Quantum wire, 2D confinement, 1D electronic system

$$\psi = A\sin k_x x \cdot \sin k_y y \cdot e^{ik_z z}$$

$$E = \frac{h^2}{8m_e^*}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right) + \frac{\hbar^2}{2m_e^*}k_z^2$$

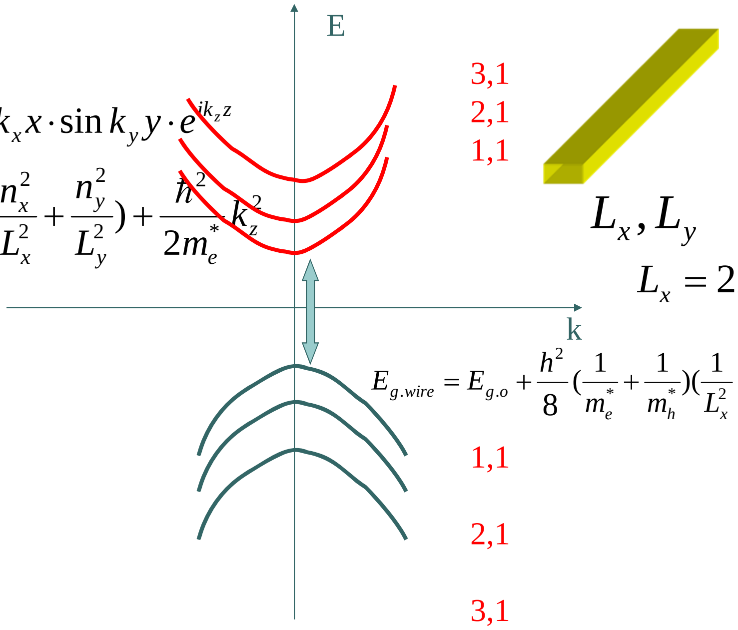
$$D(E) = \frac{\sqrt{2m_e^*}}{\pi\hbar L_x L_y}E^{-1/2}$$

$$k_F = \frac{\pi n_{1d}}{2}$$

L_x, L_y

$$\psi = A\sin k_x x \cdot \sin k_y y \cdot e^{ik_z z}$$

$$E = \frac{h^2}{8m_e^*}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right) + \frac{\hbar^2}{2m_e^*}k_z^2$$



L_x, L_y

$L_x = 2L_y$

$$E_{g.wire} = E_{g.o} + \frac{h^2}{8}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right)\left(\frac{1}{L_x^2} + \frac{1}{L_y^2}\right)$$

Quantum wire, 2D confinement, 1D electronic system

$$V_{1D} = \frac{2\pi}{L}$$

$$L_x, L_y$$

Density of states per unit length:

$$\psi = A\sin k_x x \cdot \sin k_y y \cdot e^{ik_z z}$$

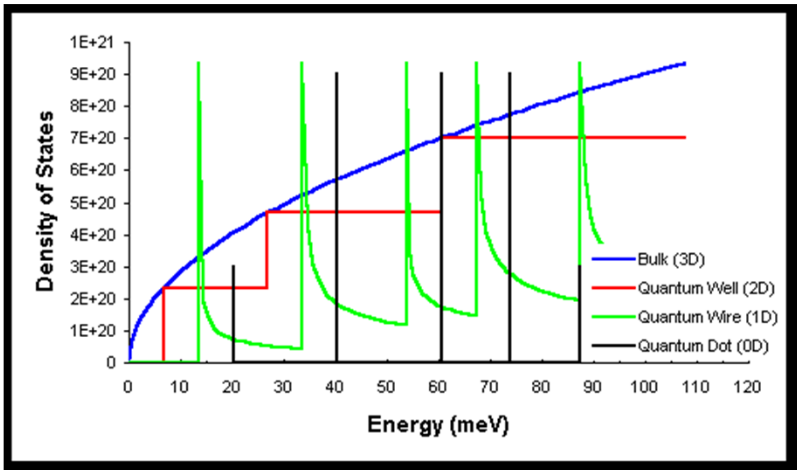
$$E = \frac{h^2}{8m_e^*}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right) + \frac{\hbar^2}{2m_e^*}k_z^2$$

$$\frac{2dk}{\frac{2\pi}{L}}\frac{1}{L.L_xL_y} \times 2 = \frac{2dk}{\pi L_xL_y}$$

$$= \frac{2}{\pi L_xL_y}\left(\frac{2mE}{\hbar^2}\right)^{-1/2}\frac{m}{\hbar^2}dE$$

$$= \frac{\sqrt{2m_e^*}}{\pi\hbar L_xL_y}E^{-1/2}dE$$

Quantum Confinement and Dimensionality



Quantum dot, 3D confinement, 0D electronic system

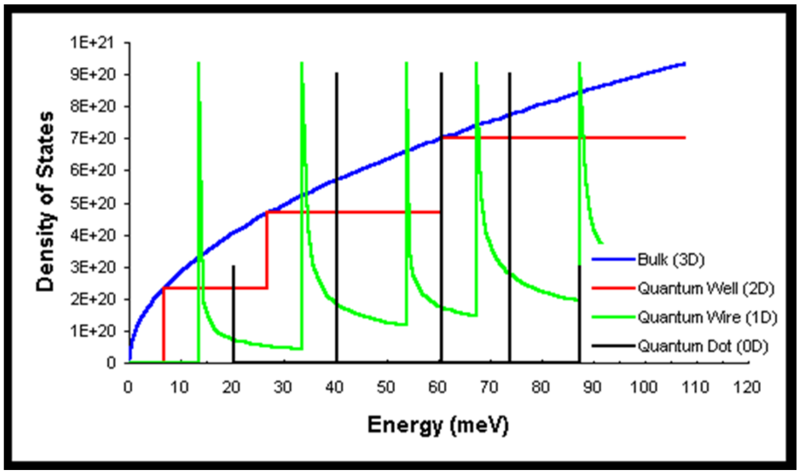
$$\psi = A\sin k_x x\cdot\sin k_y y\cdot\sin k_z z$$

$$E=\frac{h^2}{8m_e^*}\left(\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}+\frac{n_z^2}{L_z^2}\right)$$

