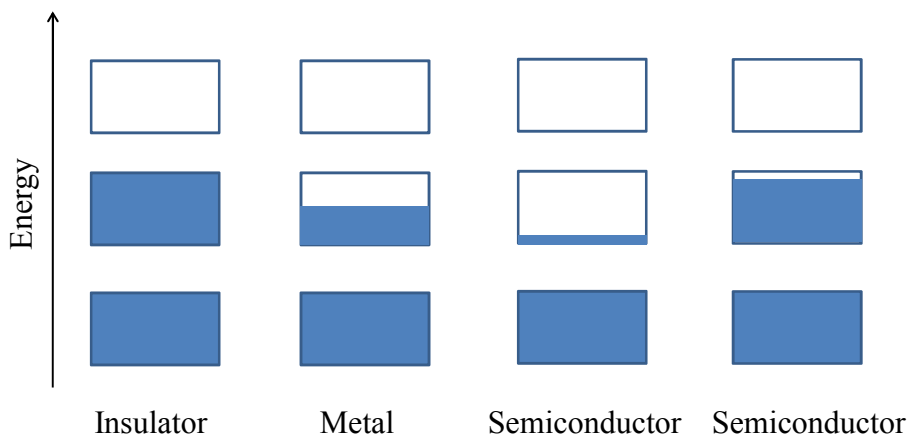


MOLECULAR ORBITAL THEORY OF BONDING

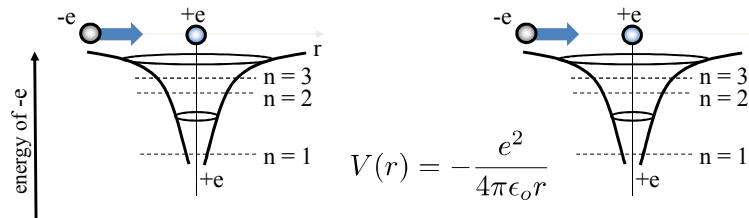
1

Energy Bands



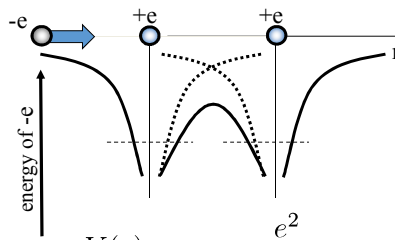
2

Atomic & Molecular Wavefunctions



$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$

Superposition of Coulomb potentials H_2 :



$$V(r) = -\frac{e^2}{4\pi\epsilon_0 |r - r_1|} - \frac{e^2}{4\pi\epsilon_0 |r - r_2|}$$

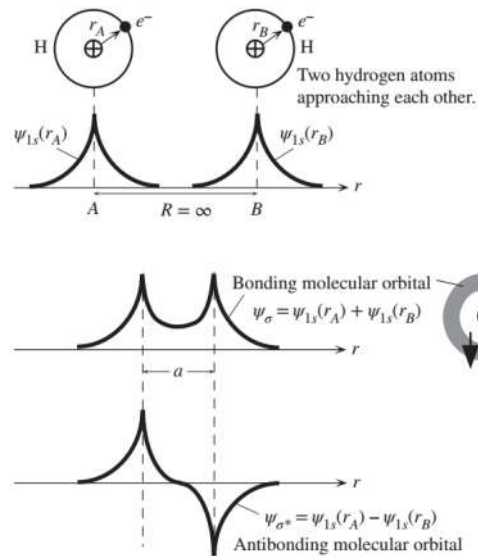
3

Hydrogen Atoms

- As the two atoms approach each other, ψ_{1s} wavefunctions overlap.
- The overlap of wavefunctions can either be in phase or out of phase \rightarrow two molecular orbitals are formed with different energies.

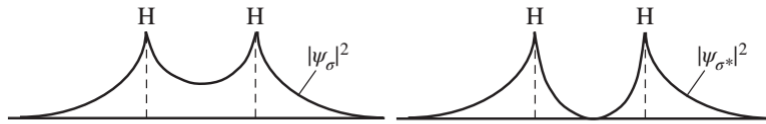
$$\psi_{\sigma} = \psi_{1s}(r_A) + \psi_{1s}(r_B)$$

$$\psi_{\sigma^*} = \psi_{1s}(r_A) - \psi_{1s}(r_B)$$



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Probability Distribution



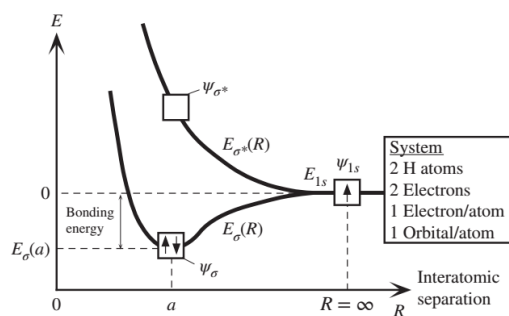
Electron probability distributions for bonding and antibonding orbitals, ψ_σ and ψ_{σ^*} .

- The first molecular orbital ψ_σ is *symmetric* and has considerable magnitude between the nuclei, whereas the second ψ_{σ^*} , is *antisymmetric* and has a node between the nuclei.

