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"

Robert S. Mulliken

PHYSICAL REVIEW VOLUME 136, NUMBER 3B 9 NOVEMEBR 1964

Inhomogeneous Electron Gas*

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(Received 18 June 1964)

This paper deals with the ground state of an interacting electron gas in an external potential $v(\mathbf{r})$. It is 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) $n(\mathbf{r}) = n_0 + \tilde{n}(\mathbf{r})$, $\tilde{n}/n_0 << 1$, and (2) $n(\mathbf{r}) = \varphi(\mathbf{r}/r_0)$ with φ arbitrary and $r_0 \to \infty$. 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.

The Nobel Prize in Chemistry 1998

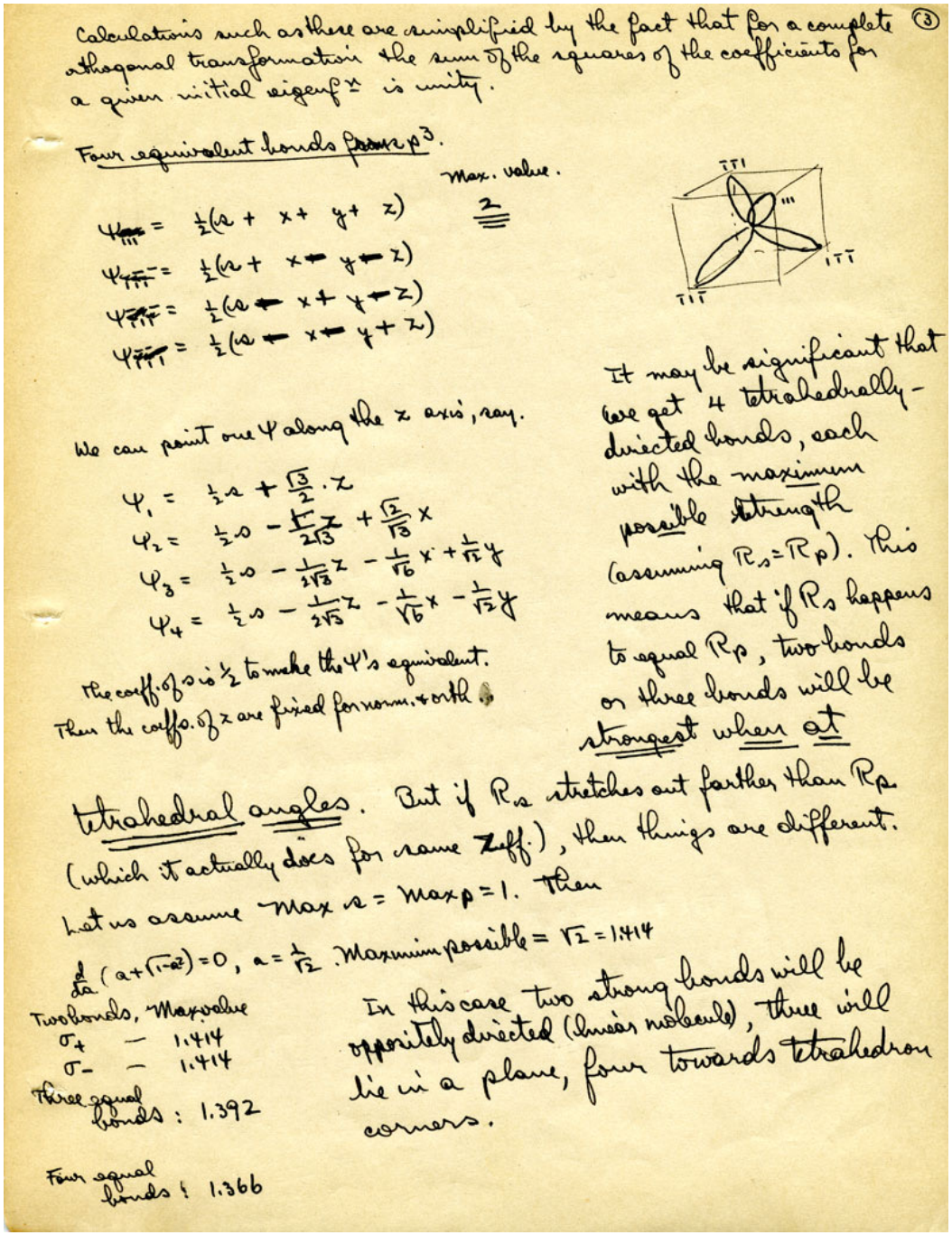
"for his development of the density-functional theory"

"for his development of computational methods in quantum chemistry"

Walter Kohn

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 eigenf^{n} is unity. ③

Four equivalent bonds from sp^3.

Max. value.

$\psi_{111} = \frac{1}{2}(s + x + y + z)$ 2

$\psi_{1\bar{1}\bar{1}} = \frac{1}{2}(s + x - y - z)$

$\psi_{\bar{1}1\bar{1}} = \frac{1}{2}(s - x + y - z)$

$\psi_{\bar{1}\bar{1}1} = \frac{1}{2}(s - x - y + z)$

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

$\psi_1 = \frac{1}{2}s + \frac{\sqrt{3}}{2}\cdot x$

$\psi_2 = \frac{1}{2}s - \frac{1}{2\sqrt{3}}z + \frac{\sqrt{2}}{\sqrt{3}}x$

$\psi_3 = \frac{1}{2}s - \frac{1}{2\sqrt{3}}z - \frac{1}{\sqrt{6}}x + \frac{1}{\sqrt{2}}y$

$\psi_4 = \frac{1}{2}s - \frac{1}{2\sqrt{3}}z - \frac{1}{\sqrt{6}}x - \frac{1}{\sqrt{2}}y$

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

It may be significant that we get 4 tetrahedrally-directed bonds, each with the maximum possible strength (assuming $R_s = R_p$). This means that if R_s happens to equal R_p, two bonds or three bonds will be strongest when at 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 max s = max p = 1. Then

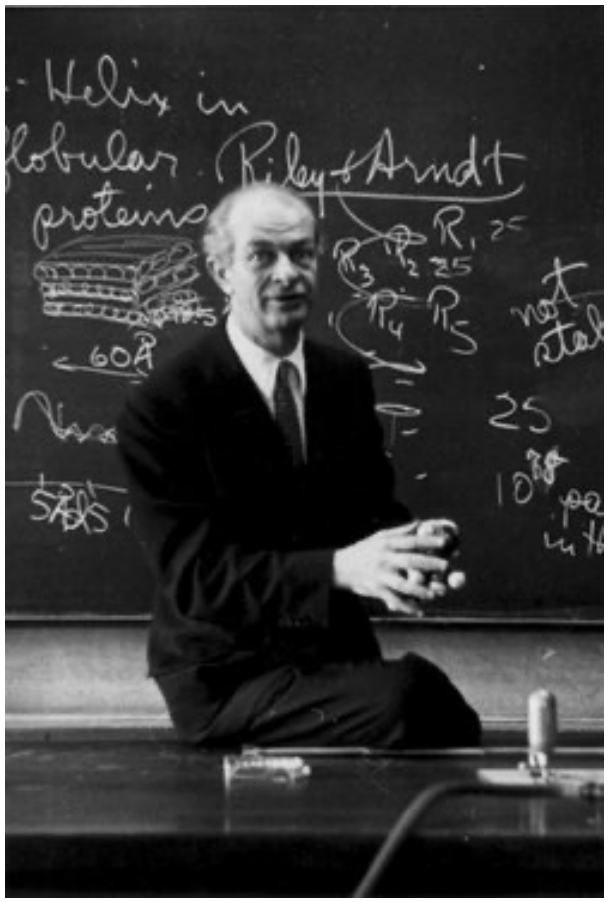
$\frac{d}{da}(a + \sqrt{1-a^2}) = 0$, $a = \frac{1}{\sqrt{2}}$. Maximum possible = $\sqrt{2} = 1.414$

Two bonds, Max value
σ_+ — 1.414
σ_- — 1.414

Three equal bonds : 1.392

Four equal bonds : 1.366

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



Linus Pauling online
at Oregon State Univ.

cf. Raty *et al.*,
Adv. Mater. **31**, 1806280 ('19)

Energy Eigenstates

- **Time-independent Schrödinger equation**

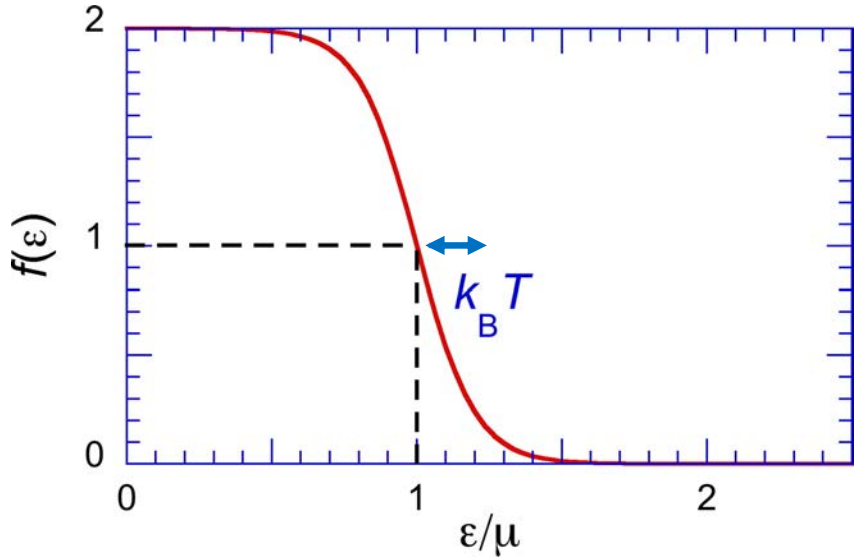
Hamiltonian operator → $H\psi_n(\mathbf{r}) = \epsilon_n \psi_n(\mathbf{r})$ ← Eigenstate