Discrete states

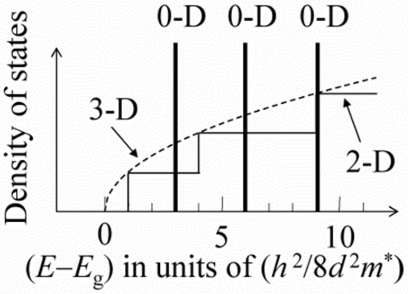
$$L_x, L_y, L_z$$

Quantum Confinement and Dimensionality

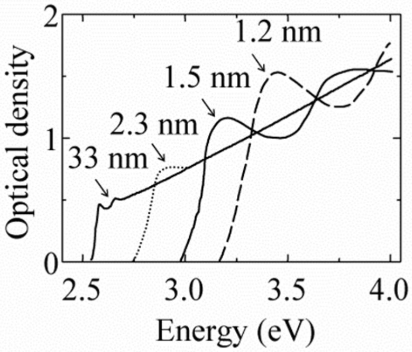


Quantum dots

Discrete atomic-like density of states

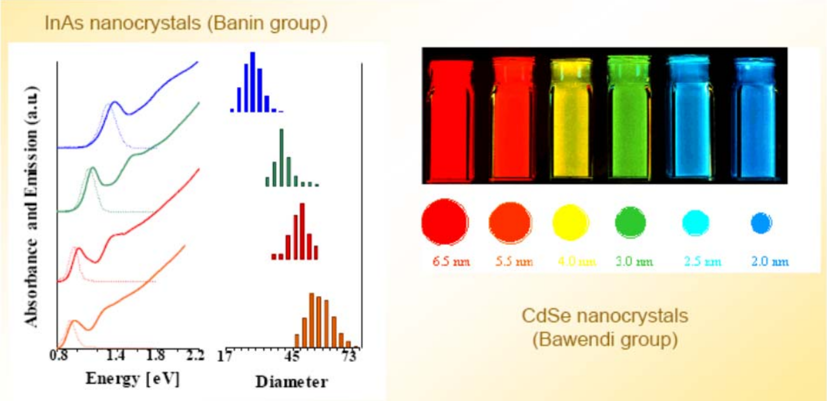


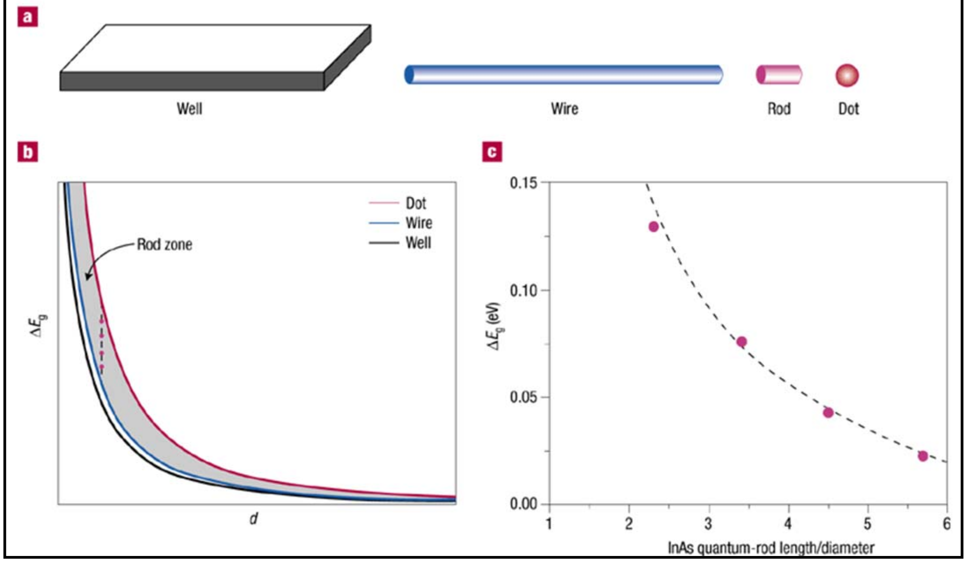
CdS quantum dots versus dot size d at 4.2K



Examples:

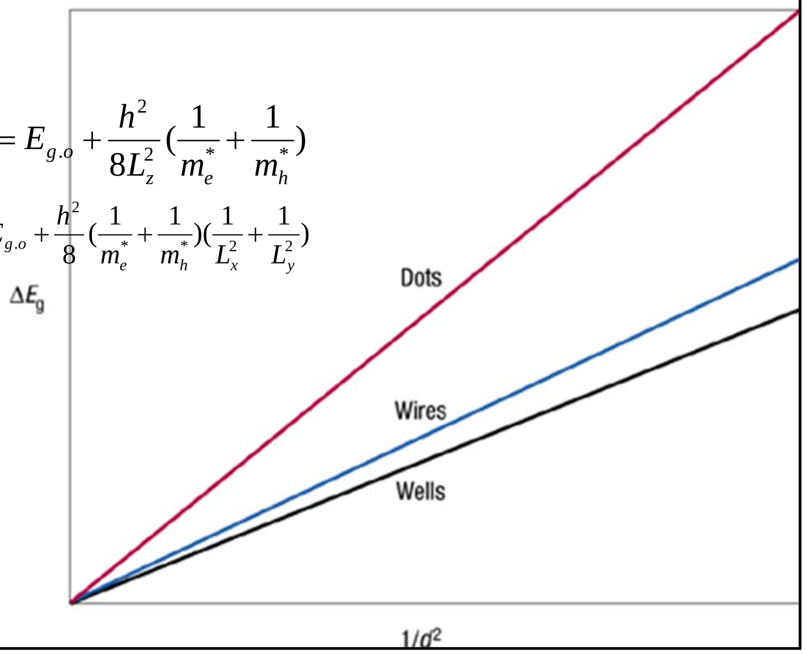
1. Semiconductor doped glass (Colour glass filters & stained glass)
2. Self-organized III-V quantum dots (eg InAs/GaAs)

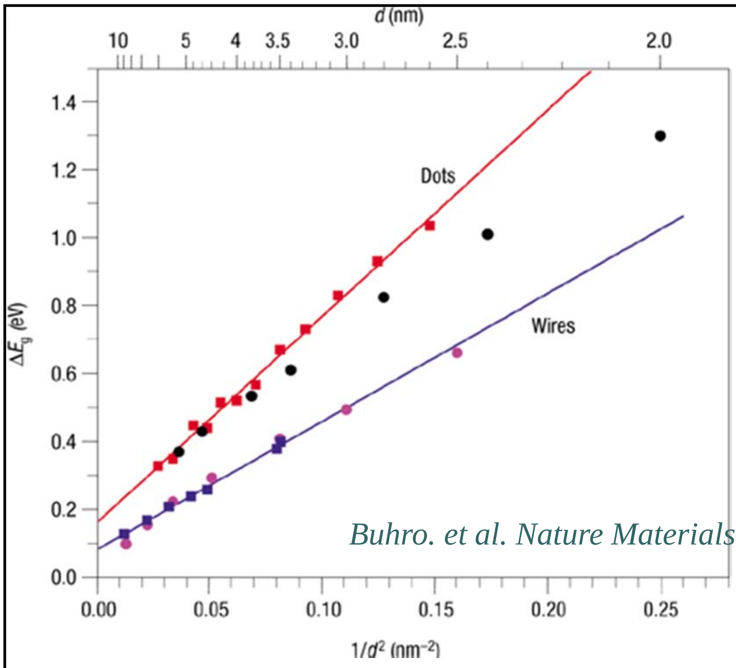




$$E_{g.well} = E_{g.o} + \frac{h^2}{8L_z^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right)$$

$$E_{g.wire} = E_{g.o} + \frac{h^2}{8}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right)\left(\frac{1}{L_x^2} + \frac{1}{L_y^2}\right)$$





