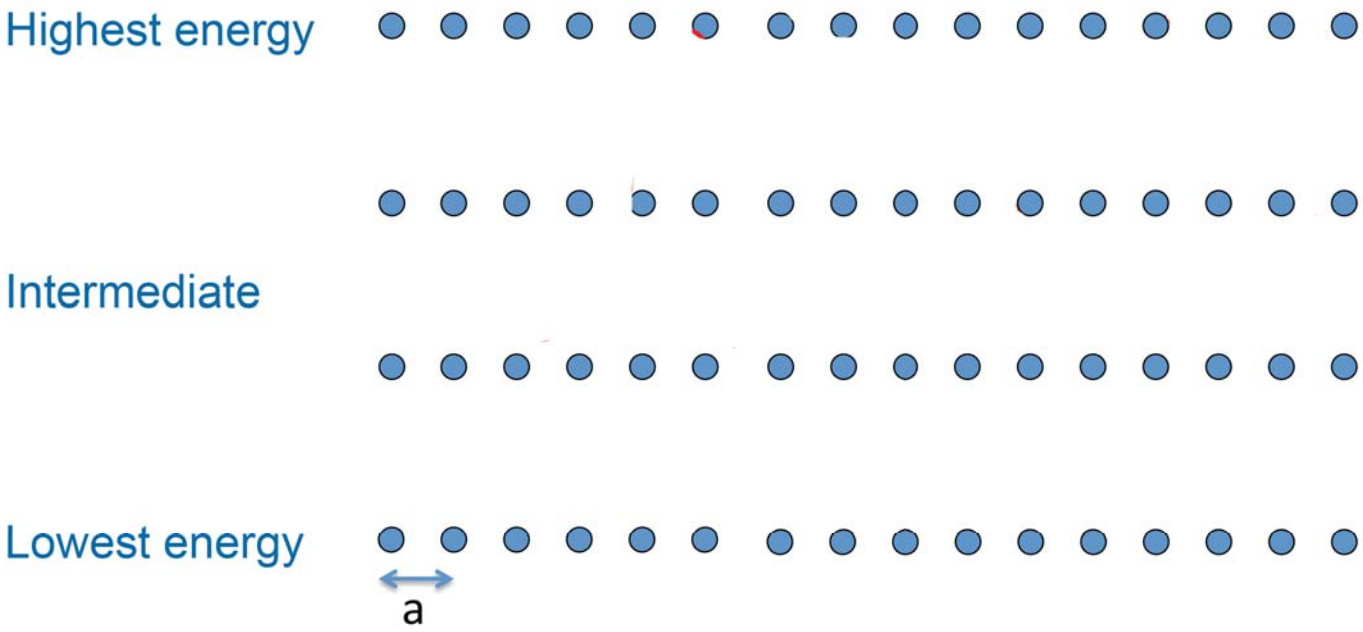
Wave functions of crystals

- Let's consider a 1D chain of atoms
- Combination of atomic orbitals to make the wavefunction of the crystal