Eigenvalue

- **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**

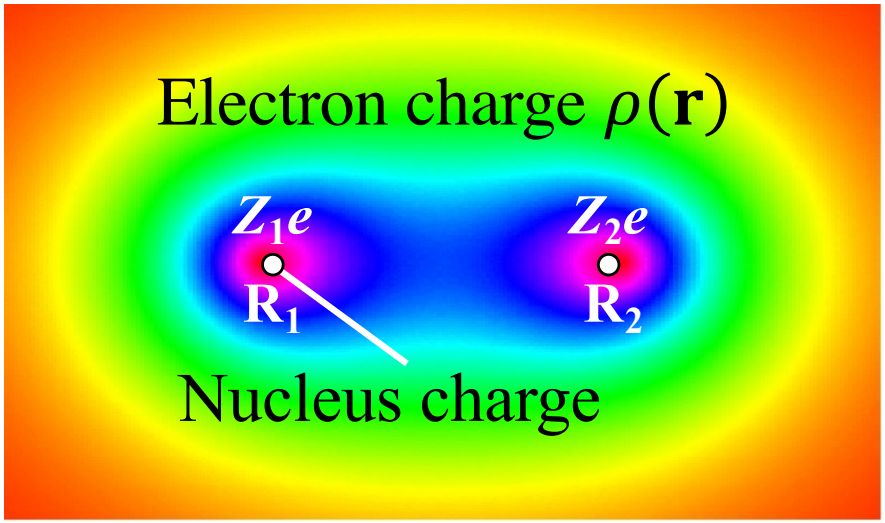
$$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial \mathbf{r}_i^2} + v(\mathbf{r})$$

- **Density functional theory**

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

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

exchange-correlation potential



See *CSCI699: Extreme-scale Quantum Simulations*
https://aiichironakano.github.io/cs699.html

Density Functional Theory

- **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)

Background: Atomic Orbitals

$$\begin{cases} n = 1,2,\cdots \\ l \in [0, n-1] \\ m \in [-l, l] \end{cases}$$

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi)$$

Radial function — Spherical harmonics

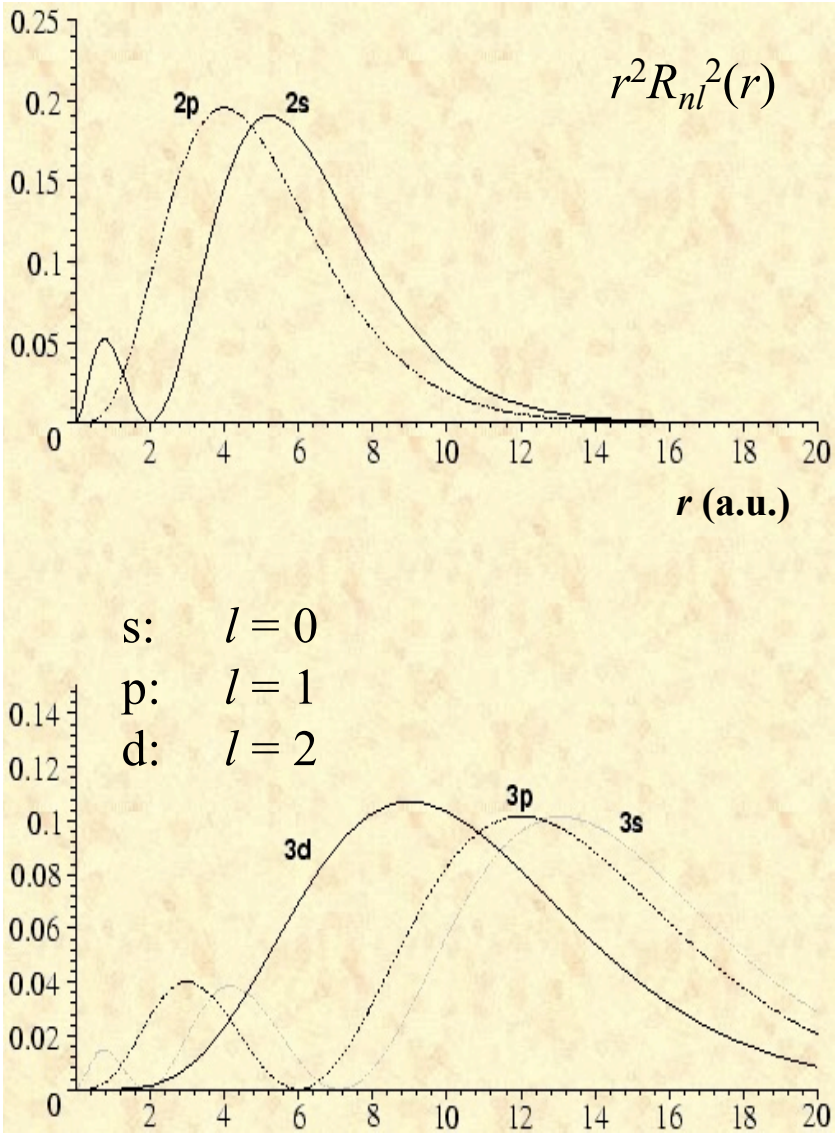
s: $l = 0$
p: $l = 1$
d: $l = 2$

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

	n	ℓ	m	$R_{n\ell}$	$Y_{\ell m}$
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	$\left(\frac{1}{2a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$	$\frac{1}{2\sqrt{\pi}}$
2p	2	1	0	$\left(\frac{1}{2a_0}\right)^{3/2}\frac{1}{\sqrt{3}}\frac{r}{a_0}e^{-r/2a_0}$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$
⋮	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

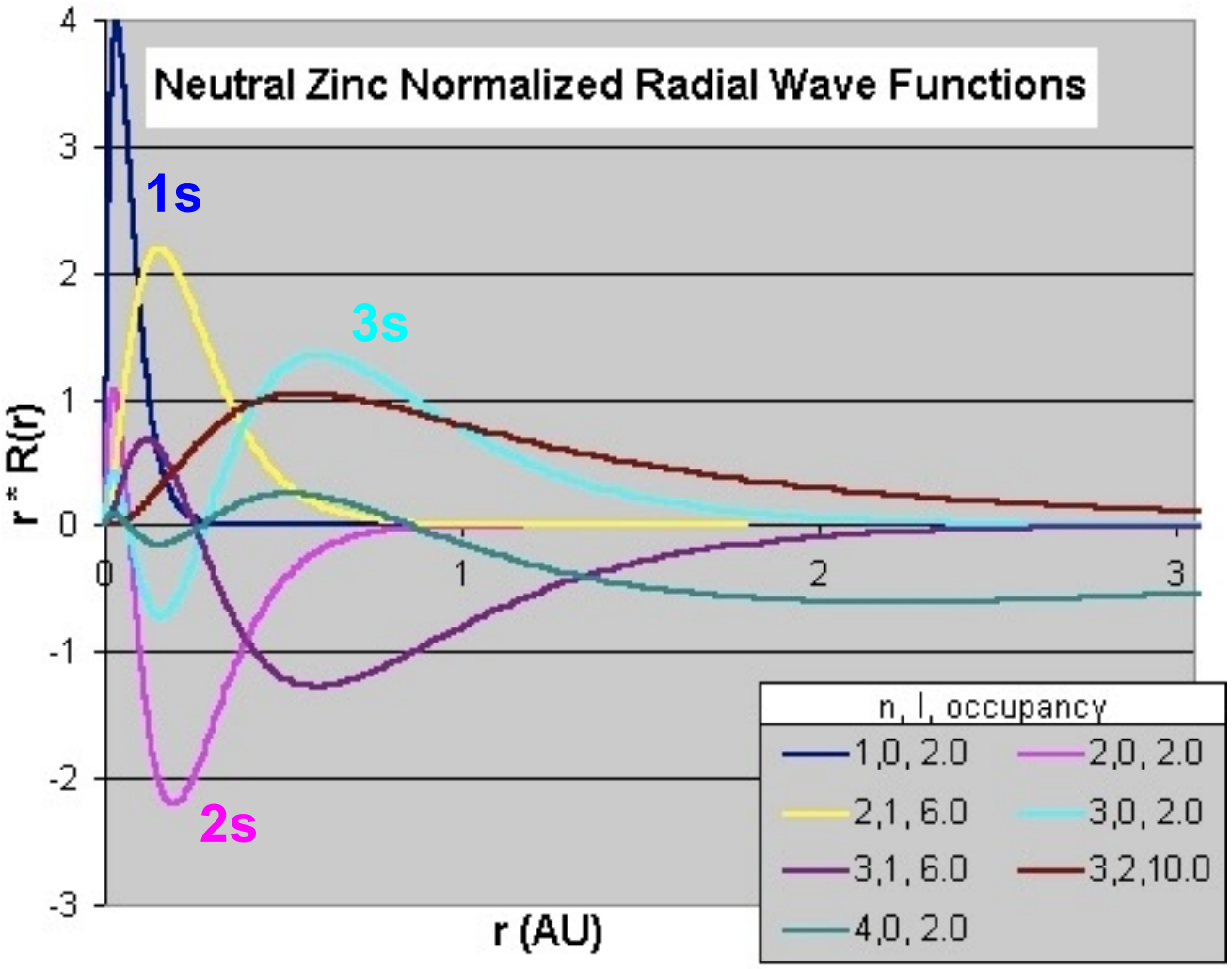
Hydrogen Eigenstates



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

Herman-Skillman Solutions for Atoms

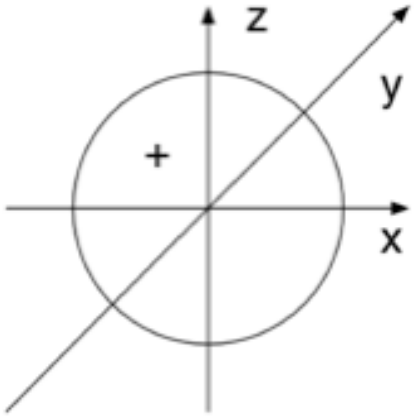
- Hartree approximation ($v_{xc} = 0$) for many-electron interaction



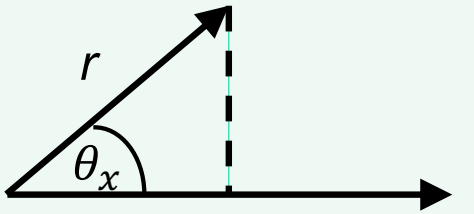
Outer shells (*i.e.*, larger *n*) still spread outward

