The Linearized Augmented Planewave (LAPW) Method

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$$E_{T}[\rho]=T_{s}[\rho]+E_{ei}[\rho]+E_{H}[\rho]+E_{xc}[\rho]+E_{ii}$$

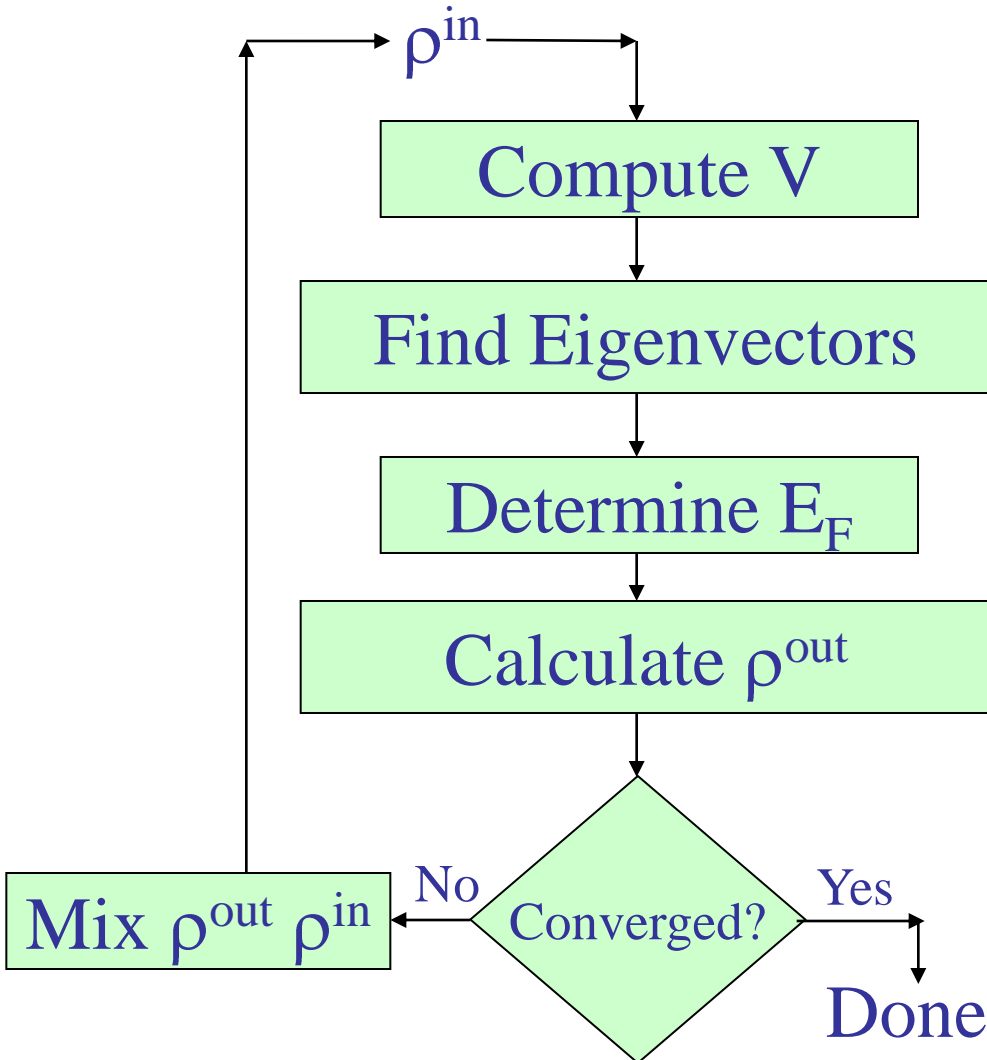$$\{T_{s}+V_{ks}[\rho,r]\}\varphi_{I}(r)=\varepsilon_{i}\varphi_{i}(r)$$

Need tools that are reliable and predictive.

CECAM, July 18, 2011

DFT ALGORITHMS

•Find φ_I and ρ to solve:

$$\{ T_s + V_{ks}[\rho,r] \} \varphi_I(r) = \varepsilon_i \varphi_i(r)$$

```
                    ρ^in
                      |
                      v
             ┌──────────────────┐
             │   Compute V      │
             └──────────────────┘
                      |
                      v
             ┌──────────────────┐
             │ Find Eigenvectors│
             └──────────────────┘
                      |
                      v
             ┌──────────────────┐
             │ Determine E_F    │
             └──────────────────┘
                      |
                      v
             ┌──────────────────┐
             │ Calculate ρ^out  │
             └──────────────────┘
                      |
                      v
  ┌──────────────┐  No  ◇
  │ Mix ρ^out ρ^in│◄─── Converged? ──── Yes
  └──────────────┘        ◇              |
                                         v
                                       Done
```

Standard Solution:

- Expand φ_I in a basis $\{\phi_j\}$.
- Many methods, PW, FE, LAPW, LMTO, LCAO ...
- For fixed V_{KS} get a linear algebra problem. (eigenvalue).

$$<\phi|H|\phi>x_i = \varepsilon_i<\phi|\phi>x_i$$

- Iterate to find self-consistent ρ.

Some Numbers:

- # φ_I ~ 10 / atom.
- # ϕ_j ~ 10's - 1000's / atom.
- # atoms (State of the Art): 100 – 1000's.

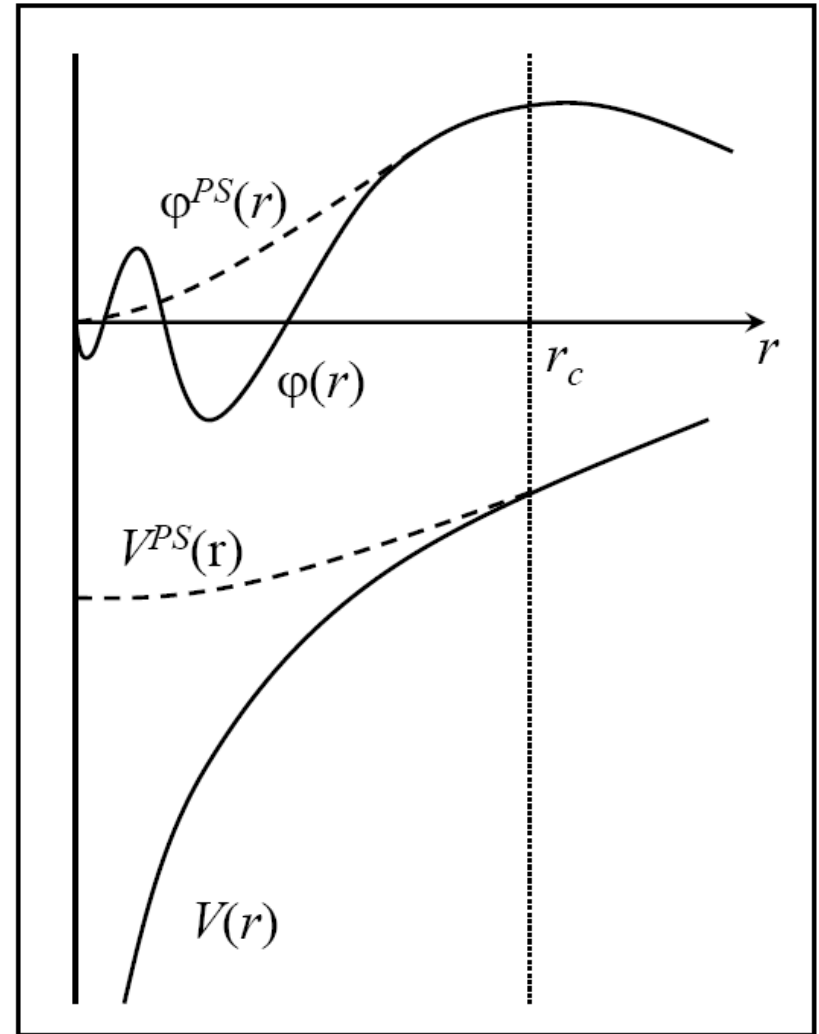# Motivation for Augmentation
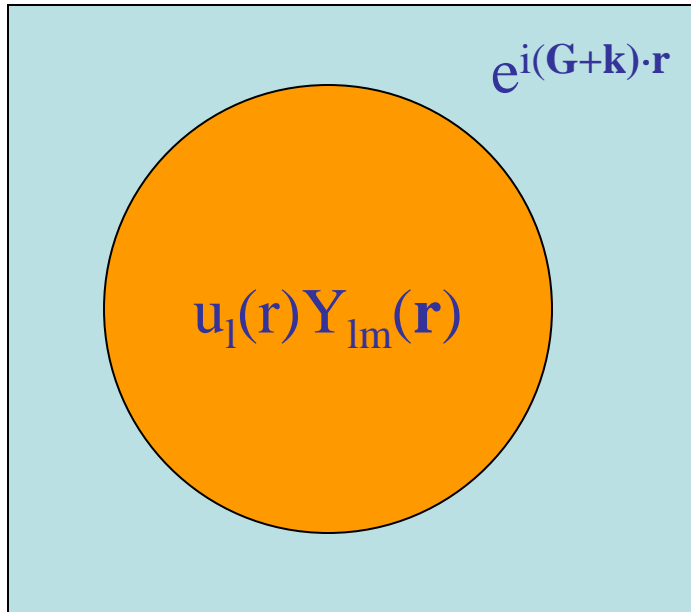
Schrödinger Equation:

$$(T+V-\varepsilon)\varphi = 0$$

For valence states: ε is small ➔

Tφ is also small except where V is strong, i.e. near the nucleus.

