

# The Solid State as a Fabric for Intertwining Chemical Bonding, Electronic Structure and Magnetism

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Vietri Sul Mare, Italy

October 3, 2011

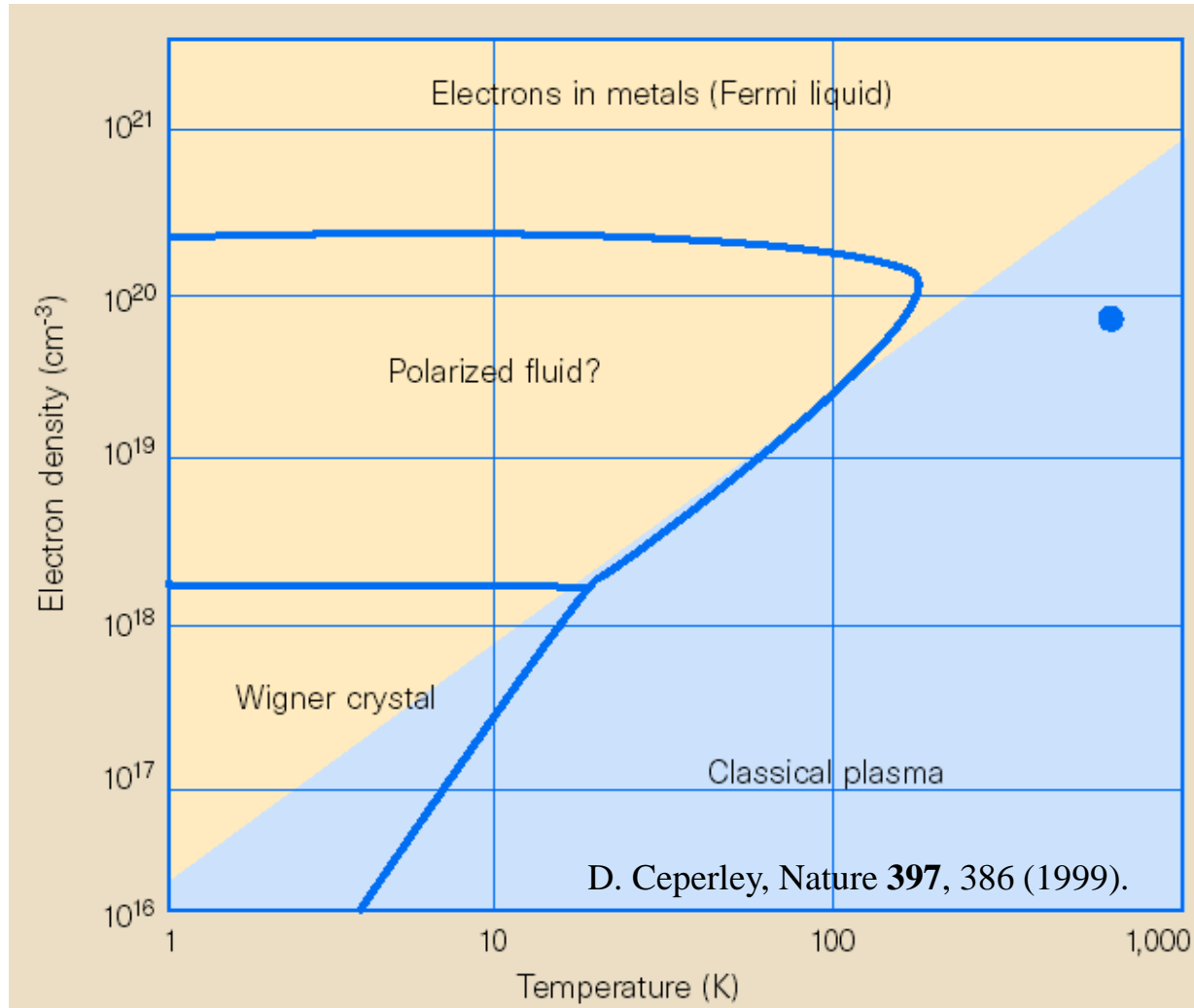
# Blueberry Muffins



The blueberries change the taste, but the muffin is still basically a muffin.

The taste does not depend much on the distribution of berries.

# The Electron Gas



***bcc Fe:***  $n_{av} = 2.2 \times 10^{24}$  e/cm<sup>3</sup> (total);  $n_{av} = 6.8 \times 10^{23}$  e/cm<sup>3</sup> (valence)

***Nothing Interesting Happens in the Uniform Electron Gas at Densities of Solids***

# The Electron Gas Now With Nuclei

1 H Hydrogen 1.007 94																	Group 18 2 He Helium 4.002 602
Group 1 3 Li Lithium 6.941	Group 2 4 Be Beryllium 9.012 182																
11 Na Sodium 22.989 770	12 Mg Magnesium 24.3050	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9	Group 10	Group 11	Group 12	Group 13 5 B Boron 10.811	Group 14 6 C Carbon 12.0107	Group 15 7 N Nitrogen 14.006 74	Group 16 8 O Oxygen 15.9994	Group 17 9 F Fluorine 18.998 4032	10 Ne Neon 20.1797
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955 910	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938 049	26 Fe Iron 55.845	27 Co Cobalt 58.933 200	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	32 Ge Germanium 72.61	33 As Arsenic 74.921 60	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.905 85	40 Zr Zirconium 91.224	41 Nb Niobium 92.906 38	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.905 50	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.904 47	54 Xe Xenon 131.29
55 Cs Cesium 132.905 45	56 Ba Barium 137.327	57 La Lanthanum 138.9055	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.078	79 Au Gold 196.966 55	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.980 38	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)
87 Fr Francium (223)	88 Ra Radium (226)	89 Ac Actinium (227)	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (263)	107 Bh Bohrium (264)	108 Hs Hassium (265) <sup>†</sup>	109 Mt Meitnerium (268) <sup>†</sup>	110 Uun* Ununittium (269) <sup>†</sup>	111 Uuu* Ununiumium (272) <sup>†</sup>	112 Uub* Ununbium (277) <sup>†</sup>		114 Uuq* Ununquadium (285) <sup>†</sup>				

**Key:**

6 — Atomic number  
 C — Symbol  
 Carbon — Name  
 12.0107 — Average atomic mass

- Metals**
- Alkali metals
  - Alkaline-earth metals
  - Transition metals
  - Other metals
- Nonmetals**
- Hydrogen
  - Semiconductors
  - Halogens
  - Noble gases
  - Other nonmetals

A team at Lawrence Berkeley National reported the discovery of elements 116 and 119 in June 1999. The same team retracted the discovery in July 2001. The discovery of element 114 has been reported but not confirmed.

<sup>†</sup> Estimated from currently available IUPAC data.  
 \* The systematic names and symbols for elements greater than 109 will be used until the approval of trivial names by IUPAC.

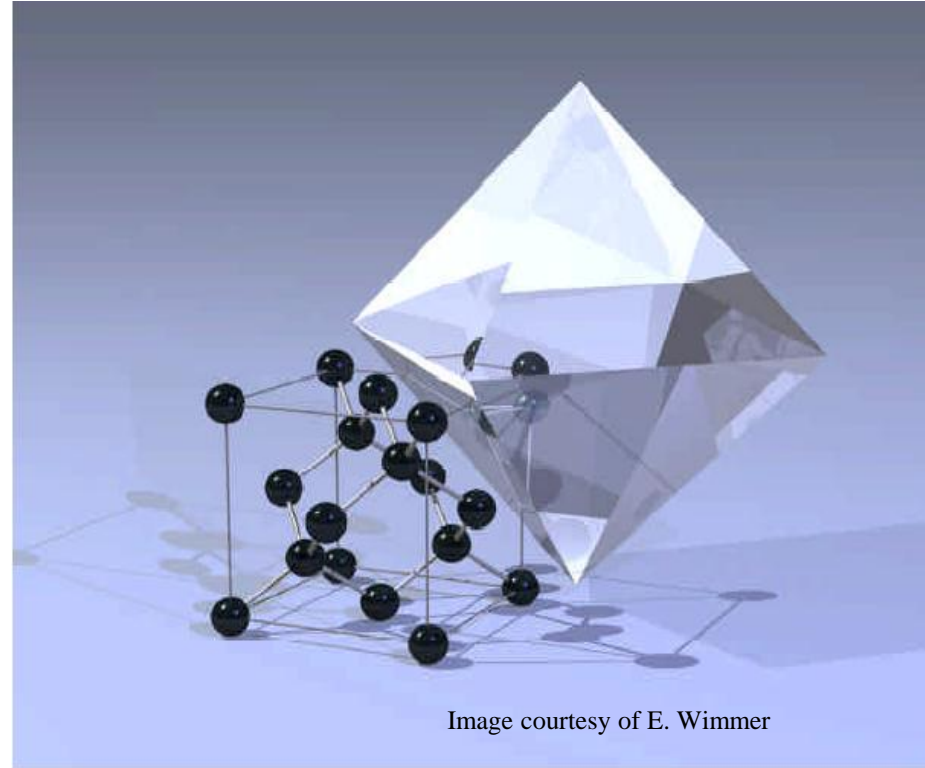
58 Ce Cerium 140.116	59 Pr Praseodymium 140.907 65	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925 34	66 Dy Dysprosium 162.50	67 Ho Holmium 164.930 32	68 Er Erbium 167.26	69 Tm Thulium 168.934 21	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
90 Th Thorium 232.0381	91 Pa Protactinium 231.035 88	92 U Uranium 238.0289	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)

The atomic masses listed in this table reflect the precision of current measurements. (Values listed in parentheses are those of the element's most stable or most common isotope.) In calculations throughout the text, however, atomic masses have been rounded to two places to the right of the decimal.

He: liquid at 0 K  
 W: melts at 3695 K

# First Principles Modeling

- Connect properties with atomic level structure.
- Sort out physical models.
- Ask “what if” questions.
- Microscopic mechanisms and **understanding**.
- Screen ideas for new/modified materials.
- Analyze failures.



# Rough Plan

## Mornings:

- **Monday:** “First Principles Calculations: The Glue that Binds Materials and Models”
- **Tuesday:** “The Wacky World of Perovskites”
- **Wednesday:** “Magnetism and Superconductivity”
- **Thursday:** “Thermoelectrics: Getting a Grip on Heat”
- **Friday:** “Electronic Structure and Chemical Bonding”

## Afternoons:

- Hands on with the DFT calculations and discussions.



“Hell, there are no rules here - we’re trying to accomplish something.”

Thomas Edison

**WARNING**

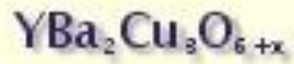


If you do not ask questions, I will.

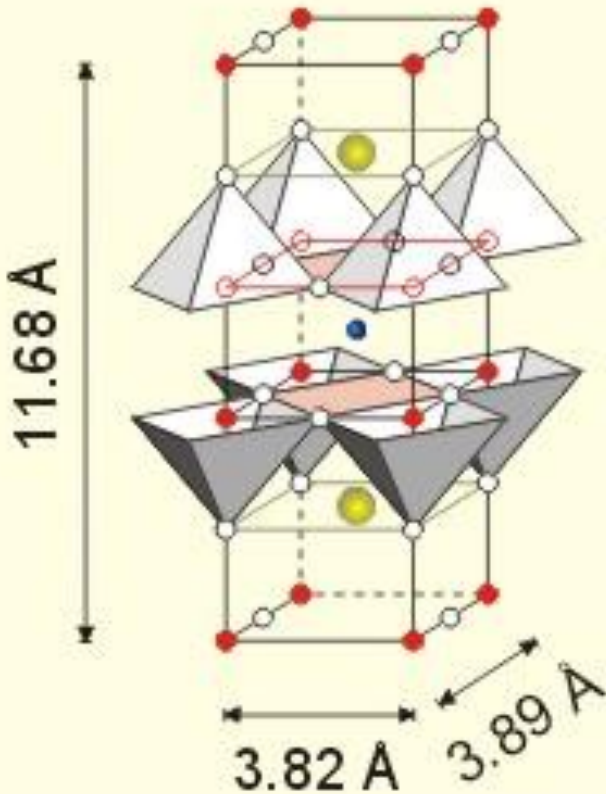
(corollary) If you do not contradict me, I will.



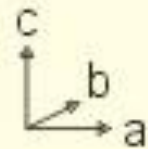
# Property Prediction and Surprises



- Y
- Ba
- Cu
- O

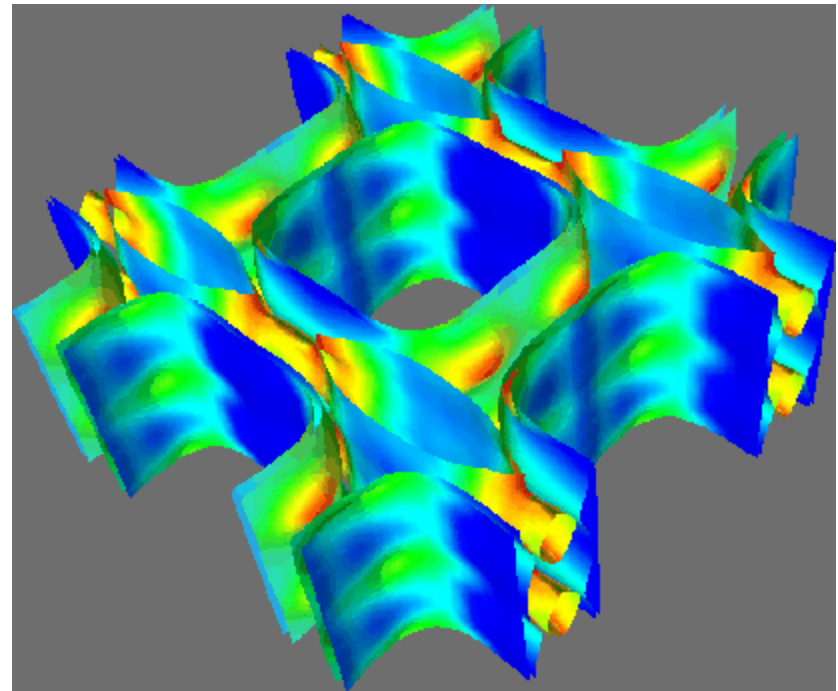


- Cu(1), O(4)
- Ba, O(1)
- Cu(2), O(2), O(3)
- Y
- Cu(2), O(2), O(3)
- Ba, O(1)
- Cu(1), O(4)



M. Opel

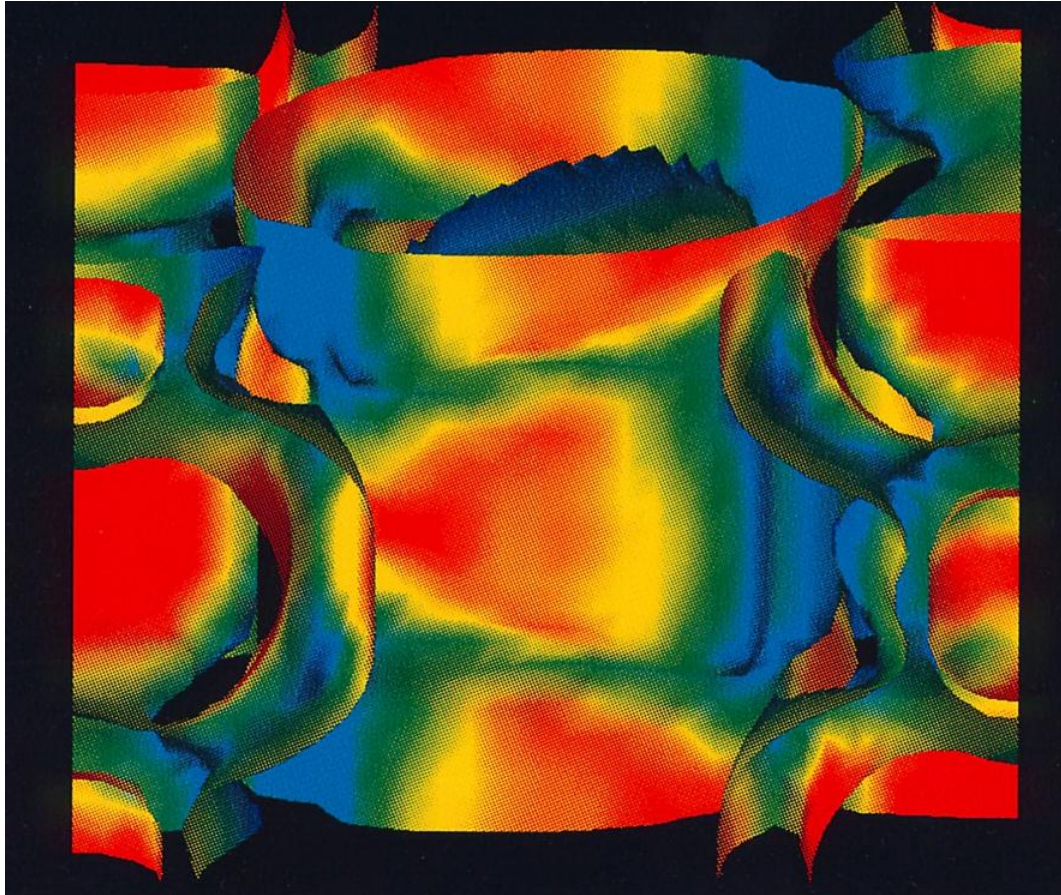
High- $T_c$  Electronic Structures are 2D