Atomic Orbitals

- **s orbital ($l = 0$)**

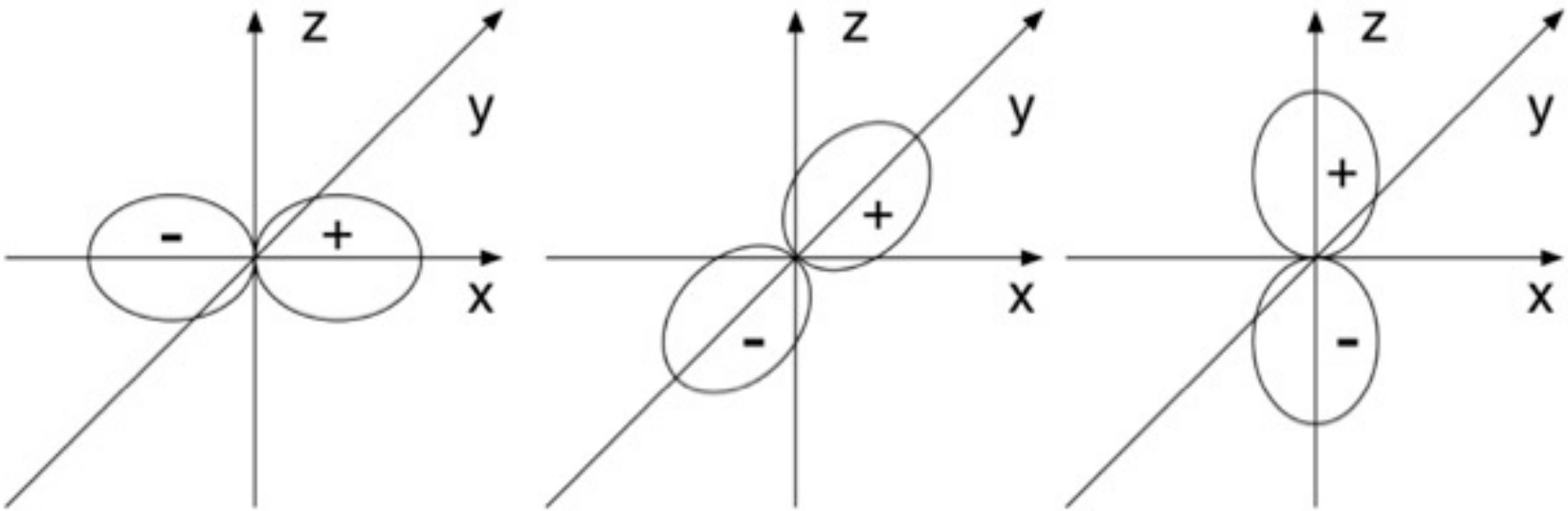


Directional cosine



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

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



Tight-Binding Model

- **Linear combination of atomic orbitals (LCAO)**

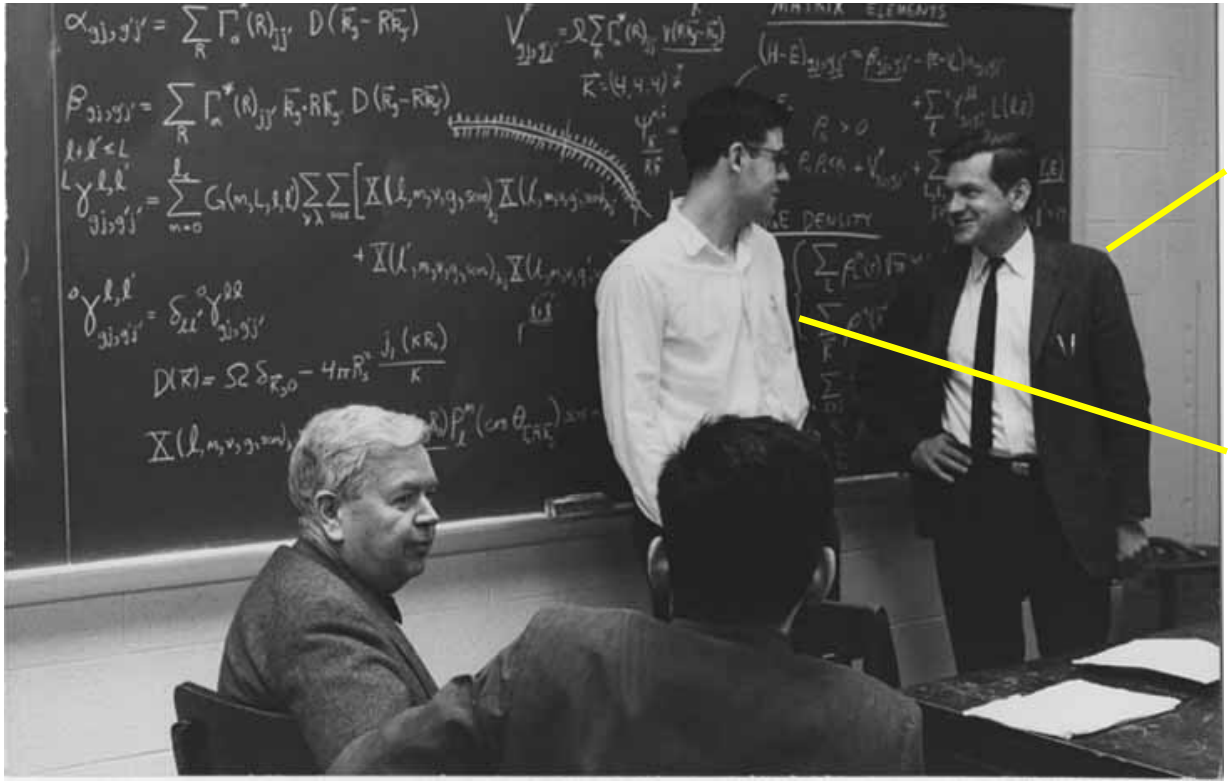
$$\psi(\vec{r}) = \sum_{i=1}^{N} \sum_{\alpha \in \{s, p_x, p_y, p_z\}} c_{i\alpha}\, \psi_\alpha(\vec{r} - \vec{r}_i)$$

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)



John Slater

George Koster

Valence Electrons

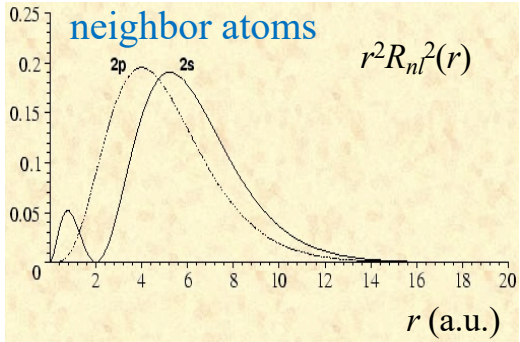
- **Example: Silicon—$1s^2 2s^2 2p^6 3s^2 3p^2$**

WebElements™ periodic table

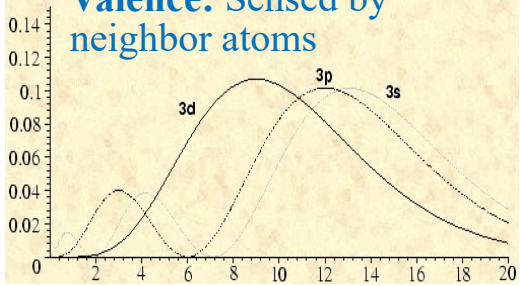
http://www.webelements.com

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												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
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		

Core: Invisible to neighbor atoms



Valence: Sensed by neighbor atoms



Electronic Configuration

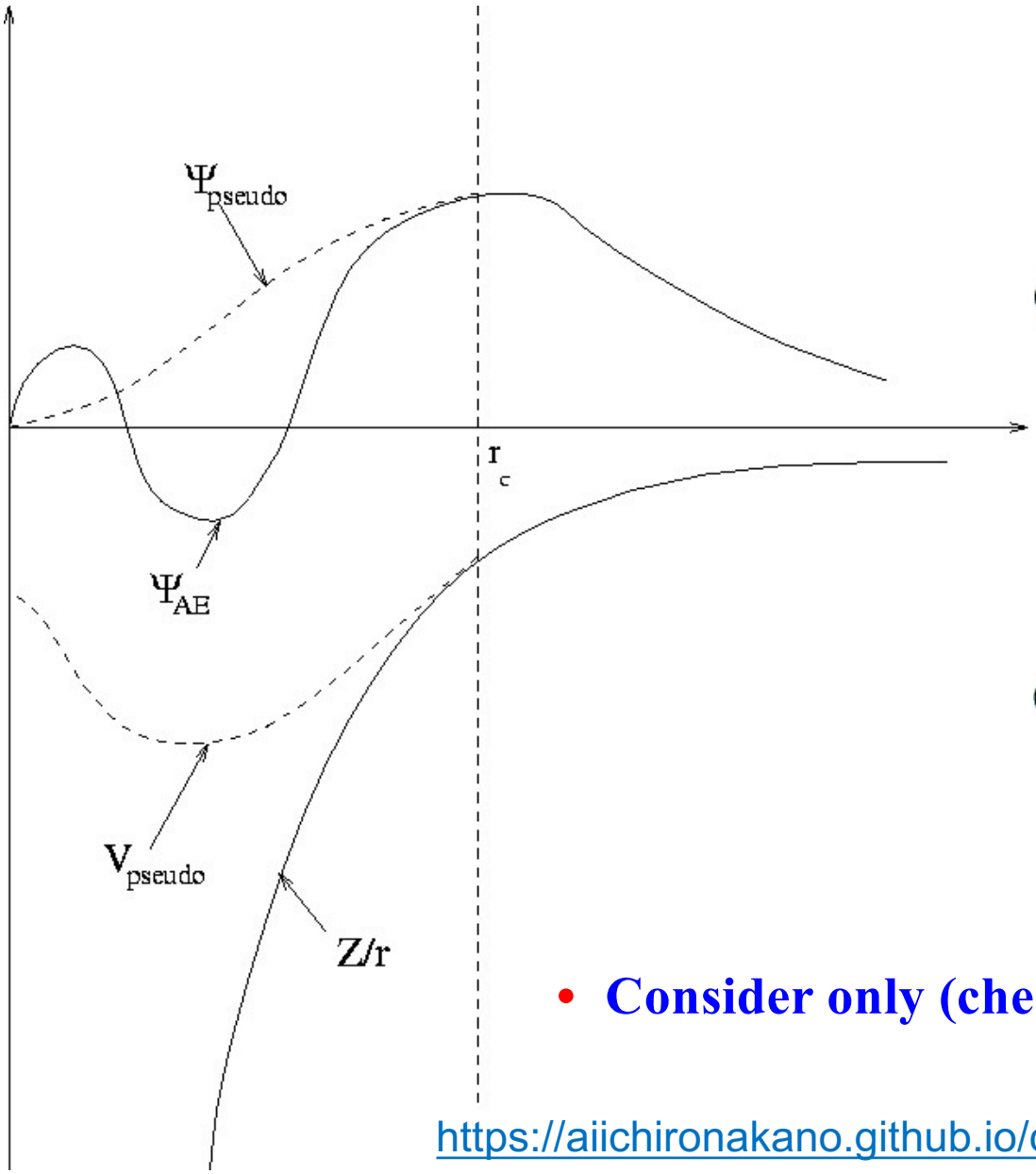
The following represents the electronic configuration and its associated term symbol for the **ground state neutral gaseous atom**. The configuration associated with silicon in its compounds is not necessarily the same.

