

Week 8: Energy Bands & Density of States Announcements

Remember the Electron Wave Functions for a H Atom?

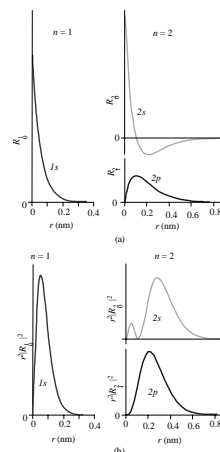


Fig. 3.21: (a) Radial wavefunctions of the electron in a hydrogenic atom for various n and ℓ values. (b) $r^2 R_{nl}^2$

Electron Wave Function with Two H Atoms

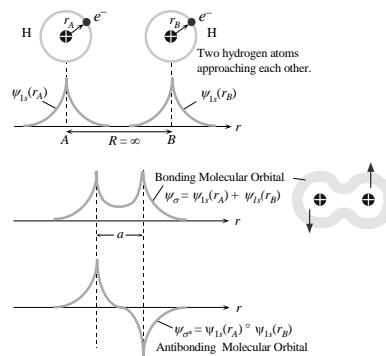


Fig. 4.1: Formation of molecular orbitals, bonding and antibonding (ψ_{σ} and ψ_{σ^*}) when two H atoms approach each other. The two electrons pair their spins and occupy the bonding orbital ψ_{σ} .

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Multi-atom Wave Functions Combine

- Two H atoms: the wavefunctions combine to form new wavefunctions
 - LCAO:
- Symmetric
 - wave are in phase
 - Constructive interference:
- Anti-symmetric
 - waves are out of phase
 - Destructive interference:

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Multi-atom Probability Function

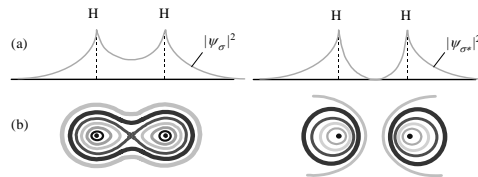


Fig. 4.2: (a) Electron probability distributions for bonding and antibonding orbitals, ψ_σ and ψ_{σ^*} . (b) Lines represent contours of constant probability (darker lines represent greater relative probability).

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Nodes of “Antibonding”

- Symmetric Waves
 - Probability peaks in center:
- Antisymmetric Waves
 - Probability goes to zero in the middle:
 - Nodes:
 - Has a higher energy

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H₂ Molecule Energy Levels

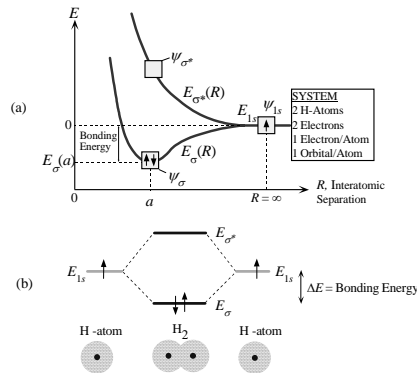


Fig. 4.3: Electron energy in the system comprising two hydrogen atoms. (a) Energy of ψ_σ and ψ_{σ^*} vs. the interatomic separation, R . (b) Schematic diagram showing the changes in the electron energy as two isolated H atoms, far left and far right, come to form a hydrogen molecule.

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Lowest Energy Configuration is Stable

- This results in bands, electrons both fill lower energy band (E_σ)
- H₂ is favorable because this lowers the energy relative to individual H atoms
- How about He?

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He₂ Molecule Energy Levels

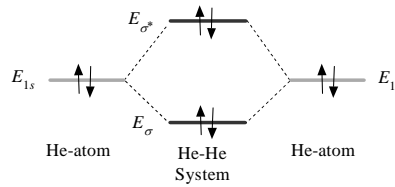


Fig. 4.5: Two He atoms have 4 electrons. When He atoms come together 2 of the electrons enter the E_{σ} and 2 the E_{σ^*} levels so that the overall energy is greater than two isolated He atoms.

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Solid (With Lots of Atoms)

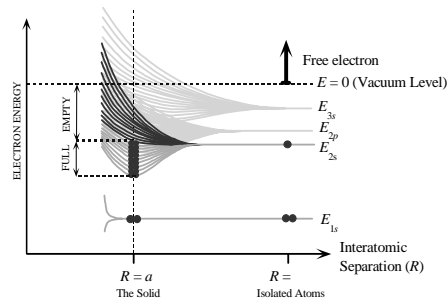


Fig. 4.9: As solid atoms are brought together from infinity, the atomic orbitals overlap and give rise to bands. Outer orbitals overlap first. The $3s$ orbitals give rise to the $3s$ band, $2p$ orbitals to the $2p$ band and so on. The various bands overlap to produce a single band in which the energy is nearly continuous.

