

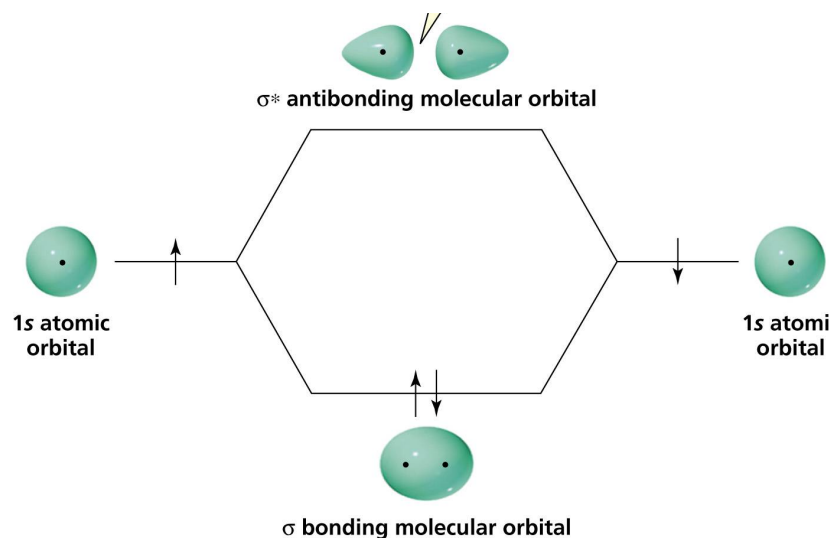
PH575 Spring 2019

Lecture #4 - Homo- & heteronuclear diatomic molecule: Sutton Ch. 2 pp 25-31

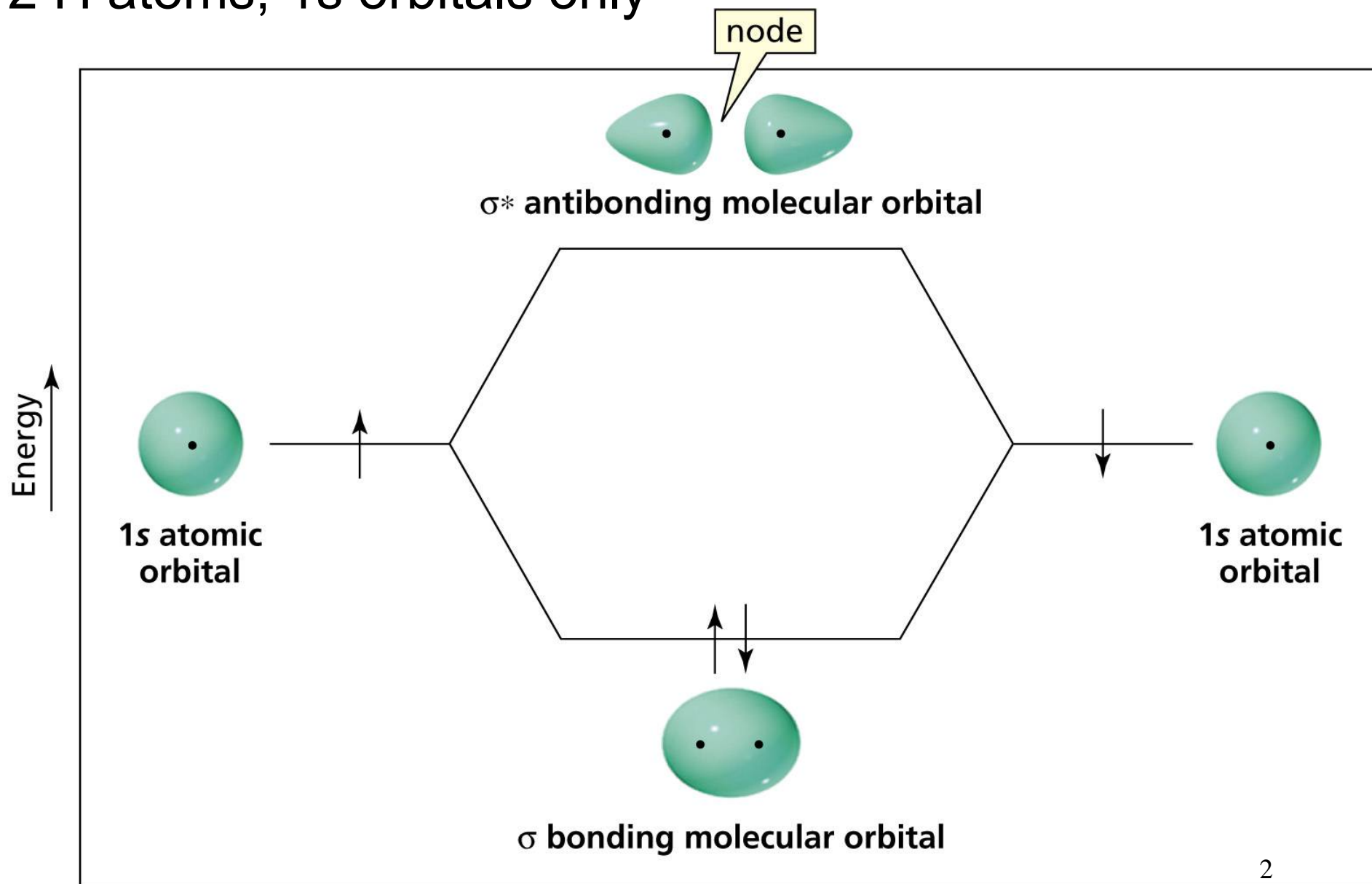
$$\langle n\ell m_\ell | n\ell m_\ell \rangle$$

$$\sum_i |i\rangle \langle i| = 1$$

$$\beta = \langle 1 | \hat{H} | 2 \rangle$$



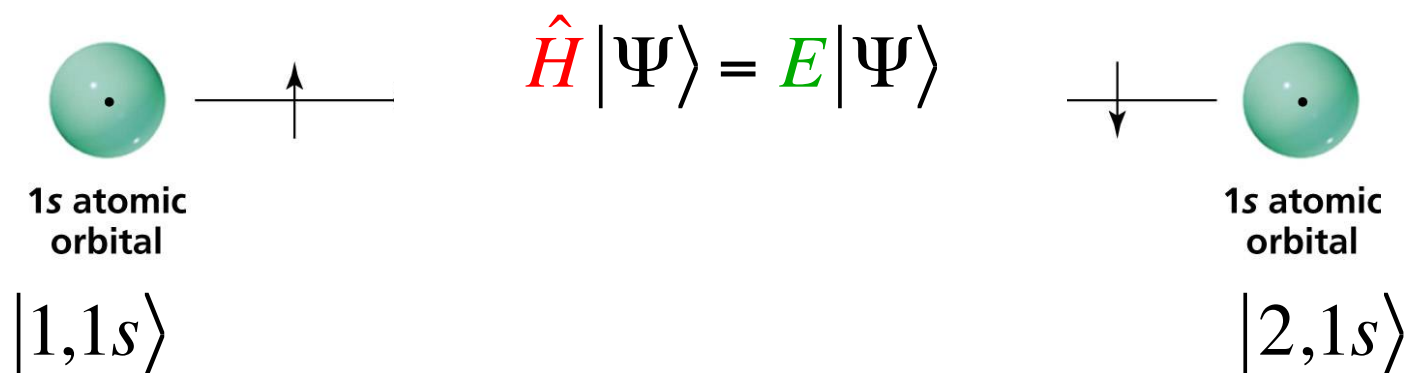
H_2 : a homonuclear diatomic molecule
2 H atoms, 1s orbitals only



