



Introduction to Pseudopotentials and Electronic Structure

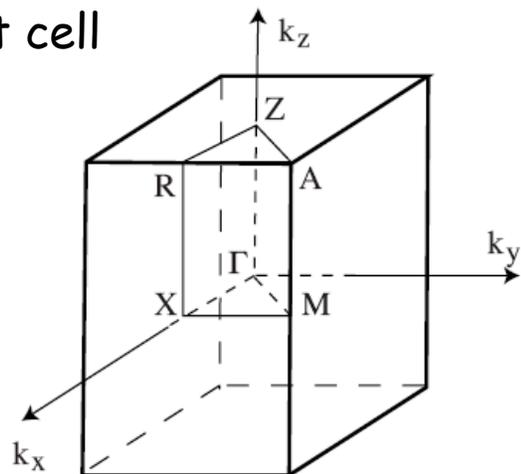
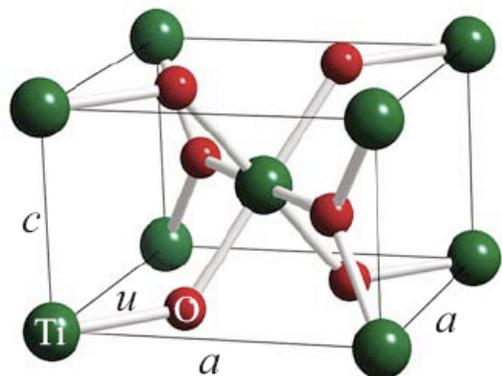
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Nov. 3, 2014
Brookhaven National Laboratory

You searched for: TOPIC: (TiO₂ 110 surface) -
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Example: rutile (TiO₂)

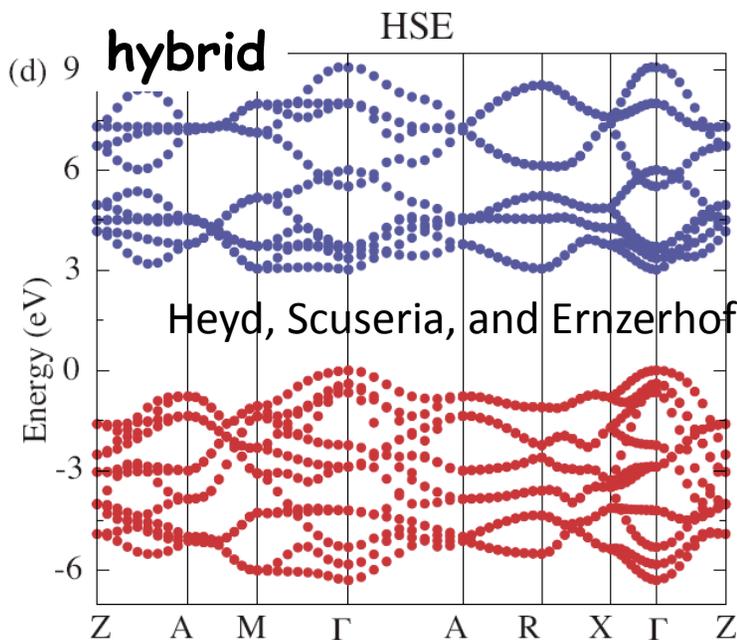
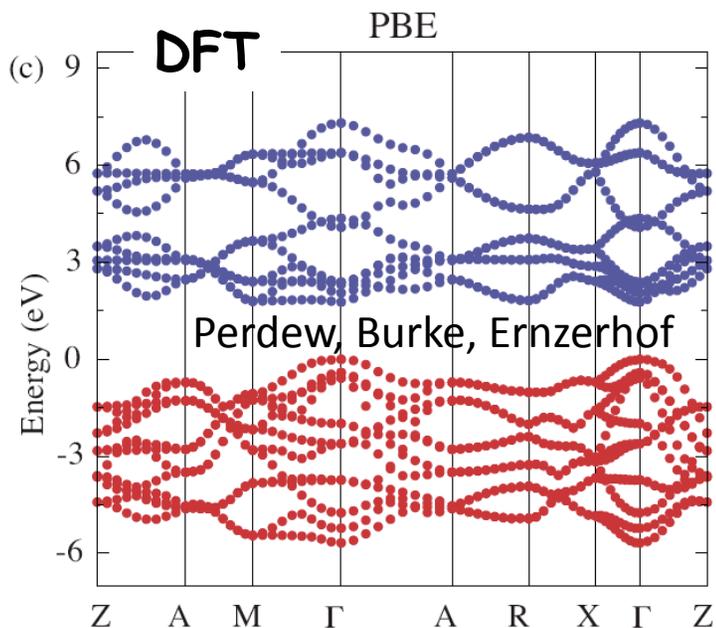
6-atom tetragonal unit cell



Hybrid functional studies of the **oxygen vacancy** in TiO₂, A. Janotti, J. B. Varley, P. Rinke, N. Umezawa, G. Kresse, and C. G. Van de Walle, PRB **81**, 085212 (2010)

Ti: 4s²3d² (4 electrons, 6 orbitals)
 O: 2s²2p⁴ (6 electrons, 4 orbitals)
 2(TiO₂) - 32 valence electrons

28 minimal basis orbitals
~1130 plane waves



12 empty bands

12 filled bands

4 oxygen 2s bands
 lower in energy

Single-particle ideas and philosophies - converging or diverging?

1. Drude, Sommerfeld, Bloch. Classical, Quantum, free to bound in solid.
2. Hartree-Fock; Slater $\rho(\vec{r})^{1/3}$ (average exchange).
3. Interacting many-body theory:
Single-particle Green's function; Landau theory; "GW" approximation
4. Hohenberg-Kohn-Sham density functional theory (DFT)

Single-particle Methods of Solution

1. Local orbitals; LCAO-Hückel
2. Plane waves
3. Augmented plane waves (APW)
4. Orthogonalized plane waves (OPW)
5. Green's function methods (KKR)
6. Pseudopotentials
7. PAW



Walter Kohn

Pseudopotentials (~1959) were born before DFT (1964) and remain partially independent. DFT "does" $\rho(r)$. What do pseudopotentials do?

Bloch's theorem: **can choose** eigenstates of a periodic Hamiltonian in the form

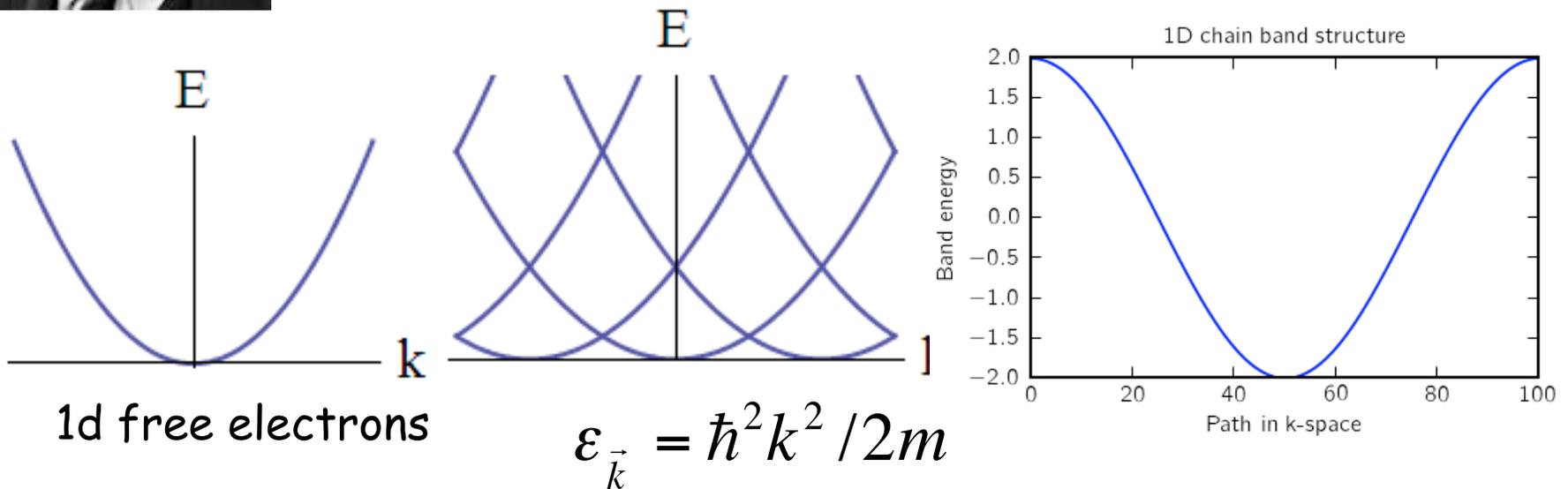


$$\hat{T}(\vec{R})\psi(\vec{r}) \equiv \psi(\vec{r} + \vec{R}) = \exp(i\vec{k} \cdot \vec{R})\psi(\vec{r}) \quad (\text{label as } \psi_{\vec{k}})$$

(eigenvalue of \hat{H} labeled as $\varepsilon_{\vec{k}}$)

(eigenvalue of translation $\hat{T}(\vec{R})$ is $\exp(i\vec{k} \cdot \vec{R})$)

\vec{k} and $\vec{k} + \vec{G}$ give the same translation eigenvalue.



1d free electrons

$$\varepsilon_{\vec{k}} = \hbar^2 k^2 / 2m$$

1d free electrons with periodicity of k -space (the reciprocal lattice)

1d single-orbital tight-binding band

LCAO: $\psi_k = \sum \exp(ikR)\phi(r-R)$ $\varepsilon_k = -2t\cos(ka)$

PHYSICAL REVIEW
volume 51 (1937)
Wave Functions in a Periodic Potential

J. C. SLATER* .

Augmented Plane Waves (APW)

The wave function is expanded in spherical harmonics and radial solutions of the wave equation within the spheres, and in plane waves outside the spheres, joining continuously at the surface. A single unperturbed function consists of a single plane wave outside the spheres, together with the necessary spherical functions within the spheres. ... It is hoped that the method will be useful for comparatively low energy excited electrons, for which the usual method of expansion in plane waves converges too slowly.

Birth of computational electronic structure theory?

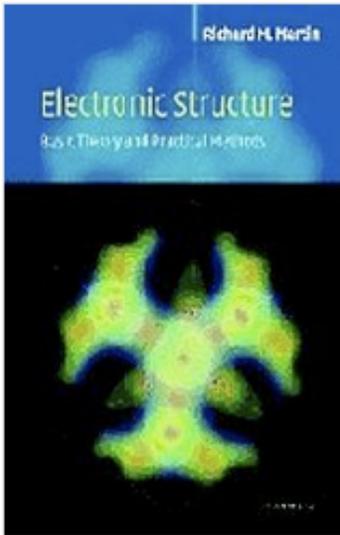


students:

Leland Allen
Don Ellis
Art Freeman
Frank Herman
George Koster
Len Mattheiss
Dick Watson
John Wood

The pseudopotential emerged ~1959 as a related way of reducing the number of plane waves needed.

