The Linearized Augmented Planewave (LAPW) Method – (WIEN2k, ELK, FLEUR)

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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.

Please Ask Questions as They Arise

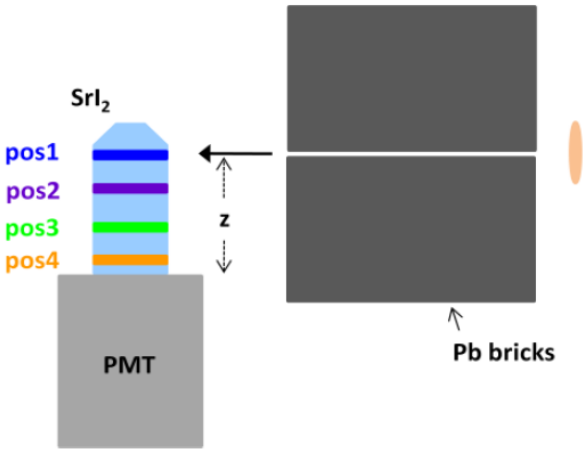
IPAM, July 23, 2014

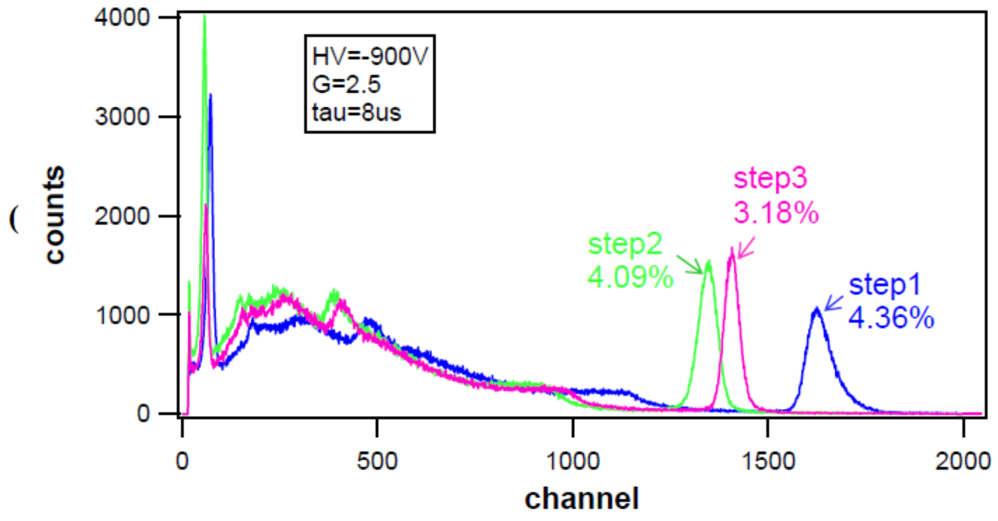
Scintillators for Radiation Detection

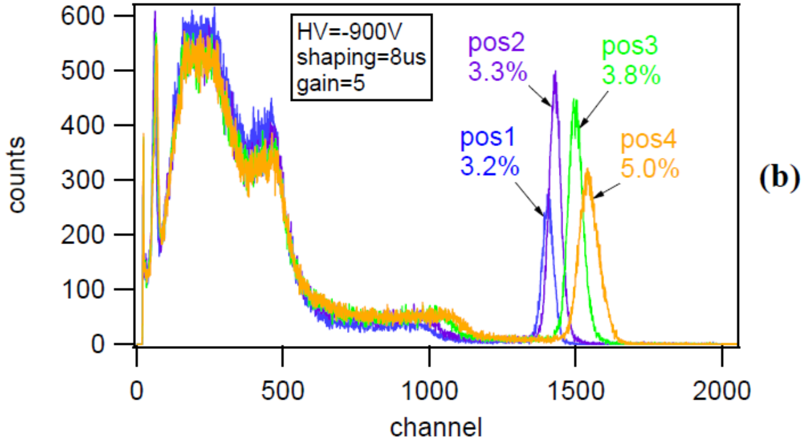
Technology for room temperature radiation detection: New trend is use of spectroscopic detection ➔ source identification.

SrI_2 (10 cm^3) packaging

~20% of photons detected



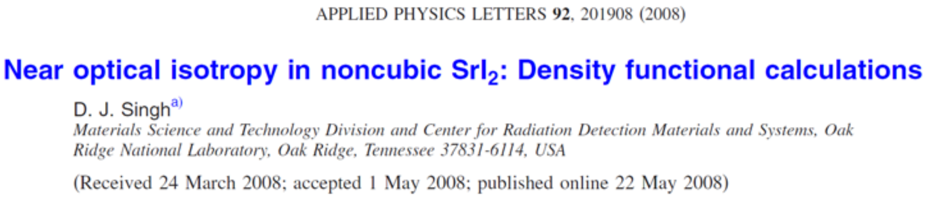




Knowledge of optical properties is important for scintillator applications.

Sturm, Cherepy, Drury, Thelin, Fisher, Magyar, Payne, Burger, Boatner, Ramey, Shah (2011)

Experiment



APPLIED PHYSICS LETTERS **92**, 201908 (2008)

Near optical isotropy in noncubic SrI_2: Density functional calculations

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EEE TRANSACTIONS ON NUCLEAR SCIENCE, VOL. 57, NO. 6, DECEMBER 2010 3827

Fabrication and Properties of Translucent SrI_2 and $Eu{:}SrI_2$ Scintillator Ceramics

Stephen R. Podowitz, Romain M. Gaumé, Wesley T. Hong, Atlal Laouar, and Robert S. Feigelson

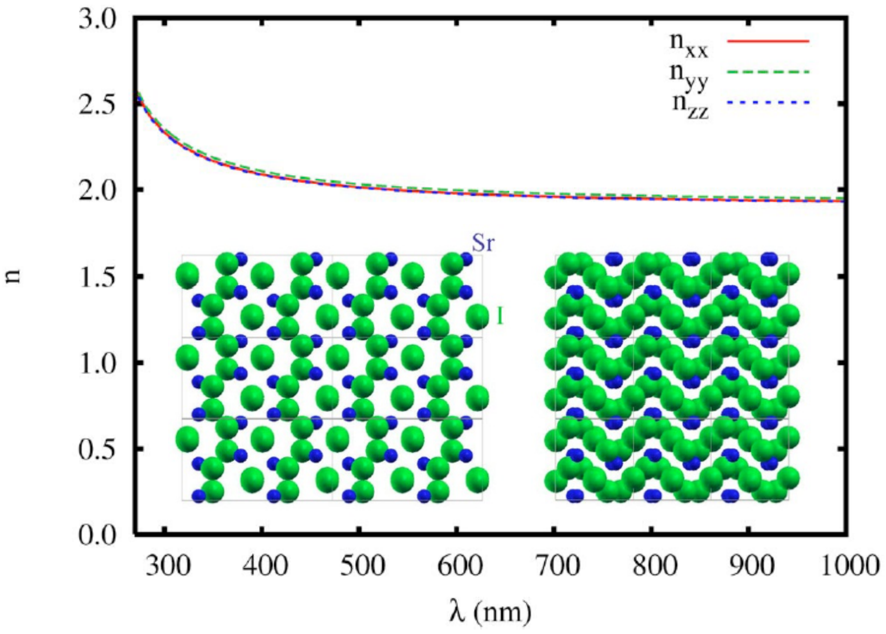


FIG. 4. (Color online) Wavelength dependent refractive index of SrI_2 as obtained with the Engel–Vosko GGA.

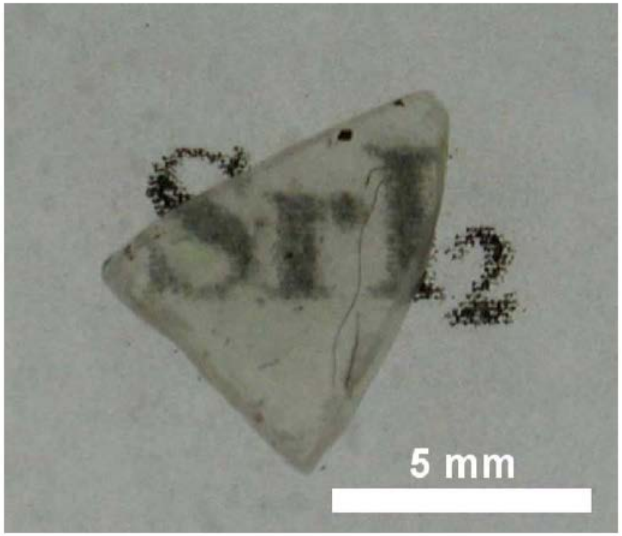
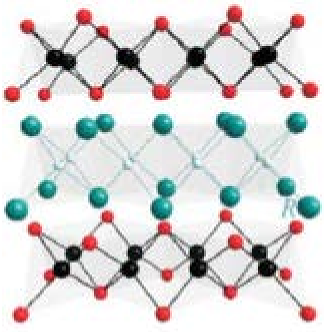


Fig. 5. Translucent ceramic sample of 0.77 mm-thick $Eu{:}SrI_2$ backlit.

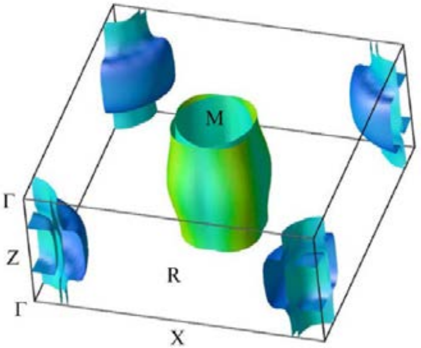
First principles theory, not fit to experiment ➔ results that can point in unanticipated directions.

LAPW and Related Methods

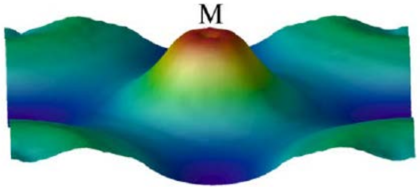
- All-electron
- Emphasis on avoidance of non-controlled approximations.
- Numerical and planewave basis sets (systematic accuracy testing, increase).
- Widely used for systems where precise treatment especially d, f states is essential.
- Generally less efficient than other methods for large systems.