Augmented Planewave (APW) Method

•J.C. Slater, *Phys. Rev.* **51**, 846 (1937); *Phys. Rev.* **81**, 385 (1951).

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

$u_l(r)Y_{lm}(\mathbf{r})$

Divide Space Into 2 Regions:

•Atom Centered Spheres

•Interstitial

"Basis" Consists of Planewaves in the Interstitial and Radial Functions in the Spheres.

$$\varphi(\mathbf{r}) = \begin{cases} \Omega^{-1/2} \sum\limits_{\mathbf{G}} c_{\mathbf{G}}\, e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}} & r \in \text{Interstitial (I)} \\[2ex] \sum\limits_{lm} A_{lm}\, u_l(r)\, Y_{lm}(\mathbf{r}) & r \in \text{Sphere (S)} \end{cases}$$

• $u_l(r)$ are the radial solutions of Schrodinger's equation at the energy of interest (i.e. the band energy).

Efficiency & Accuracy
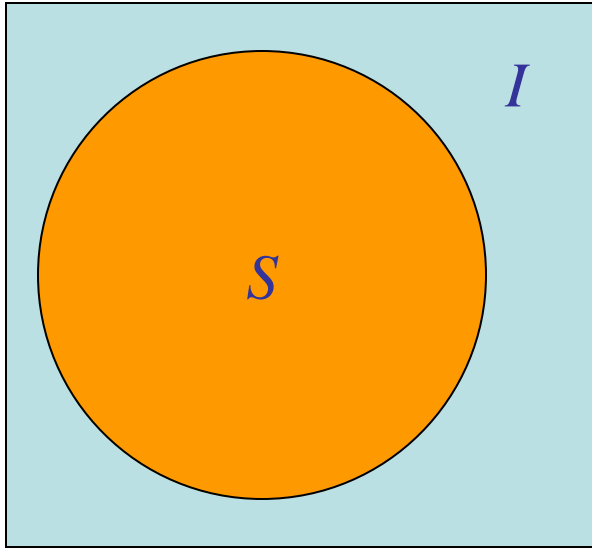
(1) Very efficient basis set.

(2) Represent all quantities as generally as possible in all regions of space and make only controlled approximations.

Spheres: Atomic-like treatment
- Numerical radial functions times Y_{lm}: can increase l_{max}
- Angular integrals are fast due to orthogonality of the Y_{lm}

Interstitial: Free space like treatment
- Planewave expansions.
- Integrals are fast due to FFT properties
  - Step function (cut out spheres) can be done exactly up to finite G_{max} by convolution with pre-computed $U(G)$

Augmented Planewave (APW) Method

$$\varphi(\mathbf{r}) = \begin{cases} \Omega^{-1/2} \sum_{\mathbf{G}} c_{\mathbf{G}} \, e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}} & r \in \text{Interstitial (I)} \\ \sum_{lm} A_{lm} \, u_l(r) \, Y_{lm}(\mathbf{r}) & r \in \text{Sphere (S)} \end{cases}$$

Key points:

1. The A_{lm} are not variational parameters. They are determined by a matching condition. That is the value of the basis functions, $\phi_{\mathbf{k}+\mathbf{G}}$ is fixed to be continuous at the sphere boundary.

2. The full crystal potential can be used because one may show that the u_l are orthogonal to "core" states.

$$[-d^2/dr^2 + l(l+1)/r^2 + V(r) - E_l] \, r u_l(r) = 0$$

So:

$$(E_2 - E_1) \, r \, u_1 \, u_2 = u_2 \, (d^2 r u_1/dr^2) - u_1 \, (d^2 r u_2/dr^2)$$

Integrate by parts to get overlap of u_1 *and* u_2. They are orthogonal if one of them is 0 on the sphere boundary.

APW: An All-Electron Method

E

valence   APW

$2p_{3/2}$
$2p_{1/2}$
$2s$

Atomic-like core package

$1s$
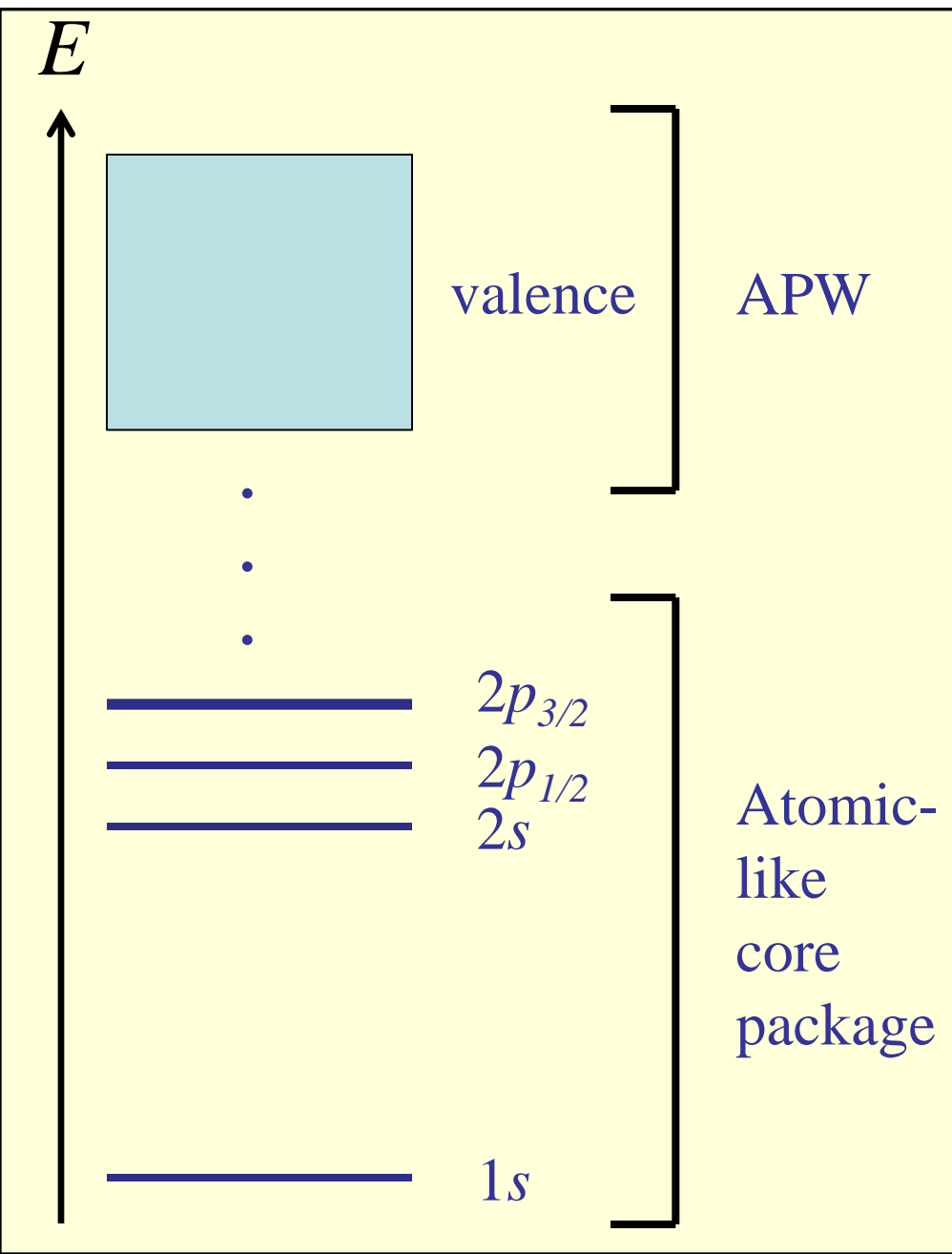
The $u_l(r)$ $Y_{lm}(\mathbf{r})$ are orthogonal core states.

➔ Can use this basis to obtain true valence states in the real potential.

(1) Calculate core states separately in each SCF cycle.

(2) Use the same potential for core and valence and calculate the charge density from the sum of these.

Augmented Planewave (APW) Method

Another Interesting Point:

- Since the basis functions are indexed by **k+G** one imagines a connection with planewave pseudopotential formalisms.

$$<A\phi|H|A\phi>x = \varepsilon< A\phi|A\phi>x \quad \equiv \quad <\phi|A^\dagger HA|\phi>x = \varepsilon<\phi|A^\dagger A\phi>x$$

$$H^{PS} \qquad\qquad\qquad S^{PS}$$

- So this is like non-norm-conserving pseudopotential.

- However, it is highly non-transferable:
  - Cannot be used at another energy (because u is very energy dependent - $\partial u/\partial E$ is usually large).
  - Cannot be used for a different potential.

- **Result**: *The APW method as written requires use of an energy dependent secular equation and is not practical for more than simple solids.*

The APW Method as a Pseudopotential

• It's highly non-transferable, but it is soft!