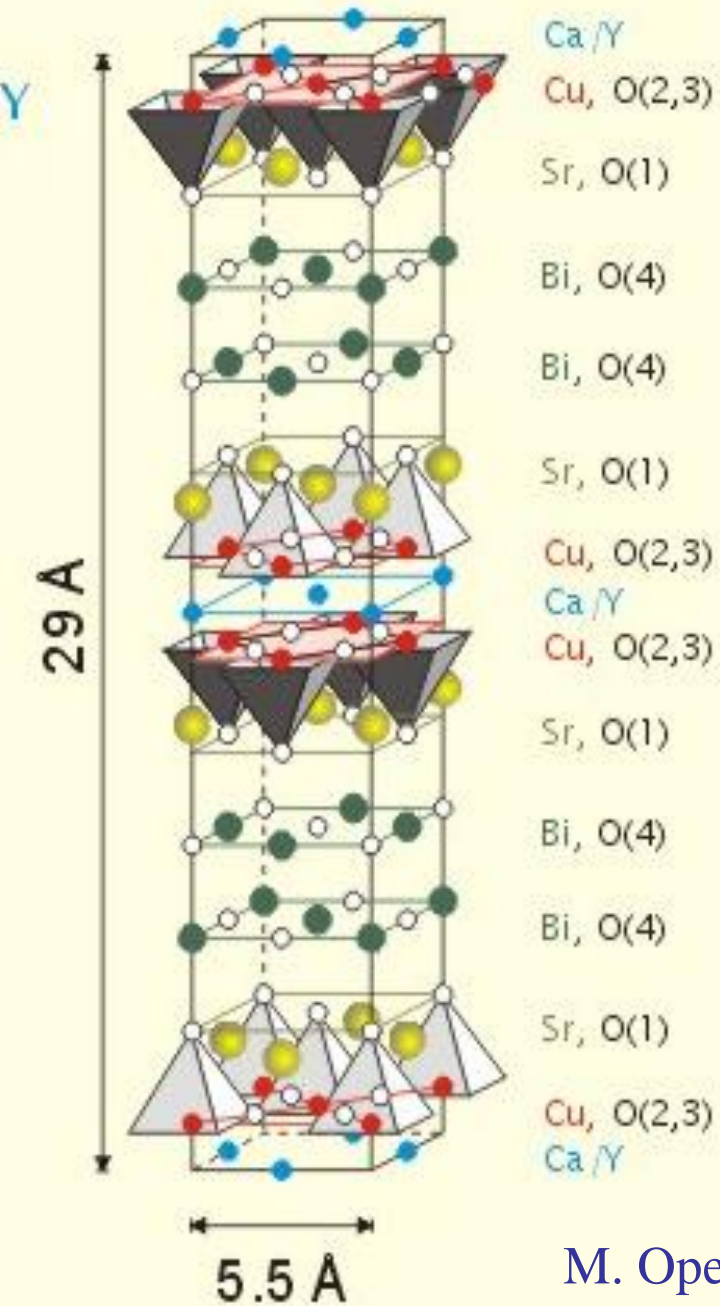
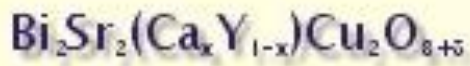
Pickett, Cohen, Krakauer, Singh

ANSWER: 1994 (Pickett and Singh, PRL) **NO!**

Fermi Surface of  $\text{YNi}_2\text{B}_2\text{C}$  ( $T_c=16\text{K}$ )



- Electronic structures are very three dimensional
- Due to strong B-C bonds
- Large electron phonon coupling is responsible for superconductivity (conventional mechanism).
- **NOT THE BASIS OF A NEW FAMILY OF HIGH TEMPERATURE SUPERCONDUCTORS**



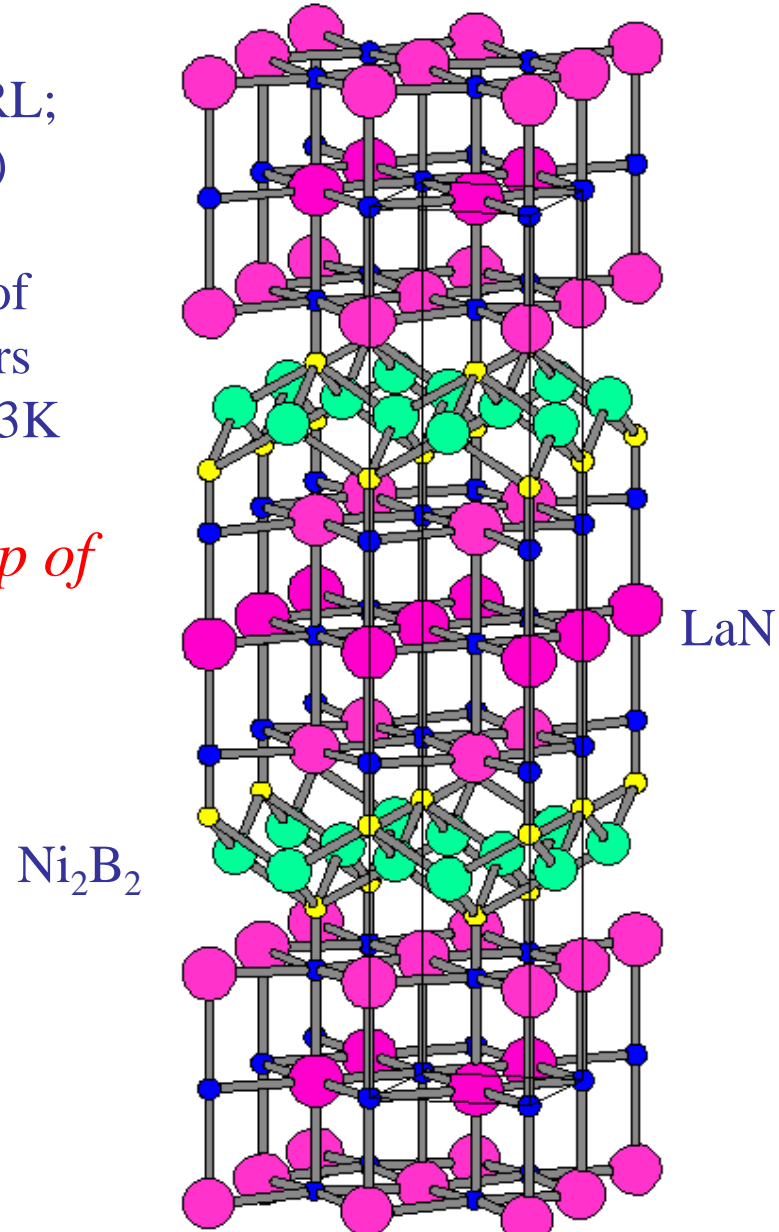
M. Opel



NEWS: 1994  
(Nagarajan, PRL;  
Cava, Nature)

A new family of  
superconductors  
with  $T_c$  up to 23K

*Is 23K the tip of  
the iceberg?*



(Fig. by Huang et al.)



Westminster Abbey, London

*“The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations that are much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.”*

P.A.M. Dirac, *Proc. Roy. Soc. (Lond)*  
**123**, 714 (1929).

$H\psi = E\psi$  : Many Body Problem, with correlated many-body wavefunctions → Too hard.

# Density Functional Theory

**Standard approach:** properties are governed by a wavefunction:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) ; H\Psi = E\Psi$$

Given the Hamiltonian, we focus on solving for the wavefunction and extract observables as expectation values of operators with this wavefunction – for  $N$  electrons this is a  $3N$  dimensional problem.

**Density Functional Theory:** Hohenberg-Kohn theorem tells us

- Energy and other observables of the ground state are given as functionals of the density  $\rho(\mathbf{r})$  which exists in 3 dimensions only.
- The ground state density is unique and is the density that minimizes this functional.

$$E = E[\rho] ; \rho = \min_{E[\rho]} \{ \rho \}$$

The functional  $E$  is proven to exist, but is not given by the theorem.

# Kohn-Sham Approach

Any density  $N$  electron density can be written as the density corresponding to an  $N$  electron Slater determinant (never mind that the true wavefunction cannot).

$$\rho(\mathbf{r}) = \sum \varphi_i(\mathbf{r})^* \varphi_i(\mathbf{r}) ; i=1,2, \dots , N$$

Where the  $\varphi_i(\mathbf{r})$  are the Kohn-Sham orbitals

→ variational principle for  $\rho$  yields a variational principle for the  $\varphi_i(\mathbf{r})$ .

Kohn and Sham then separated terms that should be large in the functional leaving a (hopefully) small remainder as the unknown functional.

$$E[\rho] = T_s[\rho] + E_{ext}[\rho] + U_{Hartree}[\rho] + E_{xc}[\rho]$$

where, like  $E$ ,  $E_{xc}$  is unknown.  $E_{xc}$  is defined by this equation.

# Kohn-Sham Equations

Use the variational principle to write single particle equations for the Kohn-Sham orbitals.

$$\{T_s + V_{ext} + V_{Hartree} + V_{xc}\} \varphi_i = \varepsilon_i \varphi_i$$

$$\rho(\mathbf{r}) = \sum \varphi_i(\mathbf{r})^* \varphi_i(\mathbf{r}) ; i=1,2, \dots , N$$

Here,  $V_{hartree}$  and  $V_{xc}$  are functionals of the density (functional derivatives of the energy terms with respect to density), so generally these equations must be solved self-consistently.

This is straightforwardly generalizable to magnetic systems via spin-density functional theory where instead of a single function one has spin-densities,  $\rho_{\uparrow}(\mathbf{r})$  and  $\rho_{\downarrow}(\mathbf{r})$  for the collinear case and a four component spinor for non-collinear.



# The Local Density Approximation

Generally one may write

$$E[\rho] = \int \rho(\mathbf{r}) \varepsilon_{xc}[\rho](\mathbf{r}) d^3\mathbf{r}$$

The local (spin) density approximation consists of taking  $\varepsilon_{xc}[\rho]$  at each point  $\mathbf{r}$  as the value for the uniform electron gas at the density for this  $\mathbf{r}$ .

This exceedingly simple approximation works remarkably well, especially considering that the electron gasses of solids are nothing close to the uniform electron gas.

# Theory of static structural properties, crystal stability, and phase transformations: Application to Si and Ge

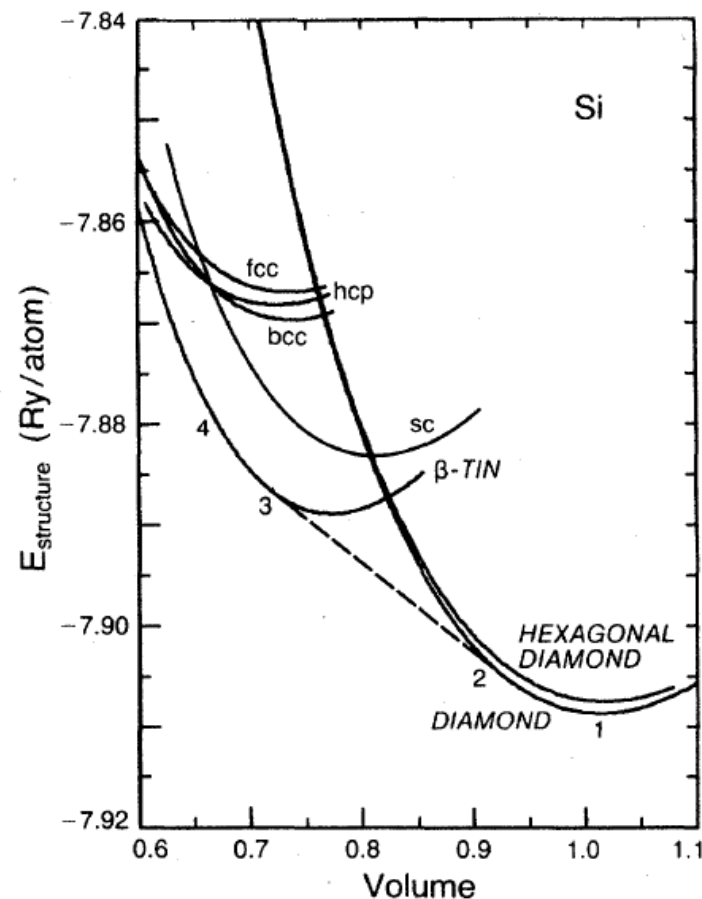
M. T. Yin\* and Marvin L. Cohen

*Department of Physics, University of California, Berkeley, California 94720  
and Materials and Molecular Research Division, Lawrence Berkeley Laboratory,  
Berkeley, California 94720*

(Received 29 March 1982)

TABLE II. Comparison of calculated and measured static properties of Si and Ge.

	Lattice constant (Å)	Cohesive energy (eV/atom)	Bulk modulus (Mbar)
Si			
Calculation	5.451	4.84	0.98
Experiment	5.429 <sup>a</sup>	4.63 <sup>b</sup>	0.99 <sup>c</sup>
Ge			
Calculation	5.655	4.26	0.73
Experiment	5.652 <sup>a</sup>	3.85 <sup>b</sup>	0.77 <sup>c</sup>



One of many early works of this type.

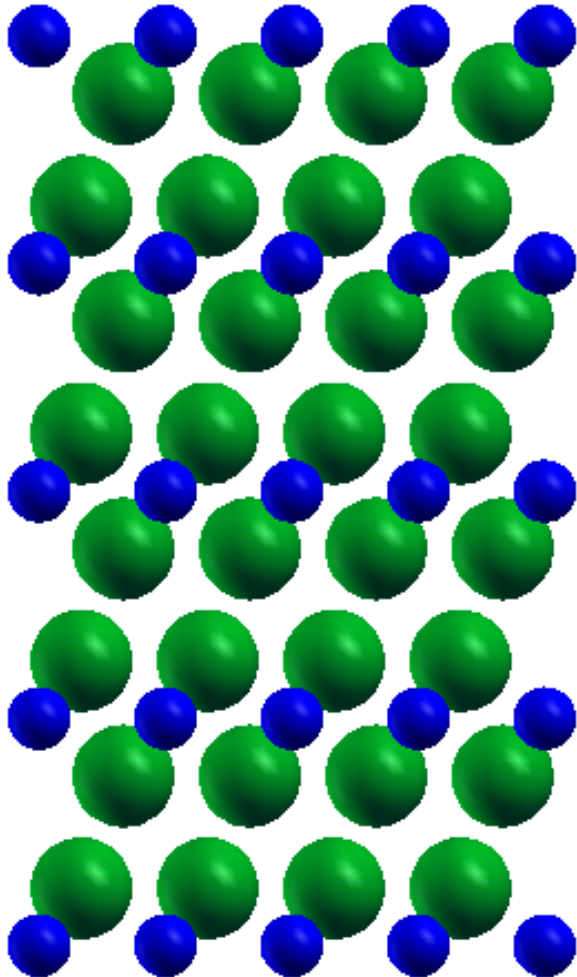
# Salt

NaCl:



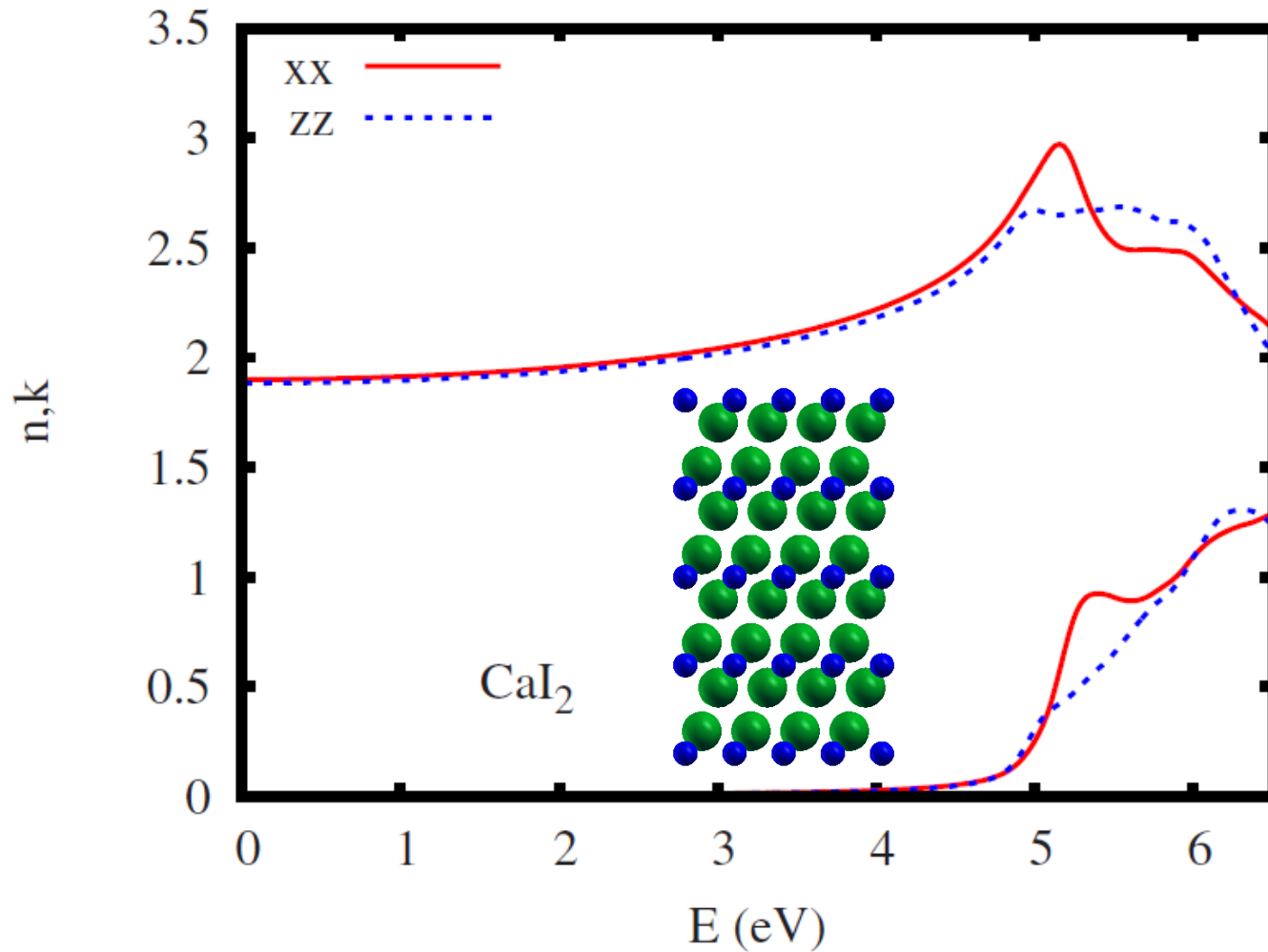
# Halides (Cl, Br, I)

- Structures generally show cations in locally symmetric anion cages, but the overall lattice structures of halides are often very non-isotropic (Pauling Rules).