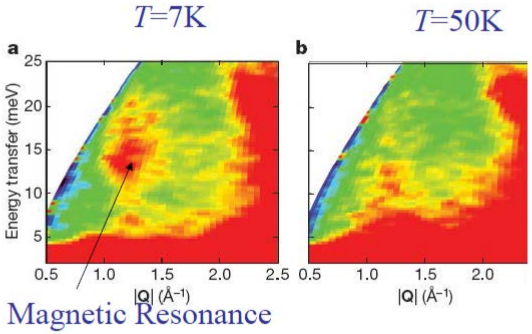
Discovery of superconductivity in F-doped LaFeAsO (Hosono) Jan. 2008



Electronic structure – not like cuprates March 2008



Spin-fluctuations and s+- state - March 2008

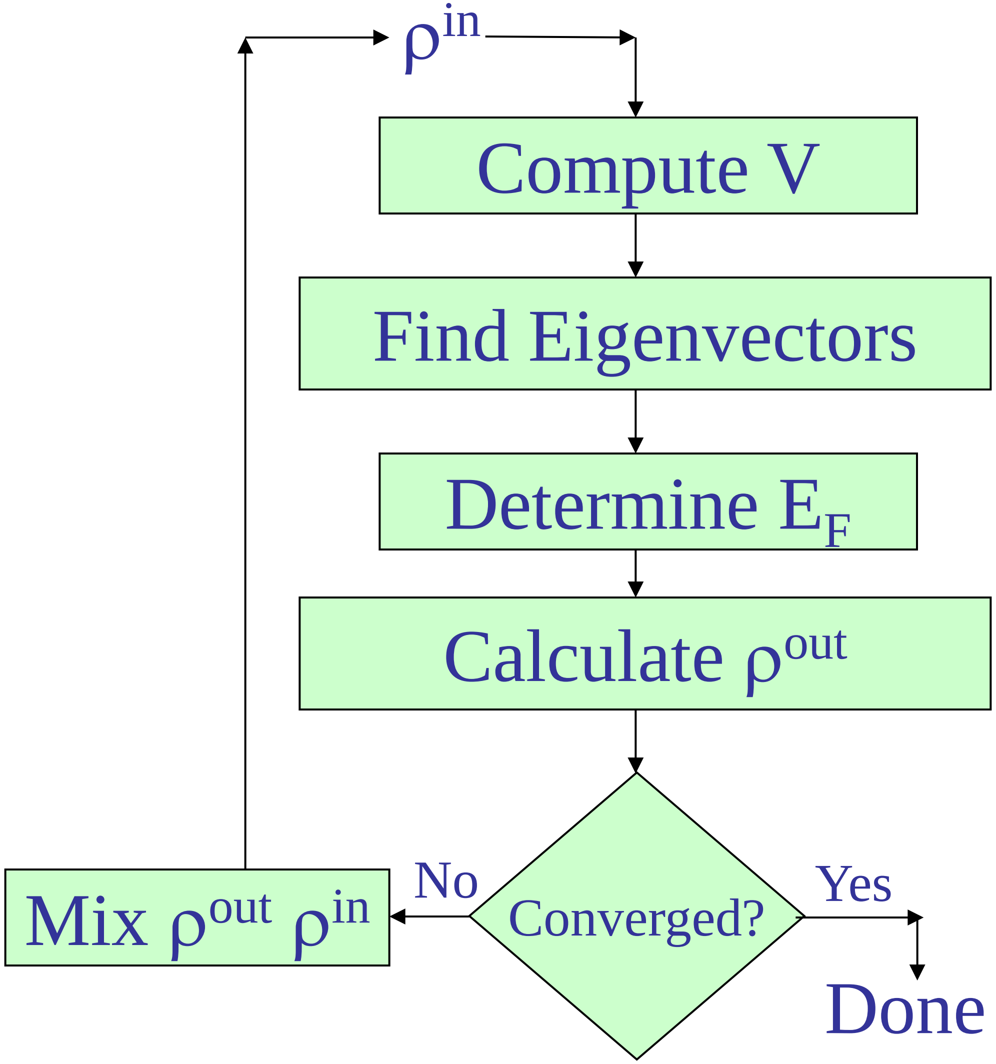


Neutron spin-resonance, Nov. 2008

DFT ALGORITHMS

•Find φ_I and ρ to solve:

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



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.

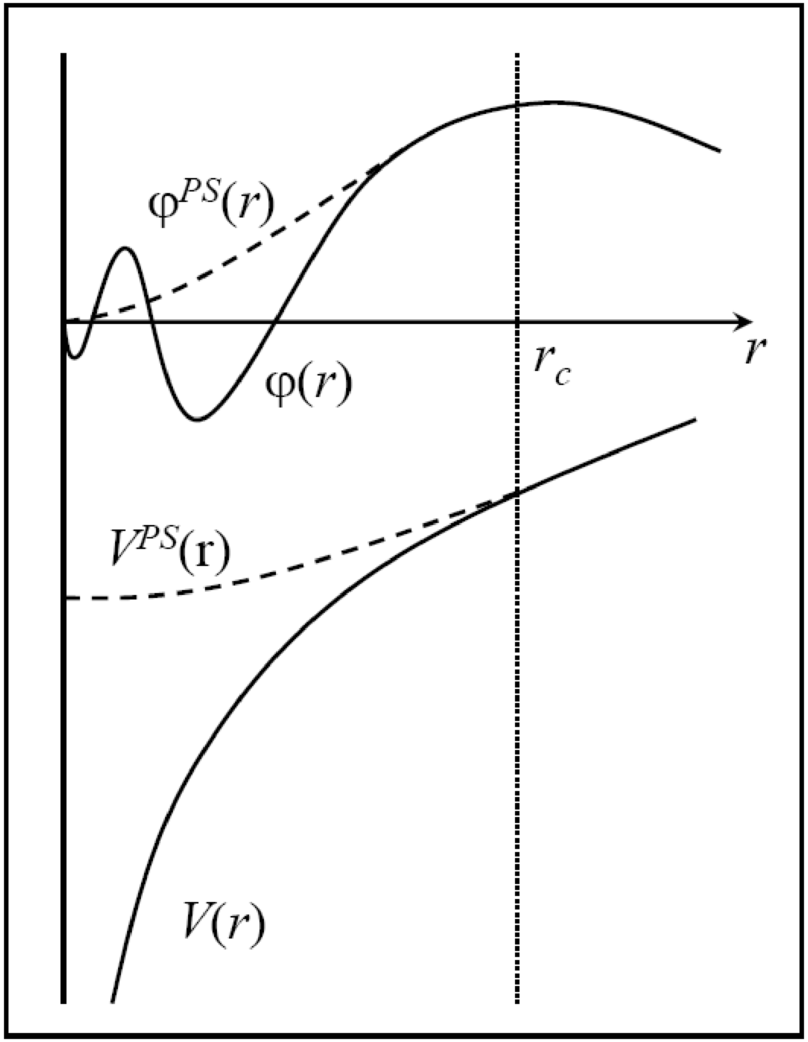
Motivation for Augmentation

Schrödinger Equation:

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

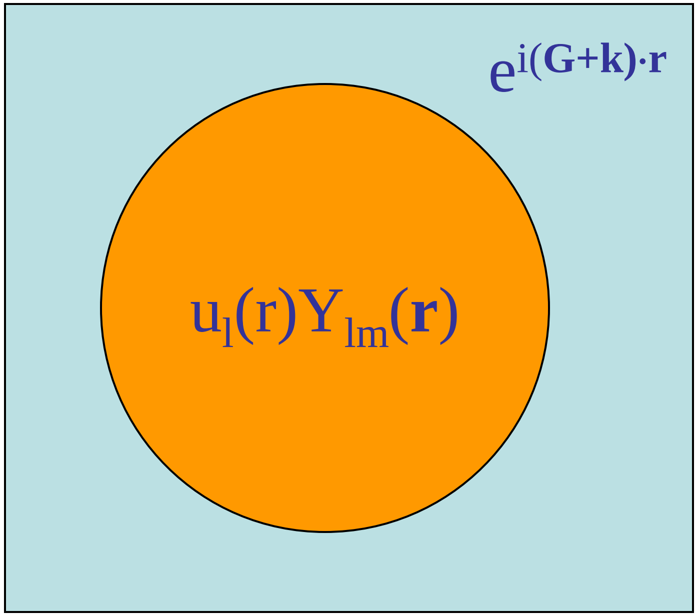
For valence states: ε is small ➔

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).



Divide Space Into 2 Regions:

- Atom Centered Spheres
- Interstitial

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

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

- u_l(r) are the radial solutions of Schrodinger’s equation at the energy of interest (i.e. the band energy).

Augmented Planewave (APW) Method

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

Key points:

1. The $A_{\ell m}$ are not variational parameters. They are determined by a matching condition. That is the value of the basis functions, $\phi_{\mathbf{k+G}}$ 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.

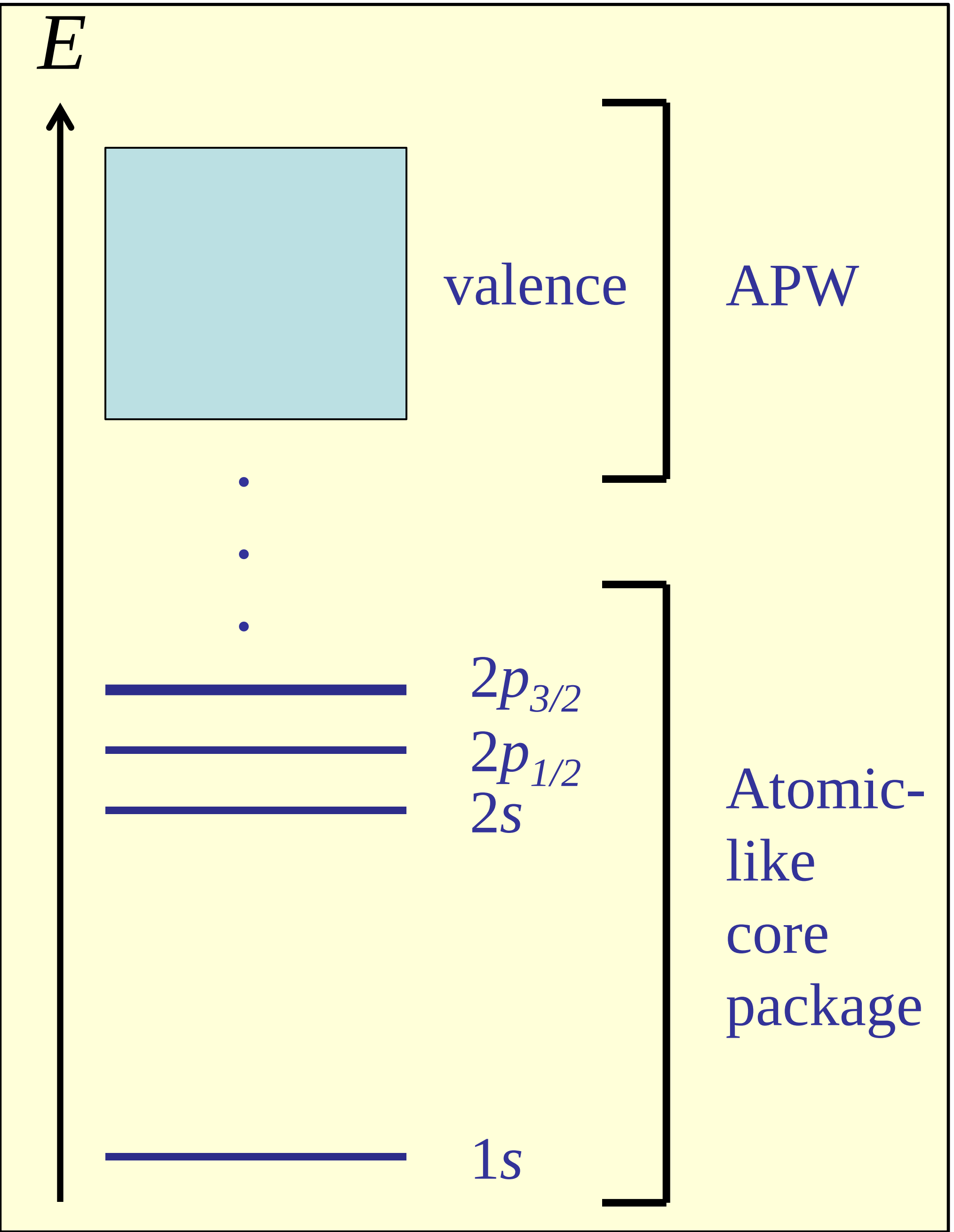
$$[\, -\mathrm{d}^2/\mathrm{d}r^2 + \ell(\ell+1)/r^2 + V(r) - E_\ell \,]\, r u_\ell(r) = 0$$

So:

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

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



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.

