

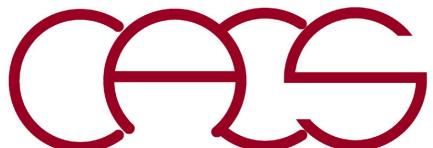
Tight-Binding Model of Electronic Structures

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Goals: Quantum eigenvalue problem
Vectors (projection &
addition theorem)

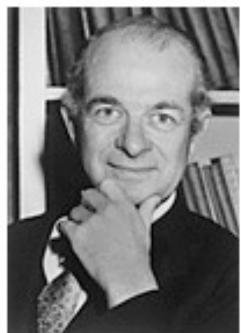


Electronic Structures



The Nobel Prize in Chemistry 1954

"for his research into the nature of the chemical bond and its application to the elucidation of the structure of complex substances"



Linus Carl Pauling

- Atomic wave functions
- Bonds
- Bands
- Reaction
- ...



The Nobel Prize in Chemistry 1981

"for their theories, developed independently, concerning the course of chemical reactions"



Kenichi Fukui



Roald Hoffmann



The Nobel Prize in Chemistry 1966

"for his fundamental work concerning chemical bonds and the electronic structure of molecules by the molecular orbital method"

PHYSICAL REVIEW

VOLUME 136, NUMBER 3B

9 NOVEMBER 1964



Robert S. Mulliken

Inhomogeneous Electron Gas*

P. HOHENBERG†

École Normale Supérieure, Paris, France

AND

W. KOHN‡

École Normale Supérieure, Paris, France and Faculté des Sciences, Orsay, France

and

University of California at San Diego, La Jolla, California

(Received 18 June 1964)

This paper deals with the ground state of an interacting electron gas in an external potential $v(r)$. It is proved that there exists a universal functional of the density, $F[n(r)]$, independent of $v(r)$, such that the expression $E = \int v(r)n(r)dx + F[n(r)]$ has as its minimum value the correct ground-state energy associated with $v(r)$. The functional $F[n(r)]$ is then discussed for two situations: (1) $n(r) = n_0 + \bar{n}(r)$, $\bar{n}/n_0 < 1$, and (2) $n(r) = \varphi(r/r_0)$ with φ 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 these methods are presented.



Walter Kohn



The Nobel Prize in Chemistry 1998

"for his development of the density-functional theory"



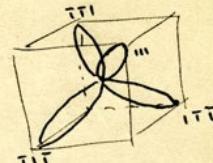
John A. Pople

Pauling's Note (1930)

Calculations such as these are simplified by the fact that for a complete orthogonal transformation the sum of the squares of the coefficients for a given initial eigen ψ is unity. ③

Four equivalent bonds from p³.

$$\begin{aligned}\psi_{111} &= \frac{1}{2}(x + y + z) & \text{Max. value.} \\ \psi_{111}^* &= \frac{1}{2}(x + y - z) \\ \psi_{111}^* &= \frac{1}{2}(x - y + z) \\ \psi_{111}^* &= \frac{1}{2}(x - y - z)\end{aligned}$$



We can point one ψ along the x axis, say.

$$\begin{aligned}\psi_1 &= \frac{1}{2}x + \frac{\sqrt{3}}{2}z \\ \psi_2 &= \frac{1}{2}x - \frac{\sqrt{3}}{2}z + \frac{\sqrt{2}}{2}y \\ \psi_3 &= \frac{1}{2}x - \frac{\sqrt{3}}{2}z - \frac{\sqrt{2}}{2}y + \frac{1}{2}y \\ \psi_4 &= \frac{1}{2}x - \frac{\sqrt{3}}{2}z - \frac{\sqrt{2}}{2}y - \frac{1}{2}y\end{aligned}$$

The coeff. of z is $\frac{1}{2}$ to make the ψ 's equivalent.
Then the coeffs. of y are fixed for norm. with x .

tetrahedral angles. But if R_s stretches out farther than R_p (which it actually does for same $Z_{eff.}$), then things are different.
Let us assume $\text{Max } s = \text{Max } p = 1$. Then

$$\frac{d}{da}(a + \sqrt{1-a^2}) = 0, a = \frac{1}{\sqrt{2}}. \text{ Maximum possible} = \sqrt{2} = 1.414$$

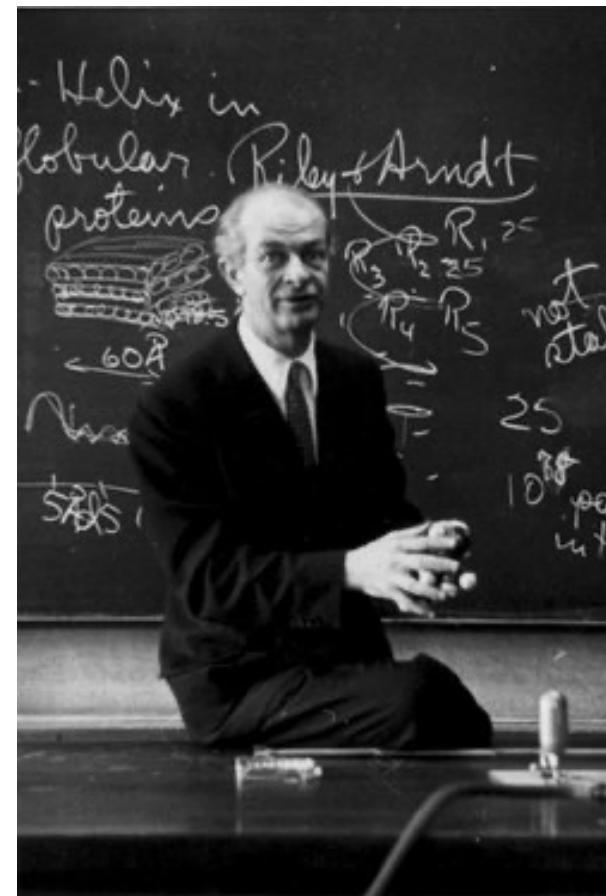
Two bonds, Max value

$$\begin{aligned}\sigma_+ &= 1.414 \\ \sigma_- &= 1.414\end{aligned}$$

Three equal bonds : 1.392

Four equal bonds : 1.366

In this case two strong bonds will be oppositely directed (linear molecule), three will lie in a plane, four towards tetrahedron corners.



[Linus Pauling online](#)
at Oregon State Univ.

cf. [Sixth bond? \(Adv. Sci. News\)](#)
[Raty et al.,](#)
[Adv. Mater. 31, 1806280 \('19\)](#)

Energy Eigenstates

- Time-independent Schrödinger equation

$$\begin{array}{ccc} \text{Hamiltonian} & \longrightarrow & \text{Eigenstate} \\ \text{operator} & & \\ & & \text{Eigenvalue} \end{array}$$

- Stationary state

$$i\hbar \frac{\partial}{\partial t} \psi(t) = H\psi(t)$$

$$\psi(t) = \exp(-i\epsilon_n t/\hbar) \psi_n$$

- Hamiltonian operator

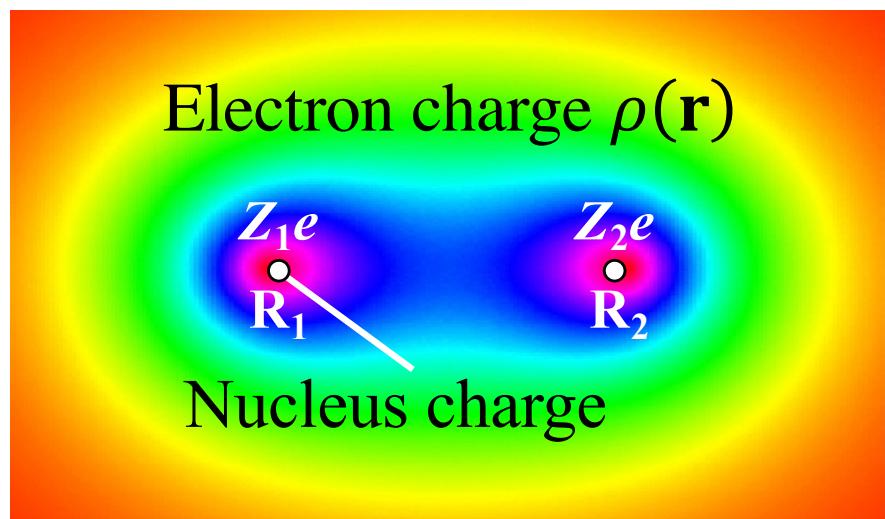
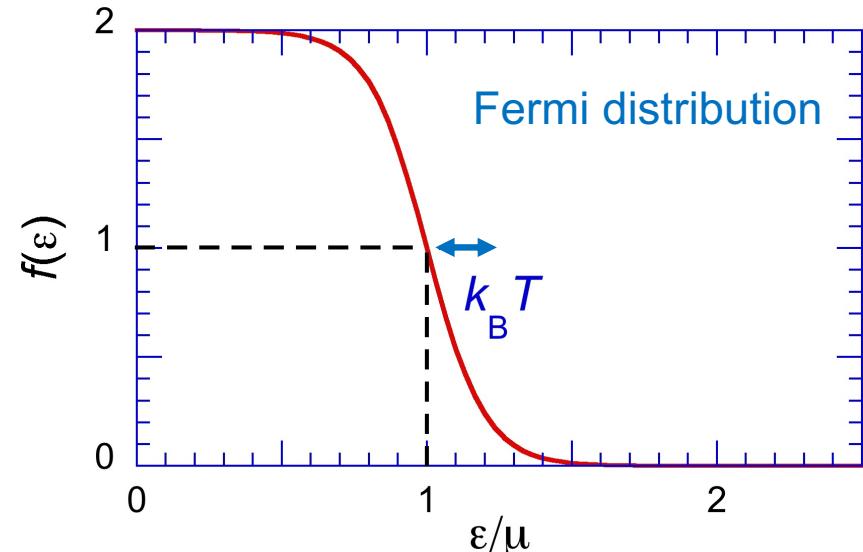
$$H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}_i^2} + v(\mathbf{r})$$

- Density functional theory

$$v(\mathbf{r}) = - \sum_I \frac{Z_I e^2}{|\mathbf{r} - \mathbf{R}_I|} + \int d\mathbf{r}' \frac{e^2 \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_n \frac{2}{\exp\left(\frac{\epsilon_n - \mu}{k_B T}\right) + 1} |\psi_n(\mathbf{r})|^2$$

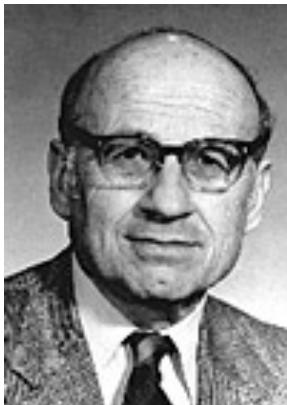
exchange-correlation potential



See PHY760: Extreme-scale Quantum Simulations
<https://aiichironakano.github.io/phys760.html>

Density Functional Theory

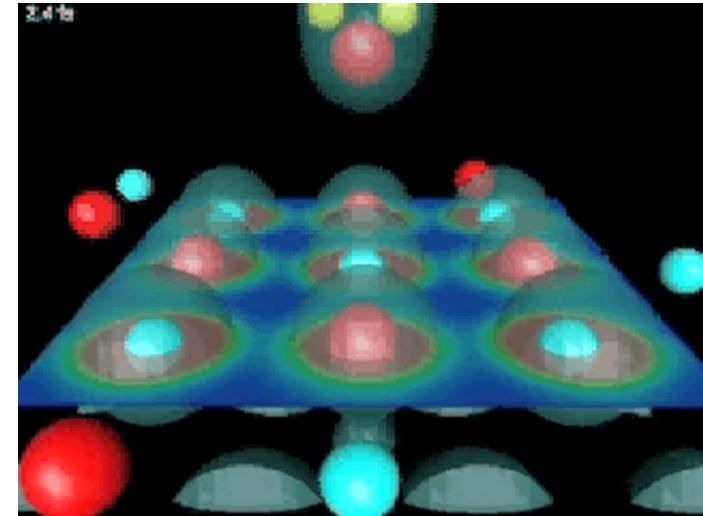
Challenge: Complexity of quantum N -body problem



Density functional theory (DFT)

(Walter Kohn, Nobel Chemistry Prize, '98)

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_{\text{el}}}) \underset{\text{red arrow}}{O(C^N)}$$
$$\{\psi_n(\mathbf{r}) | n = 1, \dots, N_{\text{el}}\} \underset{\text{red arrow}}{O(N^3)}$$



- P. Hohenberg & W. Kohn, “Inhomogeneous electron gas,”
Phys. Rev. **136**, B864 ('64)

The electronic ground state is a functional of the electron density $\rho(\mathbf{r})$

- W. Kohn & L. Sham, “Self-consistent equations including exchange & correlation effects,” *Phys. Rev.* **140**, A1133 ('65)

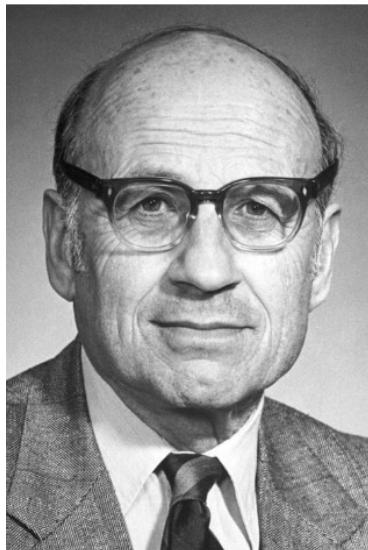
Derived a formally exact self-consistent single-electron equations for many-electron systems (*cf.* the previous page)

See DFT reading list:

<https://aiichironakano.github.io/phys516/DFT-seminar.tar.gz>

1998 Nobel Chemistry Prize

Nobel Prize in Chemistry 1998



Physicist: Algorithm

Photo from the Nobel Foundation archive.

