



**Felix Bloch** was born in Zurich, Switzerland, on October 23, 1905, as the son of Gustav Bloch and Agnes Bloch (*née* Mayer). From 1912 to 1918 he attended the public primary school and subsequently the "Gymnasium" of the Canton of Zurich, which he left in the fall of 1924 after having passed the "Matura", i.e. the final examination which entitled him to attend an institution of higher learning. Planning originally to become an engineer, he entered directly the [Federal Institute of Technology \(Eidgenössische Technische Hochschule\) in Zurich](#). After one year's study of engineering he decided instead to study physics, and changed therefore over to the Division of Mathematics and Physics at the same institution. During the following two years he attended, among others, courses given by [Debye](#), Scherrer, Weyl, as well as [Schrödinger](#), who taught at the same time at the [University of Zurich](#) and through whom he became acquainted, toward the end of this period, with the new wave mechanics. Bloch's interests had by that time turned toward theoretical physics. After Schrödinger left Zurich in the fall of 1927 he continued his studies with Heisenberg at the [University of Leipzig](#), where he received his degree of Doctor of Philosophy in the summer of 1928 with a dissertation dealing with the quantum mechanics of electrons in crystals and developing the theory of metallic conduction.

# A Simplification of the Hartree-Fock Method



J. C. SLATER

*Massachusetts Institute of Technology,\* Cambridge, Massachusetts*

**Phys. Rev. 81, 385 (1951)**

Slater's students included William Shockley, Richard Feynman, Art Freeman, Dick Watson, Lenny Mattheiss, etc.

$$\begin{aligned}
 H_1 u_i(x_1) + \left[ \sum_{k=1}^n \int u_k^*(x_2) u_k(x_2) (e^2/4\pi\epsilon_0 r_{12}) dx_2 \right] u_i(x_1) \\
 - \sum_{k=1}^n \left[ \int u_k^*(x_2) u_i(x_2) (e^2/4\pi\epsilon_0 r_{12}) dx_2 \right] u_k(x_1) \\
 = E_i u_i(x_1).
 \end{aligned}$$

Slater introduced the idea of the "exchange charge density" and then approximated it by the "average exchange charge density."

$$\begin{aligned}
 H_1 u_i(x_1) + \left[ \sum_{k=1}^n \int u_k^*(x_2) u_k(x_2) (e^2/4\pi\epsilon_0 r_{12}) dx_2 \right. \\
 \left. \frac{\sum_{j=1}^n \sum_{k=1}^n \int u_j^*(x_1) u_k^*(x_2) u_k(x_1) u_j(x_2) (e^2/4\pi\epsilon_0 r_{12}) dx_2}{\sum_{j=1}^n u_j^*(x_1) u_j(x_1)} \right] u_i(x_1) = E_i u_i(x_1)
 \end{aligned}$$

$$H_1 u_i(x_1) + \left[ \sum(k) \int u_k^*(x_2) u_k(x_2) (e^2/4\pi\epsilon_0 r_{12}) dx_2 - 3(e^2/4\pi\epsilon_0) \left\{ \frac{3}{8\pi} \sum(k) u_k^*(x_1) u_k(x_1) \right\}^{\frac{1}{2}} \right] u_i(x_1) = E_i u_i(x_1).$$

Finally, Slater introduced some notions from electron gas theory which motivated a local approximation for the Hartree-Fock exchange.

## Simplified LCAO Method for the Periodic Potential Problem

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*Massachusetts Institute of Technology, Cambridge, Massachusetts*

**Phys. Rev. 94, 1498 (1954)**

TABLE I. Energy integrals for crystal in terms of two-center integrals.

$E_{s,s}$	$(ss\sigma)$
$E_{s,p}$	$l(sp\sigma)$
$E_{s,p}$	$P(p\rho\sigma) + (1-P)(p\rho\pi)$
$E_{s,p}$	$lm(p\rho\sigma) - lm(p\rho\pi)$
$E_{s,p}$	$ln(p\rho\sigma) - ln(p\rho\pi)$
$E_{s,ss}$	$\sqrt{3}lm(sd\sigma)$
$E_{s,p^2}$	$\frac{1}{2}\sqrt{3}(P-m^2)(sd\sigma)$
$E_{s,p^2}$	$[n^2 - \frac{1}{2}(P+m^2)](sd\sigma)$
$E_{s,ss}$	$\sqrt{3}Pm(pd\sigma) + m(1-2P)(pd\pi)$
$E_{s,ss}$	$\sqrt{3}lm(pd\sigma) - 2lmn(pd\pi)$
$E_{s,ss}$	$\sqrt{3}Pn(pd\sigma) + n(1-2P)(pd\pi)$
$E_{s,p^2}$	$\frac{1}{2}\sqrt{3}l(P-m^2)(pd\sigma) + l(1-P+m^2)(pd\pi)$
$E_{s,p^2}$	$\frac{1}{2}\sqrt{3}n(P-m^2)(pd\sigma) - n(1+P-m^2)(pd\pi)$
$E_{s,p^2}$	$\frac{1}{2}\sqrt{3}n(P-m^2)(pd\sigma) - n(P-m^2)(pd\pi)$
$E_{s,p^2}$	$l[n^2 - \frac{1}{2}(P+m^2)](pd\sigma) - \sqrt{3}ln(pd\pi)$
$E_{s,p^2}$	$m[n^2 - \frac{1}{2}(P+m^2)](pd\sigma) - \sqrt{3}mn(pd\pi)$
$E_{s,p^2}$	$n[n^2 - \frac{1}{2}(P+m^2)](pd\sigma) + \sqrt{3}n(P+m^2)(pd\pi)$
$E_{ss,ss}$	$3Pm^2(dd\sigma) + (P+m^2-4Pm^2)(dd\pi) + (n^2+Pm^2)(ddd)$
$E_{ss,ss}$	$3lm^2n(dd\sigma) + ln(1-4m^2)(dd\pi) + ln(m^2-1)(ddd)$
$E_{ss,ss}$	$3Pmn(dd\sigma) + mn(1-4P)(dd\pi) + mn(P-1)(ddd)$
$E_{ss,p^2}$	$\frac{1}{2}lm(P-m^2)(dd\sigma) + 2lm(m^2-P)(dd\pi) + \frac{1}{2}lm(P-m^2)(ddd)$
$E_{ss,p^2}$	$\frac{1}{2}mn(P-m^2)(dd\sigma) - mn[1+2(P-m^2)](dd\pi) + mn[1+\frac{1}{2}(P-m^2)](ddd)$
$E_{ss,p^2}$	$\frac{1}{2}nl(P-m^2)(dd\sigma) + nl[1-2(P-m^2)](dd\pi) - nl[1-\frac{1}{2}(P-m^2)](ddd)$
$E_{ss,p^2}$	$\sqrt{3}lm[n^2 - \frac{1}{2}(P+m^2)](dd\sigma) - 2\sqrt{3}lmn^2(dd\pi) + \sqrt{3}lm(1+n^2)(ddd)$
$E_{ss,p^2}$	$\sqrt{3}mn[n^2 - \frac{1}{2}(P+m^2)](dd\sigma) + \sqrt{3}mn(P+m^2-n^2)(dd\pi) - \frac{1}{2}\sqrt{3}mn(P+m^2)(ddd)$
$E_{ss,p^2}$	$\sqrt{3}ln[n^2 - \frac{1}{2}(P+m^2)](dd\sigma) + \sqrt{3}ln(P+m^2-n^2)(dd\pi) - \frac{1}{2}\sqrt{3}ln(P+m^2)(ddd)$
$E_{s,p^2,p^2}$	$\frac{1}{2}(P-m^2)^2(dd\sigma) + [P+m^2-(P-m^2)^2](dd\pi) + [n^2 + \frac{1}{2}(P-m^2)^2](ddd)$
$E_{s,p^2,p^2}$	$\frac{1}{2}\sqrt{3}(P-m^2)[n^2 - \frac{1}{2}(P+m^2)](dd\sigma) + \sqrt{3}n^2(m^2-P)(dd\pi) + \frac{1}{2}\sqrt{3}(1+n^2)(P-m^2)(ddd)$
$E_{s,p^2,p^2}$	$[n^2 - \frac{1}{2}(P+m^2)]^2(dd\sigma) + 3n^2(P+m^2)(dd\pi) + \frac{1}{2}(P+m^2)^2(ddd)$