Connection with Planewave Methods

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

$$<A\phi|H|A\phi>x = \varepsilon< A\phi|A\phi>x \quad \equiv \quad <\phi|\underset{H^{PS}}{A^{\dagger}HA}|\phi>x = \varepsilon<\phi|\underset{S^{PS}}{A^{\dagger}A}\phi>x$$

- 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 - *∂u/∂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.*

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*(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

O.K. Andersen, Phys. Rev. B **12**, 3060 (1975).

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 $\mathring{u}(r) = \partial u(r)/\partial E$.

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

- 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

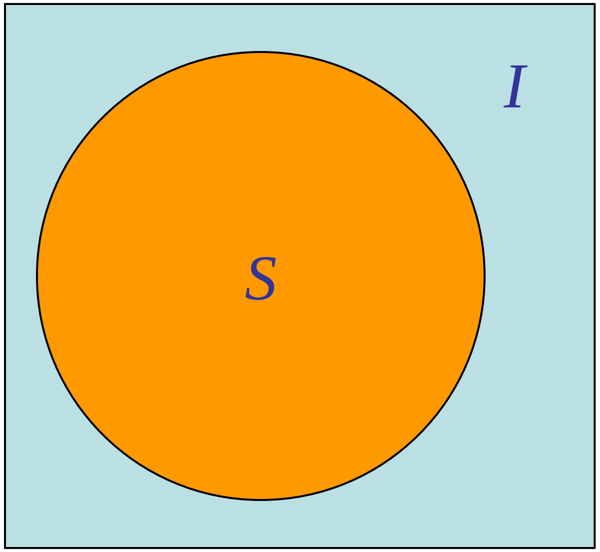
Effect of adding $\mathring{u}_l$ to the basis:

- Basis is flexible enough to use a single diagonalization (energy errors are now O(δ^4)).
- Must have additional matching conditions to connect both u and $\mathring{u}$ to the planewaves

➔ for a given level of convergence, more planewaves are needed.

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

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

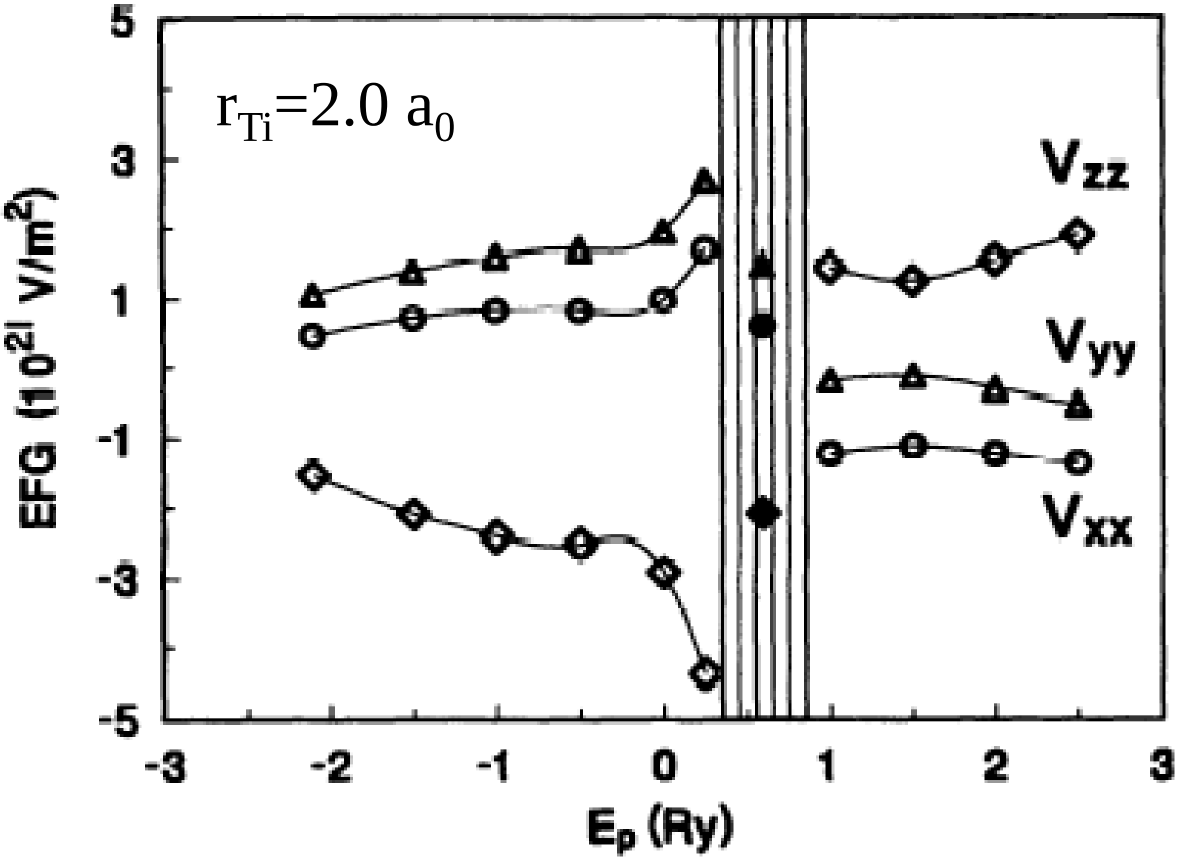
- Planewave expansions.
- Integrals are fast due to FFT properties
  - Step function (cut out spheres) can be done exactly up to finite G_{max} by convolution with pre-computed U(G)

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 $O(N)$ …

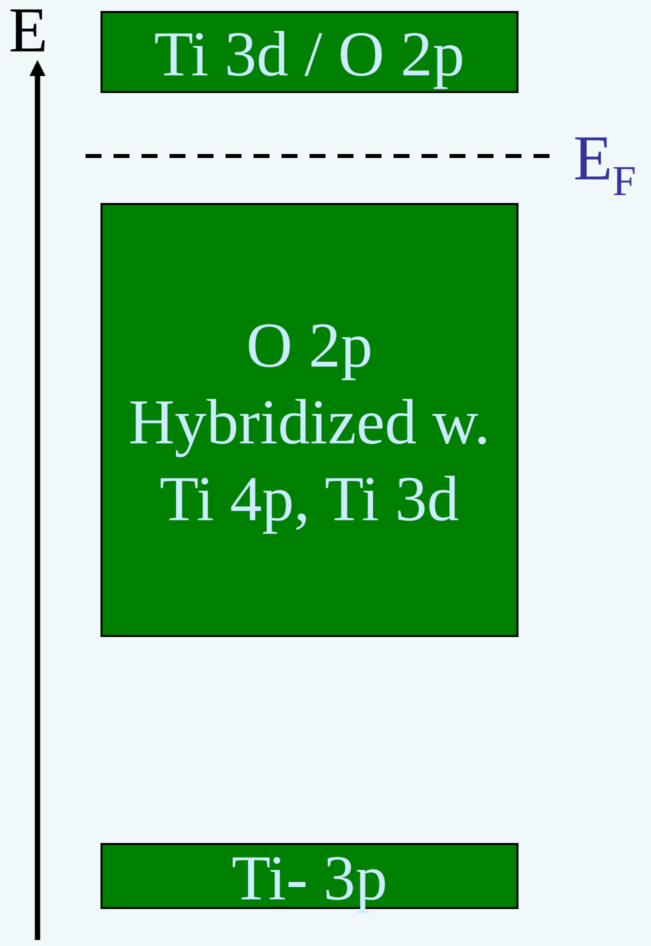
Complications in the LAPW Method

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



P. Blaha, D.J. Singh, P.I. Sorantin and K. Schwarz, Phys. Rev. B **46**, 1321 (1992).

Electronic Structure



Complications in the LAPW Method

What went wrong?

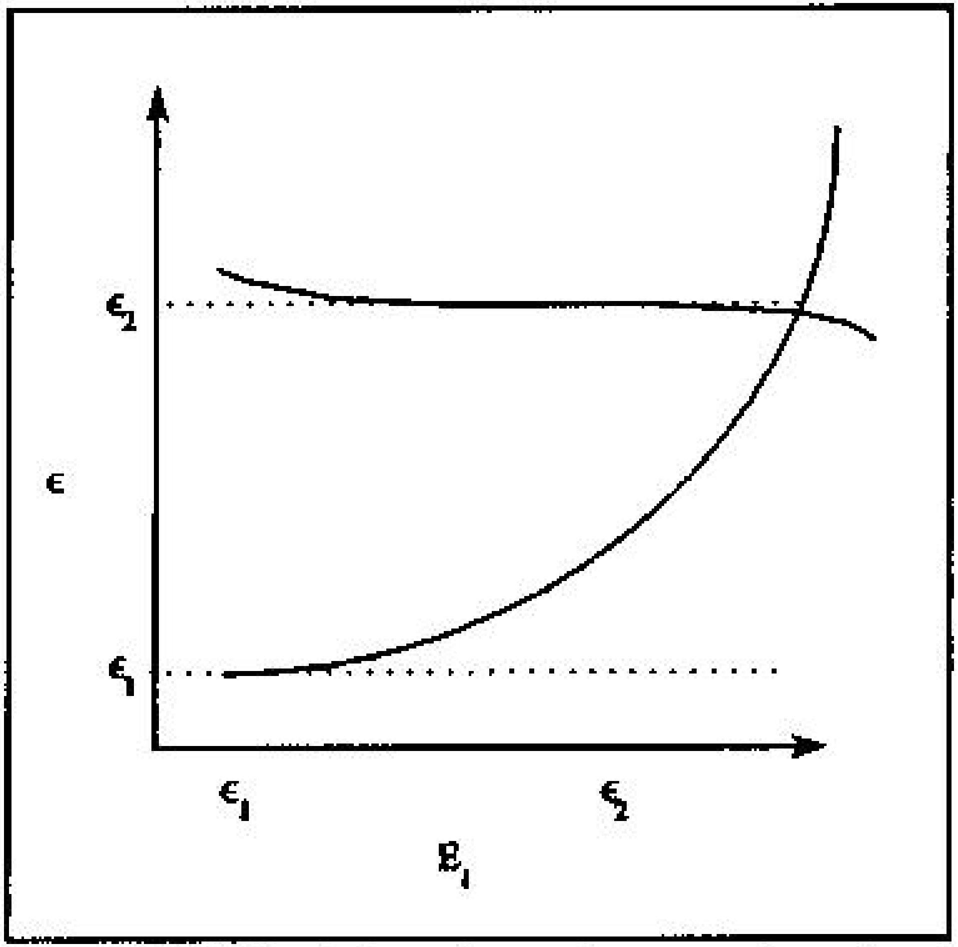


Figure 5.14 Variation of a semi-core and a valence band with E_l. The dotted lines at ϵ_1 and ϵ_2 denote the true locations of the bands.