Walter Kohn

Prize share: 1/2

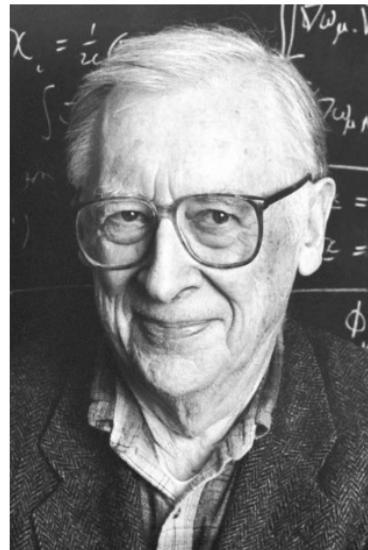


Photo from the Nobel Foundation archive.

John A. Pople

Prize share: 1/2

Chemist: Software



The Nobel Prize in Chemistry 1998 was divided equally between Walter Kohn "for his development of the density-functional theory" and John A. Pople "for his development of computational methods in quantum chemistry"

Walter Kohn (1923-2016)

Book chapter No access

DENSITY FUNCTIONAL THEORY OF SUPERCONDUCTORS REGARDED AS TWO-COMPONENT PLASMAS

Walter KOHN

Pages 331-335

 Purchase

Book chapter No access

GREEN'S FUNCTION AND DYNAMIC CORRELATIONS OF ELECTRONS IN METALS

Aiichiro NAKANO and Setsuo ICHIMARU

Pages 337-340

 Purchase

Strongly Coupled Plasma Physics

Proceedings of Yamada Conference XXIV on Strongly Coupled Plasma Physics, Lake Yamanaka, Japan, August 29–September 2, 1989



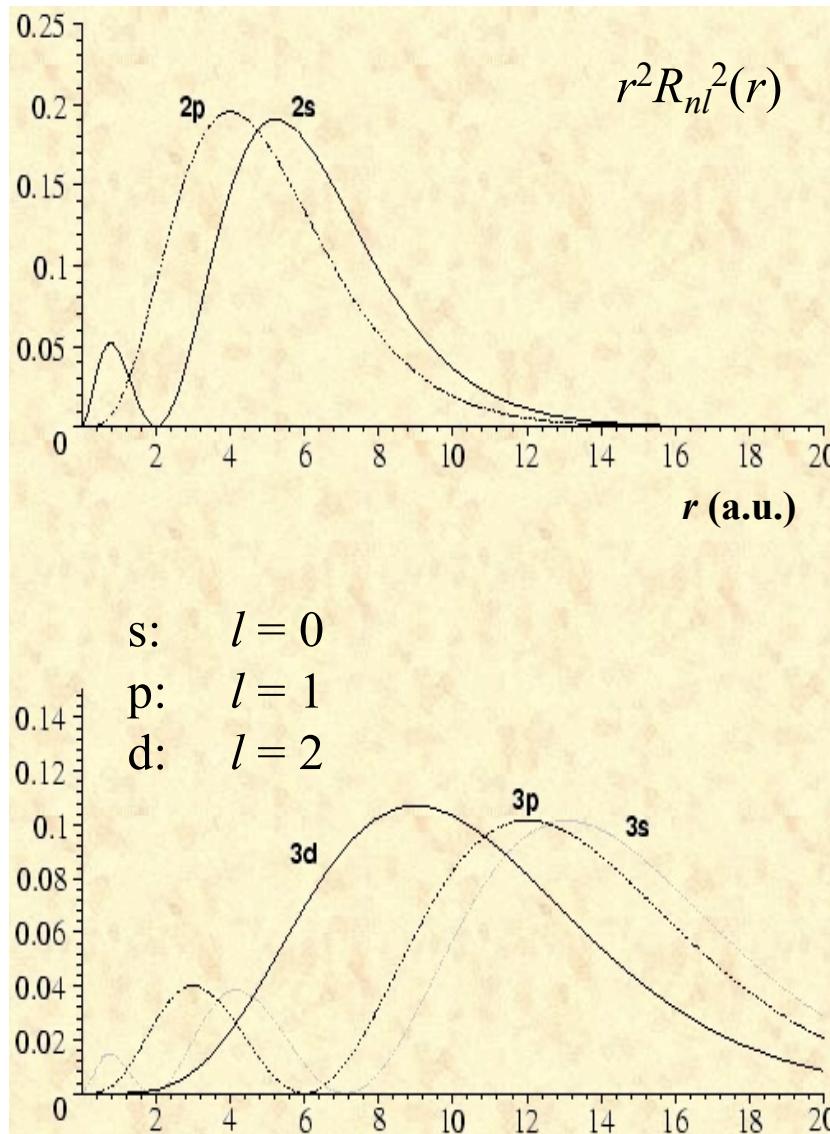
Background: Atomic Orbitals

$$\begin{cases} n = 1, 2, \dots \\ l \in [0, n-1] \\ m \in [-l, l] \end{cases} \quad \psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi) \quad \begin{array}{ll} \text{Radial function} & \text{Spherical harmonics} \end{array} \quad \begin{array}{ll} \text{s: } l=0 & \\ \text{p: } l=1 & \\ \text{d: } l=2 & \end{array}$$

- Hydrogen eigenstates ($\rho = v_{xc} = 0$)

	n	ℓ	m	$R_{nl\ell}$	$Y_{\ell m}$
1s	1	0	0	$2 \left(\frac{1}{a_0} \right)^{3/2} e^{-r/a_0}$	$\frac{1}{2\sqrt{\pi}}$
2s	2	0	0	$\left(\frac{1}{2a_0} \right)^{3/2} \left(2 - \frac{r}{a_0} \right) e^{-r/2a_0}$	$\frac{1}{2\sqrt{\pi}}$
	2	1	0	$\left(\frac{1}{2a_0} \right)^{3/2} \frac{1}{\sqrt{3}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{2} \sqrt{\frac{3}{\pi}} \cos \theta$
2p	2	1	± 1	$\left(\frac{1}{2a_0} \right)^{3/2} \frac{1}{\sqrt{3}} \frac{r}{a_0} e^{-r/2a_0}$	$\pm \frac{1}{2} \sqrt{\frac{3}{2\pi}} \sin \theta e^{\pm i\phi}$
:					Laguerre polynomial

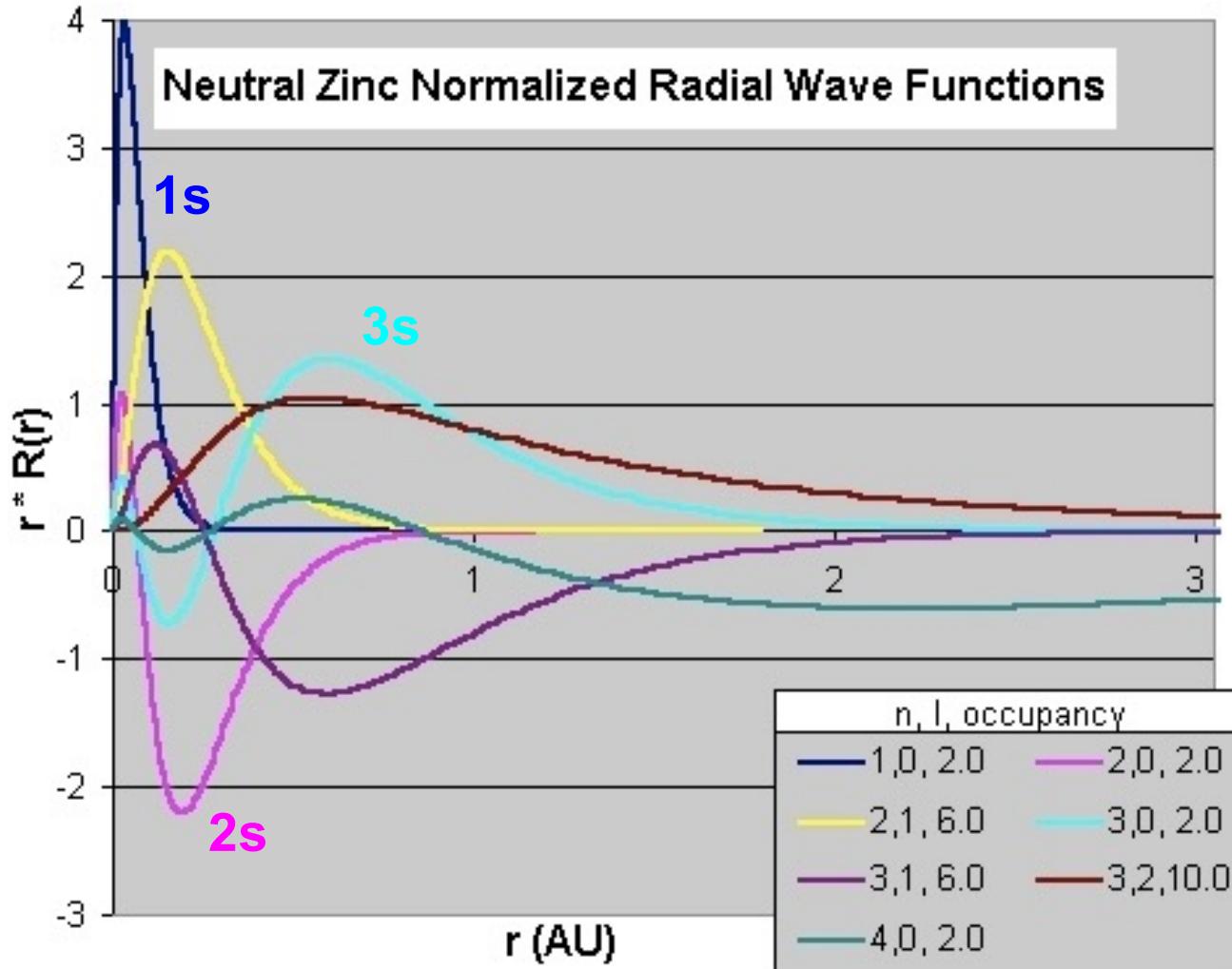
Hydrogen Eigenstates



Outer shells (*i.e.*,
larger n) spread
outward

Herman-Skillman Solutions for Atoms

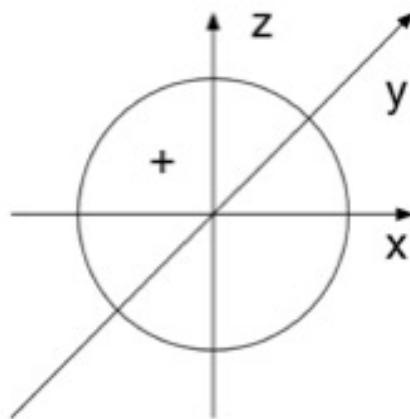
- Hartree approximation ($v_{xc} = 0$) for many-electron interaction



Outer shells (*i.e.*, larger n) still spread outward

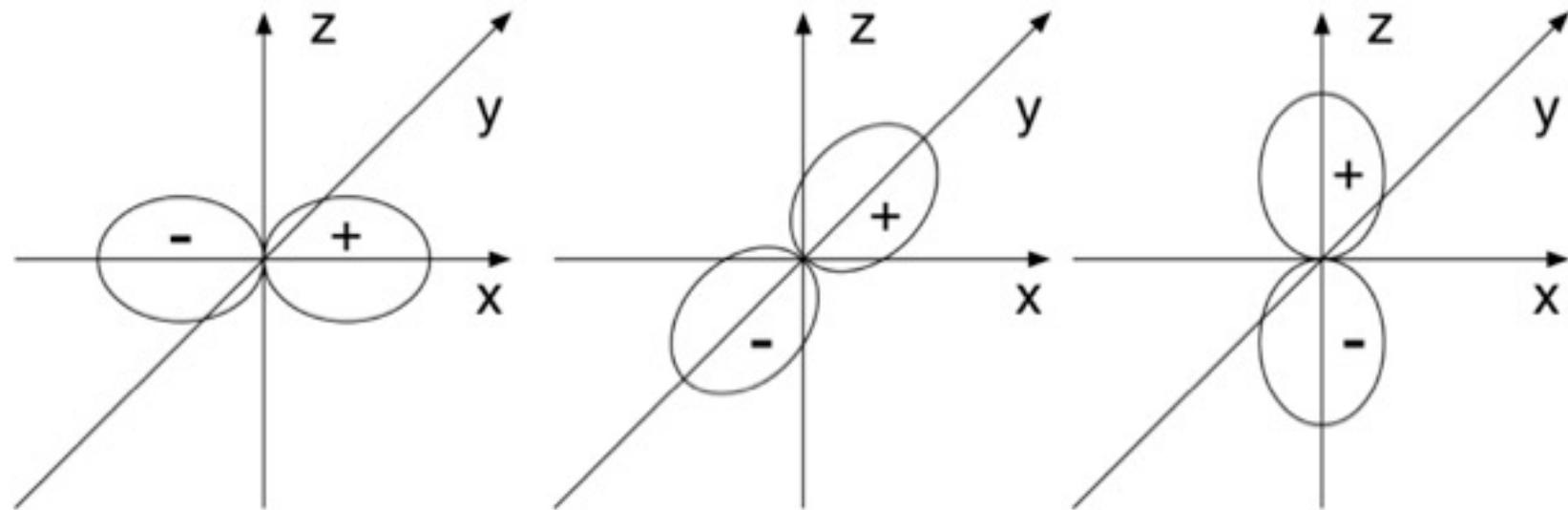
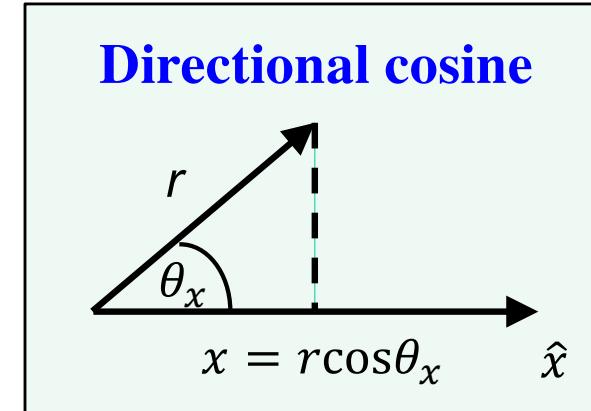
Atomic Orbitals