Goal: find molecular orbitals, $|\Psi\rangle$
and their energies, E

$$|\Psi\rangle = \langle 1,1s|\Psi\rangle|1,1s\rangle + \langle 2,1s|\Psi\rangle|2,1s\rangle$$

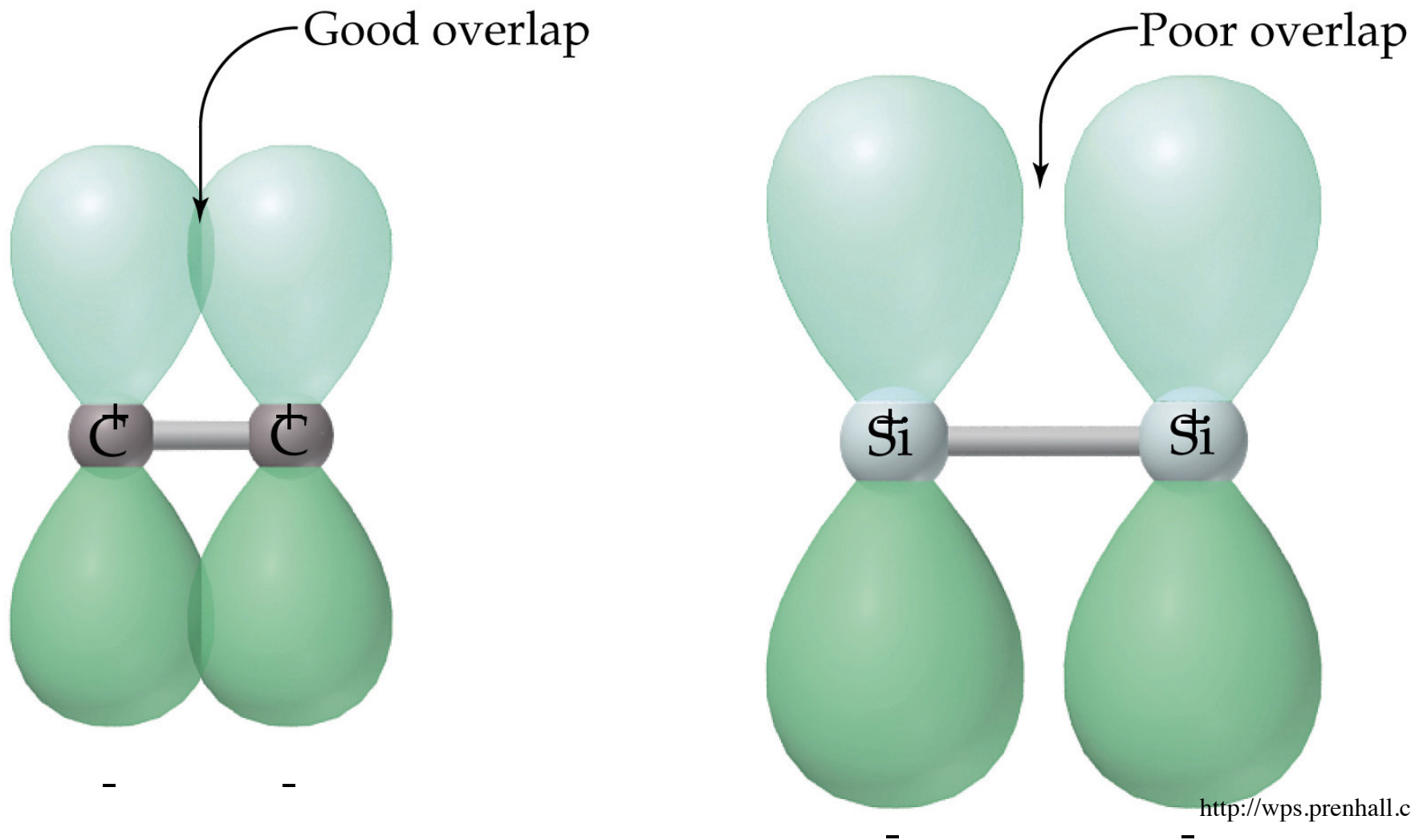
$$|\Psi\rangle = c_1|1,1s\rangle + c_2|2,1s\rangle$$



We know these atomic orbitals, and their energies. These are the basis kets.

Assume orthogonal (not quite true, but OK) $\langle 1,1s|2,1s\rangle = 0$ 3

Overlap of atomic orbitals on different atoms



A large overlap integral *requires* spatial overlap, but spatially overlapping orbitals can still have zero overlap if the signs are appropriately arranged. e.g 2s is orthogonal to 2p on same⁴ atom.

We want to find molecular orbitals, and their energies, E

$$\hat{H}|\Psi\rangle = E|\Psi\rangle$$

$$|\Psi\rangle = c_1|1,1s\rangle + c_2|2,1s\rangle$$

$$\hat{H} [c_1|1,1s\rangle + c_2|2,1s\rangle] = E [c_1|1,1s\rangle + c_2|2,1s\rangle]$$

On-site
matrix
element
 $H_{11}=E_0$
(assume
known)

Project onto basis ket #1

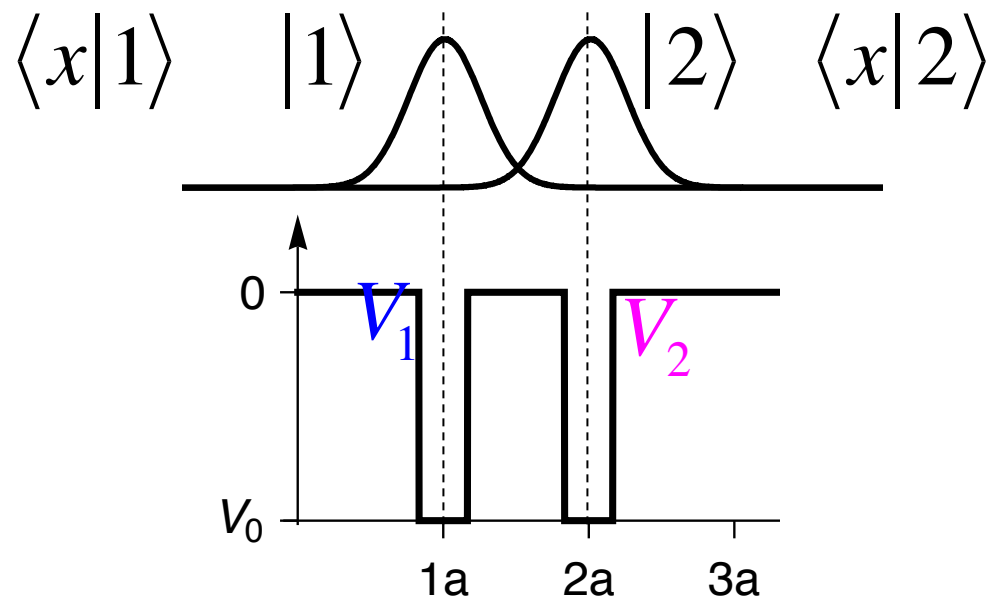
$$c_1 \langle 1,1s | \hat{H} | 1,1s \rangle + c_2 \langle 1,1s | \hat{H} | 2,1s \rangle = E \left[c_1 \underbrace{\langle 1,1s | 1,1s \rangle}_? + c_2 \underbrace{\langle 1,1s | 2,1s \rangle}_? \right]$$

Hopping
matrix
element
 $H_{12}=\beta$
(assume
known)

On-site energy: $\langle 1 | \hat{H} | 1 \rangle = \langle 1 | -\frac{\hbar^2}{2m} \nabla^2 + V_1(r) + V_2(r) | 1 \rangle$

$$E_0 = E_{1,atomic} + \langle 1 | V_2(r) | 1 \rangle$$

On-site energy is approximately the atomic energy, but small correction due to other potential. WF 1 is small where V_2 is large and vice versa (note: e-e interactions neglected).