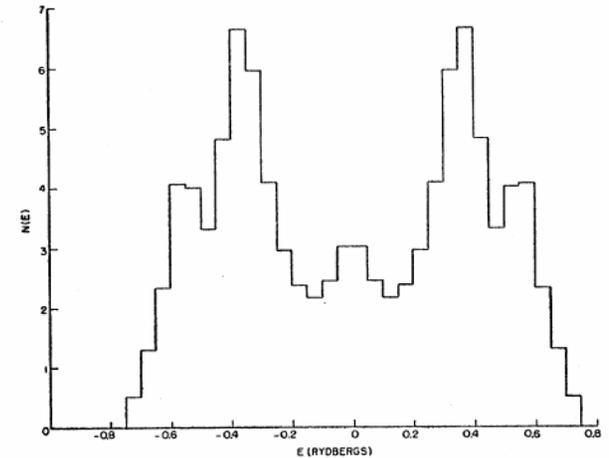
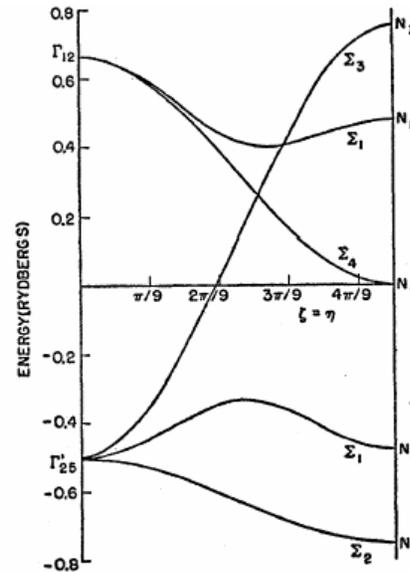


FIG. 3. Density of states curve for body-centered structure calculated using Fletcher and Wohlfarth's parameters for the nearest-neighbor  $d$  interactions. The total area under the  $N(E)$  curve is five corresponding to five states.

# Inhomogeneous Electron Gas\*

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proved that there exists a universal functional of the density,  $F[n(\mathbf{r})]$ , independent of  $v(\mathbf{r})$ , such that the expression  $E \equiv \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})]$  has as its minimum value the correct ground-state energy associated with  $v(\mathbf{r})$ . The functional  $F[n(\mathbf{r})]$  is then discussed for two situations: (1)  $n(\mathbf{r}) = n_0 + \tilde{n}(\mathbf{r})$ ,  $\tilde{n}/n_0 \ll 1$ , and (2)  $n(\mathbf{r}) = \varphi(\mathbf{r}/r_0)$  with  $\varphi$  arbitrary and  $r_0 \rightarrow \infty$ . In both cases  $F$  can be expressed entirely in terms of the correlation energy and linear and higher order electronic polarizabilities of a uniform electron gas. This approach also sheds some light on generalized Thomas-Fermi methods and their limitations. Some new extensions of

## Self-Consistent Equations Including Exchange and Correlation Effects\*

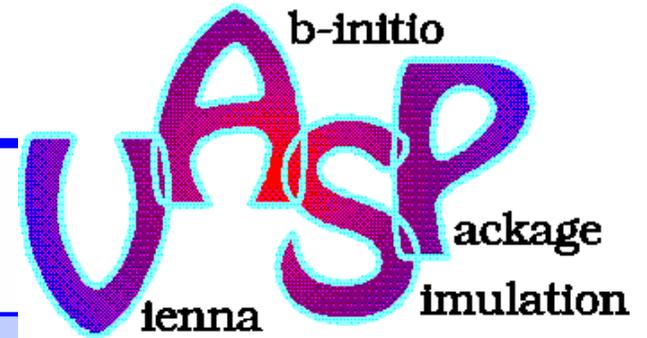
W. KOHN AND L. J. SHAM

*University of California, San Diego, La Jolla, California*

From a theory of Hohenberg and Kohn, approximation methods for treating an inhomogeneous system of interacting electrons are developed. These methods are exact for systems of slowly varying or high density. For the ground state, they lead to self-consistent equations analogous to the Hartree and Hartree-Fock equations, respectively. In these equations the exchange and correlation portions of the chemical potential of a uniform electron gas appear as additional effective potentials. (The exchange portion of our effective potential differs from that due to Slater by a factor of  $\frac{2}{3}$ .) Electronic systems at finite temperatures and in

**Phys. Rev. 136, B864 (1964)**

**Phys. Rev. 140, A1133 (1965)**



*Density-functional theory - HKS theorem*

**Hohenberg-Kohn-Sham theorem:**

- (1) The ground-state energy of a many-body system is a unique functional of the particle density,  $E_0 = E[n_0(\vec{r})]$ .
- (2) The functional  $E[n_0(\vec{r})]$  has its minimum relative to variations  $\delta n(\vec{r})$  of the particle density at the equilibrium density  $n_0(\vec{r})$ ,

$$E = E[n_0(\vec{r})] = \min \{E[n(\vec{r})]\} \tag{1}$$
$$\left. \frac{\delta E[n(\vec{r})]}{\delta n(\vec{r})} \right|_{n(\vec{r})=n_0(\vec{r})} = 0$$