- s orbital ($l = 0$)



- p orbital ($l = 1$): Cartesian representation

$$\psi_{n1m}(r, \theta, \phi) \rightarrow \left(\frac{3}{4\pi}\right)^{1/2} R_{n1}(r) \begin{cases} x/r \\ y/r \\ z/r \end{cases} \quad r = \sqrt{x^2 + y^2 + z^2}$$



Tight-Binding Model

- Linear combination of atomic orbitals (LCAO)

$$\psi(\vec{r}) = \sum_{i=1}^N \sum_{\alpha \in \{s, p_x, p_y, p_z\}} c_{i\alpha} \psi_{\alpha}(\vec{r} - \vec{r}_i)$$

PHYSICAL REVIEW

VOLUME 94, NUMBER 6

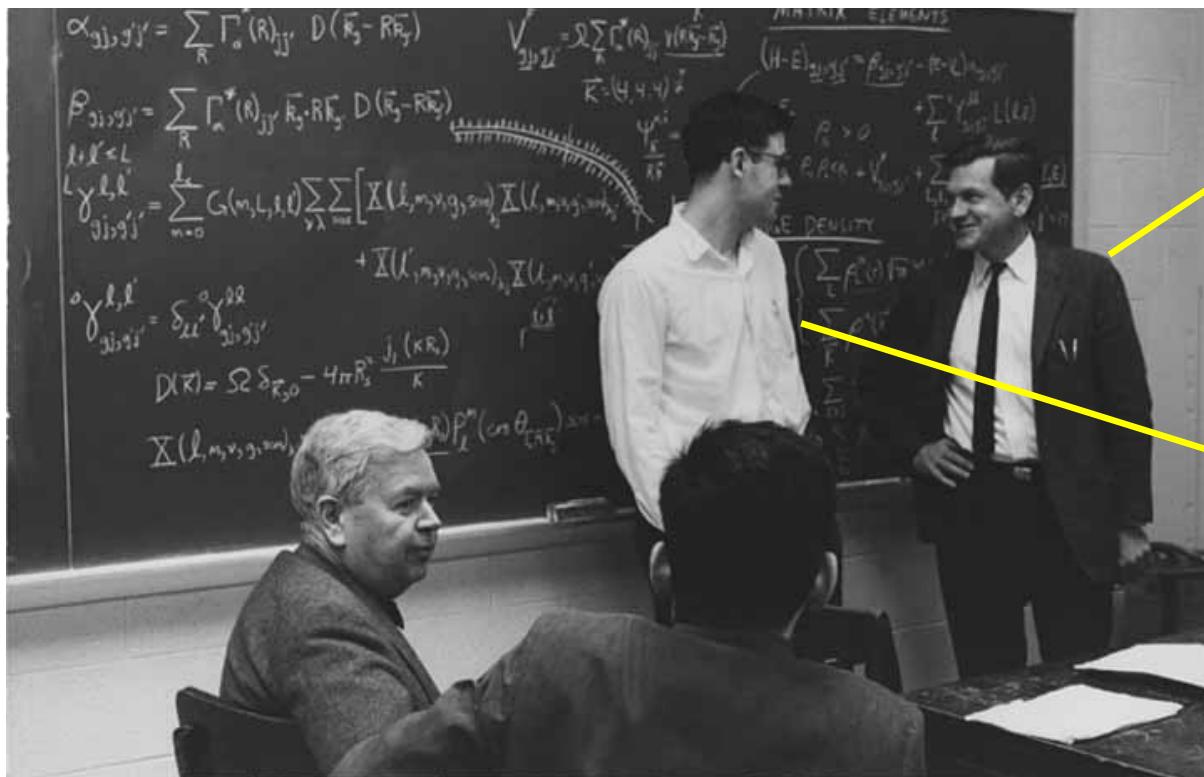
JUNE 15, 1954

Simplified LCAO Method for the Periodic Potential Problem*

J. C. SLATER AND G. F. KOSTER†

Massachusetts Institute of Technology, Cambridge, Massachusetts

(Received February 17, 1954)



Valence Electrons

- Example: Silicon— $1s^22s^22p^63s^23p^2$

WebElements™ periodic table

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
Period																			
1	1 H															2 He			
2	3 Li	4 Be																	
3	11 Na	12 Mg																	
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
*Lanthanoids		*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb			
**Actinoids		**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No			

Electronic Configuration

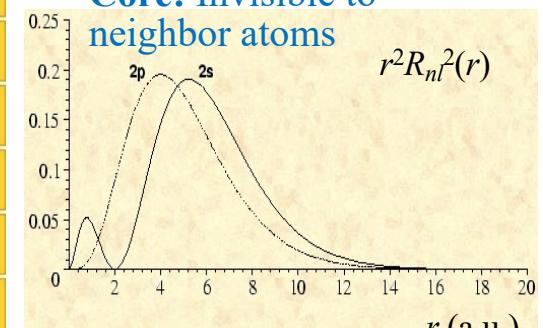
The following represents the electronic configuration and its associated term symbol for the **ground state neutral gaseous atom**. The configuration associated with silicon in its compounds is not necessarily the same.

- Ground state electron configuration: [Ne].3s².3p²
- Shell structure: 2.8.4

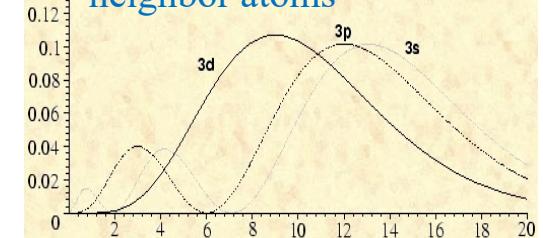
<http://www.webelements.com>

Core: Invisible to neighbor atoms

$$r^2 R_n(r)$$

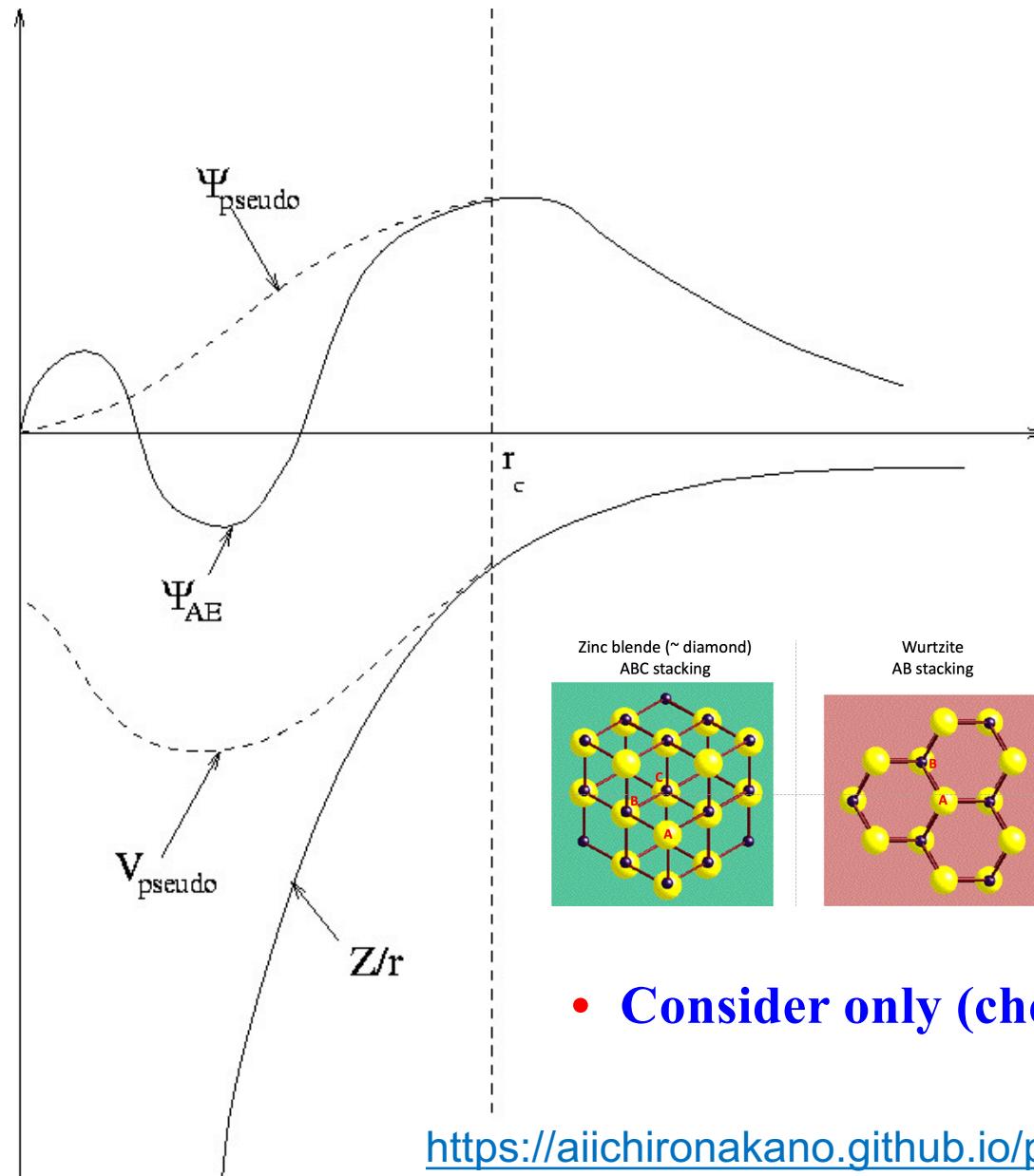


Valence: Sensed by neighbor atoms

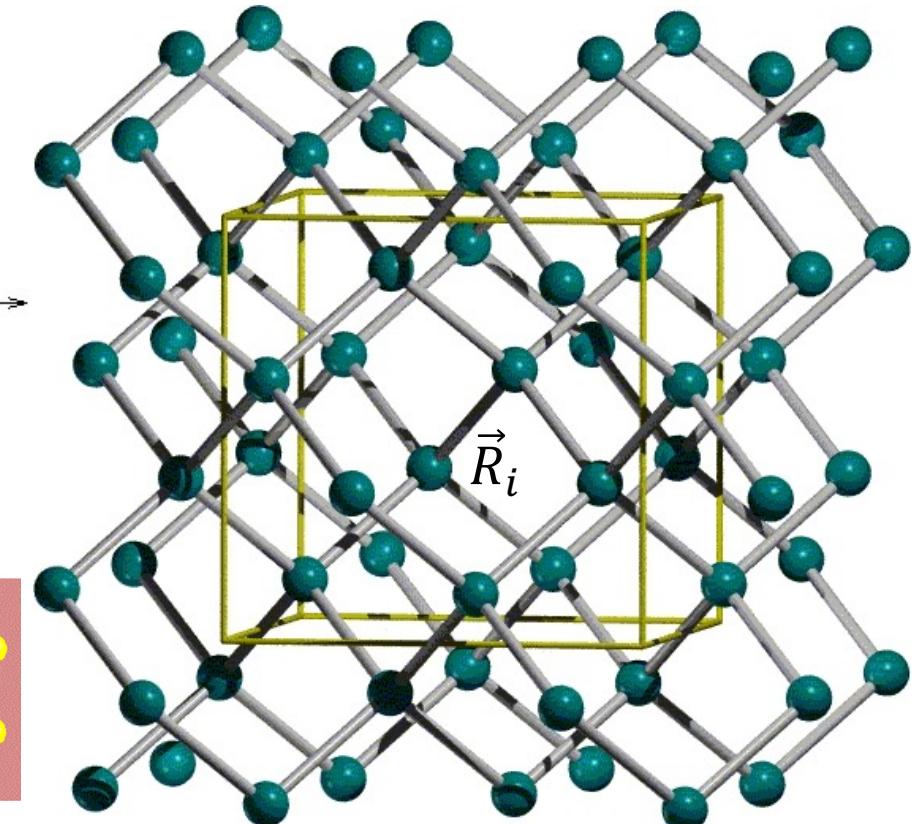


Pseudopotential

- Silicon— $1s^2 2s^2 2p^6 3s^2 3p^2$



$$\psi(\vec{r}) = \sum_{i=1}^N \sum_{\alpha \in \{s, p_x, p_y, p_z\}} c_{i\alpha} \psi_{\alpha}(\vec{r} - \vec{R}_i)$$



