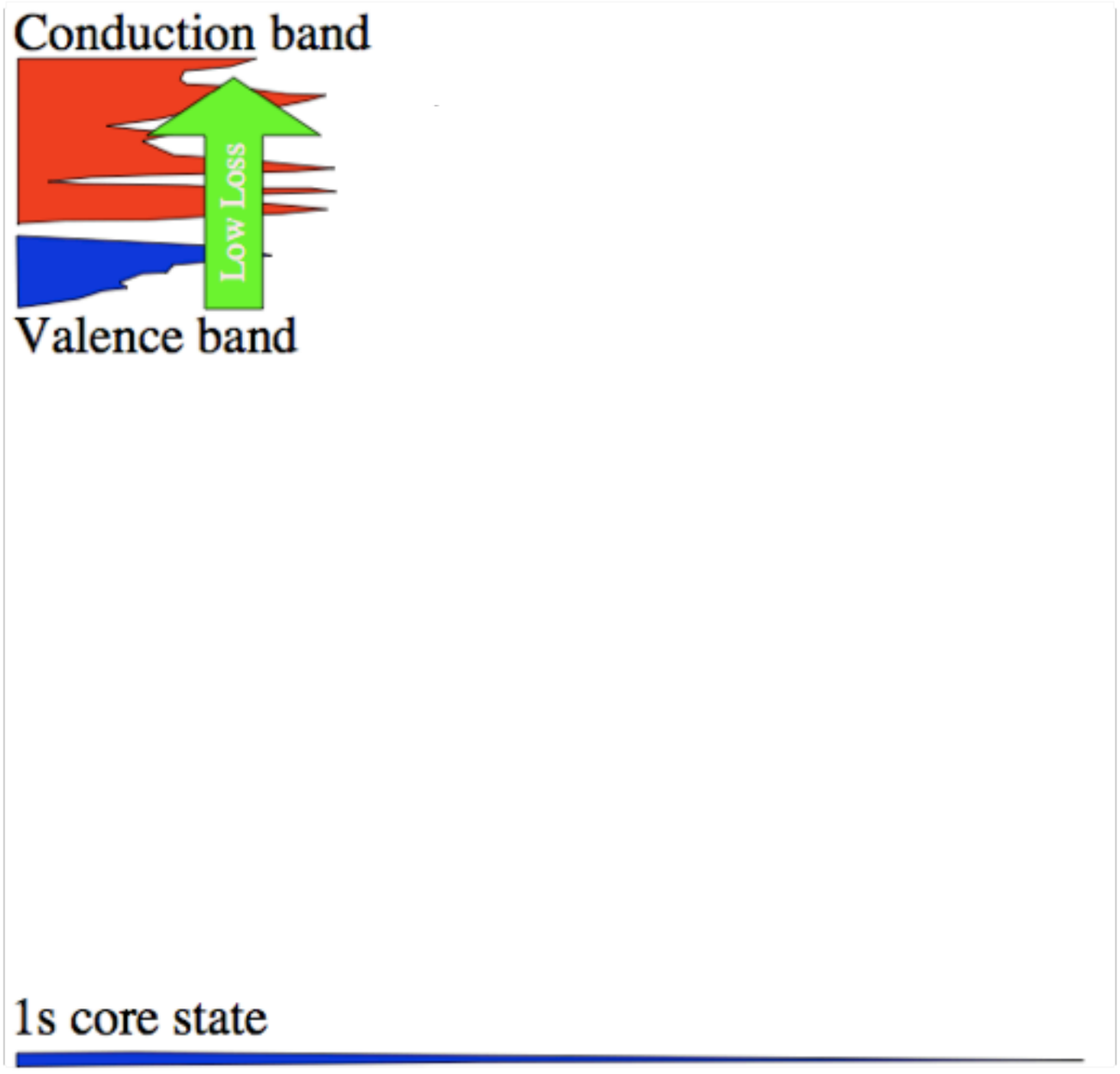
	CASTEP		All electron
	Uncorrected	Corrected	
Carbon			
$1s \rightarrow 2p$	0.03997	0.04313	0.04316
Silicon			
$1s \rightarrow 3p$	0.00065	0.00472	0.00471
$2s \rightarrow 3p$	0.06207	0.03164	0.03168
$2p \rightarrow 3s$	0.09308	0.05213	0.05196
$2p \rightarrow 3d$	—	—	0.05262