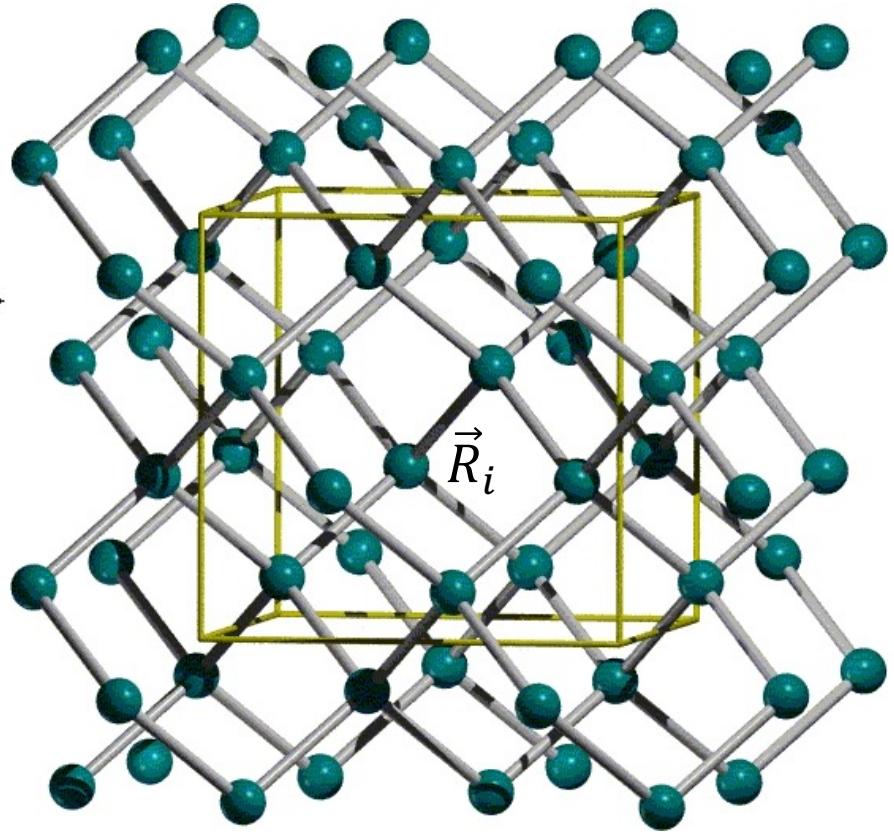
- **Ground state electron configuration:** [Ne].$3s^2.3p^2$
- **Shell structure:** 2.8.4

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**

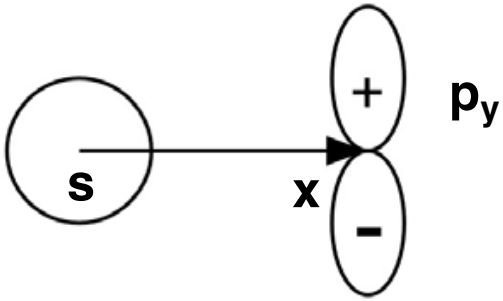
https://aiichironakano.github.io/cs699-lecture.html

Hamiltonian Matrix Elements

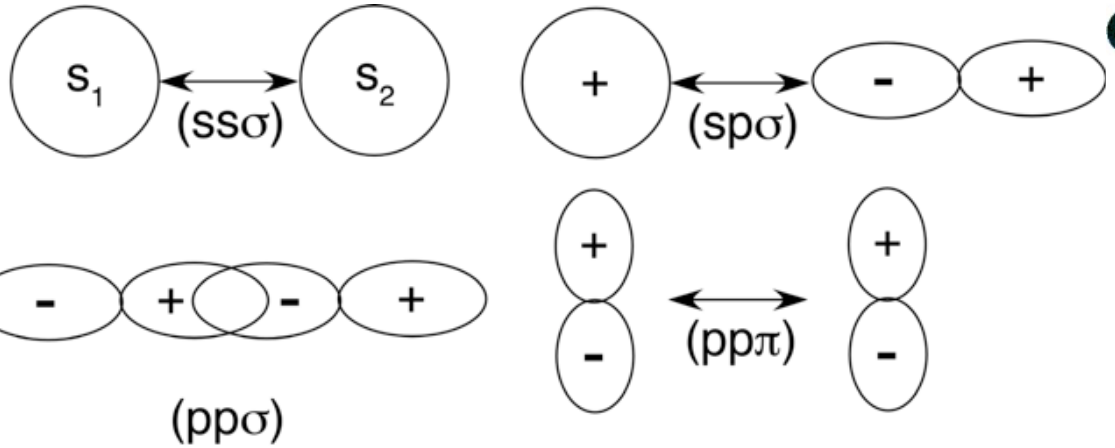
$$H_{i\prime\alpha\prime,i\alpha} = \int d\vec{r}\, \psi^*_{\alpha\prime}(\vec{r} - \vec{R}_{i\prime}) \left(-\frac{\nabla^2}{2} + v(\vec{r}) \right) \psi_\alpha(\vec{r} - \vec{R}_i)$$

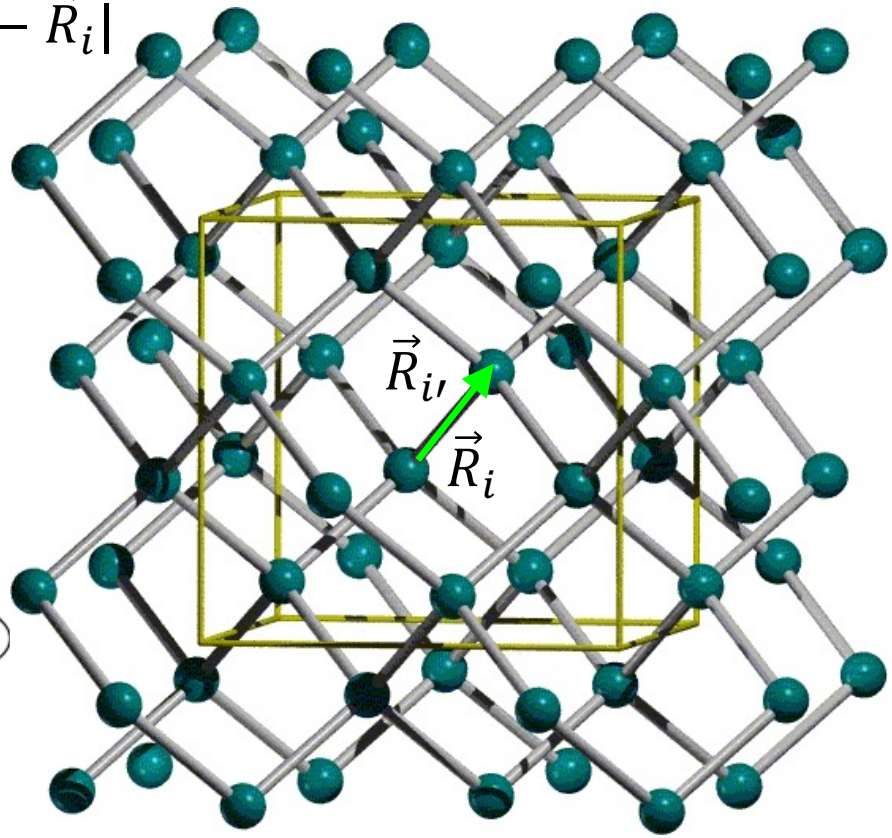
cf. slide 6

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



- **Nonvanishing matrix elements**





Overlap Integrals

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

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

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)

https://aiichironakano.github.io/phys516/Kwon-TBSi-PRB94.pdf

Eigenvalue Problem

$$H|\psi\rangle = \varepsilon|\psi\rangle \qquad |\psi\rangle = \sum_{i=1}^{N} \sum_{\alpha\in\{s,p_x,p_y,p_z\}} c_{i\alpha}\,|i\alpha\rangle$$

$$\sum_{i\alpha} c_{i\alpha}\langle i'\alpha'|H|i\alpha\rangle = \varepsilon \sum_{i\alpha} c_{i\alpha}\langle i'\alpha'|i\alpha\rangle$$

$$\langle i'\alpha'|i\alpha\rangle = \delta_{ii'}\delta_{\alpha\alpha'}$$

$$\sum_{i\alpha} H_{i'\alpha',i\alpha}c_{i\alpha} = \varepsilon c_{i'\alpha'}$$

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

- **$4N\times4N$ matrix:**
  $\kappa = 4(i-1)+\alpha$, where $i \in \{1, 2, ..., N\}$ & $\alpha \in \{1\leftrightarrow s, 2\leftrightarrow p_x, 3\leftrightarrow p_y, 4\leftrightarrow p_z\}$

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

Eigen Decomposition

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

  $\langle\kappa'|\times \quad H|\psi\rangle = \varepsilon|\psi\rangle$

  $\langle\kappa'|H|\psi\rangle = \varepsilon\langle\kappa'|\psi\rangle$

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

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

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

  $\sum_\kappa H_{\kappa'\kappa} C_{\kappa n} = C_{\kappa' n}\varepsilon_n = \sum_{n'} C_{\kappa' n'} \overbrace{\delta_{n'n}\varepsilon_n}^{E_{n'n}} = \sum_{n'} C_{\kappa' n'} E_{n'n}$

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

  $\mathbf{C} = \left[\mathbf{c}^{(1)} \cdots \mathbf{c}^{(4N)}\right]$

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

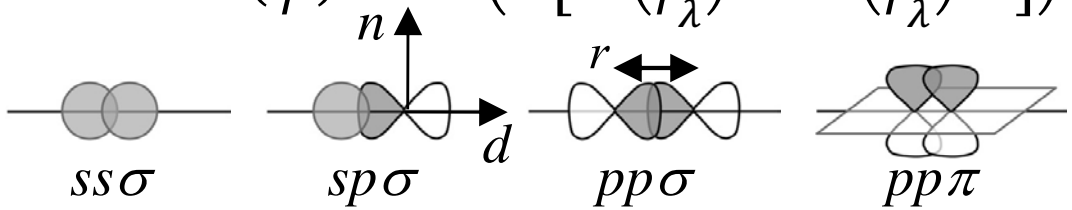
- **Orthonormality:** $\delta_{nn'} = \sum_{\kappa=1}^{4N} c_\kappa^{(n)} c_\kappa^{(n')} = \sum_{\kappa=1}^{4N} C_{n\kappa}^T C_{\kappa n'} = (\mathbf{C}^T\,\mathbf{C})_{nn'}$ or $\mathbf{I} = \mathbf{C}^\mathbf{T}\mathbf{C}$