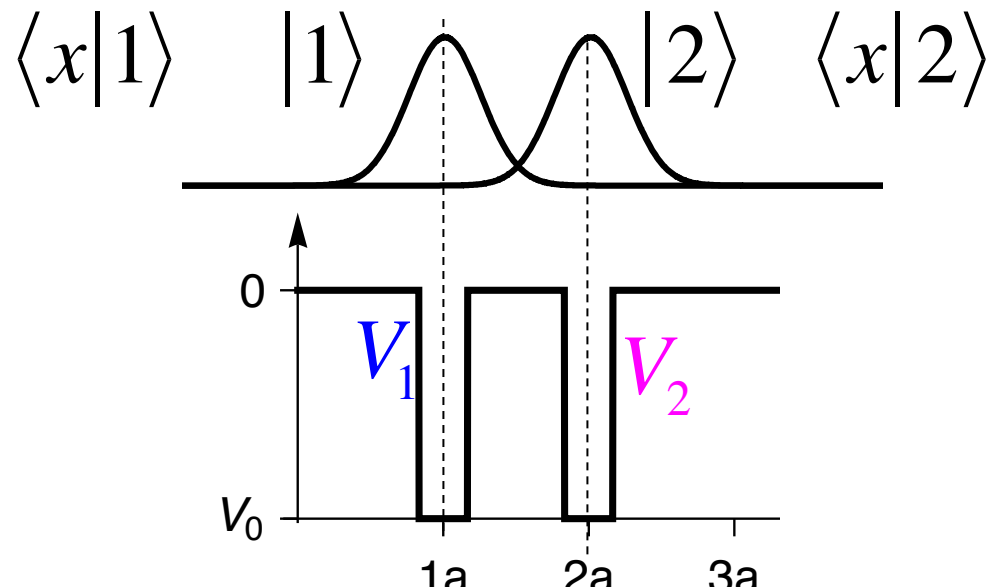
Hopping energy:

$$\langle 1 | \hat{H} | 2 \rangle = \langle 1 | -\frac{\hbar^2}{2m} \nabla^2 + V_1(r) + V_2(r) | 2 \rangle$$

$$\beta = E_{1,atomic} \langle 1 | 2 \rangle + \langle 1 | V_2(r) | 2 \rangle$$

$$\beta = \langle 1 | V_2(r) | 2 \rangle$$

Hopping energy is integral of individual potential and both atomic wave functions. Could have additional contribution if there is n-n overlap.



We want to find molecular orbitals, and their energies, E

$$c_1 E_0 + c_2 \beta = E c_1$$

$$c_1 \beta + c_2 E_0 = E c_2$$

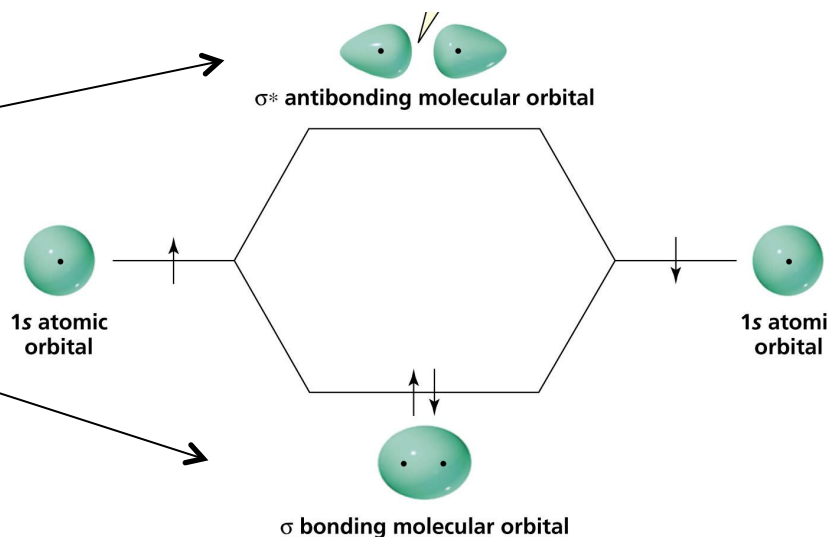
Project onto basis kets

$$\begin{vmatrix} E_0 - E & \beta \\ \beta & E_0 - E \end{vmatrix} = 0$$

Linear algebra \Rightarrow quadratic eqn

$$E_a = E_0 - \beta$$

$$E_b = E_0 + \beta$$



$$\beta = \langle 1, 1s | V_2(r) | 2, 1s \rangle < 0$$

For overlapping s orbitals, β is negative. This is because s orbitals are +ve everywhere and $V_2 < 0$ (attractive potential)