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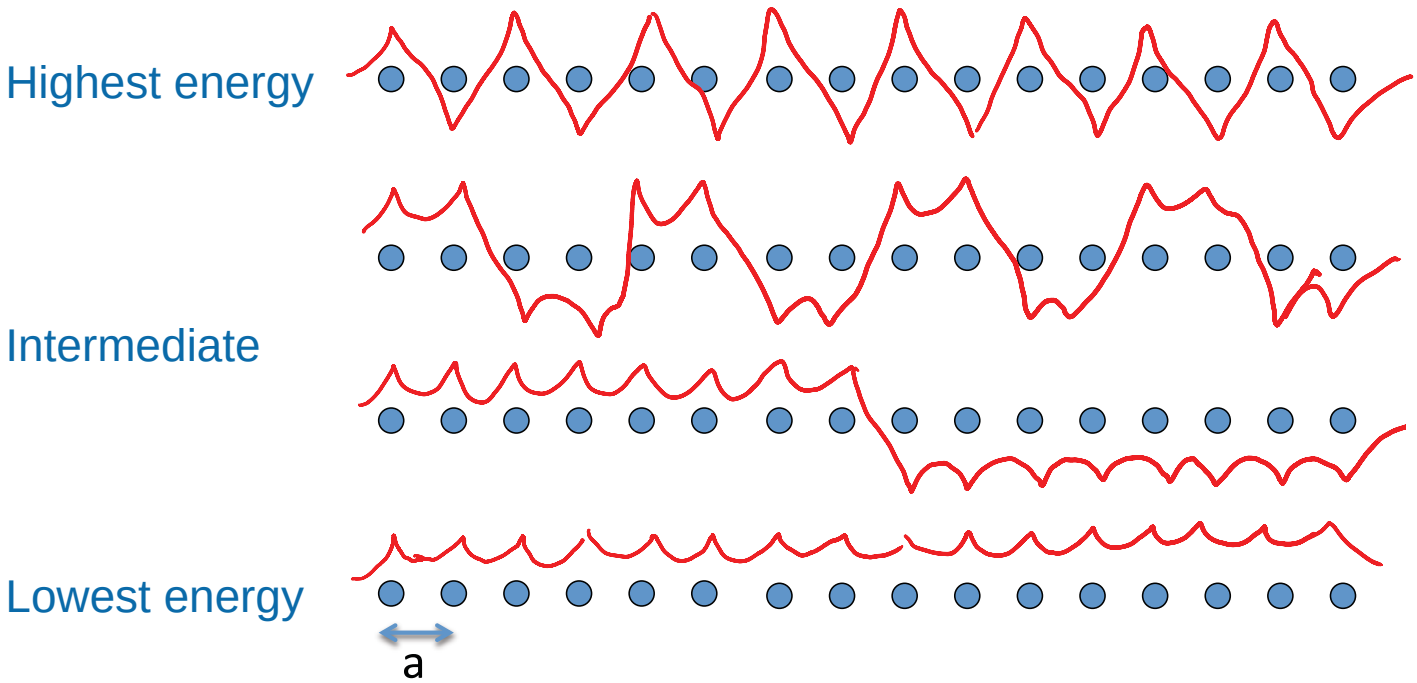
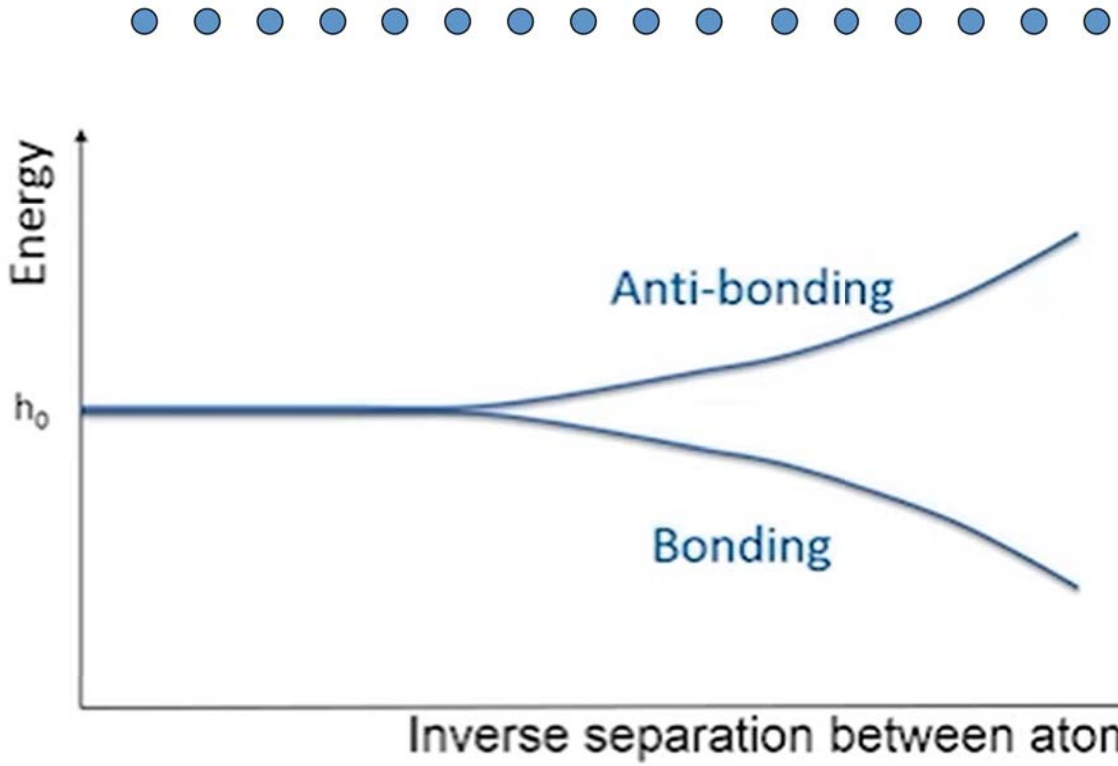
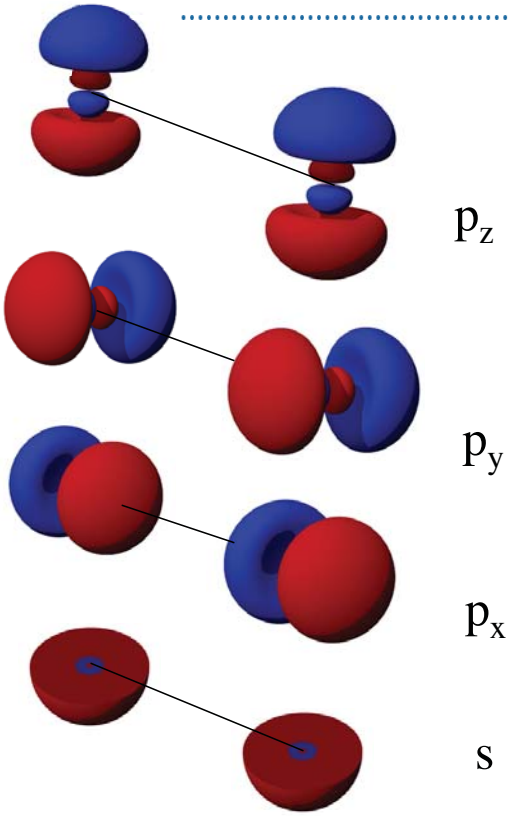