Buhro. et al. Nature Materials, 2003, 2, 517

$$\psi = A\sin k_z z \cdot e^{i(k_x x + k_y y)}$$

$$E = \frac{h^2 n_z^2}{8 m_e^* L_z^2} + \frac{\hbar^2}{2m_e^*}(k_x^2 + k_y^2)$$

$$\psi = A\sin k_x x \cdot \sin k_y y \cdot e^{ik_z z}$$

$$E = \frac{h^2}{8m_e^*}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right) + \frac{\hbar^2}{2m_e^*}k_z^2$$

$$\psi = A\sin k_x x \cdot \sin k_y y \cdot \sin k_z z$$

$$E = \frac{h^2}{8m_e^*}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$

	2D		1D			0D		
State	**E/E $_0$**		**E/E $_0$**	**Degenerate States**		**E/E $_0$**	**Degenerate States**	
1	1	1	2	(1,1)	1	3	(1,1,1)	1
2	4	1	5	(2,1),(1,2)	2	6	(2,1,1),(1,2,1),(1,1,2)	3
3	9	1	8	(2,2)	1	9	(2,2,1),(1,2,2),(2,1,2)	3
4	16	1	10	(3,1),(1,3)	2	11	(3,1,1),(1,3,1),(1,1,3)	3
5	25	1	13	(3,2),(2,3)	2	12	(2,2,2)	1
6	36	1	17	(4,1),(1,4)	2	14	(3,2,1),(3,1,2),(2,3,1) (2,1,3),(1,3,2),(1,2,3)	6
7	49	1	18	(3,3)	1	17	(3,2,2),(2,3,2),(2,2,3)	3
8	64	1	20	(4,2),(2,4)	2	18	(4,1,1),(1,4,1),(1,1,4)	3
9	81	1	25	(4,3),(3,4)	2	21	(4,2,1),(4,1,2),(1,4,2) (1,2,4),(2,4,1),(2,1,4)	6
10	100	1	26	(5,1),(1,5)	2	27	(3,3,3)	1

Tight Binding Model

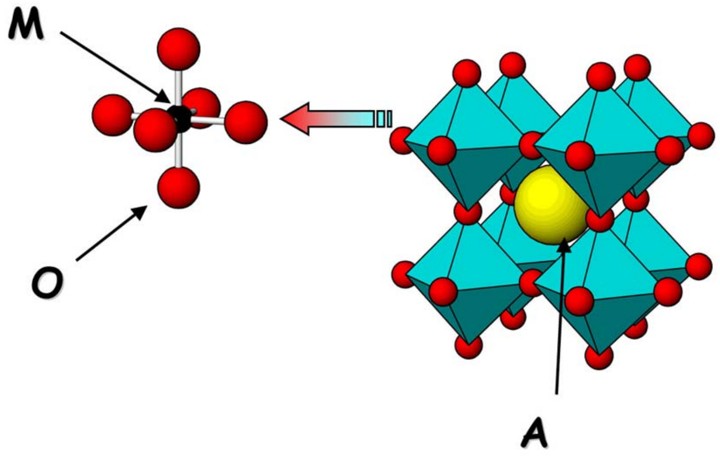
Calculation of Energy Band

Reading: **Burdett Chpt 1-3**
Hoffman p1-21

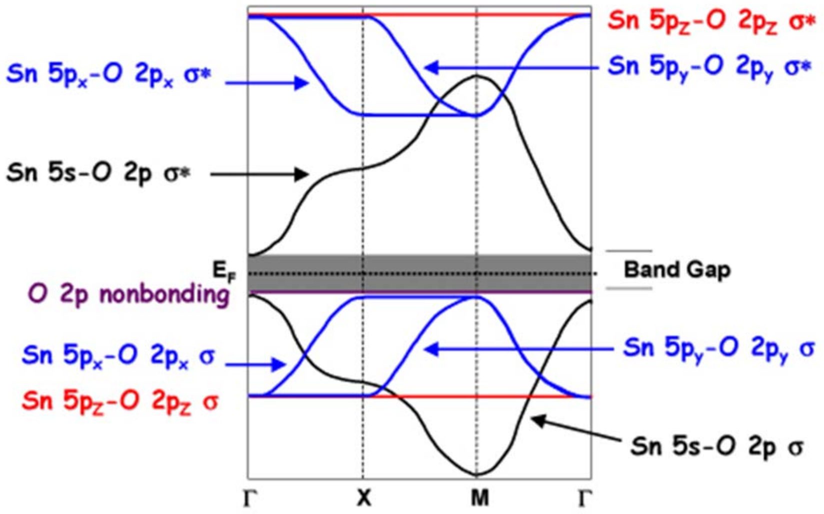
For MO Theory:

Chemical structure and bonding (Gray/Decock)