We want to find molecular orbitals, and their energies, E

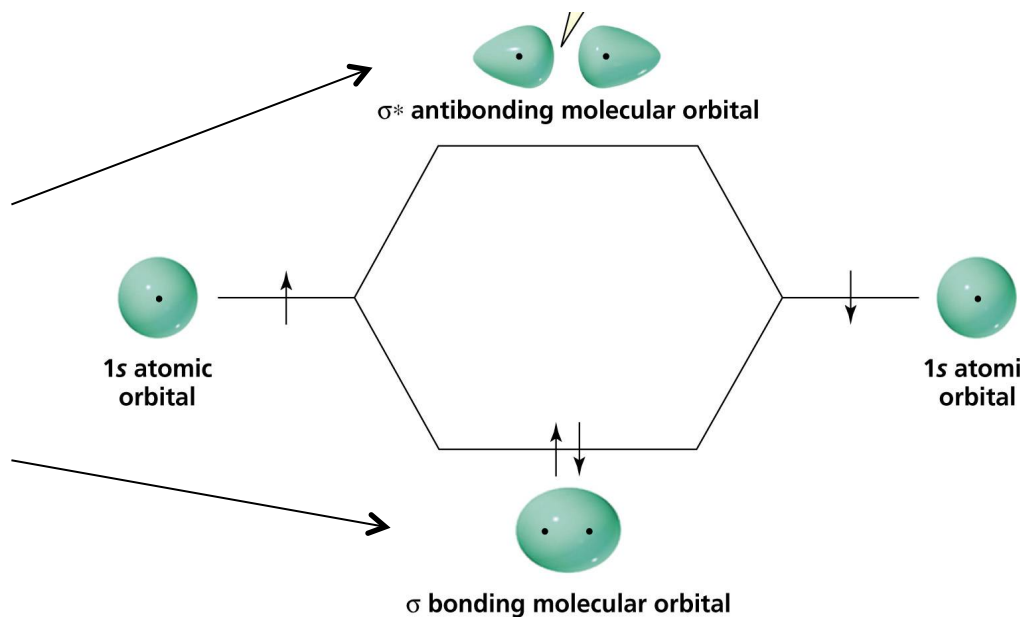
$$c_1 E_0 + c_2 \beta = E c_1$$

$$c_1 \beta + c_2 E_0 = E c_2$$

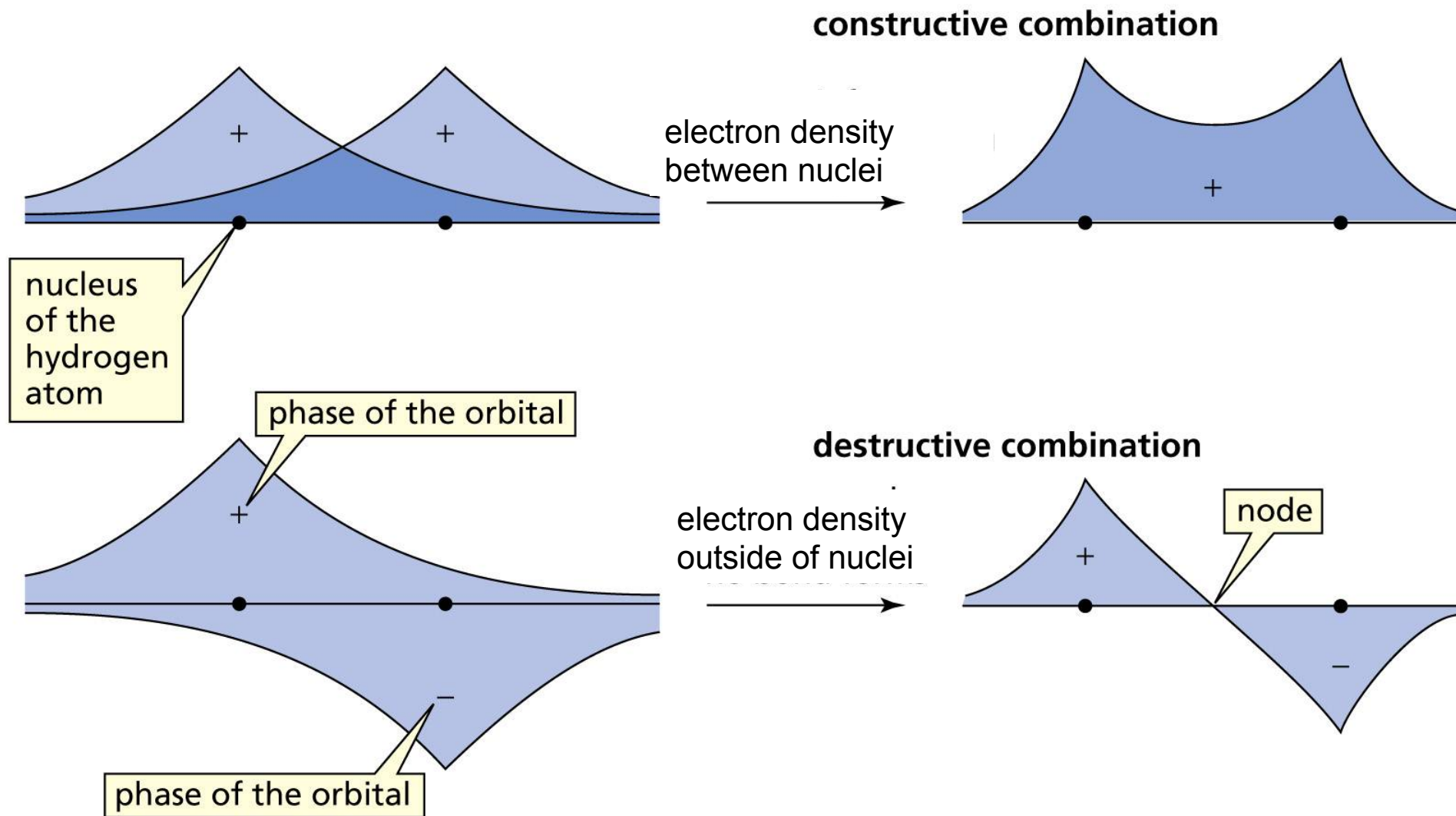
Now we can find the c 's for each of E_b and E_a , and hence the corresponding Ψ_b and Ψ_a .