COPPER

← APW Band Structure of Cu using a planewave cutoff of 8.4 Ry.
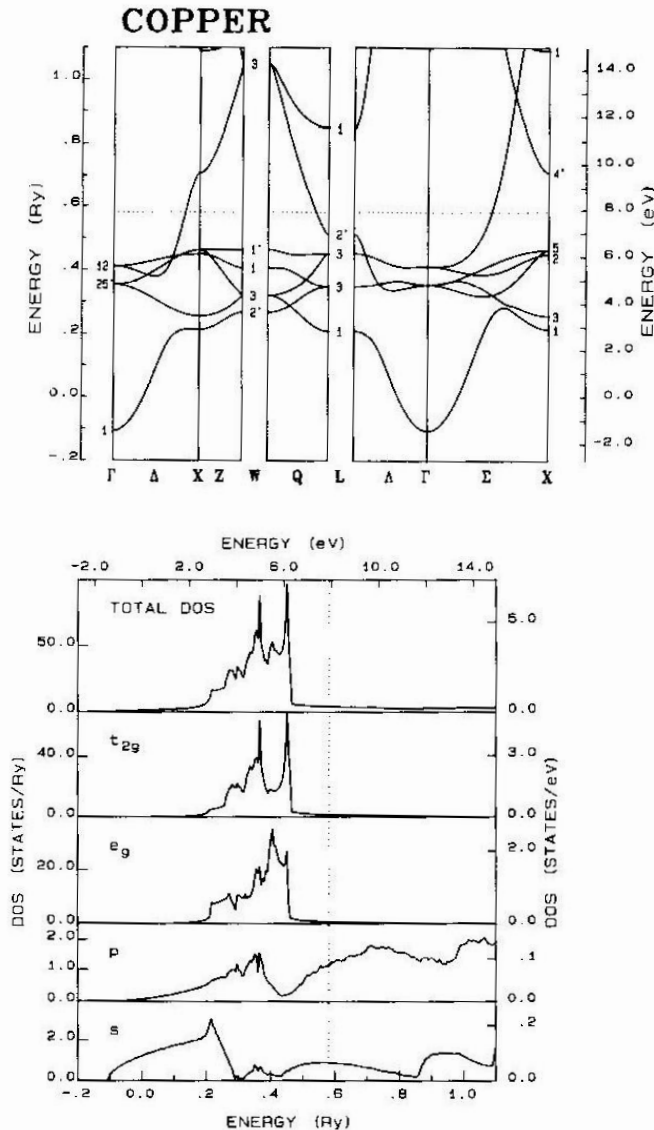
There is a trade-off between transferability and softness (nothing is free). The story of linearization and local orbitals is related to this.

D.A. Papaconstantopoulos, 1986

Problems with the APW Method

1) Must solve secular equation for each energy band: prohibitive for many bands. No clear way to make full-potential.

2) Asymptote problem: cannot match at energies where $u(\mathrm{r})$ is zero on the sphere boundary. This will in general happen at some energy – particular problem for d and f band materials.

The Linearized Augmented Planewave (LAPW) Method

Key Ideas:

- The problem with the APW method is the energy dependence of the secular equation which is a result of the energy dependence of the augmenting function.

- Solution: Add variational freedom: particularly $\mathring{u}(r) = \partial u(r)/\partial E$.

$$\varphi(\mathbf{r}) = \begin{cases} \Omega^{-1/2} \sum_{\mathbf{G}} c_{\mathbf{G}} \, e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}} & r \in I \\[2ex] \sum_{lm} (A_{lm} \, u_l(r) + B_{lm} \, \mathring{u}_l(r)) \, Y_{lm}(\mathbf{r}) & r \in S \end{cases}$$

- Where A_{lm} *and* B_{lm} are determined by matching the value and derivative of the basis functions at the sphere boundary.

THE LAPW METHOD

Results of adding $\mathring{u}_l$ to the basis:

1. Basis is flexible enough to use a single diagonalization (energy errors are now $O(\delta^4)$).

2. Must have additional matching conditions to connect both u and $\mathring{u}$ to the planewaves. This means that for a given level of convergence, more planewaves are needed.

3. The transferability also extends to variations in the potential: this enables full-potential methods.

The full potential, all electron, nature combined with the flexible basis (fully flexible in the interstitial) made the (F)LAPW method the state of the art for calculating electronic structures, especially for transition elements and their compounds – Many groups developed codes 1980 – present.

Early Impact

Many works starting in 1980's showing predictive calculations for complex materials and surfaces with d and f elements.

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Instability of the Ideal Tungsten (001) Surface

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$YBa_2Cu_3O_7$
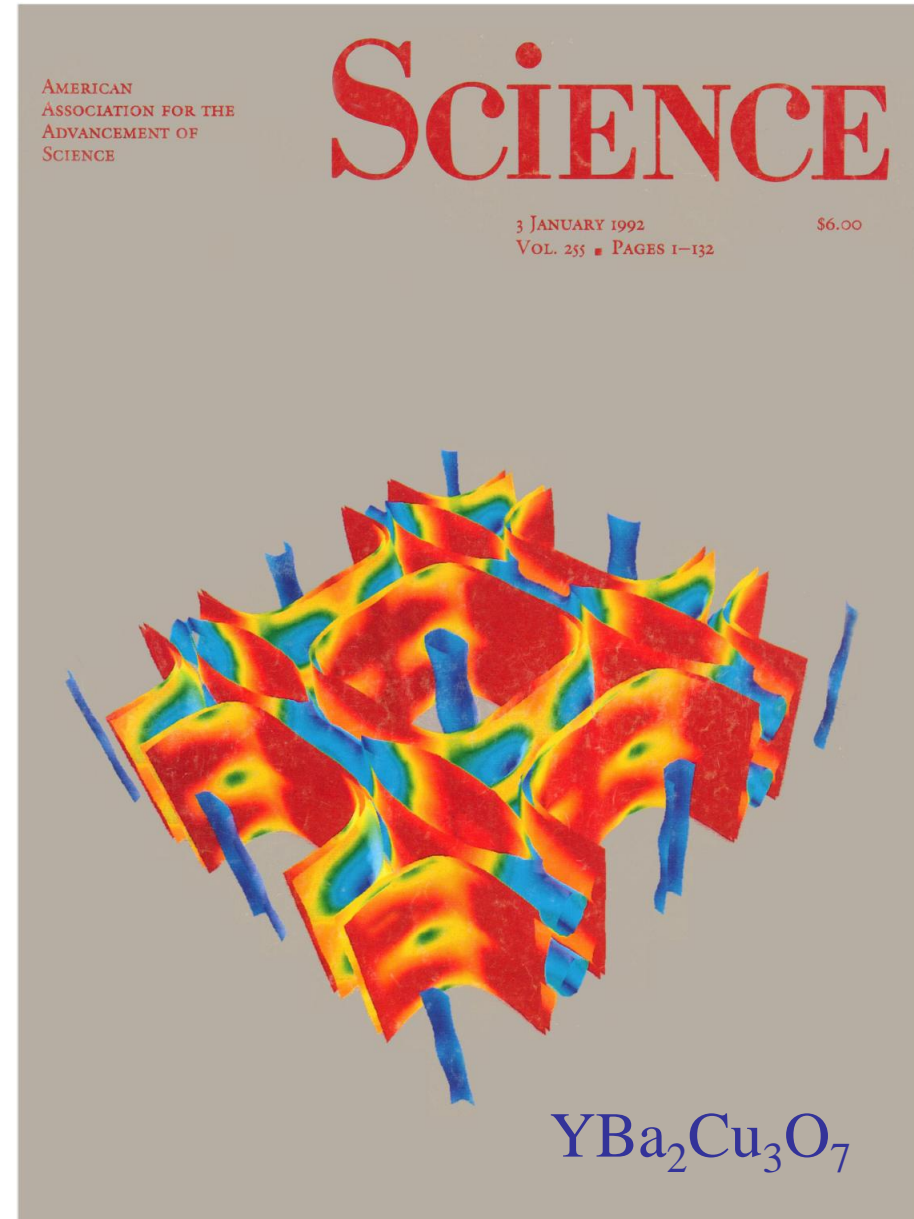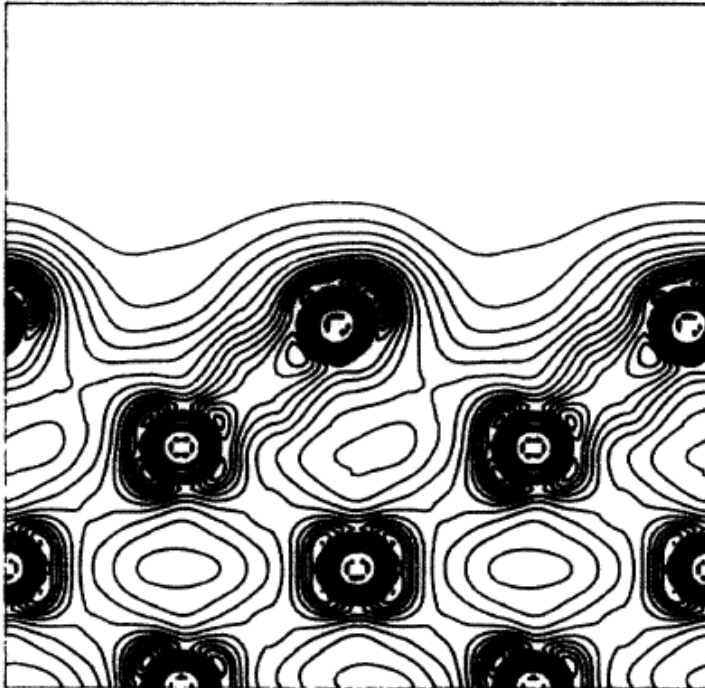
PROPERTIES OF THE LAPW METHOD

- All electron method: Core states are included.