Energy dependence

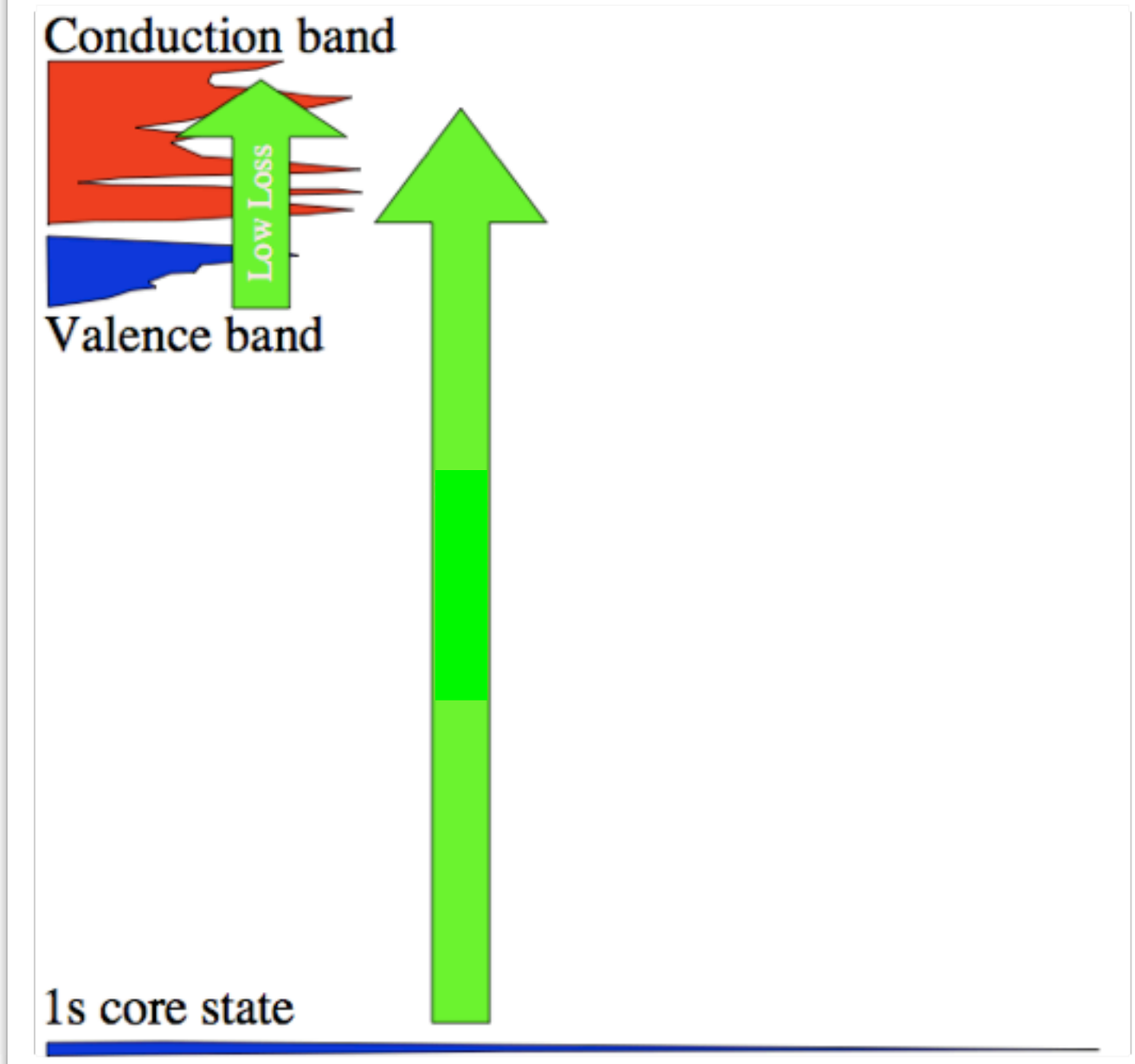


Si L23

Core hole effects



Core hole effects



*

Theoretical approaches

Weak
Perturbative approach - Clogston-Wolff

Strong
Atomic multiplet theory

In many insulators it is somewhere inbetween and is a challenge ...