### *Proof - HKS theorem*

Reductio ad absurdum:

$$H = T + V_{ee} + V \quad (2)$$

is the Hamiltonian of a many-electron system in an external potential  $V(\vec{r})$  and with an electron-electron interaction  $V_{ee}$ . In the ground-state this system has the energy  $E_0$ , with  $E_0 = \langle \psi_0 | H | \psi_0 \rangle$  and the particle density  $n_0(\vec{r}) = |\langle \psi_0 | \vec{r} \rangle|^2$ . Let us assume that a different external potential  $V'$  leads to a different ground-state  $\psi'_0$ , but to the same particle density:  $n'_0(\vec{r}) = |\langle \psi'_0 | \vec{r} \rangle|^2 = n_0(\vec{r})$ . According to the variational principle it follows that

$$\begin{aligned} E'_0 < \langle \psi_0 | H' | \psi_0 \rangle &= \langle \psi_0 | (H + V' - V) | \psi_0 \rangle \\ &= E_0 + \langle \psi_0 | (V' - V) | \psi_0 \rangle \end{aligned} \quad (3)$$

### *Proof - HKS theorem*

$$E'_0 < E_0 + \int n_0(\vec{r})[V'(\vec{r}) - V(\vec{r})]d^3r \quad (4)$$

Starting from

$$E_0 < \langle \psi'_0 | H | \psi'_0 \rangle \quad (5)$$

and using  $n'_0(\vec{r}) = n_0(\vec{r})$  it follows

$$\begin{aligned} E_0 &< E'_0 + \int n'_0(\vec{r})[V(\vec{r}) - V'(\vec{r})]d^3r \\ &= E'_0 + \int n_0(\vec{r})[V(\vec{r}) - V'(\vec{r})]d^3r \end{aligned} \quad (6)$$

in direct contradiction to the results obtained above. Hence  $n'_0(\vec{r})$  and  $n_0(\vec{r})$  must be different and  $V(\vec{r})$  is a unique functional of  $n(\vec{r})$ .

The variational property of the Hohenberg-Kohn-Sham functional is a direct consequence of the general variational principle of quantum mechanics.

## *HKS theorem - Variational principle*

With

$$\begin{aligned} F[n(\vec{r})] &= \langle \psi | T + V_{ee} | \psi \rangle \\ E[n(\vec{r})] &= F[n(\vec{r})] + \int n(\vec{r})V(\vec{r})d^3r \end{aligned} \quad (7)$$

it follows

$$\begin{aligned} E[(n'(\vec{r}))] &= \langle \psi' | T + V_{ee} | \psi' \rangle + \langle \psi' | V | \psi' \rangle \\ &= F[n'(\vec{r})] + \int n'(\vec{r})V(\vec{r})d^3r \\ &> \langle \psi_0 | T + V_{ee} | \psi_0 \rangle + \langle \psi_0 | V | \psi_0 \rangle = E[n_0(\vec{r})] \\ &= F[n_0(\vec{r})] + \int n_0(\vec{r})V(\vec{r})d^3r \end{aligned} \quad (8)$$

and hence

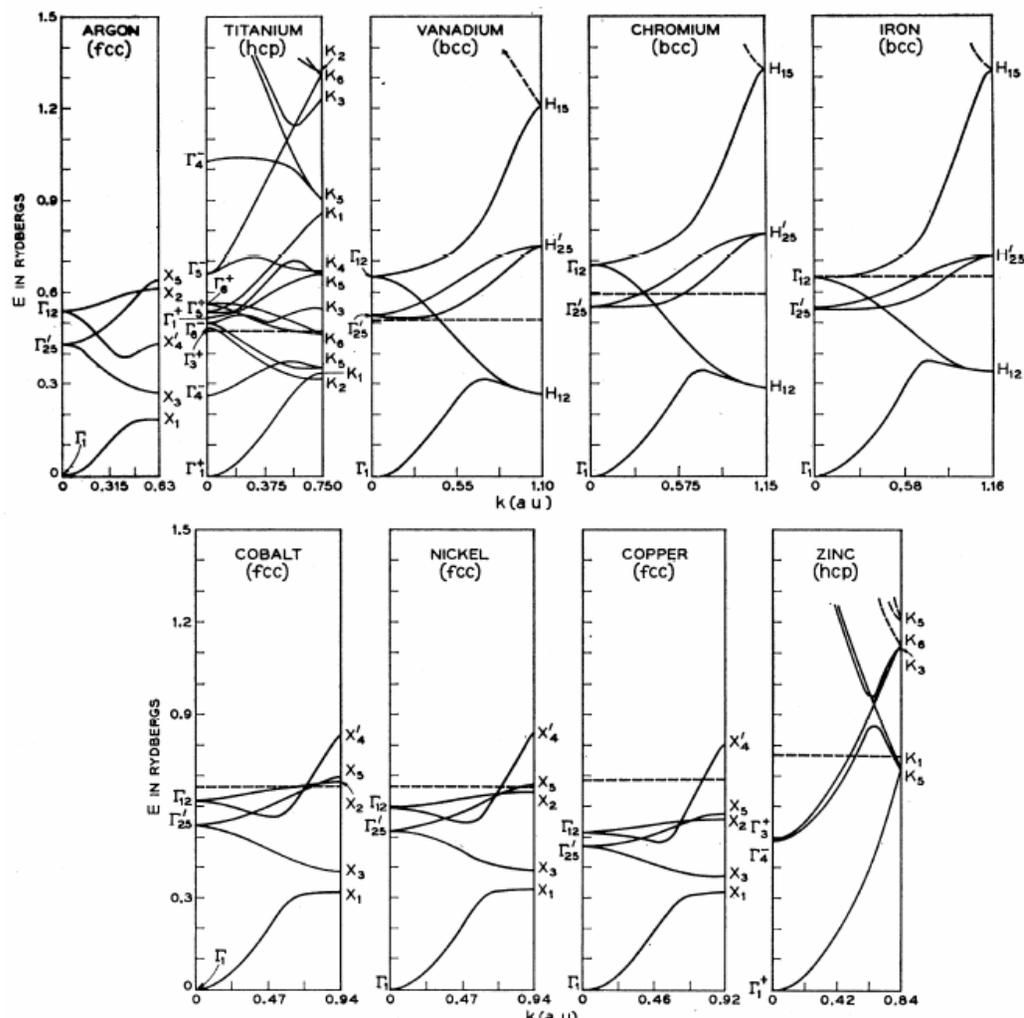
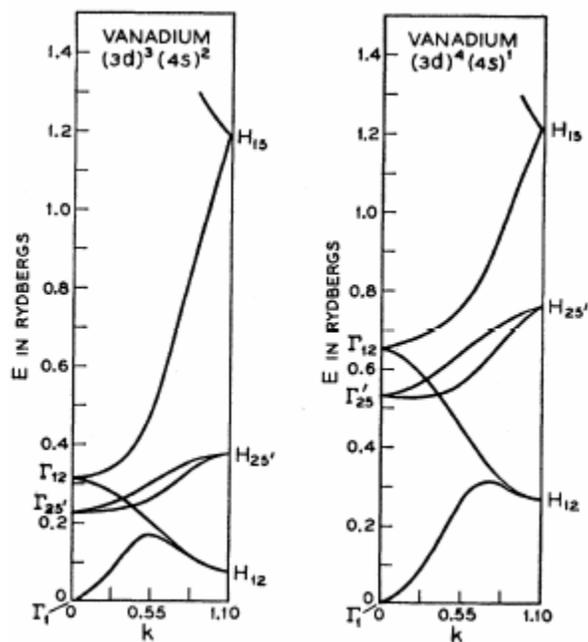
$$\begin{aligned} E_0 = E[n_0(\vec{r})] &= \min \{E[n(\vec{r})]\} \\ \frac{\delta E[n(\vec{r})]}{\delta n(\vec{r})} \Big|_{n(\vec{r})=n_0(\vec{r})} &= 0 \end{aligned} \quad (9)$$