  - φ is the true wavefunction, ρ is the true charge density …

  - Can calculate properties that depend on the details of the wavefunction near the nucleus: EFG's *etc.*

  - Relativity can be included – scalar relativistic, spin-orbit …

  - No special treatment for core-valence interactions is needed.

- Atom centered representation:

  - LDA+U, interpretation of transition element orbital populations.

  - Matrix elements are complicated.

  - IBS terms in forces, linear response …

  - Basis functions are extended – not very amenable to $O(N)$ …

CHOICE OF SPHERE RADII
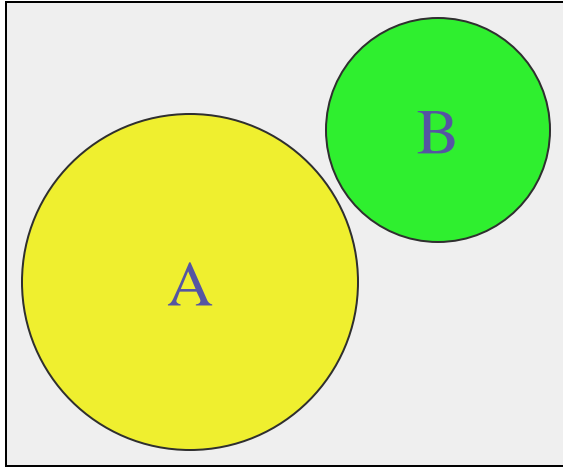
Size of basis,

$$n_b \propto G_{max}^3$$

Compute time,

$$t \propto n_b^3 \propto G_{max}^9$$

For most atoms, with "normal radii", a given level of convergence is reached for a certain, atom dependent value of rG_{max}.

Typical rG_{max} values for good convergence (always check):

Transition elements:	9	*Should consider*
f-electron materials:	9.5	*in setting radii, which*
Simple elements (B,C,N,O)	7	*are computational*
Simple metals (Al, Si, …)	6	*not physical parameters.*

Example (B2 NiAl)

Chemical Sense *vs.* Computational Sense
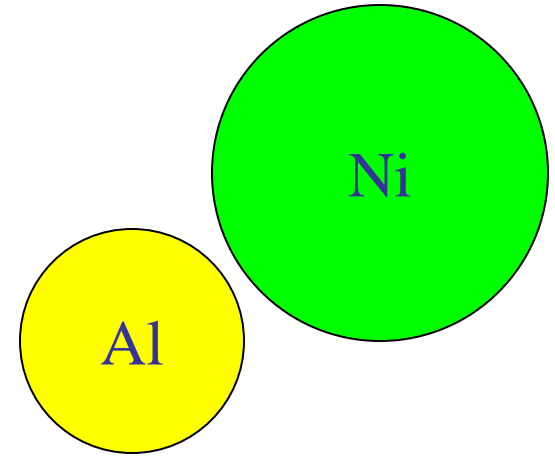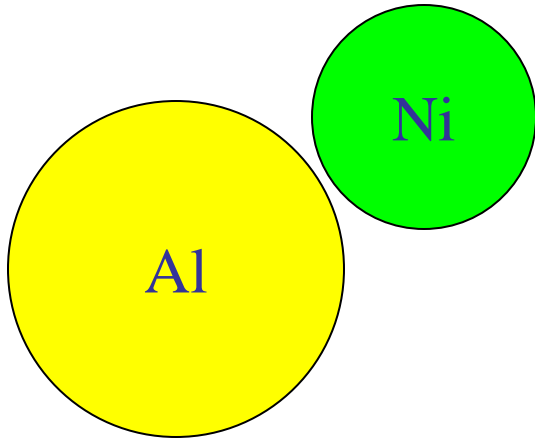
$r_{Al} = 2.8$ bohr

$r_{Ni} = 1.9$ bohr

$r_{Al}G_{max} = 6$ ➜ $G_{max} = 2.15$

$r_{Ni}G_{max} = 9$ ➜ $G_{max} = 4.74$

$r_{Al} = 1.9$ bohr

$r_{Ni} = 2.8$ bohr

$r_{Al}G_{max} = 6$ ➜ $G_{max} = 3.15$

$r_{Ni}G_{max} = 9$ ➜ $G_{max} = 3.21$

$$(4.74/3.21)^9 = 33$$

Complications in the LAPW Method

EFG Calculation for Rutile TiO_2 as a function of the Ti p linearization energy

Electronic Structure
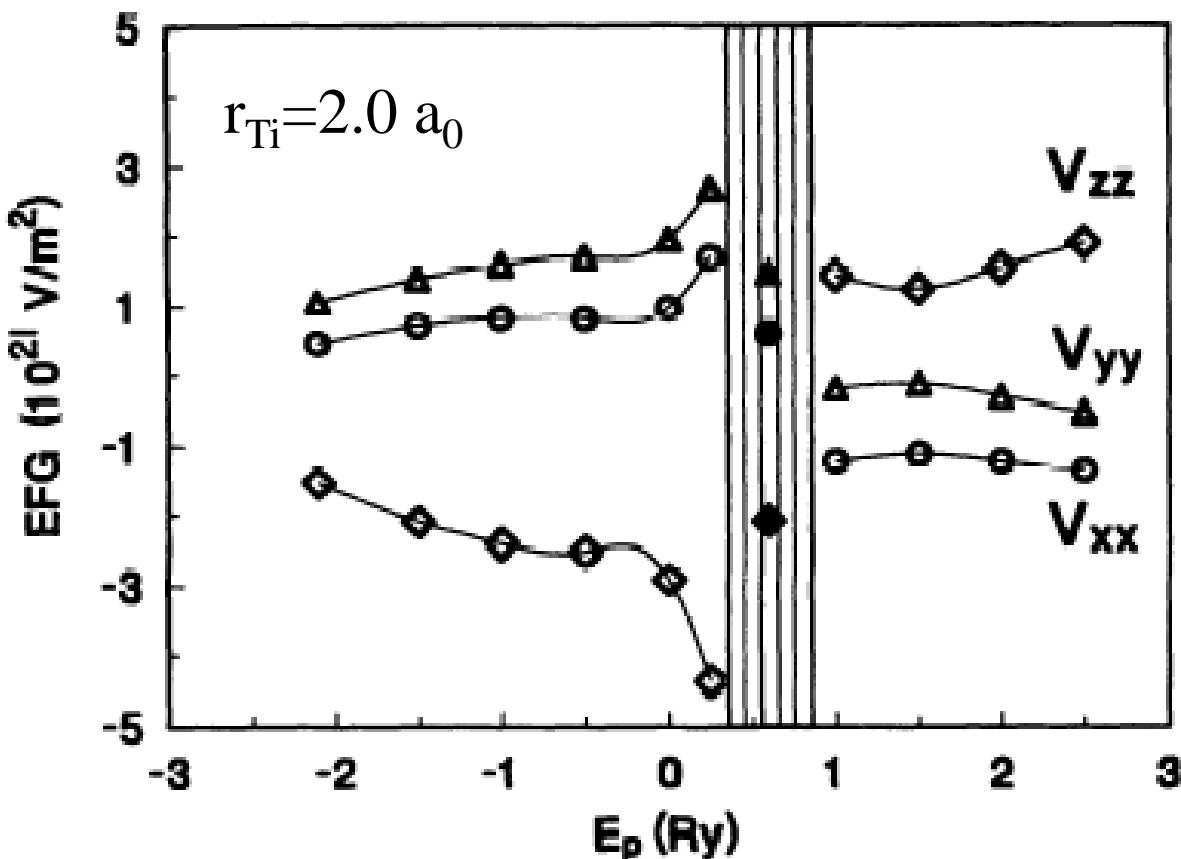
P. Blaha, D.J. Singh, P.I. Sorantin and K. Schwarz, Phys. Rev. B **46**, 1321 (1992).
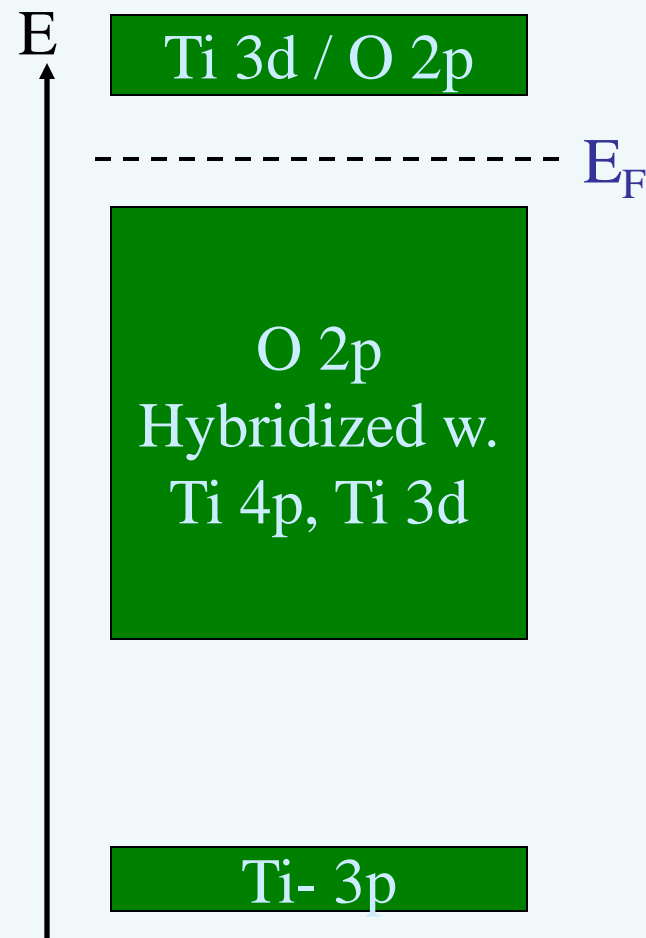
Complications in the LAPW Method