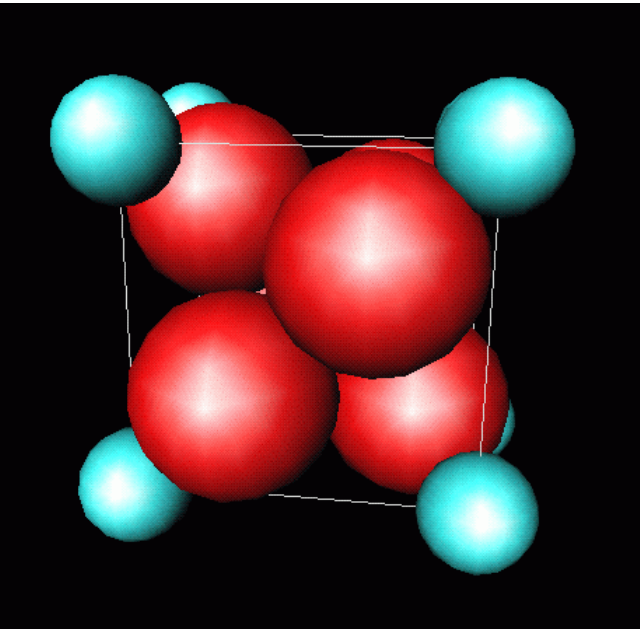
The LAPW method requires non-overlapping spheres

⇨ *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 *ů* orthogonal to them. On the other hand, the valence states may have significant contributions from the same *l*.

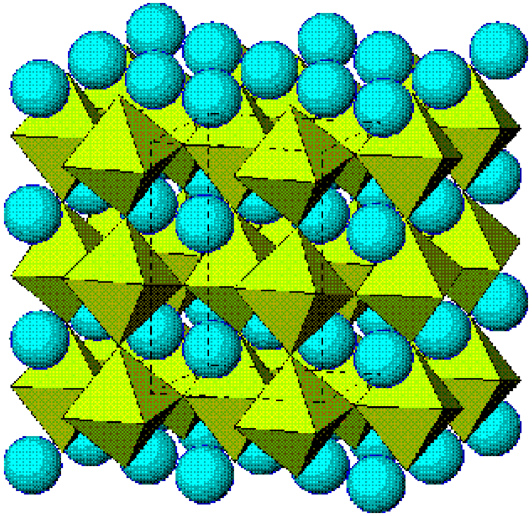
Complications in the LAPW Method

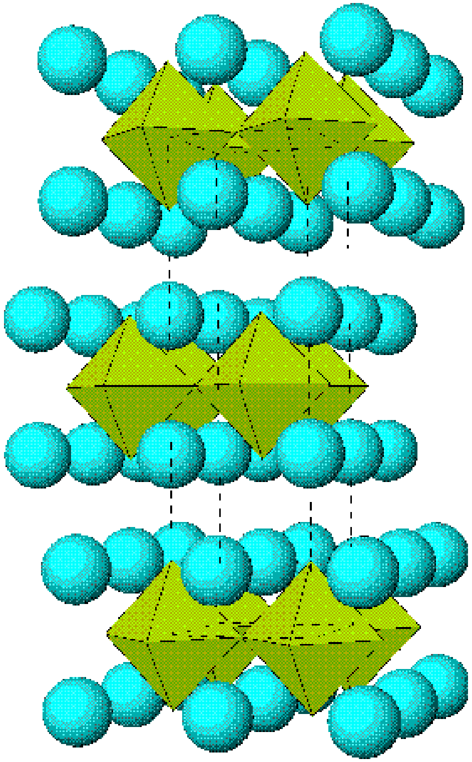
Solution?: Use large spheres to get orthogonality to core states:
Unfortunately, crystal structures don't generally allow this.



Rutile Structure

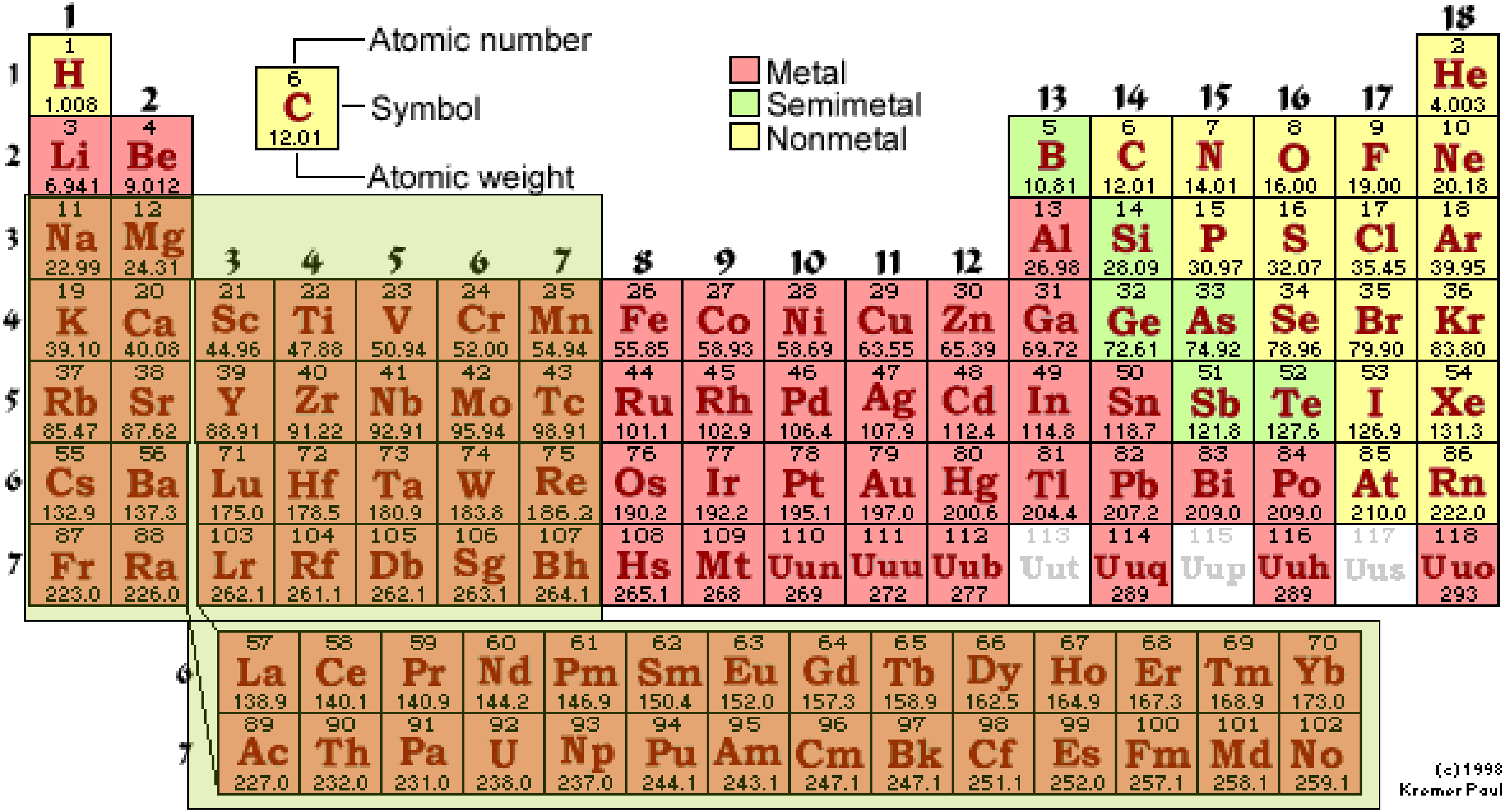
Perovskite





Layered Perovskite

Complications in the LAPW Method

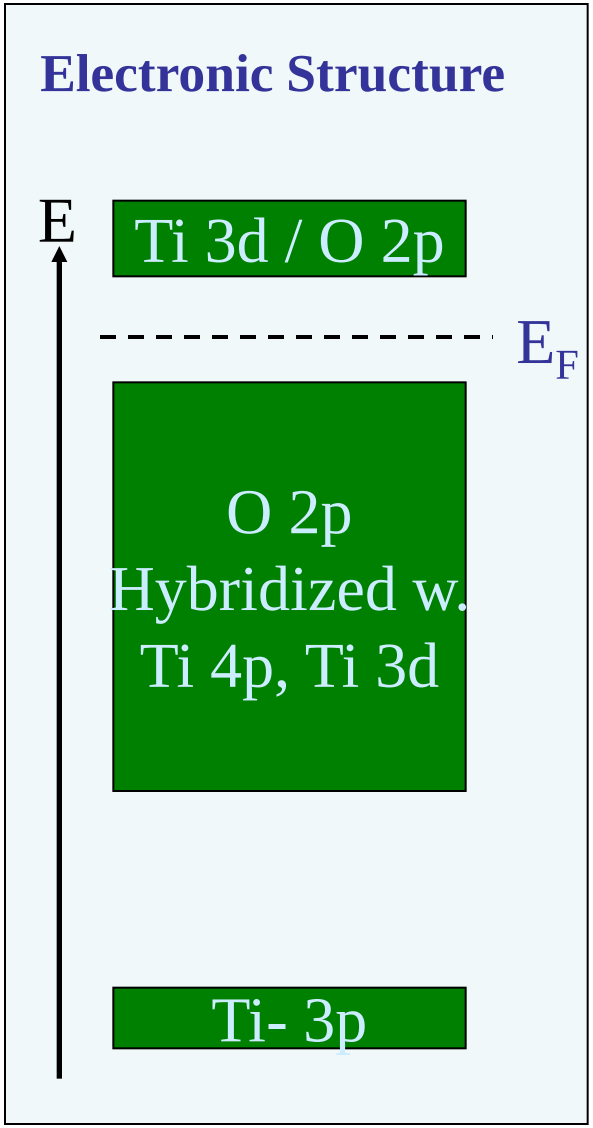


	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H 1.008																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	71 Lu 175.0	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po 209.0	85 At 210.0	86 Rn 222.0
7	87 Fr 223.0	88 Ra 226.0	103 Lr 262.1	104 Rf 261.1	105 Db 262.1	106 Sg 263.1	107 Bh 264.1	108 Hs 265.1	109 Mt 268	110 Uun 269	111 Uuu 272	112 Uub 277	113 Uut	114 Uuq 289	115 Uup	116 Uuh 289	117 Uus	118 Uuo 293

6	57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm 146.9	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0
7	89 Ac 227.0	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu 244.1	95 Am 243.1	96 Cm 247.1	97 Bk 247.1	98 Cf 251.1	99 Es 252.0	100 Fm 257.1	101 Md 258.1	102 No 259.1

🟩 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.