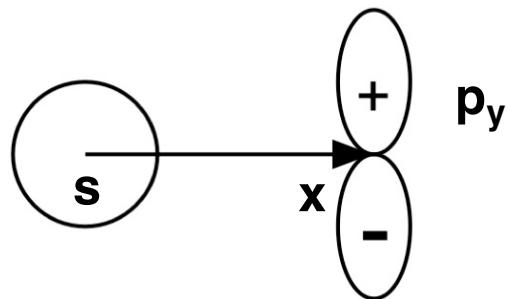
- Consider only (chemically active) valence electrons

Hamiltonian Matrix Elements

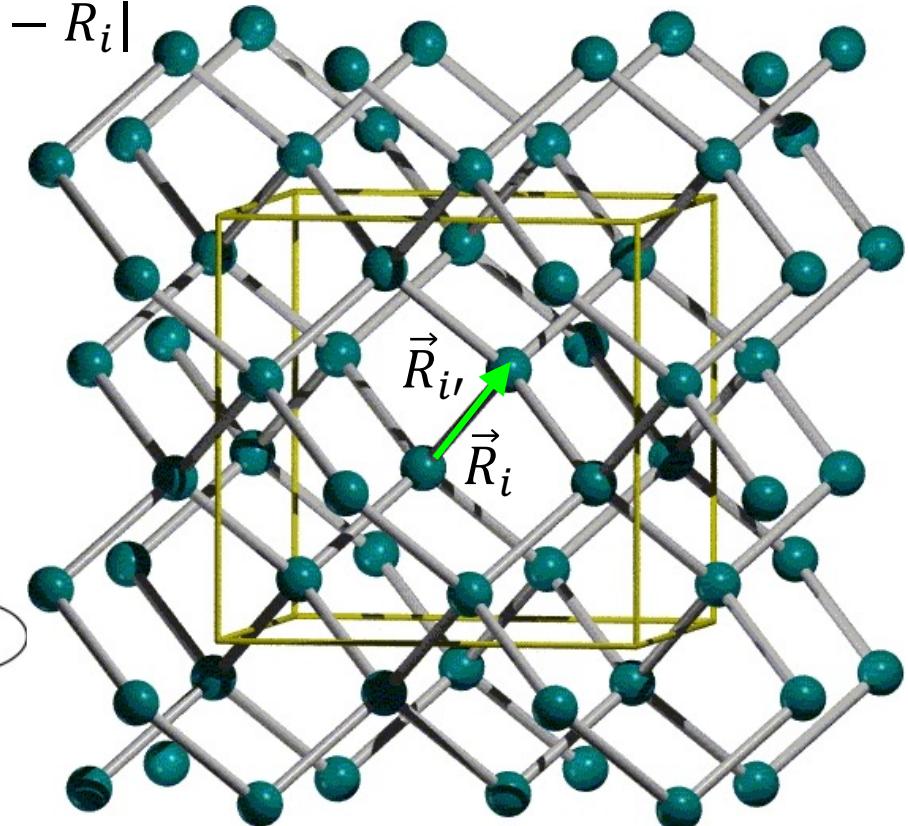
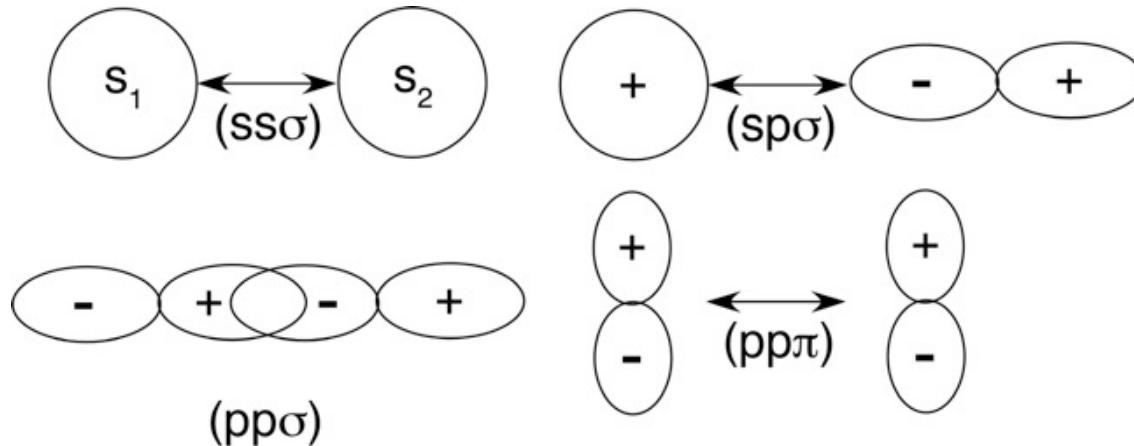
$$H_{i'\alpha',i\alpha} = \int d\vec{r} \psi_{\alpha'}^*(\vec{r} - \vec{R}_{i'}) \left(-\frac{\nabla^2}{2} + v(\vec{r}) \right) \psi_\alpha(\vec{r} - \vec{R}_i)$$

cf. slide 8

- Exponential decay $\sim \exp(-R_{ii'}/a)$ $R_{ii'} = |\vec{R}_{i'} - \vec{R}_i|$
- Many elements are 0 by symmetry



- Nonvanishing matrix elements



Overlap Integrals

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

$E_{s,s}$	$(ss\sigma)$
$E_{s,z}$	$l(sp\sigma)$
$E_{z,z}$	$l^2(pp\sigma) + (1-l^2)(pp\pi)$
$E_{x,y}$	$lm(pp\sigma) - lm(pp\pi)$
$E_{x,z}$	$ln(pp\sigma) - ln(pp\pi)$

J. C. Slater & G. F. Koster, *Phys. Rev.* **94**, 1498 ('54)

Parameterization:

- L. Goodwin, A. J. Skinner & D. G. Pettifor, *Europhys. Lett.* **9**, 701 ('89)
- I. Kwon *et al.*, *Phys. Rev. B* **49**, 7242 ('94)

Eigenvalue Problem

$$H|\psi\rangle = \varepsilon|\psi\rangle \quad |\psi\rangle = \sum_{i=1}^N \sum_{\alpha \in \{s, p_x, p_y, p_z\}} c_{i\alpha} |i\alpha\rangle$$
$$\sum_{i\alpha} c_{i\alpha} \langle i'\alpha' | H | i\alpha \rangle = \varepsilon \sum_{i\alpha} c_{i\alpha} \langle i'\alpha' | i\alpha \rangle$$
$$\langle i'\alpha' | i\alpha \rangle = \delta_{ii'} \delta_{\alpha\alpha'}$$
$$\sum_{i\alpha} H_{i'\alpha', i\alpha} c_{i\alpha} = \varepsilon c_{i'\alpha'}$$

$$H_{i'\alpha', i\alpha} = \langle i'\alpha' | H | i\alpha \rangle = \int d\vec{r} \psi_{\alpha'}^*(\vec{r} - \vec{R}_{i'}) \left(-\frac{\nabla^2}{2} + v(\vec{r}) \right) \psi_\alpha(\vec{r} - \vec{R}_i)$$

- **4N×4N matrix:**

$\kappa = 4(i-1) + \alpha$, where $i \in \{1, 2, \dots, N\}$ & $\alpha \in \{1 \leftrightarrow s, 2 \leftrightarrow p_x, 3 \leftrightarrow p_y, 4 \leftrightarrow p_z\}$

$$\sum_{\kappa} H_{\kappa', \kappa} c_{\kappa} = \varepsilon c_{\kappa'}, \text{ or } \mathbf{C}^T \mathbf{H} \mathbf{C} = \mathbf{E}$$

Matrix-vector multiplication

See the next slide

Eigen Decomposition

- **4N-dim. vector:** $|\kappa\rangle = |4(i-1) + \alpha\rangle$ $i = 1, \dots, N$; $\alpha \in \{3s, 3p_x, 3p_y, 3p_z\}$

$$\langle \kappa' | \times \begin{array}{l} H|\psi\rangle = \varepsilon |\psi\rangle \\ \langle \kappa' | H |\psi\rangle = \varepsilon \langle \kappa' | \psi\rangle \end{array}$$

- **Closure approximation (assume completeness, i.e., narrow the world)**

$$\sum |\kappa\rangle \langle \kappa| = 1 \Leftrightarrow |\psi\rangle = \sum |\kappa\rangle \langle \kappa| \psi\rangle$$

$$\therefore \sum_{\kappa} \overbrace{\langle \kappa' | H | \kappa \rangle}^{H_{\kappa' \kappa}} \underbrace{\langle \kappa | \psi_n \rangle}_{c_{\kappa}^{(n)} = C_{\kappa n}} = \varepsilon_n \underbrace{C_{\kappa' n}}_{E_{n' n}} \quad (n = 1, \dots, 4N)$$

$$\sum_{\kappa} H_{\kappa' \kappa} C_{\kappa n} = C_{\kappa' n} \varepsilon_n = \sum_{n'} C_{\kappa' n'} \underbrace{\delta_{n' n} \varepsilon_n}_{E_{n' n}} = \sum_{n'} C_{\kappa' n'} E_{n' n}$$

- **Matrix eigenvalue problem:** $\mathbf{H}\mathbf{C} = \mathbf{CE}$

$$\mathbf{C} = [\mathbf{c}^{(1)} \dots \mathbf{c}^{(4N)}] \quad \text{Column-aligned eigenvectors}$$

$$\mathbf{E} = \begin{bmatrix} \varepsilon_1 & & \\ & \ddots & \\ & & \varepsilon_{4N} \end{bmatrix}$$

- **Orthonormality:** $\delta_{nn'} = \sum_{\kappa=1}^{4N} c_{\kappa}^{(n)} c_{\kappa}^{(n')} = \sum_{\kappa=1}^{4N} C_{n\kappa}^T C_{\kappa n'} = (\mathbf{C}^T \mathbf{C})_{nn'}$, or $\mathbf{I} = \mathbf{C}^T \mathbf{C}$
- **Eigen decomposition:** $\mathbf{C}^T \mathbf{H} \mathbf{C} = \mathbf{E}$ ($\because \mathbf{C}^T \times \mathbf{H} \mathbf{C} = \mathbf{C}^T \times \mathbf{C} \mathbf{E} = \mathbf{E}$)

Silicon Tight-Binding Parameters

Inter-atom

$$h_\lambda(r) = \begin{cases} \langle s_1 | H | s_2 \rangle & \lambda = ss\sigma \\ \langle s_1 | H | p_{2d} \rangle & \lambda = sp\sigma \\ \langle p_{1d} | H | p_{2d} \rangle & \lambda = pp\sigma \\ \langle p_{1n} | H | p_{2n} \rangle & \lambda = pp\pi \end{cases} = h_\lambda(r_0) \left(\frac{r_0}{r}\right)^n \exp\left(n \left[-\left(\frac{r}{r_\lambda}\right)^{n_\lambda} + \left(\frac{r_0}{r_\lambda}\right)^{n_\lambda} \right]\right)$$

Intra-atom

$$\begin{cases} \langle s | H | s \rangle = E_s \\ \langle p_x | H | p_x \rangle = \langle p_y | H | p_y \rangle = \langle p_z | H | p_z \rangle = E_p \end{cases}$$

r_0 (Å)	n	E_s (eV)	E_p (eV)
2.360352	2	-5.25	1.20

λ	$ss\sigma$	$sp\sigma$	$pp\sigma$	$pp\pi$
$h_\lambda(r_0)$ (eV)	-2.038	1.745	2.75	-1.075
n_λ	9.5	8.5	7.5	7.5
r_λ (Å)	3.4	3.55	3.7	3.7

- **Atomic unit:** length—Bohr radius, $a_B = 0.5291772083$ Å;
energy—Hartree energy, $E_H = 27.2113834$ eV

I. Kwon *et al.*, Phys. Rev. B 49, 7242 ('94)

Projection of s-p Integrals

$$|p_\alpha\rangle = \hat{a} \bullet \hat{d}|p_d\rangle + \hat{a} \bullet \hat{n}|p_n\rangle \quad (\hat{a} = \hat{x}, \hat{y}, \hat{z}; \hat{a} \bullet \hat{a} = 1) \quad \text{projection}$$