What went wrong?
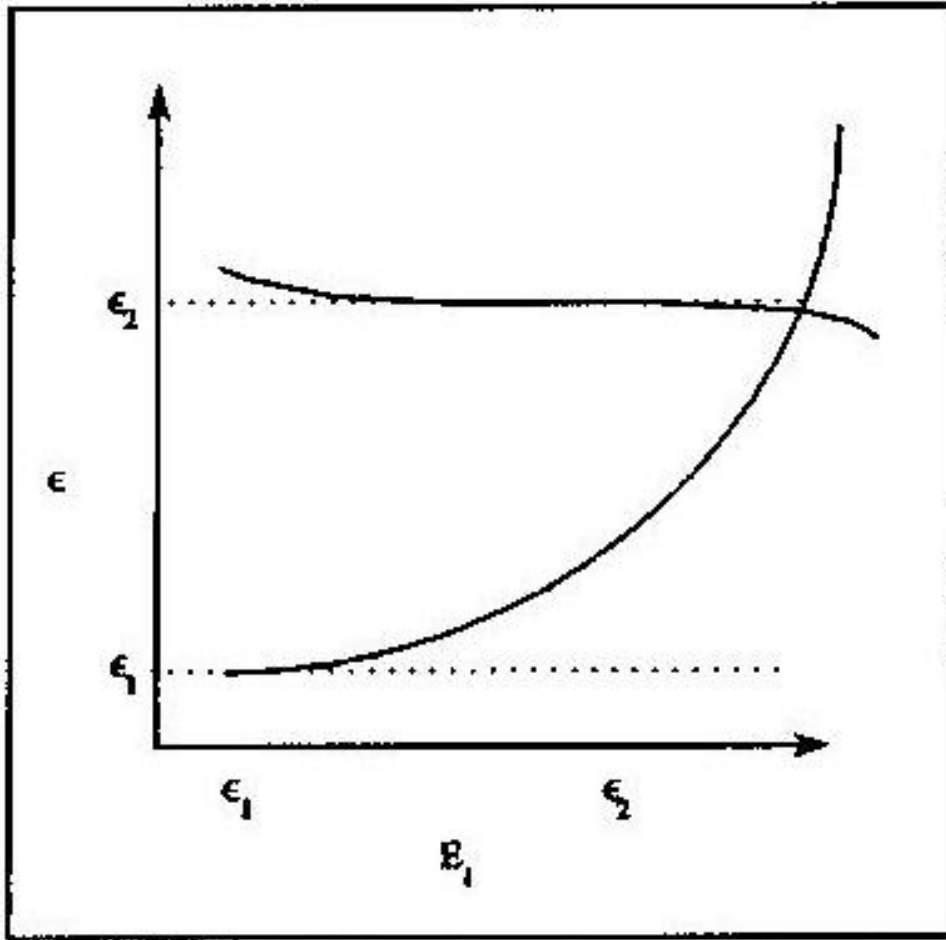
Figure 5.14 Variation of a semi-core and a valence band with E_l. The dotted lines at ϵ_1 and ϵ_2 denote the true locations of the bands.

The LAPW method requires non-overlapping spheres

⇨*There are serious limits to how large R_{MT} can be especially in oxides, nitrides, carbides.*

But for many elements there are extended core states that are not close enough to zero on the sphere boundary to have the u and $\mathring{u}$ orthogonal to them. On the other hand, the valence states may have significant contributions from the same l.

Complications in the LAPW Method

Solution?: Use large spheres to get orthogonality to core states:
Unfortunately, crystal structures don't generally allow this.
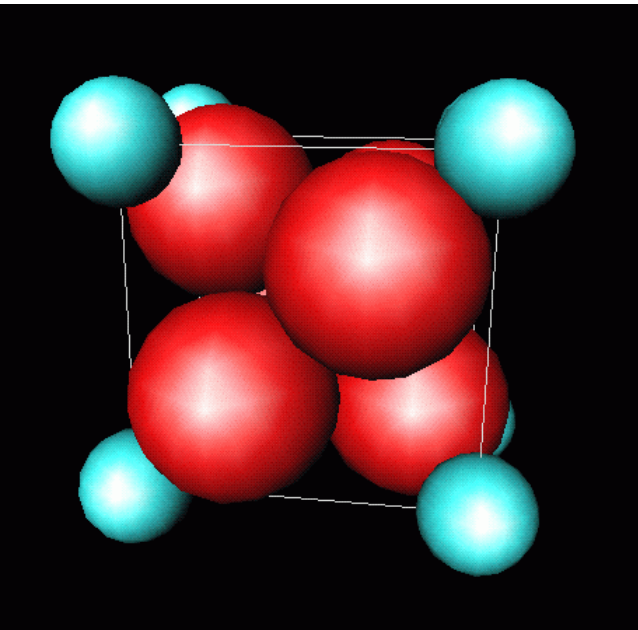
Perovskite

Rutile Structure
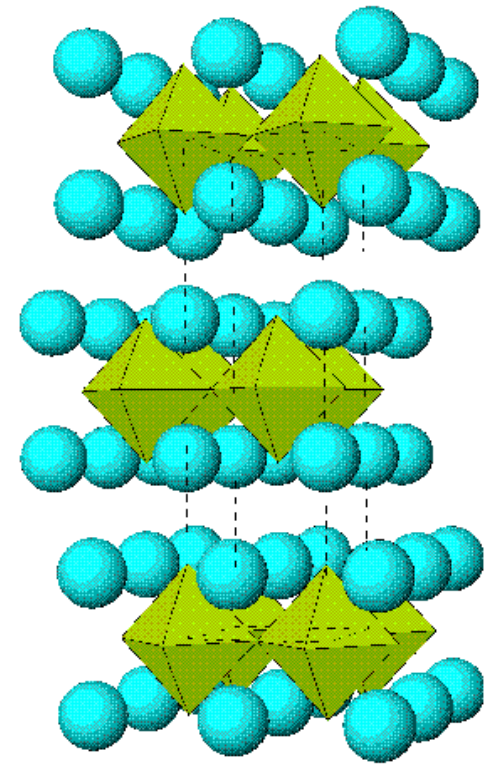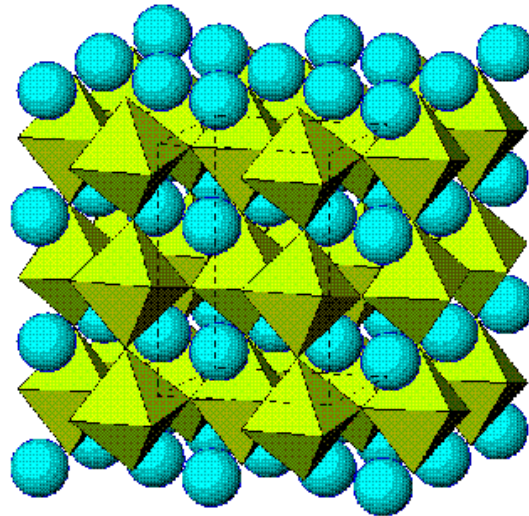
Layered Perovskite

Complications in the LAPW Method

Problems with semi-core states

ONE SOLUTION

Electronic Structure
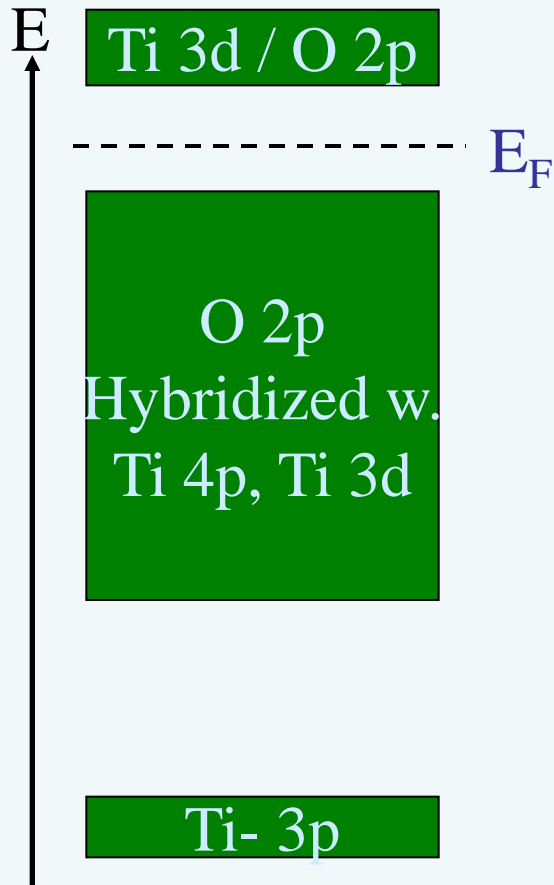
Treat all the states in a single energy window:

- Automatically orthogonal.
- Need to add variational freedom.
- Could invent quadratic or cubic APW methods.

$$\varphi(\mathbf{r}) = \left\{ \begin{array}{l} \Omega^{-1/2} \sum_{\mathbf{G}} c_{\mathbf{G}}\, e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}} \\ \sum_{lm} (A_{lm}u_l(r) + B_{lm}\mathring{u}_l(r) + C_{lm}\ddot{u}_l(r))\, Y_{lm}(\mathbf{r}) \end{array} \right.$$

Problem*: This requires an extra matching condition, e.g. second derivatives continuous ⇨ method will be impractical due to the high planewave cut-off needed.*

THE LAPW+LO METHOD

LAPW+LO basis is:

$$\varphi(\mathbf{r}) = \begin{cases} \Omega^{-1/2} \sum_{\mathbf{G}} c_{\mathbf{G}}\, e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}} \\[1em] \sum_{lm} (A_{lm}u_l(r)+B_{lm}\mathring{u}_l(r))\, Y_{lm}(\mathbf{r}) + \\[1em] \sum_{lm} c_{lm}(A'_{lm}u_l(r)+B'_{lm}\mathring{u}_l(r)+u^{(2)}_l(r))\, Y_{lm}(\mathbf{r}) \end{cases}$$

The variational coefficients are: (1) $c_{\mathbf{G}}$ and (2) c_{lm}

Subsidiary (non-variational) coefficients are A_{lm} B_{lm} A'_{lm} & B'_{lm}

- A_{lm} and B_{lm} are determined by matching the value and derivative on the sphere boundary to the planewaves as usual.

- A'_{lm} and B'_{lm} are determined by matching the value and derivative on the sphere boundary to zero. Thus this part $(A'_{lm}u_l(r)+B'_{lm}\mathring{u}_l(r)+u^{(2)}_l(r))\, Y_{lm}(\mathbf{r})$ is formally a local orbital.

THE LAPW+LO METHOD

Key Points:

1. The local orbitals need (and should) only be used for those atoms and angular momenta where they are needed.

2. The local orbitals do not serve as surrogate atomic wavefunctions in the sense that they are in mixed basis planewave codes: They are just another way to handle the augmentation. They look very different from atomic functions.

3. We are trading a large number of extra planewave coefficients for some c_{lm}.

Shape of H and S

THE LAPW+LO METHOD

D. Singh, Phys. Rev. B **43**, 6388 (1991).

SLAPW-4
Cubic APW

La
$R_{MT} = 3.3\ a_0$

QAPW
SLAPW-3

LAPW+LO

RK_{max}
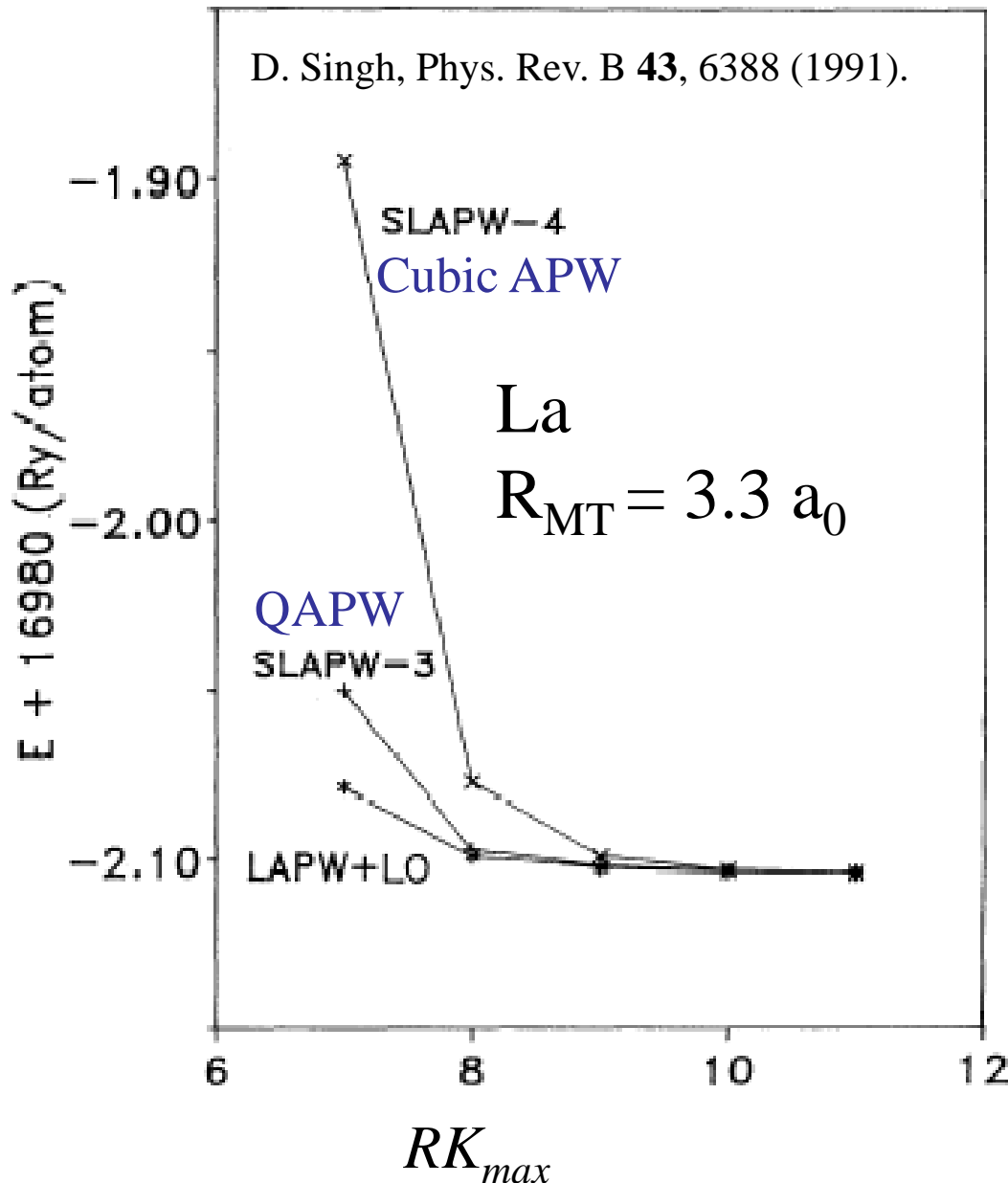
LAPW+LO converges like LAPW. The LO adds a few basis functions (i.e. 3 per atom for p states). Can also use LO to relax linearization errors, e.g. for a narrow d or f band.

Suggested settings:

Two "energy" parameters, one for u and $\mathring{u}$ and the other for $u^{(2)}$. Choose one at the semi-core position and the other at the valence.