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

***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:

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

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

Subsidiary (non-variational) coefficients are $A_{\ell m}$ $B_{\ell m}$ $A'_{\ell m}$ & $B'_{\ell m}$

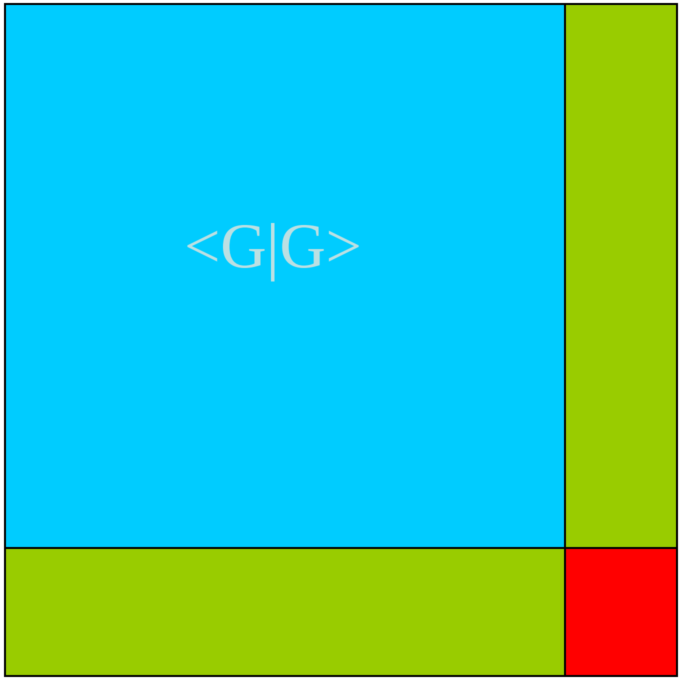
- $A_{\ell m}$ and $B_{\ell m}$ are determined by matching the value and derivative on the sphere boundary to the planewaves as usual.
- $A'_{\ell m}$ and $B'_{\ell m}$ are determined by matching the value and derivative on the sphere boundary to zero. Thus this part $(A'_{\ell m} u_\ell(r) + B'_{\ell m} \mathring{u}_\ell(r) + u^{(2)}_\ell(r))\, Y_{\ell m}(\mathbf{r})$ is formally a local orbital.

THE LAPW+LO METHOD

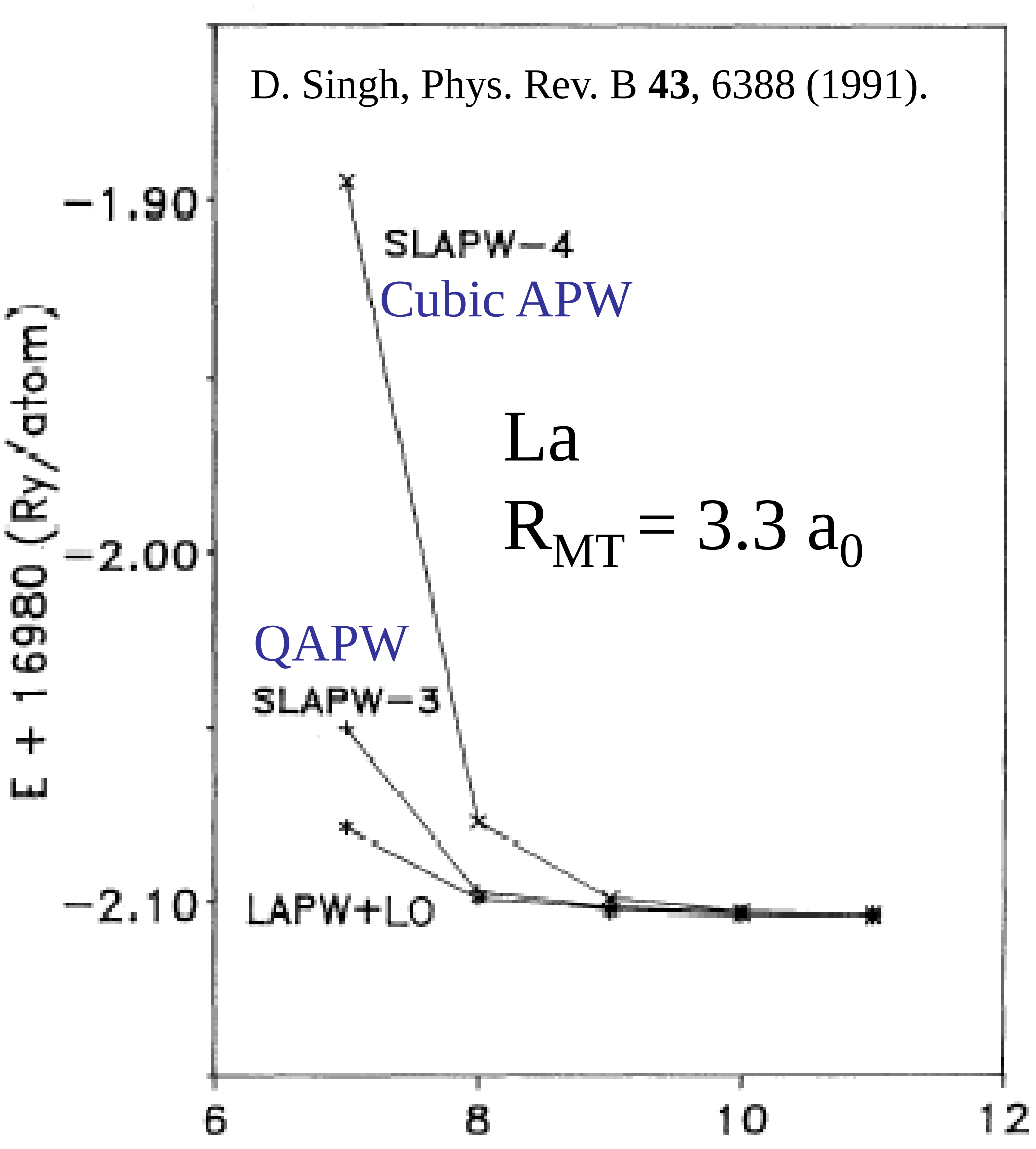
Key Points:

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



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 $\dot{u}$ and the other for $u^{(2)}$. Choose one at the semi-core position and the other at the valence.

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.

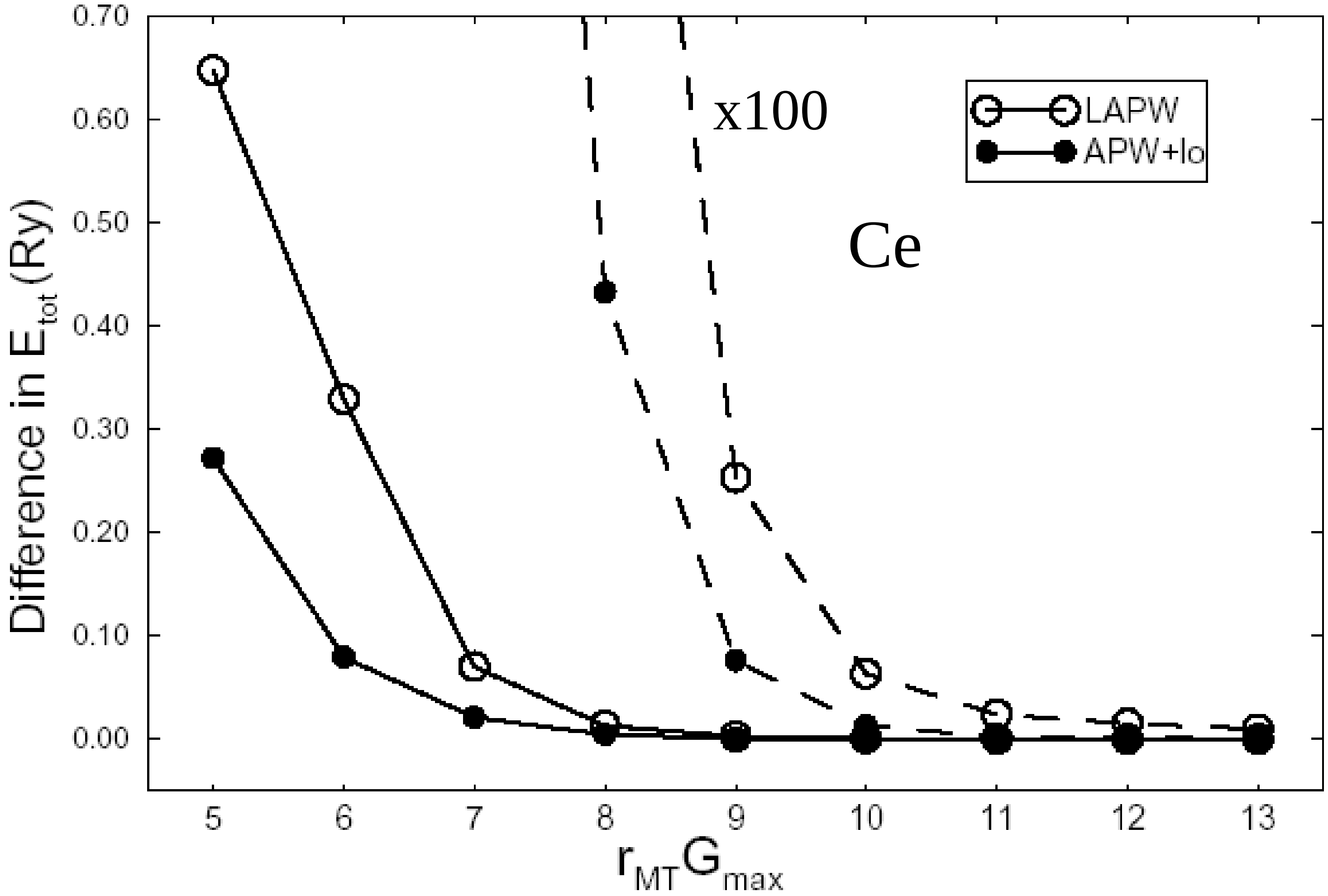
Then it is advantageous *for selected atoms and* ℓ, to use local orbitals to go back to the APW method.

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

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 3*d* channel, and LAPW for all others.

- Another useful setting is LAPW+LO to treat O 2*s* and APW+LO for O 2*p* (gives lower RKmax).

Critical Parameters in the LAPW Method

The Sphere Radii (R_{MT}):

- Large spheres give lower cost: $t \sim R^{-9}$ ➔ 10% increase in radius gives almost factor of 2 saving in run time.
- Can't have too much core leakage.
- Can't have too large effective Rkmax (>15 or so) for any atom ➔ numerical problems.
- Can't overlap – choose according to rules about needed Rk_{max} for different atoms:

For well converged (may get away with less)

	LAPW	APW+LO
Simple light sp atoms (Si,C,B,Al)	6.	5.5
Harder sp atoms (e.g. O)	7.	6.
Transition elements	9.	7.-8.
f-elements	9.-9.5	8.

Critical Parameters in the LAPW Method

The choice of basis (linearization parameters, local orbitals, LAPW vs. APW+lo):

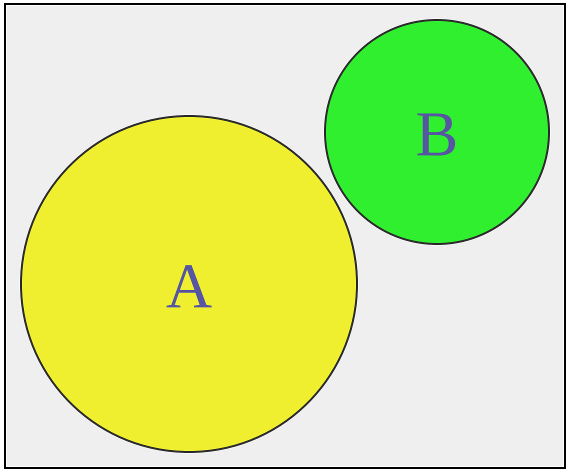
For atoms with semicore: default of WIEN2K (APW+LO), (“1” in last column of lines in case.in1) gives lower Rkmax but is less accurate than LAPW+LO if converged (case “0” in last column – need to change for both lines of that state).