Richard M. Martin, *Electronic Structure: Basic Theory and Practical Methods* Cambridge (2004)



How many plane waves are needed? $\sim (G_{\max}/G_{\min})^3$
 Crude estimate for s-orbitals: $\lambda_{\min} \sim 2a_B/Z$
 $(G_{\max}/G_{\min})^3 \sim (Za/2\sqrt{3}a_B)^3 \sim 71,400$ for Si.

With a smooth pseudopotential, $\lambda_{\min} \sim a_B$ works.
 ~ 200 plane waves for Si.

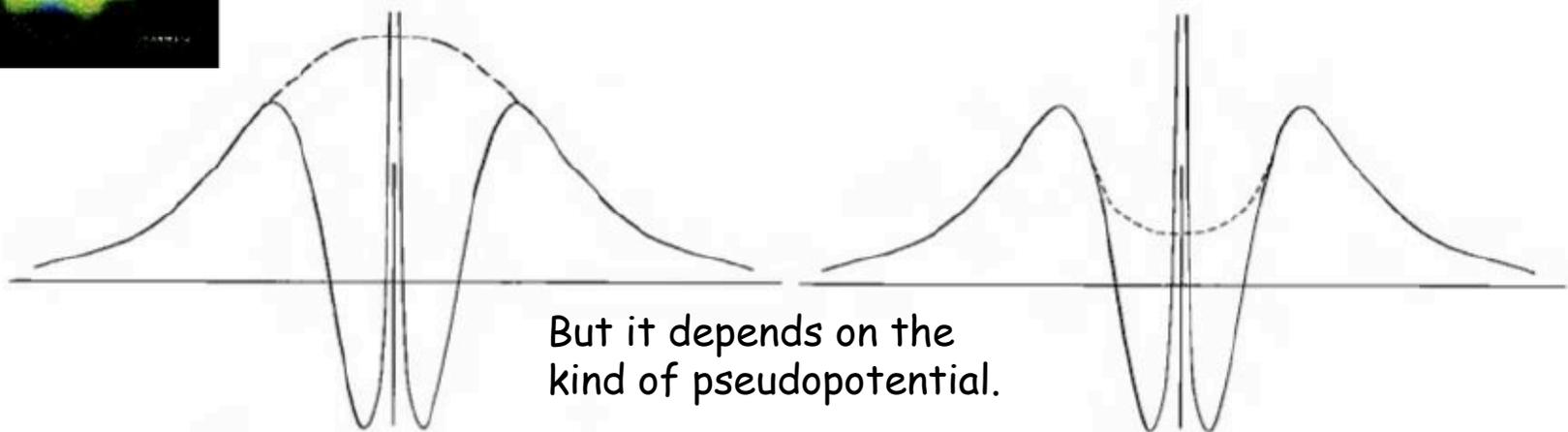


Figure 11.2. Schematic example of a valence function that has the character of a 3s orbital near

Bloch's theorem $\psi_{\mathbf{k}}(\vec{r} + \vec{R}) = e^{i\vec{k} \cdot \vec{R}} \psi_{\mathbf{k}}(\vec{r})$

"k" is short for \vec{k}, n, σ (all the quantum numbers of the state).
Let there be a "single-particle" Hamiltonian. Then:

Need to solve (in a primitive cell): $H\psi_{\mathbf{k}} = \epsilon_{\mathbf{k}}\psi_{\mathbf{k}}$

Two issues:

1. What is H?
2. How to solve?

Most methods of solution expand ψ in a "basis set." The simplest basis set adapted to Bloch's theorem is plane-waves.

$$\psi_{\mathbf{k}}(\vec{r}) = \sum_{\vec{G}} c_{\mathbf{k}}(\vec{G}) e^{i(\vec{k} + \vec{G}) \cdot \vec{r}}$$

This is a Bloch wave, since $\exp(i\vec{G} \cdot \vec{R}) = 1$
They are complete, orthogonal, and bias-free.

Dimensionless units

"Rydberg atomic units" $\hbar = e/\sqrt{2} = 2m = 1$

"Hartree atomic units" $\hbar = e = m = 1$

In both systems, the unit of length is the Bohr radius:

$$a_B = \hbar^2 / me^2 = \hbar^2 / (2m)(e^2/2) = 1$$

Simplified notation; drop the label "k".

$$|g\rangle = e^{i(\vec{k} + \vec{G}) \cdot \vec{r}} \quad |\psi\rangle = \sum_g c_g |g\rangle \quad c_g = \langle g | \psi \rangle$$

Determine the expansion coefficients c_g (secular equation.)

$$\sum_{g'} (H_{g,g'} - \epsilon \delta_{g,g'}) c_{g'} = 0$$

$$H(\vec{k} + \vec{G}, \vec{k} + \vec{G}') = H_{g,g'} = \langle g | H | g' \rangle$$

$$H_{g,g'} = \begin{pmatrix} (\vec{k} + \vec{G}_1)^2 & V(\vec{G}_1 - \vec{G}_2) & \cdots & V(\vec{G}_1 - \vec{G}_N) \\ V(\vec{G}_2 - \vec{G}_1) & (\vec{k} + \vec{G}_2)^2 & \cdots & V(\vec{G}_2 - \vec{G}_N) \\ \vdots & \vdots & \ddots & \vdots \\ V(\vec{G}_N - \vec{G}_1) & V(\vec{G}_N - \vec{G}_2) & \cdots & (\vec{k} + \vec{G}_N)^2 \end{pmatrix}$$

This is only one of many matrix versions of the Schrödinger equation

$$\psi = \sum_{n=1}^{\infty} \alpha_n |n\rangle \quad \text{where } \{|n\rangle\} \text{ is a **complete, orthonormal** set of states.}$$

$$\hat{H}\psi = \sum_{n=1}^{\infty} \alpha_n \hat{H}|n\rangle = \sum_{n=1}^{\infty} \alpha_n E|n\rangle = E\psi$$

$$\text{Left project by } \langle m| \quad \sum_{n=1}^{\infty} \alpha_n \langle m|H|n\rangle = \sum_{n=1}^{\infty} \alpha_n E \langle m|n\rangle = E\alpha_m$$

$$\begin{pmatrix} \langle 1|H|1\rangle & \cdots & \langle 1|H|N\rangle & \cdots \\ \vdots & \ddots & \vdots & \cdots \\ \langle N|H|1\rangle & \cdots & \langle N|H|N\rangle & \cdots \\ \vdots & \cdots & \cdots & \ddots \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \vdots \\ \alpha_N \\ \vdots \end{pmatrix} = E \begin{pmatrix} \alpha_1 \\ \vdots \\ \alpha_N \\ \vdots \end{pmatrix}$$

Exact version of
one-electron
Schroedinger eqn.
(assuming we know H!)

Truncated version of the matrix formulation - variational accuracy

Theorem: if $H\psi = E\psi$ and we expand ψ in a (finite, truncated) orthonormal basis,

$$\psi = \sum_{n=1}^{\overset{N}{\circlearrowleft}} \alpha_n |n\rangle$$

then the **states that are stationary under variation of all coefficients**

$$\frac{\delta}{\delta \alpha_n^*} [\langle \psi | H | \psi \rangle - \lambda \langle \psi | \psi \rangle] = 0$$

obey the matrix eigenvalue equation

$$\begin{pmatrix} \langle 1 | H | 1 \rangle & \cdots & \langle 1 | H | N \rangle \\ \vdots & \ddots & \vdots \\ \langle N | H | 1 \rangle & \cdots & \langle N | H | N \rangle \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \vdots \\ \alpha_n \end{pmatrix} = \lambda \begin{pmatrix} \alpha_1 \\ \vdots \\ \alpha_n \end{pmatrix}$$

Basis functions are **often not orthogonal or normalized**.
 This creates a "**generalized**"
 Hermitean eigenvalue problem.

$$\hat{H} \begin{pmatrix} \alpha_1 \\ \vdots \\ \alpha_N \\ \vdots \end{pmatrix} = E \hat{S} \begin{pmatrix} \alpha_1 \\ \vdots \\ \alpha_N \\ \vdots \end{pmatrix}$$

$$\hat{H} = \begin{pmatrix} \langle 1|H|1\rangle & \cdots & \langle 1|H|N\rangle & \cdots \\ \vdots & \ddots & \vdots & \cdots \\ \langle N|H|1\rangle & \cdots & \langle N|H|N\rangle & \cdots \\ \vdots & \cdots & \cdots & \ddots \end{pmatrix} \quad \hat{S} = \begin{pmatrix} \langle 1|1\rangle & \cdots & \langle 1|N\rangle & \cdots \\ \vdots & \ddots & \vdots & \cdots \\ \langle N|1\rangle & \cdots & \langle N|N\rangle & \cdots \\ \vdots & \cdots & \cdots & \ddots \end{pmatrix}$$

Linear algebra methods solve this with little added difficulty.
 One approach:

$$\hat{H}\psi = E\hat{S}\psi \quad \text{and} \quad \phi = \hat{S}^{1/2}\psi$$

$$\rightarrow \hat{H}_{\text{eff}}\psi = E\psi \quad \text{where} \quad \hat{H}_{\text{eff}} = \hat{S}^{-1/2}\hat{H}\hat{S}^{-1/2}$$

More annoyingly, efficient basis functions (or a “pseudopotential”) tend to be **energy-dependent**. Then it is not a linear problem any more.

$$\hat{H}(E) \begin{pmatrix} \alpha_1 \\ \vdots \\ \alpha_N \\ \vdots \end{pmatrix} = E \hat{S}(E) \begin{pmatrix} \alpha_1 \\ \vdots \\ \alpha_N \\ \vdots \end{pmatrix}$$

Solve iteratively?
Lose nice linear algebra theorems.

$$\hat{H}(E)|\psi\rangle = E\hat{S}(E)|\psi\rangle$$

$$\hat{H}(E)|\psi\rangle = E\hat{S}(E)|\psi\rangle$$

Linearized approximations: LAPW (O. K. Andersen), etc.