THE COST OF PLANEWAVES

Si$_{46}$ Clathrate

E. Richter
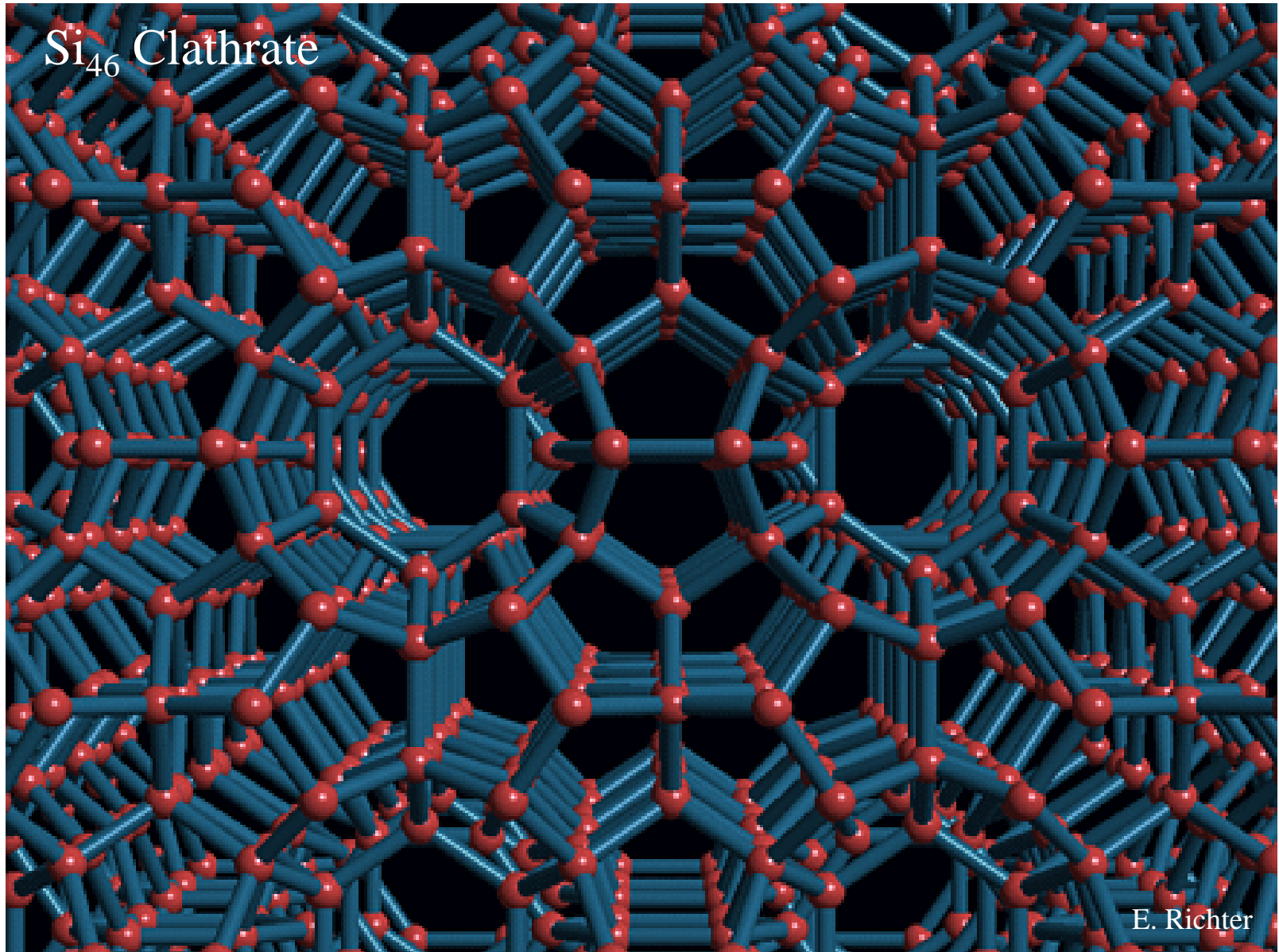
Example of a structure with short bonds and large open spaces

THE APW+LO METHOD

In certain cases it is highly advantageous to lower RK_{MAX} even at the expense of some local orbitals:

- Structures with short bonds and large empty spaces.

- Structures with some "hard" atoms embedded in a matrix of "soft" atoms: *e.g.* Mn impurities in Ge.

Then it is advantageous *for selected atoms and l*, to use local orbitals to go back to the APW method.

$$\varphi(\mathbf{r}) = \begin{cases} \Omega^{-1/2} \sum_{\mathbf{G}} c_{\mathbf{G}} \, e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}} \\ \sum_{lm} (A_{lm} u_l(r)) \, Y_{lm}(\mathbf{r}) + \\ \sum_{lm} c_{lm}(A'_{lm} u_l(r) + u^{(2)}_l(r)) \, Y_{lm}(\mathbf{r}) \end{cases}$$

n.b. now we only match the value on the boundary for these *l*. This means that there are extra APW-like kinetic energy terms in the Hamiltonian and forces.

Convergence of the APW+LO Method

E. Sjostedt, L. Nordstrom and D.J. Singh, Solid State Commun. **114**, 15 (2000).
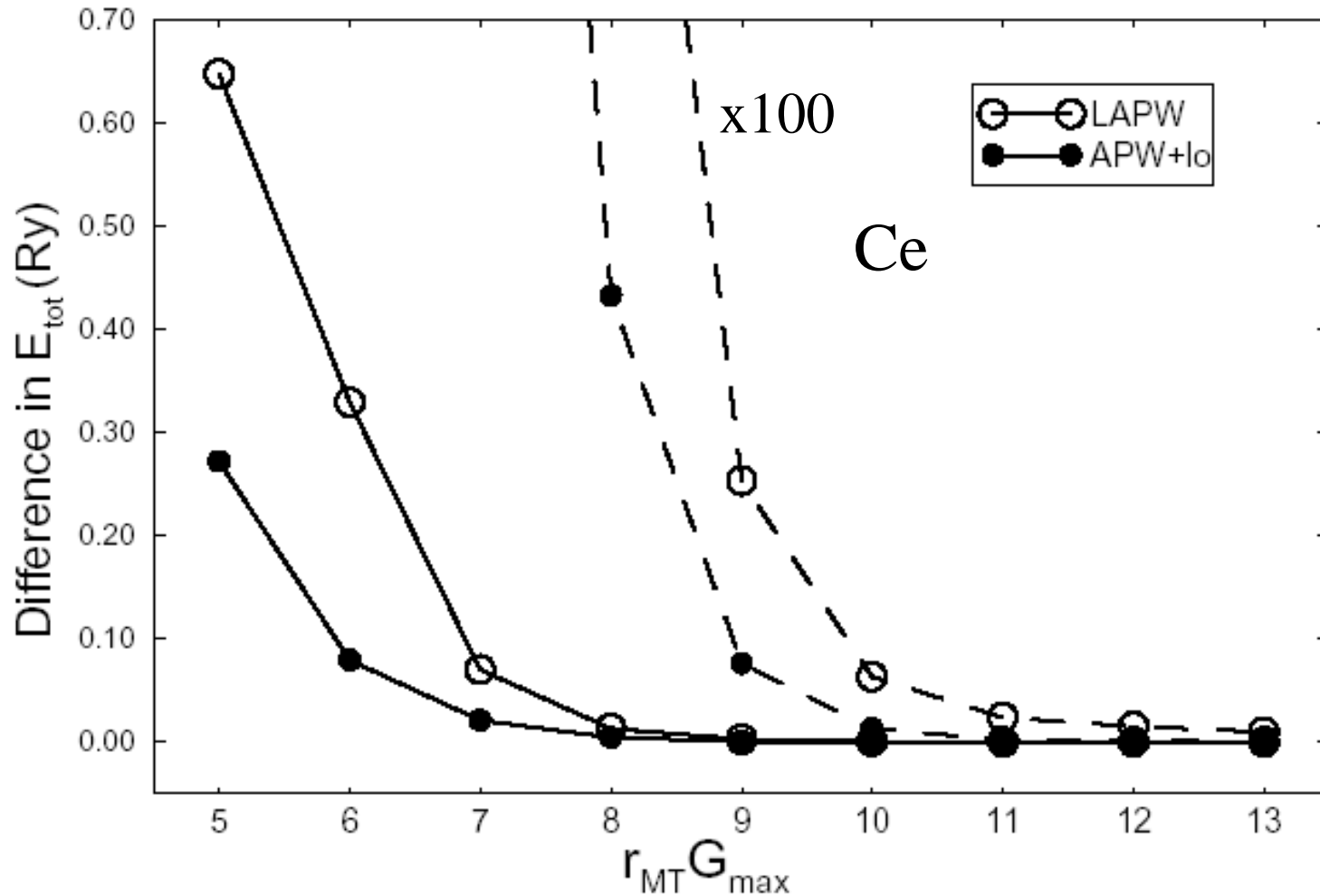
REMARKS ON THE APW+LO METHOD

- APW+LO is equivalent to LAPW not LAPW+LO. It is not suitable for handling semicore states. For this LAPW+LO or APW+2LO should be used.

- There is no requirement that all atoms or angular momenta be augmented in the same way (see Madsen *et al.*). This can be exploited by using APW+LO *only for those atoms and l for which a high G_{max} would otherwise be needed*. For example, with Mn in Ge one might use APW+LO only for the Mn $3d$ channel, and LAPW for all others.

How to Set Linearization Parameters

Extended Core States?

NO → Set E_ℓ at the center of the relevant states. As needed, control linearization errors by reducing R_α or adding local orbitals. → Done

YES → Local Orbital Capability?

NO → Maximize R_α → Ghost Bands?