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N atoms

- N (large number) atoms together in a solid
 - N different wave functions
 - N ways of combining wave functions
 - N different energy levels for each wave function
- Two electrons per a level results
 - Example of Li: 3 electrons per atom
 - » 1 electron per atom in 2s band

Band Structure of Li

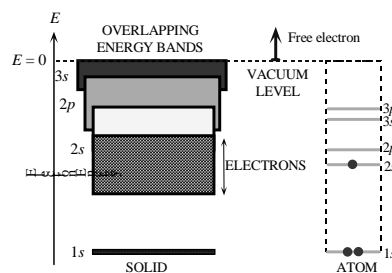


Fig. 4.10: In a metal the various energy bands overlap to give a single band of energies that is only partially full of electrons. There are states with energies up to the vacuum level where the electron is free.

Metal Fermi Energy & Work Function

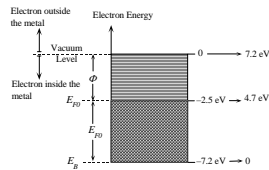


Fig. 4.11: Typical electron energy band diagram for a metal. All the valence electrons are in an energy band which they only partially fill. The top of the band is the vacuum level where the electron is free from the solid ($PE = 0$).
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■ E_{F0} : Fermi Energy (at 0K)

- Energy from bottom of valence band to highest energy state that is full
- States below this are all full: above this are empty (at 0K)

■ Φ : Work function

- Energy required to pull electron from its outermost full state to vacuum
- Energy from highest energy state that is full to vacuum (free electron)

Valence Electrons for Semiconductors

■ Some major semiconductors are:

- Column IV: Si, Ge
- Column III-V: GaAs, InP
- Column II-VI: HgTe, CdS

- Si and Ge act like they have four valence electrons when in reality they have 1 full s shell and 2 electrons in a p shell

Lone Si Atom Electronic Structure

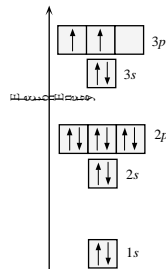


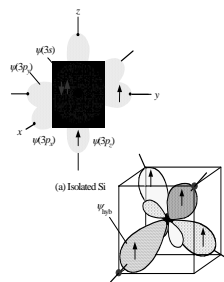
Fig. 4.14: The electronic structure of Si.

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Sp³ Hybridization



(b) Si preparing to bond
 Fig. 4.15: (a). Si is in Group IV in the Periodic Table. An isolated Si atom has 2 electrons in the 3s and 2 electrons in the 3p orbitals. (b) When Si is about to bond, the one 3s-orbital and the three 3p-orbitals become perturbed and mixed to form four hybridized orbitals, ψ_{hyb} , called sp^3 orbitals which are directed towards the corners of a tetrahedron. The ψ_{3s} orbital has a large major lobe and a

- When two (or more) silicon atoms near each other
 - the Ψ_s , Ψ_{px} , Ψ_{pz} , and Ψ_{pz} orbitals overlap to form 4 Ψ_{hyb} orbitals
- We call this sp^3 hybridization

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Covalently Bonding

- To fill the four sp^3 orbitals, 8 electrons are needed

Silicon Covalently Bonds

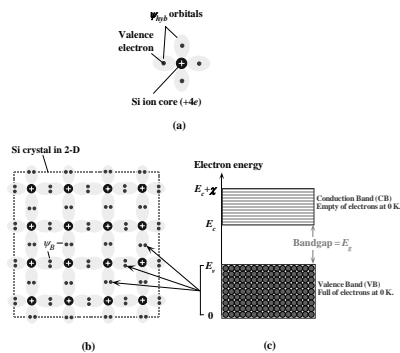


Fig. 5.1: (a) A simplified two dimensional illustration of a Si atom with four hybrid orbitals, ψ_{sp^3} . Each orbital has one electron. (b) A simplified two dimensional view of a region of the Si crystal showing covalent bonds. (c) The energy band diagram at absolute zero of temperature.

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Semiconductor Terms

- Conduction band:
- Valence band:
- Bandgap energy:
- Fermi energy:

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Si Orbitals and Bands

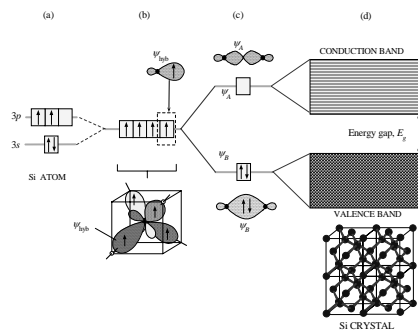


Fig. 4.16: (a) Formation of energy bands in the Si crystal first involves hybridization of $3s$ and $3p$ orbitals to four identical ψ_{hyb} orbitals which make 109.5° with each other as shown in (b). (c) ψ_{hyb} orbitals on two neighboring Si atoms can overlap to form ψ_B or ψ_A . The first is a bonding orbital (full) and the second is an antibonding orbital (empty). In the crystal ψ_B overlap to give the valence band (full) and ψ_A overlap to give the conduction band (empty).