$$\hat{H}(E) \approx \hat{H}(E_0) + (E - E_0)\hat{H}'_{E_0}$$

$$\hat{S}(E) \approx \hat{S}(E_0) + (E - E_0)\hat{S}'_{E_0}$$

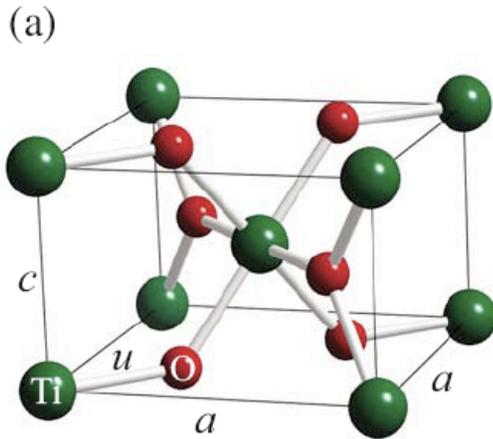
This leads to a generalized linear Hermitean eigenvalue problem:

$$\left[\hat{H}(E_0) - E_0 \right] |\psi\rangle = (E - E_0) \left[1 + E_0 \hat{S}'_{E_0} - \hat{H}'_{E_0} \right] |\psi\rangle$$

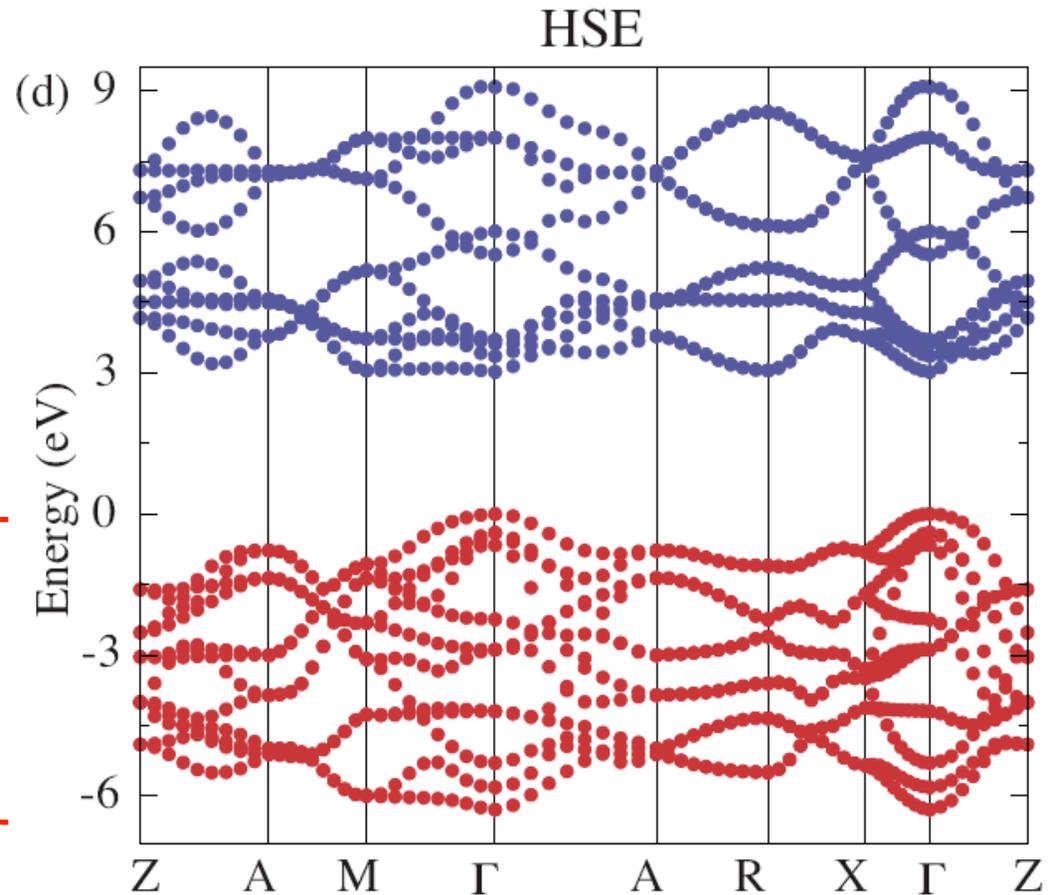
and works only in an energy interval around E_0 .

The soft letter ell (L): "linearized" (LAPW) or "local" (LDA)

Back to rutile

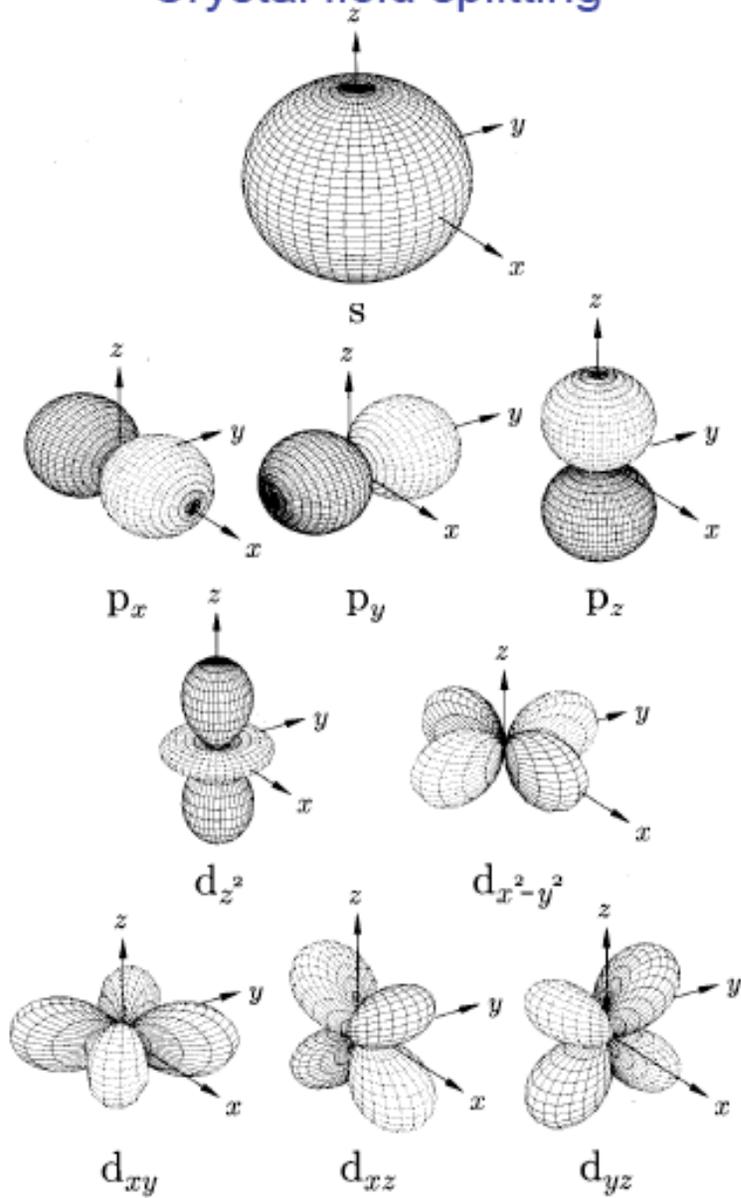


4 x 3 oxygen 2p levels
 $p(x)$, $p(y)$, $p(z)$
bonded with 2 x 2 Ti E_g levels
 $d(3z^2-r^2)$, $d(3x^2-r^2)$, $d(3y^2-r^2)$



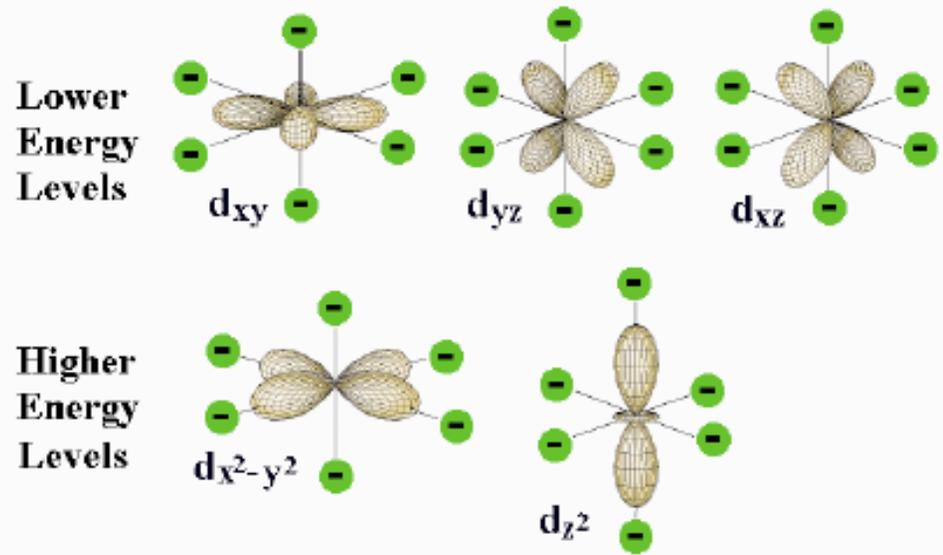
Local orbital picture **necessary** to describe covalent orbital mixing chemistry.

Crystal field splitting

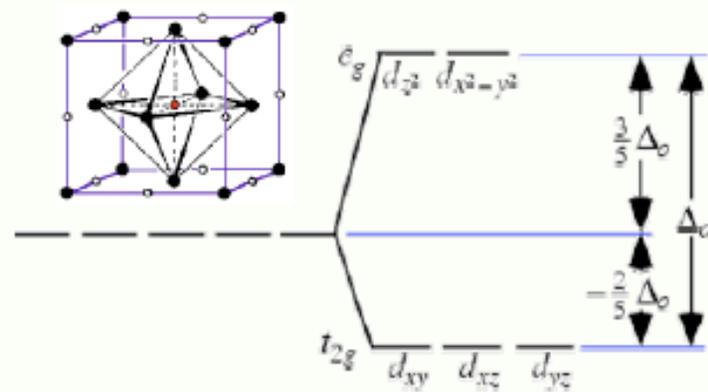


covalent bonding/anti-bonding splitting.

In a crystal, crystal field is usually more important than the LS coupling



octahedral (O_h) crystal field splitting



Different symmetries would have different splitting patterns

"Oxygen vacancies in rutile TiO_2 were simulated by removing one O atom from a supercell with 72 atoms."