Single particle approach

Beyond the "sudden" approximation

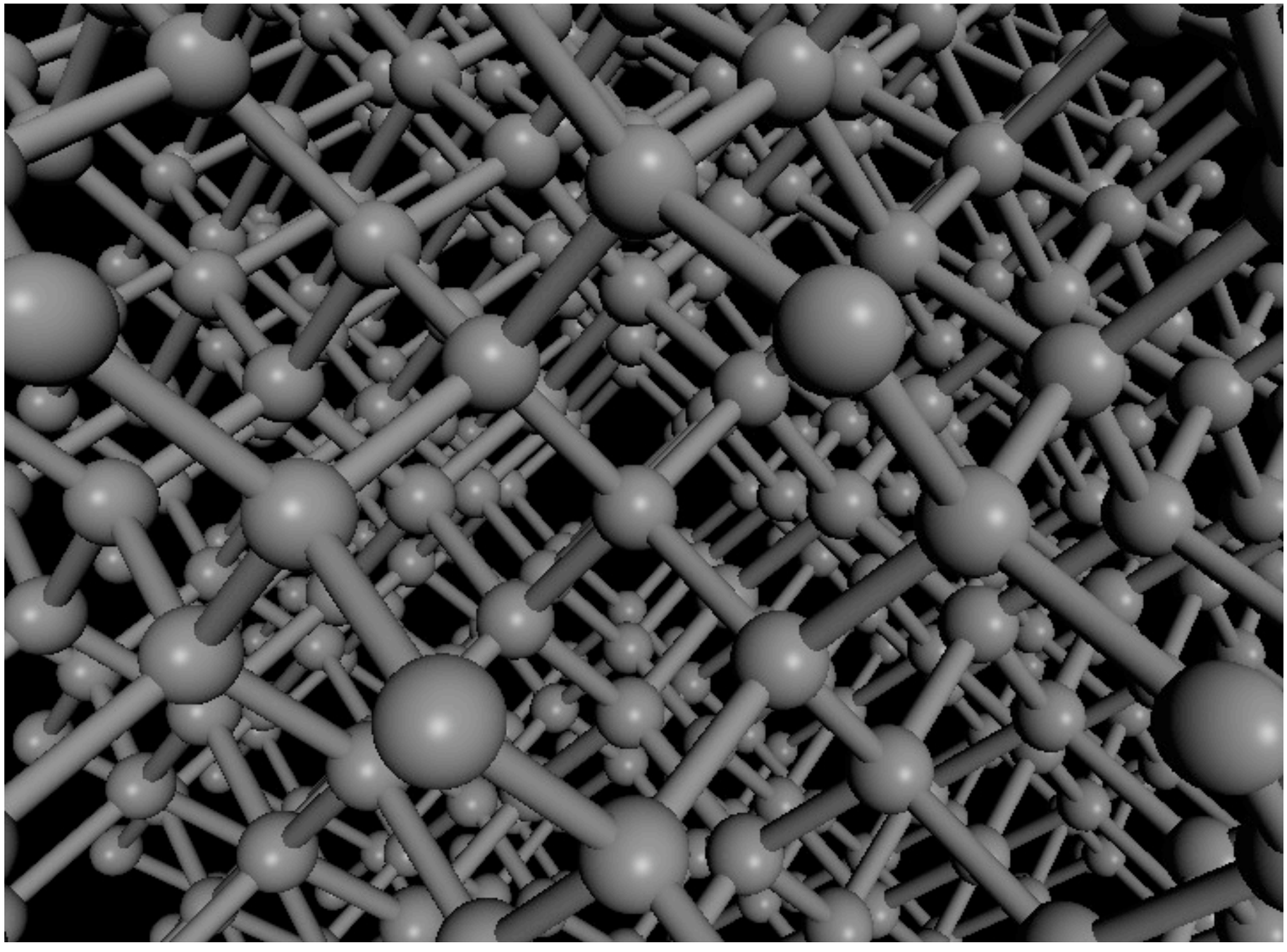
Exploit separation of timescales:

1) Core electron ejected
2) Lattice remains fixed
3) Final states relax

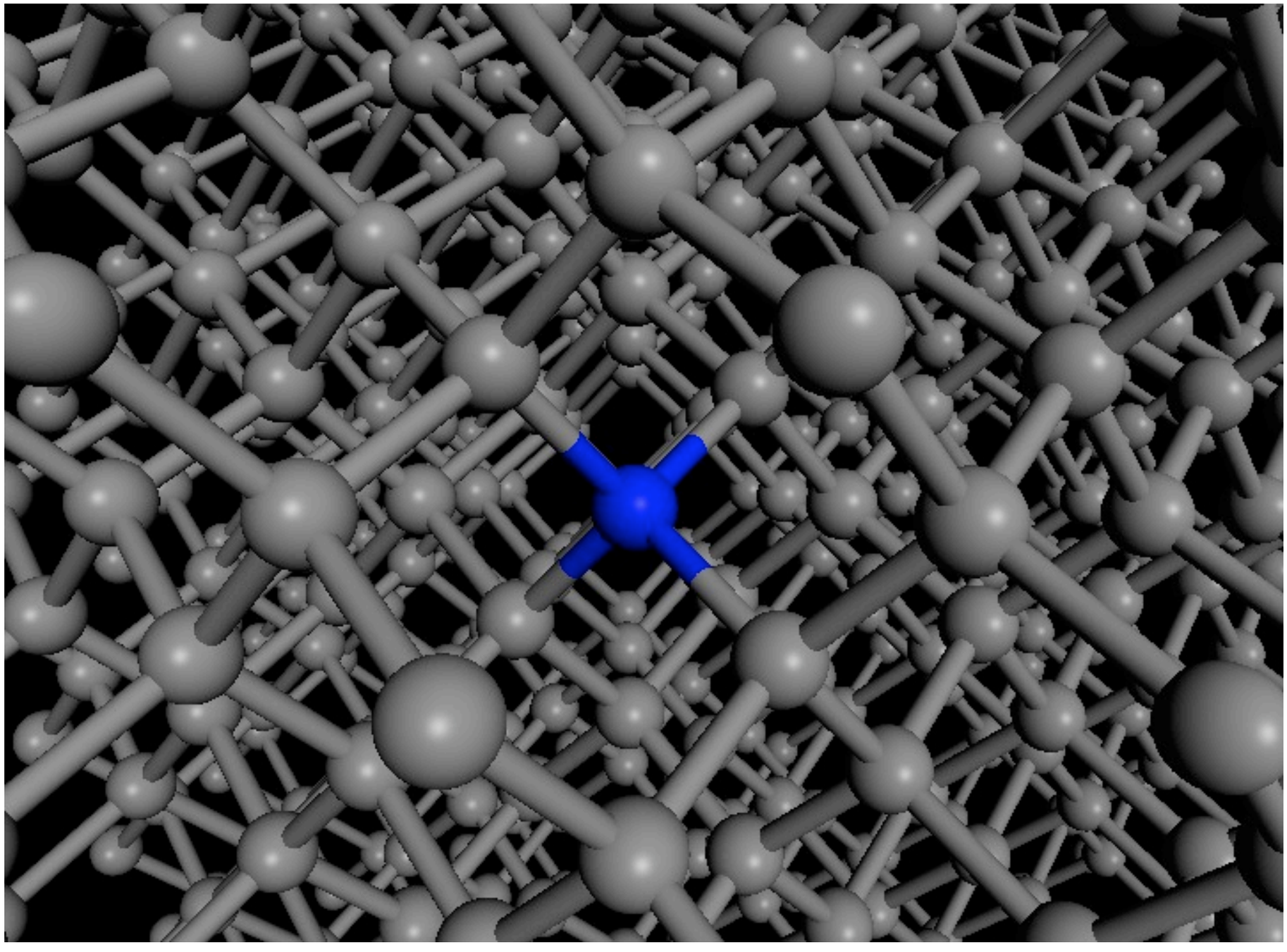
Initial core state from an atomic calculation

