Fundamentals of Solid State Physics

Electronic Properties - The Tight-Binding Model

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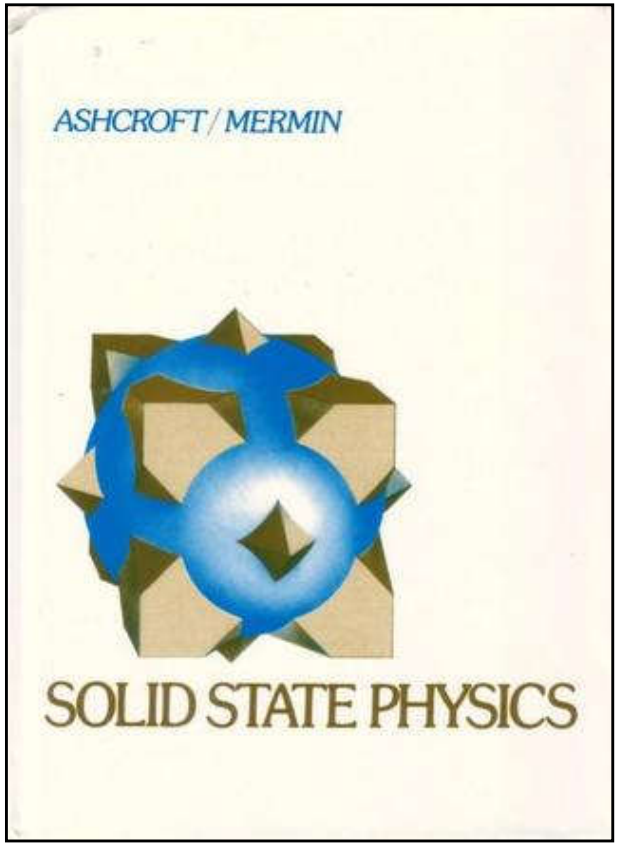
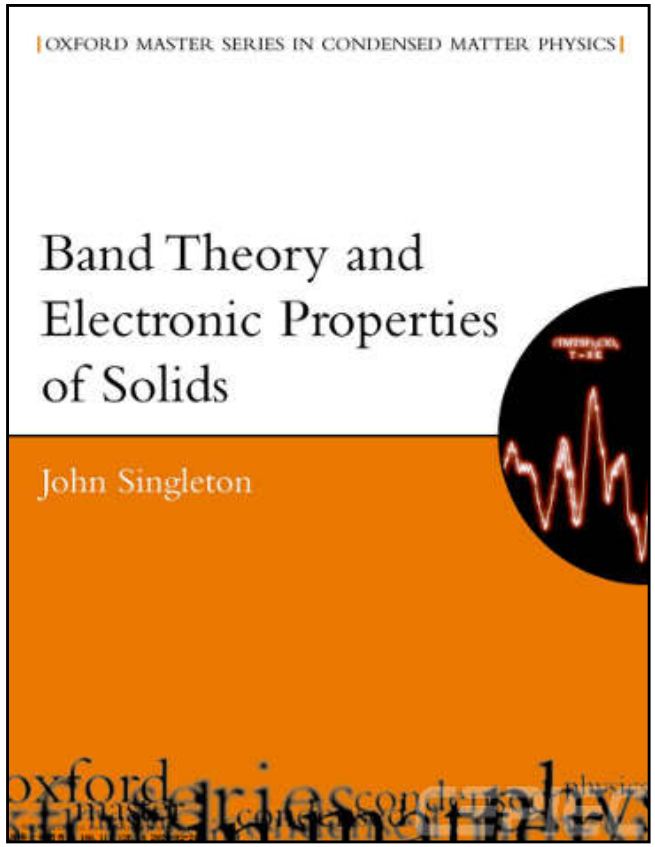
Further Reading

- **Ashcroft & Mermin, Chapter 10**
- **Singleton, Chapter 4**





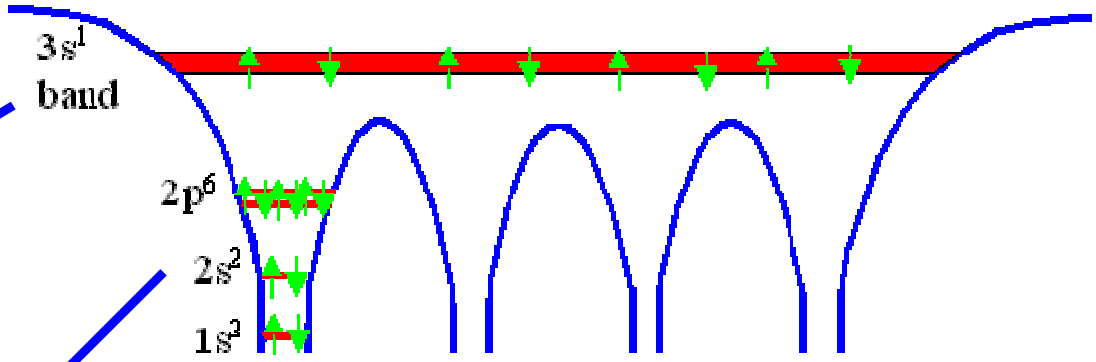
Real Electrons in Solids

Electrons are in *periodic* potentials

→ **Bloch Wave**

$$\psi(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r})\cdot u_{\mathbf{k}}(\mathbf{r})$$