# Energy Bands for the Iron Transition Series\*

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**Phys. Rev. 134, A970 (1964)**  
**(cited 264 times)**



# New Method for Calculating Wave Functions in Crystals and Molecules

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**Phys. Rev. 116, 287 (1959)**

<sup>†</sup> National Science Foundation Postdoctoral Fellow.

<sup>‡</sup> National Science Foundation Predoctoral Fellow.

<sup>1</sup> C. Herring, Phys. Rev. **57**, 1169 (1940).

<sup>2</sup> V. Heine, Proc. Roy. Soc. (London) **A240**, 340 (1957).

<sup>3</sup> F. Herman, Phys. Rev. **88**, 1210 (1952); **93**, 1214 (1954).

<sup>4</sup> J. C. Slater, Phys. Rev. **92**, 603 (1953).

We begin by imagining that we *know* the exact crystal wave function  $\psi_\alpha$  which transforms according to an irreducible representation of the cubic point group  $\Gamma_\alpha$  which has *s* or *p* atomic symmetry.<sup>7</sup> Since  $\psi_\alpha$  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  $\varphi$  to be a single plane wave Herring's<sup>1</sup> results would follow.

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

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**Phys. Rev. 141, 789-796 (1966) [cited 1217 times]**

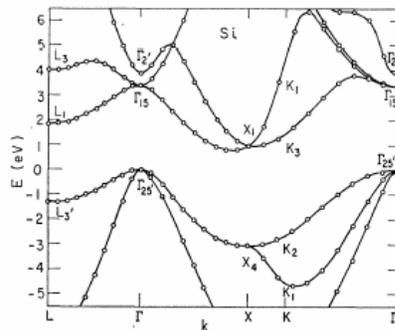
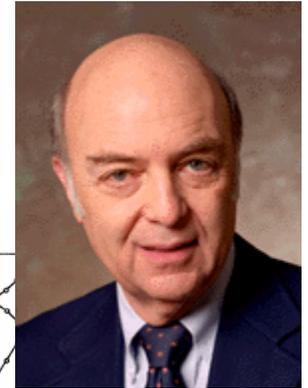


FIG. 1. Band structure of Si.

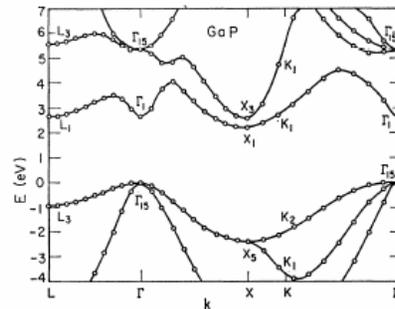


FIG. 4. Band structure of GaP.

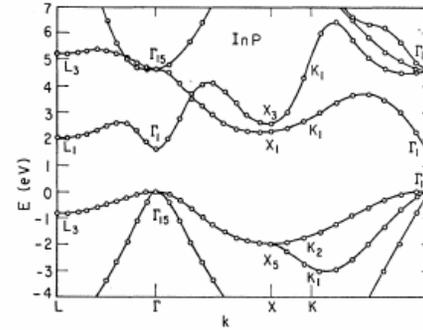


FIG. 7. Band structure of InP.

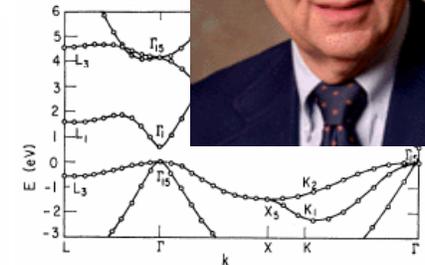


FIG. 10. Band structure of InS.

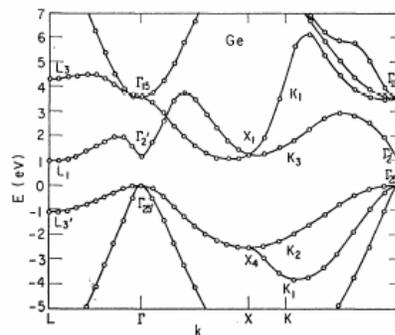


FIG. 2. Band structure of Ge.

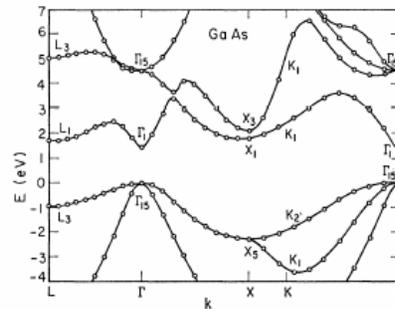


FIG. 5. Band structure of GaAs.

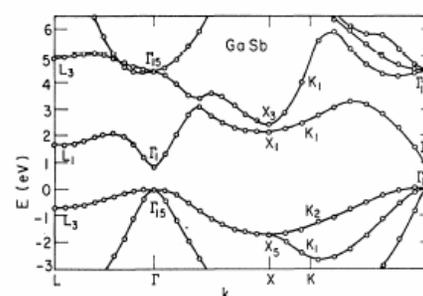


FIG. 8. Band structure of GaSb.

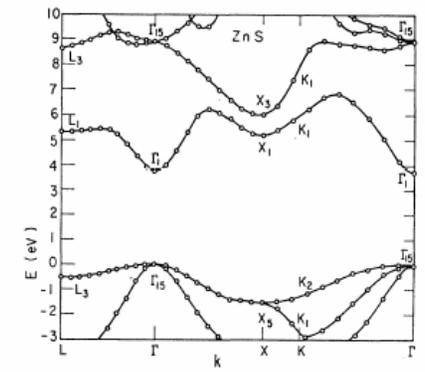


FIG. 11. Band structure of ZnS.