Molecules vs. solids

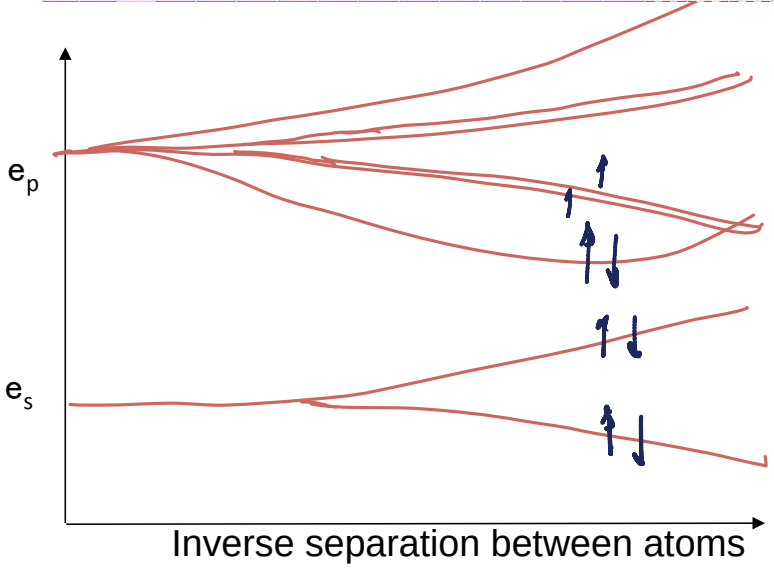


Remember: bring 2 Si together



From wikipedia

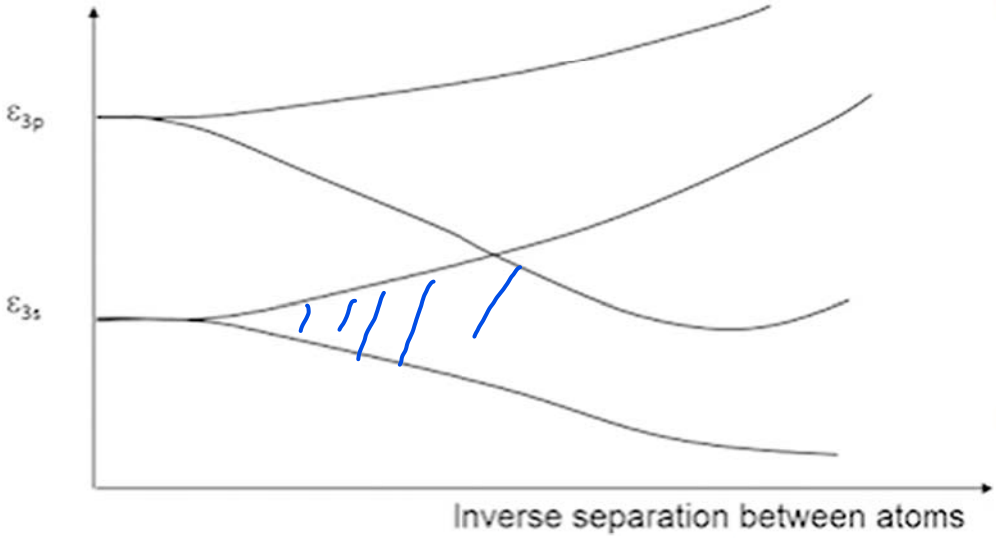
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe



Adapted from: W. Harrison, "Electronic structure and the properties of solids"
Images from Wikipedia

Making a crystal: lots of Si atoms together

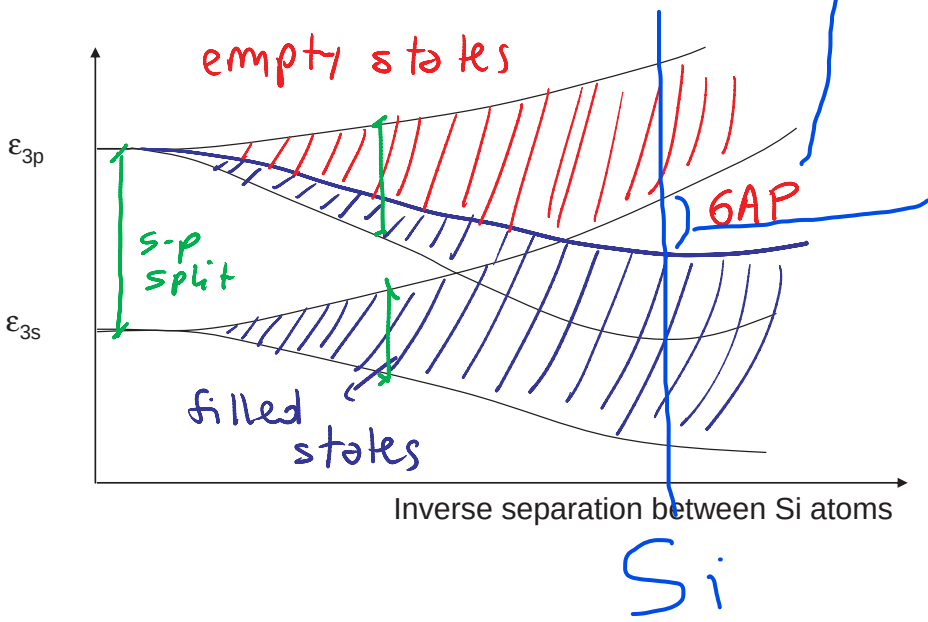
The s and p states overlap



Column IV band gaps

- C: 5.5 eV
- Si: 1.2 eV
- Ge: 0.6 eV
- Sn: 0.0 eV
  - Low T: a-Sn (diamond)
  - High T: b-Sn (tetragonal)
- Pb: fcc metal

Making a crystal: lots of Si atoms together

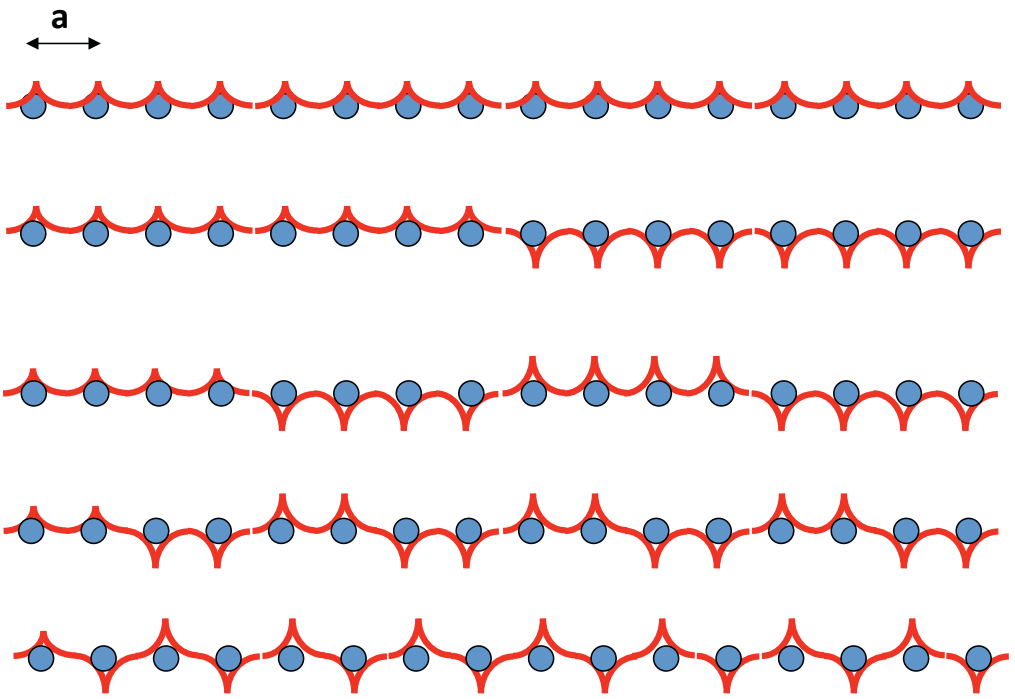


Column IV band gaps

C: 5.5 eV
Si: 1.2 eV
Ge: 0.6 eV
Sn: 0.0 eV
Low T
a-Sn (diamond)
b-Sn (tetragonal)
Pb: fcc metal

- Bonding/anti-bonding splitting larger than s-p splitting:
  - Covalent bonding dominates, insulators and semiconductors
- s-p splitting larger than bonding anti-bonding splitting
  - Metallic bonding, closed packed structures