$$\Psi_a = \frac{1}{\sqrt{2}} (|1,1s\rangle - |2,1s\rangle)$$

$$\Psi_b = \frac{1}{\sqrt{2}} (|1,1s\rangle + |2,1s\rangle)$$



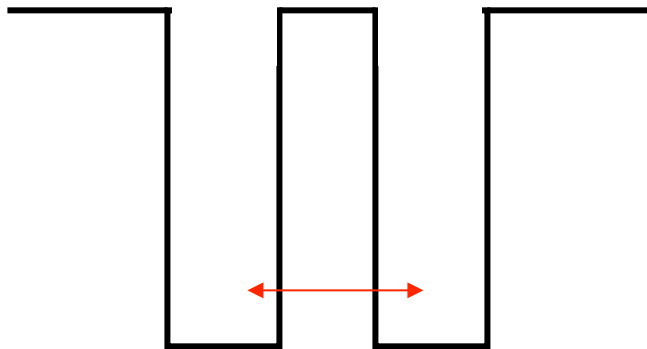
H₂ molecule



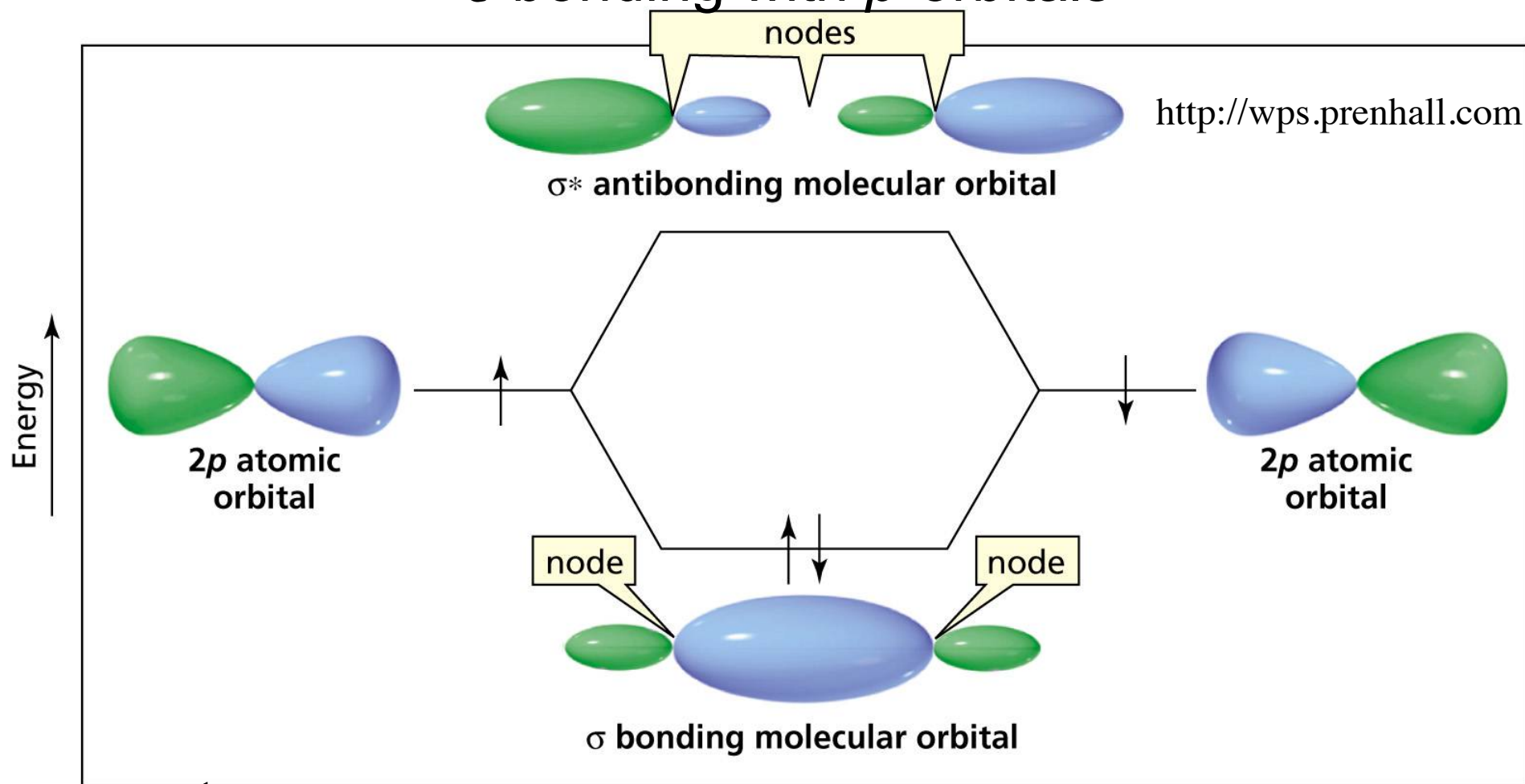
H₂ molecule

Bonding is a quantum mechanical phenomenon that results from the interference of quantum waves!

To view bonding as the "sharing" of electrons, we can show (Sutton p33-31) that an electron oscillates from atom #1 to atom #2 at a frequency $2\beta/h$. How does it overcome the large ionization potential? It tunnels! Again a quantum mechanical phenomenon.