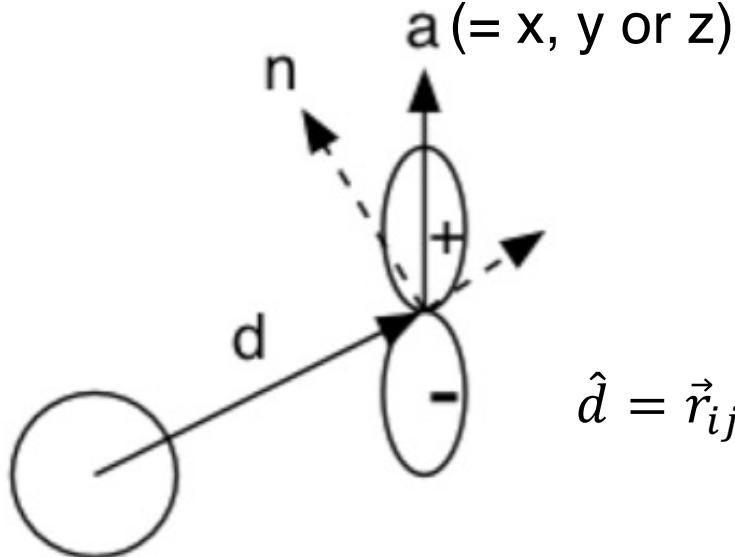
$$\because |p_\alpha\rangle = \cos(\chi - \theta) = \cos\chi\cos\theta + \sin\chi\sin\theta = \cos\theta|p_d\rangle + \sin\theta|p_n\rangle \quad \text{addition theorem}$$

$$= \hat{a} \bullet \hat{d}|p_d\rangle + \cos(\pi/2 - \theta)|p_n\rangle = \hat{a} \bullet \hat{d}|p_d\rangle + \hat{a} \bullet \hat{n}|p_n\rangle$$

$$\cos\chi = p_d$$

$$\sin\chi = \cos\left(\frac{\pi}{2} - \chi\right) = p_n$$

cf. slide 11

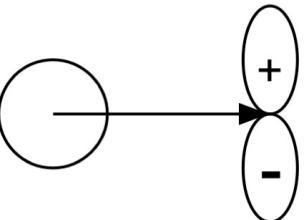
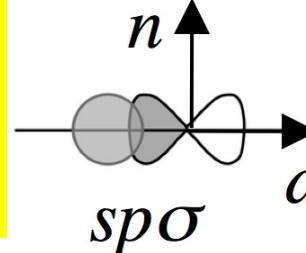
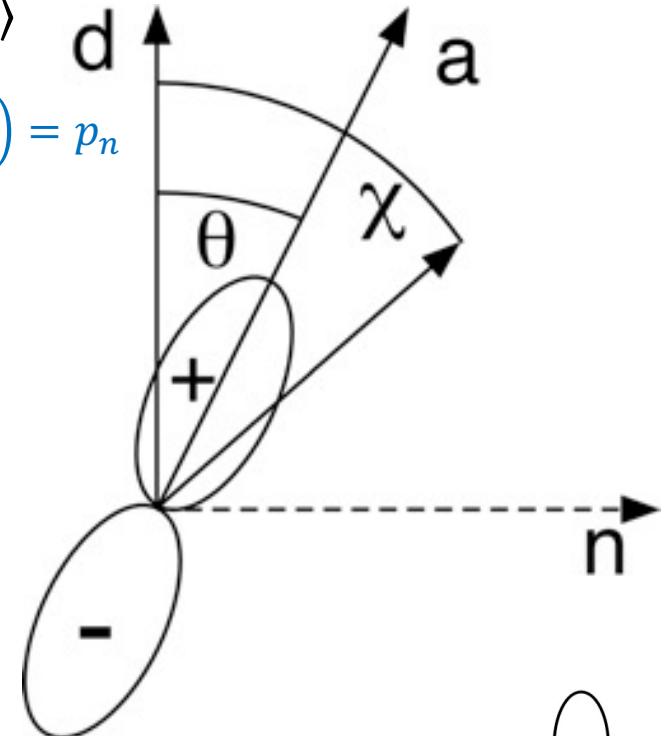


Basis function

$$\langle s | H | p_a \rangle = \langle s | H (\hat{a} \bullet \hat{d}|p_d\rangle + \hat{a} \bullet \hat{n}|p_n\rangle) \rangle = (\hat{a} \bullet \hat{d}) h_{sp\sigma}$$

Hamiltonian matrix element

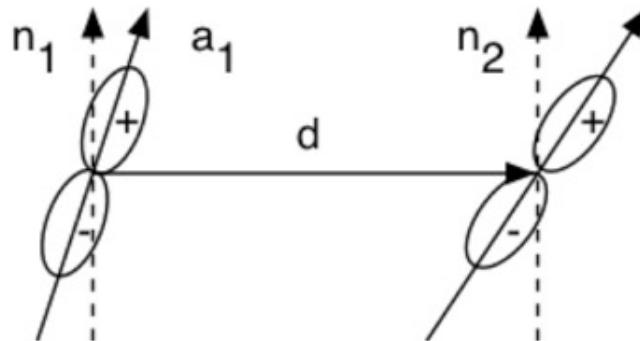
$$\begin{pmatrix} \langle s_1 | H | p_{2x} \rangle \\ \langle s_1 | H | p_{2y} \rangle \\ \langle s_1 | H | p_{2z} \rangle \end{pmatrix} = - \begin{pmatrix} \langle p_{1x} | H | s_2 \rangle \\ \langle p_{1y} | H | s_2 \rangle \\ \langle p_{1z} | H | s_2 \rangle \end{pmatrix} = \begin{pmatrix} d_x h_{sp\sigma}(r) \\ d_y h_{sp\sigma}(r) \\ d_z h_{sp\sigma}(r) \end{pmatrix}$$



$$\langle s | H | p_n \rangle = 0$$

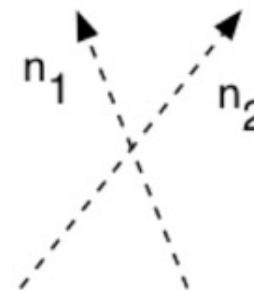
Projection of p-p Integrals

$$|p_1\rangle = \hat{a}_1 \cdot \hat{d} |p_{d1}\rangle + \hat{a}_1 \cdot \hat{n}_1 |p_{n1}\rangle$$



Side view of vector d

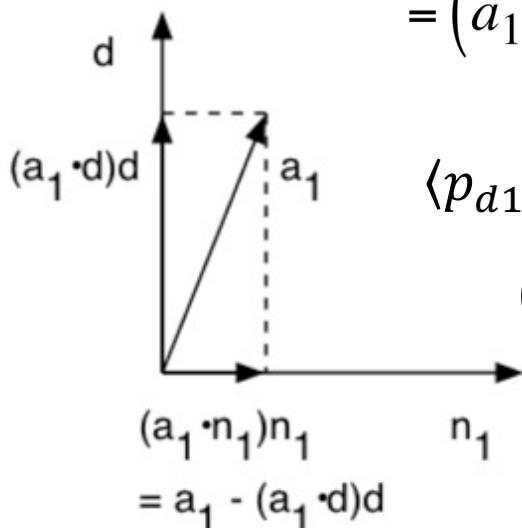
$$|p_2\rangle = \hat{a}_2 \cdot \hat{d} |p_{d2}\rangle + \hat{a}_2 \cdot \hat{n}_2 |p_{n2}\rangle$$



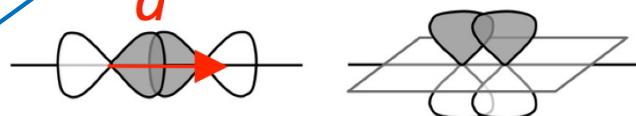
View from vector d direction

$$\langle p_1 | H | p_2 \rangle = (\hat{a}_1 \cdot \hat{d} \langle p_{d1} | + \hat{a}_1 \cdot \hat{n}_1 \langle p_{n1} |) H (\hat{a}_2 \cdot \hat{d} | p_{d2} \rangle + \hat{a}_2 \cdot \hat{n}_2 | p_{n2} \rangle)$$

$$= (\hat{a}_1 \cdot \hat{d}) (\hat{a}_2 \cdot \hat{d}) \langle p_{d1} | H | p_{d2} \rangle + (\hat{a}_1 \cdot \hat{n}_1 \langle p_{n1} |) H (\hat{a}_2 \cdot \hat{n}_2 | p_{n2} \rangle)$$



$$\langle p_{d1} | H | p_{d2} \rangle = h_{pp\sigma}(r)$$



$$(\hat{a}_1 \cdot \hat{n}_1 \langle p_{n1} |) H (\hat{a}_2 \cdot \hat{n}_2 | p_{n2} \rangle) = (\hat{a}_1 \cdot \hat{n}_1) (\hat{a}_2 \cdot \hat{n}_2) \langle p_{n1} | H | p_{n2} \rangle$$

$$= (\hat{a}_1 \cdot \hat{n}_1) (\hat{a}_2 \cdot \hat{n}_2) (\hat{n}_1 \cdot \hat{n}_2) h_{pp\pi}(r)$$

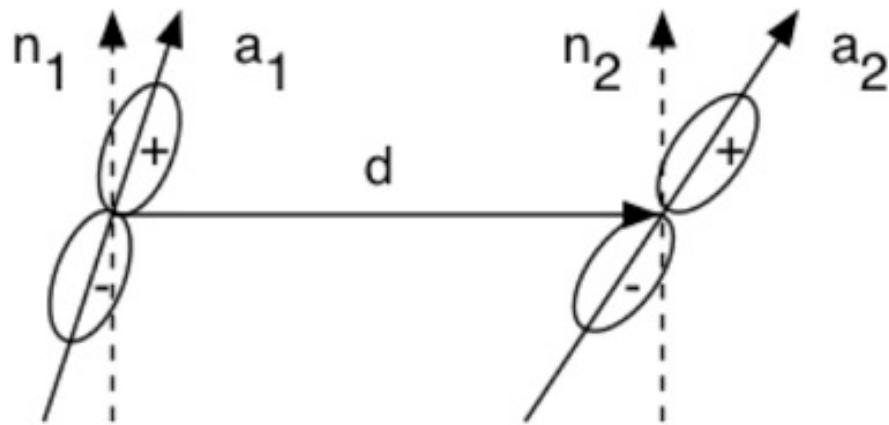
$$= ((\hat{a}_1 \cdot \hat{n}_1) \hat{n}_1) \cdot ((\hat{a}_2 \cdot \hat{n}_2) \hat{n}_2) h_{pp\pi}(r)$$

$$= (\hat{a}_1 - (\hat{a}_1 \cdot \hat{d}) \hat{d}) \cdot (\hat{a}_2 - (\hat{a}_2 \cdot \hat{d}) \hat{d}) h_{pp\pi}(r)$$

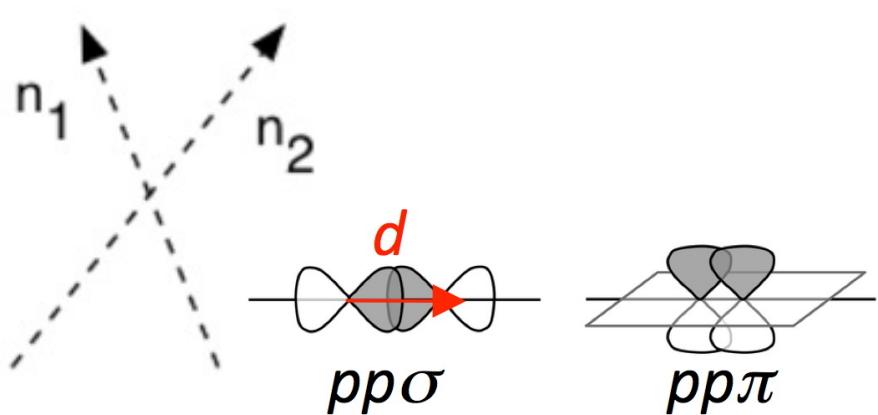
$$(\hat{a}_1 \cdot \hat{n}_1) \hat{n}_1 = \hat{a}_1 - (\hat{a}_1 \cdot \hat{d}) \hat{d}$$

\because 2D completeness: $1 = |d\rangle\langle d| + |n\rangle\langle n|$

Projection of p-p Integrals



Side view of vector d



View from vector d direction

$$= \begin{pmatrix} d_x^2 h_{pp\sigma} + (1 - d_x^2) h_{pp\pi} & d_x d_y (h_{pp\sigma} - h_{pp\pi}) & d_x d_z (h_{pp\sigma} - h_{pp\pi}) \\ d_y d_x (h_{pp\sigma} - h_{pp\pi}) & d_y^2 h_{pp\sigma} + (1 - d_y^2) h_{pp\pi} & d_y d_z (h_{pp\sigma} - h_{pp\pi}) \\ d_z d_x (h_{pp\sigma} - h_{pp\pi}) & d_z d_y (h_{pp\sigma} - h_{pp\pi}) & d_z^2 h_{pp\sigma} + (1 - d_z^2) h_{pp\pi} \end{pmatrix} \begin{pmatrix} \hat{x} \bullet \hat{d}, \hat{y} \bullet \hat{d}, \hat{z} \bullet \hat{d} \\ = (d_x, d_y, d_z) \end{pmatrix}$$

TB Hamiltonian Matrix

$$H = \begin{pmatrix} & & j & \\ & & \vdots & \\ s_i s_j & s_i p_{jx} & s_i p_{jy} & s_i p_{jz} \\ i \dots & p_{ix} s_j & p_{ix} p_{jx} & p_{ix} p_{jy} & p_{ix} p_{jz} & \dots \\ p_{iy} s_j & p_{iy} p_{jx} & p_{iy} p_{jy} & p_{iy} p_{jz} & & \\ p_{iz} s_j & p_{iz} p_{jx} & p_{iz} p_{jy} & p_{iz} p_{jz} & & \\ & \vdots & & & & \\ & & \text{---} & & & \\ & & & & & \text{---} \\ & & & & & \text{---} \\ & & & & & \text{---} \end{pmatrix}$$

ss σ

$i \neq j$

$\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$

$r = |\vec{r}_{ij}|$

$\hat{d} = \vec{r}_{ij}/r = (d_x, d_y, d_z)$

$nAtom \times nAtom$ blocks, each 4×4

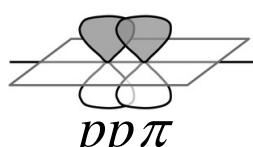
$i=j$

$E_s \quad 0 \quad 0 \quad 0$

$0 \quad E_p \quad 0 \quad 0$

$0 \quad 0 \quad E_p \quad 0$

$0 \quad 0 \quad 0 \quad E_p$



$H_{i'\alpha',i\alpha} = \langle i'\alpha' | H | i\alpha \rangle$

$= \int d\vec{r} \psi_{\alpha'}^*(\vec{r} - \vec{R}_{i'}) \left(-\frac{\nabla^2}{2} + v(\vec{r}) \right) \psi_{\alpha}(\vec{r} - \vec{R}_i)$