$\text{CaI}_2$  – light yield is  $>100,000$  ph/MeV with  $\text{Eu}^{2+}$  activators (Hofstadter, 1964, Cherepy, 2008), but this has not proven useful because of *difficulties with crystal growth* – very anisotropic, micaceous, rhombohedral material that invariably cracks.

# Optical Properties of $\text{CaI}_2$

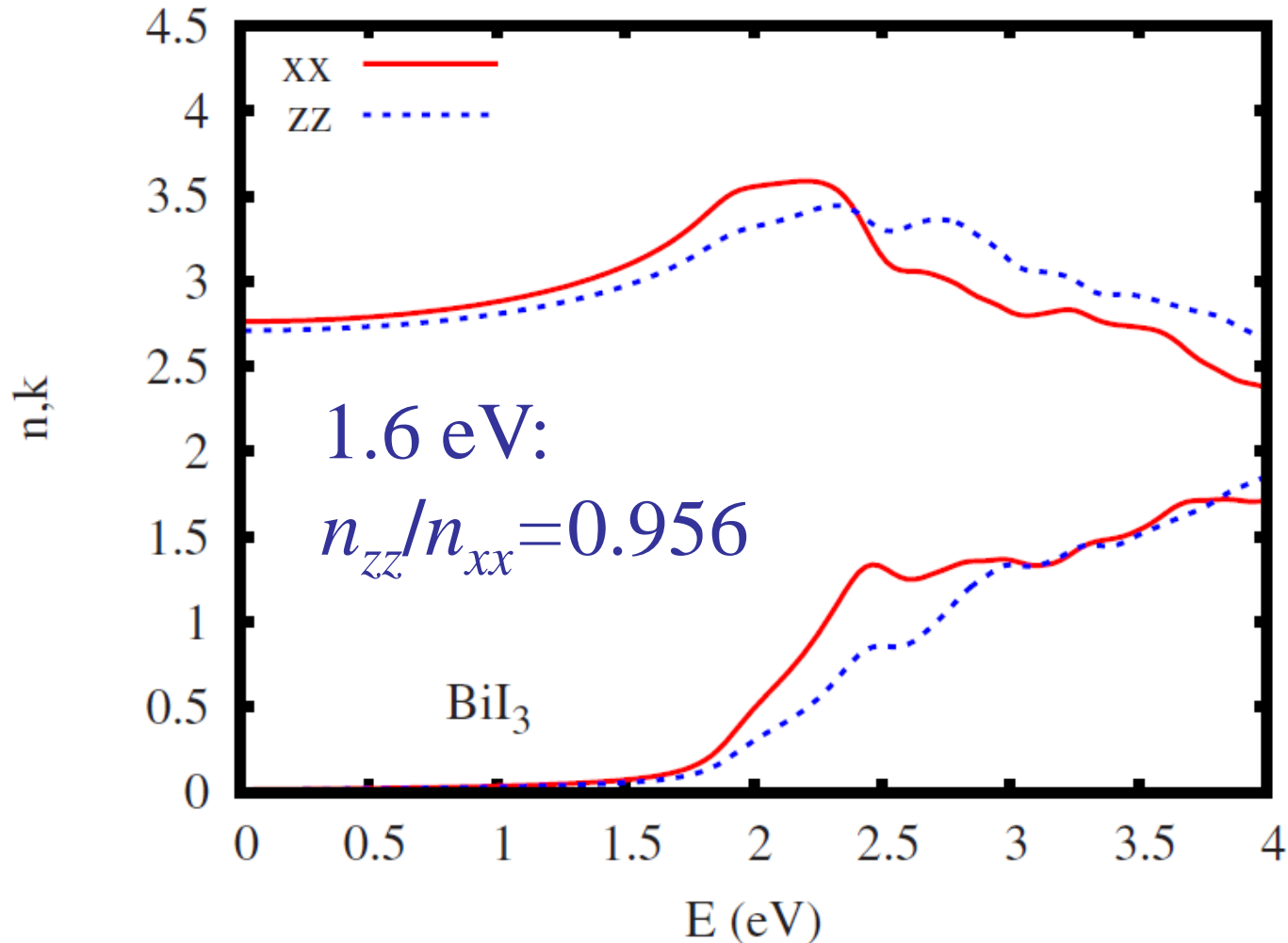


Low energy  
limit:

$$n_{zz}/n_{xx} = 0.991$$

*Not the expected result*

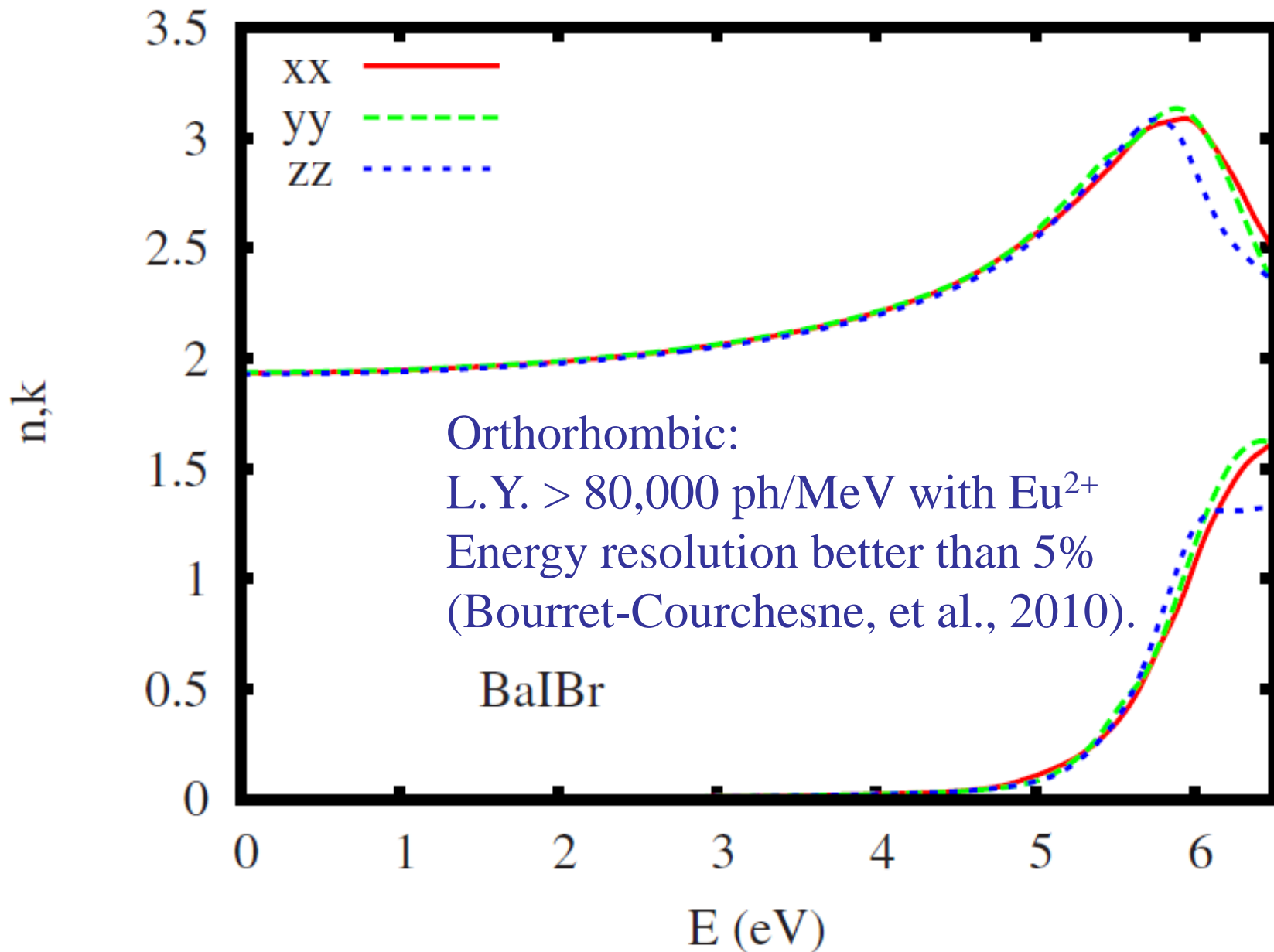
# Not All Halides Are Near Isotropic



Measurements (G.E. Jellison, Jr., et al.):  $n_{AV}(1.6 \text{ eV})=3.1$

First principles:  $n_{AV}(1.6 \text{ eV})=3.11$  *in excellent agreement*

# But we found that many are: BaI Br



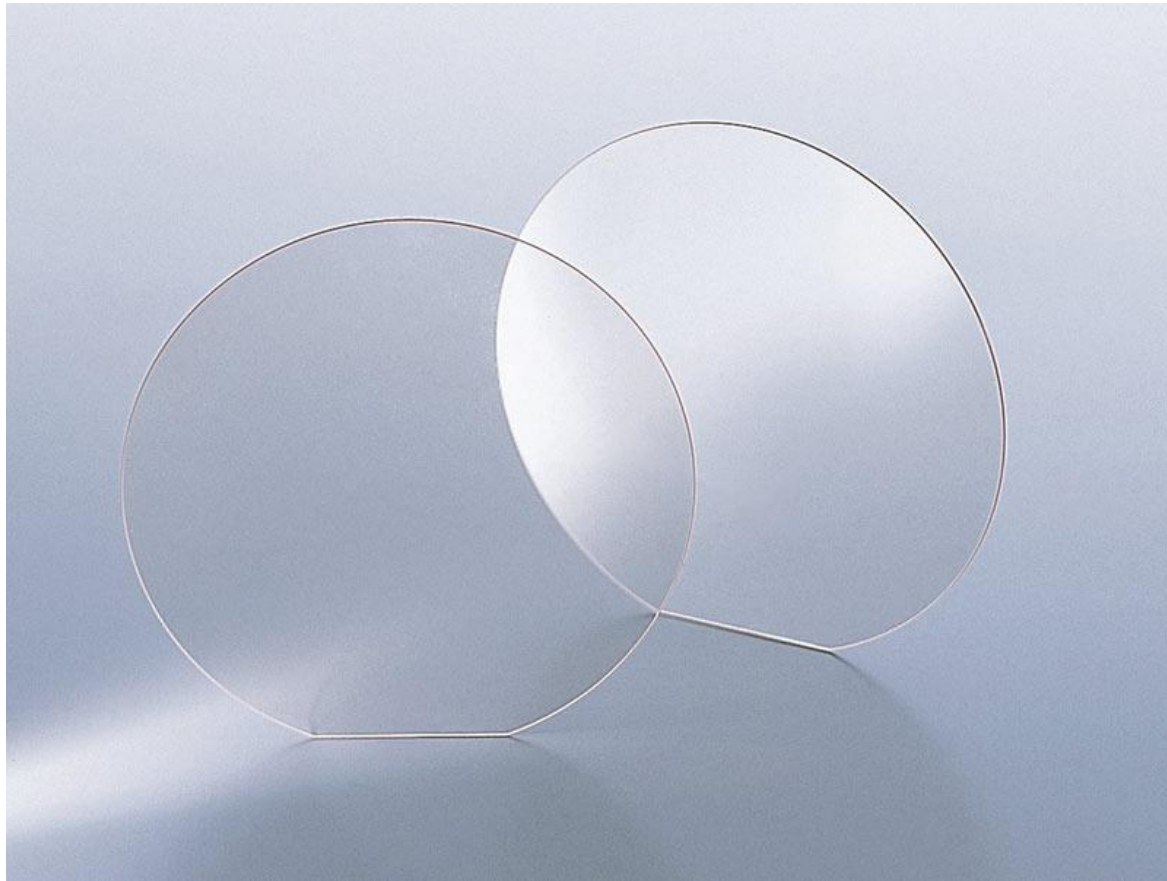
# Transparent Ceramics

## Key:

High density ceramic.

Low light scattering due to use of cubic (isotropic) materials.

*Crystal growth is not part of the process.*



Casio transparent ceramic camera lens (2004).

*Opportunity for lower-cost manufactured scintillators with uniform characteristics.*



# Predictive Theory

APPLIED PHYSICS LETTERS 92, 201908 (2008)

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

3827

## Near optical isotropy in noncubic $\text{SrI}_2$ : Density functional calculations

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Materials Science and Technology Division and Center for Radiation Detection Materials and Systems, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6114, USA

(Received 24 March 2008; accepted 1 May 2008; published online 22 May 2008)

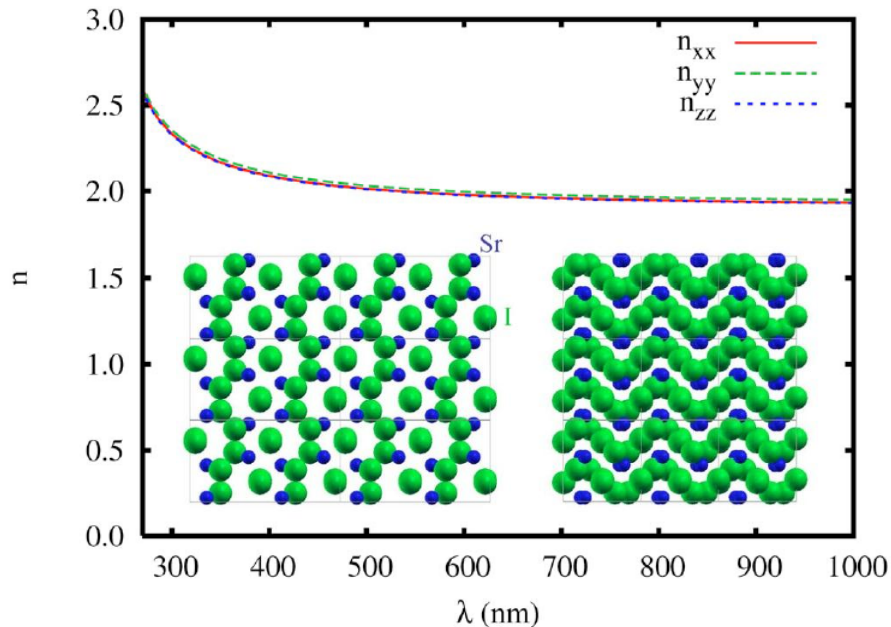


FIG. 4. (Color online) Wavelength dependent refractive index of  $\text{SrI}_2$  as obtained with the Engel-Vosko GGA.

## Fabrication and Properties of Translucent $\text{SrI}_2$ and $\text{Eu:SrI}_2$ Scintillator Ceramics

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

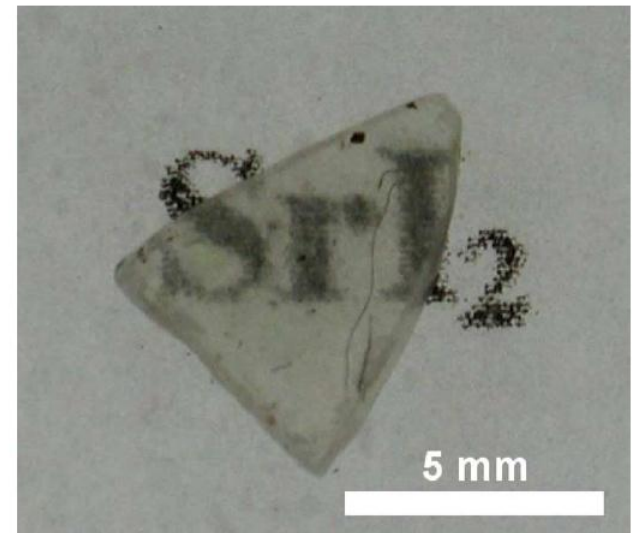


Fig. 5. Translucent ceramic sample of 0.77 mm-thick  $\text{Eu:SrI}_2$  backlit.

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

# Modern Density Functionals

$$E[\rho] = \int \rho(\mathbf{r}) \varepsilon_{xc}[\rho](\mathbf{r}) d^3\mathbf{r}$$

(1) Local (spin) density approximation:  $\varepsilon_{xc}[\rho](\mathbf{r}) = \varepsilon_{local}(\rho(\mathbf{r}))$

- Widely used, especially for metals.

(2) Generalized gradient approximations (GGA, Langreth, Perdew):

$$\varepsilon_{xc}[\rho](\mathbf{r}) = \varepsilon_{gga}(\rho(\mathbf{r}), |\nabla\rho(\mathbf{r})|)$$

- Much improved binding energies compared to LDA (chemical accuracy).
- Not gradient expansions, but sophisticated functionals based on exact scaling relations for the inhomogeneous electron gas (electron gas in solids is very non-uniform – can't use gradient expansions).
- New versions, e.g. PBE-SOL, Wu-Cohen, give almost uniform improvement over LDA in structural properties.