YES → Use local orbitals to treat semi-core states. → Done

Ghost Bands?
NO → Done
YES → Raise E_ℓ
YES → Lower E_ℓ to semi-core position. Reduce R_α as needed.
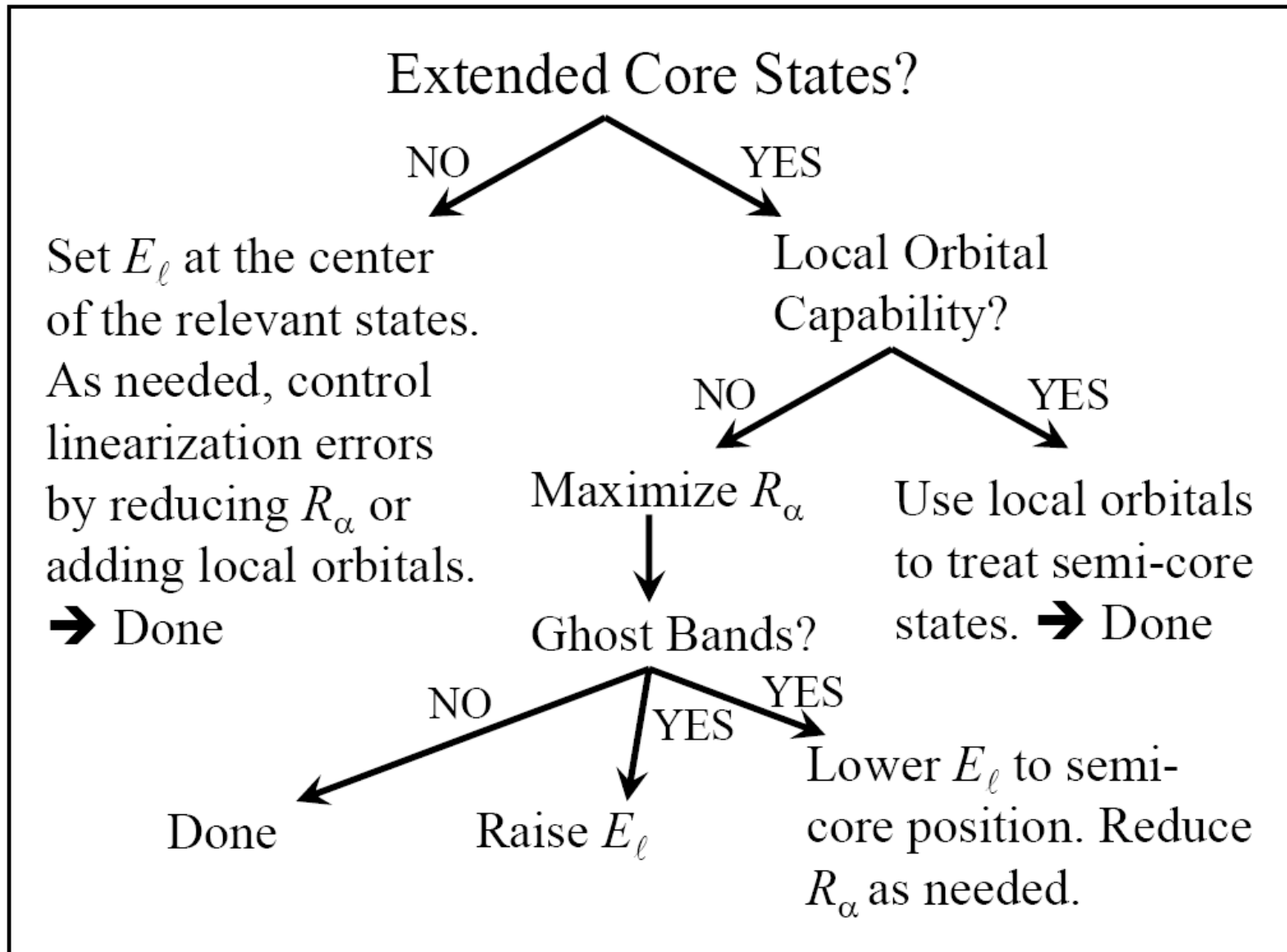
Charge Density, Potential, etc.

Interstitial

Sphere

$\rho(\mathbf{r})$, $V(\mathbf{r})$: Lattice Harmonics

$\varphi(\mathbf{r})$: Atomic-like Functions

$\rho(\mathbf{r})$, $V(\mathbf{r})$: Stars
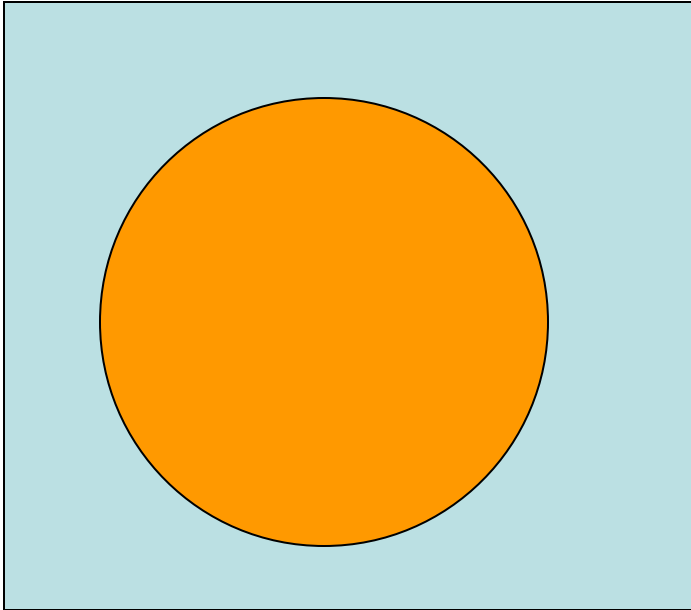
$\varphi(\mathbf{r})$: Planewaves
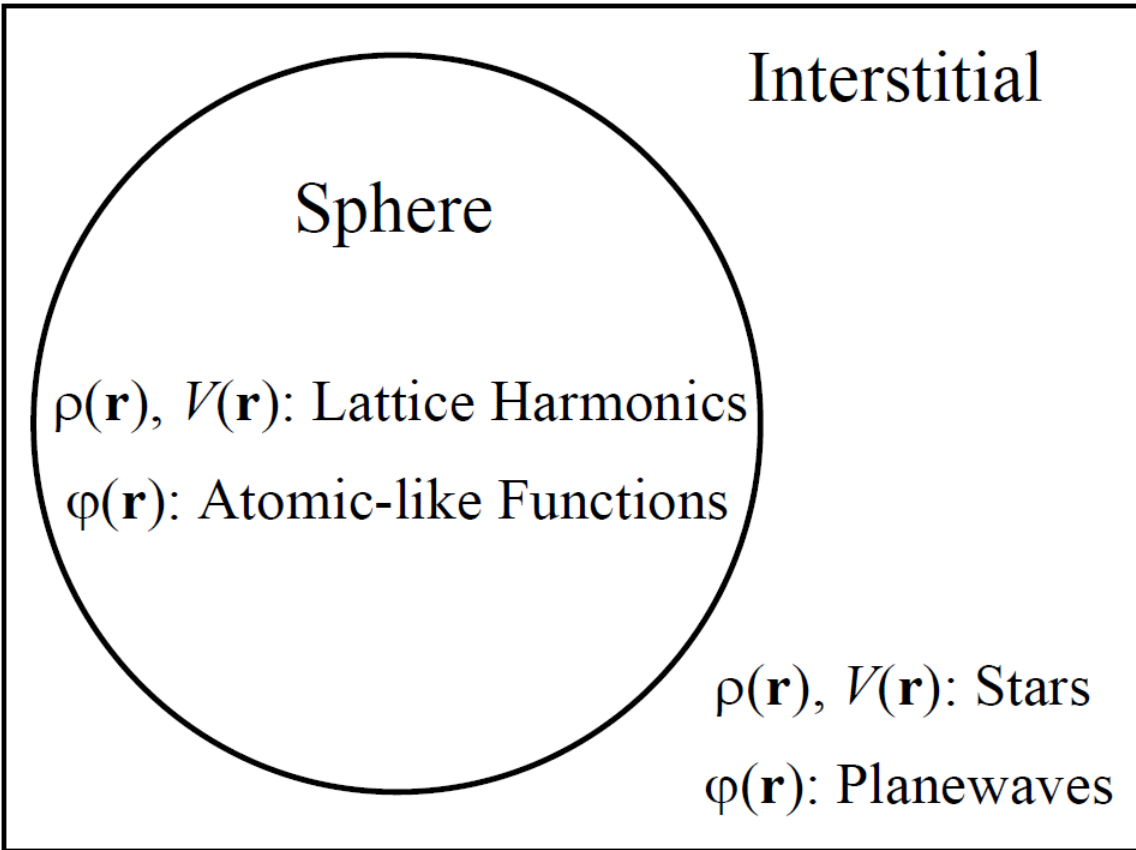
- Normally exploit lattice symmetry:
  - Stars in interstitial.
  - Lattice harmonics in spheres.
  - Only store for inequivalent atoms.

Allows for fast evaluation of Coulomb potential via multipole approach.

Multipole Method for Coulomb Potential

M. Weinert.

1. Evaluate multipole moments of ρ inside spheres.
2. Construct a smooth charge density (the pseudocharge) that is the same as the real charge outside the sphere, and has the same multipoles inside
   - n.b. can construct a smooth charge with a given multipole that is zero outside a sphere

3. Use Fourier transform method to get V ➔ exact in interstitial, but not in spheres.
4. Integrate Poisson's equation inward from sphere on radial grids to get V inside spheres.

➔ fast method comparable to planewaves

$$V_C(\mathbf{G}) = \frac{4\pi\rho(\mathbf{G})}{|\mathbf{G}|^2}$$

References

1. D.J. Singh and L. Nordstrom, *Planewaves, Pseudopotentials and the LAPW Method* (Springer, 2005). **Details about the LAPW method, connection with pseudopotentials and inner workings of codes.**

2. O.K. Andersen, Phys. Rev. B **12**, 3060 (1975). **Formalism for the LAPW method.**

3. D. Singh, Phys. Rev. B **43**, 6388 (1991). **Local orbitals.**

4. E. Sjostedt, L. Nordstrom and D.J. Singh, Solid State Commun. **114**, 15 (2000). **APW+LO method.**

5. J.C. Slater, Phys. Rev. **51**, 846 (1937). **APW method.**

6. T.L. Loukes, *The Augmented Planewave Method* (Benjamin, 1967). **Details about APW implementation.**