12 primitive cells \rightarrow **336 orbitals in a minimal basis**

"We used a plane-wave basis set with a cutoff of 400 eV"

400 eV = $k_{\text{max}}^2 = (2\pi/\lambda_{\text{min}})^2$ corresponds to a minimum wave-length of 0.6 Å

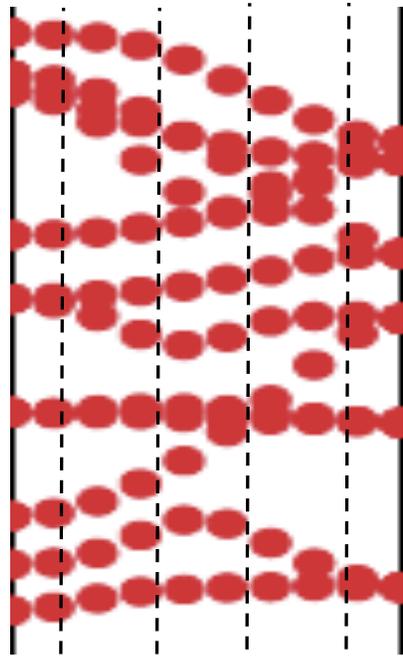
$$\rightarrow k_{\text{max}} = 5.42 \text{ a.u.} \rightarrow V_{\text{k-space}} (4\pi/3)k_{\text{max}}^3 = 667 \text{ a.u.}$$

The super-cell has dimensions $V = 2a \times 2a \times 3c = 748 \text{ \AA}^3 = 5,055 \text{ a.u.}$
The Brillouin zone volume $V_{\text{BZ}} = (2\pi)^3/V = 0.049 \text{ a.u.}$

The matrix dimension is $V_{\text{k-space}}/V_{\text{BZ}} =$ **13,600 plane waves**
Plane waves enlarge the basis set by 40
and the computer time by $(40)^3 = 64,000$

"... integrations over the Brillouin zone were performed using a $2 \times 2 \times 2$ mesh of special k points."

Self-consistent potential $V(r)$ depends on charge density $\rho(r)$



0 $(\pi/a)(1,0,0)$

Discrete k-mesh of special points used to evaluate $\rho(r)$.

$$\left[\hat{T} + \hat{V}(\vec{r}, \rho[\vec{r}']) - \epsilon_k \right] \psi_k(\vec{r}) = 0$$

$$\rho(\vec{r}) = \sum_k^{\text{occ}} |\psi_k(\vec{r})|^2$$

Birth of the pseudopotential

New Method for Calculating Wave Functions in Crystals and Molecules¹



JAMES C. PHILLIPS[†] AND LEONARD KLEINMAN[‡]
Department of Physics, University of California, Berkeley, California

Phys. Rev. 116, 287 (1959)

[†] National Science Foundation Postdoctoral Fellow.

[‡] National Science Foundation Predoctoral Fellow.

¹ C. Herring, Phys. Rev. 57, 1169 (1940).

² V. Heine, Proc. Roy. Soc. (London) A240, 340 (1957).

³ F. Herman, Phys. Rev. 88, 1210 (1952); 93, 1214 (1954).

⁴ J. C. Slater, Phys. Rev. 92, 603 (1953).



We begin by imagining that we *know* the exact crystal wave function ψ_α which transforms according to an irreducible representation of the cubic point group Γ_α which has *s* or *p* atomic symmetry.⁷ Since ψ_α must be orthogonal to the core states of similar symmetry, we have

$$\psi_\alpha = \varphi_\alpha + \sum_n a_n^\alpha \varphi_\alpha^n, \quad (2.1)$$

$$a_n^\alpha = -(\varphi_\alpha, \varphi_\alpha^n). \quad (2.2)$$

If we had chosen φ to be a single plane wave Herring's¹ results would follow.



Conyers Herring

real wave - function : $\psi(\vec{r}) = \langle \vec{r} | \psi \rangle$

pseudo wave - function : $\tilde{\psi}(\vec{r}) = \langle \vec{r} | \tilde{\psi} \rangle$

$$|\tilde{\psi}\rangle \equiv |\psi\rangle - \sum_i |i\rangle \langle i | \psi \rangle$$

$\sum_i |i\rangle \langle i|$ is the projection operator that orthogonalizes ψ to the (somewhat arbitrary?) states $|i\rangle$.

$H|\psi\rangle = E|\psi\rangle$ defines an effective Hamiltonian $\tilde{H}\tilde{\psi} = E\tilde{\psi}$.

If $H = T + V$ ($V =$ potential), then $\tilde{H} = T + \tilde{V}$ ($\tilde{V} =$ pseudopotential).

DFT is not yet born. People were guessing that V "existed" (Slater showed how to "guess" it quite well). Then \tilde{V} is a weaker potential, a non-local operator, that also exists and has pseudo-wavefunctions for its solution.

So, brave computational scientist, proceed to guess \tilde{V} !

R. M. Martin, *Electronic Structure ...*

Pseudopotential for a problem where the 1-electron potential is "known":

$$\hat{H} \psi_i^v(\mathbf{r}) = \left[-\nabla^2 + V(\mathbf{r}) \right] \psi_i^v(\mathbf{r}) = \varepsilon_i^v \psi_i^v(\mathbf{r})$$

$$\hat{H}^{\text{PKA}} \tilde{\psi}_i^v(\mathbf{r}) \equiv \left[-\nabla^2 + \hat{V}^{\text{PKA}} \right] \tilde{\psi}_i^v(\mathbf{r}) = \varepsilon_i^v \tilde{\psi}_i^v(\mathbf{r})$$

Phillips-Kleinman-Antoncik

$$\hat{V}^{\text{PKA}} = V + \hat{V}^R \quad \hat{V}^R \tilde{\psi}_i^v(\mathbf{r}) = \sum_j (\varepsilon_j^v - \varepsilon_j^c) \langle \psi_j^c | \tilde{\psi}_i^v \rangle \psi_j^c(\mathbf{r})$$

The full self-consistent treatment was not an option until 15 years later. The full apparatus of non-local (and **energy-dependent**) potentials was over the top. Simpler approaches were encouraged.

"SL" = semi-local

$$\hat{V}_{\text{SL}} = \sum_{lm} |Y_{lm}\rangle V_l(r) \langle Y_{lm}|$$

Band Structures and Pseudopotential Form Factors for Fourteen Semiconductors of the Diamond and Zinc-blende Structures*

MARVIN L. COHEN† AND T. K. BERGSTRESSER

Department of Physics, University of California, Berkeley, California

Phys. Rev. 141, 789-796 (1966) [cited 1336 times]

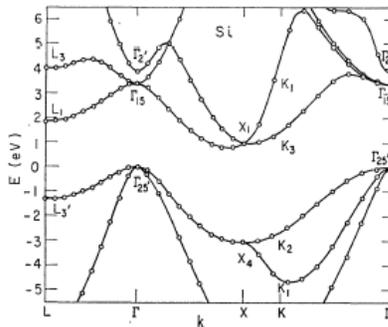
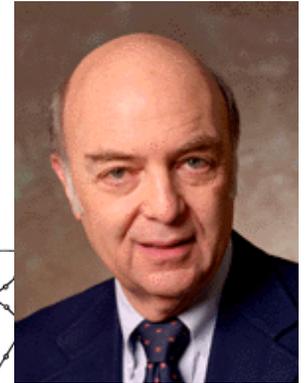


FIG. 1. Band structure of Si.

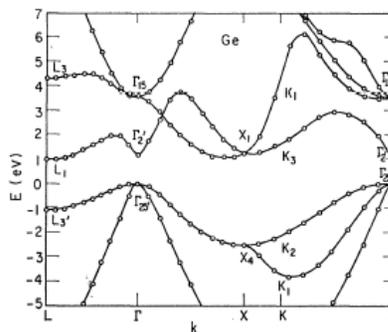


FIG. 2. Band structure of Ge.

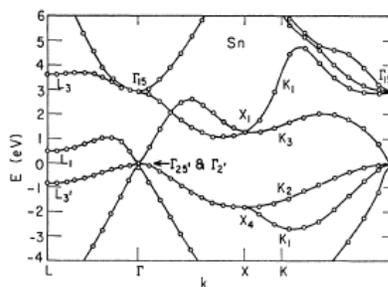


FIG. 3. Band structure of Sn.

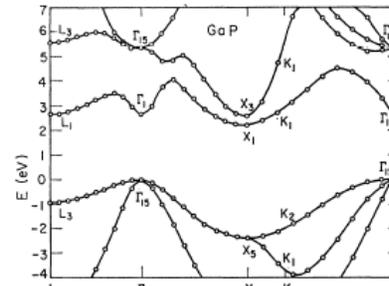


FIG. 5. Band structure of GaAs.

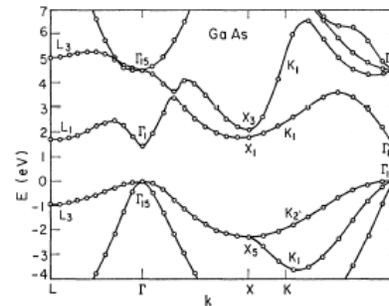


FIG. 6. Band structure of AlSb.

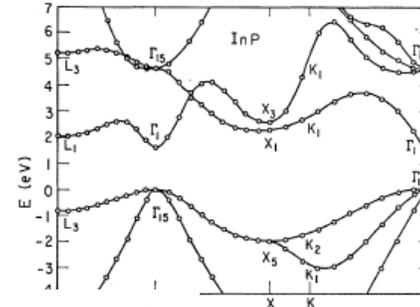


FIG. 8. Band structure of GaSb.

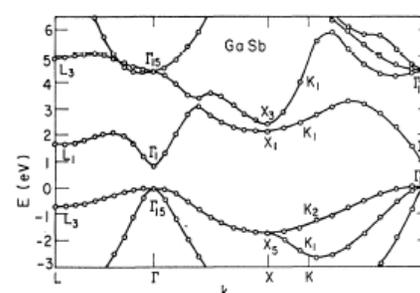


FIG. 9. Band structure of InAs.

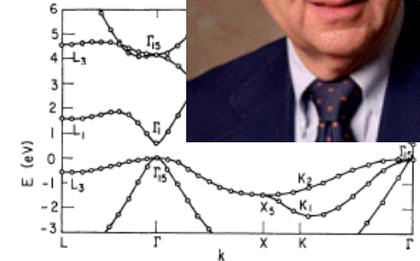


FIG. 10. Band structure of InSb.

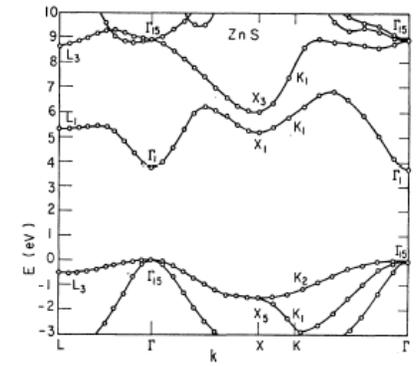


FIG. 11. Band structure of ZnS.