# Modern Density Functionals

(3) Hybrid functionals (Becke and others):

- Mixture of GGA and Hartree-Fock exchange on the Kohn-Sham orbitals.
- Common in chemistry and semiconductor physics (band gaps are better than standard LDA or GGA's).

(4) Van der Waal's Functionals (Langreth, Lundqvist):

- Non-local functionals that incorporate dispersion interactions.
- Surface science, molecular systems, water, DNA, carbon materials, etc.

# **Applications of DFT Calculations**

### Large-scale screening of metal hydrides for hydrogen storage from first-principles calculations based on equilibrium reaction thermodynamics†

Ki Chul Kim,<sup>a</sup> Anant D. Kulkarni,<sup>b</sup> J. Karl Johnson<sup>b</sup> and David S. Sholl<sup>\*a</sup>

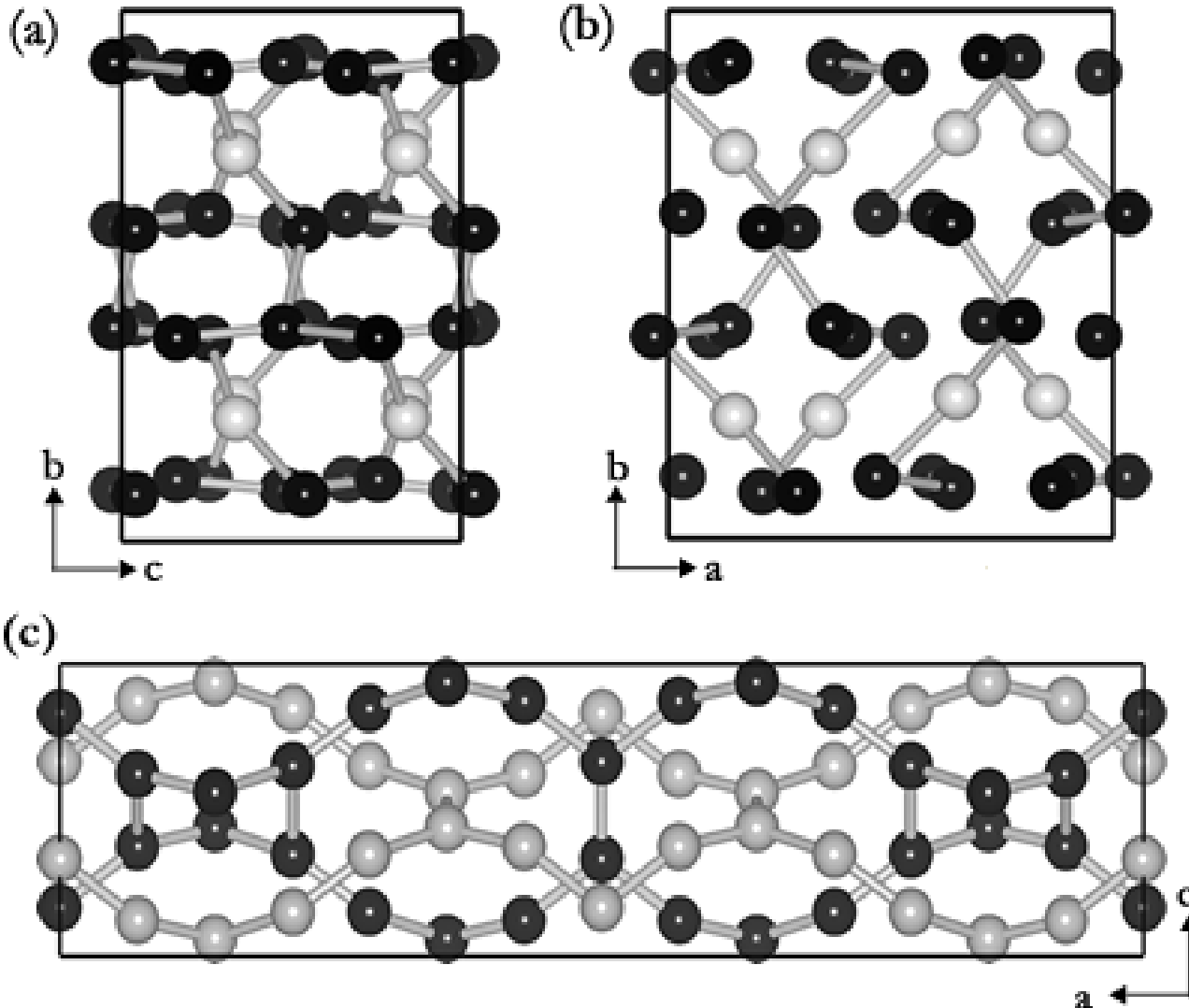
**Table 2** Promising single-step reactions identified from our screening approach. The reactions are divided into six categories.  $\Delta U_0$  is the change of the reaction enthalpy at 0 K and  $\Delta S_{\text{conf}}$  is the configurational entropy. The configurational entropy is only listed for systems having partial occupancies. The term  $T\Delta S_{\text{conf}}$  is evaluated at the temperature estimated to produce 1 bar of  $\text{H}_2$ ,  $T_{\text{est}}$ , from eqn (3). The enthalpy changes at 0 K for reactions involving  $\text{LiBH}_4$  used the DFT total energy of *ortho*- $\text{LiBH}_4$ . The selection criteria for these reactions are  $>6$  wt.% and  $15 \leq \Delta U_0 \leq 75$  kJ mol<sup>-1</sup>  $\text{H}_2$ . For systems having  $T\Delta S_{\text{conf}} \neq 0$  the figure of merit for comparing reactions is  $\Delta U_0 - T\Delta S_{\text{conf}}$

Reaction	wt. %	$\Delta U_0$ ( $T\Delta S_{\text{conf}}$ ) (kJ mol <sup>-1</sup> $\text{H}_2$ )
Interesting reactions (3 reactions)		
$\text{MgH}_2 \rightarrow \text{Mg} + \text{H}_2$	7.66	64.7
$\text{LiH} + 2\text{LiNH}_2 + \text{KBH}_4 \rightarrow \text{Li}_3\text{BN}_2 + \text{KH} + 4\text{H}_2$	7.48	43.6 (-7.2)
$2\text{MgH}_2 + \text{Mg}(\text{NH}_2)_2 \rightarrow \text{Mg}_3\text{N}_2 + 4\text{H}_2$	7.4	26
Reactions involving $\text{B}_{12}\text{H}_{12}$ species (13 reactions)		
$\text{LiBH}_4 \rightarrow (5/6)\text{LiH} + (1/12)\text{Li}_2\text{B}_{12}\text{H}_{12} + (13/12)\text{H}_2$	10.03	62.1
$4\text{LiBH}_4 + 5\text{Si} + 10\text{Mg}(\text{BH}_4)_2 \rightarrow 5\text{Mg}_2\text{Si} + 2\text{Li}_2\text{B}_{12}\text{H}_{12} + 36\text{H}_2$	9.46	41
$5\text{Si} + 12\text{Mg}(\text{BH}_4)_2 \rightarrow 5\text{Mg}_2\text{Si} + 2\text{MgB}_{12}\text{H}_{12} + 36\text{H}_2$	9.21	43.6
$5\text{Si} + 10\text{Mg}(\text{BH}_4)_2 + 2\text{Ca}(\text{BH}_4)_2 \rightarrow 5\text{Mg}_2\text{Si} + 2\text{CaB}_{12}\text{H}_{12} + 36\text{H}_2$	8.85	41.2
$2\text{LiBH}_4 + 5\text{Mg}(\text{BH}_4)_2 \rightarrow 5\text{MgH}_2 + \text{Li}_2\text{B}_{12}\text{H}_{12} + 13\text{H}_2$	8.36	43.1
$5\text{Si} + 10\text{Mg}(\text{BH}_4)_2 + 4\text{KBH}_4 \rightarrow 5\text{Mg}_2\text{Si} + 2\text{K}_2\text{B}_{12}\text{H}_{12} + 36\text{H}_2$	8.1	37.3 (-2.9)
$\text{Mg}(\text{BH}_4)_2 \rightarrow (5/6)\text{MgH}_2 + (1/6)\text{MgB}_{12}\text{H}_{12} + (13/6)\text{H}_2$	8.09	47.1
$\text{LiSc}(\text{BH}_4)_4 \rightarrow (2/5)\text{LiBH}_4 + \text{ScH}_2 + (3/10)\text{Li}_2\text{B}_{12}\text{H}_{12} + (22/5)\text{H}_2$	7.97	24.1
$5\text{Mg}(\text{BH}_4)_2 + \text{Ca}(\text{BH}_4)_2 \rightarrow 5\text{Mg}_2\text{Si} + \text{CaB}_{12}\text{H}_{12} + 12\text{H}_2$	7.72	42.1

Energies and densities are the fundamental quantities in DFT.

# Structures

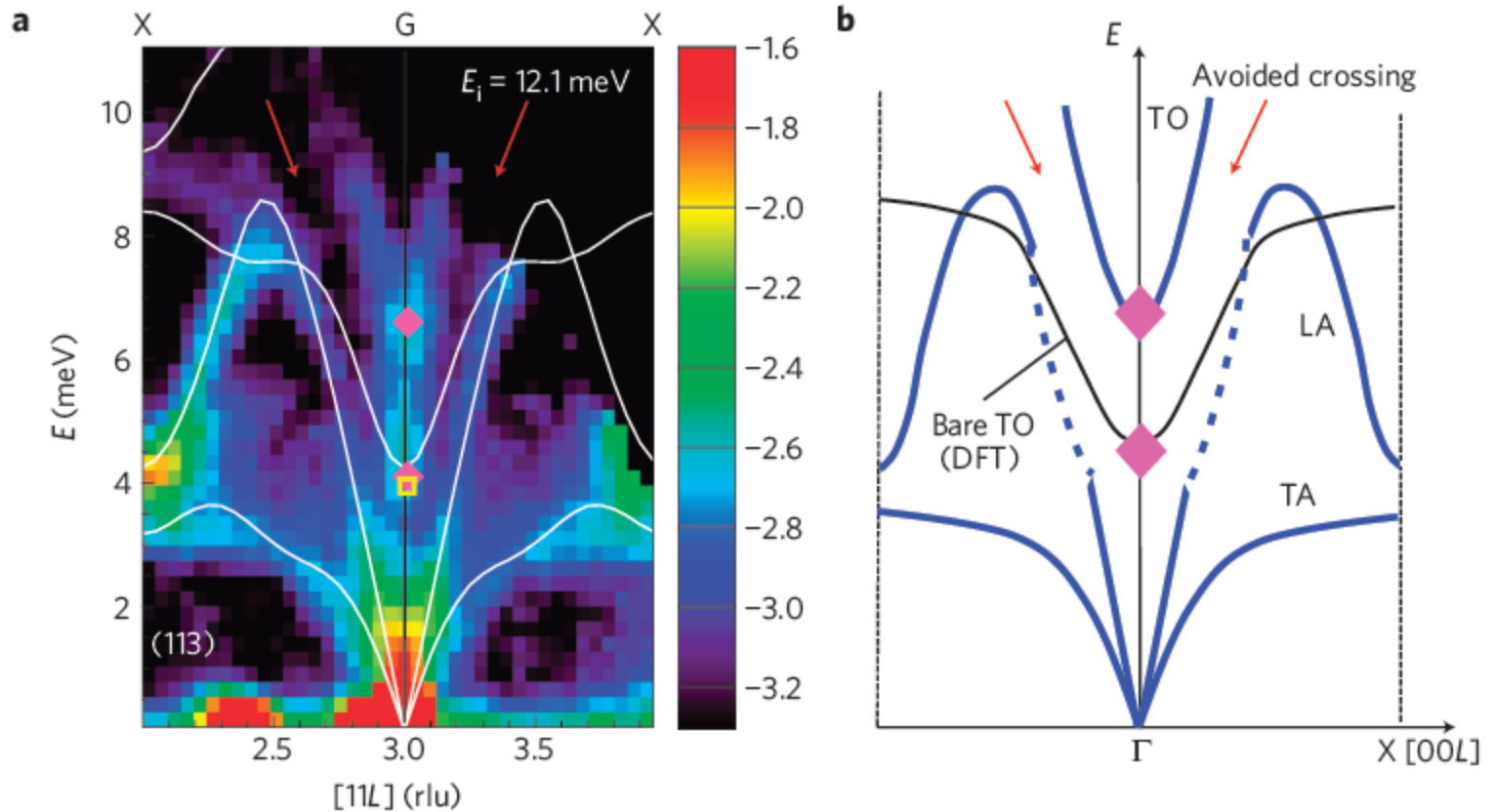
Predicted high pressure phases of Li (Yanming Ma)



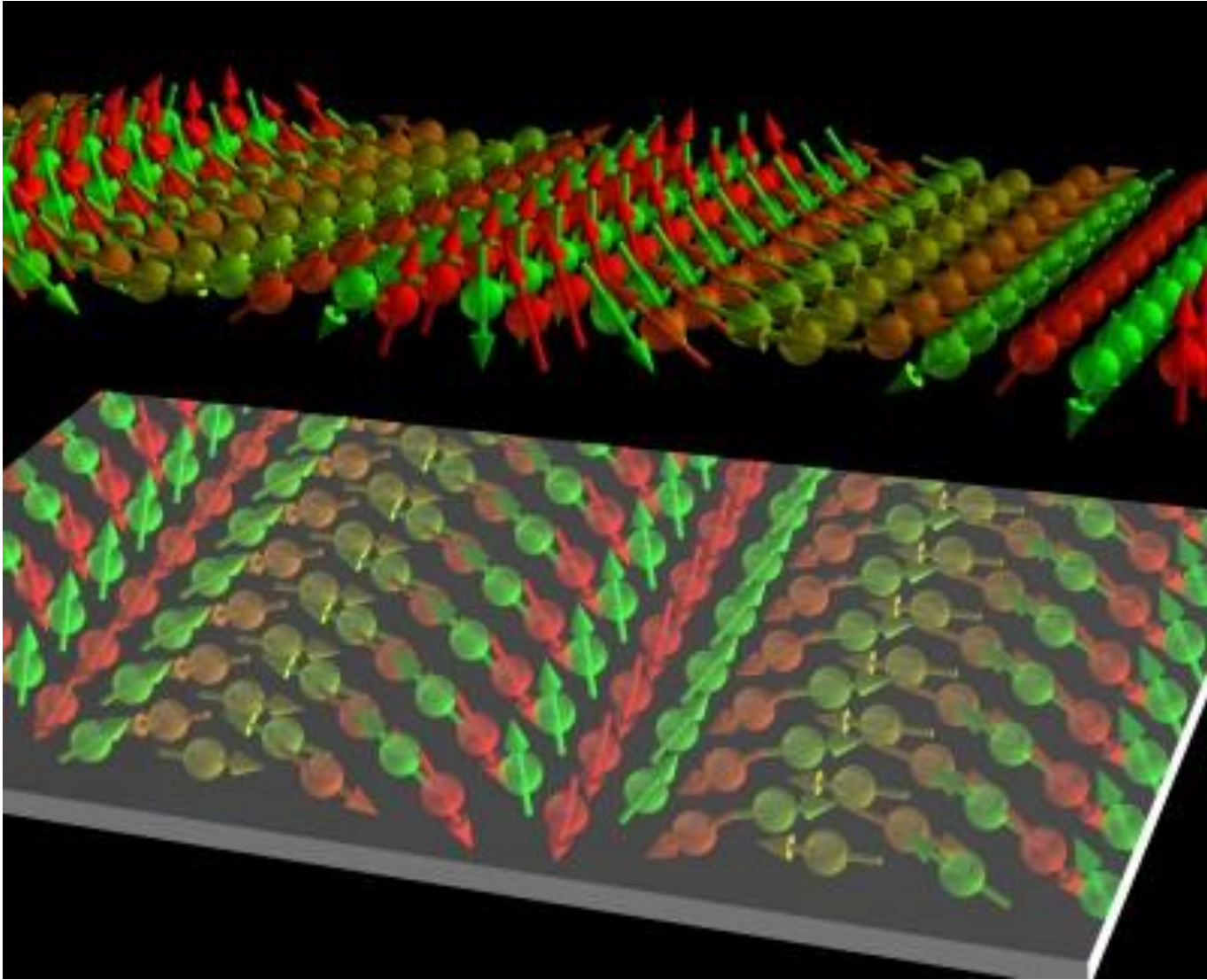
# Dynamics

## Giant anharmonic phonon scattering in PbTe

O. Delaire<sup>1\*</sup>, J. Ma<sup>1</sup>, K. Marty<sup>1</sup>, A. F. May<sup>2</sup>, M. A. McGuire<sup>2</sup>, M-H. Du<sup>2</sup>, D. J. Singh<sup>2</sup>, A. Podlesnyak<sup>1</sup>, G. Ehlers<sup>1</sup>, M. D. Lumsden<sup>1</sup> and B. C. Sales<sup>2</sup>