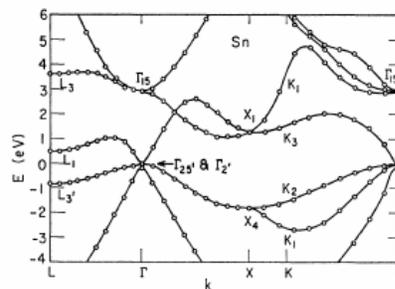


FIG. 3. Band structure of Sn.

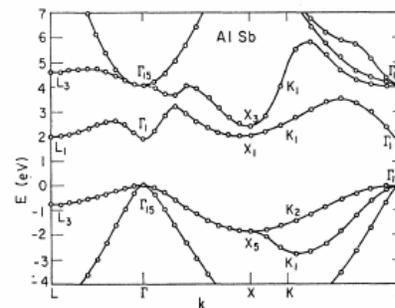


FIG. 6. Band structure of AlSb.

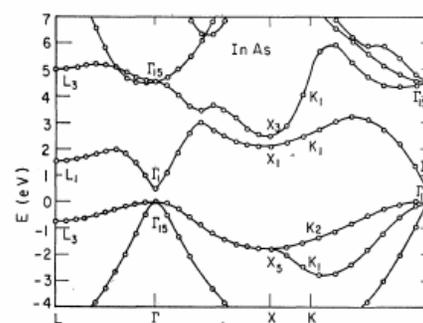


FIG. 9. Band structure of InAs.

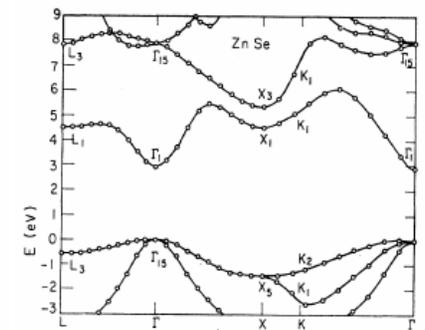


FIG. 12. Band structure of ZnSe.

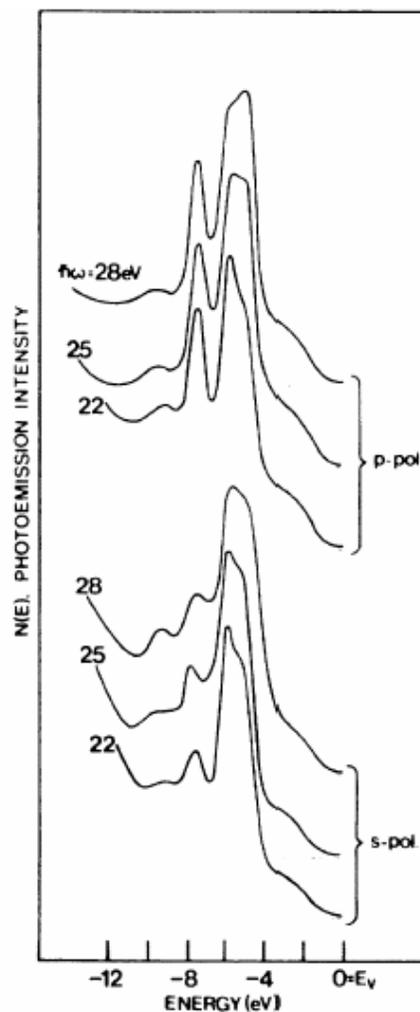
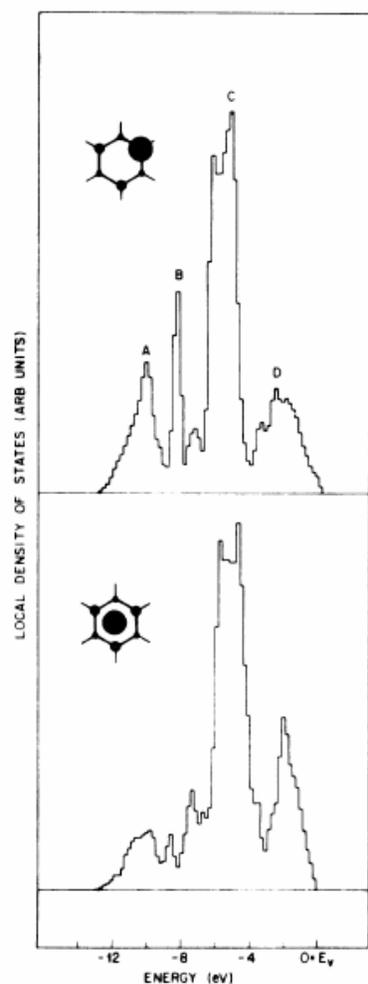
# Chemisorption-Site Geometry from Polarized Photoemission: Si(111)Cl and Ge(111)Cl<sup>†</sup>

M. Schluter, J. E. Rowe, and G. Margaritondo\*  
*Bell Laboratories, Murray Hill, New Jersey 07974*

and

K. M. Ho and Marvin L. Cohen  
*Physics Department, University of California, Berkeley, California 94270, and Molecular and Materials  
Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94270*