Can do set-ups like (to lower Rkmax from 7. to maybe 6.5)
WIEN2k for O:

```
     0.30     3  0
    0   -1.55    0.002  CONT 0          LAPW
    0    0.30    0.000  CONT 0          +LO
    1    0.30    0.000  CONT 1          APW+lo
```

Similar in ELK

CHOICE OF SPHERE RADII



Size of basis,

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

Compute time,

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

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

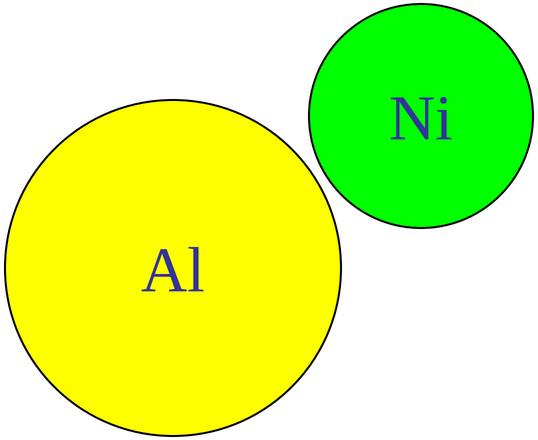
Typical rG_{max} values for good convergence (always check):

Transition elements:	9
f-electron materials:	9.-9.5
Simple elements (O,F,Cl)	7
Soft simple elements (Al, Si, …)	6

Should consider in setting radii, which are computational not physical parameters.

Example (B2 NiAl)

Chemical Sense *vs.* Computational Sense

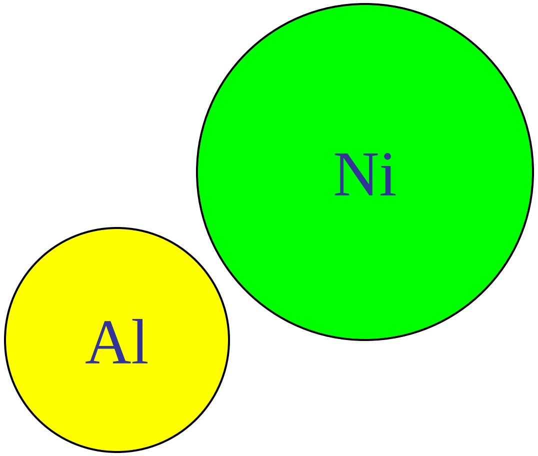


$r_{Al} = 2.8$ bohr

$r_{Ni} = 1.9$ bohr

$r_{Al}G_{max} = 6 \rightarrow G_{max} = 2.15$

$r_{Ni}G_{max} = 9 \rightarrow G_{max} = 4.74$



$r_{Al} = 1.9$ bohr

$r_{Ni} = 2.8$ bohr

$r_{Al}G_{max} = 6 \rightarrow G_{max} = 3.15$

$r_{Ni}G_{max} = 9 \rightarrow G_{max} = 3.21$

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

Critical Parameters in the LAPW Method

The choice of valence and core states:

Including semicore states means that you need high Rkmax for that atom: e.g. Se without semi-core 3d can use Rkmax=7., Se with semicore 3d needs Rkmax=9.

Semicore cannot leak out – this constraint affects choice of radius.

Critical Parameters in the LAPW Method

The planewave cut-off:

Should always check – change Rkmax and check energy and forces to make sure nothing important changes.

If in any doubt about an LAPW calculation make small changes in the sphere radii and see if anything changes – almost everything except zone sampling depends on sphere radii.

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.**

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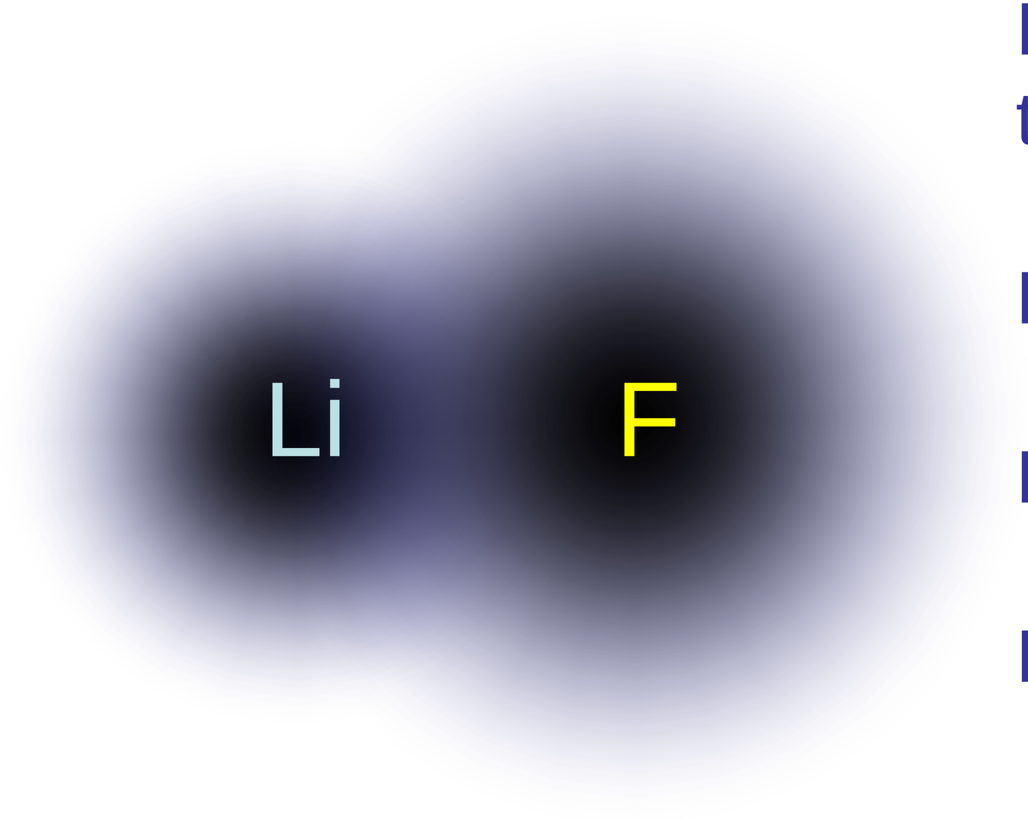
3. D. Singh, Phys. Rev. B **43**, 6388 (1991). **Local orbitals.**

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.**

How Do We Know What is What



How do we understand this in useful terms:

$Li^+ F^-$?

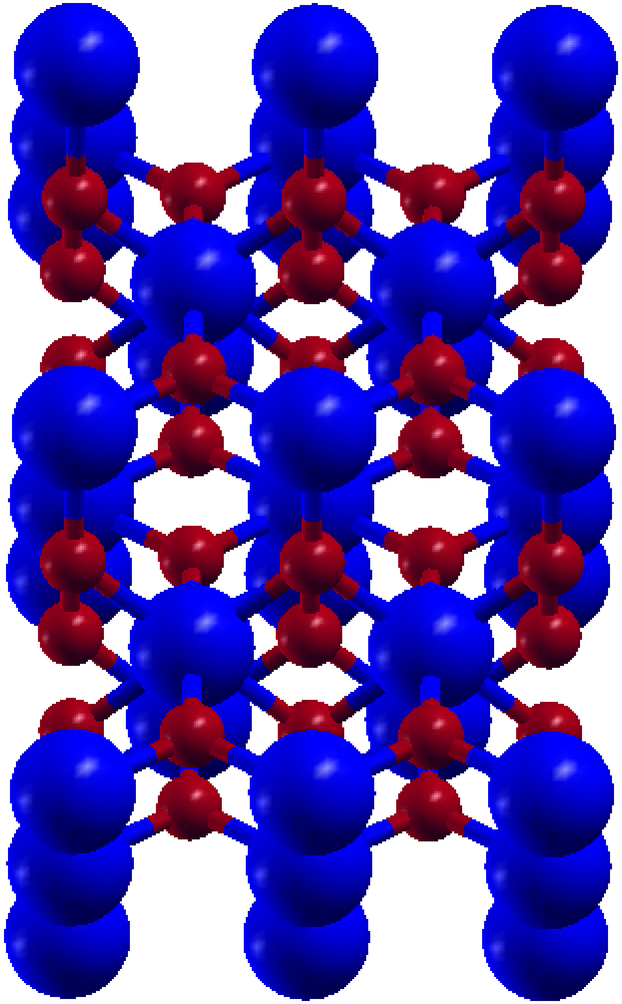
LiF (covalent)?

$Li^- F^+$?

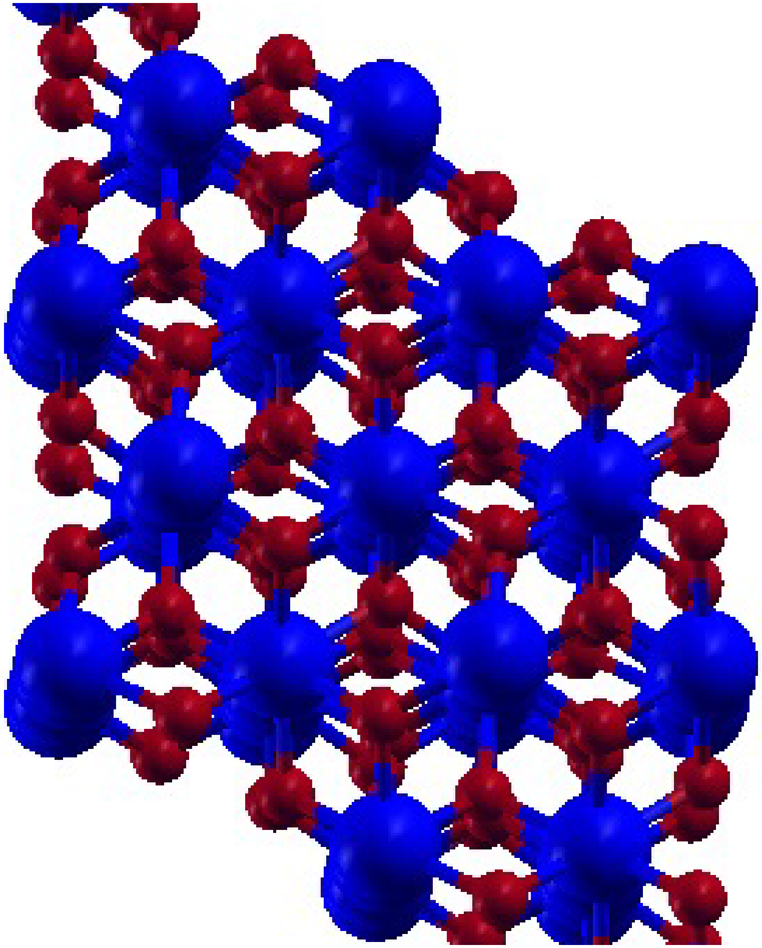
Note: *An expansion in radial functions times spherical harmonics is complete ➔ Expansion about more than one site is over-complete (ambiguous).*

An Example: Two Titanium Oxides

TiO_2

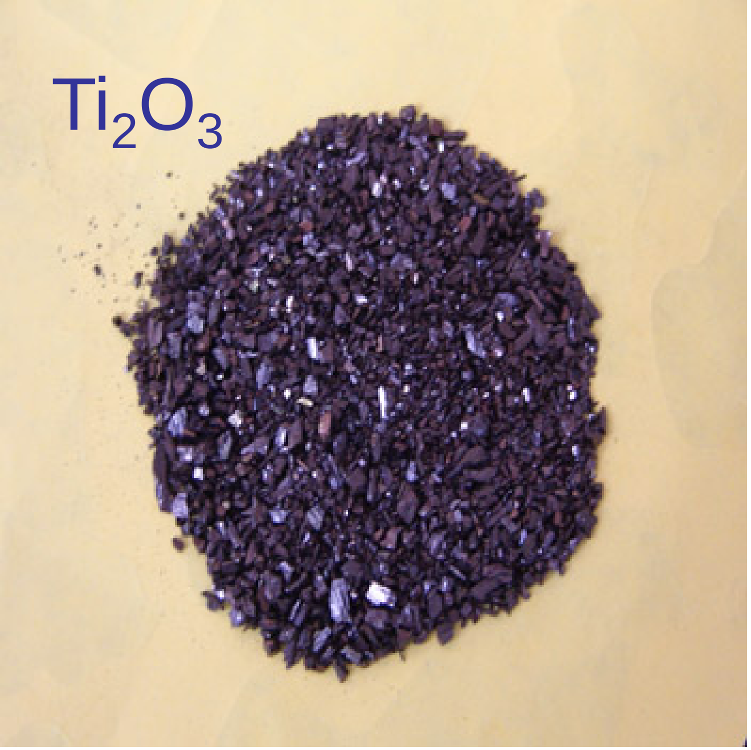


Ti_2O_3



Both have Ti octahedrally coordinated by O.