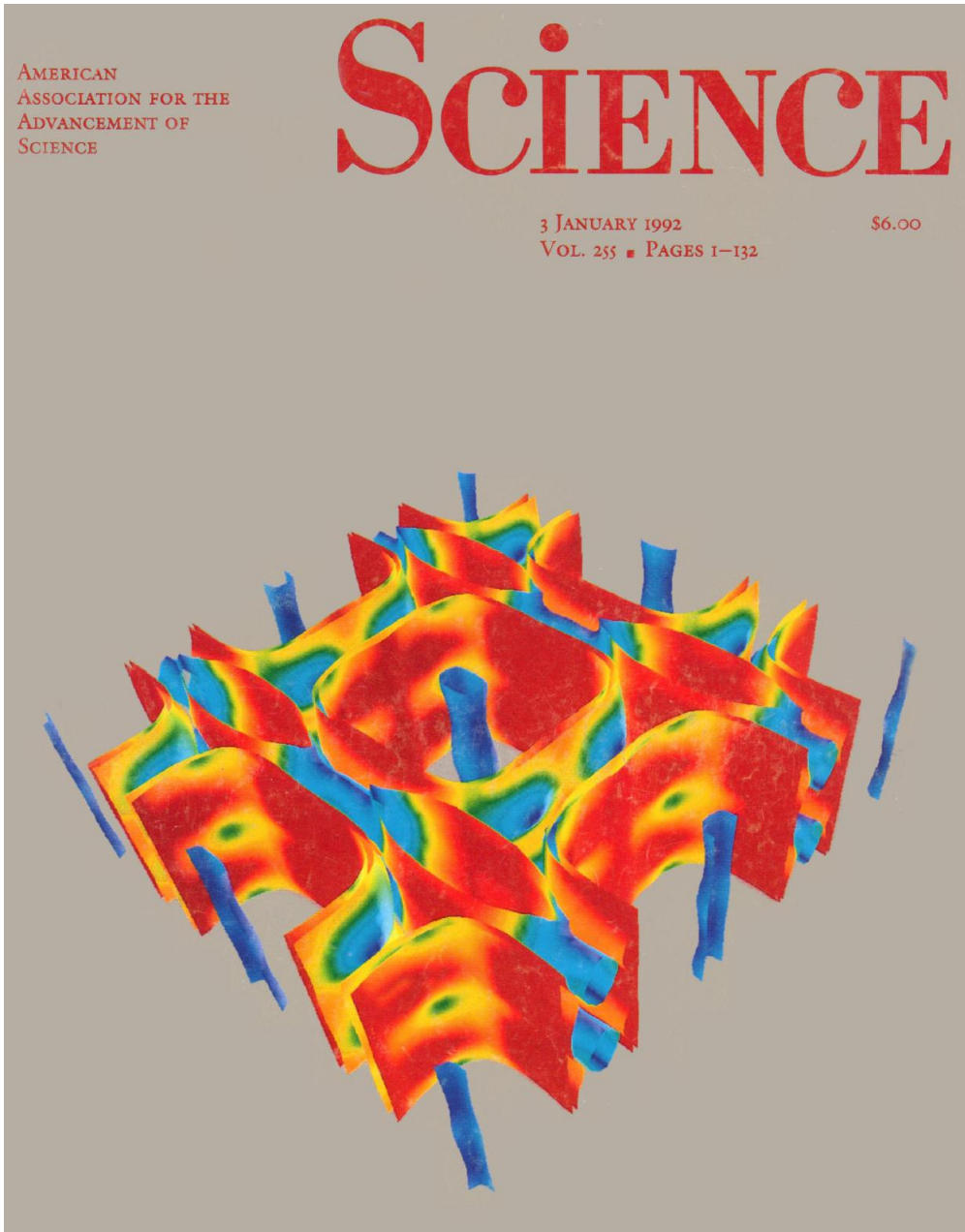
# Magnetism



S. Blugel, Julich, Germany: Non-collinear magnetism on a thin film.

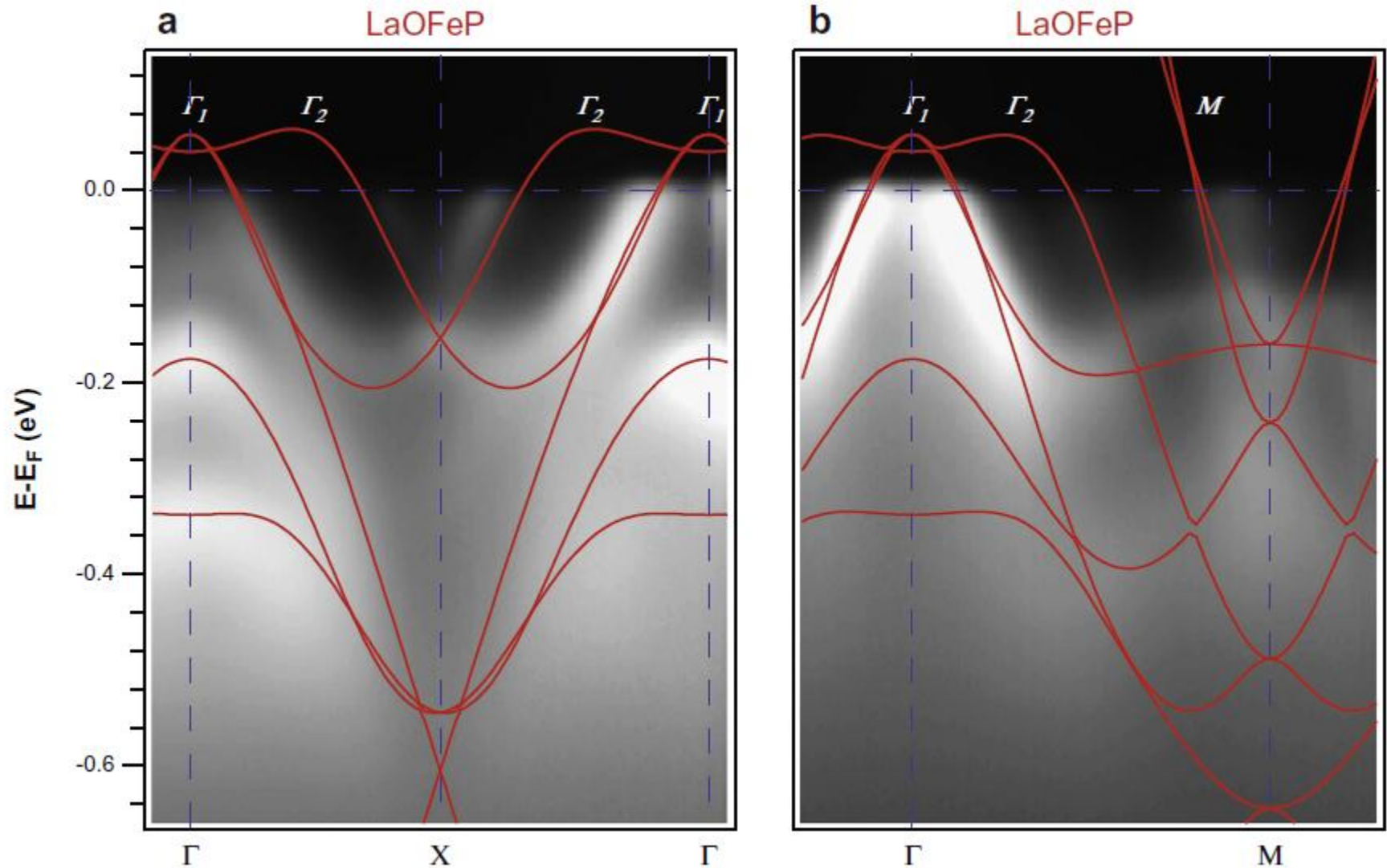


# Fermi Surfaces



Based on Kohn-Sham eigenvalues, which are not fundamentally related to excitation energies in exact DFT – but this is known to be predictive and useful based on experience.

# Band Structures



D.H Lu (2009)

# Band Structure Related Quantities

- Optical properties.
- Excitation energies.
- Electronic transport.
- Electron-Phonon interactions.
- etc.

None of these are fundamental in DFT, but they are often quite accurate, and the inaccuracies are well established from much experience.

This is very useful because DFT is tractable, microscopic and predictive.

# SOME NUMBERS

Binding energy of Fe:	2541.025 Ry	
bcc-fcc energy difference in Fe:	0.013 Ry	(austenite-ferrite in steels)
Binding of PZT (Piezoelectrics):	46730.476 Ry	
Ferroelectric instability in PZT:	0.006 Ry	
Binding of Mn-ferrite (oxide mag.):	15987.192 Ry	
Magnetic coupling of Mn-ferrite:	0.070 Ry	

***Small differences between very large energies are the keys to materials properties***

**→ We rely on careful choice of numerical methods and error cancellation in the differences.**

# References: DFT and Methods

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2. S. Lundqvist and N.H. March, *Theory of the Inhomogeneous Electron Gas* (Plenum, N.Y., 1983). *Excellent book on DFT.*
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5. J. Ihm, A. Zunger and M.L. Cohen, *J. Phys. C* **12**, 4409 (1979). Total energy formalism for norm conserving pseudopotentials.
6. D.J. Singh and L. Nordstrom, *Planewaves, Pseudopotentials and the LAPW Method*, 2<sup>nd</sup> Ed. (Springer, 2006). *Book about the LAPW method with some discussion of pseudopotentials.*
7. V. Eyert, *The Augmented Spherical Wave Method* (Springer, Berlin, 2007). *A detailed description of the ASW (closely related to LMTO) method.*
8. Richard M. Martin, *Electronic Structure of Matter* (Cambridge University Press, 2004). *Excellent overview of electronic structure methods and calculations.*

# The Linearized Augmented Planewave (LAPW) Method

$$E_T[\rho] = T_s[\rho] + E_{ei}[\rho] + E_H[\rho] + E_{xc}[\rho] + E_{ii}$$

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

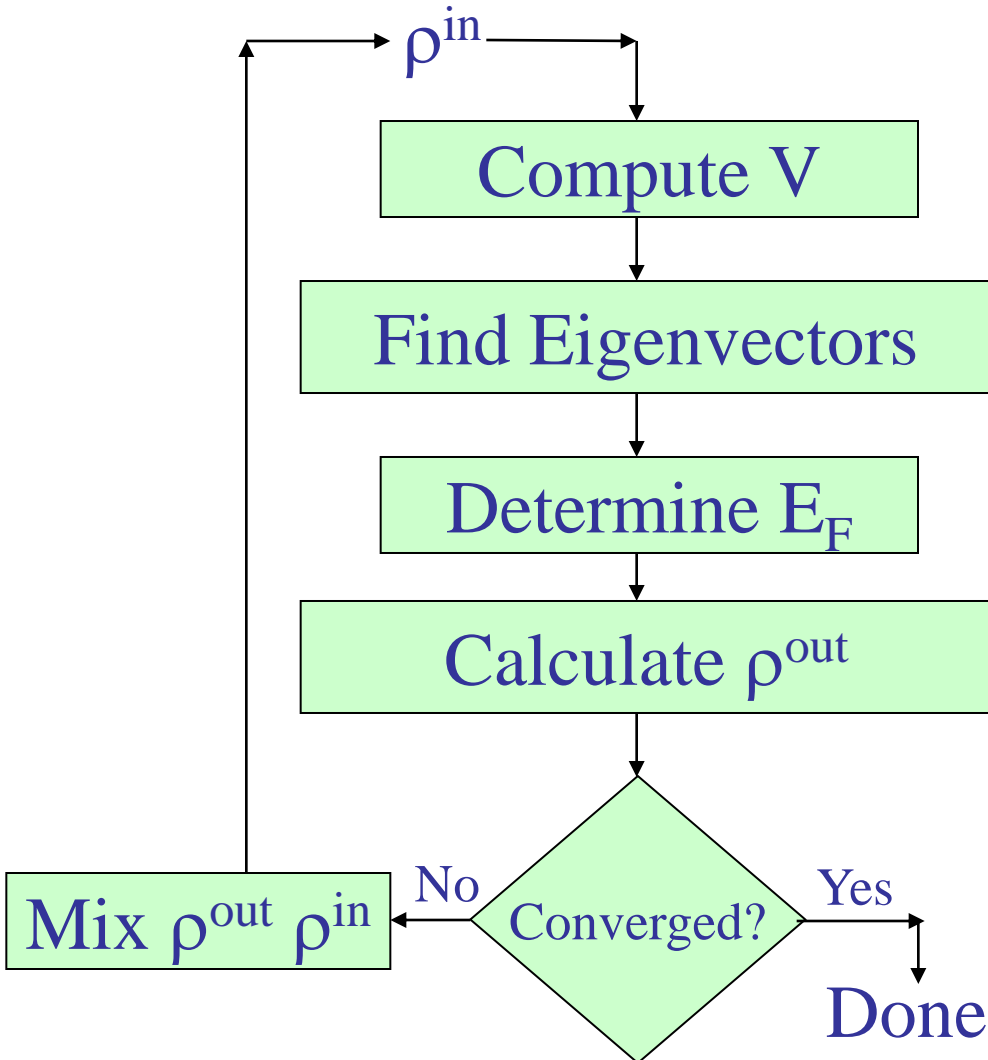
*Need tools that are reliable and predictive.*



# DFT ALGORITHMS

- Find  $\varphi_I$  and  $\rho$  to solve:

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



## Standard Solution:

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

(eigenvalue).

$$\langle \phi | H | \phi \rangle x_i = \varepsilon_i \langle \phi | \phi \rangle x_i$$

- Iterate to find self-consistent  $\rho$ .

## Some Numbers:

- #  $\varphi_i \sim 10$  / atom.
- #  $\phi_j \sim 10$ 's - 1000's / atom.
- # atoms (State of the Art): 100 – 1000's.

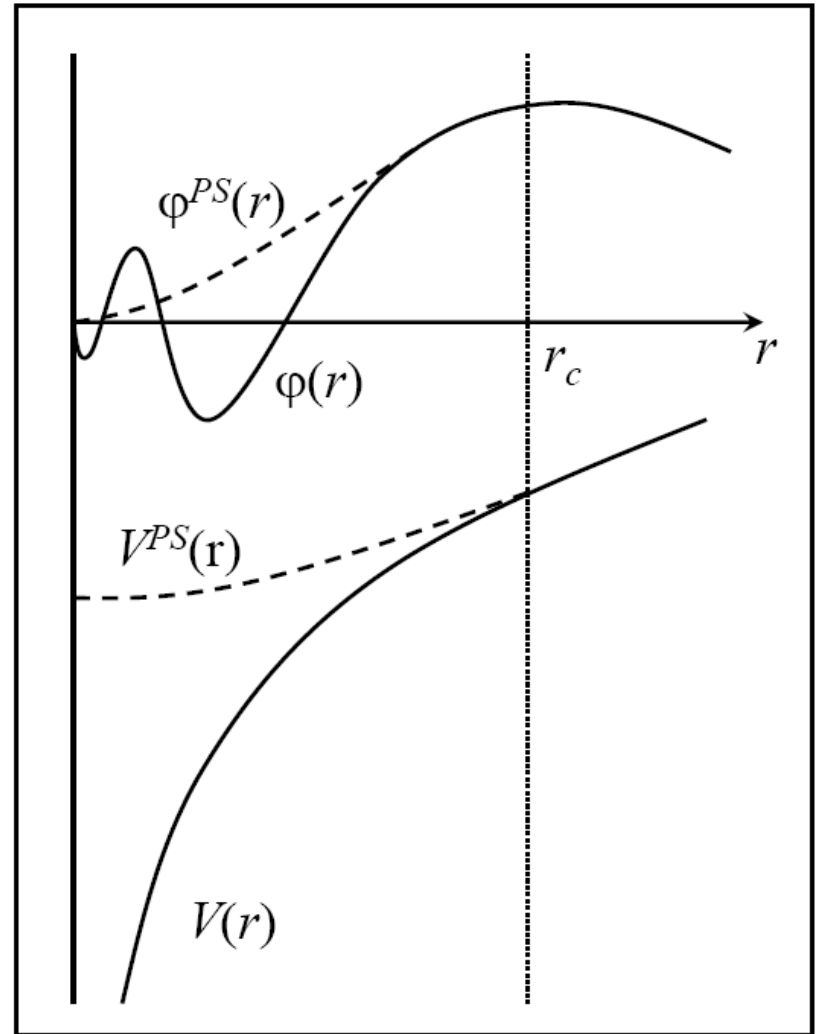
# Motivation for Augmentation

Schrödinger Equation:

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

For valence states:  $\varepsilon$  is small  $\rightarrow$

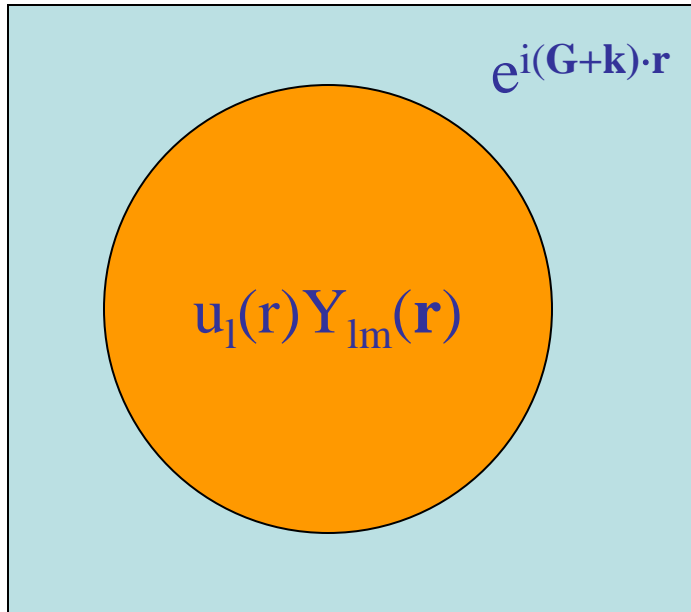
*$T\varphi$  is also small except where  $V$  is strong, i.e. near the nucleus.*





# Augmented Planewave (APW) Method

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



Divide Space Into 2 Regions:

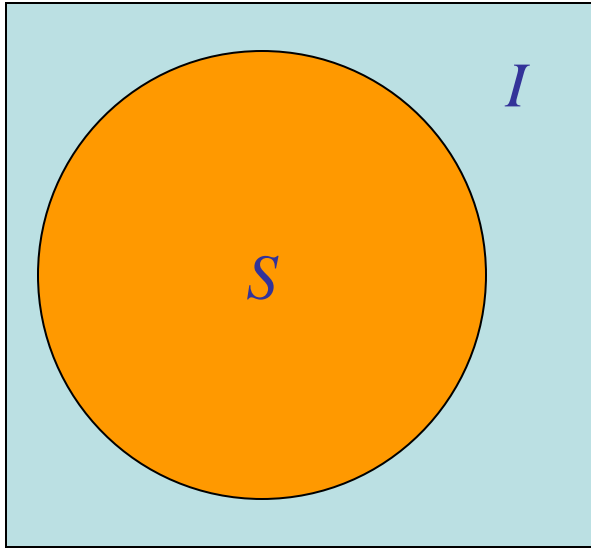
- Atom Centered Spheres
- Interstitial

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

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

- $u_l(r)$  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

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

## 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.

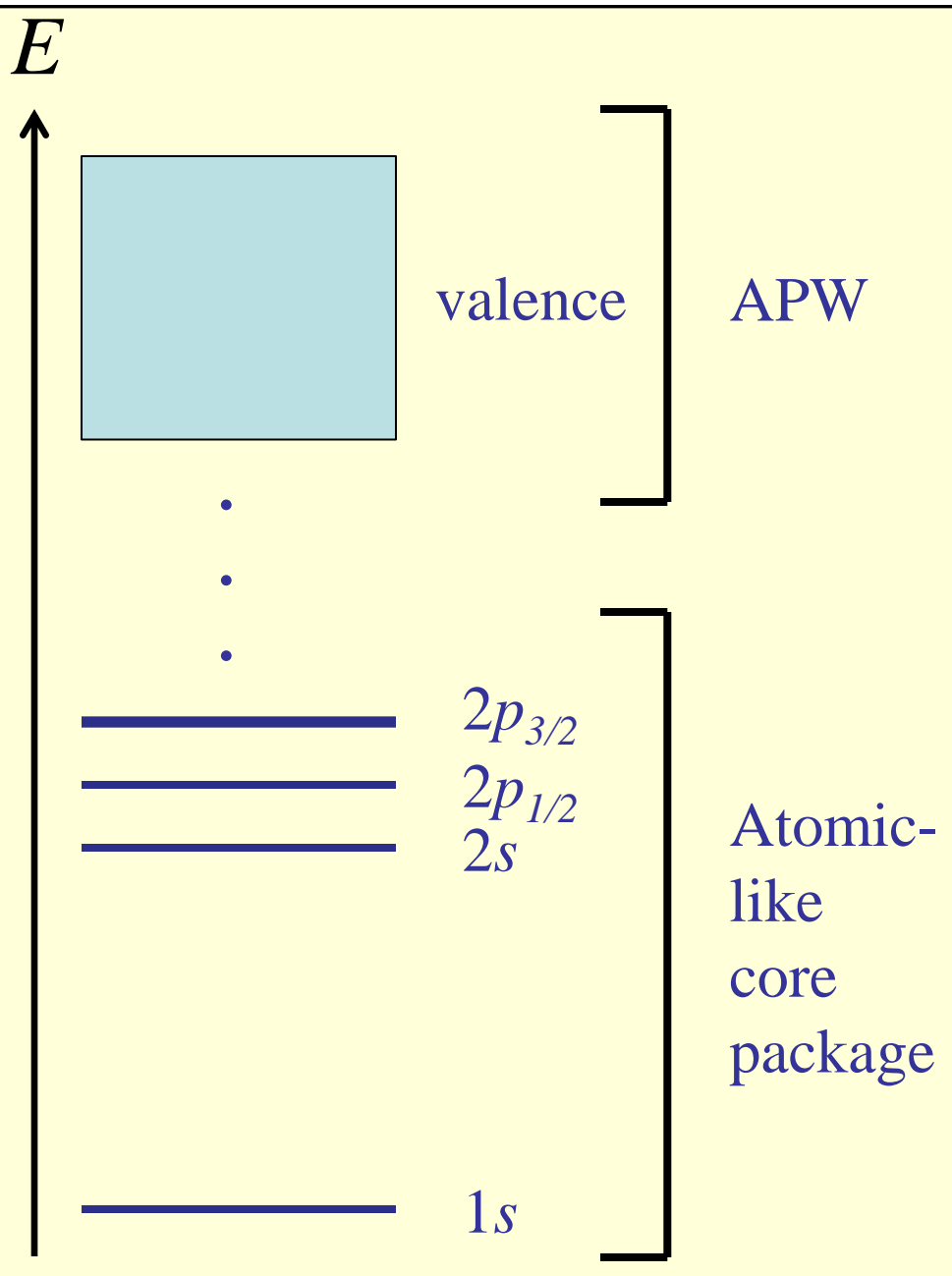
$$[ -d^2/dr^2 + l(l+1)/r^2 + V(r) - E_l ] ru_l(r) = 0$$

So:

$$(E_2 - E_1) r u_1 u_2 = u_2 (d^2 ru_1/dr^2) - u_1 (d^2 ru_2/dr^2)$$

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



The  $u_l(\mathbf{r}) Y_{lm}(\mathbf{r})$  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  $\mathbf{k}+\mathbf{G}$  one imagines a connection with planewave pseudopotential formalisms.

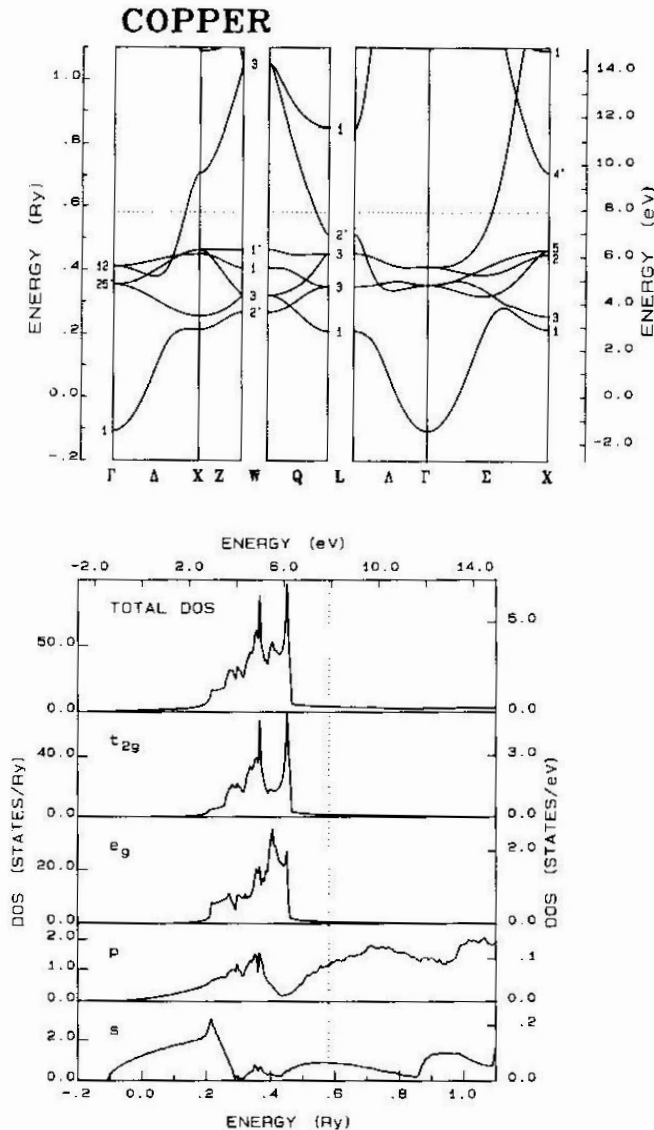
$$\langle A\phi | H | A\phi \rangle_{\mathbf{x}} = \varepsilon \langle A\phi | A\phi \rangle_{\mathbf{x}} \quad \equiv \quad \langle \phi | \underbrace{A^\dagger H A}_{H^{\text{PS}}} | \phi \rangle_{\mathbf{x}} = \varepsilon \langle \phi | \underbrace{A^\dagger A}_{S^{\text{PS}}} | \phi \rangle_{\mathbf{x}}$$

- 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 -  $\partial u / \partial E$  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!

← 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.*

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

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

- 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  $\hat{u}_l$  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  $\hat{u}$  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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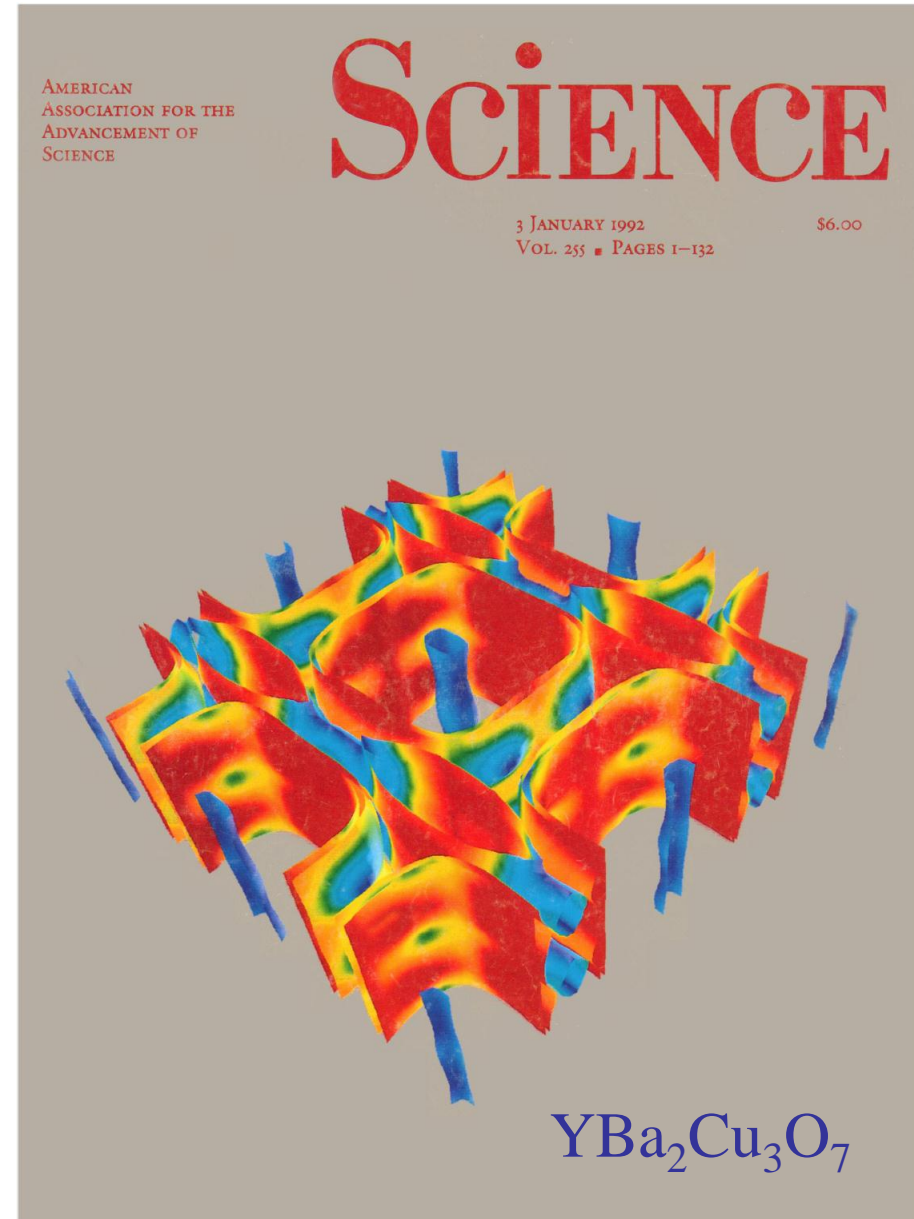
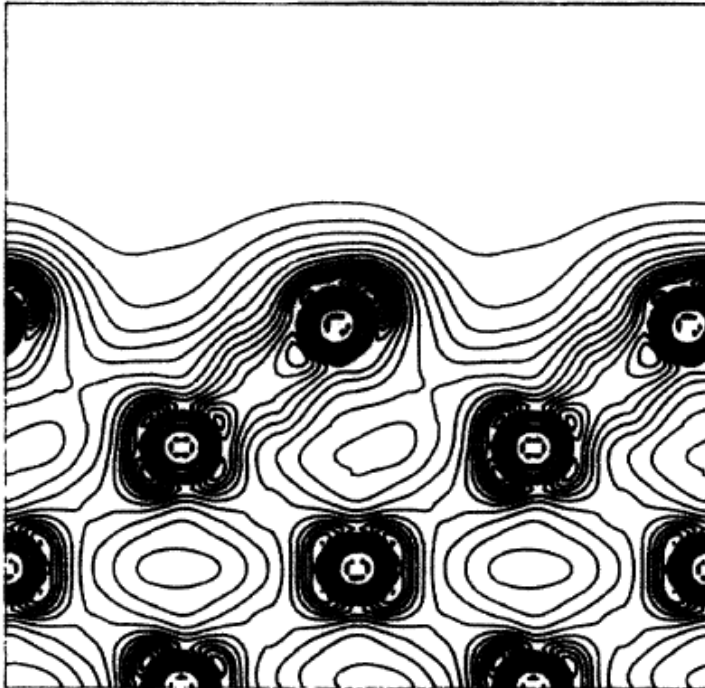
PHYSICAL REVIEW LETTERS

29 DECEMBER 1986

## Instability of the Ideal Tungsten (001) Surface

David Singh, Su-Huai Wei,<sup>(a)</sup> and Henry Krakauer

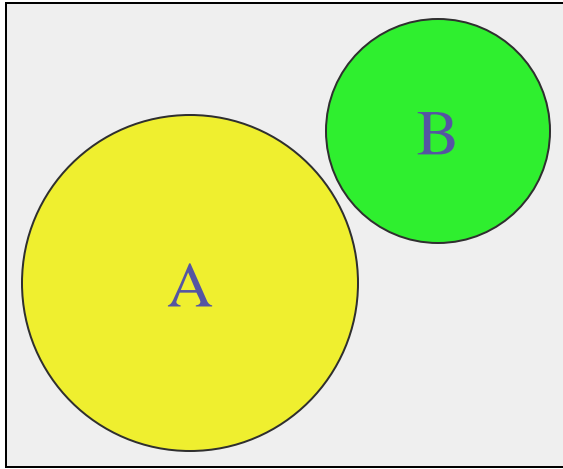
*Department of Physics, College of William and Mary, Williamsburg, Virginia 23185*



# PROPERTIES OF THE LAPW METHOD

- All electron method: Core states are included.
  - $\varphi$  is the true wavefunction,  $\rho$  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):

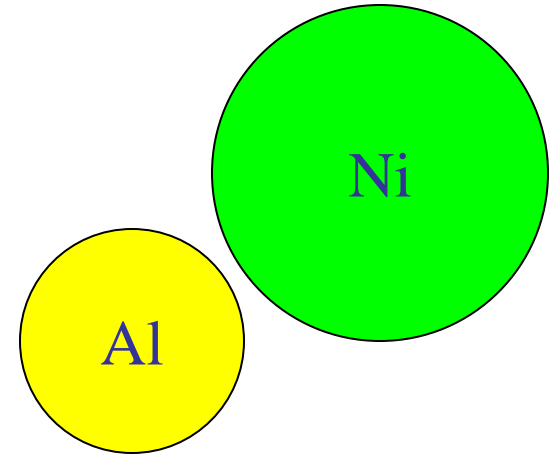
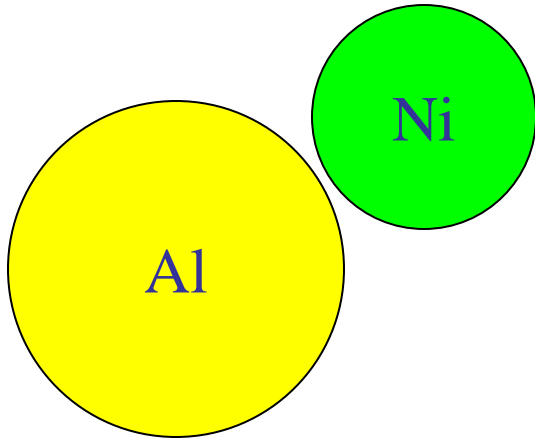
Transition elements:	9	<i>Should consider</i>
f-electron materials:	9.5	<i>in setting radii, which</i>
Simple elements (B,C,N,O)	7	<i>are computational</i>
Simple metals (Al, Si, ...)	6	<i>not physical parameters.</i>

# Example (B2 NiAl)

Chemical Sense

vs.