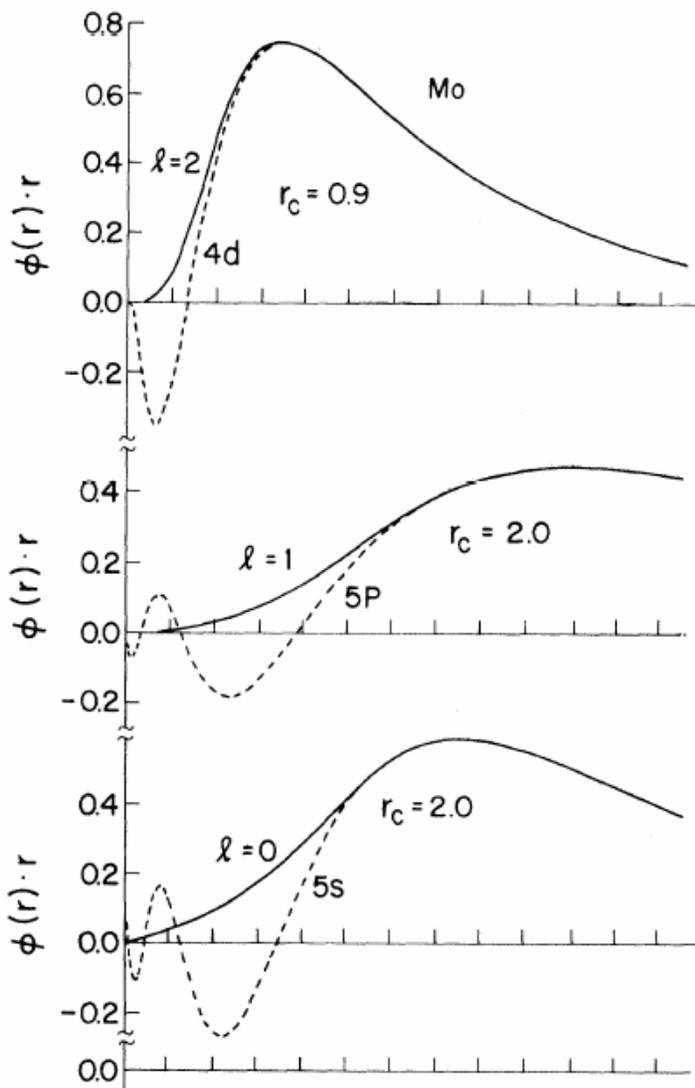
**Phys. Rev. Lett. 37, 1632 (1976)**



# Norm-Conserving Pseudopotentials

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

**Phys. Rev. Letters 43, 1494 (1979)**



## 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)**

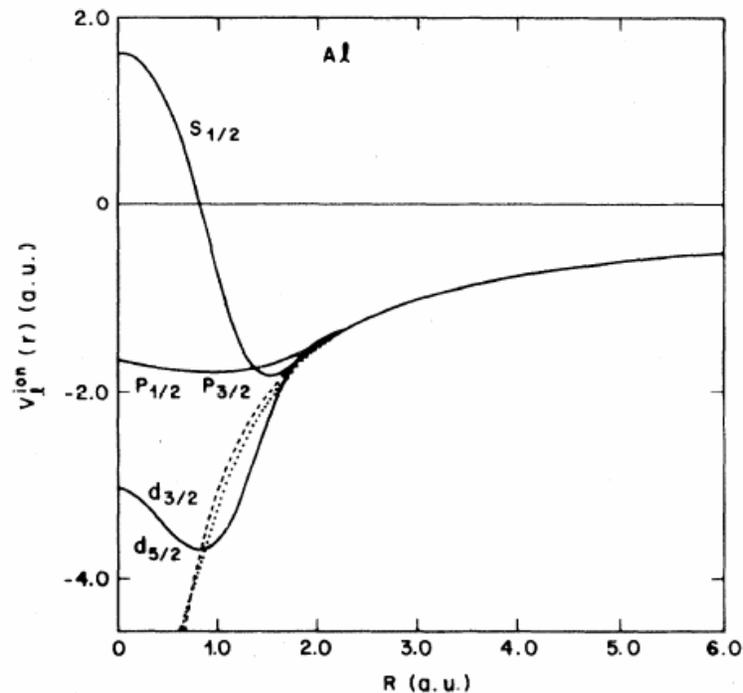


FIG. 3. Ion-core pseudopotentials for aluminum.

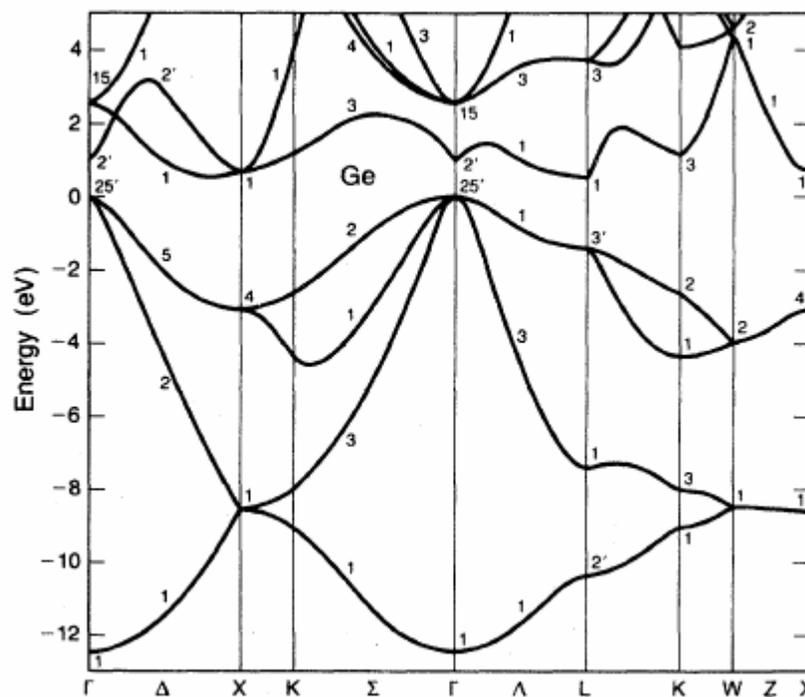
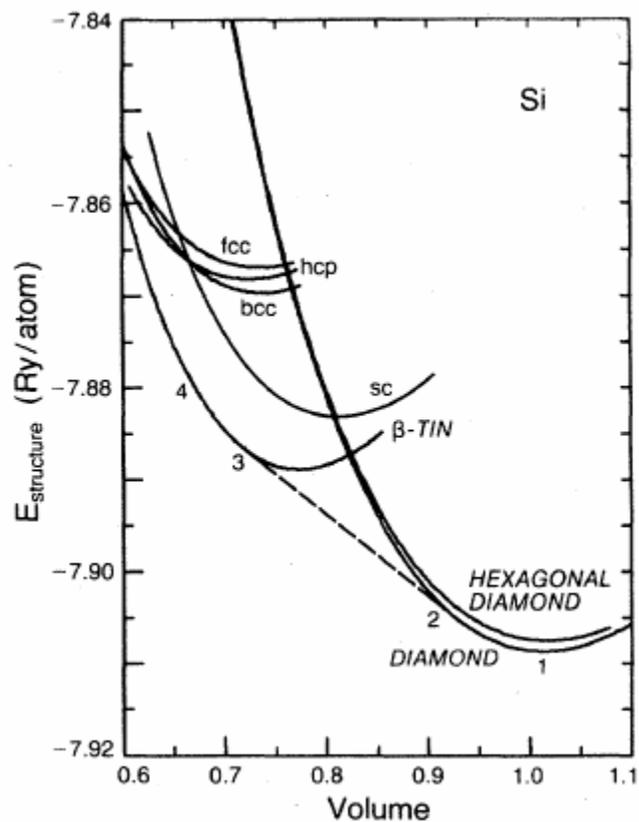
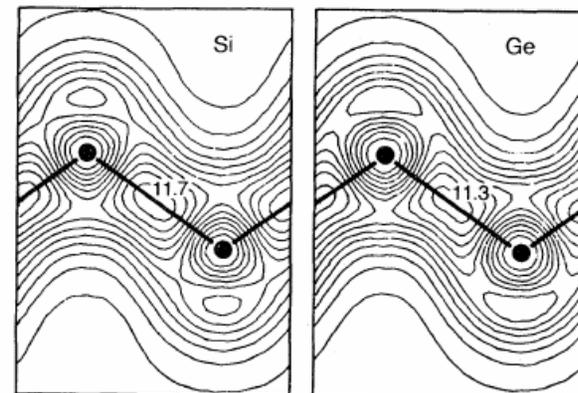
# Theory of static structural properties, crystal stability, and phase transformations: Application to Si and Ge

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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.