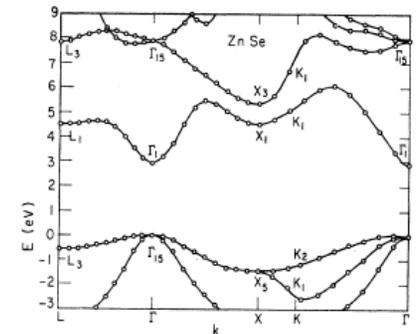


FIG. 12. Band structure of ZnSe.

Empirical pseudopotentials

"Empirical pseudo-potential method" local version

$$\begin{aligned} \vec{a} &= a\left(0, \frac{1}{2}, \frac{1}{2}\right) & \vec{A} &= \frac{2\pi}{a}(\bar{1} 11) \\ \text{fcc structure: } \vec{b} &= a\left(\frac{1}{2}, 0, \frac{1}{2}\right) & \vec{B} &= \frac{2\pi}{a}(1 \bar{1} 1) \\ \vec{c} &= a\left(\frac{1}{2}, \frac{1}{2}, 0\right) & \vec{C} &= \frac{2\pi}{a}(11 \bar{1}) \end{aligned}$$

5 smallest reciprocal lattice vector (RLV) types

$$\vec{G}_3 = \frac{2\pi}{a}(111), \vec{G}_4 = \frac{2\pi}{a}(200), \vec{G}_8 = \frac{2\pi}{a}(220), \vec{G}_{11} = \frac{2\pi}{a}(311), \vec{G}_{12} = \frac{2\pi}{a}(222)$$

matrix elements $\langle \vec{k} | V | \vec{k} + \vec{G}_3 \rangle = V(|\vec{G}_3|) \equiv V_3$ are the same for all 12 vectors

Diamond structure: fcc with a basis of **two identical atoms** at locations τ_1 and τ_2 .

$$\langle \vec{k} | V | \vec{k} + \vec{G} \rangle = V(\vec{G})S(\vec{G}) \text{ where } S(\vec{G}) = \left(e^{i\vec{G}\cdot\tau_1} + e^{i\vec{G}\cdot\tau_2} \right) / 2$$

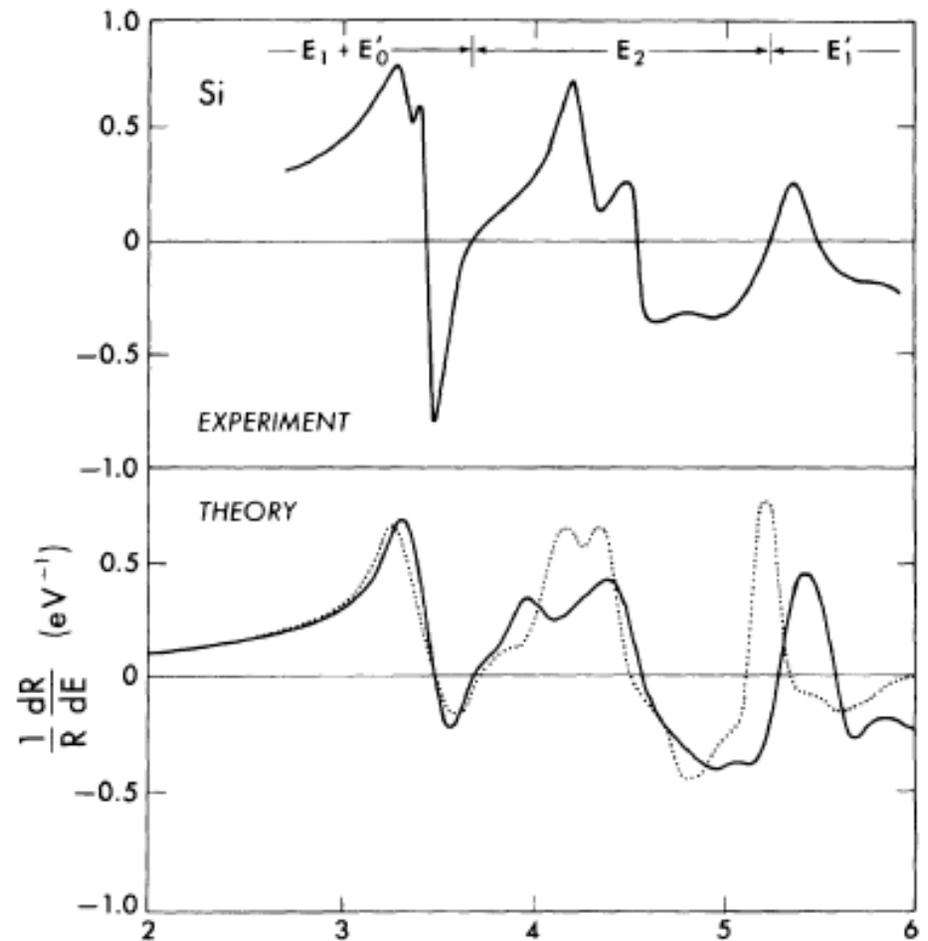
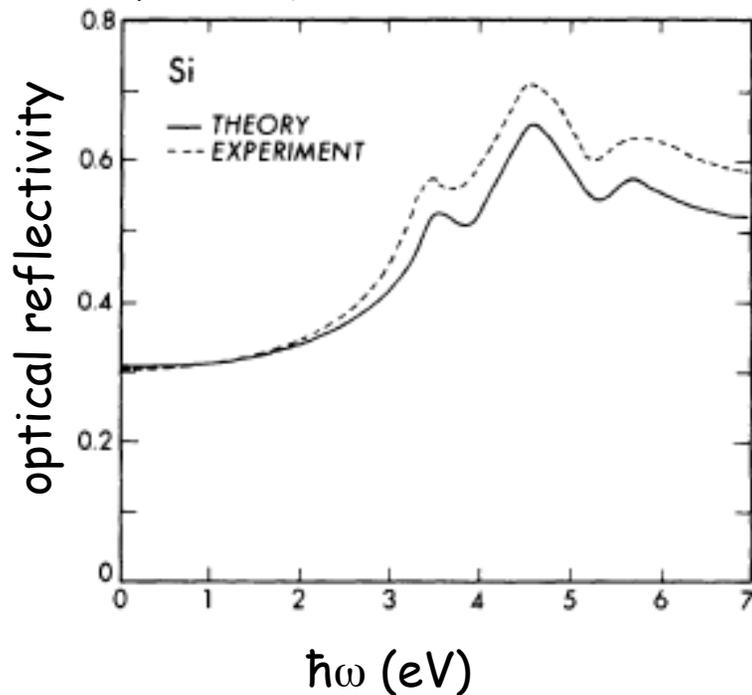
Note - destructive interference kills structure factor $S(G)$ for certain G 's.

$$S(\vec{G}_4) = S(\vec{G}_{12}) = 0$$

Three numbers (V_3, V_8, V_{11}) give a "good" band structure for C, Si, Ge, Sn.

Empirical pseudopotentials are adjusted until theory "agrees" with optical experiment.

There are aspects of experiment lying outside "quasi-particle theory:" excitonic effects, for example. Two particle Green's function, Bethe-Salpeter equation.



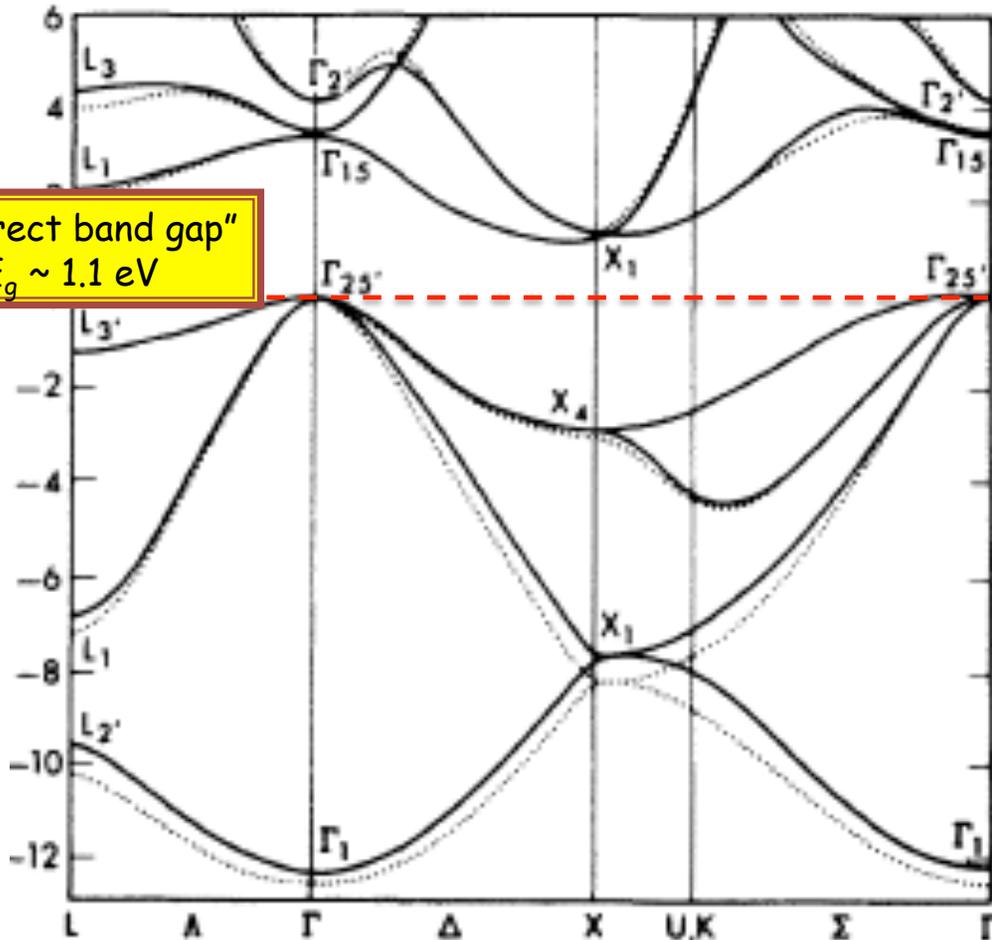
H. R. Philipp and H. Ehrenreich, *Phys. Rev.* **129**, 1550 (1963).

R. R. L. Zucca, J. P. Walter, Y. R. Shen, and M. L. Cohen, *Solid State Commun.* **8**, 627 (1970).

James R. Chelikowsky and Marvin L. Cohen
Nonlocal pseudopotential calculations for the electronic structure of eleven ...conductors
 Phys. Rev. B 14, 556-582 (1976)

2 atoms/cell, 4 valence electrons \rightarrow 4 occupied bands.