- **Eigen decomposition:** $\mathbf{C}^T\mathbf{HC} = \mathbf{E}$ ($\because \mathbf{C}^T \times \mathbf{HC} = \mathbf{C}^T \times \mathbf{CE} = \mathbf{E}$)

Silicon Tight-Binding Parameters

Inter-atom

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



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	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

- **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

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

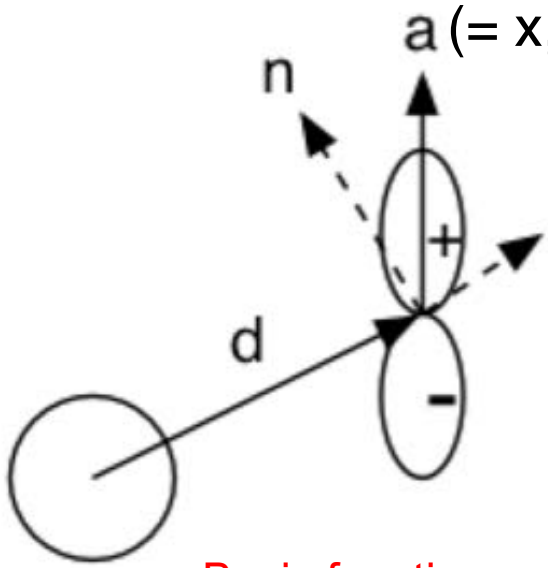
$\because |p_\alpha\rangle = \cos(\chi-\theta) = \cos\chi\cos\theta + \sin\chi\sin\theta = \cos\theta|p_d\rangle + \sin\theta|p_n\rangle$ **addition theorem**

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

$\cos\chi = p_d$

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

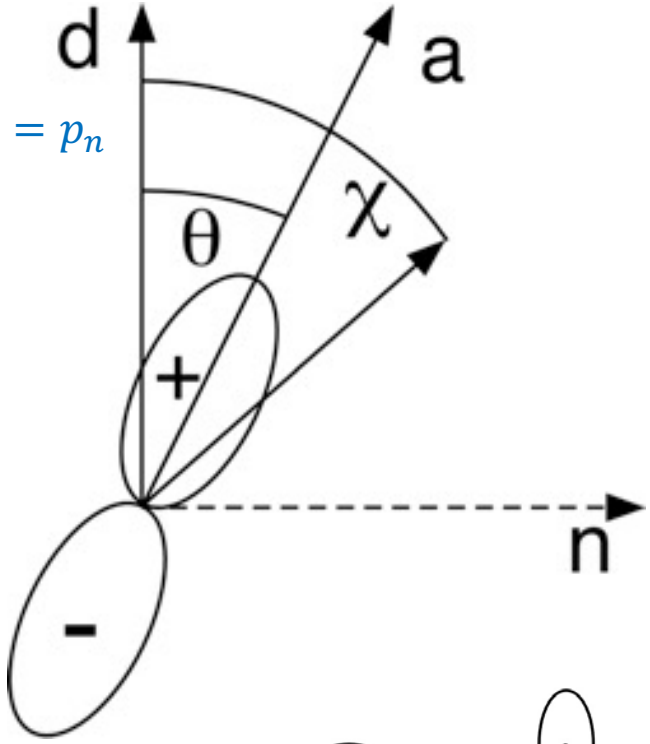
cf. slide 9



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

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

$$\hat{d} = \vec{r}_{ij}/r = \left(\overbrace{\hat{x}\bullet\hat{d}}^{d_x}, \overbrace{\hat{y}\bullet\hat{d}}^{d_y}, \overbrace{\hat{z}\bullet\hat{d}}^{d_z}\right)$$

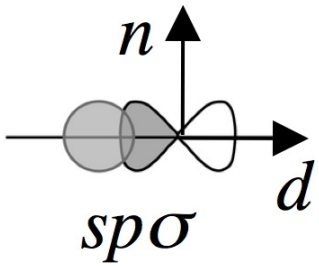


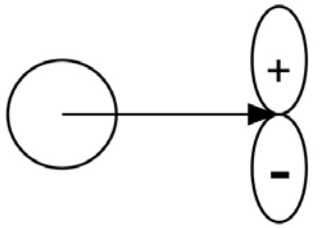
Basis function

Hamilton matrix element

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

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

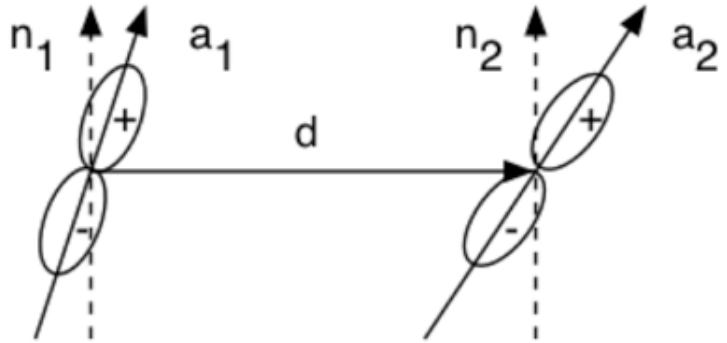




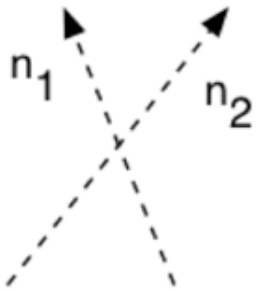
$\langle s|H|p_n\rangle = 0$

Projection of p-p Integrals

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



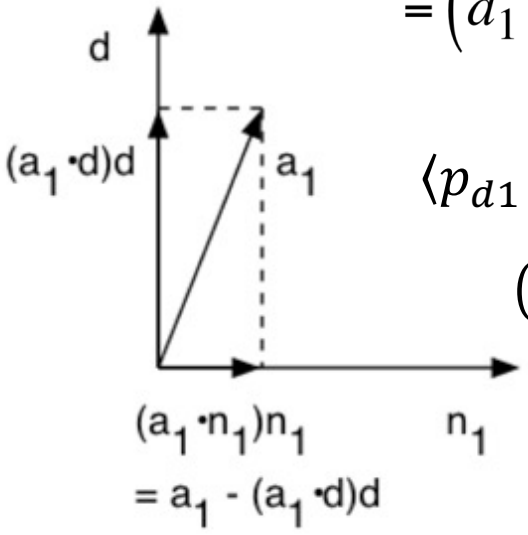
Side view of vector d



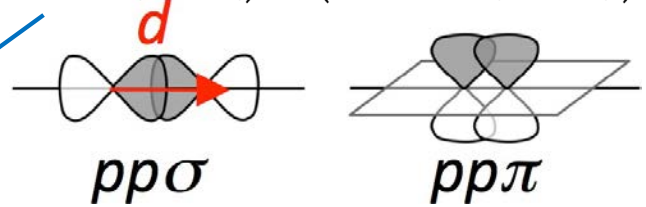
View from vector d direction

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

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



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



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

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

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

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

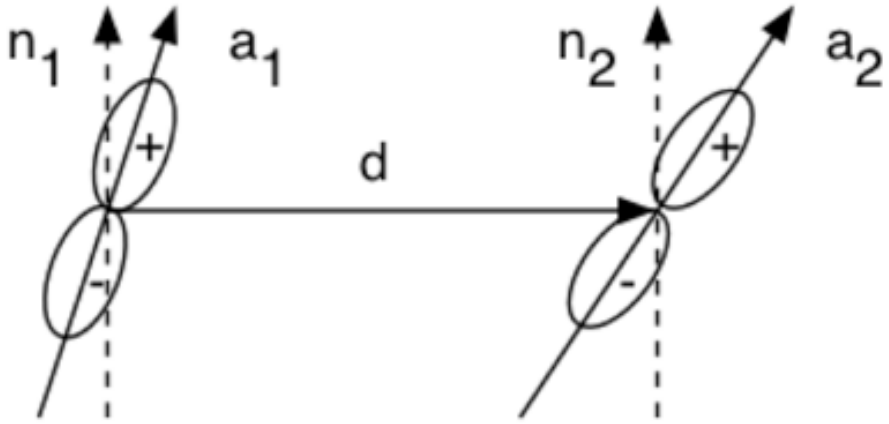
$$\left(\hat{a}_1 \bullet \hat{n}_1\right)\hat{n}_1 = \hat{a}_1 - \left(\hat{a}_1 \bullet \hat{d}\right)\hat{d}$$

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

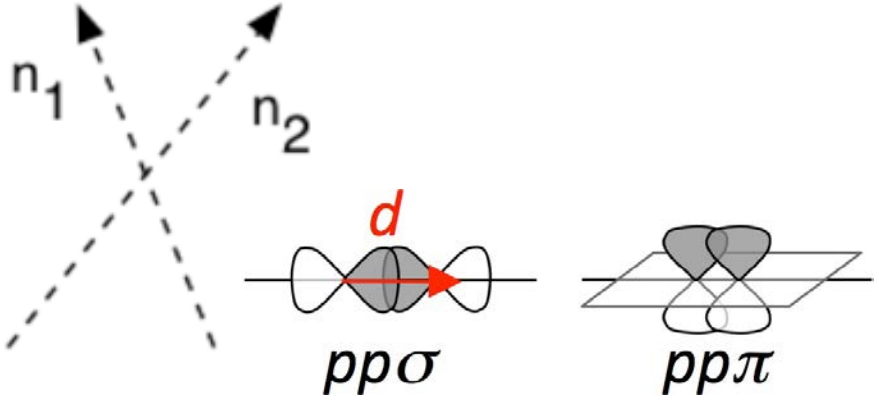
Projection of p-p Integrals

$$\langle p_1|H|p_2\rangle = (\hat{a}_1 \bullet \hat{d}) \bullet (\hat{a}_2 \bullet \hat{d}) h_{pp\sigma}(r) + (\hat{a}_1 - (\hat{a}_1 \bullet \hat{d})\hat{d}) \bullet (\hat{a}_2 - (\hat{a}_2 \bullet \hat{d})\hat{d}) h_{pp\pi}(r)$$

projection onto $\hat{d}$ — projection out of $\hat{d}$



Side view of vector d



View from vector d direction

$$\begin{pmatrix} \langle p_{1x}|H|p_{2x}\rangle & \langle p_{1x}|H|p_{2y}\rangle & \langle p_{1x}|H|p_{2z}\rangle \\ \langle p_{1y}|H|p_{2x}\rangle & \langle p_{1y}|H|p_{2y}\rangle & \langle p_{1y}|H|p_{2z}\rangle \\ \langle p_{1z}|H|p_{2x}\rangle & \langle p_{1z}|H|p_{2y}\rangle & \langle p_{1z}|H|p_{2z}\rangle \end{pmatrix} (\hat{x} \bullet \hat{d}, \hat{y} \bullet \hat{d}, \hat{z} \bullet \hat{d}) = (d_x, d_y, d_z)$$