# Unified Approach for Molecular Dynamics and Density-Functional Theory



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and

M. Parrinello

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International School for Advanced Studies, Trieste, Italy*



**Phys. Rev. Letters 55, 2471 (1985)**

$$L = \sum_i \frac{1}{2} \mu \int_{\Omega} d^3r |\dot{\psi}_i|^2 + \sum_I \frac{1}{2} M_I \dot{R}_I^2 + \sum_{\nu} \frac{1}{2} \mu_{\nu} \dot{\alpha}_{\nu}^2 - E[\{\psi_i\}, \{R_I\}, \{\alpha_{\nu}\}]$$

where the  $\psi_i$  are subject to the holonomic constraints

$$\int_{\Omega} d^3r \psi_i^*(\mathbf{r}, t) \psi_j(\mathbf{r}, t) = \delta_{ij}. \quad (4)$$

$$E[\{\psi_i\}, \{R_I\}, \{\alpha_{\nu}\}] = \sum_i \int_{\Omega} d^3r \psi_i^*(\mathbf{r}) [- (\hbar^2/2m) \nabla^2] \psi_i(\mathbf{r}) + U[n(\mathbf{r}), \{R_I\}, \{\alpha_{\nu}\}].$$

**Simultaneous iterative diagonalization, iterative self-consistency  
and evolution of classical atomic trajectories**

$$\mu \ddot{\psi}_i(\mathbf{r}, t) = - \delta E / \delta \psi_i^*(\mathbf{r}, t) + \sum_k \Lambda_{ik} \psi_k(\mathbf{r}, t),$$

$$M_I \ddot{R}_I = - \nabla_{R_I} E,$$

$$\mu_{\nu} \ddot{\alpha}_{\nu} = - (\partial E / \partial \alpha_{\nu}), \quad \text{external constraints}$$



*Theory of quasiparticle surface states in semiconductor surfaces*  
 Mark S. Hybertsen and Steven G. Louie, Phys. Rev. B **38**, 4033 (1988)

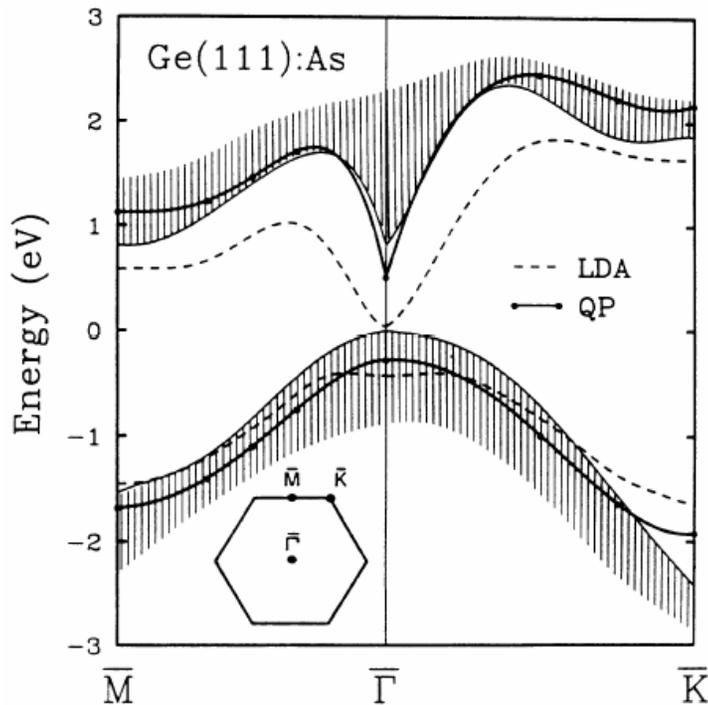
$$[T + V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r})]\psi(\mathbf{r}) + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}'; E^{\text{QP}})\psi(\mathbf{r}') = E^{\text{QP}}\psi(\mathbf{r})$$

$$\Sigma(\mathbf{r}, \mathbf{r}'; E) = \frac{i}{2\pi} \int d\omega e^{-i\delta\omega} G(\mathbf{r}, \mathbf{r}'; E - \omega) W(\mathbf{r}, \mathbf{r}'; \omega)$$

"GW" approximation (Hedin)

$$W(\mathbf{r}, \mathbf{r}'; \omega) = \frac{1}{\Omega} \int d\mathbf{r}'' \epsilon^{-1}(\mathbf{r}, \mathbf{r}''; \omega) V_C(\mathbf{r}'' - \mathbf{r}')$$

$\epsilon^{-1}$  is the time-ordered dielectric matrix

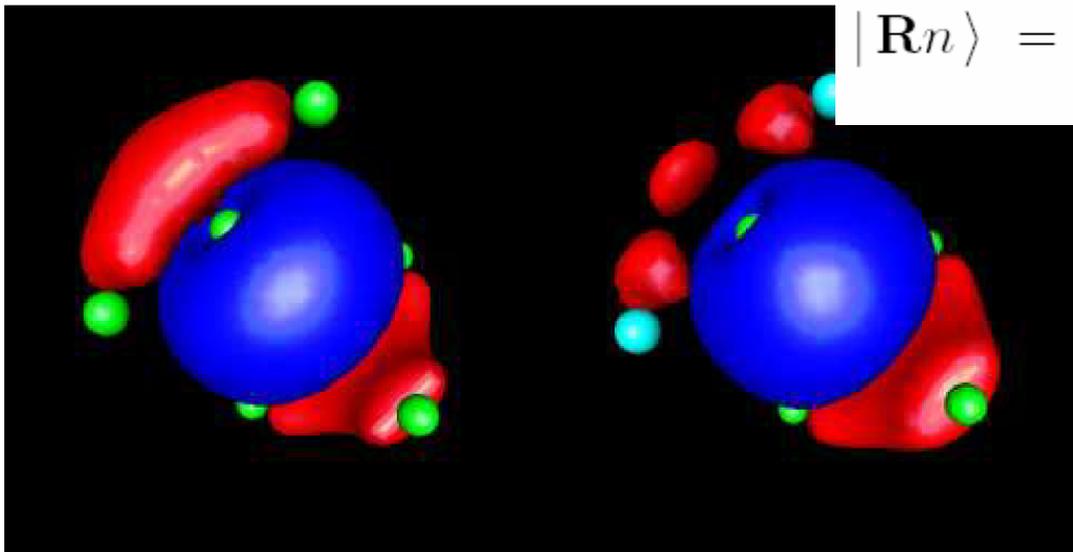


*Quasiparticle calculation of valence band offset of AlAs-GaAs(001)*  
 S. B. Zhang, D. Tománek, Steven G. Louie, Marvin L. Cohen  
 and Mark S. Hybertsen Department of Physics, University of California,  
 Berkeley, California 94720, USA