Final states from self consistent calculation
with a single excited atom

Supercell approximation



Supercell approximation



Excited atom

Z+1 approximation
(eg replace C with N)

Constrained calculation
(only possible with AE code)

Excited pseudopotentials
(need to be able to generate PSPs)

On-the-fly pseudopotentials

A feature unique to CASTEP

Remember and use the generation data for PAW

```
%BLOCK SPECIES_POT
C 2|1.4|1.4|1.3|6|10|12|20:21(qc=6)[]
%ENDBLOCK SPECIES_POT
```

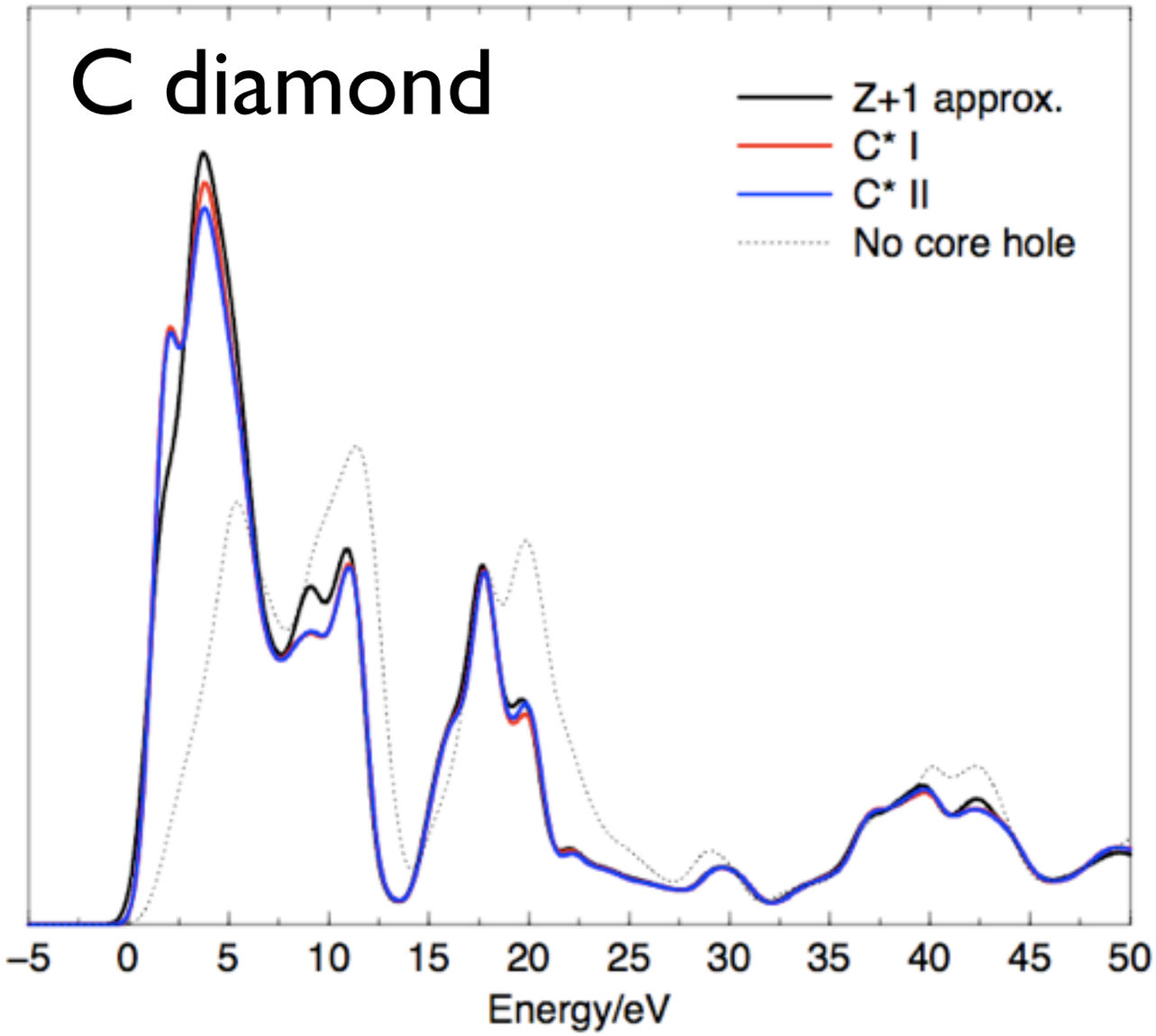
Great power - and responsibility

TEST!!!