"Indirect band gap"
 $E_g \sim 1.1$ eV



empirical nonlocal pseudopotential (solid line) and
 empirical local pseudopotential (dashed line).

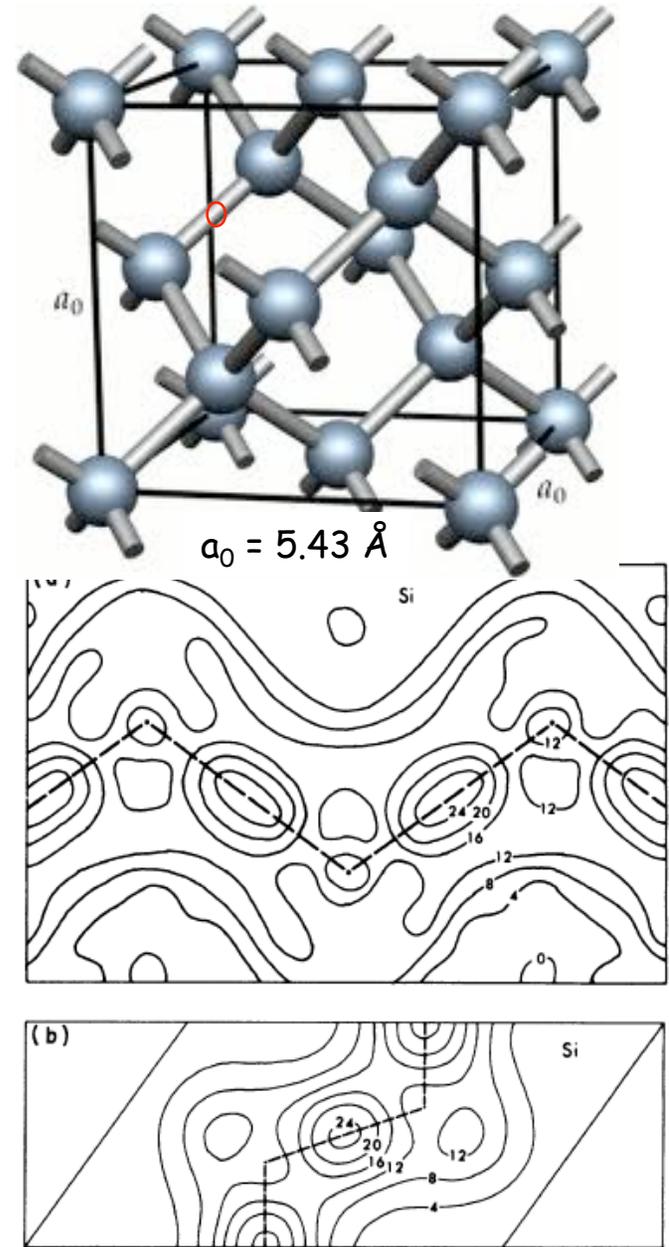
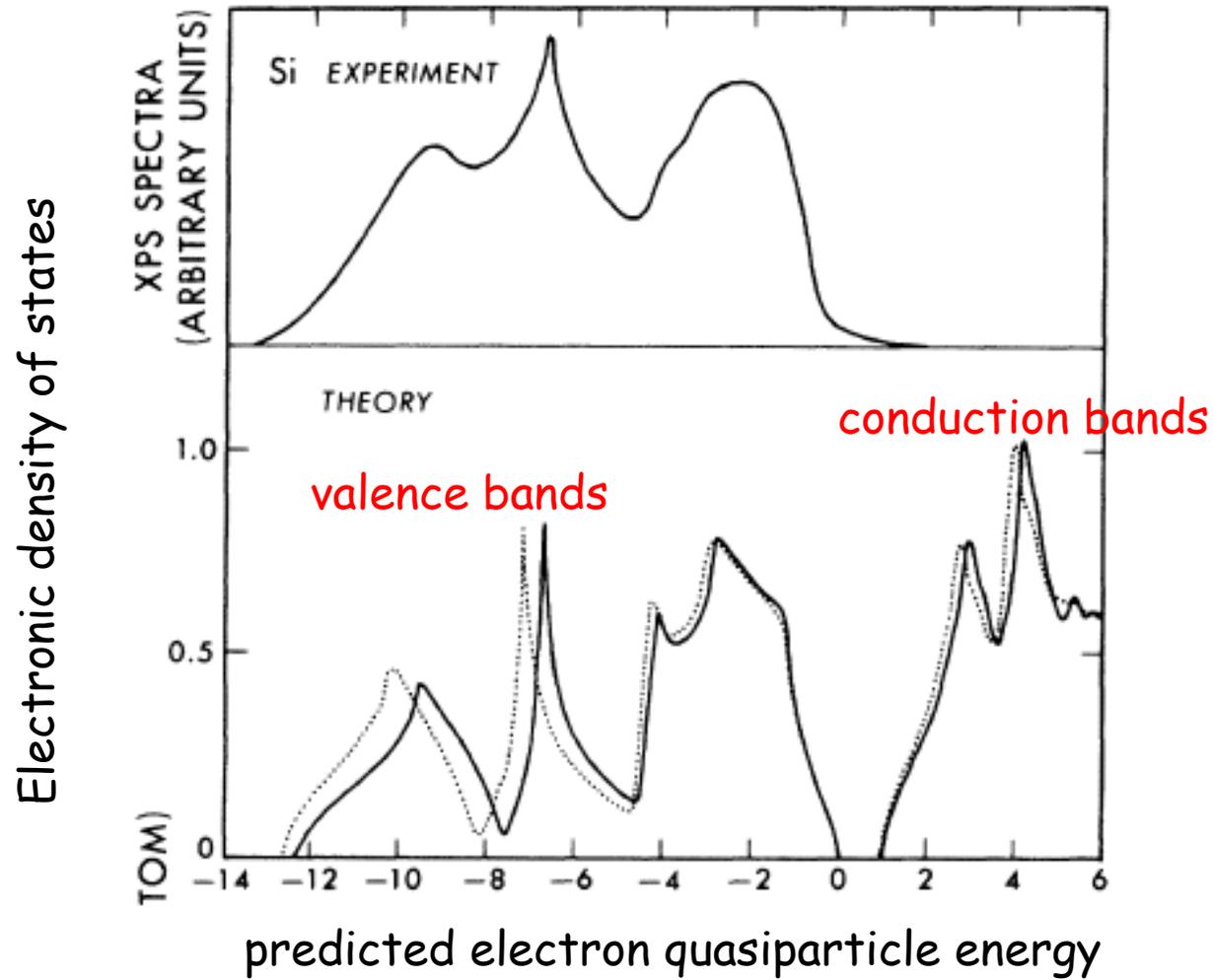


FIG. 5. Valence charge density as determined by Yang and Coppens (Ref. 9) from x-ray experimental data. (b) Valence charge density as calculated by a nonlocal pseudopotential. In both cases the contours are in units of e/Ω_e .

This is a wonderful way to study bulk solids - supplemented by chemical local basis insights.



Around 1980, self-consistent calculations had become attainable.
“**Ab initio**” (i.e. non-empirical, no adjusting) had become desirable.

Why? It **worsened** quasiparticle properties.

The “band-gap problem” emerged with ab initio theory.

Answer: surface physics!

DFT promises ground state properties, especially total energy -
These had not been the target of previous semi-empirical approaches.

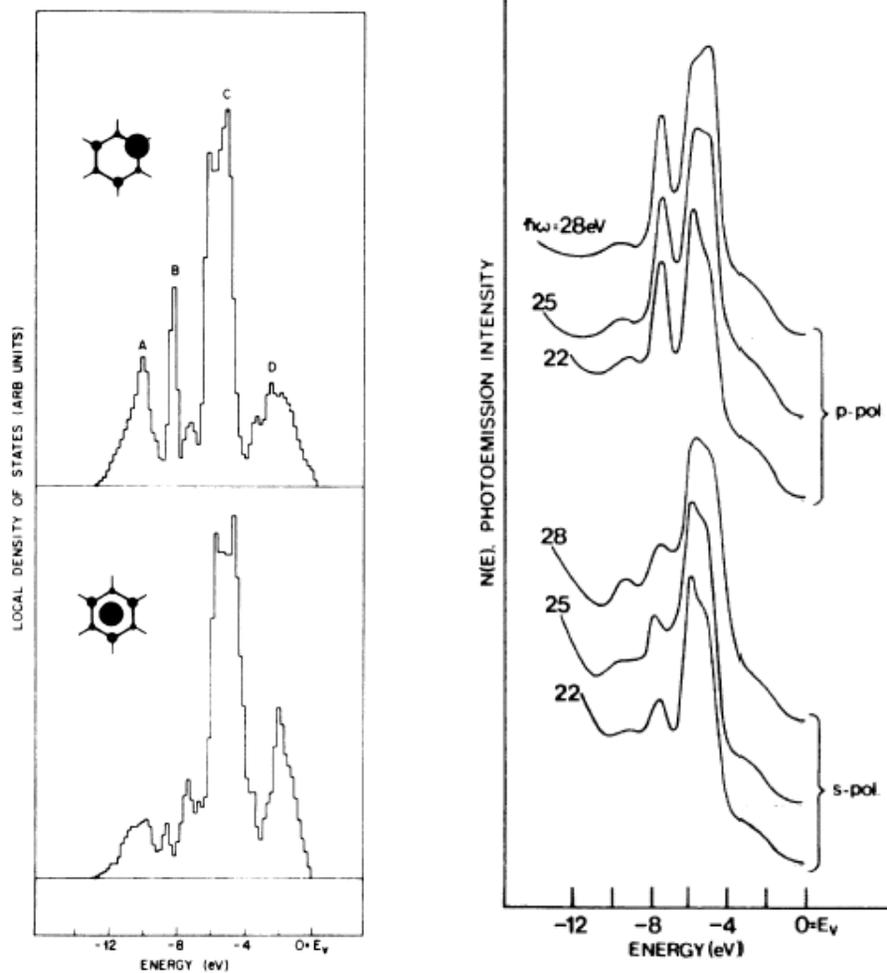
Chemisorption-Site Geometry from Polarized Photoemission: Si(111)Cl and Ge(111)Cl[†]

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Bell Laboratories, Murray Hill, New Jersey 07974

and

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

Phys. Rev. Lett. 37, 1632 (1976)