σ bonding with *p*-orbitals

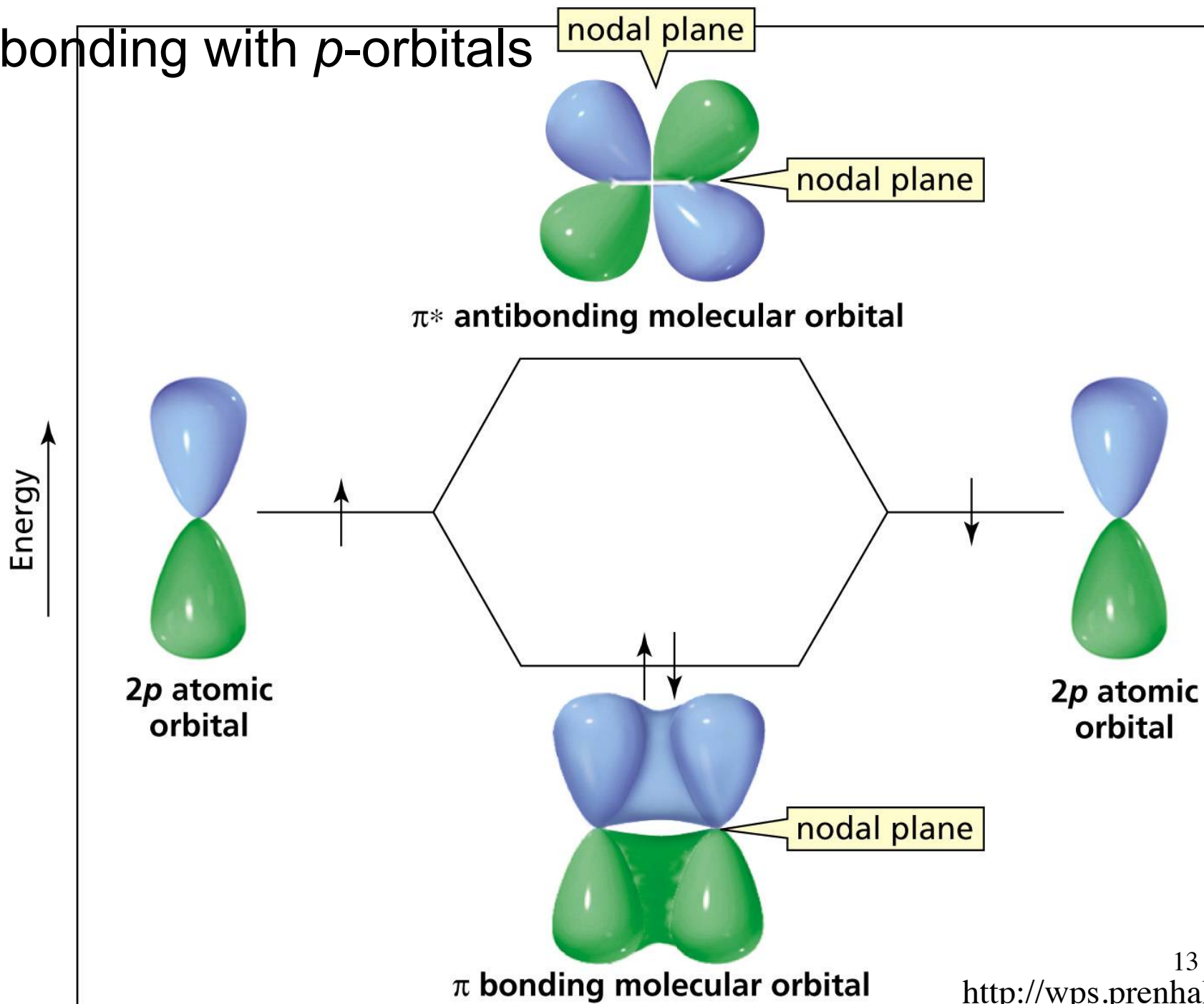


$$\Psi_a = \frac{1}{\sqrt{2}} (|1, p\rangle + |2, p\rangle)$$

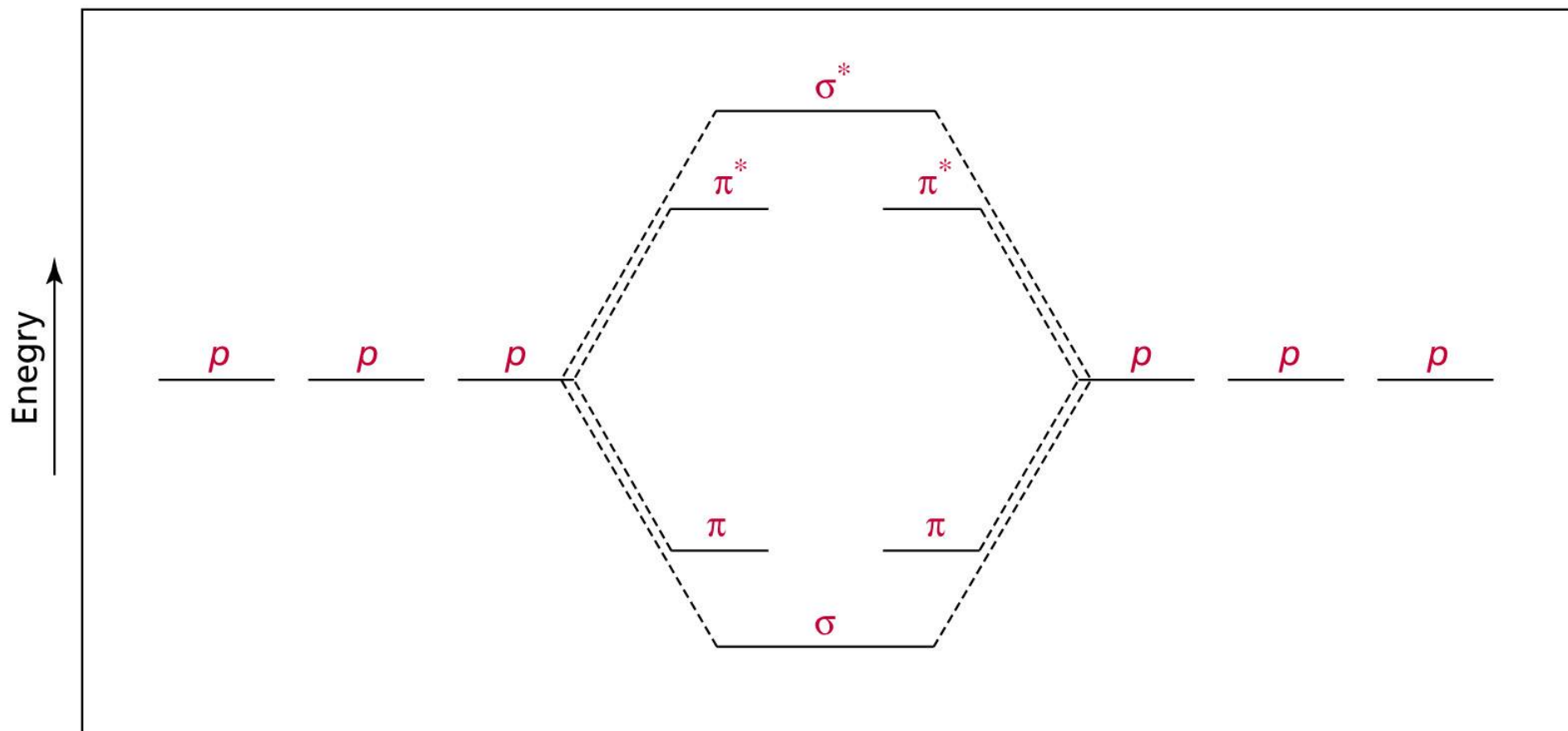
$$\Psi_b = \frac{1}{\sqrt{2}} (|1, p\rangle - |2, p\rangle)$$

Why is the –ve sign associated with the bonding orbital in this example?

π bonding with p -orbitals

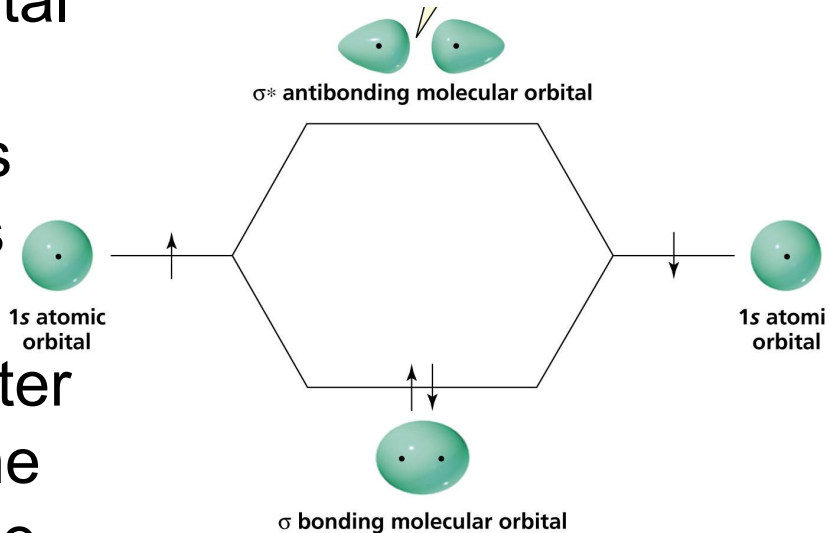


MO diagram for p -orbitals



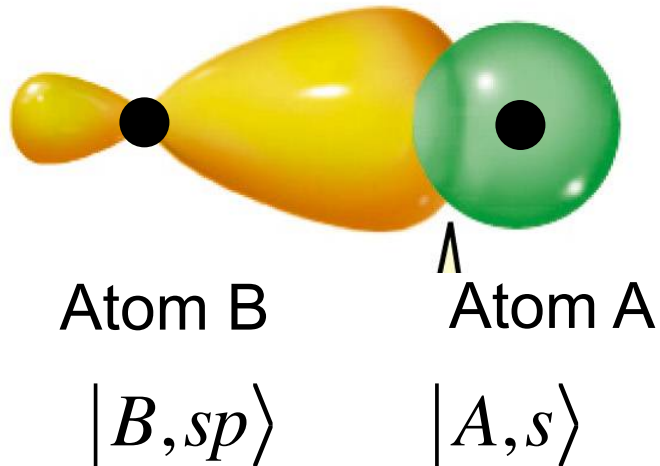
- H_2 molecule has 2 atoms and the 2 molecular orbitals are (relatively) close in energy, one higher and one lower than the energy of the atomic orbital

- The hopping term represents tunneling of electrons across the potential barrier between atoms (see Sutton). The faster the tunneling, the stronger the interaction, and the bigger the splitting.



- The orbitals are bonding (electron density between nuclei tending to draw nuclei together), or antibonding (electron density on opposite sides of nuclei, causing nuclear repulsion)

Heteronuclear diatomic molecule



E_A —

$$\langle B | \hat{H} | B \rangle = E_B \quad \langle A | \hat{H} | A \rangle = E_A$$