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)

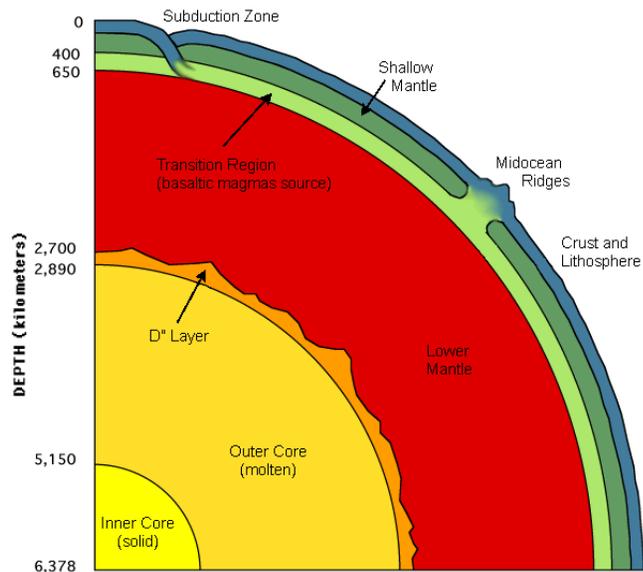
*Electric polarization as a bulk quantity and its relation to surface charge*, David Vanderbilt and R. D. King-Smith, Phys. Rev. B **48**, 4442 (1993)



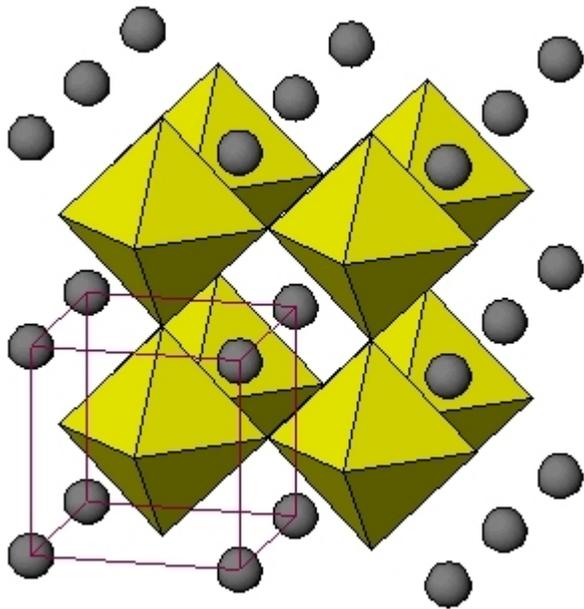
$$|\mathbf{R}n\rangle = \frac{V}{(2\pi)^3} \int_{BZ} |\psi_{n\mathbf{k}}\rangle e^{i\varphi_n(\mathbf{k}) - i\mathbf{k}\cdot\mathbf{R}} d\mathbf{k}$$

Nicola Marzari and David Vanderbilt, *Maximally localized generalized Wannier functions for composite energy bands*, Phys. Rev. B **56**, 12847 (1997)

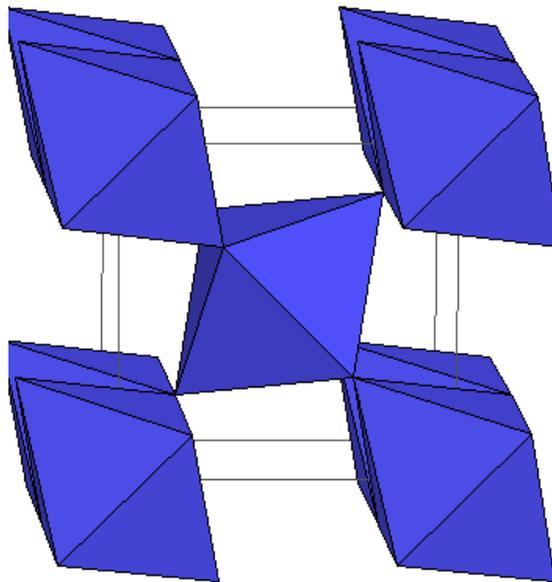
Figure 1: Amplitude isosurface contours for maximally-localized Wannier functions in Si (left panel) and GaAs (right panel). Red and blue contours are for isosurfaces of identical absolute value but opposite signs; Si and As atoms are in green, Ga in cyan. Each unit cell displays four (spin-unpolarized) equivalent WFs, localized around the centers of the four covalent bonds; breaking of inversion symmetry in GaAs polarizes the WFs towards the more electronegative As anion.



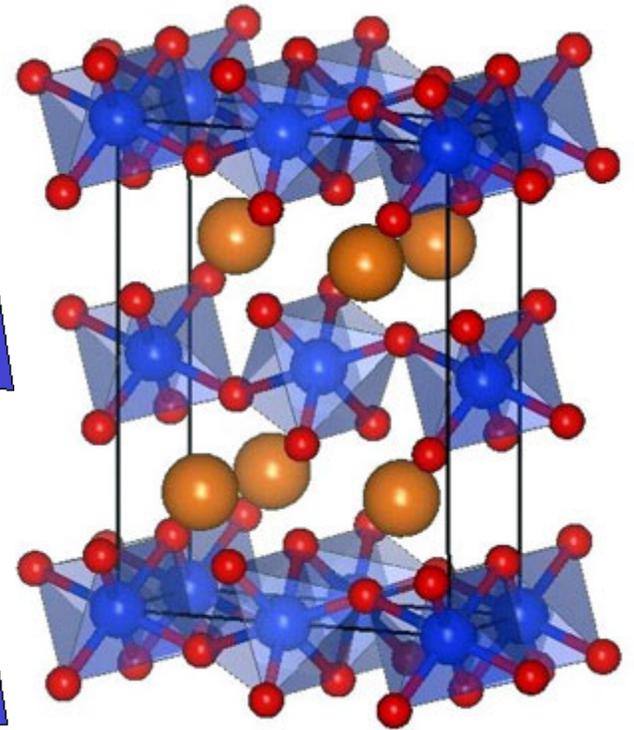
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Perovskite  
 $ABX_3$



Rutile  
 $BX_2$



New phase  
 $ABX_3$