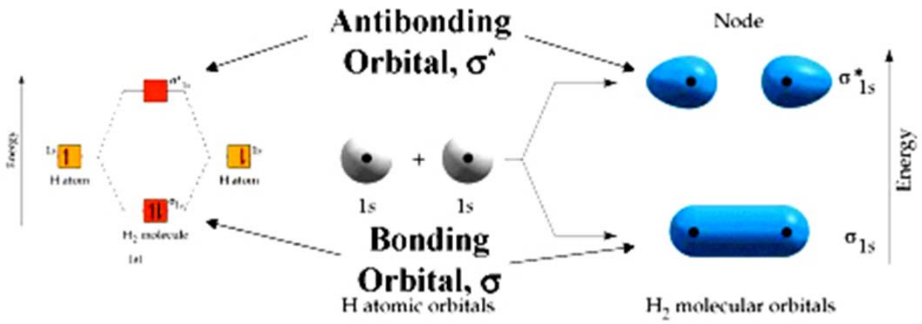
Perovskite Crystal Structure

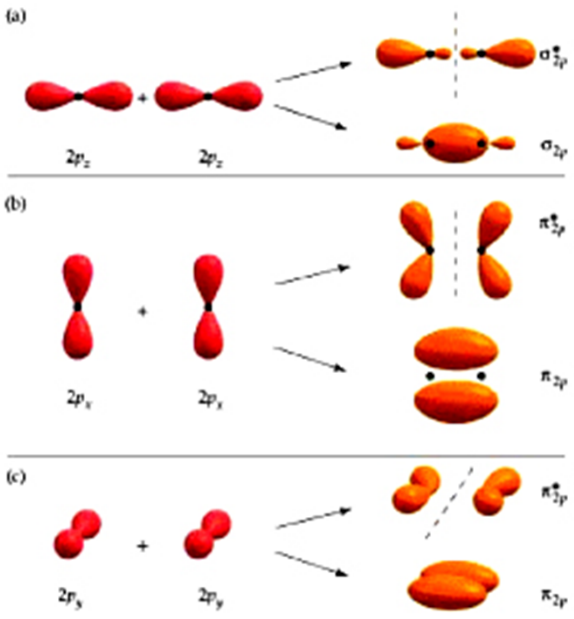


Ba_2SnO_4: Band Structure

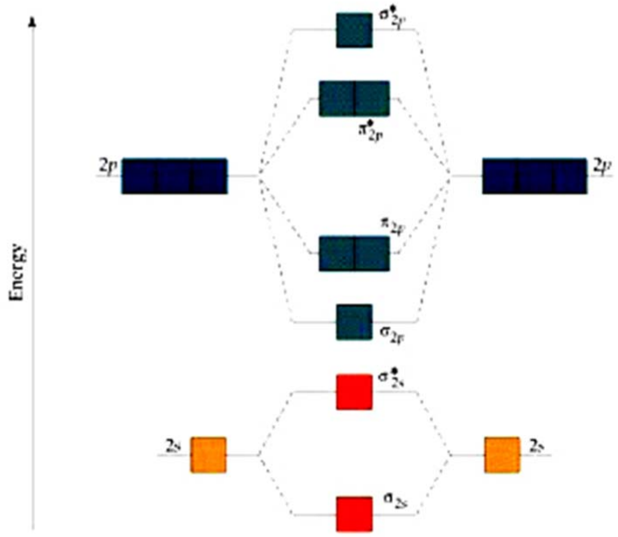


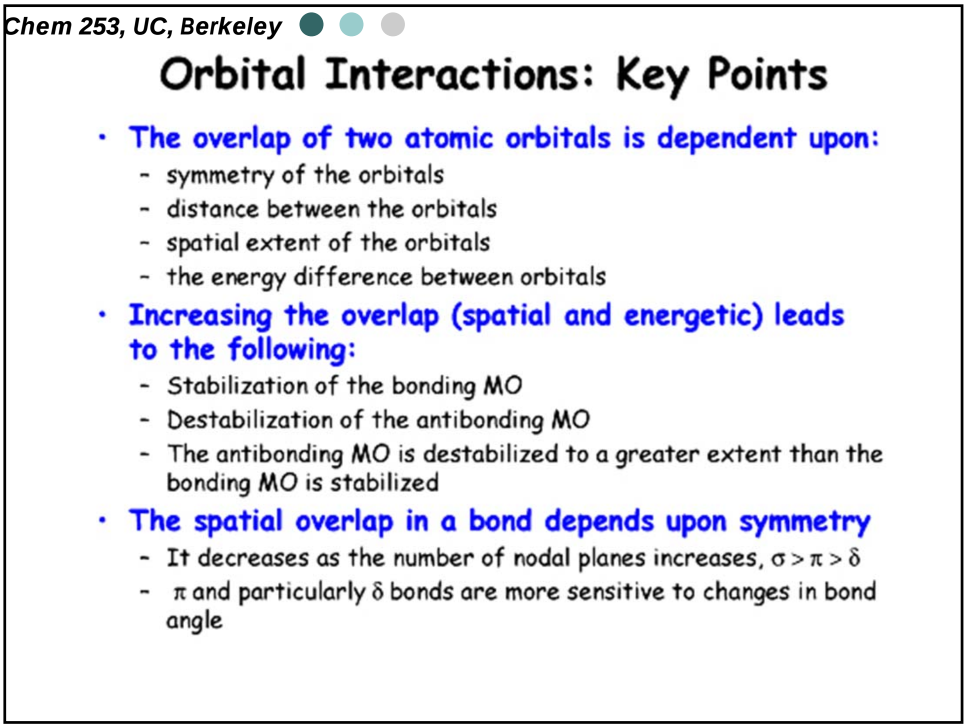
Molecular Orbital Theory





Diatomic Molecules





Orbital Interactions: Key Points

- **The overlap of two atomic orbitals is dependent upon:**
  - symmetry of the orbitals
  - distance between the orbitals
  - spatial extent of the orbitals
  - the energy difference between orbitals
- **Increasing the overlap (spatial and energetic) leads to the following:**
  - Stabilization of the bonding MO
  - Destabilization of the antibonding MO
  - The antibonding MO is destabilized to a greater extent than the bonding MO is stabilized
- **The spatial overlap in a bond depends upon symmetry**
  - It decreases as the number of nodal planes increases, $\sigma > \pi > \delta$
  - π and particularly δ bonds are more sensitive to changes in bond angle

Elementary Band Theory for Molecules

Schrödinger equation

$$\boxed{\hat{H}\psi = E\psi}$$

Solving the Schrödinger equation
after applying simplifications

tight binding approach

LCAO: linear combination of atomic wavefunctions, the Atomic Orbitals ϕ

$\boxed{\psi = \sum_i c_i\phi_i}$ ϕ is normalized, thus $\int \phi_i^2 d\tau = 1$

with $d\tau = \partial x \partial y \partial z$

Calculate the expectation value of $\hat{H}$:

$$E = \frac{\int \psi\hat{H}\psi d\tau}{\int \psi^2 d\tau}$$

c_i: coefficients
AO's: basis set

For a minimal E: $\partial E/\partial c_i = 0$

Elementary Band Theory for Molecules

Case studies: 1) the diatomic case

$$\psi = \sum_i c_i\phi_i = c_1\phi_1 + c_2\phi_2$$

For a minimal E: $\partial E/\partial c_i = 0$, i.e.
$\partial E/\partial c_1 = 0$ and $\partial E/\partial c_2 = 0$
=> two solutions

$$\boxed{E = \frac{\int \psi\hat{H}\psi d\tau \longrightarrow \text{numerator (I)}}{\int \psi^2 d\tau \longrightarrow \text{denominator (II)}}}$$

$$\int \psi\hat{H}\psi d\tau = \int (c_1\phi_1 + c_2\phi_2)\hat{H}(c_1\phi_1 + c_2\phi_2)d\tau$$

Using the analogy $(a + b)^2 = a^2 + 2ab + b^2$:

$$= \int (c_1^2\phi_1\hat{H}\phi_1 + 2c_1c_2\phi_1\hat{H}\phi_2 + c_2^2\phi_2\hat{H}\phi_2)d\tau$$

$$= c_1^2\boxed{\int \phi_1\hat{H}\phi_1 d\tau} + 2c_1c_2\boxed{\int \phi_1\hat{H}\phi_2 d\tau} + c_2^2\boxed{\int \phi_2\hat{H}\phi_2 d\tau} \rightarrow$$

Coulomb-integral
$\alpha_2 < 0$

Coulomb-integral
$\alpha_1 < 0$

resonance-integral
$\beta_{12} < 0$ if bonding

Case studies: the diatomic case, continued

$$\psi = \sum_i c_i\phi_i = c_1\phi_1 + c_2\phi_2$$

Numerator (I): $\int\psi\hat{H}\psi d\tau = c_1^2\alpha_1 + 2c_1c_2\beta_{12} + c_2^2\alpha_2$

Denominator (II): $\int\psi^2 d\tau = \int(c_1\phi_1 + c_2\phi_2)^2 d\tau$

$$= \int(c_1^2\phi_1^2 + 2c_1c_2\phi_1\phi_2 + c_2^2\phi_2^2)d\tau$$

$$= c_1^2\underbrace{\boxed{\int\phi_1^2 d\tau}}_{=1} + 2c_1c_2\underbrace{\boxed{\int\phi_1\phi_2 d\tau}}_{\text{overlap}} + c_2^2\underbrace{\boxed{\int\phi_2^2 d\tau}}_{=1}$$