Core hole effects

Put the core hole in the pseudopotential

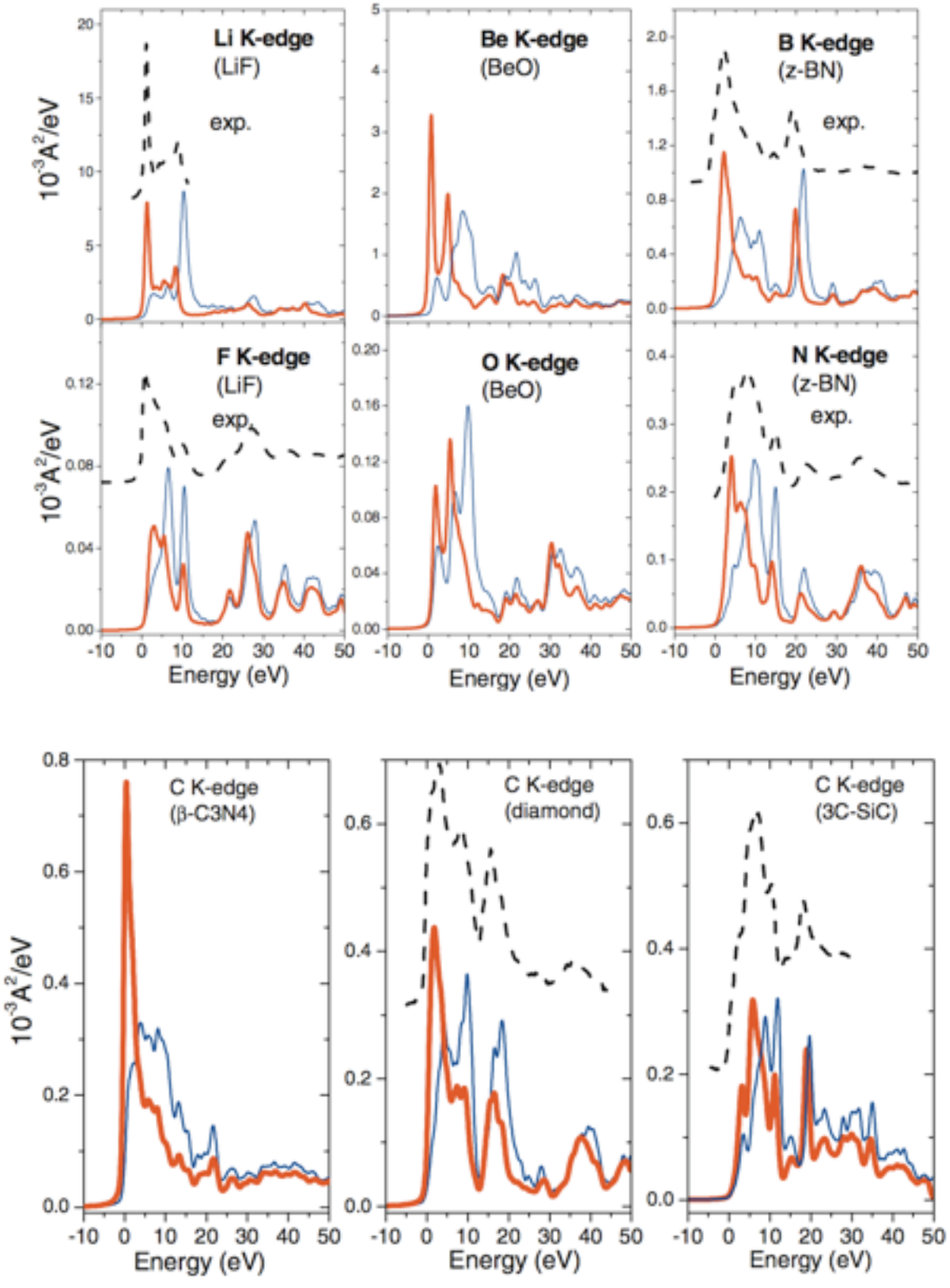
Use the supercell approximation