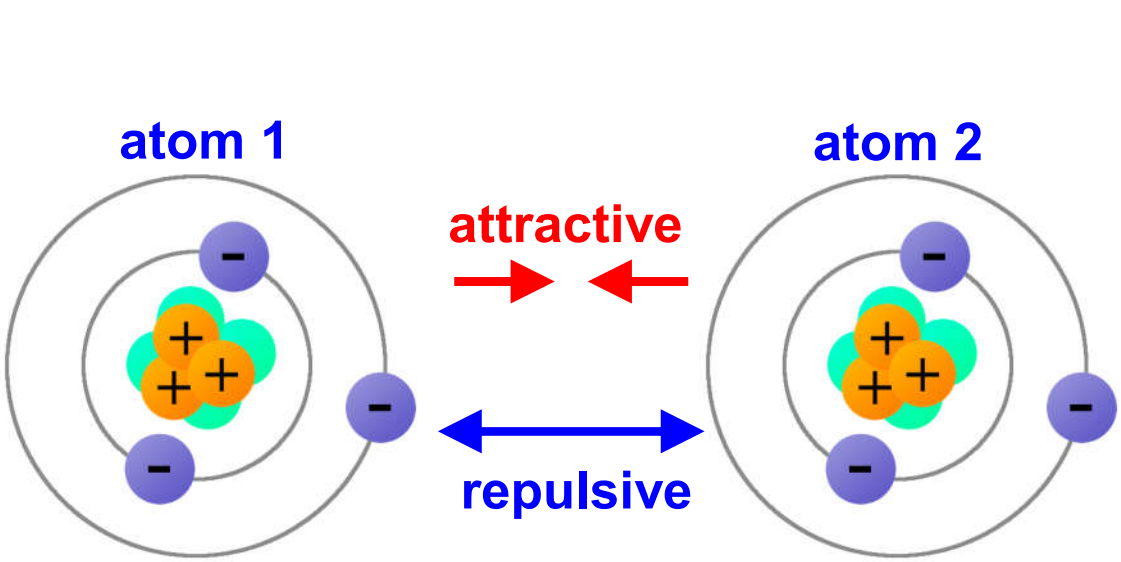
Nearly Free Electron Model
"近自由"近似

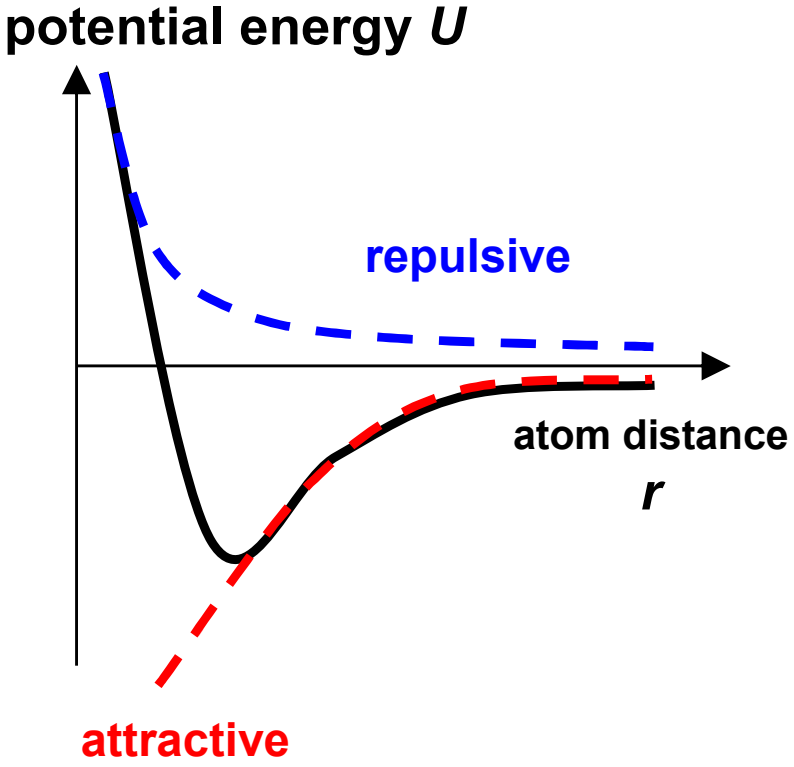


Sodium (Na) [$1s^2$ $2s^2$ $2p^6$] $3s^1$

Tight Binding Model
"紧束缚"近似

Atomic Bonding





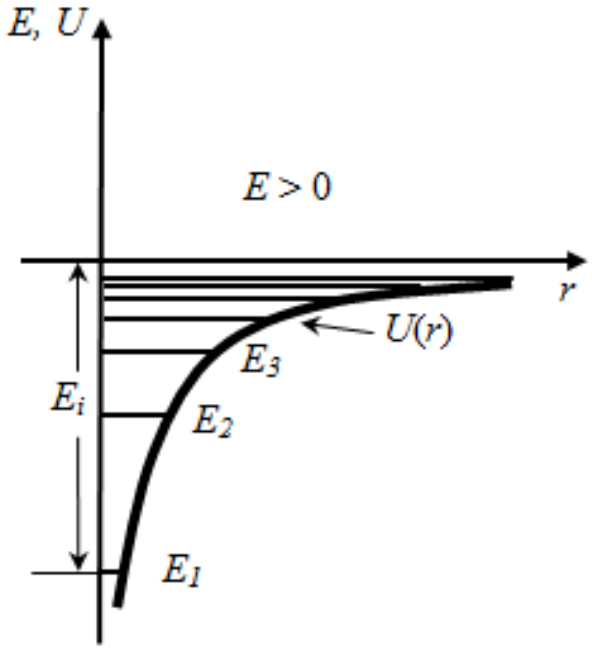
- **Interatomic Potential *U***
  - attraction: electrostatic (+ –)
  - repulsion: electrostatic (+ + /– –)
    and Pauli exclusion principle

What are the quantum mechanic explanations?