$S_{12} \geq 0$ if bonding

$$\Rightarrow \int\psi^2 d\tau = c_1^2 + 2c_1c_2S_{12} + c_2^2$$

$\partial E/\partial c_1 = 0$

$$\frac{\partial E}{\partial c_1} = \frac{\partial}{\partial c_1}\;\frac{c_1^2\alpha_1 + 2c_1c_2\beta_{12} + c_2^2\alpha_2}{c_1^2 + 2c_1c_2S_{12} + c_2^2} = 0$$

Case studies: the diatomic case, continued

$$(\alpha_1 - E)c_1 + (\beta_{12} - ES_{12})c_2 = 0$$

$$(\beta_{12} - ES_{12})c_1 + (\alpha_2 - E)c_2 = 0$$

Secular determinant = 0

$$0 = \begin{vmatrix} \alpha_1 - E & \beta_{12} - ES_{12} \\ \beta_{12} - ES_{12} & \alpha_2 - E \end{vmatrix}$$

General rule:

$$0 = \begin{vmatrix} A & B \\ C & D \end{vmatrix} = AD - BC$$

$$0 = (\alpha_1 - E)(\alpha_2 - E) - (\beta_{12} - ES_{12})(\beta_{12} - ES_{12})$$

Case studies: 1a) the diatomic homoatomic case, e.g. H_2

$$\alpha_1 = \alpha_2 = \alpha$$

$$0 = (\alpha - E)(\alpha - E) - (\beta - ES)(\beta - ES) = (\alpha - E)^2 - (\beta - ES)^2$$

$$\Rightarrow (\alpha - E) = \pm(\beta - ES)$$

Case studies: the diatomic homoatomic case, e.g. H_2

$\alpha - E = \pm (\beta - ES)$: **two solutions, A and B**

A

$\alpha - E = -(\beta - ES)$

$\alpha + \beta = E(1 + S)$

$\boxed{E = (\alpha + \beta)/(1+S)}$

$c_1 = 1/\sqrt{[2(1 + S)]} = c_2$

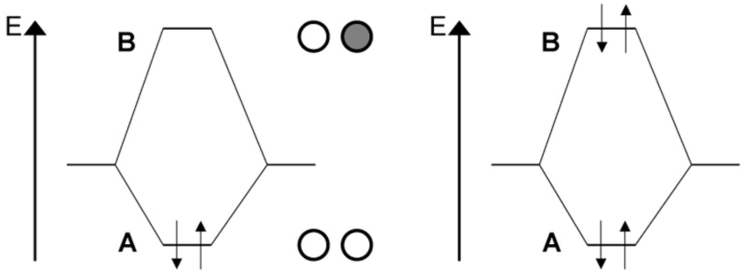
B

$\alpha - E = \beta - ES$

$\alpha - \beta = E(1 - S)$

$\boxed{E = (\alpha - \beta)/(1-S)}$

$c_1 = 1/\sqrt{[2(1 - S)]} = -c_2$



H_2

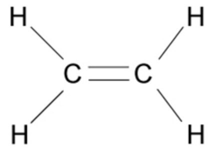
"He_2"

Calculated without any approximation

Case studies: more complex molecules

Conjugated molecules, e.g. ethene, C_2H_4, and butadiene, C_4H_6

C_2H_4



VB: **sp²** for each C atom

Consider only the π bonds:

$$\psi = \sum_i c_i\phi_i = c_1\phi_1 + c_2\phi_2$$

Problem solved by analogy: $\boxed{E_1 = (\alpha + \beta)/(1+S),\ E_2 = (\alpha - \beta)/(1-S)}$

C_4H_6 $\quad \psi = \sum_i c_i\phi_i = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4$

Secular determinant = 0

$$0 = \begin{vmatrix} \alpha_1 - E & \beta_{12} - ES_{12} & \beta_{13} - ES_{13} & \beta_{14} - ES_{14} \\ \beta_{21} - ES_{21} & \alpha_2 - E & \beta_{23} - ES_{23} & \beta_{24} - ES_{24} \\ \beta_{31} - ES_{31} & \beta_{32} - ES_{32} & \alpha_3 - E & \beta_{34} - ES_{34} \\ \beta_{41} - ES_{41} & \beta_{42} - ES_{42} & \beta_{43} - ES_{43} & \alpha_4 - E \end{vmatrix}$$

C_4H_6, continued ….

Problem 'solution' by approximation(s):

1. approx.: set $\beta_{ij} = 0$ unless adjacent atoms → **Extended Hückel**
2. approx.: set $S_{ij} = 0$ → **Simple Hückel**

Hückel determinant:

$$\boxed{| H_{ij} - E | = 0}$$

Extended Hückel determinant:

$$\boxed{| H_{ij} - S_{ij}E | = 0}$$

$H_{ii} = \alpha_i = \int \phi_i \hat{H} \phi_i d\tau$ Coulomb integral ≡ - **ionization potential**

$\boxed{H_{ii} = -I_i}$

$H_{ij} = \beta_{ij} = \int \phi_i \hat{H} \phi_j d\tau$ resonance integral

H_{ij} is proportional to the average of H_{ii} and H_{jj}

Ionization potential [eV] examples for Hückel calculations

	B	C	N	O	F
2s:	14.0	19.4	25.6	32.3	40.2
2p:	8.3	10.6	13.2	15.8	18.6

C_4H_6, continued ….

ethene, or H_2:

$E_1 = (\alpha + \beta)/(1+S)$, $E_2 = (\alpha - \beta)/(1-S)$ **no approx.**

$E_1 = (\alpha + \beta)/(1+S)$, $E_2 = (\alpha - \beta)/(1-S)$ **Extended Hückel**

$E_1 = (\alpha + \beta)$, $E_2 = (\alpha - \beta)$ **Simple Hückel**

C_4H_6, secular determinant in the **Simple Hückel** approximation

$$0 = \begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix}$$

C_4H_6, continued ….

$0 = (\alpha - E)^4 - 3(\alpha - E)^2\beta^2 + 4\beta^4$

solve in analogy to

$ax^4 + bx^2 + c = 0$, with $u = x^2$:

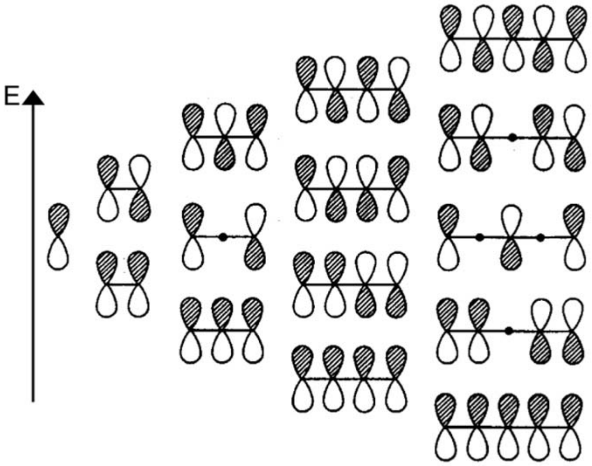
$au^2 + bu + c = 0$

=> $E = \alpha \pm 1.62\beta$, $E = \alpha \pm 0.62\beta$

Simple Hückel

General scheme for 'linear' polyenes

Simple Hückel



C_2H_4: $E = \alpha \pm \beta$; C_3H_5: $E = \alpha \pm \sqrt{2}\beta$, α;

C_4H_6: $\alpha \pm 1.6\beta$, $\alpha \pm 0.6\beta$; C_nH_{n+2}: $E = \alpha \pm 2\beta$, ….