A Chemist's View



Electronegativity:

Ti: 1.54 O: 3.44

Large difference means O is O^{2-} and therefore we have Ti^{4+} and Ti^{3+} respectively. These are known common valence states of Ti.

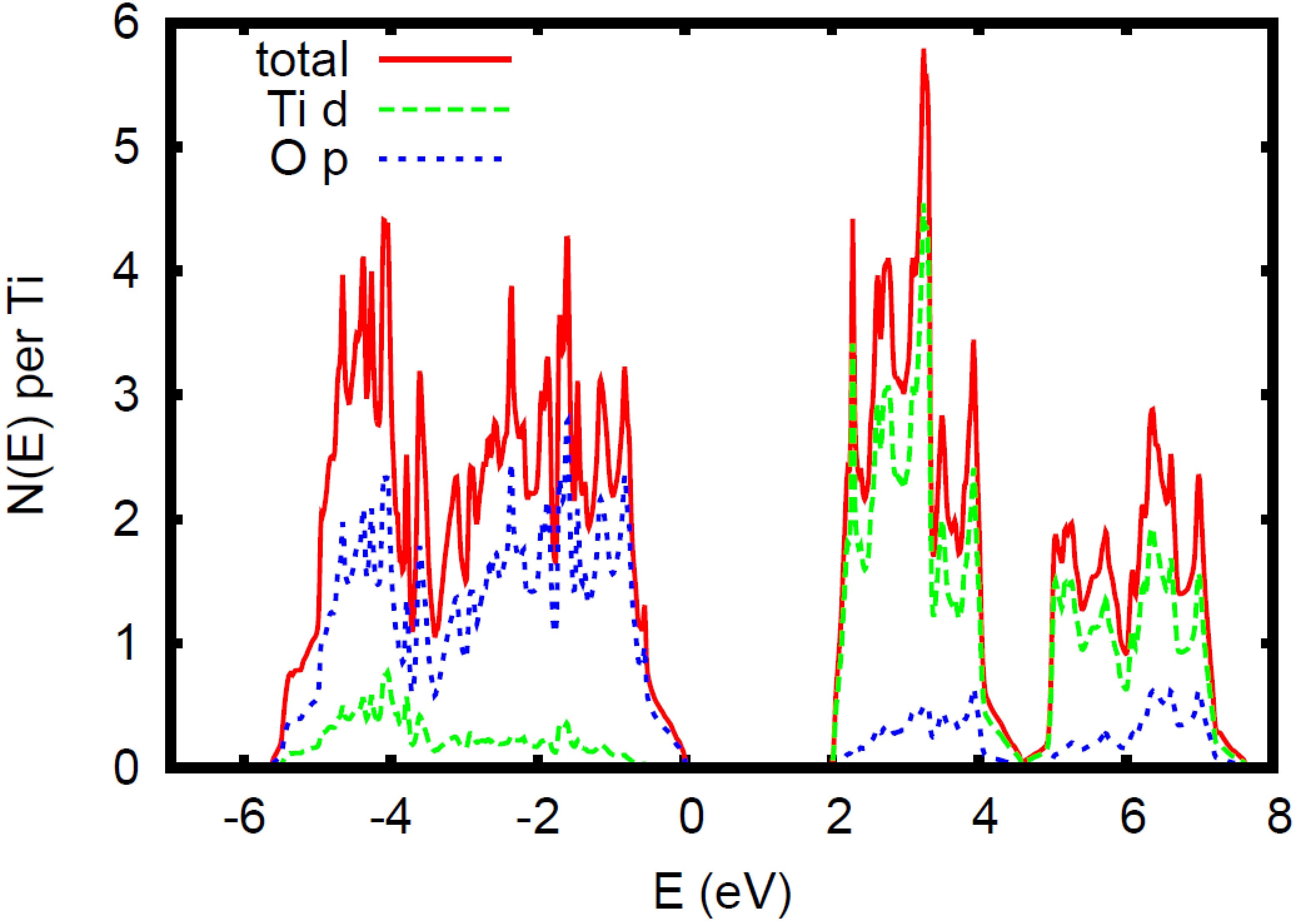
22
47.88
4,3
3560
1935
4.54
Ti
$[Ar]3d^2 4s^2$
Titanium

Things are not always so simple:

- Smaller electronegativity differences (e.g. $BaFe_2As_2$).
- Metals (e.g. $PdCoO_2$).
- Multiple mixed valence ions (e.g. $MnFe_2O_4$ – $Mn^{2+}Fe^{3+}$; $Mn^{4+}Fe^{2+}$ etc.).