— E_B

On-site integrals

$$\langle A | \hat{H} | B \rangle = \langle B | \hat{H} | A \rangle = \beta$$

Off-site integral

$$|\Psi\rangle = c_A |A\rangle + c_B |B\rangle$$

General form of MO

$$\hat{H} |\Psi\rangle = E |\Psi\rangle$$

Schrödinger eigenvalue equation

Want to find these molecular orbitals, and their energies, E

$$c_A E_A + c_B \beta = E c_A$$

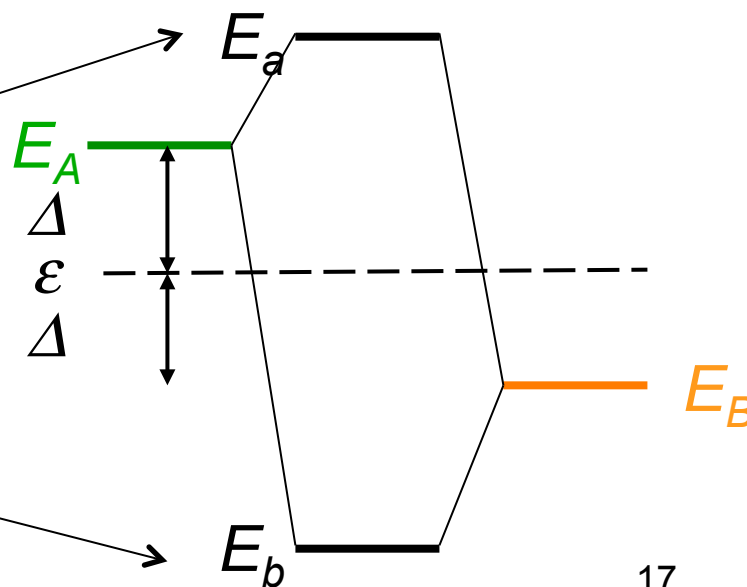
$$c_A \beta + c_B E_B = E c_B$$

Project onto basis
kets

$$\begin{vmatrix} E_A - E & \beta \\ \beta & E_B - E \end{vmatrix} = 0 \quad \text{Linear algebra} \Rightarrow \text{quadratic eqn}$$

$$E_a = \varepsilon + \left(\Delta^2 + \beta^2 \right)^{1/2}$$

$$E_b = \varepsilon - \left(\Delta^2 + \beta^2 \right)^{1/2}$$



Want to find these molecular orbitals, and their energies, E

$$c_A E_A + c_B \beta = E c_A$$

$$c_A \beta + c_B E_B = E c_B$$

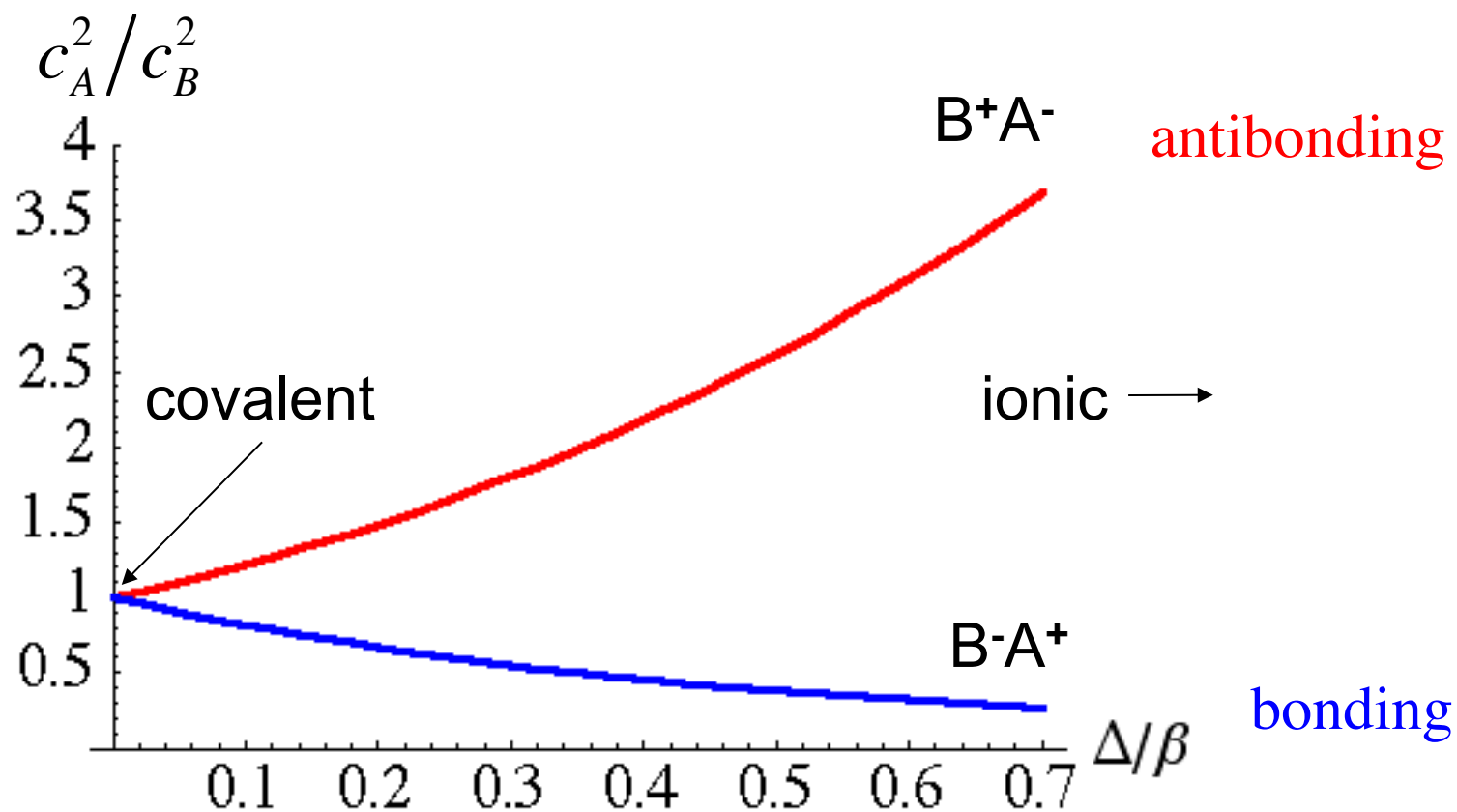
Now we can find the c 's for each of E_b and E_a , and hence the corresponding Ψ_b and Ψ_a .

$$\frac{c_{A,a}^2}{c_{B,a}^2} = \frac{1}{1 + 2(\Delta / \beta)^2 - 2(\Delta / \beta) \left(1 + (\Delta / \beta)^2\right)^{1/2}}$$

$$\frac{c_{A,b}^2}{c_{B,b}^2} = \frac{1}{1 + 2(\Delta / \beta)^2 + 2(\Delta / \beta) \left(1 + (\Delta / \beta)^2\right)^{1/2}}$$

$$\frac{c_{A,a}^2}{c_{B,a}^2} = \frac{1}{1 + 2(\Delta / \beta)^2 - 2(\Delta / \beta) \left(1 + (\Delta / \beta)^2 \right)^{1/2}}$$

$$\frac{c_{A,b}^2}{c_{B,b}^2} = \frac{1}{1 + 2(\Delta / \beta)^2 + 2(\Delta / \beta) \left(1 + (\Delta / \beta)^2 \right)^{1/2}}$$