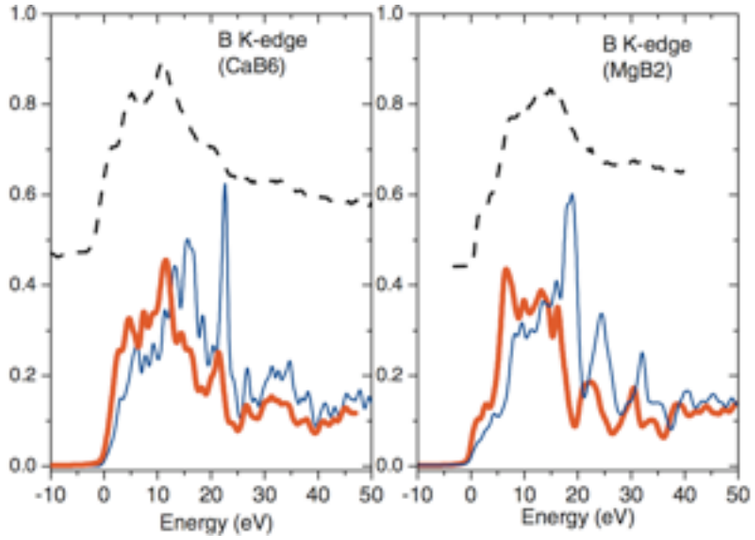


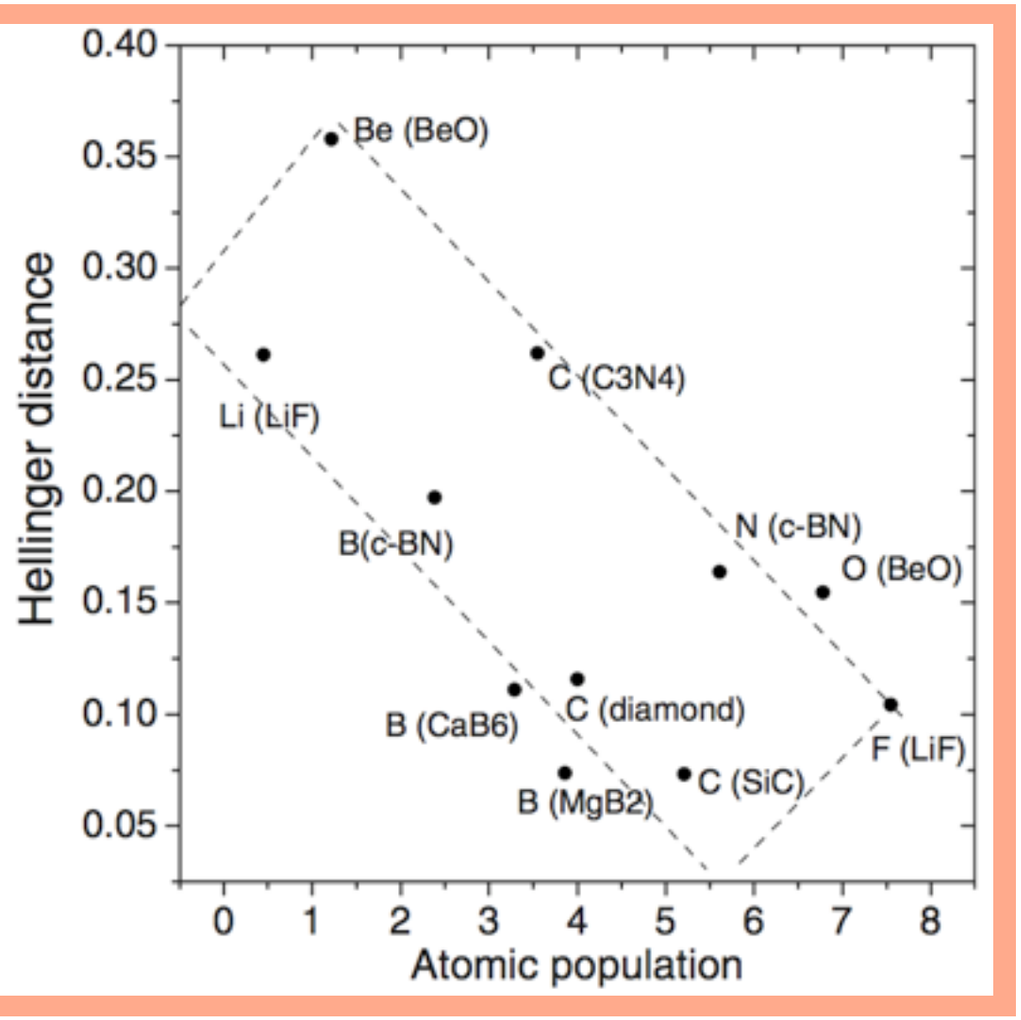
The strength of the core hole effect varies considerably from material to material