Apply periodic boundary condition (pick the minimum image)

$$\begin{pmatrix} h_{ss\sigma} & d_x h_{sp\sigma} & d_y h_{sp\sigma} & d_z h_{sp\sigma} \\ -d_x h_{sp\sigma} & d_x^2 h_{pp\sigma} + (1 - d_x^2) h_{pp\pi} & d_x d_y (h_{pp\sigma} - h_{pp\pi}) & d_x d_z (h_{pp\sigma} - h_{pp\pi}) \\ -d_y h_{sp\sigma} & d_y d_x (h_{pp\sigma} - h_{pp\pi}) & d_y^2 h_{pp\sigma} + (1 - d_y^2) h_{pp\pi} & d_y d_z (h_{pp\sigma} - h_{pp\pi}) \\ -d_z h_{sp\sigma} & d_z d_x (h_{pp\sigma} - h_{pp\pi}) & d_z d_y (h_{pp\sigma} - h_{pp\pi}) & d_z^2 h_{pp\sigma} + (1 - d_z^2) h_{pp\pi} \end{pmatrix}$$

$js \quad jp_x \quad jp_y \quad jp_x$

$is \quad ip_x \quad ip_y \quad ip_x$

TB Matrix Elements

$$\begin{cases} \langle s | H | s \rangle = E_s \\ \langle p_x | H | p_x \rangle = \langle p_y | H | p_y \rangle = \langle p_z | H | p_z \rangle = E_p \end{cases}$$

r_0 (Å)	n	E_s (eV)	E_p (eV)
2.360352	2	-5.25	1.20

$$\begin{pmatrix} h_{ss\sigma} & d_x h_{sp\sigma} & d_y h_{sp\sigma} & d_z h_{sp\sigma} \\ -d_x h_{sp\sigma} & d_x^2 h_{pp\sigma} + (1 - d_x^2) h_{pp\pi} & d_x d_y (h_{pp\sigma} - h_{pp\pi}) & d_x d_z (h_{pp\sigma} - h_{pp\pi}) \\ -d_y h_{sp\sigma} & d_y d_x (h_{pp\sigma} - h_{pp\pi}) & d_y^2 h_{pp\sigma} + (1 - d_y^2) h_{pp\pi} & d_y d_z (h_{pp\sigma} - h_{pp\pi}) \\ -d_z h_{sp\sigma} & d_z d_x (h_{pp\sigma} - h_{pp\pi}) & d_z d_y (h_{pp\sigma} - h_{pp\pi}) & d_z^2 h_{pp\sigma} + (1 - d_z^2) h_{pp\pi} \end{pmatrix}$$

$$h_\lambda(r) = \begin{cases} \langle s_1 | H | s_2 \rangle & \lambda = ss\sigma \\ \langle s_1 | H | p_{2d} \rangle & \lambda = sp\sigma \\ \langle p_{1d} | H | p_{2d} \rangle & \lambda = pp\sigma \\ \langle p_{1n} | H | p_{2n} \rangle & \lambda = pp\pi \end{cases} = h_\lambda(r_0) \left(\frac{r_0}{r}\right)^n \exp\left(n \left[-\left(\frac{r}{r_\lambda}\right)^{n_\lambda} + \left(\frac{r_0}{r_\lambda}\right)^{n_\lambda}\right]\right)$$

λ	ssσ	spσ	ppσ	ppπ
$h_\lambda(r_0)$ (eV)	-2.038	1.745	2.75	-1.075
n_λ	9.5	8.5	7.5	7.5
r_λ (Å)	3.4	3.55	3.7	3.7

Overlap Integrals

$$\begin{pmatrix} h_{ss\sigma} & d_x h_{sp\sigma} & d_y h_{sp\sigma} & d_z h_{sp\sigma} \\ -d_x h_{sp\sigma} & d_x^2 h_{pp\sigma} + (1 - d_x^2) h_{pp\pi} & d_x d_y (h_{pp\sigma} - h_{pp\pi}) & d_x d_z (h_{pp\sigma} - h_{pp\pi}) \\ -d_y h_{sp\sigma} & d_y d_x (h_{pp\sigma} - h_{pp\pi}) & d_y^2 h_{pp\sigma} + (1 - d_y^2) h_{pp\pi} & d_y d_z (h_{pp\sigma} - h_{pp\pi}) \\ -d_z h_{sp\sigma} & d_z d_x (h_{pp\sigma} - h_{pp\pi}) & d_z d_y (h_{pp\sigma} - h_{pp\pi}) & d_z^2 h_{pp\sigma} + (1 - d_z^2) h_{pp\pi} \end{pmatrix}$$

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

$E_{s,s}$	$(ss\sigma)$
$E_{s,z}$	$l(sp\sigma)$
$E_{z,z}$	$l^2(pp\sigma) + (1 - l^2)(pp\pi)$
$E_{x,y}$	$lm(pp\sigma) - lm(pp\pi)$
$E_{x,z}$	$ln(pp\sigma) - ln(pp\pi)$

J. C. Slater & G. F. Koster, *Phys. Rev.* **94**, 1498 ('54)

Eigenvalue Problem

$$H|\psi\rangle = \varepsilon|\psi\rangle \quad |\psi\rangle = \sum_{i=1}^N \sum_{\alpha \in \{s, p_x, p_y, p_z\}} c_{i\alpha} |i\alpha\rangle$$
$$\sum_{i\alpha} c_{i\alpha} \langle i'\alpha' | H | i\alpha \rangle = \varepsilon \sum_{i\alpha} c_{i\alpha} \langle i'\alpha' | i\alpha \rangle$$
$$\langle i'\alpha' | i\alpha \rangle = \delta_{ii'} \delta_{\alpha\alpha'}$$
$$\sum_{i\alpha} H_{i'\alpha', i\alpha} c_{i\alpha} = \varepsilon c_{i'\alpha'}$$

$$H_{i'\alpha', i\alpha} = \langle i'\alpha' | H | i\alpha \rangle = \int d\vec{r} \psi_{\alpha'}^*(\vec{r} - \vec{R}_{i'}) \left(-\frac{\nabla^2}{2} + v(\vec{r}) \right) \psi_\alpha(\vec{r} - \vec{R}_i)$$

- **4N×4N matrix:**

$\kappa = 4(i-1) + \alpha$, where $i \in \{1, 2, \dots, N\}$ & $\alpha \in \{1 \leftrightarrow s, 2 \leftrightarrow p_x, 3 \leftrightarrow p_y, 4 \leftrightarrow p_z\}$

$$\sum_{\kappa} H_{\kappa', \kappa} c_{\kappa} = \varepsilon c_{\kappa'} \text{ or } \mathbf{C}^T \mathbf{H} \mathbf{C} = \mathbf{E}$$

cf. slide 23 for Hamiltonian matrix elements

Spectral
decomposition

Numerical Recipes Routines

eigen.c

```

double **h; // Hamiltonian matrix
double *d; // Eigenvalues
double *e;
...
/* Allocate memory for matrices & vectors*/
n4 = 4*nAtom; // Hamiltonian matrix size with s-p basis
h = dmatrix(1,n4,1,n4); // Use h[1:n4][1:n4]
d = dvector(1,n4); // d[1:n4]
e = dvector(1,n4); // e[1:n4]

/* Set up the Hamiltonian matrix elements h here */

/* Diagonalize the Hamiltonian matrix */
tred2(h,n4,d,e);
tqli(d,e,n4,h); CTHC = E

```

double**

h

double*

h[0]

h[1]

...

double

h[1][0]

h[1][1]

...

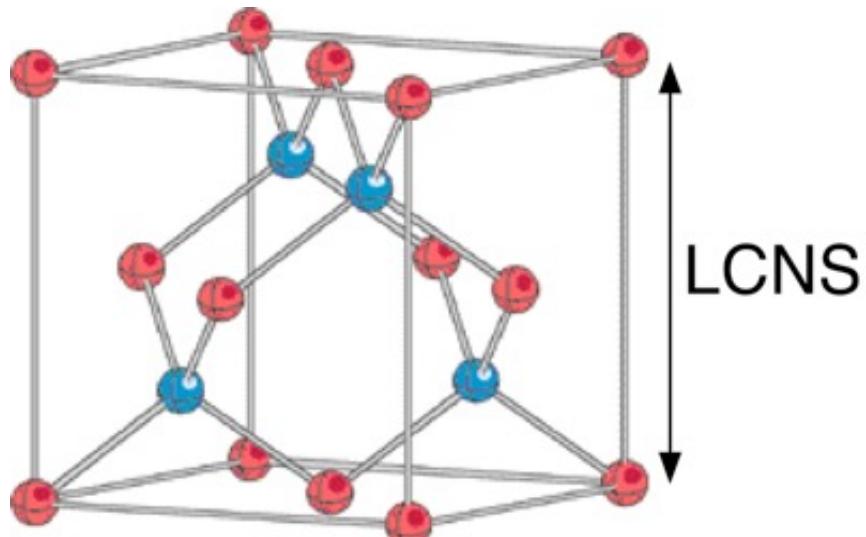
\mathbf{H} in $\xrightarrow{\text{tred2}}$ out $\mathbf{C}, \mathbf{d}, \mathbf{e}$ in $\xrightarrow{\text{tqli}}$ \mathbf{C}', \mathbf{d}' = eigenvectors, eigenvalues

$$\mathbf{C}^T \mathbf{H} \mathbf{C} = \begin{bmatrix} & & \\ & \text{e} & \\ & & \end{bmatrix}_{\mathbf{d}}$$

$$\mathbf{C}'^T \mathbf{H} \mathbf{C}' = \begin{bmatrix} & & \\ & & \\ & & \end{bmatrix}_{\mathbf{d}'}$$

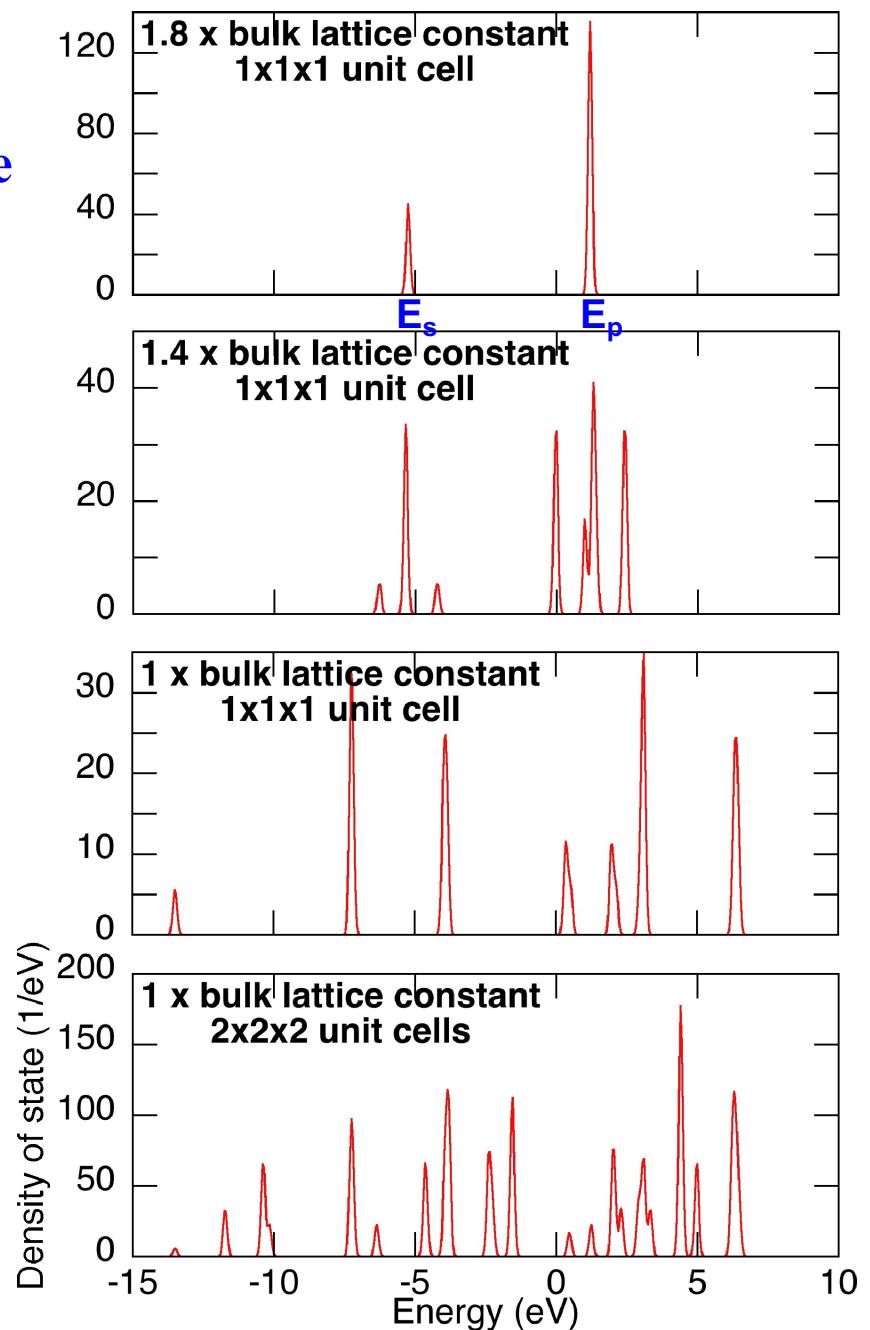
Example

- Si crystal: $1 \times 1 \times 1$ or $2 \times 2 \times 2$ cubic unit cells (8 atoms per unit cell), with lattice constant = 1.8, 1.4 & $1 \times$ bulk crystalline lattice constant (5.43 \AA or 10.2622 a.u.)