Isolated Atoms

- **Hydrogen atom**

$$V(\mathbf{r}) = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{\mathbf{r}}$$



$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\cdot\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

→

$$\psi(r,\theta,\varphi) = R_{nl}(r)\cdot Y_{lm}(\theta,\varphi)$$

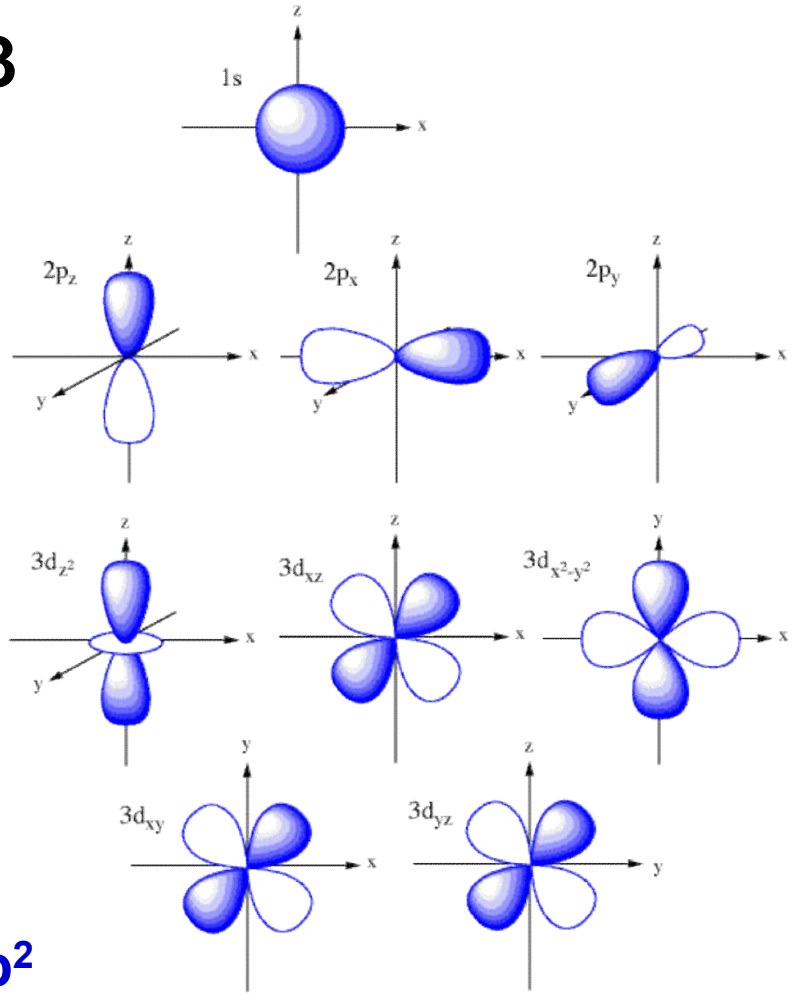
$$E_n = -\frac{13.6\,\text{eV}}{n^2}$$

***n*, *l*, *m* - quantum numbers**

m_S - spin (+1/2, -1/2)

Isolated Atoms

- Angular momentum: $l = 0, 1, 2, 3$
- Atomic orbitals: s p d f



- Examples
  - Hydrogen (H) $1s^1$
  - Helium (He) $1s^2$
  - Lithium (Li) $[1s^2]\ 2s^1$
  - Carbon (C) $[1s^2]\ 2s^2\ 2p^2$
  - Neon (Ne) $[1s^2]\ 2s^2\ 2p^6$
  - Sodium (Na) $[1s^2\ 2s^2\ 2p^6]\ 3s^1$
  - Silicon (Si) $[1s^2\ 2s^2\ 2p^6]\ 3s^2\ 3p^2$

core electrons

valence electrons

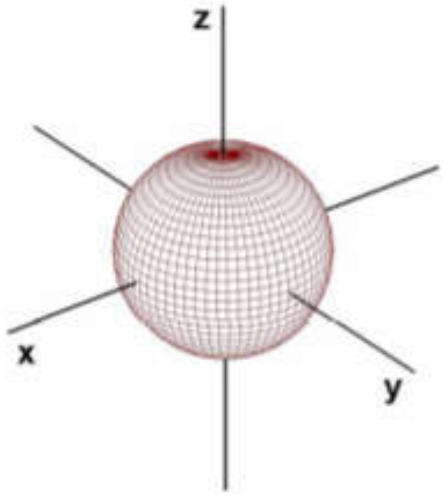
Hydrogen Atom

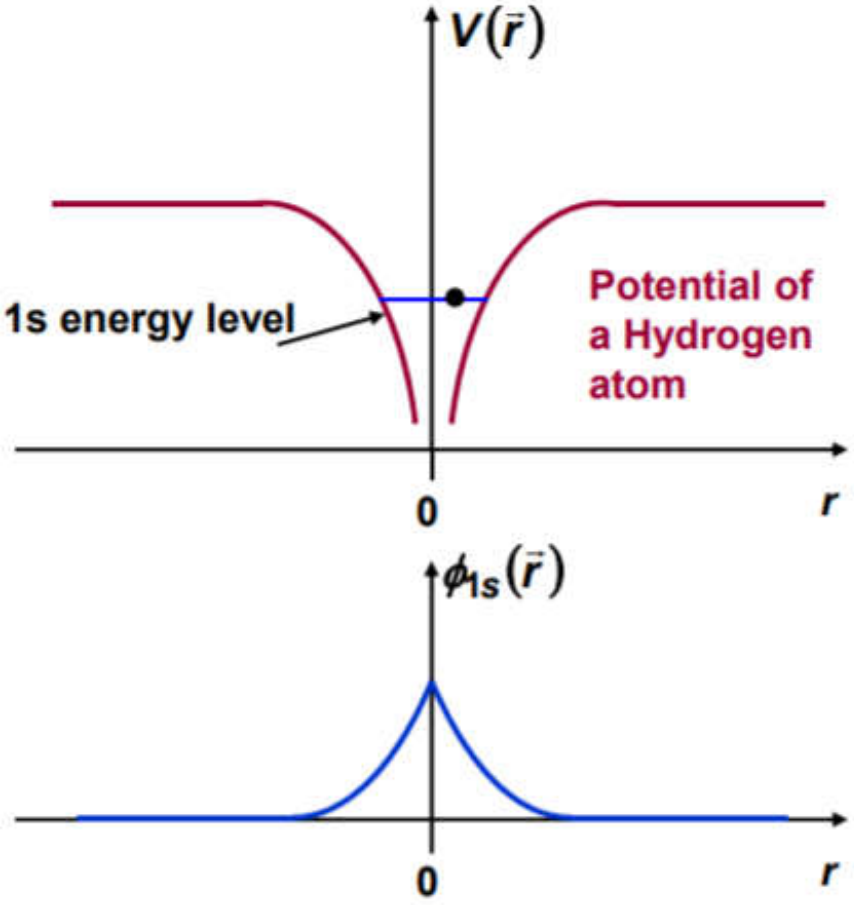
$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r})+V(\mathbf{r})\cdot\psi(\mathbf{r})=E\psi(\mathbf{r})$$