Screening

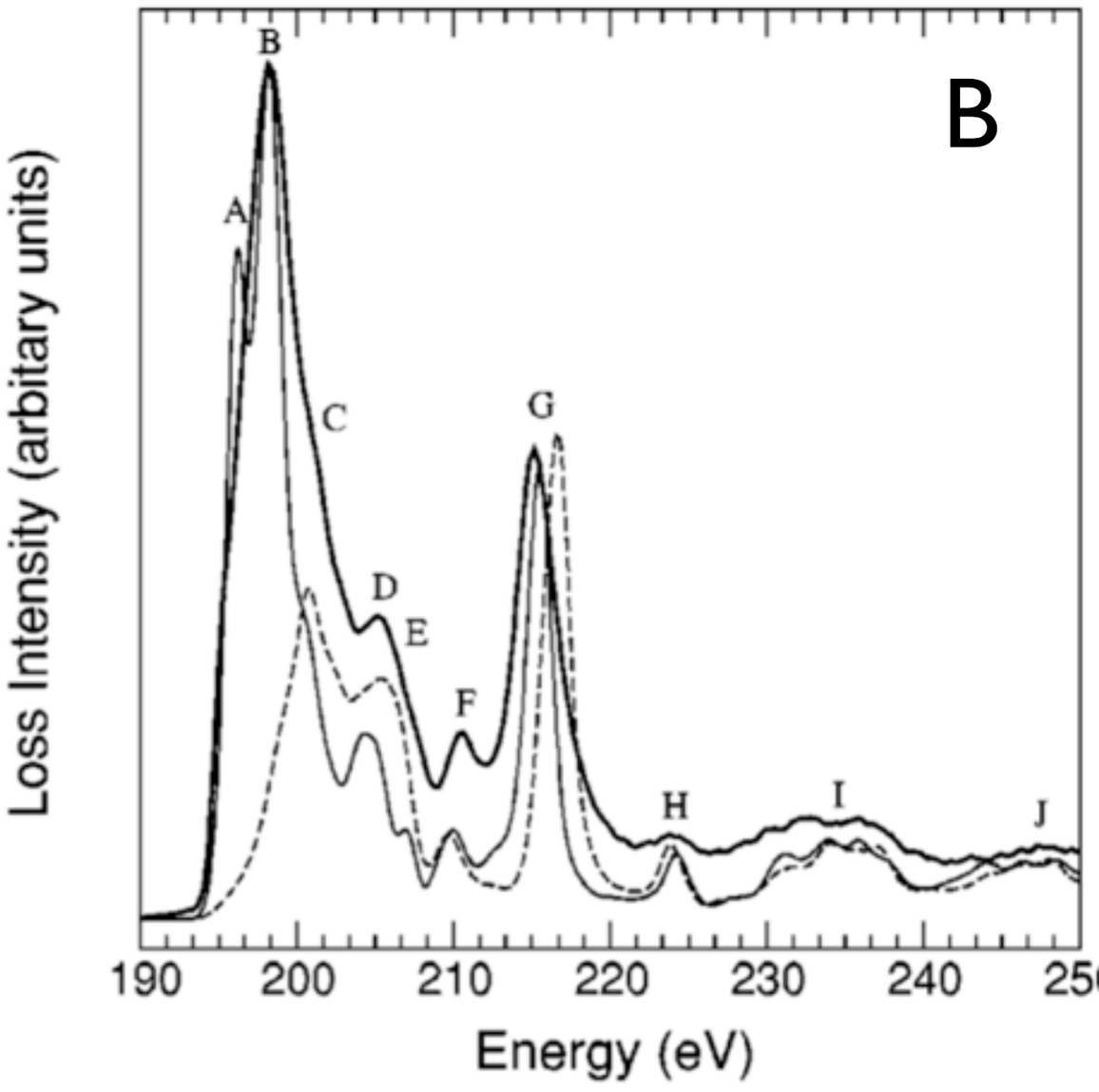
Core hole strength

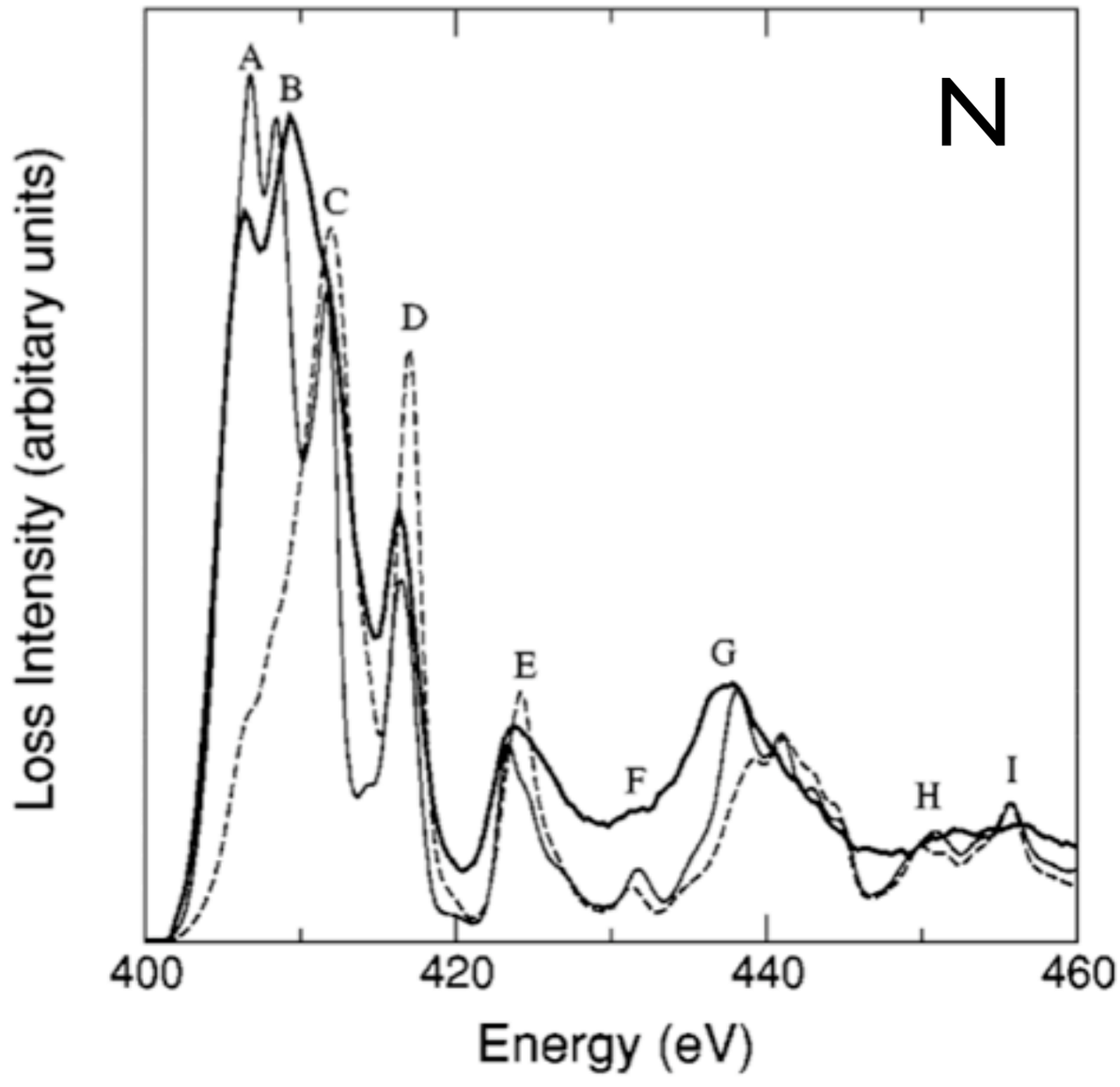






Boron Nitride





"Cubic boron nitride: experimental and theoretical energy-loss near edge structure",
Jayawardane, Pickard, Brown and Payne,
Phys. Rev. B, **64**, 115107 (2001)

Theory overview

	Theory	Methods	Features
I	*Atomic calculation*	atomic multiplet [96], multiconfigurational Dirac Fock (MCDF)	basic edge shapes, L2,3 ratio, multiplet fine structure, crystal field splitting can be included
II	*Single scattering*	EXAFS and EXELFS methods [92]	reflections from neighbouring atoms, describes extended structure above ~50eV
III	*Multiple scattering*	XANES methods [26]	multiple reflections, *not* self-consistent, poor description of threshold
IV	*Self-consistent band theory*	muffin tin — augmented plane wave (APW) [9], augmented spherical wave (ASW) [37, 100], Korringa-Kohn-Rostoker (KKR) [58] ...	self-consistent potentials, all electron, directly interpretable local angular momentum resolved DOS
		pseudopotential — pseudo-atomic orbital [102] and planewave [15]	pseudo-atomic orbitals give direct interpretation of DOS, but the inadequate basis leads to failure at high energies. Planewaves are discussed in the current work
V	*Inclusion of core effects*		

Why plane waves?

Ease of use

Large complex low symmetry problems

Structural relaxation

Complications

Excited state lifetimes determine the energy dependent broadening

Where should the excited electron be put?

Linking with multiplet theory

Beyond the dipole approximation

Magnetism

How well does KS describe the excited states?

The challenge is to tackle these without losing the efficiency that allows realistic systems to be investigated

Bibliography

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First principles methods using CASTEP	Clark et al	Zeitschrift fur Kristallographie **220**, 567-570 (2005)
Ab initio EELS with a plane wave basis set	Pickard et al	Electron microscopy and analysis 1997 **147**, 211-214 (1995)
Ab initio EELS: beyond the fingerprint	Pickard et al	Electron microscopy and analysis 1995 **153**, 179-182 (1997)
Cubic boron nitride: experimental and theoretical energy-loss near edge structure	Jayawardane et al	PRB **64**, 115107 (2001)
Theory of core hole effects in 1s core level spectroscopy of the first-row elements	Gao et al	PRB **77**, 115122 (2008)

Direct link to thesis:
Ab initio electron energy loss spectroscopy

http://www.tcm.phy.cam.ac.uk/~cjp20/old/thesis.tar.gz