Electronegativity

TABLE 1.3 The Electronegativities of Selected Elements^a

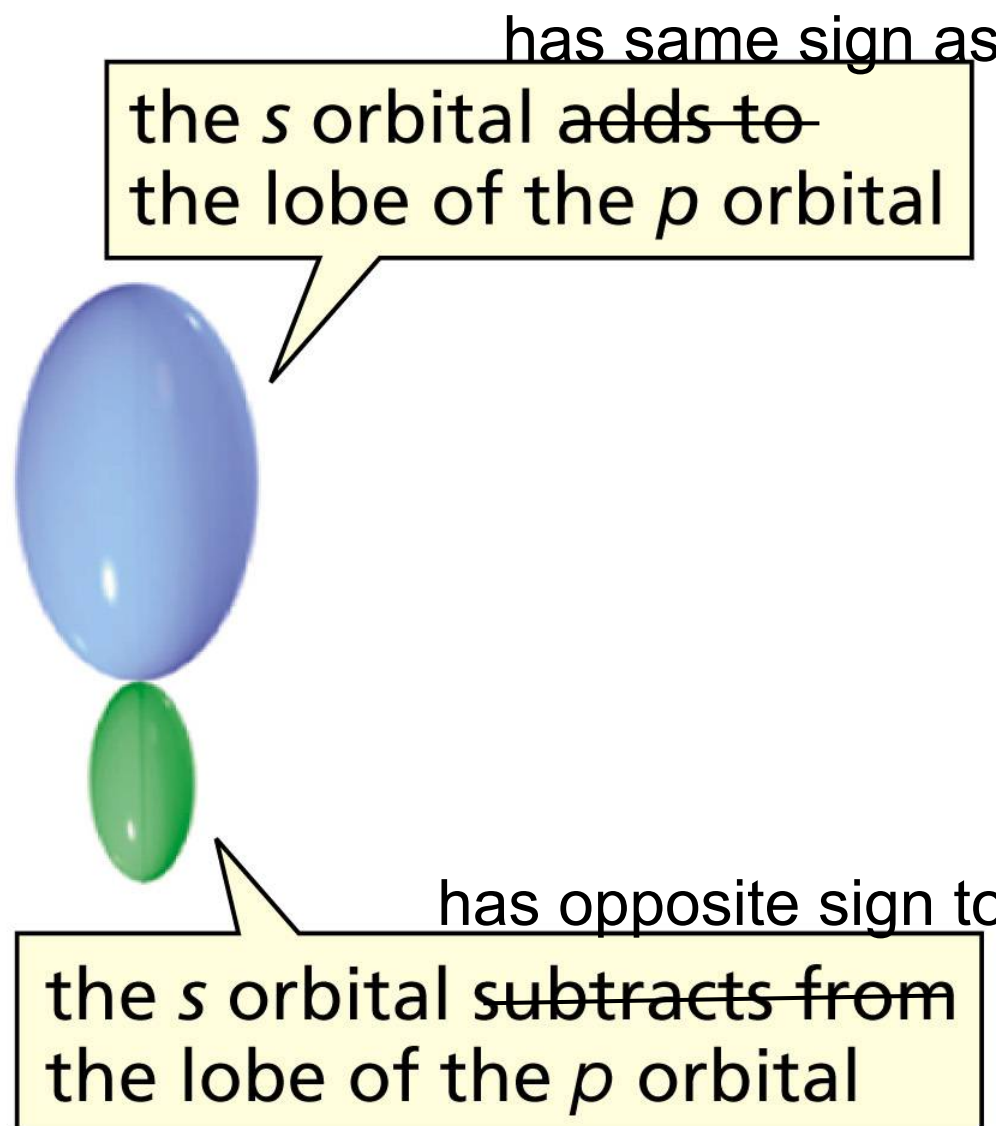
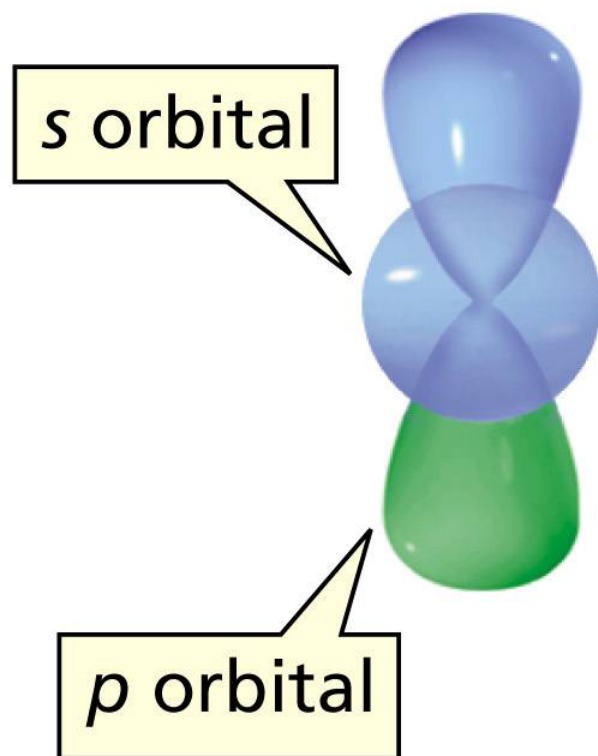
IA	IIA	IB	IIB	IIIA	IVA	VA	VIA	VIIA
H 2.1								
Li 1.0	Be 1.5			B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2			Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0							Br 2.8
								I 2.5

increasing electronegativity

increasing electronegativity

^aElectronegativity values are relative, not absolute. As a result, there are several scales of electronegativities. electronegativities listed here are from the scale devised by Linus Pauling.





sp^3 -hybridization

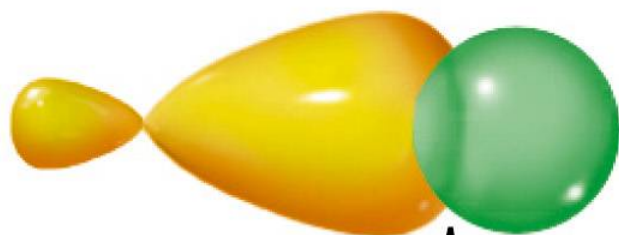


This commonly shown picture is actually inaccurate. It shows 1s-2p hybridization. One always sees 2s-2p hybridization. 2s electron distribution is different from 1s!

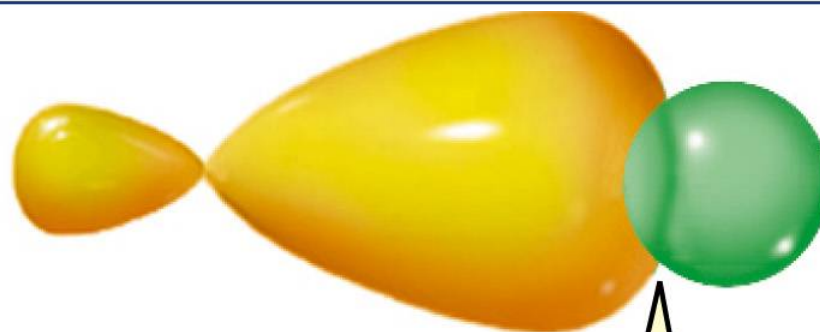
HF and HCl

Table 1.6 Hydrogen–Halogen Bond Lengths and Bond Strengths

Hydrogen halide		Bond length (Å)	Bond strength	
			kcal/mol	kJ/mol
H—F		0.917	136	571
H—Cl		1.2746	103	432
H—Br		1.4145	87	366
H—I		1.6090	71	298



overlap of an s orbital
with a 2 sp^3 orbital



overlap of an s orbital
with a 3 sp^3 orbital

Overlap of the bonding sp^3 hybrid orbital of F and Cl with H in HF and HCl.

Overlap of the 1s orbital of hydrogen is better with the smaller $2sp^3$ hybrid orbital of fluorine than with the larger $3sp^3$ hybrid orbital of chlorine, resulting in a shorter, stronger bond in HF than in HCl.