Computational Sense



$$r_{Al} = 2.8 \text{ bohr}$$

$$r_{Ni} = 1.9 \text{ bohr}$$

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

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

$$r_{Al} = 1.9 \text{ bohr}$$

$$r_{Ni} = 2.8 \text{ bohr}$$

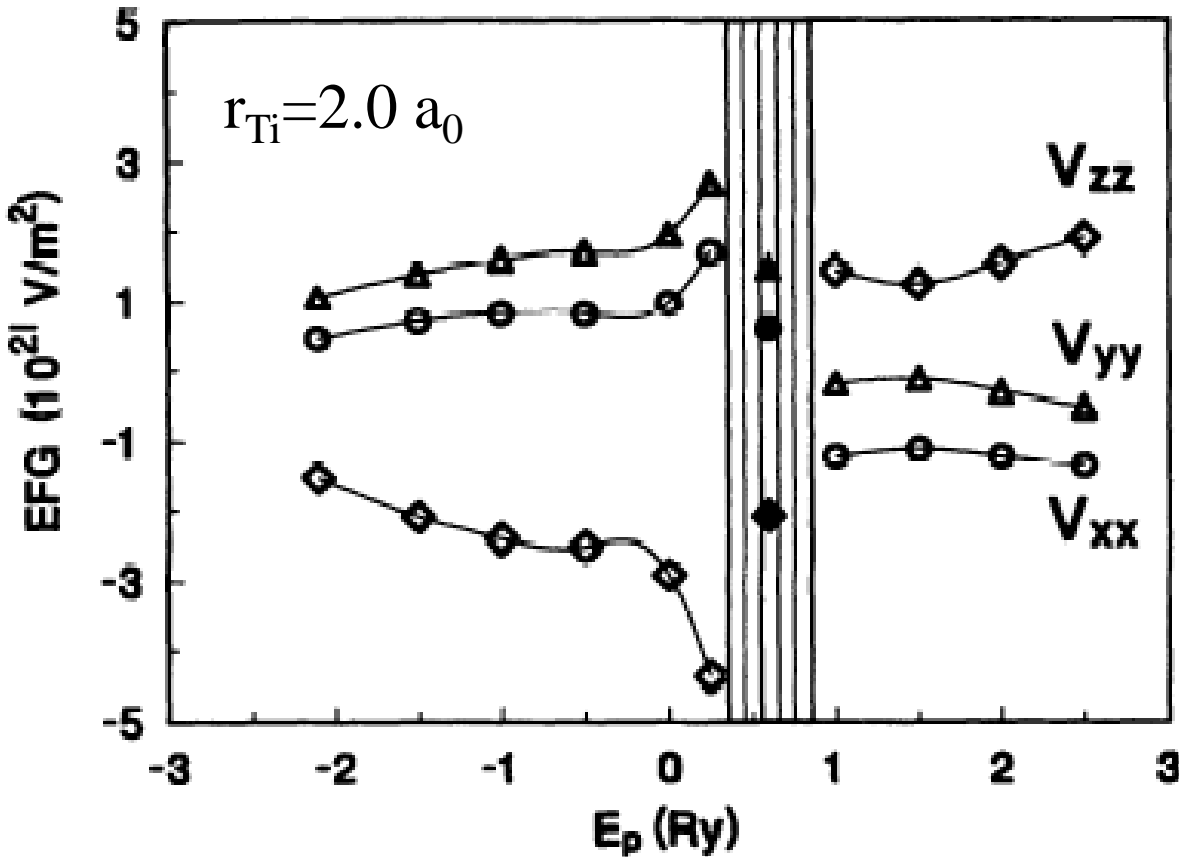
$$r_{Al} G_{max} = 6 \rightarrow G_{max} = 3.15$$

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

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

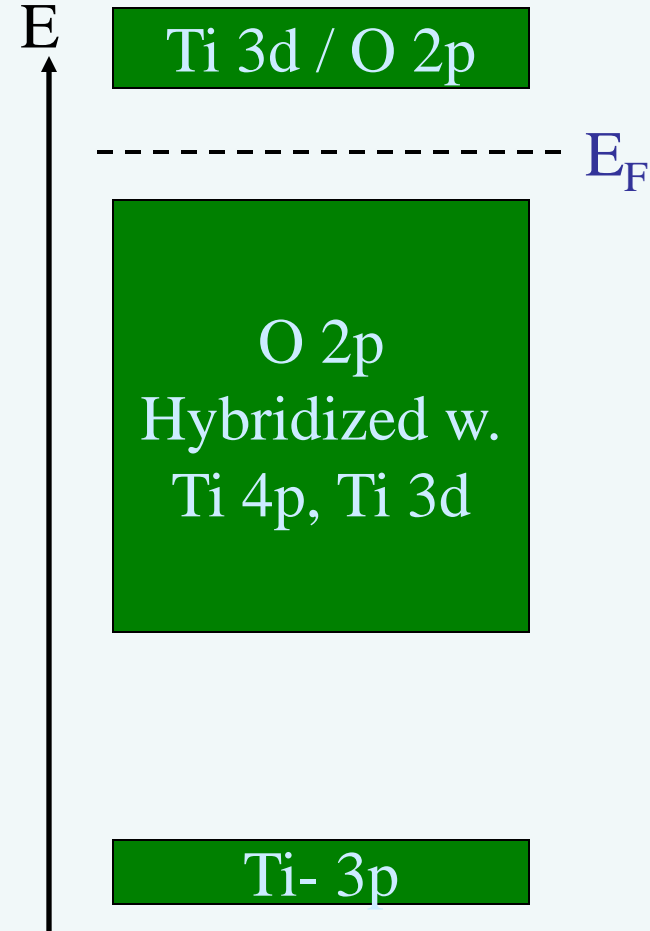
# Complications in the LAPW Method

EFG Calculation for Rutile  $\text{TiO}_2$  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?

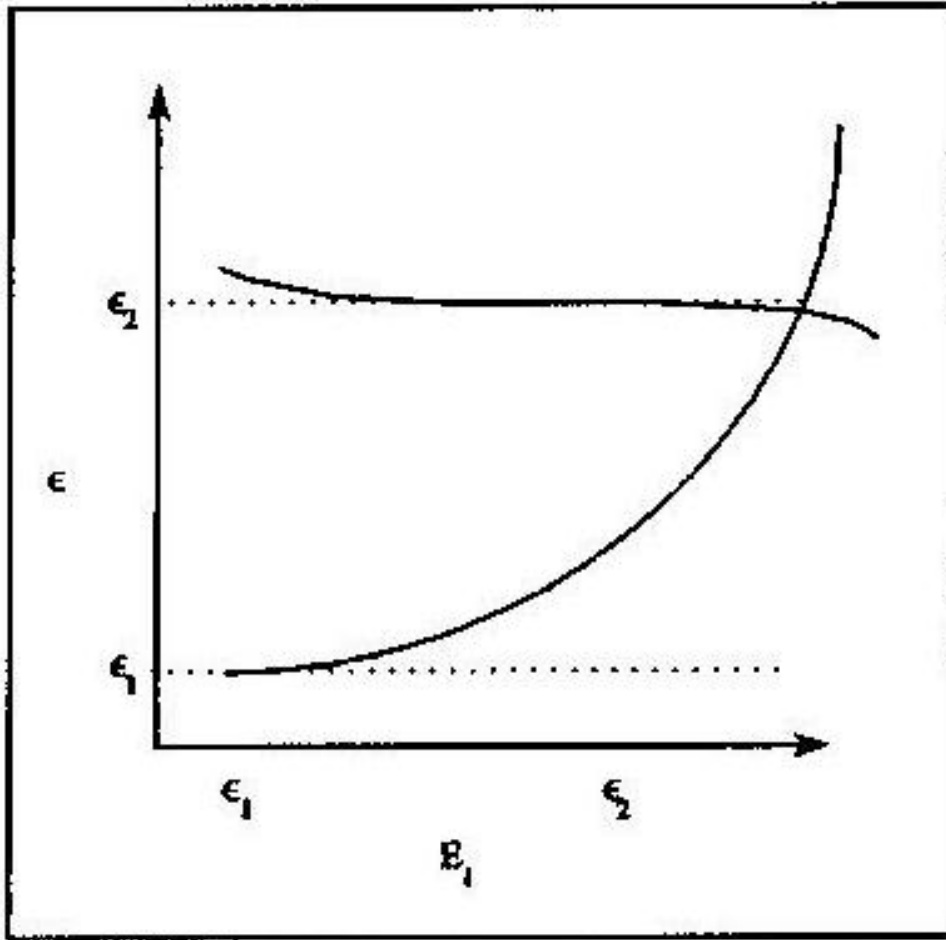


Figure 5.14 Variation of a semi-core and a valence band with  $E_T$ . The dotted lines at  $\epsilon_1$  and  $\epsilon_2$  denote the true locations of the bands.

The LAPW method requires non-overlapping spheres

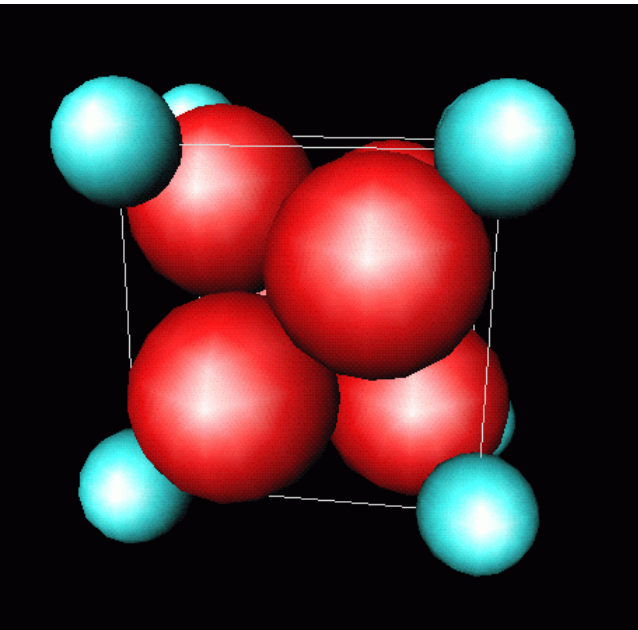
$\Rightarrow$  There are serious limits to how large  $R_{MT}$  can be especially in oxides, nitrides, carbides.

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  $\dot{u}$  orthogonal to them. On the other hand, the valence states may have significant contributions from the same  $l$ .

# Complications in the LAPW Method

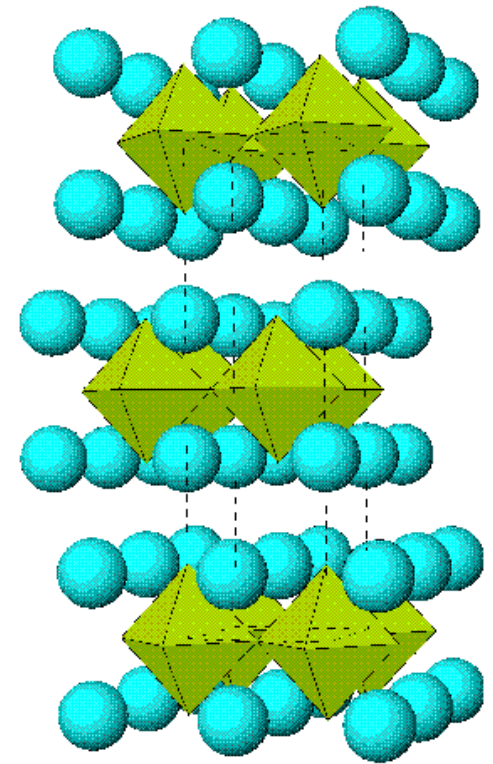
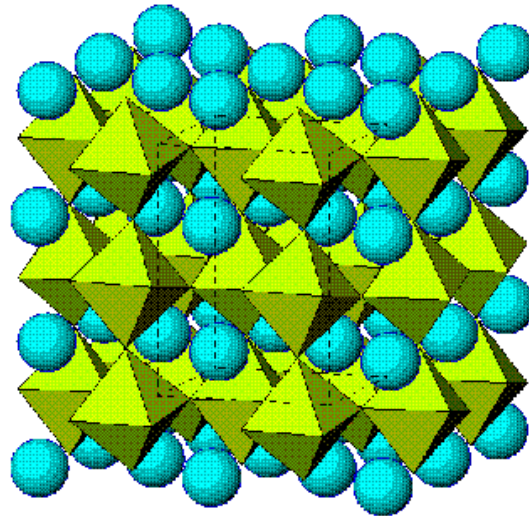
*Solution?: Use large spheres to get orthogonality to core states:*

*Unfortunately, crystal structures don't generally allow this.*



Rutile Structure

Perovskite



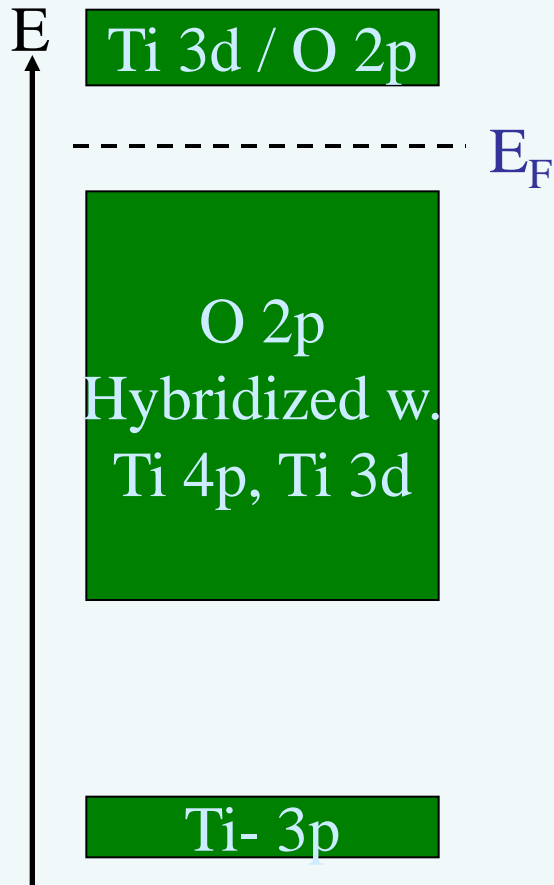
Layered Perovskite





# 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.

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

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

# THE LAPW+LO METHOD

LAPW+LO basis is:

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

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  $(A'_{lm}u_l(\mathbf{r})+B'_{lm}\dot{u}_l(\mathbf{r})+u^{(2)}_l(\mathbf{r})) Y_{lm}(\mathbf{r})$  is formally a local orbital.

# THE LAPW+LO METHOD

## Key Points:

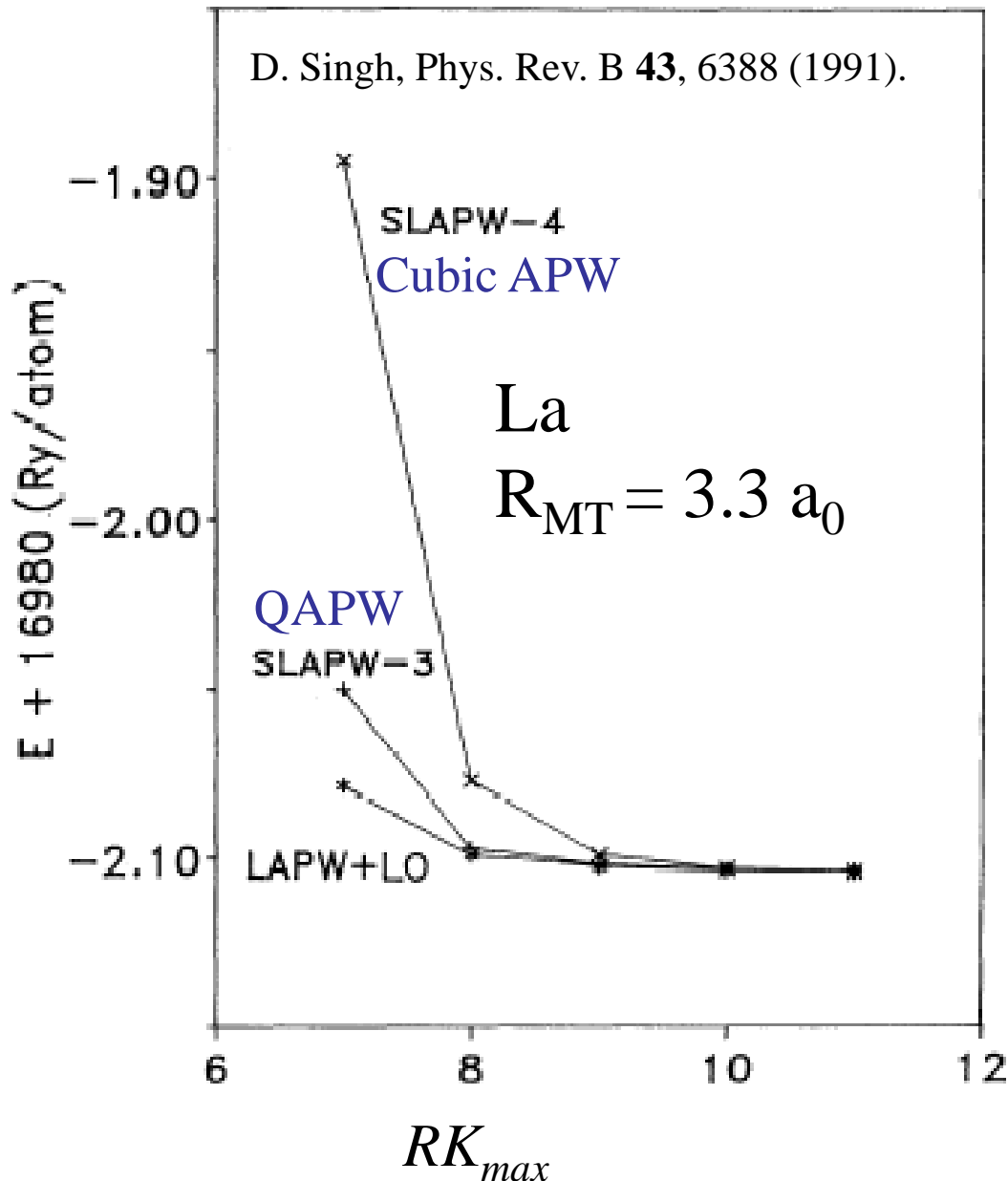
1. The local orbitals need (and should) only be used for those atoms and angular momenta where they are needed.
2. The local orbitals do not serve as surrogate atomic wavefunctions in the sense that they are in mixed basis plane wave codes: They are just another way to handle the augmentation. They look very different from atomic functions.
3. We are trading a large number of extra plane wave coefficients for some  $c_{lm}$ .