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Semiconductor Band Structure

- At 0K, VB is full (electrons can't conduct)
- Electrons can be excited into the CB by various means such as heat or light
 - excitation leaves behind a hole

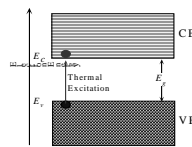


Fig. 4.17: Energy band diagram of a semiconductor.

Conductivity of Semiconductors and Metals

- Our next goal is to relate the conductivity of semiconductors and metals to the band structure
- To accomplish this we want to calculate the density of states and density of electrons as a function of energy in the bands
- To do the math we are going to treat our semiconductors and metals as electrons in a box
 - Fairly accurate portrayal of electron sea around lattice atoms

Density of States in a Band

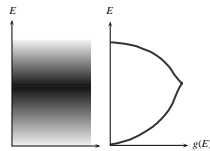


Fig. 4.20: The density of states, $g(E)$ vs E in an energy band.

- The density of states $g(E)$ varies across a band
- $g(E)$ is the density of states at any one energy
- $S_v(E')$: total number of states per unit volume with energy less than E

$$S_v(E') = \int_0^{E'} g(E) dE$$

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Solve for E in a 2-D Square

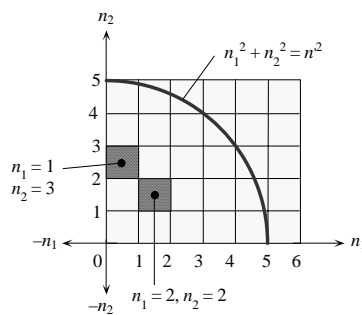


Fig. 4.21: Each state, electron wavefunction in the crystal, can be represented by a box at n_1, n_2 .

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Solve for E in a 3-D Box

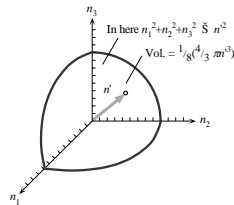


Fig. 4.22: In three dimensions, the volume defined by a sphere of radius n' and the positive axes n_1 , n_2 and n_3 , is all the possible combinations of positive n_1 , n_2 and n_3 , values which satisfy $n_1^2 + n_2^2 + n_3^2 = n'^2$.

- States with E less than E' will be those with $n_1^2 + n_2^2 + n_3^2 < n'^2$
- From electron in a box model:

$$E' = \frac{h^2}{8m_e L^2} (n'^2)$$

- The number of orbitals less n' are marked out by the volume of that sphere

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Total Number of States $E < E'$

$$S_{\text{orb}}(n') = \frac{1}{8} \left(\frac{4}{3} \pi n'^3 \right) = \frac{1}{6} (\pi n'^3)$$

$$S(n') = 2S_{\text{orb}}(n') = \frac{1}{3} (\pi n'^3)$$

$$S(E') = \frac{\pi L^3 (8m_e E')^{3/2}}{3h^3}$$

$$S_v(E) = \frac{\pi (8m_e E)^{3/2}}{3h^3}$$

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Solve for $g(E)$

- Now use the total number of sites for electrons $S_V(E')$ to solve for the density of sites for electrons at any E : $g(E)$

$$\frac{dS_V(E)}{dE} = g(E) = 8\pi\sqrt{2}\left(\frac{m_e}{h^2}\right)^{3/2}\sqrt{E}$$

- This E is relative to zero
 - remember our integral was looking at energies from bottom (0) up to E'
- We can also go the other way
 - an integral from E' to E_{top}
 - this would result in a $g(E)$ with a $E_{\text{top}} - E$ term in it

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Density of States in a Band

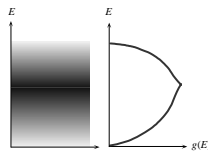


Fig. 4.20: The density of states, $g(E)$ vs E in an energy band.

- We end up with a parabola: we have to look at in two steps because we know the density of states must go to 0 at each band edge

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Solve for Density of Electrons

- $g(E)$ is the density of sites for electrons at any E
- We can combine this with the probability that the site is full (has an electron in it): $f(E)$
- This will tell us the density of electrons: n

$$n = \int_{\text{band}} f(E)g(E)dE$$