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

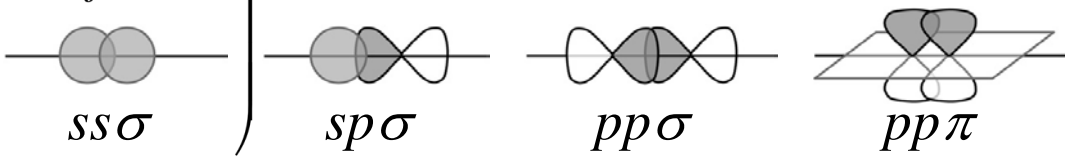
TB Hamiltonian Matrix

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

nAtom×*nAtom* blocks, each 4×4

$i = j$

$$\begin{pmatrix} E_s & 0 & 0 & 0 \\ 0 & E_p & 0 & 0 \\ 0 & 0 & E_p & 0 \\ 0 & 0 & 0 & E_p \end{pmatrix}$$



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

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

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

$i \neq j$

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

Apply periodic boundary condition (pick the minimum image)

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

js jp_x jp_y jp_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.

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

$l = d_x, m = d_y, n = d_z$

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

Eigenvalue Problem

$$H|\psi\rangle = \varepsilon|\psi\rangle \qquad |\psi\rangle = \sum_{i=1}^{N} \sum_{\alpha\in\{s,p_x,p_y,p_z\}} c_{i\alpha}\,|i\alpha\rangle$$

$$\sum_{i\alpha} c_{i\alpha}\langle i'\alpha'|H|i\alpha\rangle = \varepsilon \sum_{i\alpha} c_{i\alpha}\langle i'\alpha'|i\alpha\rangle$$

$$\langle i'\alpha'|i\alpha\rangle = \delta_{ii'}\delta_{\alpha\alpha'}$$

$$\sum_{i\alpha} H_{i'\alpha',i\alpha} c_{i\alpha} = \varepsilon c_{i'\alpha'}$$

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

- **$4N\times4N$ matrix:**
  $\kappa = 4(i-1)+\alpha$, where $i \in \{1, 2, ..., N\}$ & $\alpha \in \{1\leftrightarrow s, 2\leftrightarrow p_x, 3\leftrightarrow p_y, 4\leftrightarrow p_z\}$

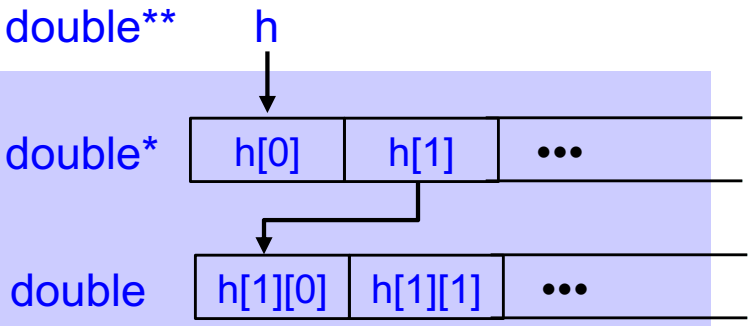
$$\sum_{\kappa} H_{\kappa'\kappa} c_{\kappa} = \varepsilon c_{\kappa'} \text{ or } \mathbf{C^T H C = E}$$