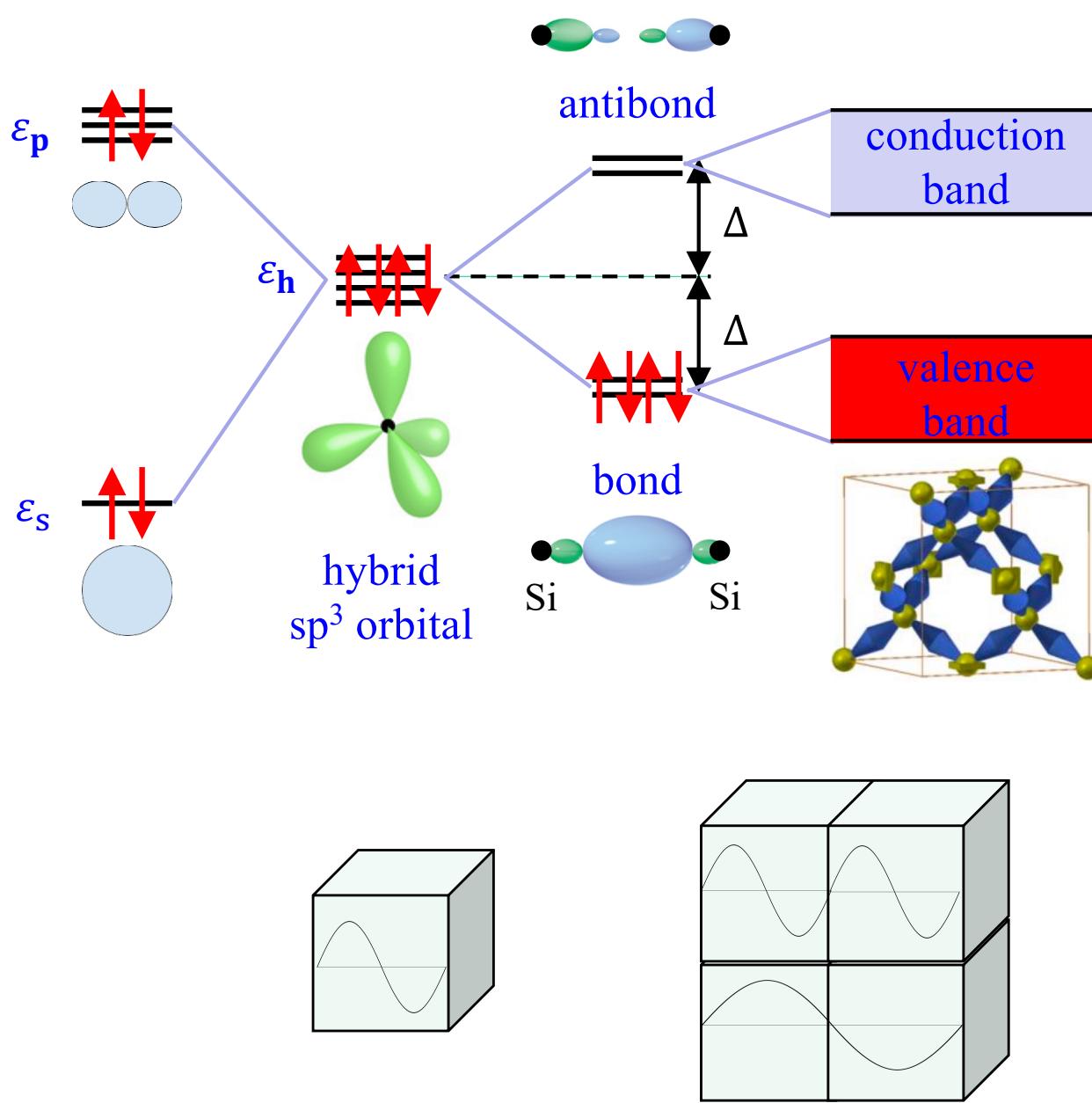


- Density of states: $\sigma = 0.1 \text{ eV}$

$$D(\varepsilon) = \sum_{n=1}^{n^4} \frac{1}{\sqrt{\pi}\sigma} \exp\left(-\frac{(\varepsilon - \varepsilon_n)^2}{\sigma^2}\right)$$



Energy Band in a Nutshell



$$H = \begin{bmatrix} \varepsilon_h & \Delta \\ \Delta & \varepsilon_h \end{bmatrix}$$

$$\begin{aligned} |H - \lambda I| &= \begin{vmatrix} \varepsilon_h - \lambda & \Delta \\ \Delta & \varepsilon_h - \lambda \end{vmatrix} \\ &= (\lambda - \varepsilon_h)^2 - \Delta^2 = 0 \end{aligned}$$

$$\therefore \lambda_{\pm} = \varepsilon_h \pm \Delta$$

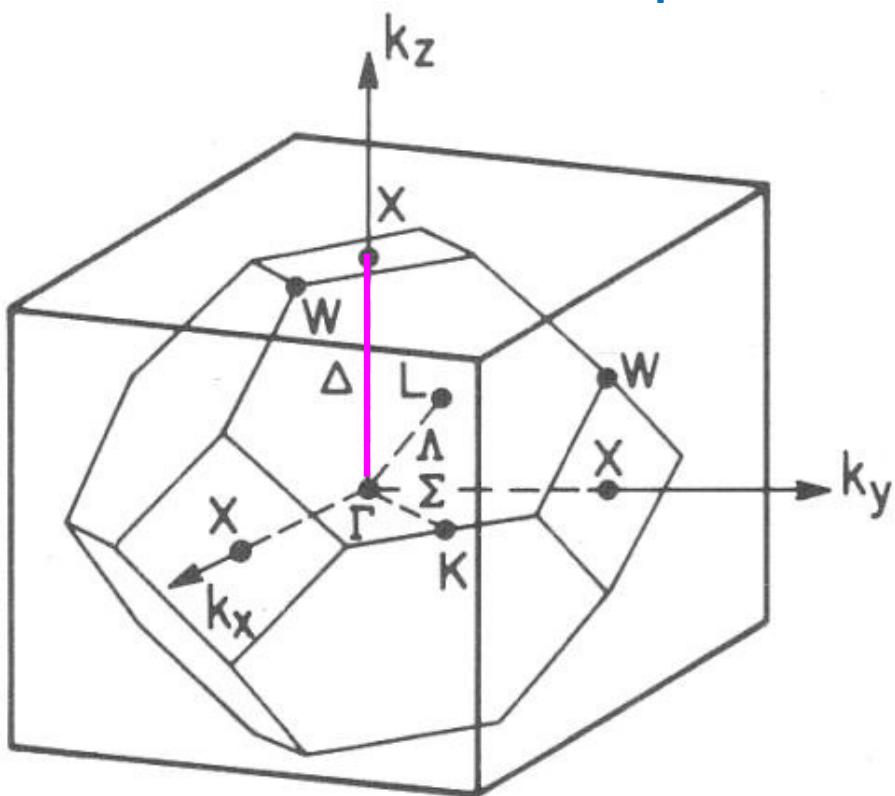
$$\begin{bmatrix} \varepsilon_s & \varepsilon_p & e^{-cr} & \varepsilon_p \\ \varepsilon_p & \varepsilon_p & \varepsilon_s & \varepsilon_p \\ e^{-cr} & \varepsilon_s & \varepsilon_p & \varepsilon_p \\ & \varepsilon_p & \varepsilon_p & \varepsilon_p \end{bmatrix}$$

Band: Infinite Lattice

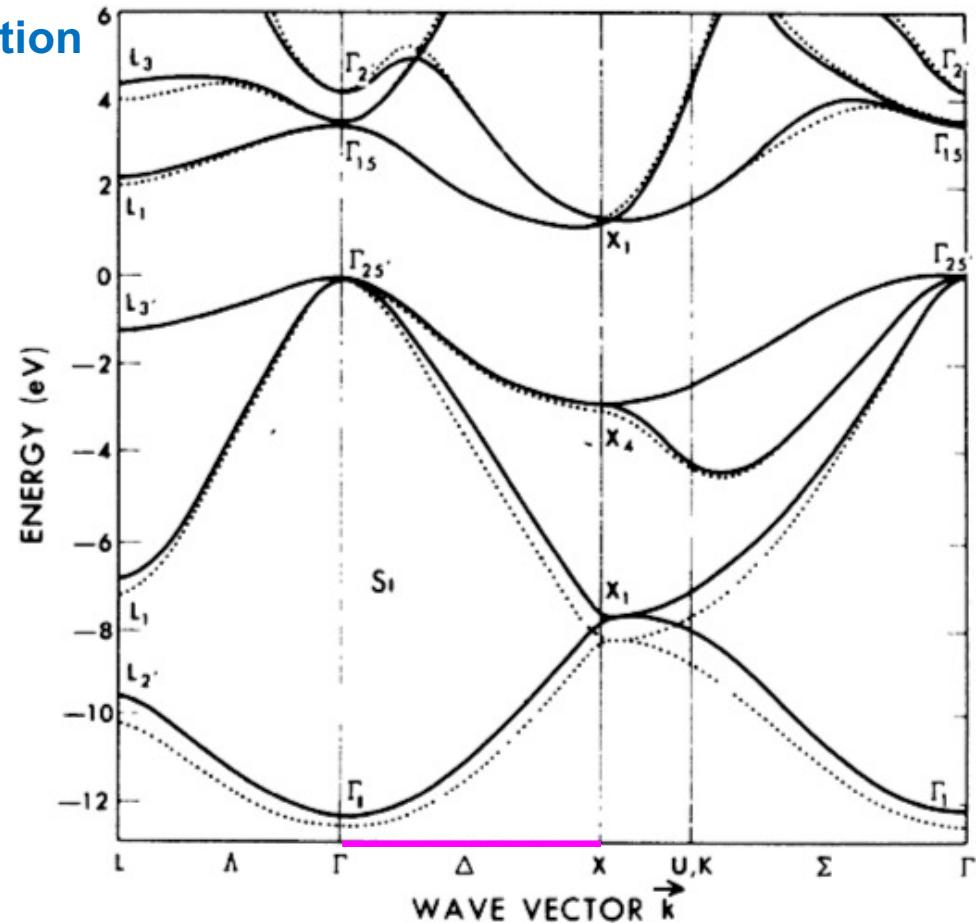
- **Bloch theorem:** $\psi_{n\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r})u_{n,\mathbf{k}}(\mathbf{r})$