for 1s orbital →

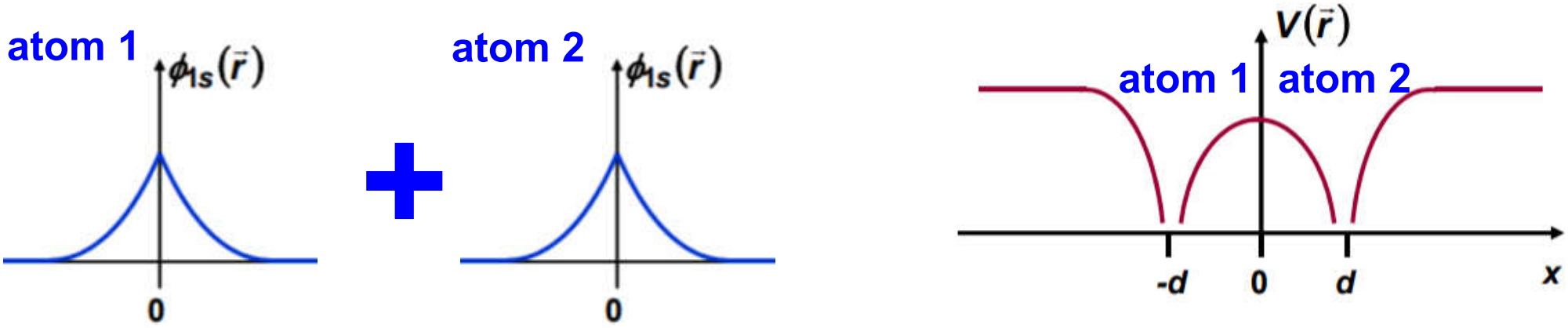
$$\phi_{1s}(\mathbf{r})=\frac{1}{\sqrt{\pi a_0^3}}e^{-r/a_0}$$

$$E_{1s}=-13.6\,\text{eV}$$





Hydrogen Molecule H-H



$$\hat{H}_m \psi(\mathbf{r}) = E\psi(\mathbf{r})$$

$$\hat{H}_m = -\frac{\hbar^2}{2m}\nabla^2 + V_1(\mathbf{r}) + V_2(\mathbf{r})$$

Linear Combination of Atomic Orbitals (LCAO)

$$\psi(\mathbf{r}) = c_1\phi_1(\mathbf{r}) + c_2\phi_2(\mathbf{r})$$

Hydrogen Molecule H-H

Homework 5.5

For ϕ_1 and ϕ_2

$$\hat{H}_0\phi(\mathbf{r}) = E_{1s}\phi(\mathbf{r})$$

$$\hat{H}_0 = -\frac{\hbar^2}{2m}\nabla^2 + V_0(\mathbf{r})$$

Take the integral

$$\int \phi_1^* \hat{H}_m \psi d\mathbf{r} = \int \phi_1^* E \psi d\mathbf{r}$$

$$\rightarrow \quad c_1\int \phi_1^* \hat{H}_m \phi_1 d\mathbf{r} + c_2\int \phi_1^* \hat{H}_m \phi_2 d\mathbf{r} = c_1 E\int \phi_1^* \phi_1 d\mathbf{r} + c_2 E\int \phi_1^* \phi_2 d\mathbf{r}$$

Hydrogen Molecule H-H

Homework 5.5

$$c_1\int \phi_1^* \hat{H}_m \phi_1 d\mathbf{r} + c_2 \int \phi_1^* \hat{H}_m \phi_2 d\mathbf{r} = c_1 E \int \phi_1^* \phi_1 d\mathbf{r} + c_2 E \int \phi_1^* \phi_2 d\mathbf{r}$$

We have

$$\int \phi_1^* \phi_1 d\mathbf{r} = 1$$

$$\int \phi_1^* \phi_2 d\mathbf{r} = 0$$

$$\int \phi_1^* \hat{H}_m \phi_1 d\mathbf{r} \approx \int \phi_1^* \hat{H}_0 \phi_1 d\mathbf{r} = \int \phi_1^* E_{1s} \phi_1 d\mathbf{r} = E_{1s} \int \phi_1^* \phi_1 d\mathbf{r} = E_{1s}$$

$$\int \phi_1^* \hat{H}_m \phi_2 d\mathbf{r} \approx -V_{ss\sigma} < 0$$

Hydrogen Molecule H-H

Homework 5.5

We have

$$c_1 E_{1s} - c_2 V_{ss\sigma} = c_1 E$$

Similarly

$$-c_1 V_{ss\sigma} + c_2 E_{1s} = c_2 E$$

→

$$\begin{pmatrix} E_{1s} - E & -V_{ss\sigma} \\ -V_{ss\sigma} & E_{1s} - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