Electronic bands in crystals



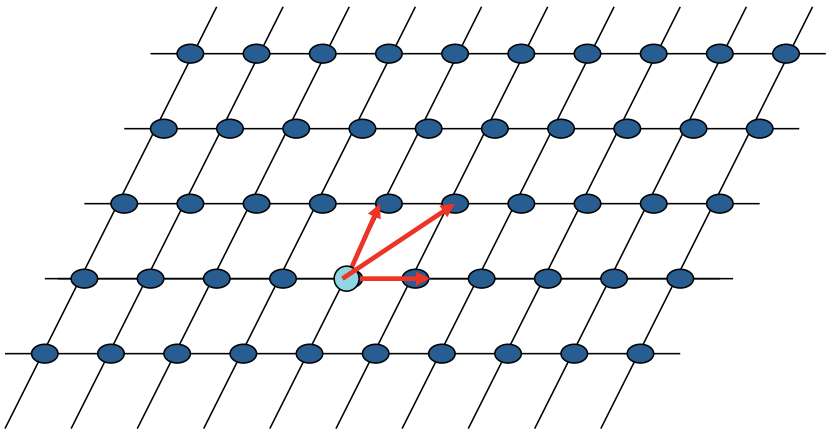
How do we describe the ~10^{24} crystal wavefunctions?

Background: Bravais lattice and basis

Bravais lattice: collection of points generated by three non-collinear vectors

$$r_{lmn} = l \cdot \vec{a}_1 + m \cdot \vec{a}_2 + n \cdot \vec{a}_3$$

Two dimensional Bravais lattice



Perfect crystal: Bravais lattice + basis (atoms)

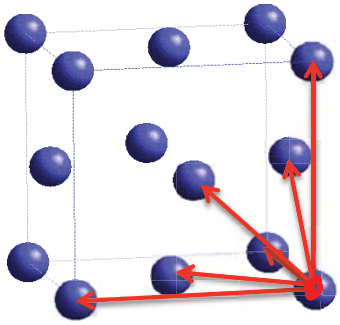
14 Bravais Lattices in 3D

The 7 lattice systems	The 14 Bravais lattices			
Triclinic	P $\alpha, \beta, \gamma \neq 90°$			
Monoclinic	P $\beta \neq 90°$ $\alpha, \gamma = 90°$	C $\beta \neq 90°$ $\alpha, \gamma = 90°$		
Orthorhombic	P $a \neq b \neq c$	C $a \neq b \neq c$	I $a \neq b \neq c$	F $a \neq b \neq c$
Tetragonal	P $a \neq c$	I $a \neq c$		
Rhombohedral	P $\alpha = \beta = \gamma \neq 90°$			
Hexagonal	P			
Cubic	P (pcc)	I (bcc)	F (fcc)	

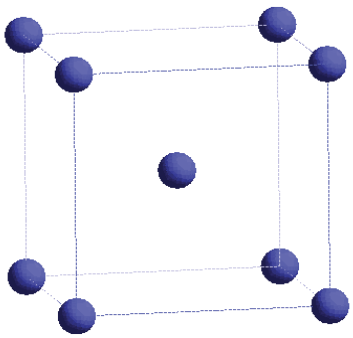
http://en.wikipedia.org/wiki/Bravais_lattice

Background: Crystal structures

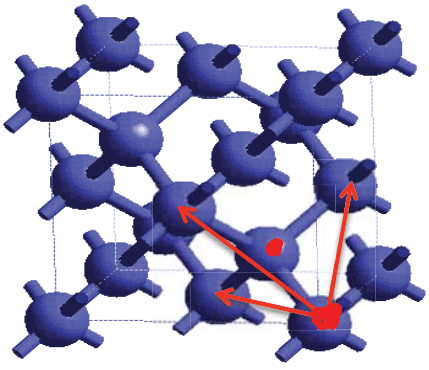
Face centered cubic



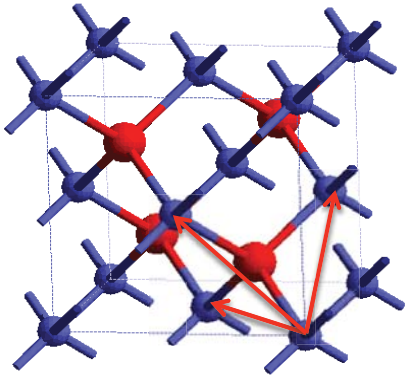
Body centered cubic



Diamond



Zincblende



Background: Reciprocal space

Functions with the periodicity of the Bravais lattice can be written using plane waves as a basis set:

$$e^{i\vec{G}\vec{r}}$$

With: $\vec{G}\left(n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3\right) = n'2\pi$

The vectors that satisfy that condition also make a Bravais lattice in k-space: the reciprocal lattice with basis set b_1, b_2, b_3

$$\vec{G} = n_1\vec{b}_1 + n_2\vec{b}_2 + n_3\vec{b}_3$$

$$\vec{a}_i\vec{b}_j = 2\pi\delta_{ij}$$

Background: Dirac's notation

Wavefunction $\psi(r)$ Represented with a *ket*: $|\psi\rangle$

Complex conjugate of wavefunction: $\psi^*(r)$ *bra*: $\langle\psi|$

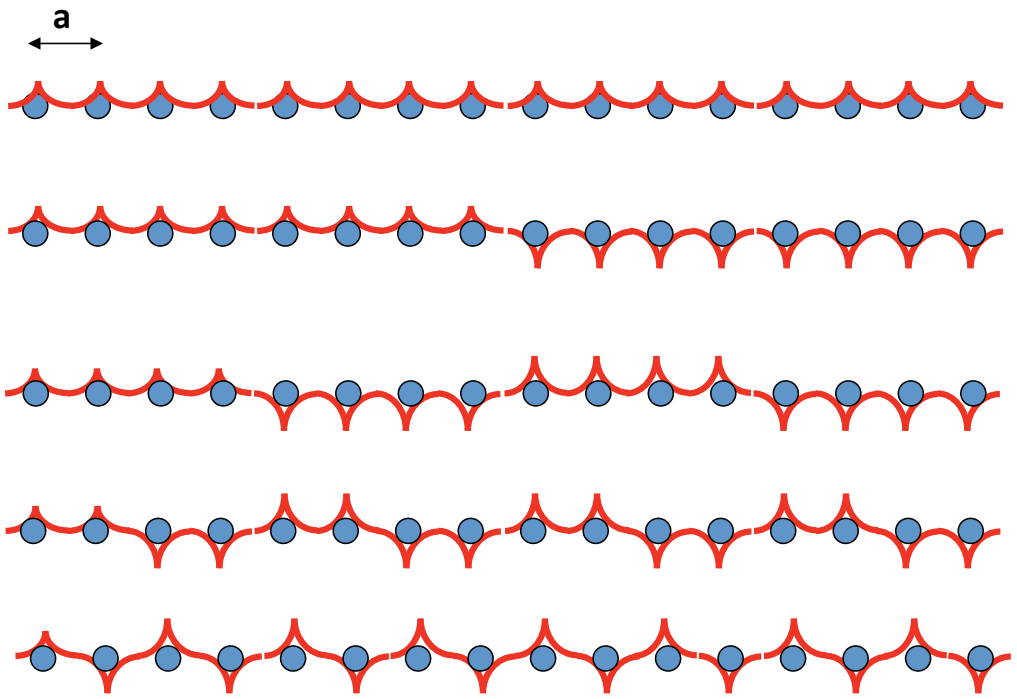
When a *braket* is formed integration is implied:

$$\langle\psi_1|\psi_2\rangle = \int \psi_1^*(r)\psi_2(r)d^3r$$

Expectation values

$$\langle\psi_1|O|\psi_2\rangle = \int \psi_1^*(r)O\psi_2(r)d^3r$$

Back to: Electronic bands in crystals



How do we describe the ~10^{24} crystal wavefunctions?

LCAO in crystals

Atomic orbital centered in atom *n*

$$|\psi_{xtal}\rangle = \sum_n a_n |n\rangle = a_n |n\rangle$$

Sum is implied for repeated indexes

$$H\, a_n |n\rangle = E\, a_n |n\rangle$$ Schrödinger Equation

Multiply by: $\langle m|$

$$\langle m|H\, a_n |n\rangle = \langle m|E\, a_n |n\rangle$$

$$a_n \langle m|H|n\rangle = E a_n \langle m|n\rangle$$

Only interactions between nearest neighbors + neglect overlap

$$a_{m-1}\langle m|H|m-1\rangle + a_m \langle m|H|m\rangle + a_{m+1}\langle m|H|m+1\rangle = a_m E$$

LCAO in crystals

$$-V_2 a_{m-1} + h_0 a_m - V_2 a_{m+1} = a_m E$$

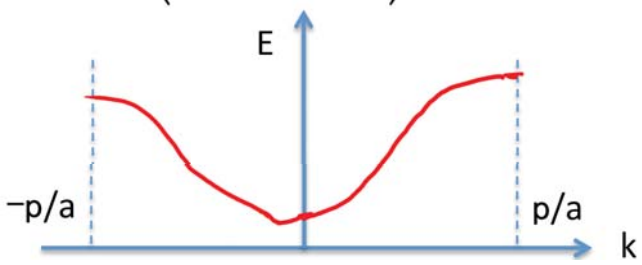
Ansatz: $a_m(k) = e^{ikR_m} = e^{ikam}$

$$-V_2 e^{ik(m-1)a} + h_0 e^{ikma} - V_2 e^{ik(m+1)a} = E e^{ikma}$$

$$-V_2 e^{-ika} + h_0 - V_2 e^{ika} = E$$

$$-V_2 e^{-ika} + h_0 - V_2 e^{ika} = E = h_0 - V_2\left(e^{-ika} + e^{ika}\right)$$

$$E(k) = h_0 - 2V_2 \cos(ka)$$



First Brillouin Zone

Are all k values allowed or physically meaningful?

$$\psi_{xtal}(k) = e^{ikan}|n\rangle$$

$$\psi_{xtal}\left(k + \frac{2\pi}{a}\right) = e^{i\left(k+\frac{2\pi}{a}\right)an}|n\rangle = e^{i\frac{2\pi}{a}an} e^{ikan}|n\rangle$$

$$\psi_{xtal}(k) = \psi_{xtal}\left(k + \frac{2\pi}{a}\right)$$

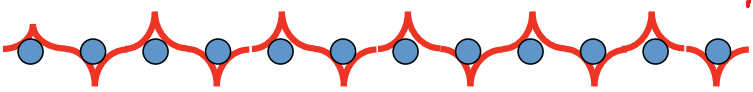
Values of k: $-\frac{\pi}{a} < k \leq \frac{\pi}{a}$

- In 3D values of k are restricted to the First Brillouin Zone
  - Points in k-space that are closer to the origin than to any other point of the reciprocal lattice

Band diagrams AKA E-k diagrams

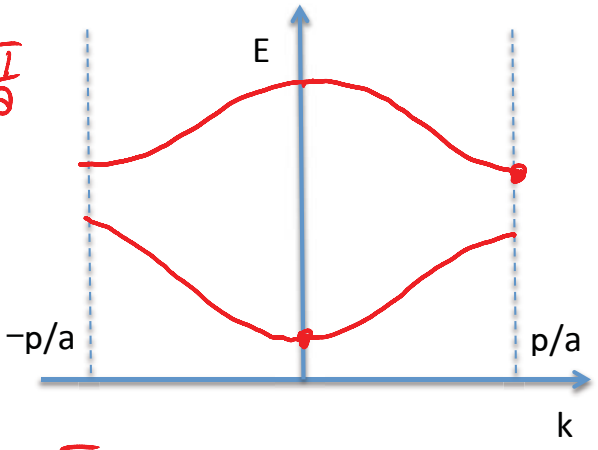
s-type orbitals

$k = 0$



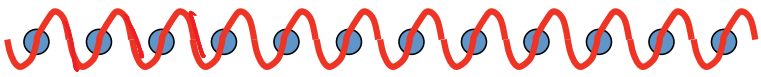
$k = \frac{\pi}{a}$

$$E_{1s}(k) = h_{0,1s} - 2V_{2,1s}\cos(ka)$$



p-type orbitals

$k = \frac{\pi}{a}$

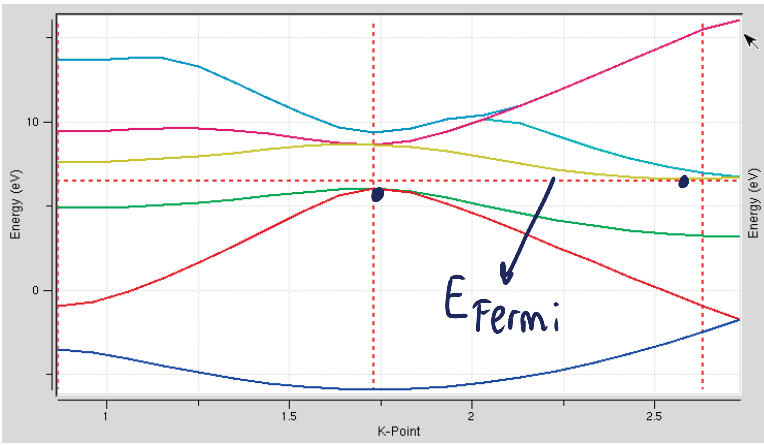


$k = a$

- Each band denotes an atomic orbital
- K tells you how the WF changes from unit cell to unit cell