Simple Hückel

General scheme for 'linear' polyenes

C_nH_{n+2}: n atoms, n π orbitals, j energy levels with j = 1, 2, 3, …, n

$\boxed{E_j = \alpha + 2\beta\cos(j\pi)/(n+1)}$

Examples:

ethene, C_2H_4, n = 2:

$E_1 = \alpha + 2\beta\cos\pi/3 = \alpha + \beta$

$E_2 = \alpha + 2\beta\cos(2\pi)/3 = \alpha - \beta$

allyl, C_3H_5, n = 3:

$E_1 = \alpha + 2\beta\cos\pi/4 = \alpha + \sqrt{2}\beta$ …

Cyclic (C_nH_n) vs. 'linear' polyenes (C_nH_{n+2})

e.g., cyclobutadiene vs. butadiene

different secular determinants!

Simple Hückel

Cyclic vs. 'linear' polyenes

cyclobutadiene

$$0 = \begin{vmatrix} \alpha - E & \beta & 0 & \enclose{circle}{\beta} \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ \enclose{circle}{\beta} & 0 & \beta & \alpha - E \end{vmatrix}$$

=> $E = \alpha \pm 2\beta, \alpha, \alpha$

butadiene

$$0 = \begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix}$$

=> $E = \alpha \pm 1.62\beta$, $E = \pm 0.62\beta$

C_nH_n: n atoms, n π orbitals, j energy levels with

j = ±1, ±2, ±3, …, ±n/2 if n even

j = 0, ±1, ±2, ±3, …, ±(n-1)/2 if n odd

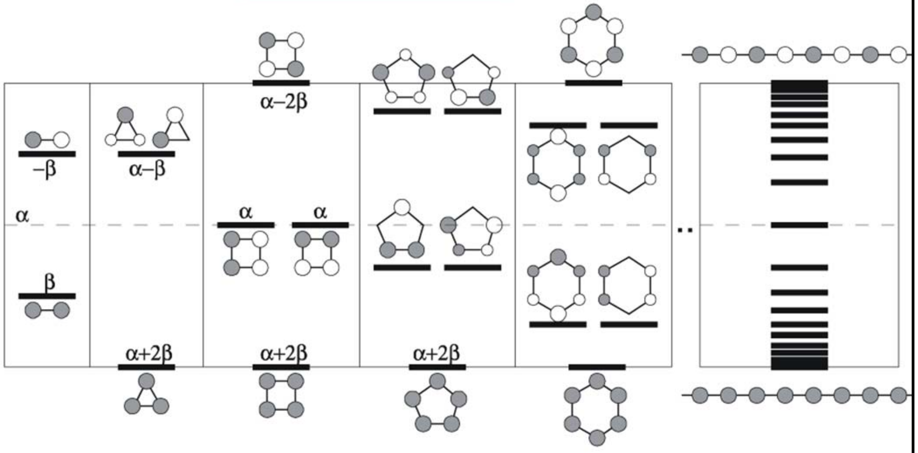
$\boxed{E_j = \alpha + 2\beta\cos(2j\pi)/n}$

Cyclobutadiene: n = 4, j = ±1, ±2

=> $E_2 = \alpha + 2\beta\cos(4\pi)/4 = \alpha - 2\beta$

Cyclic polyenes

$E_j = \alpha + 2\beta\cos(2j\pi)/n$



Cyclic polyenes

$E_j = \alpha + 2\beta\cos(2j\pi)/n$

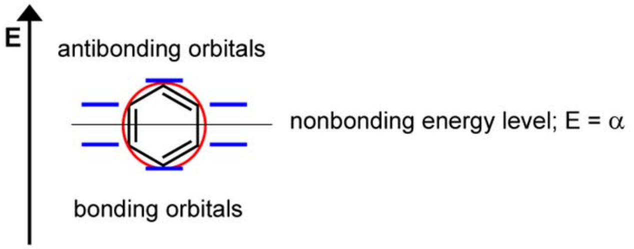
Frost's circles:

tool for estimating the π MO's for cyclic polyenes

Construction:

1) draw the polyene schematically, with one vertex at the bottom
2) draw a circle around the center, which touches all vertices

=> DONE! The energy levels are, where the corners of the polyene touch the circle.



E

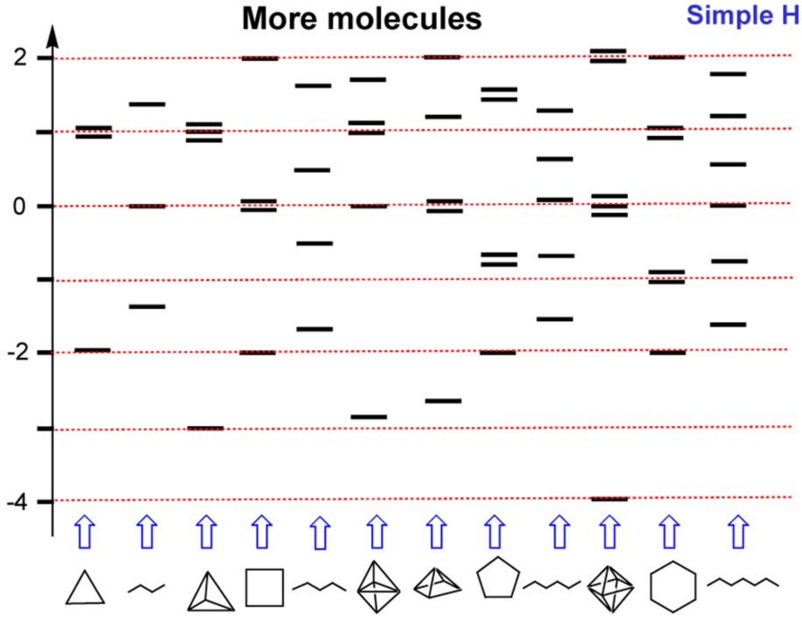
antibonding orbitals

nonbonding energy level; E = α

bonding orbitals

More molecules

Simple Hückel



Elementary Band Theory for Extended Solids

Energy bands in solids arise from overlapping

atomic orbitals => **crystal orbitals** (that make up the bands)

Recipe: use **LCAO** (tight binding) **approach**

Crystal = regular periodic array => translational symmetry

Periodic boundary condition requires: $\psi(x+Na) = \psi(x)$.
I.e. each wavefunction must be **symmetry equivalent** to the one in the neighboring cells.
A function u(x) which is unaltered when moving from one lattice point to another is called a **Bloch function** [u(x) = u(x+Na)].