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Hydrogen Atoms

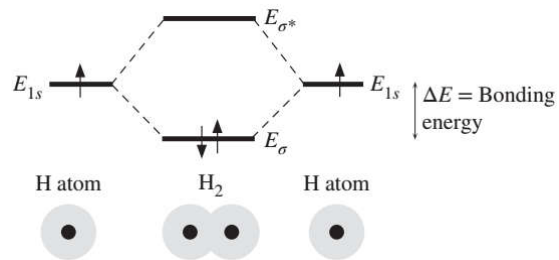
- As R decreases and the two H atoms get closer, the energy of the ψ_σ orbital state passes through a minimum at $R = a$.
- The wavefunction ψ_σ corresponding to the lowest electron energy is called the bonding orbital, and ψ_{σ^*} is the antibonding orbital.



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Hydrogen Atoms

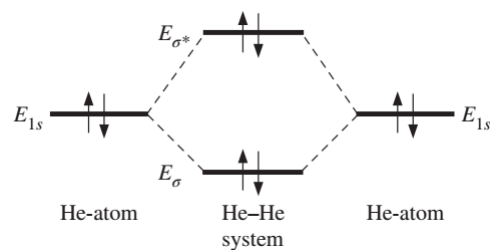
- The changes in the electron energy as two isolated H atoms, far left and far right, come together to form a hydrogen molecule.
- E_{1s} , splits into two, E_{σ} and E_{σ^*} .



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He Atoms

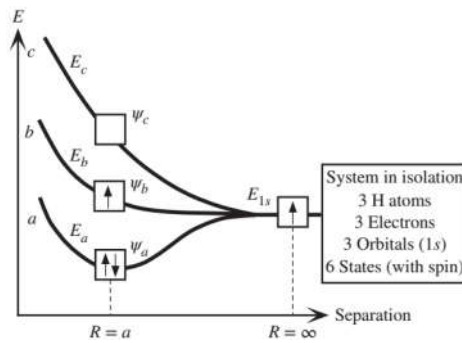
- Consider what happens when two He atoms come together.
- When He atoms come together, two of the electrons enter the E_{σ} level and two the E_{σ^*} level, so the overall energy is greater than two isolated He atoms.
- Quantum mechanical calculations show that the antibonding energy level E_{σ^*} shifts higher than the bonding level E_{σ} shifts lower.
- The overlap of full atomic orbital states does not lead to bonding.
- We need an overlap of half-occupied orbitals, as in the H₂ molecule, to form a bond between two atoms.



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3 Hydrogen Atoms

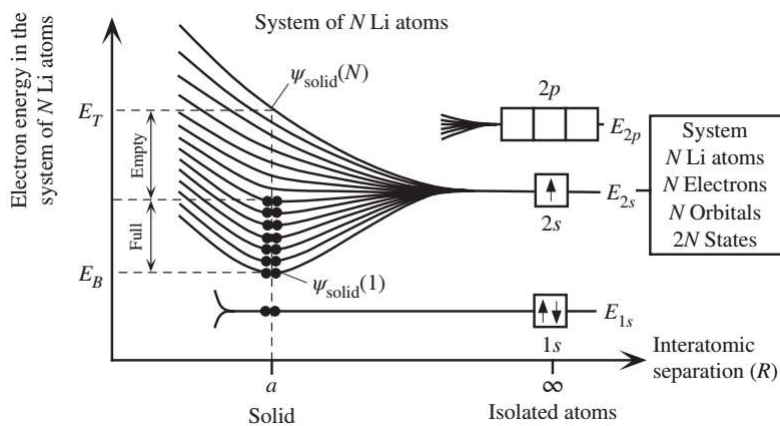
- Three separate molecular orbital states, ψ_a , ψ_b , and ψ_c , from three ψ_{1s} atomic states.
- Although H_2 and H_3 both have two electrons in the lowest energy level, H_3 also has an extra electron at the higher energy level (E_b), which tends to increase the net energy of the atom. Thus, the H_3 molecule is much less stable than the H_2 molecule.



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Li Atoms

- Consider N Li (lithium) atoms are brought close together.



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Bloch Theorem

- **Bloch wave:** A type of wavefunction for a particle in a periodically repeating environment → consider an electron in a crystal.
- A wavefunction ψ is a Bloch wave if it has the form:

$$\psi(\vec{k}, \vec{r}) = e^{i\vec{k} \cdot \vec{r}} u(\vec{k}, \vec{r})$$

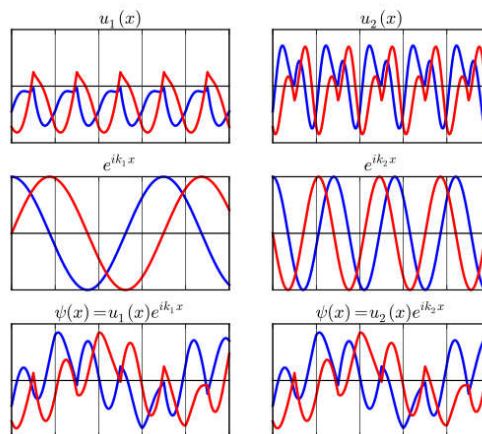
$u(\vec{k}, \vec{r})$: Periodic function with the same periodicity as the crystal

$$u(\vec{k}, \vec{r} + \vec{R}) = u(\vec{k}, \vec{r})$$

A plane wave modulated by a function that has periodicity of the potential.

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Bloch Theorem



A Bloch wave (bottom) can be broken up into the product of a periodic function (top) and a plane-wave (center). Blue is real part, red is imaginary part. The left side and right side represent the same Bloch wave broken up in two different ways, involving the wave vector k_1 (left) or k_2 (right). The difference $(k_1 - k_2)$ is a reciprocal lattice vector.

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