→

$$\det \begin{pmatrix} E_{1s} - E & -V_{ss\sigma} \\ -V_{ss\sigma} & E_{1s} - E \end{pmatrix} = 0$$

Hydrogen Molecule H-H

Homework 5.5

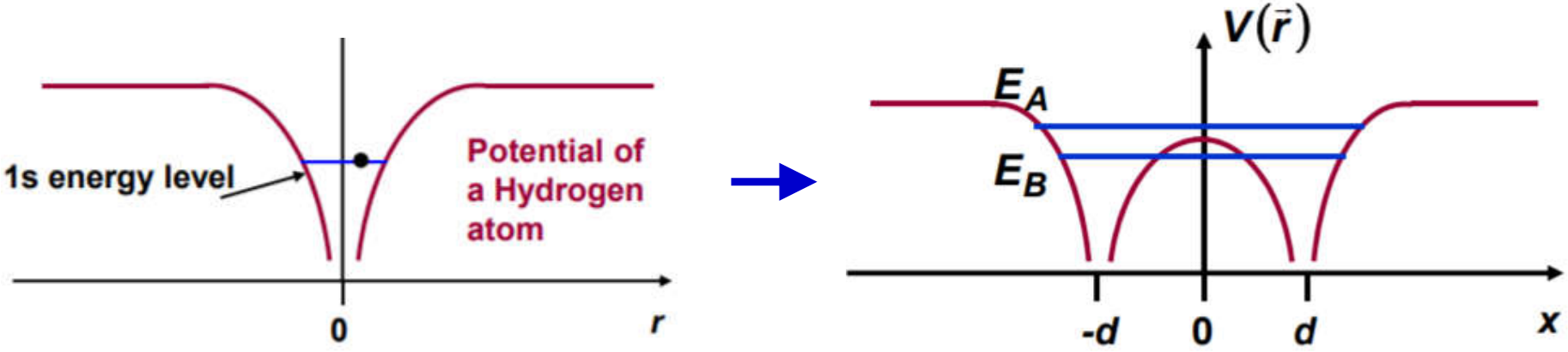
We have two solutions:

bonding molecular orbital (MO)

$$E_B = E_{1s} - V_{ss\sigma}$$

anti-bonding molecular orbital (MO)

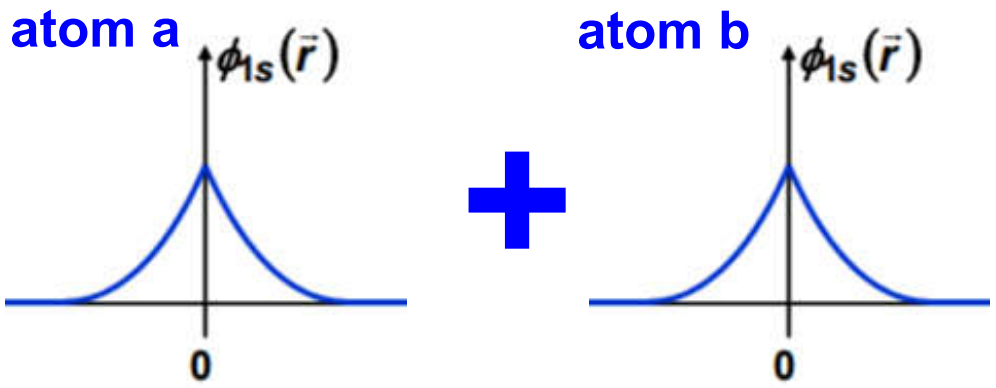
$$E_A = E_{1s} + V_{ss\sigma}$$

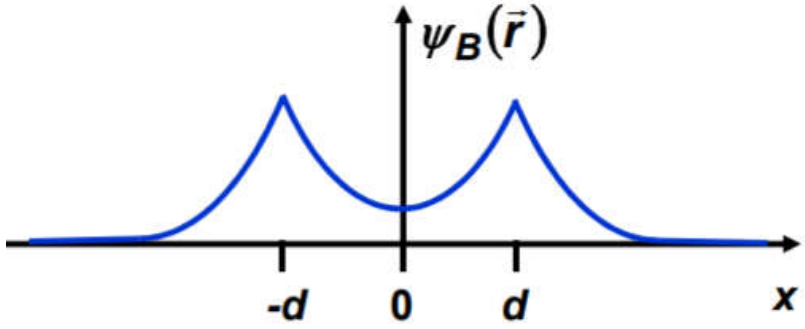


Pauli exclusion principle:

Two electrons cannot be in the same energy state

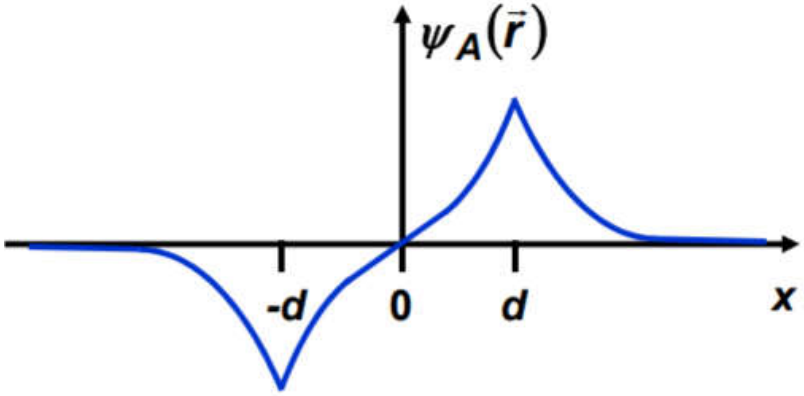
Hydrogen Molecule H-H





$$\psi_B(\mathbf{r}) \sim [\phi_1(\mathbf{r}) + \phi_2(\mathbf{r})]$$

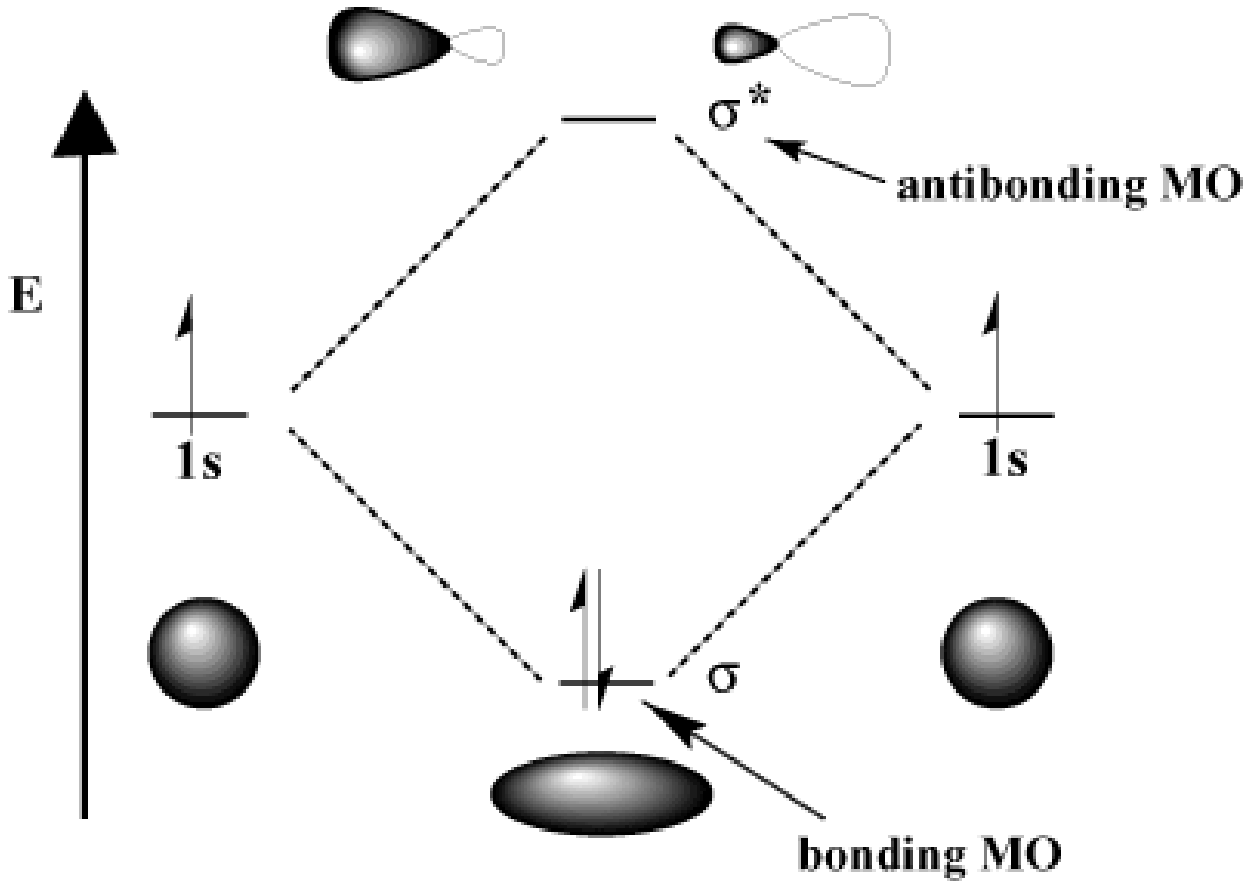
bonding orbital



$$\psi_A(\mathbf{r}) \sim [\phi_1(\mathbf{r}) - \phi_2(\mathbf{r})]$$

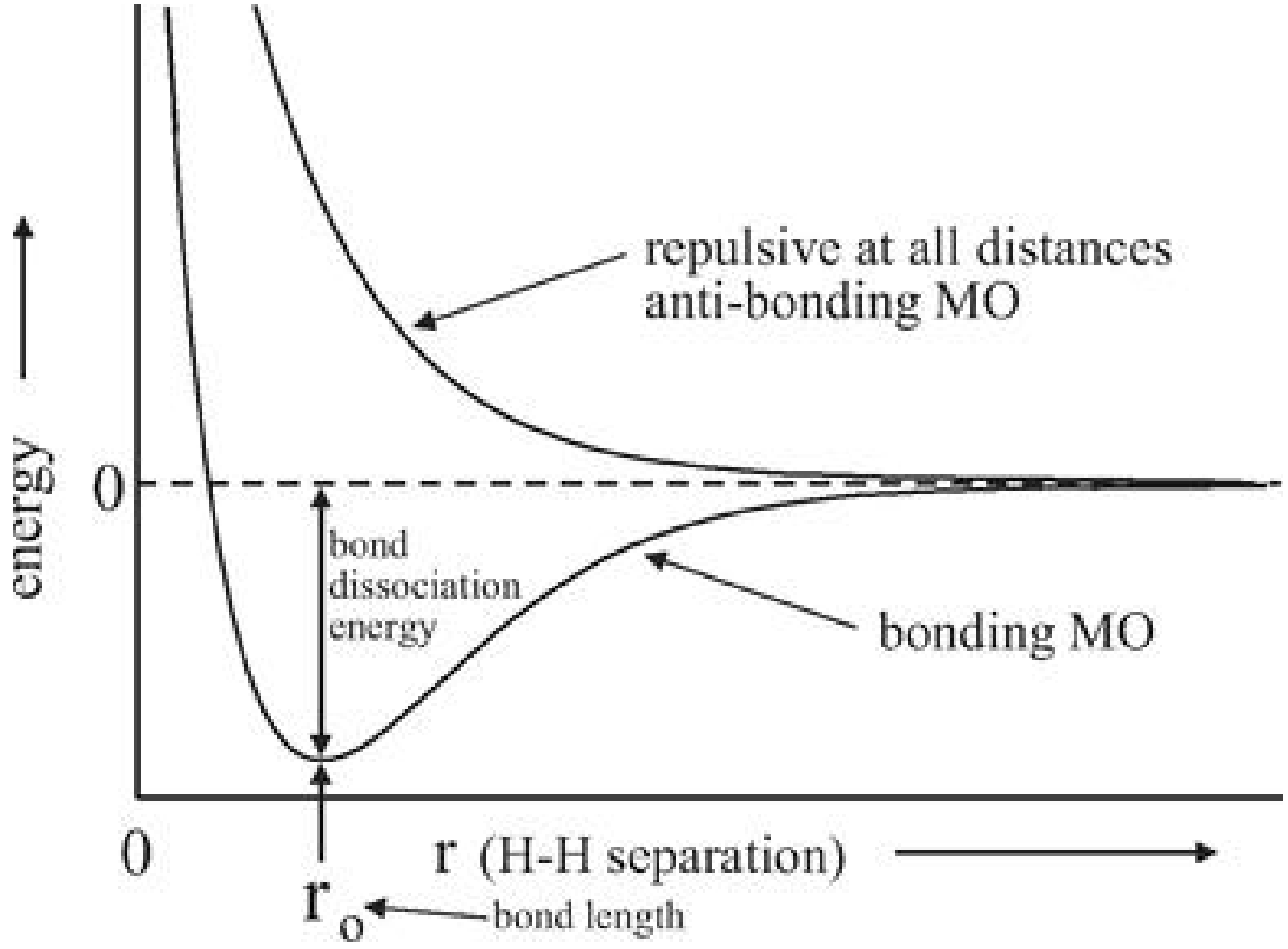
anti-bonding orbital

Hydrogen Molecule H-H



The two 1s orbitals on each Hydrogen atom combine to generate *two* molecular orbitals (MO):
the bonding MO and the anti-bonding MO,
with energy splitting

Hydrogen Molecule H-H



bonding energy vs. atom separation

A General Molecule A-B

Example: H-F, C-O, ...

Linear Combination of Atomic Orbitals (LCAO)

$$\psi(\mathbf{r}) = c_1\phi_1(\mathbf{r}) + c_2\phi_2(\mathbf{r})$$

For an electron, probabilities in A and B are different

$$P_A = \frac{c_1^2}{c_1^2 + c_2^2}$$

$$P_B = \frac{c_2^2}{c_1^2 + c_2^2}$$

A General Molecule A-B

Polarity (极性) f

$$f = \left| \frac{P_A - P_B}{P_A + P_B} \right| = \left| \frac{c_1^2 - c_2^2}{c_1^2 + c_2^2} \right|$$

For H-H, C-C, ...

$$|c_1| = |c_2| \longrightarrow f = 0$$

nonpolar bonding
covalent (共价键)

For H-F, C-H, Na-Cl, ...

$$|c_1| \neq |c_2| \longrightarrow 0 < f < 1$$

polar bonding
covalent or ionic (离子键)