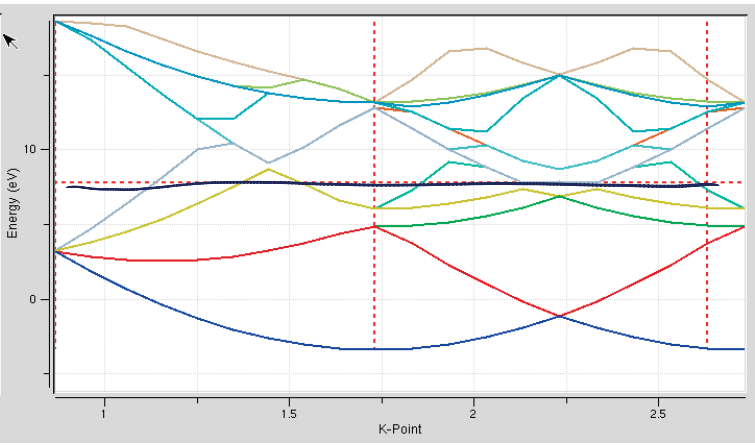
Electronic band structure of crystals

DFT band structure of Si
Quantum Espresso tool

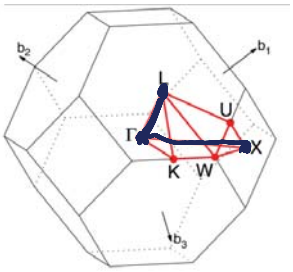


L: p/a(1,1,1) G X: p/a(1,0,0)

DFT band structure of Al
Quantum Espresso tool

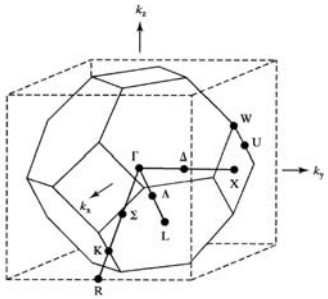


L: p/a(1,1,1) G X: p/a(1,0,0)



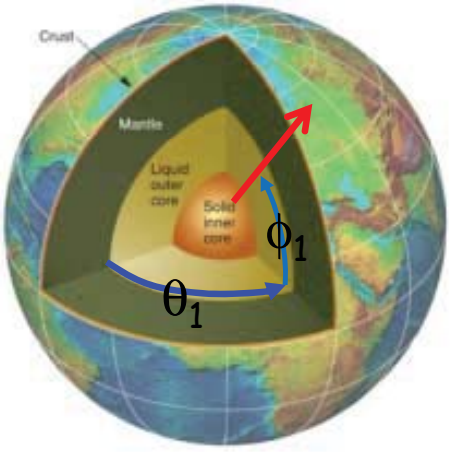
First Brillouin zone (fcc)
W. Setyawan, S. Curtarolo,
Computational Materials Science 299–312, 49 (2010)

Analogy for E-k Diagram: 4D info thiough 2D Plots

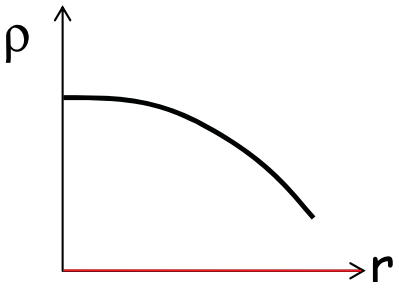


Density (x,y,z)

4D information

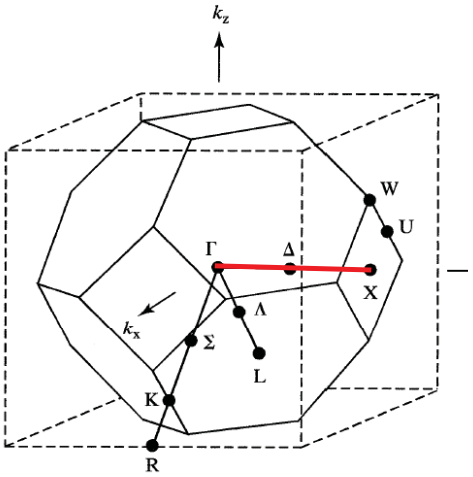


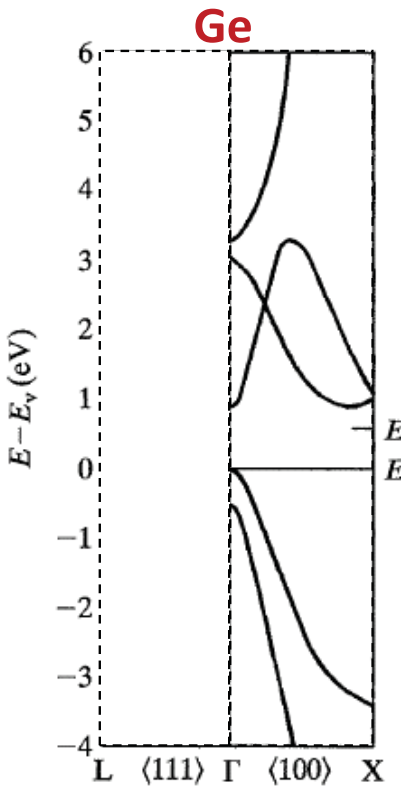
Cut along (θ_1, ϕ_1) …



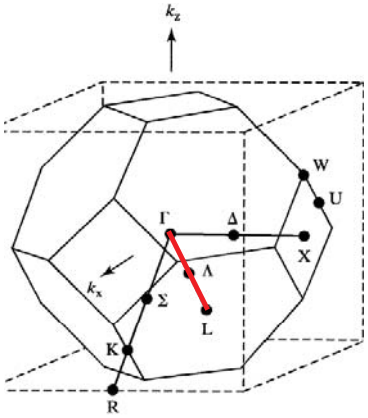
A series of line-sections can
Represent the 4D info in 2D plots