Benefit of "ab initio": total energy

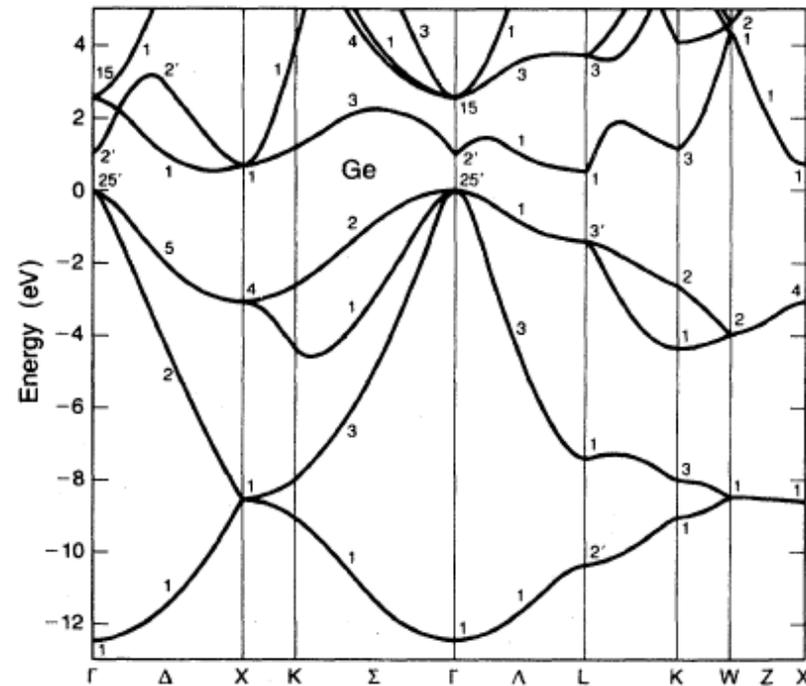
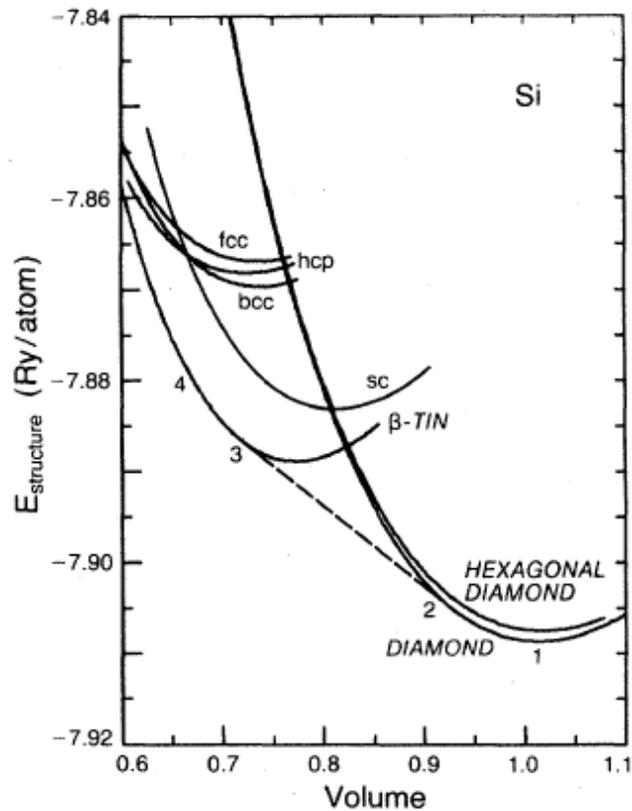
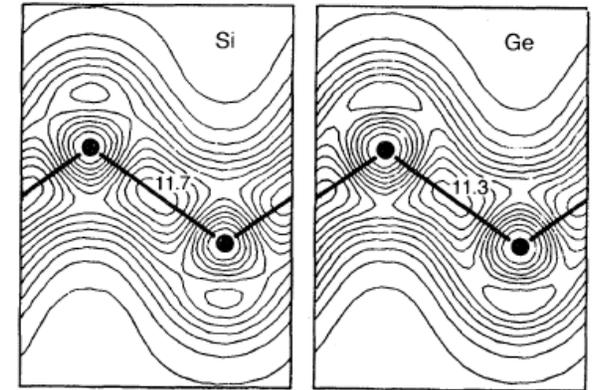
Theory of static structural properties, crystal stability, and phase transformations: Application to Si and Ge

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,

Phys. Rev. B26, 5668 (1982)

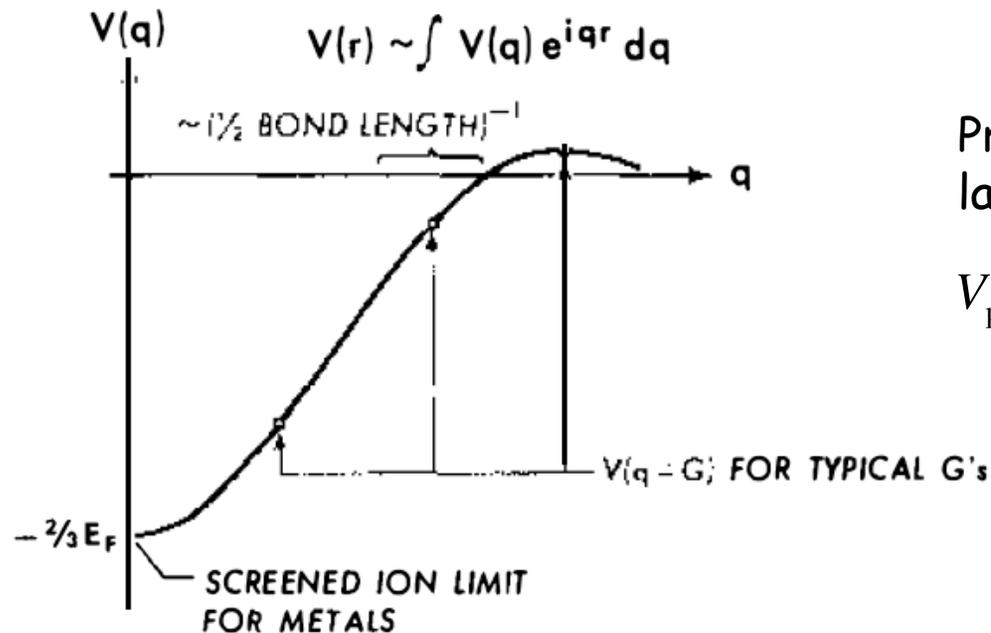
Valence charge density (110 plane)



using a plane-wave basis set with a kinetic-energy cutoff (E_{pw}) of 11.5 Ry at which point the overall convergent error of eigenvalues is about 0.05 eV.

Note: We are no longer assuming we "know" V ; we claim that Hohenberg-Kohn-Sham theory has taught us how to construct V .

[More accurately, has given us license to invent ways to construct V .]



Previous view: $H = T + V_{\text{pseudo}}$. At large distances, it must equal

$$V_{\text{pseudo}}(q) = -\frac{4\pi Z_{\text{valence}} e^2}{\epsilon(q) q^2} \rightarrow \frac{2}{3} \epsilon_{\text{Fermi}}$$

Crystal potential $V(\vec{r}) = \sum_{\vec{G}} V(\vec{G}) S(\vec{G}) e^{i\vec{G} \cdot \vec{r}}$

"all electron" DFT

$$V(\vec{r}) = -\frac{Z_{\text{tot}} e^2}{|\vec{r}|} + \int d^3 r' \frac{\rho_{\text{tot}}(\vec{r}')}{|\vec{r} - \vec{r}'|} + V_{\text{XC}}[\rho_{\text{tot}}]$$

$$\rho_{\text{tot}}(\vec{r}) = \sum_i^{\text{tot, occupied}} |\psi_i(\vec{r})|^2$$

"Valence only" DFT

$$\tilde{V}(\vec{r}) = -\frac{Z_{\text{valence}} e^2}{|\vec{r}|} + V_{\text{NLcorr}} + \int d^3 r' \frac{\rho_{\text{valence}}(\vec{r}')}{|\vec{r} - \vec{r}'|} + V_{\text{XC}}[\rho_{\text{valence}}]$$

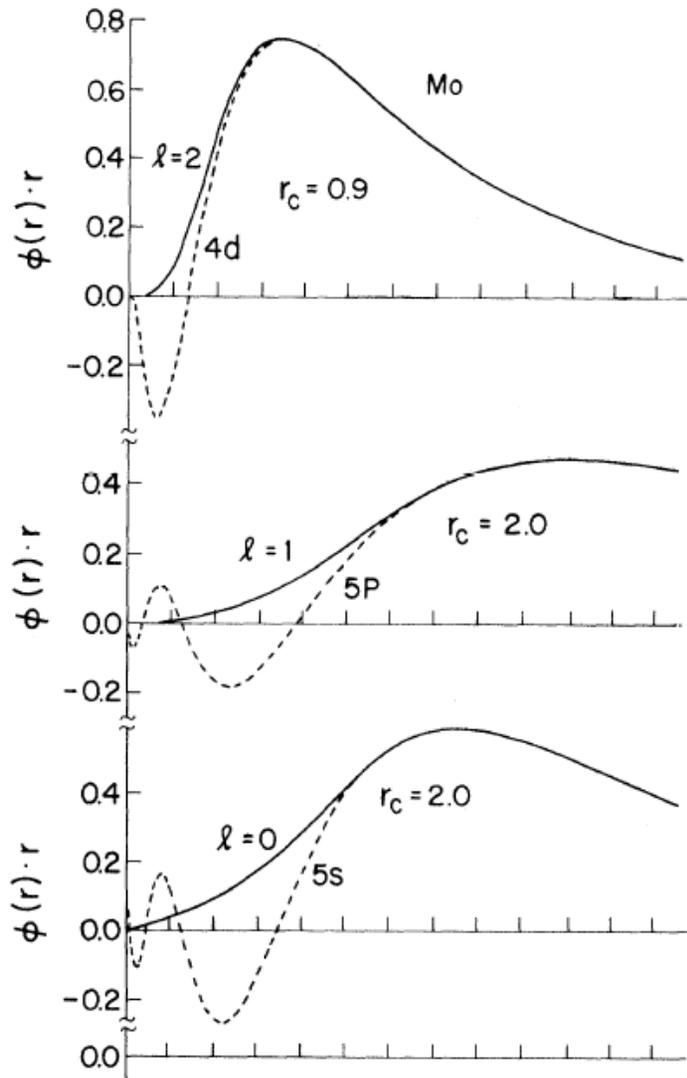
$$\rho_{\text{valence}}(\vec{r}) = \sum_i^{\text{valence, occupied}} |\tilde{\psi}_i(\vec{r})|^2$$

The pseudopotential allows wavefunctions to behave smoothly in the core region, but self-consistent screening is NOT contained in this pseudo part; it changes with environment.