cf. slide 21 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);
```

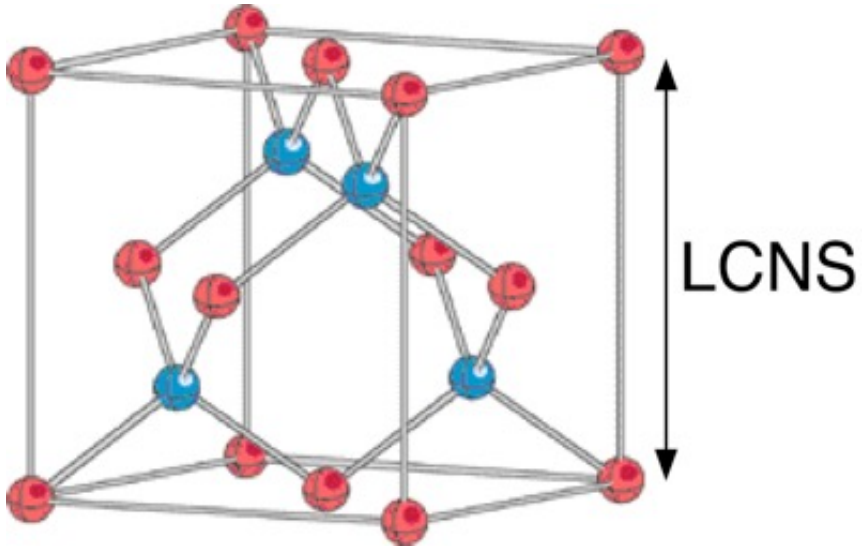
$\mathbf{C}^T\mathbf{H}\mathbf{C} = \mathbf{E}$

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

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

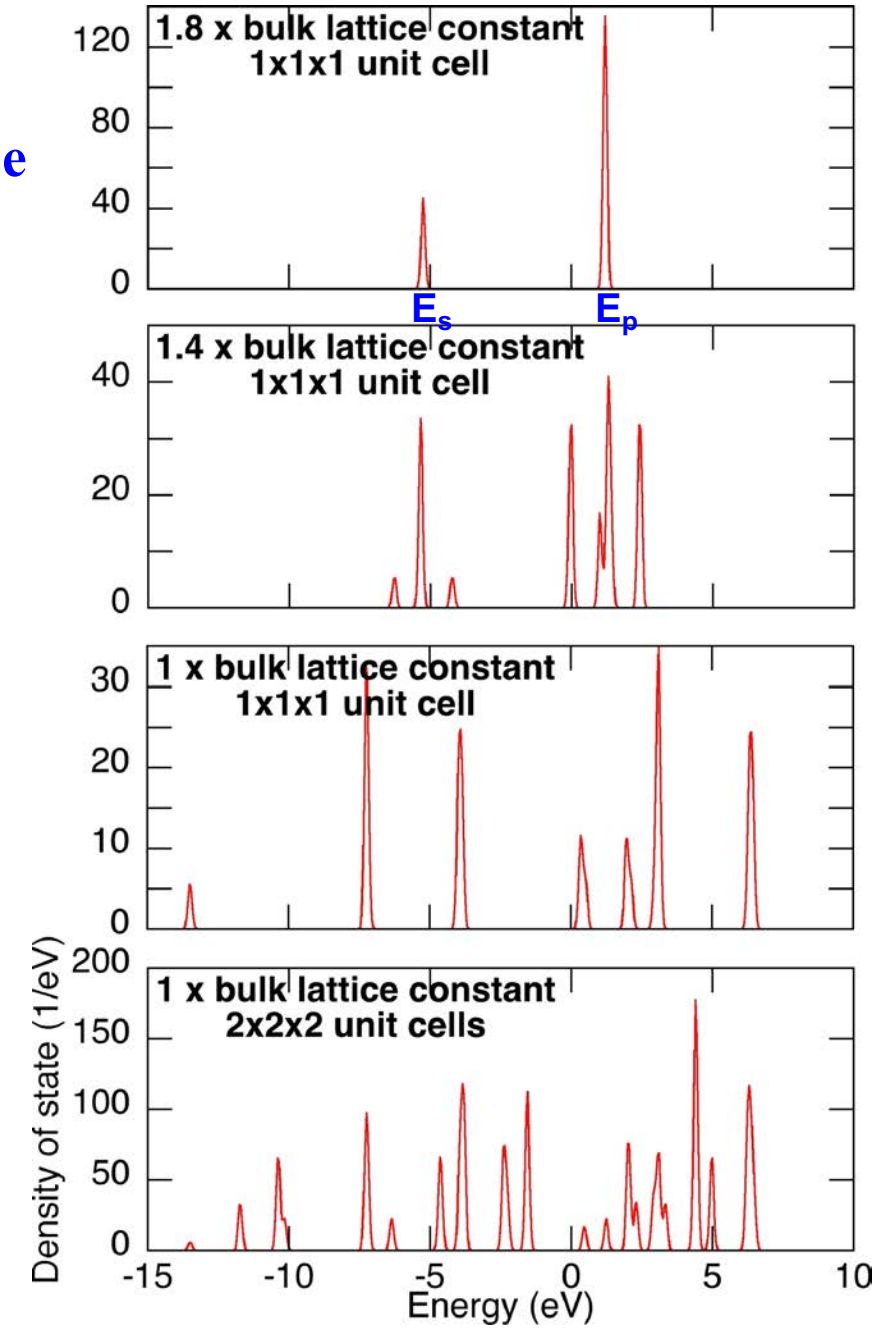
Example

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

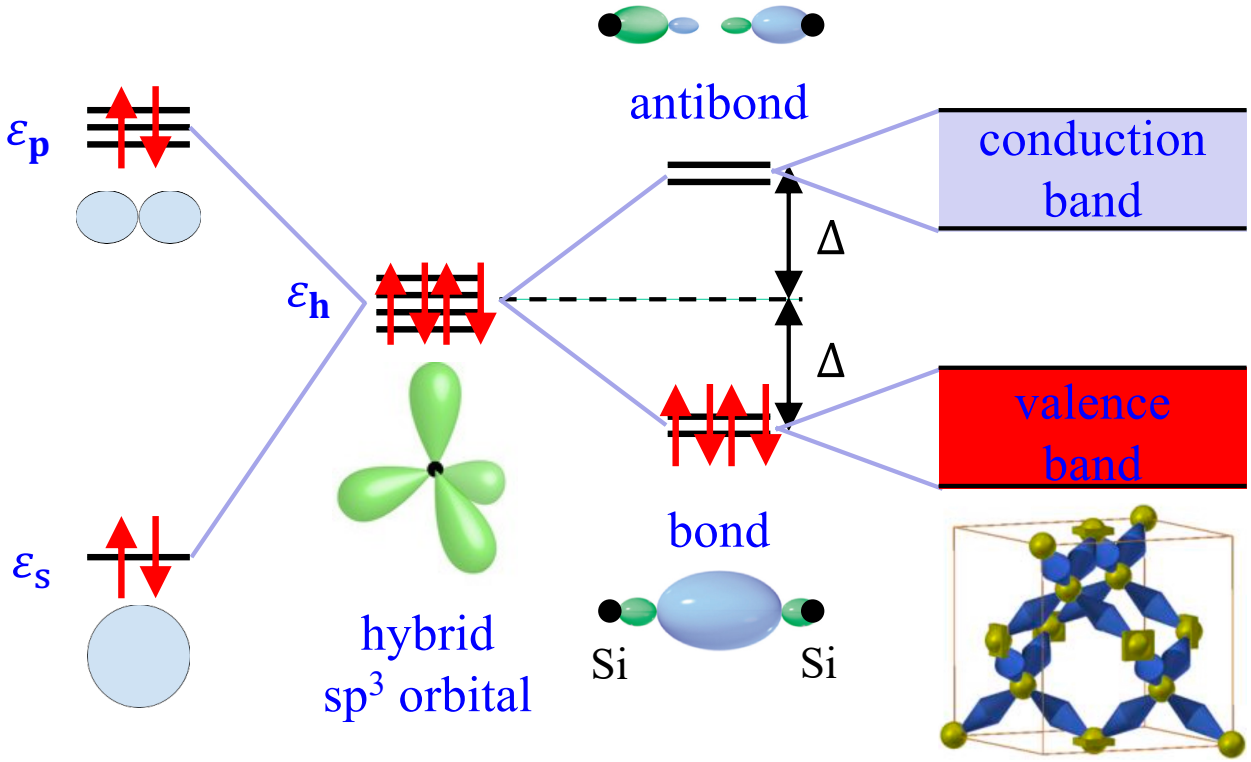


- **Density of states: σ = 0.1 eV**

$$D(\varepsilon) = \sum_{n=1}^{n4} \frac{1}{\sqrt{\pi}\sigma} \exp\left(-\frac{(\varepsilon - \varepsilon_n)^2}{\sigma^2}\right)$$



Energy Band in a Nutshell

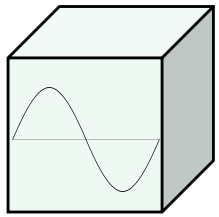


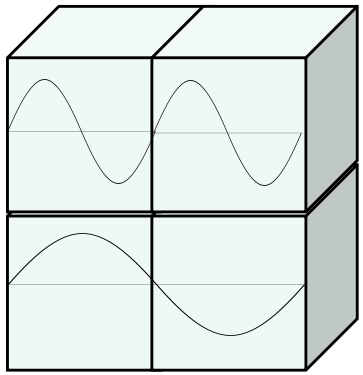
$$H = \begin{bmatrix} \varepsilon_h & \Delta \\ \Delta & \varepsilon_h \end{bmatrix}$$

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

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

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

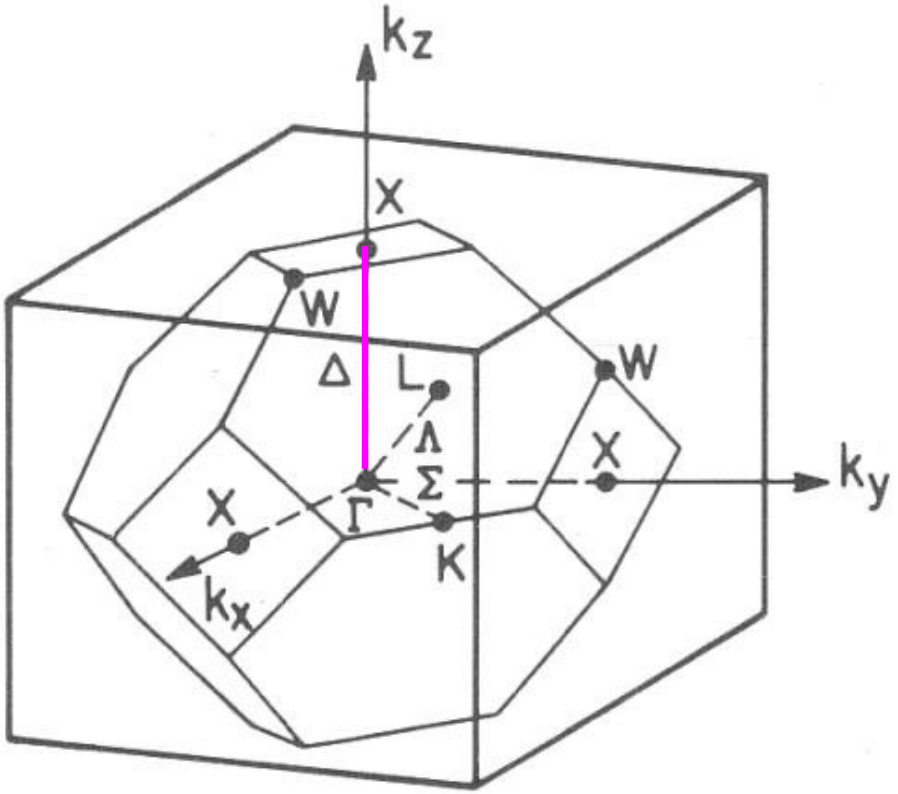




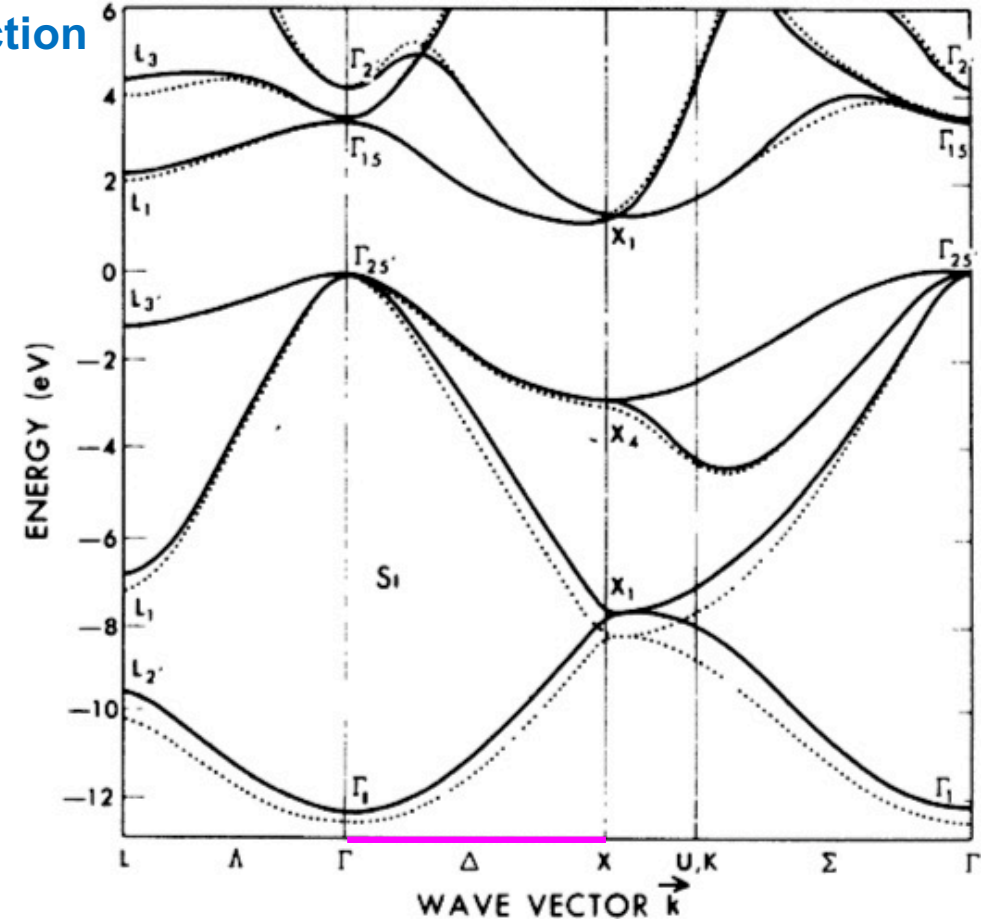
Band: Infinite Lattice