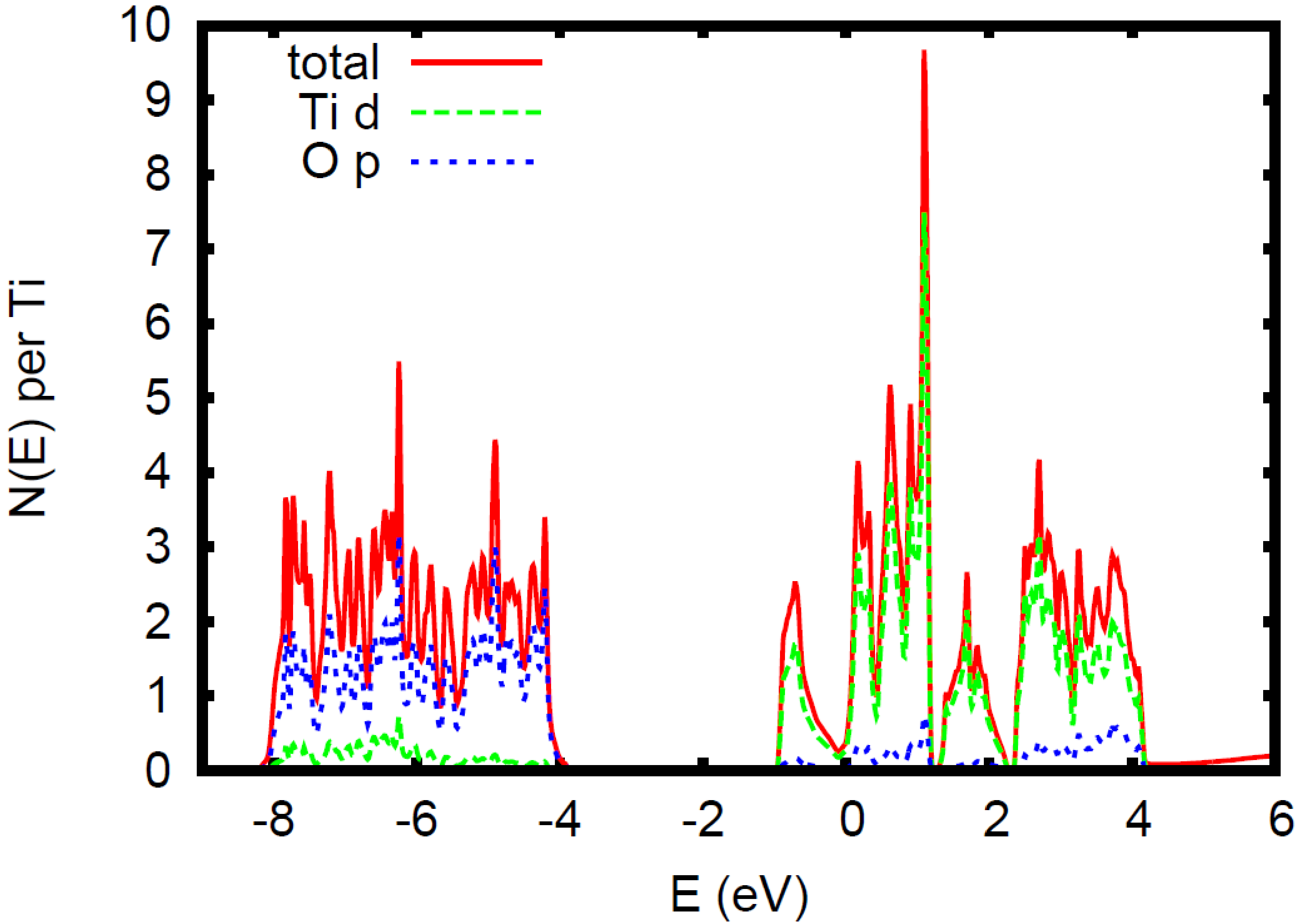
Density of States for TiO_2

LAPW calculation with r_{Ti}=2.0 bohr, r_O=1.6 bohr

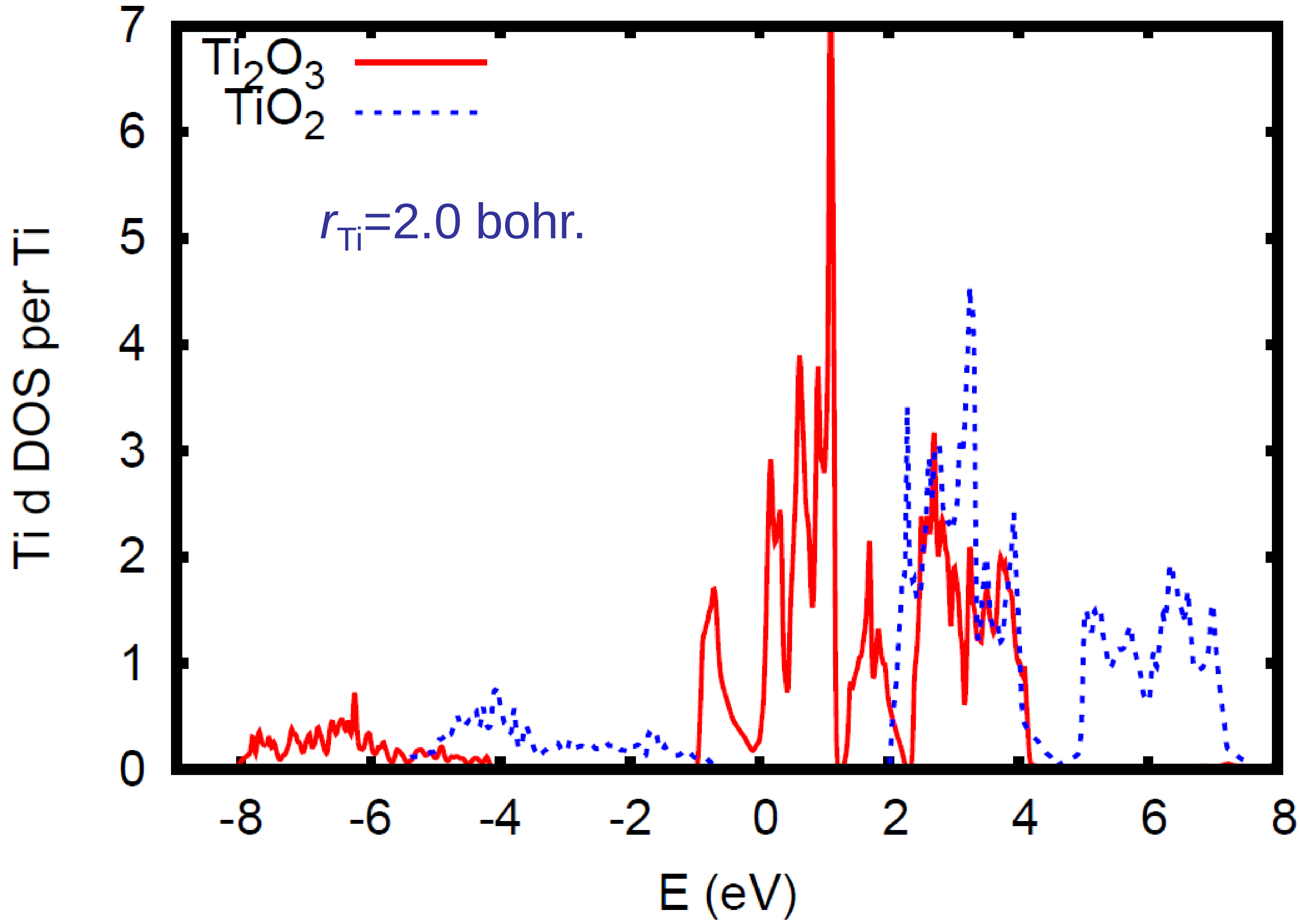


Density of States for Ti_2O_3

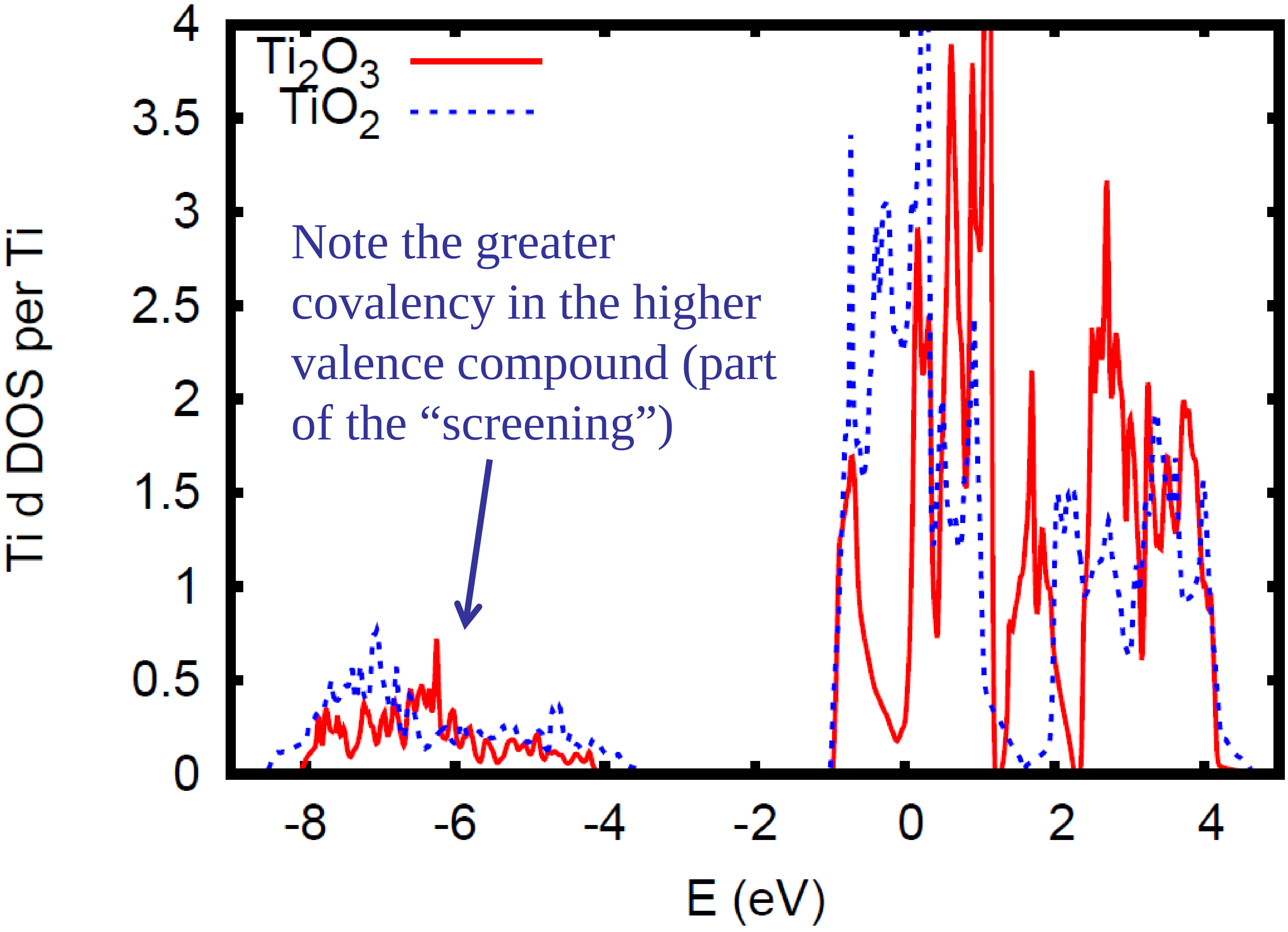
LAPW calculation with r_{Ti}=2.0 bohr, r_O=1.6 bohr



Comparison of Ti d Projections



Ti d Projections with 3 eV Shift



Note the greater covalency in the higher valence compound (part of the "screening")

Deep Core Level Positions

- Reflect the Coulomb potential, which should vary with valence.
- Experimentally accessible quantities.
- Absolute position is arbitrary in a solid state calculation: Need to look either at differences or relative to some physical reference, e.g. Fermi level.

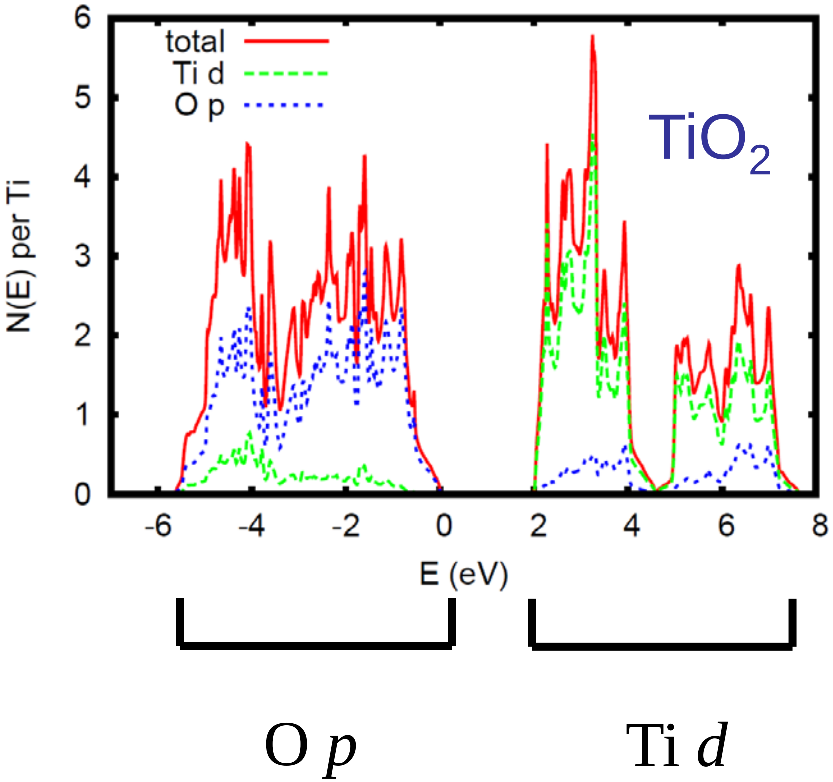
O 1*s* – Ti 1*s* (PBE GGA).

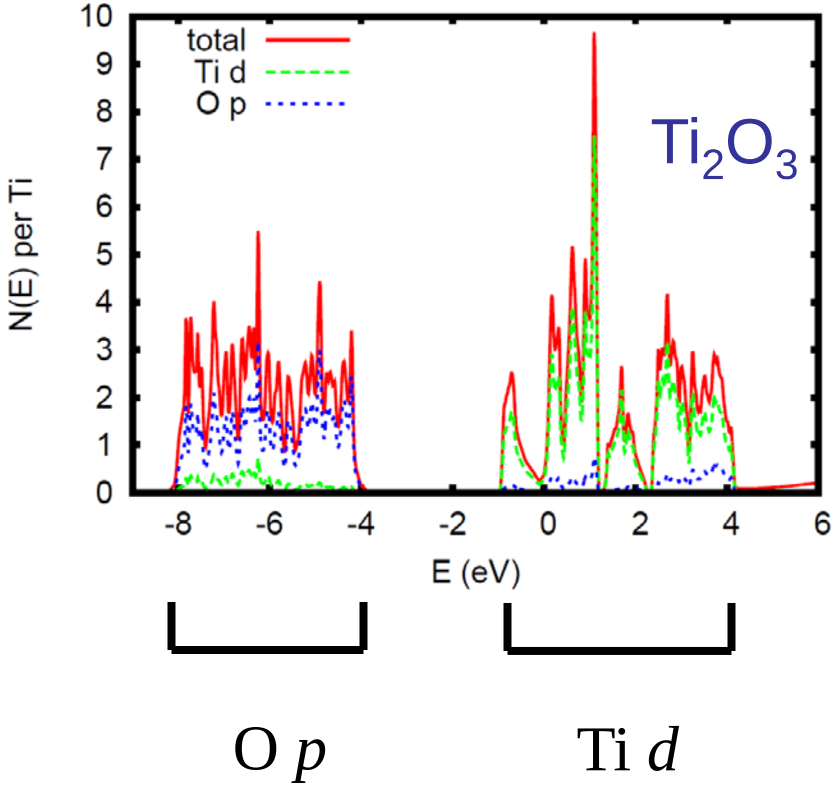
TiO_2: 4357.73 eV
Ti_2O_3: 4356.09 eV

- Difference is > 1 eV and can be used to characterize valence. However, the differences in non-oxides/halides are smaller, and this is indirect (relies on reference compounds).
- Higher binding energy for metal ion means higher valence.
- Can be misleading for hypothetical crystal structures.

What Can Be Done for TiO_2 / Ti_2O_3

- Do DFT calculations; find band characters and then count.





12 O *p* bands occupied (24 *e*) per cell (Ti_2O_4), no occupied *d* bands ➔ Ti^{4+}

18 O *p* bands occupied (36 *e*) per cell (Ti_4O_6), 2 occupied *d* bands ➔ Ti^{3+}

Questions?