$$\phi(r) = \frac{e^{ik\cdot r}}{\sqrt{V}}u(r)$$

Bloch's theorem

$$\boxed{\psi_k = \sum_n e^{ikna}\,\phi_n}$$

(a solution of the Schrödinger equation)

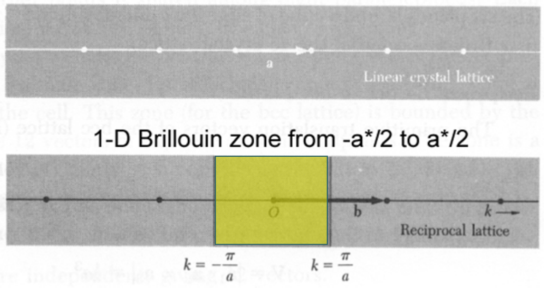
$$\psi_k = \sum_n \{(\cos kna + i\sin kna)\phi_n\}$$

Elementary Band Theory for Extended Solids

$$\boxed{\psi_k = \sum_n \{(\cos kna + i\sin kna)\phi_n\}}$$

$$\psi(k) = \sum_n e^{inka}\phi_n$$

1-dimensional case



1-D Brillouin zone from -a*/2 to a*/2

a* = 2π/a

$$\boxed{-\pi/a \le k \le \pi/a}$$

Consider k = 0: **zone center Γ**

cos(kna) = cos(0) = 1

sin(kna) = sin(0) = 0

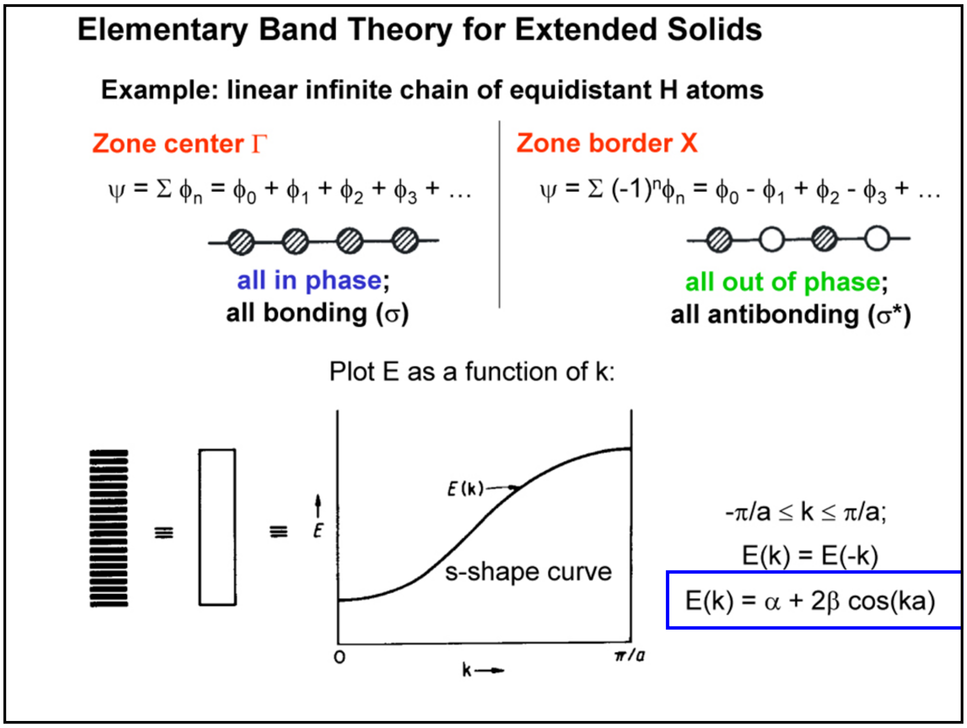
$\psi = \Sigma\, \phi_n = \phi_0 + \phi_1 + \phi_2 + \phi_3 + \ldots$

Consider k = π/a: **zone border X**

cos(kna) = cos(πn) = $(-1)^n$

sin(kna) = sin(πn) = 0

$\psi = \Sigma\, (-1)^n\phi_n = \phi_0 - \phi_1 + \phi_2 - \phi_3 + \ldots$



Elementary Band Theory for Extended Solids

Example: linear infinite chain of equidistant H atoms

Zone center Γ

$\psi = \Sigma\, \phi_n = \phi_0 + \phi_1 + \phi_2 + \phi_3 + \ldots$

all in phase;
all bonding (σ)

Zone border X

$\psi = \Sigma\, (-1)^n \phi_n = \phi_0 - \phi_1 + \phi_2 - \phi_3 + \ldots$

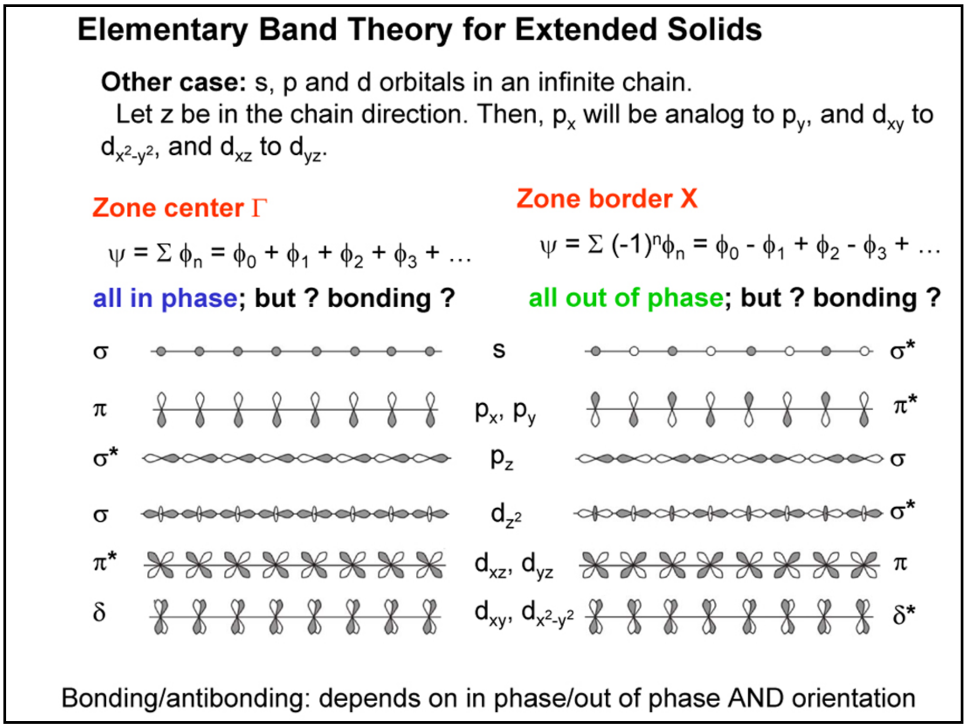
all out of phase;
all antibonding (σ*)

Plot E as a function of k:

$-\pi/a \le k \le \pi/a$;

$E(k) = E(-k)$

$\boxed{E(k) = \alpha + 2\beta \cos(ka)}$



Elementary Band Theory for Extended Solids

Other case: s, p and d orbitals in an infinite chain.
Let z be in the chain direction. Then, p_x will be analog to p_y, and d_{xy} to $d_{x^2-y^2}$, and d_{xz} to d_{yz}.