## Shape of H and S



# THE LAPW+LO METHOD

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

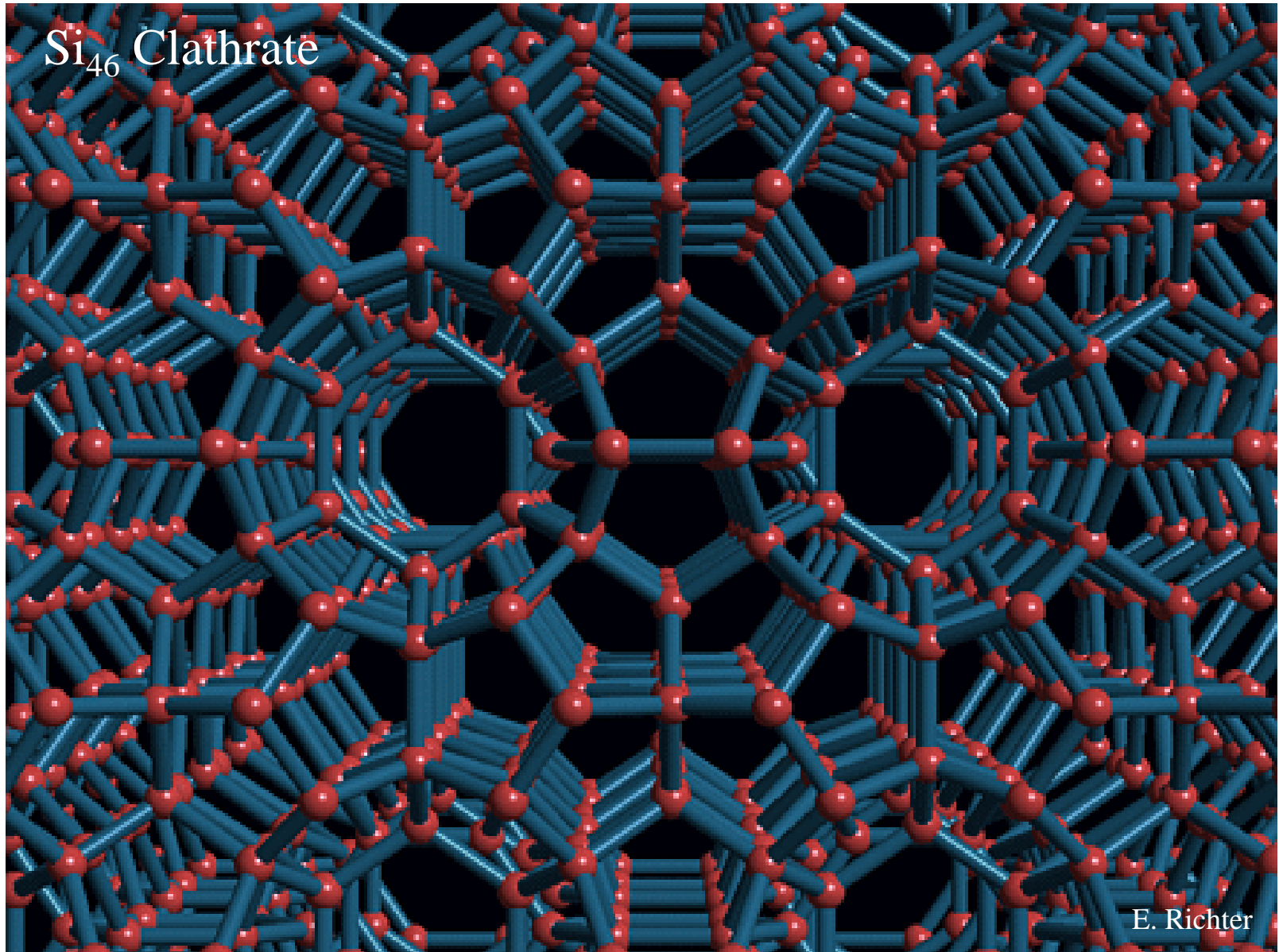


LAPW+LO converges like LAPW. The LO adds a few basis functions (i.e. 3 per atom for p states). Can also use LO to relax linearization errors, e.g. for a narrow  $d$  or  $f$  band.

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 COST OF PLANEWAVES



Example of a structure with short bonds and large open spaces

# THE APW+LO METHOD

In certain cases it is highly advantageous to lower  $RK_{\text{MAX}}$  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.

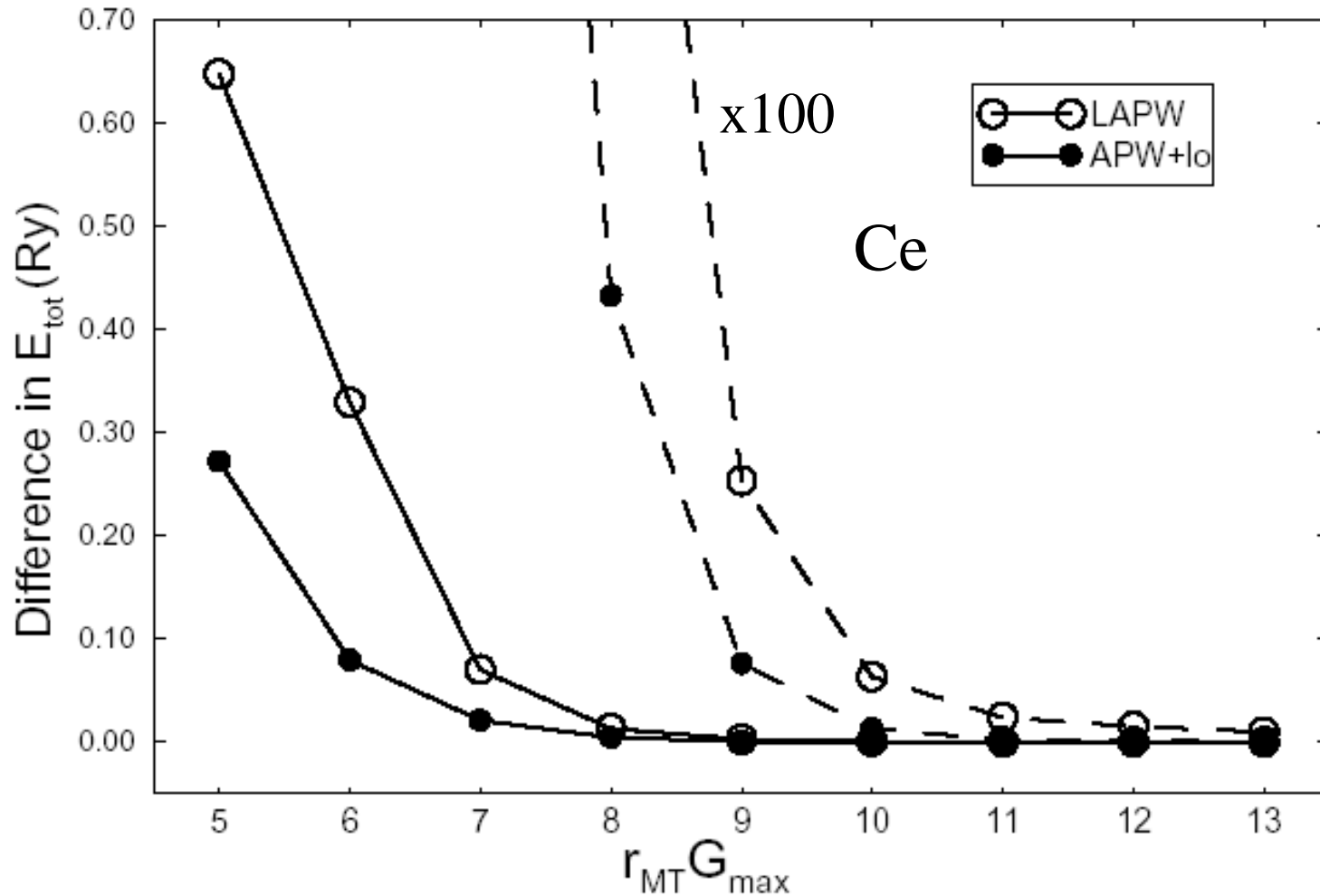
Then it is advantageous *for selected atoms and  $l$* , to use local orbitals to go back to the APW method.

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

*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. Sjöstedt, L. Nordström and D.J. Singh, Solid State Commun. **114**, 15 (2000).

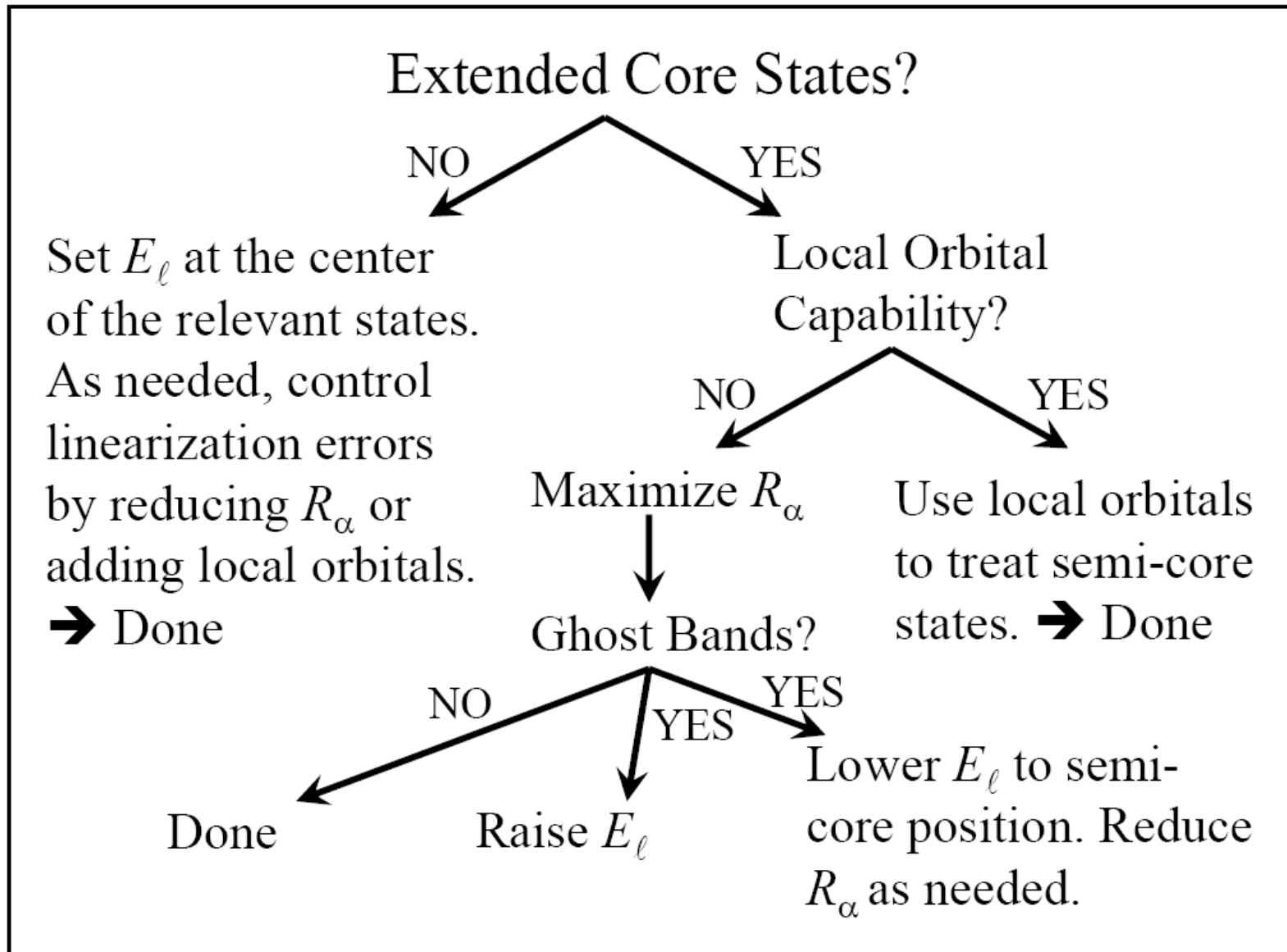




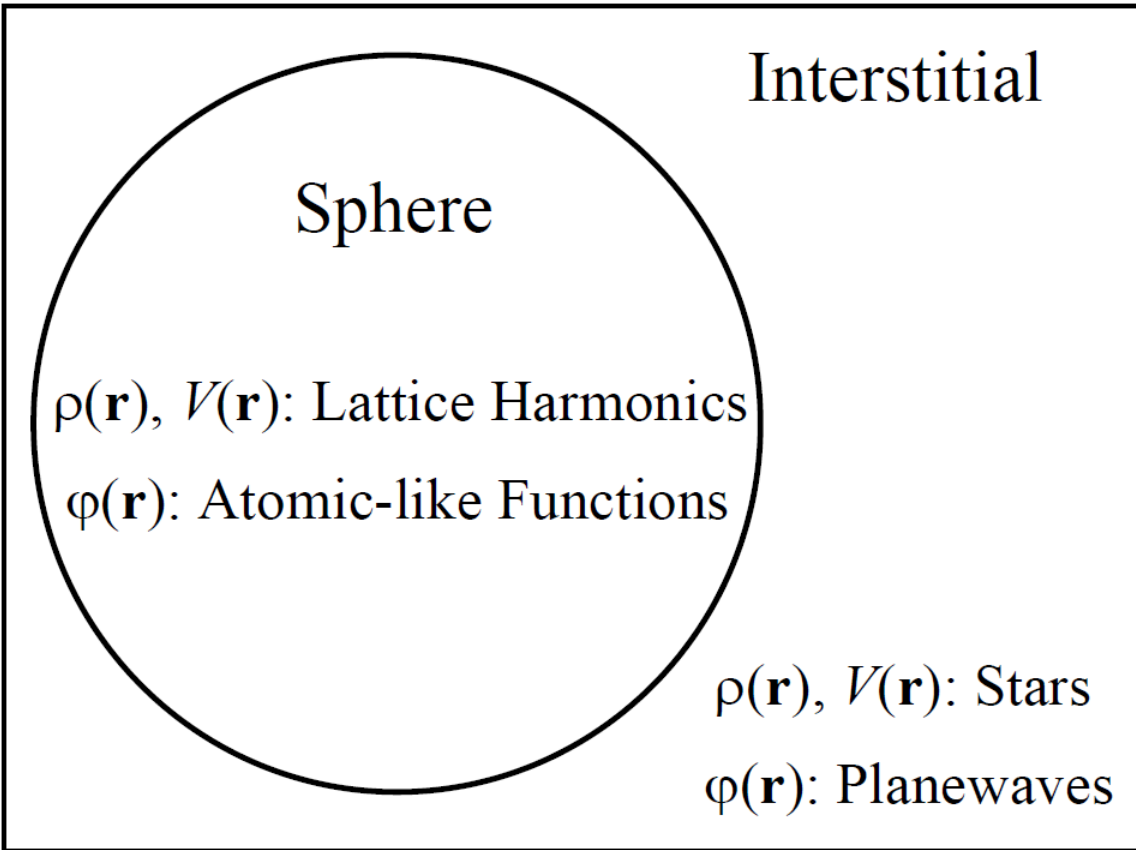
# REMARKS ON THE APW+LO METHOD

- 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



# Charge Density, Potential, etc.

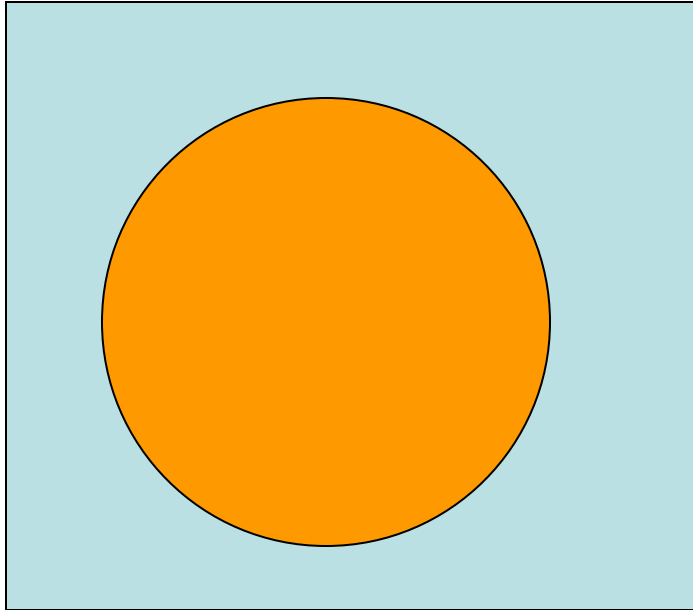


- Normally exploit lattice symmetry:
  - Stars in interstitial.
  - Lattice harmonics in spheres.
  - Only store for inequivalent atoms.

Allows for fast evaluation of Coulomb potential via multipole approach.

# Multipole Method for Coulomb Potential

M. Weinert.



1. Evaluate multipole moments of  $\rho$  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  $V \rightarrow$  exact in interstitial, but not in spheres.
4. Integrate Poisson's equation inward from sphere on radial grids to get  $V$  inside spheres.

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