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

band index periodic function

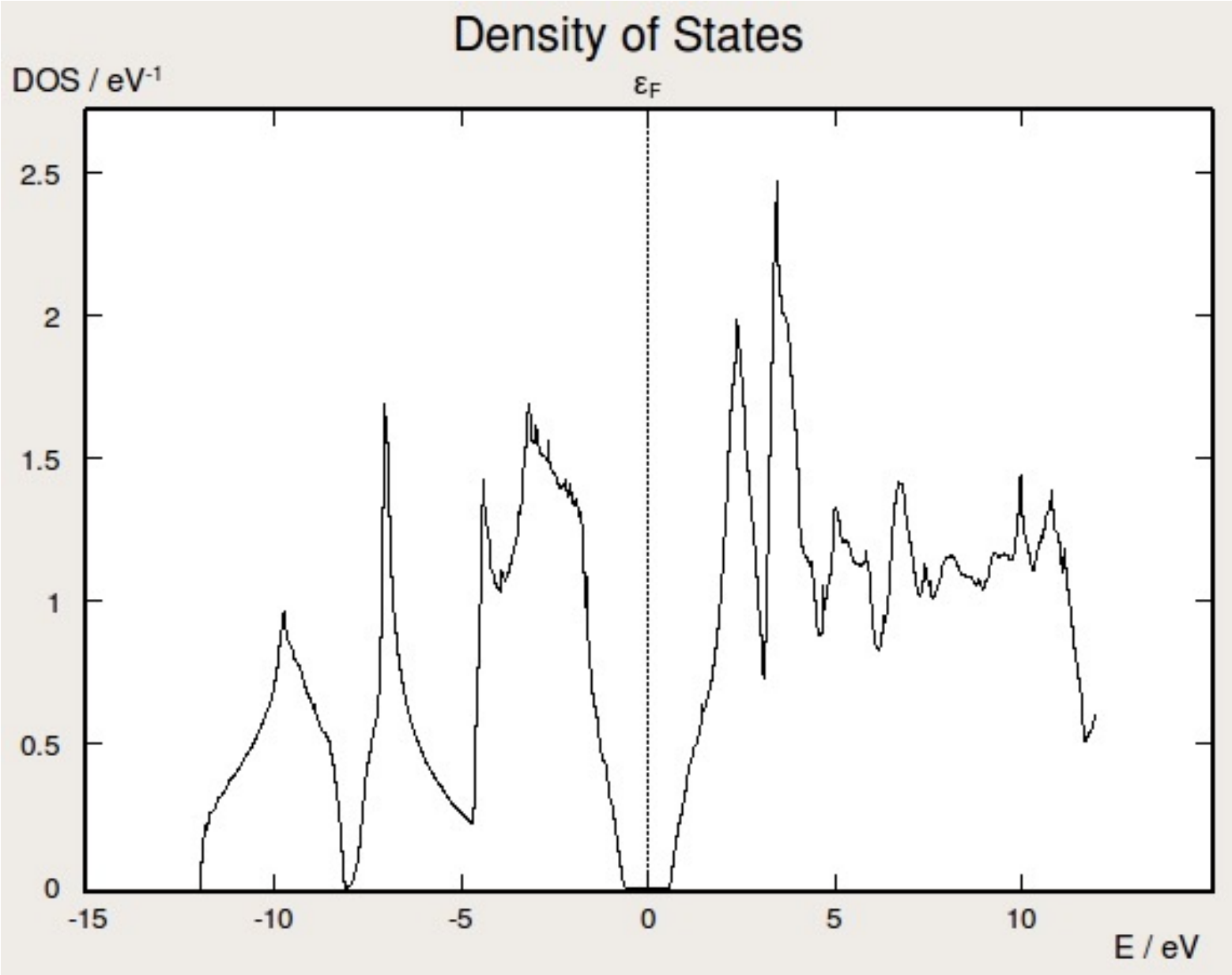


Brillouin zone of Si crystal



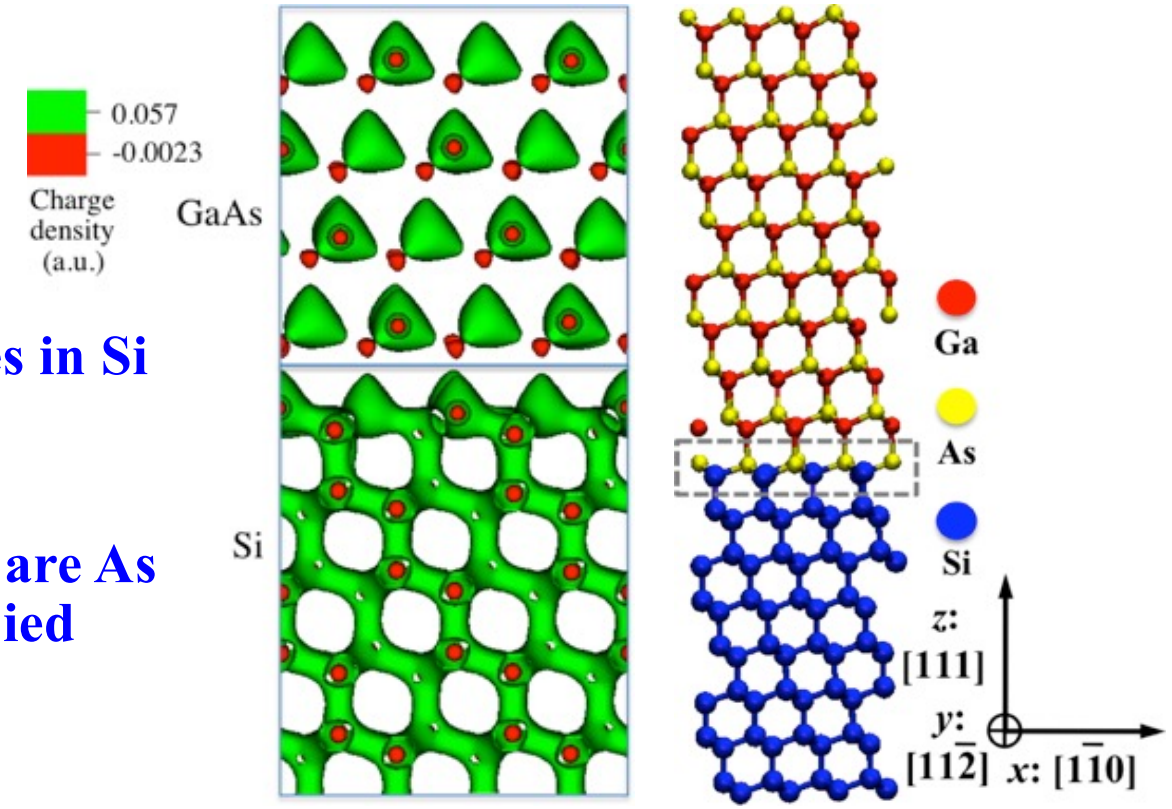
J. R. Chelikowsky & M. L. Cohen, *Phys. Rev. B* **10**, 5095 ('74)

Density of States: Silicon Crystal



http://quantumwise.com

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)**

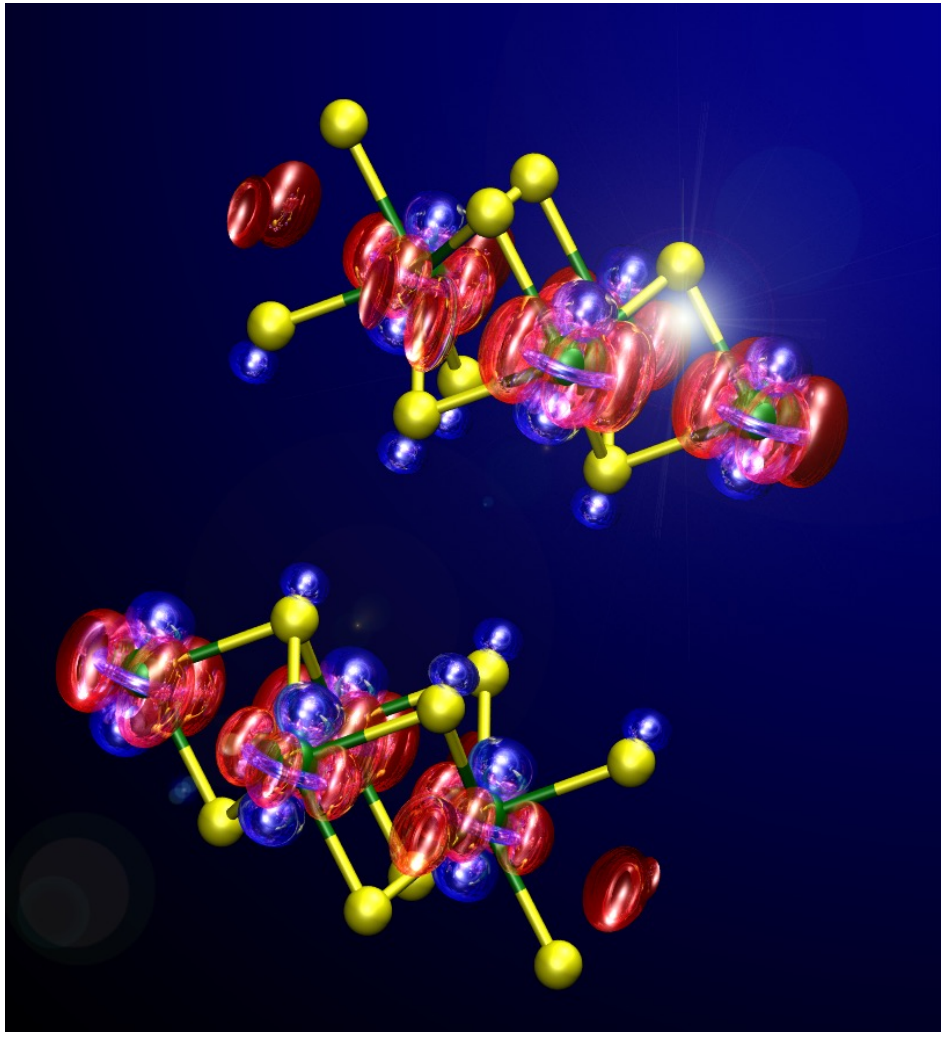
Projection of Kohn-Sham wave functions onto atomic orbitals

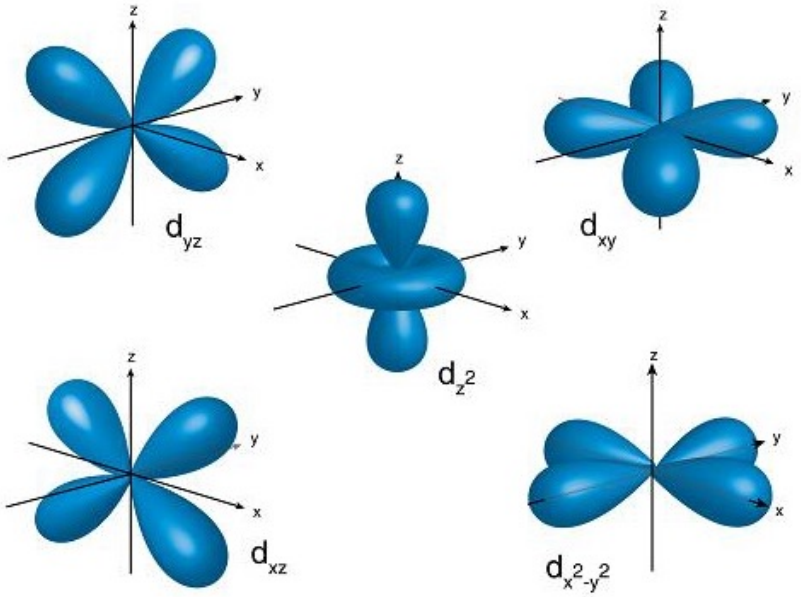
	Band	Ga 4s	Ga 4p	Ga 4d	As 4s	As 4p	As 4d	Total
	1150	0.0000	0.1157	0.0708	0.0000	0.8033	0.0101	1
	1151	0.0000	0.1158	0.0709	0.0000	0.8033	0.0100	1
Occupied	1152	0.0000	0.1166	0.0713	0.0000	**0.8017**	0.0104	1
Unoccupied	1153	**0.6763**	0.0000	0.0000	**0.3236**	0.0001	0.0000	1

Z. Yuan *et al.*, *J. Appl. Phys.* **114**, 074316 ('13); *Nano Lett.* **13**, 4925 ('13)

Wave Functions in $MoSe_2$ Bilayer

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





Electron
Hole

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