Zone center Γ

$\psi = \Sigma\, \phi_n = \phi_0 + \phi_1 + \phi_2 + \phi_3 + \ldots$

all in phase; but ? bonding ?

Zone border X

$\psi = \Sigma\, (-1)^n \phi_n = \phi_0 - \phi_1 + \phi_2 - \phi_3 + \ldots$

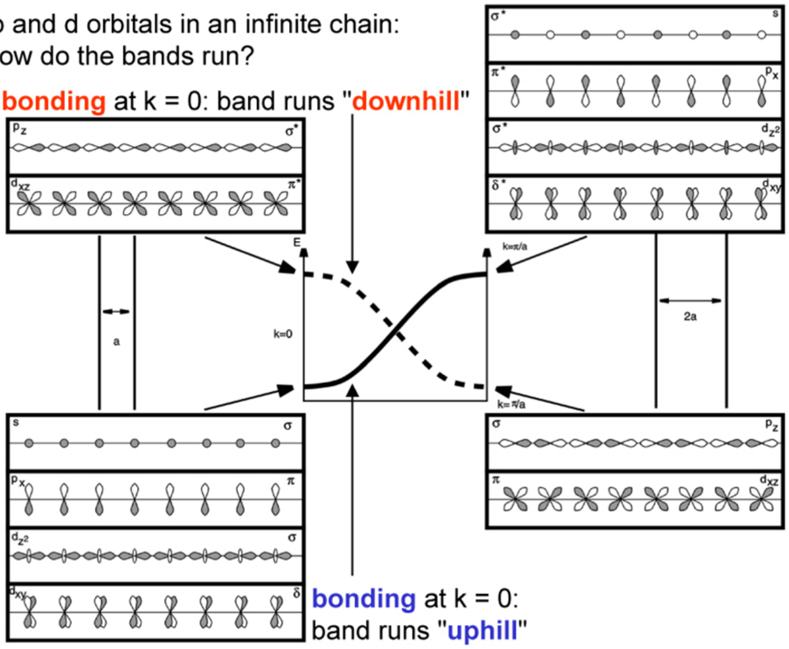
all out of phase; but ? bonding ?

σ	s	σ*
π	p_x, p_y	π*
σ*	p_z	σ
σ	d_{z^2}	σ*
π*	d_{xz}, d_{yz}	π
δ	d_{xy}, $d_{x^2-y^2}$	δ*

Bonding/antibonding: depends on in phase/out of phase AND orientation

Elementary Band Theory for Extended Solids

s, p and d orbitals in an infinite chain:
how do the bands run?



antibonding at k = 0: band runs "**downhill**"

bonding at k = 0:
band runs "**uphill**"

Chem 253, UC, Berkeley

How to calculate E(k)?

$$\psi\ (k) = \sum_n e^{inka}\phi_n$$

Crystal Schrodinger Equation: $H\psi(k) = E(k)\psi(k)$

$$E(k) = \frac{<\psi^*(k)|\hat{H}|\psi(k)>}{<\psi^*(k)|\psi(k)>}$$

$$\downarrow$$

$$\boxed{\begin{array}{l} <\phi^*{}_m|\phi_n> = 1....(m=n) \\ <\phi^*{}_m|\phi_n> = 0....(m \neq n) \end{array}}$$

$$<\psi^*(k)|\psi(k)> = \sum_{m,n} <\phi^*{}_m|\phi_n> = N$$

$$\psi\ (k) = \sum_n e^{inka}\phi_n$$

$$< \psi^*(k)\left|\hat{H}\right|\psi(k) >$$

1. m=n

$$< \psi^*(k)\left|\hat{H}\right|\psi(k) > = \sum_n < \phi^*{}_n\left|\hat{H}\right|\phi_n > = N\alpha$$

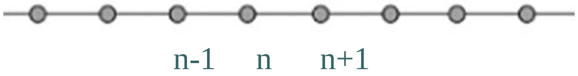
2. m≠n, consider only the nearest neighbor

$$< \phi^*{}_n\left|\hat{H}\right|\phi_{n\pm1} > = \beta$$

$$E(k) = \frac{< \psi^*(k)\left|\hat{H}\right|\psi(k) >}{< \psi^*(k)\left|\psi(k)\right. >}$$

$$......... = \frac{N\alpha + N\beta(e^{ika} + e^{-ika})}{N}$$

$$.......... = \alpha + 2\beta\cos ka$$



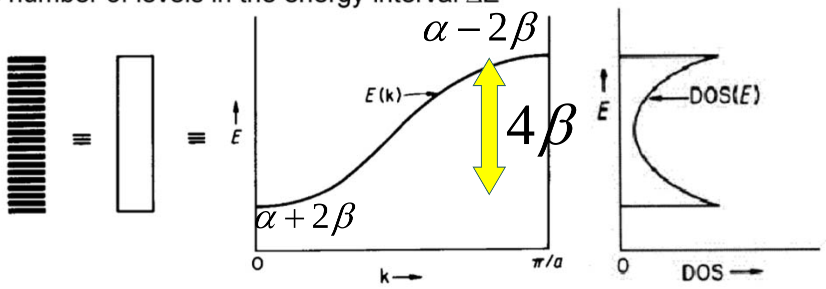
$$E(k) = \left\langle\ e^{-ikna}\phi_n\left|\hat{H}\right|\left\{e^{ik(n-1)a}\phi_{n-1} + e^{ikna}\phi_n + e^{ik(n+1)a}\phi_{n+1}\right\}\ \right\rangle$$

$$......... = \alpha + 2\beta\cos ka$$

Elementary Band Theory for Extended Solids

Densities of states (DOS)

≡ number of levels in the energy interval ΔE



DOS is proportional to the inverse slope of the band;

steep bands (large overlap) => small DOS

flat bands (small overlap) => large DOS

DOS(E_F) determines properties

e.g., electrical conductivity, magnetic susceptibility, specific heat ...

DOS(E_F) = 0: always nonmetallic

DOS(E_F) > 0: often metallic

Elementary Band Theory for Extended Solids

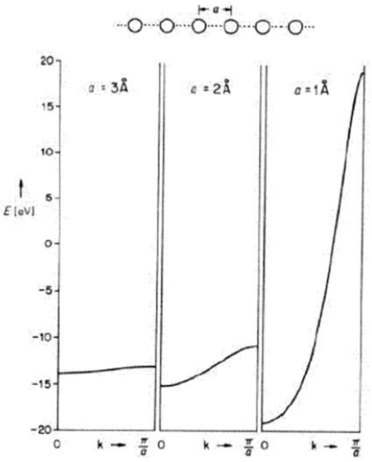
Bandwidth (dispersion)

The difference between highest and lowest level of one band.

The bandwidth is determined by the **overlap** between the interacting orbitals.

The smaller the distance between the atoms, the larger the bandwidth.

4β



Infinite chain of H atoms