band index

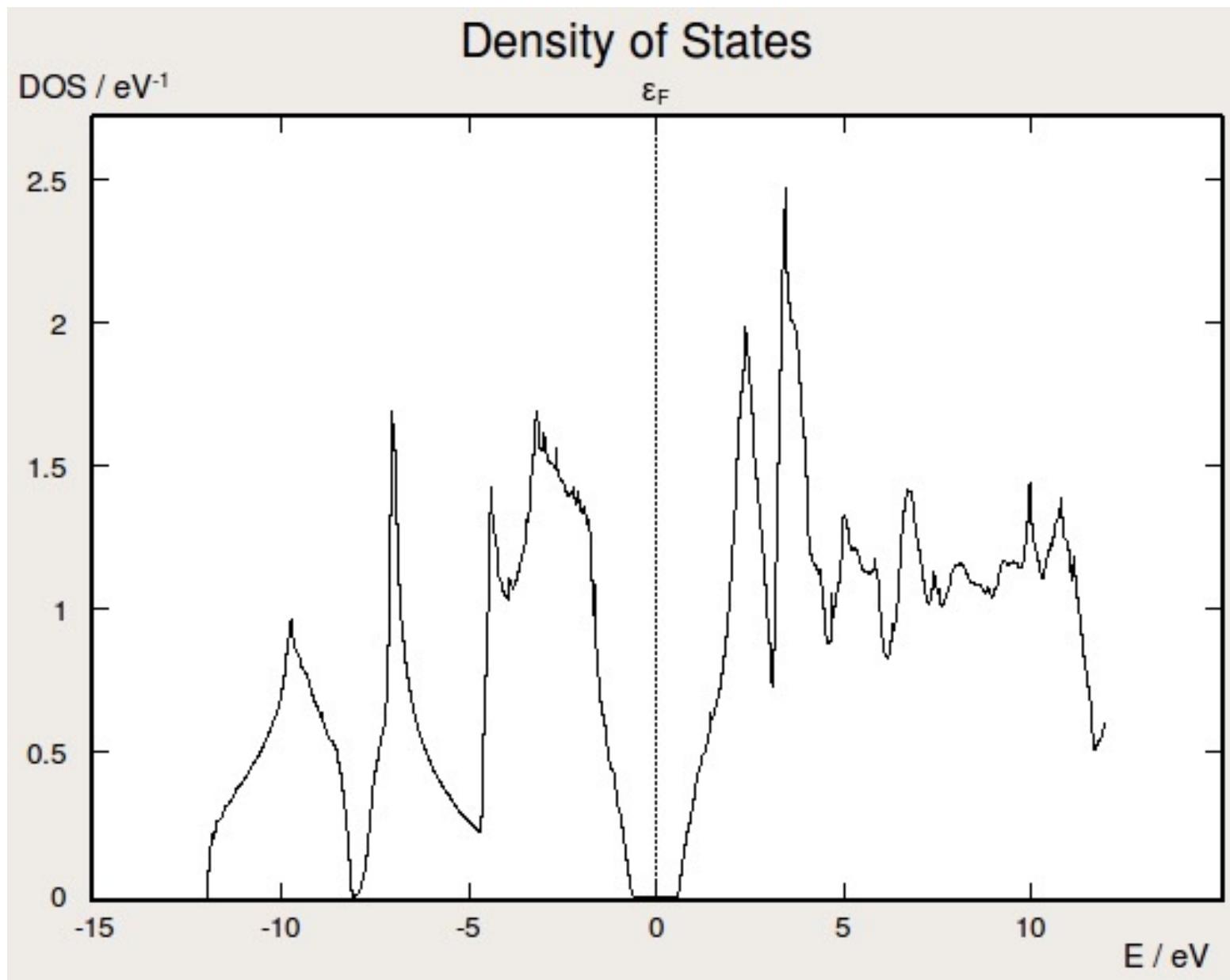
periodic function



Brillouin zone of Si crystal

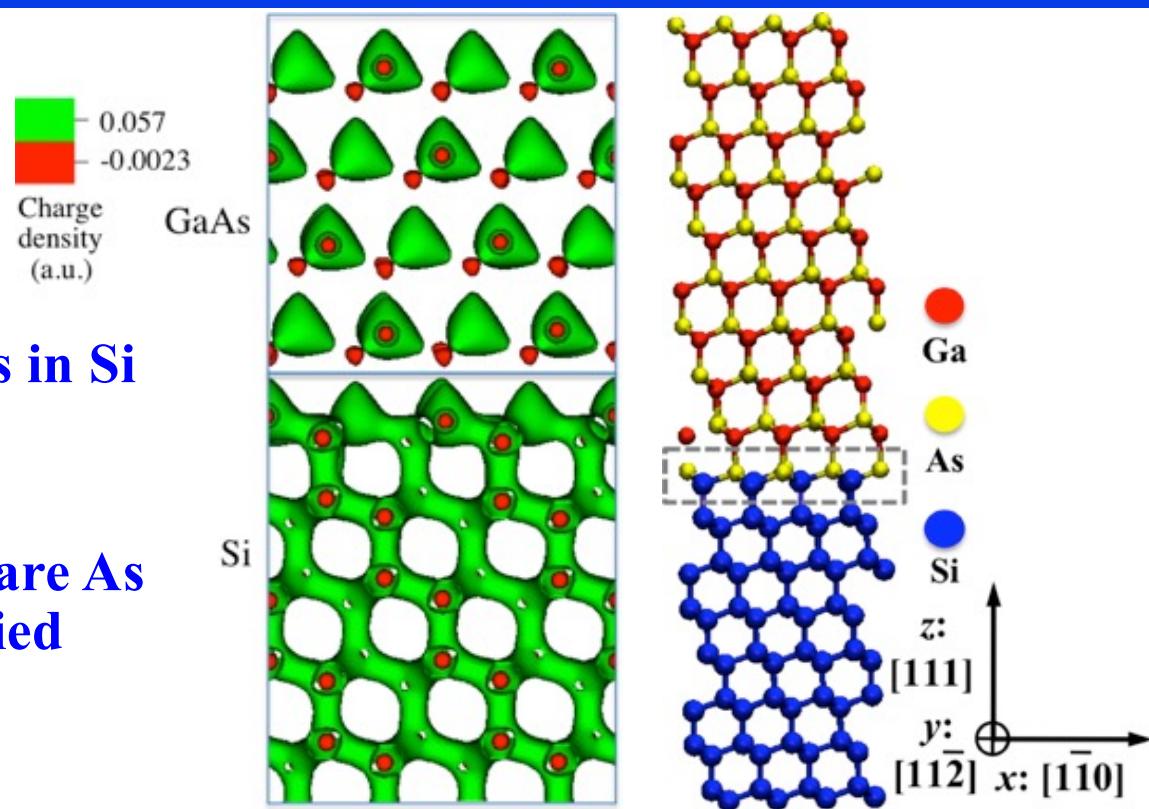


Density of States: Silicon Crystal



Charge Density at GaAs/Si (111) Interface

- Highest occupied states in Si have the hybrid sp^3 character
- Occupied GaAs states are As p-like (lowest unoccupied states are s-like)

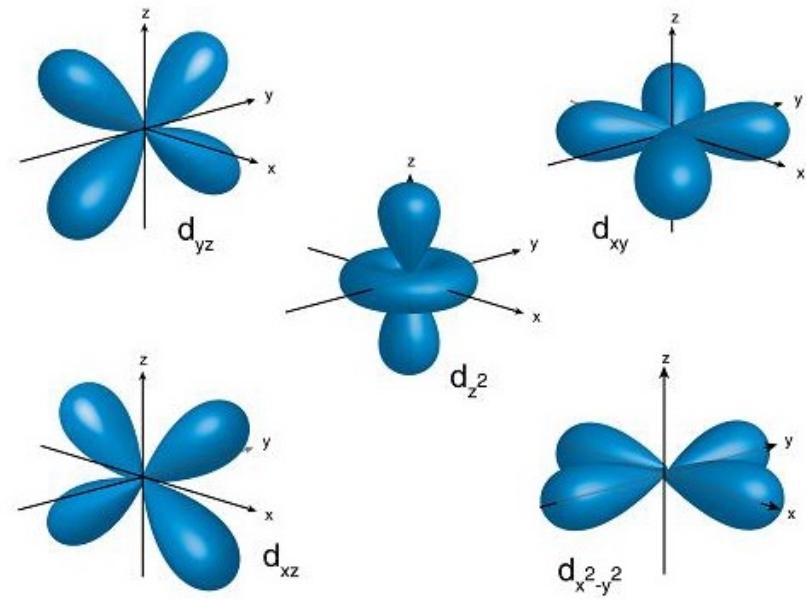
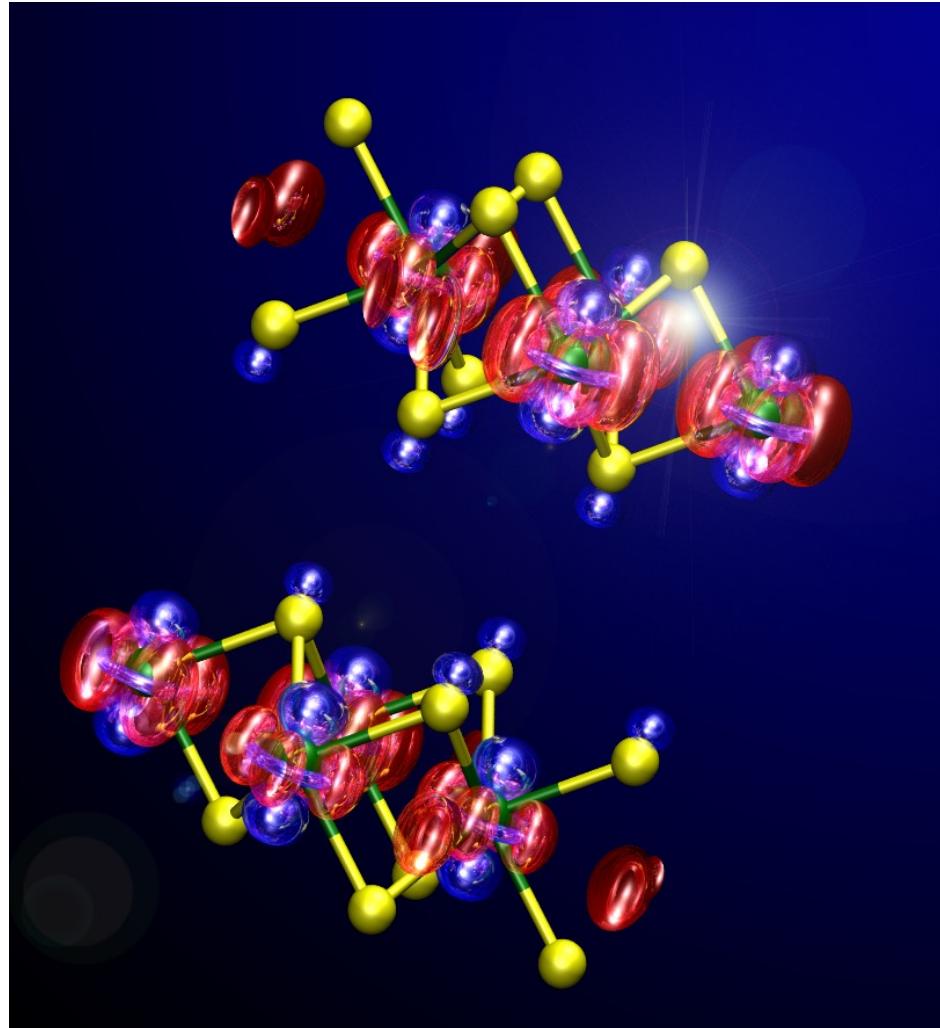


Projection of Kohn-Sham wave functions onto atomic orbitals

	Band	Ga 4s	Ga 4p	Ga 4d	As 4s	As 4p	As 4d	Total
Occupied	1150	0.0000	0.1157	0.0708	0.0000	0.8033	0.0101	1
	1151	0.0000	0.1158	0.0709	0.0000	0.8033	0.0100	1
	1152	0.0000	0.1166	0.0713	0.0000	0.8017	0.0104	1
Unoccupied	1153	0.6763	0.0000	0.0000	0.3236	0.0001	0.0000	1

Wave Functions in MoSe₂ Bilayer

- Highest occupied states (blue) are d_{z2}-like
- Lowest unoccupied states (red) are d_{xy}-like



M.-F. Lin *et al.*, *Nature Commun.* **8**, 1745 ('17); L. Bassman *et al.*, *Nano Lett.* **18**, 4653 ('18);
I. Tung *et al.*, *Nature Photon.* **13**, 425 ('19)

NRL Tight-Binding Archive

	Ia	IIa	IIIb	IVb	Vb	VIb	VIIb	VIII				Ib	IIb	IIIa	IVa	Va	VIa	VIIa	VIIIa
K	¹ H																	² He	
L	³ Li	⁴ Be												⁵ B	⁶ C	⁷ N	⁸ O	⁹ F	¹⁰ Ne
M	¹¹ Na	¹² Mg												¹³ Al	¹⁴ Si	¹⁵ P	¹⁶ S	¹⁷ Cl	¹⁸ Ar
N	¹⁹ K	²⁰ Ca	²¹ Sc	²² Ti	²³ V	²⁴ Cr	²⁵ Mn	²⁶ Fe	²⁷ Co	²⁸ Ni	²⁹ Cu	³⁰ Zn	³¹ Ga	³² Ge	³³ As	³⁴ Se	³⁵ Br	³⁶ Kr	
O	³⁷ Rb	³⁸ Sr	³⁹ Y	⁴⁰ Zr	⁴¹ Nb	⁴² Mo	⁴³ Tc	⁴⁴ Ru	⁴⁵ Rh	⁴⁶ Pd	⁴⁷ Ag	⁴⁸ Cd	⁴⁹ In	⁵⁰ Sn	⁵¹ Sb	⁵² Te	⁵³ I	⁵⁴ Xe	
P	⁵⁵ Cs	⁵⁶ Ba	⁵⁷ La	⁷² Hf	⁷³ Ta	⁷⁴ W	⁷⁵ Re	⁷⁶ Os	⁷⁷ Ir	⁷⁸ Pt	⁷⁹ Au	⁸⁰ Hg	⁸¹ Tl	⁸² Pb	⁸³ Bi	⁸⁴ Po	⁸⁵ At	⁸⁶ Rn	
Q	⁸⁷ Fr	⁸⁸ Ra	⁸⁹ Ac	¹⁰⁴ Rf	¹⁰⁵ Db	¹⁰⁶ Sg													
Lanthanides		⁵⁸ Ce	⁵⁹ Pr	⁶⁰ Nd	⁶¹ Pm	⁶² Sm	⁶³ Eu	⁶⁴ Gd	⁶⁵ Tb	⁶⁶ Dy	⁶⁷ Ho	⁶⁸ Er	⁶⁹ Tm	⁷⁰ Yb	⁷¹ Lu				
Actinides		⁹⁰ Th	⁹¹ Pa	⁹² U	⁹³ Np	⁹⁴ Pu	⁹⁵ Am	⁹⁶ Cm	⁹⁷ Bk	⁹⁸ Cf	⁹⁹ Es	¹⁰⁰ Fm	¹⁰¹ Md	¹⁰² No	¹⁰³ Lr				

Tight-Binding Overlap Parameters

In the paper [Applications of a new tight-binding total energy method for transition and noble metals: Elastic constants, vacancies, and surfaces of monatomic metals \[Phys. Rev. B 54, 4519-30 \(1996\)\]](#), we assumed the overlap matrix elements had the form

$$S_{ll'm}(R) = (a + b R + c R^2) \exp(-d^2 R) f(r), \quad (1)$$

where a, b, c, d were fitting parameters and f(r) is a cutoff function. The parameters l and l' indicate the angular momentum of the two wave functions, and m indicates the behavior of the matrix element under rotation. Obviously we must have some additional conditions on S. For example, since S is supposed to represent overlapping normalized wave functions, we must have

Silicon (Si) -- sp parameterization

```

1                               (One atom type in this file)
12.5   0.5                     (RCUT and SCREENL for 1-1 interactions)
4                               (Orbitals for atom 1)
28.086                         (Atomic Weight of Atom 1)
2.0   2.0   0.0                 (formal spd valence occupancy for atom 1)
  .110356625153E+01    0   1   lambda (equation 7)
  -.532334619024E-01   0   2   a_s    (equation 9)
...

```