Norm-Conserving Pseudopotentials

D. R. Hamann, M. Schlüter, and C. Chiang
Bell Laboratories, Murray Hill, New Jersey 07974

Phys. Rev. Letters 43, 1494 (1979)



“Transferable” (at a cost:
more plane waves than would
be needed to fit only the
valence region.

Pseudopotentials that work: From H to Pu

G. B. Bachelet,* D. R. Hamann, and M. Schlüter
Bell Laboratories, Murray Hill, New Jersey 07974

Phys. Rev. B 26, 4199 (1982)

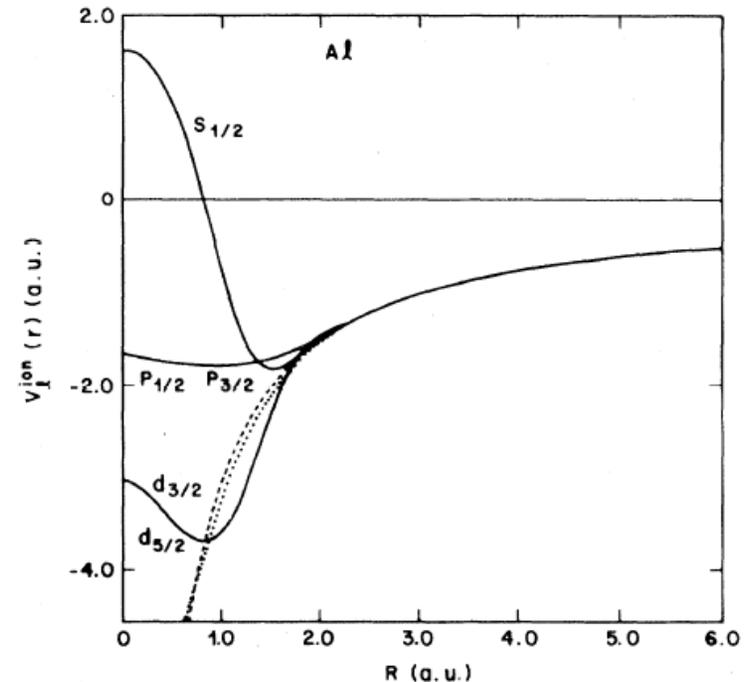


FIG. 3. Ion-core pseudopotentials for aluminum.

Kari Laasonen, Roberto Car, Changyol Lee, and David Vanderbilt,
*Implementation of Ultra-Soft Pseudopotentials in Ab-initio
Molecular Dynamics*, Phys. Rev. B **43**, 6796 (1991)

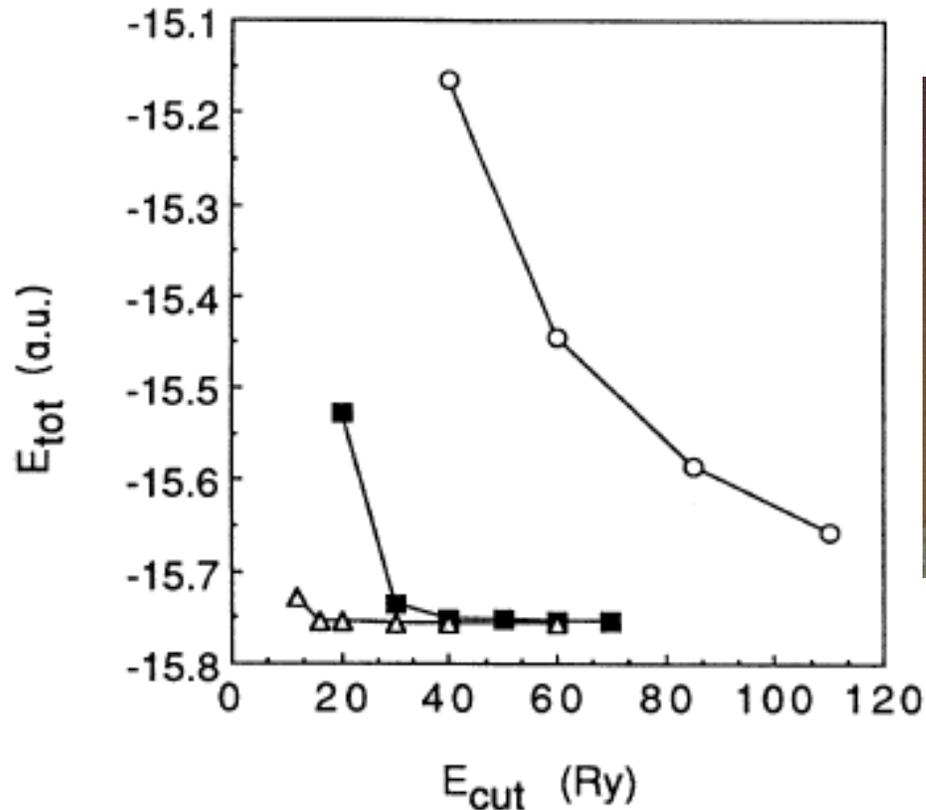


FIG. 1. Total energy of ground-state oxygen atom vs plane-wave cutoff for Bachelet-Hamann-Schlüter pseudopotential (open circles) and for Vanderbilt pseudopotential with $r_c = 1.2$ a.u. (solid squares) and $r_c = 1.8$ a.u. (open triangles).

Phys. Rev. B 50, 17953 (1994)



Projector augmented-wave method

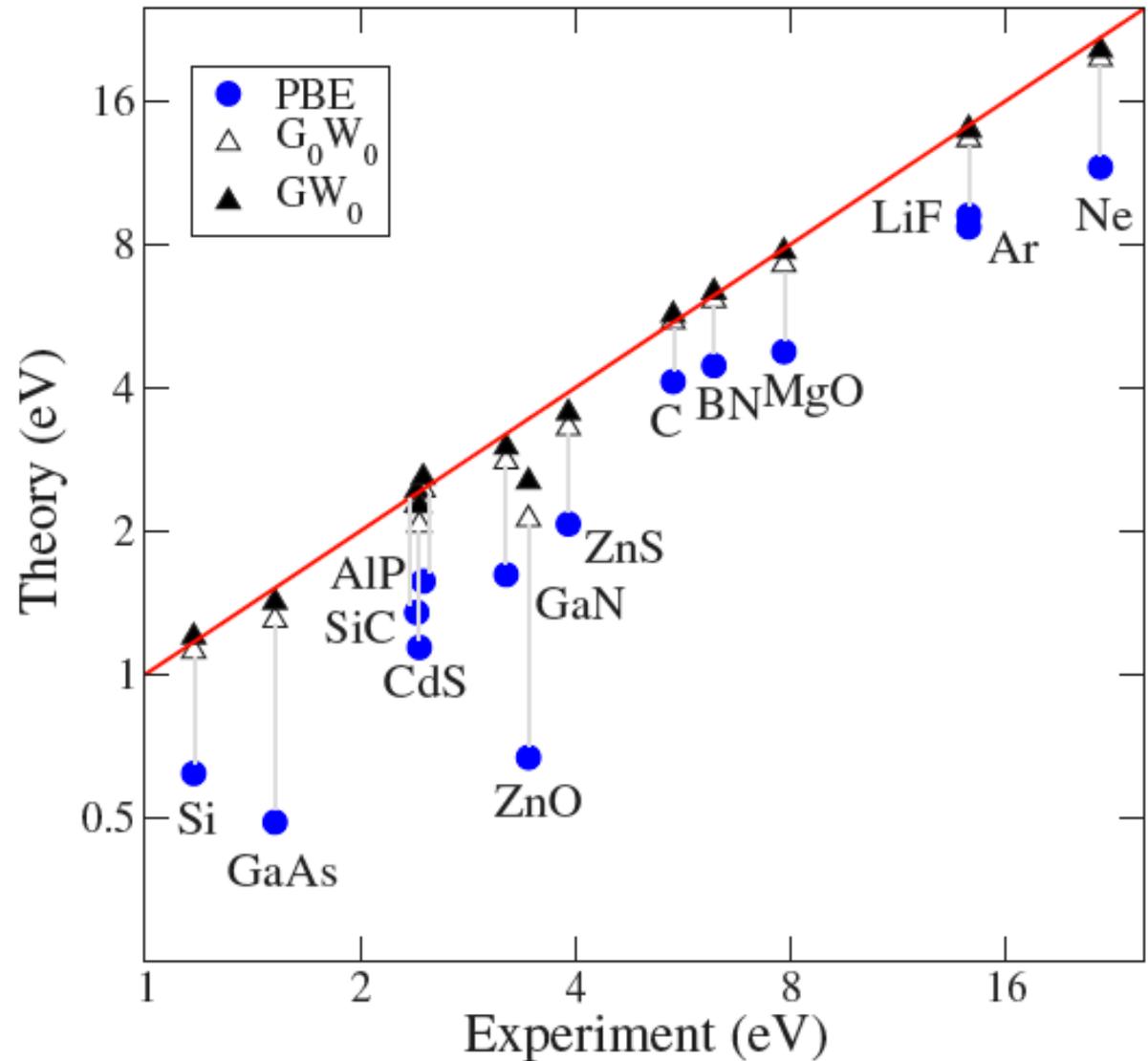
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IBM Research Division, Zurich Research Laboratory, CH-8803 Rüschlikon, Switzerland

(Received 13 June 1994; revised manuscript received 22 August 1994)

An approach for electronic structure calculations is described that generalizes both the pseudopotential method and the linear augmented-plane-wave (LAPW) method in a natural way. The method allows high-quality first-principles molecular-dynamics calculations to be performed using the original fictitious Lagrangian approach of Car and Parrinello. Like the LAPW method it can be used to treat first-row and transition-metal elements with affordable effort and provides access to the full wave function. The augmentation procedure is generalized in that partial-wave expansions are not determined by the value and the derivative of the envelope function at some muffin-tin radius, but rather by the overlap with localized projector functions. The pseudopotential approach based on generalized separable pseudopotentials can be regained by a simple approximation.

M. Shishkin and G. Kresse, Phys. Rev. B 75, 235102 (2007)
Self-consistent GW calculations for semiconductors and insulators



Thank you to all my electronic structure collaborators, especially

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Warren Pickett

Bill Butler

Jim Davenport

Mike Weinert

Renata Wentzcovitch

Mark Hybertsen

Jim Muckerman

Marivi Fernandez-Serra

Artem Oganov

and Manuel Cardona, who watched me do one by myself.