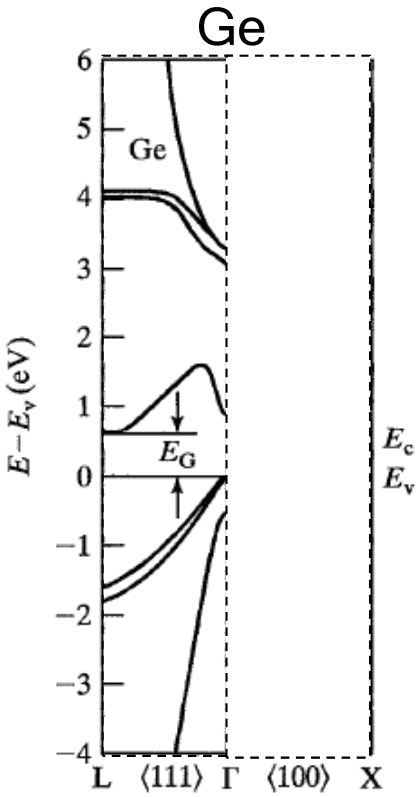
E-k along Γ-X Direction



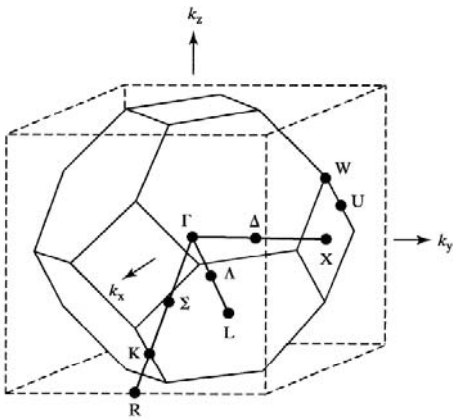


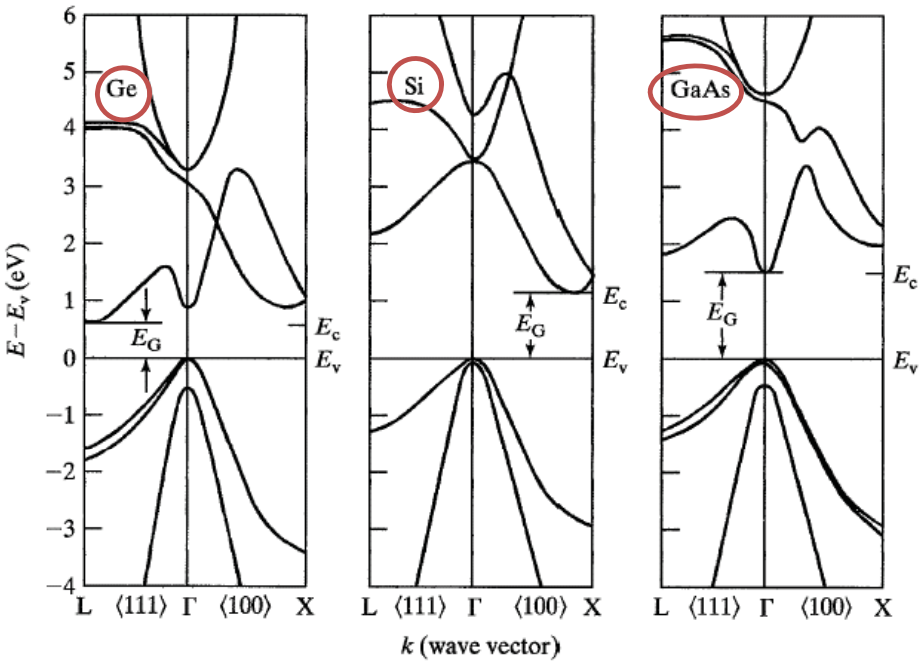
E-k along Γ-L direction





E-k Diagram

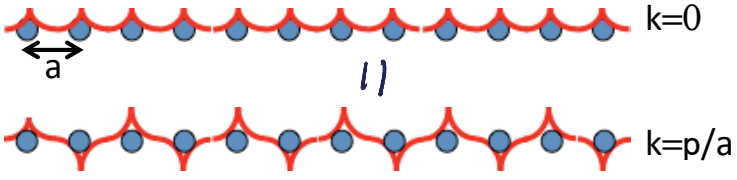


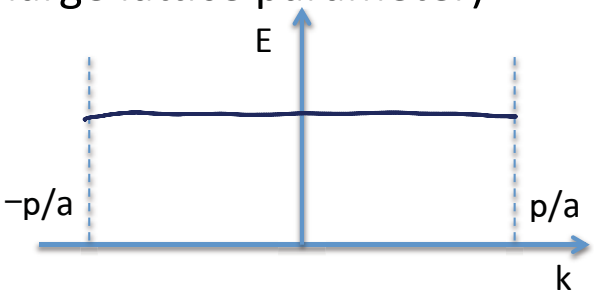


- 3 valence bands (light hole, heavy hole, split-off) valence bands near k=0 is essentially E ~ k^2
- Minima may not be at zone center
- (Ge: 8 L valleys, Si: 6 X valleys, and GaAs: Γ valleys)

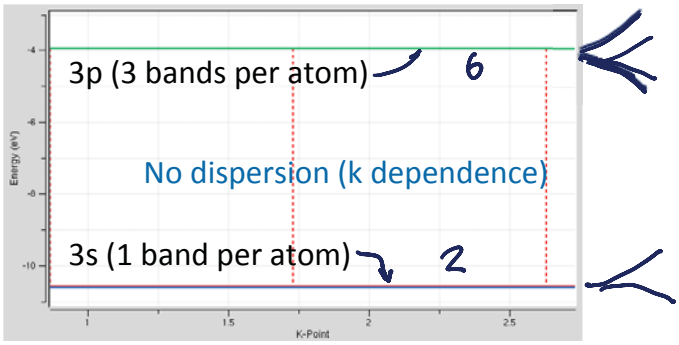
How does the Si band form?

Let's consider an isolated Si atom (very large lattice parameter)

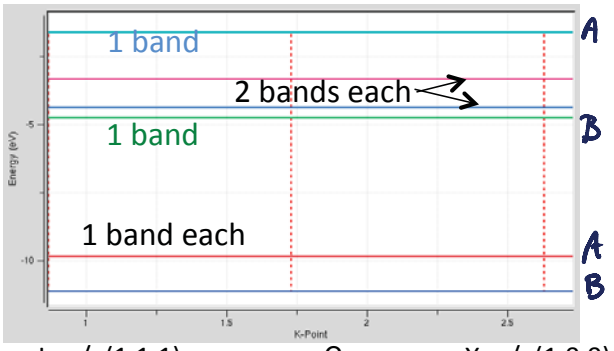




Band structure of the Si atom and Si_2 molecule

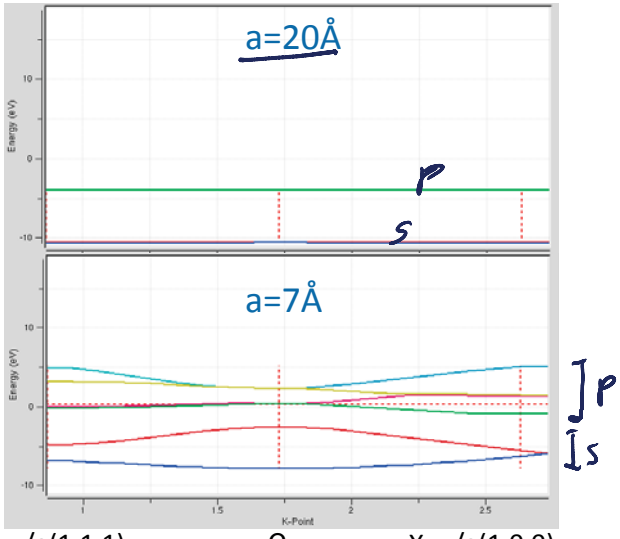


L: p/a(1,1,1) G X: p/a(1,0,0)

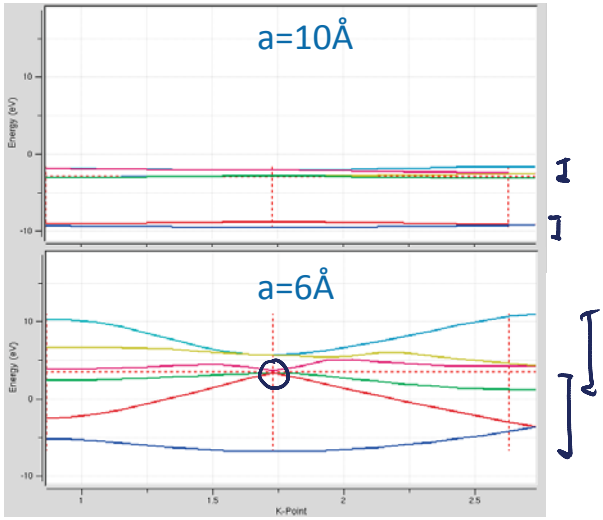


L: p/a(1,1,1) G X: p/a(1,0,0)

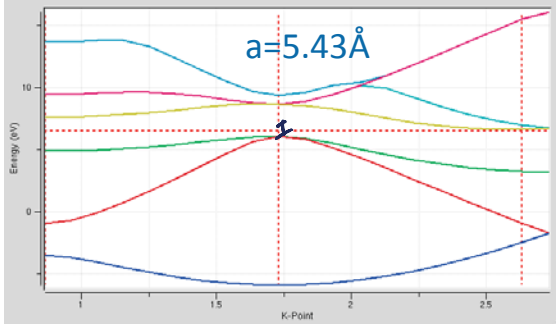
How does the Si band structure form?

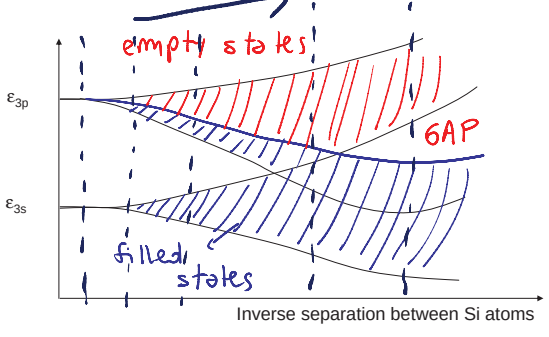


L: p/a(1,1,1) G X: p/a(1,0,0)



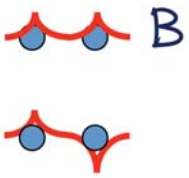
L: p/a(1,1,1) G X: p/a(1,0,0)

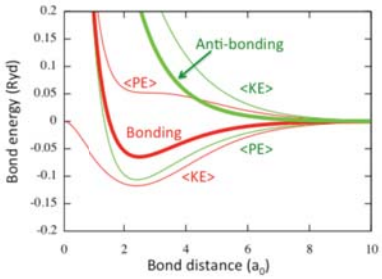


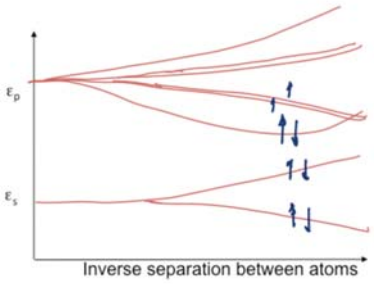


summary

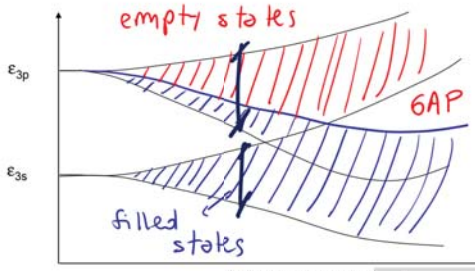
Molecules

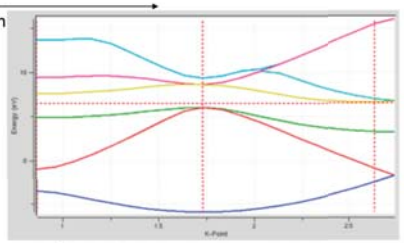






Crystals





Additional reading

Atoms and Molecules: An Introduction for Students of Physical Chemistry,
M. Karplus, Richard Needham Porter

Electronic Structure and the Properties of Solids: The Physics of the Chemical Bond,
Walter Harrison

Solid State Physics
Neil Ashcroft and David Mermin

Introduction to Solid State Physics
Charles Kittel