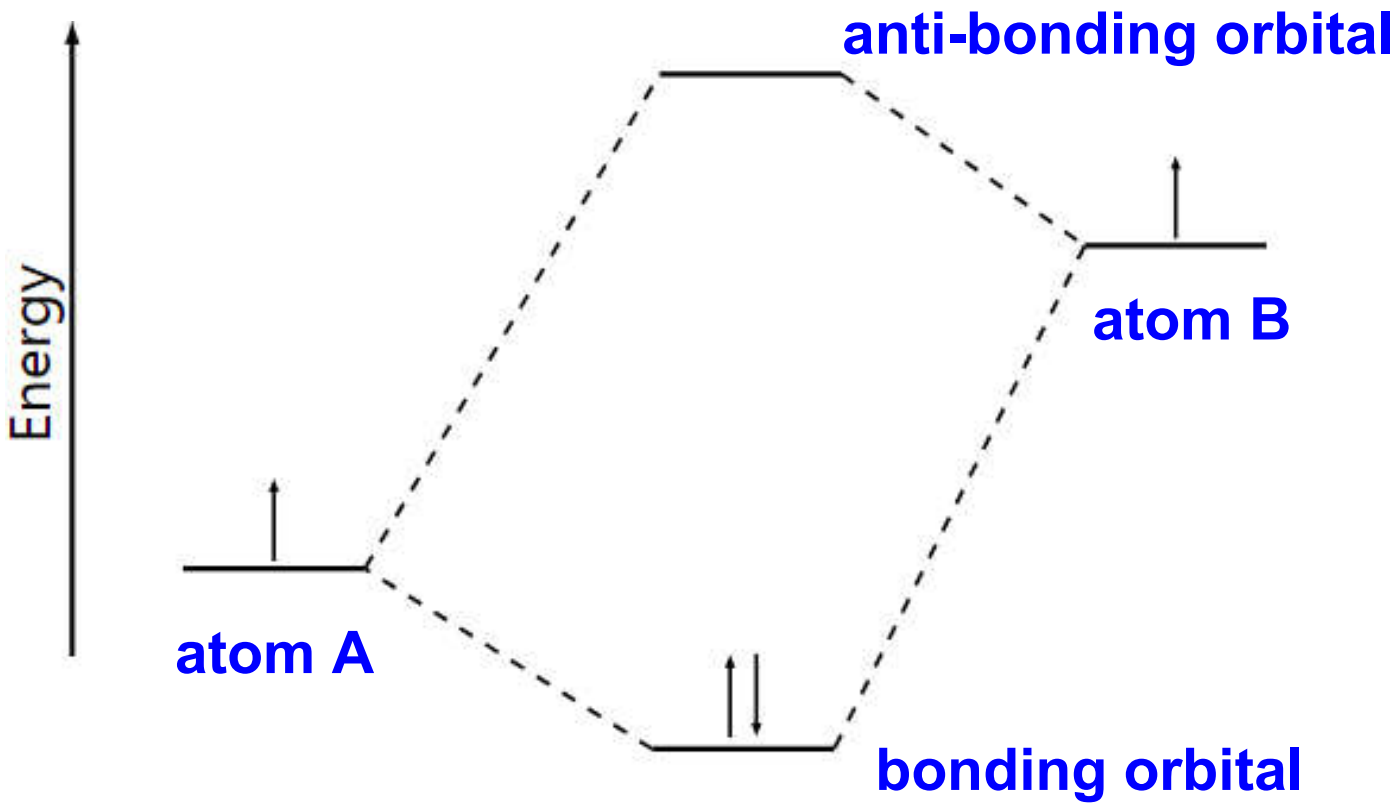
A General Molecule A-B

Polarity (极性) f

$$f = \left| \frac{P_A - P_B}{P_A + P_B} \right| = \left| \frac{c_1^2 - c_2^2}{c_1^2 + c_2^2} \right|$$

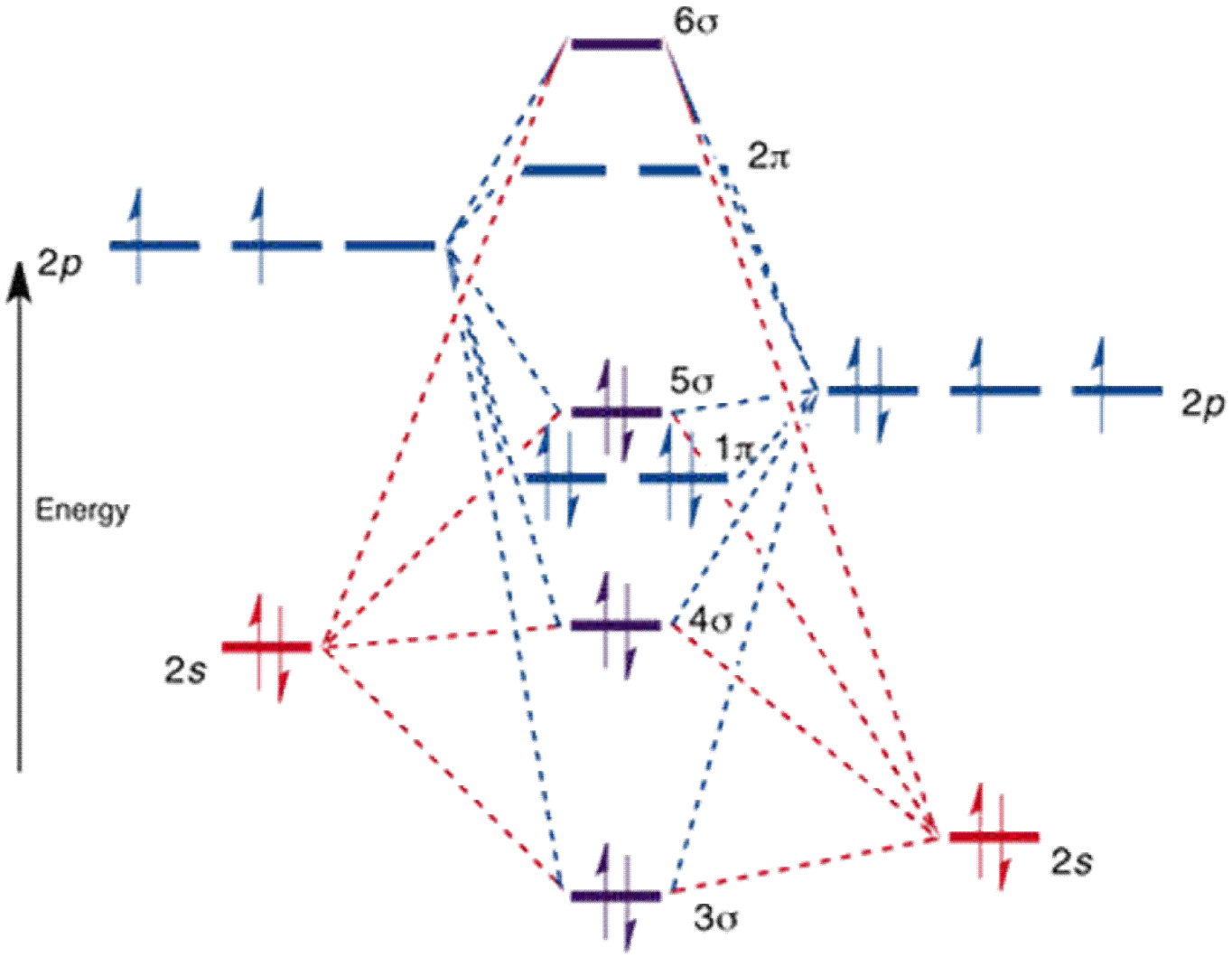
	C	Si	SiC	GaAs	ZnO	NaCl
polarity f	0	0	0.177	0.310	0.616	0.8

A General Molecule A-B



Example: H-F, ...

Another Example: C-O bonding

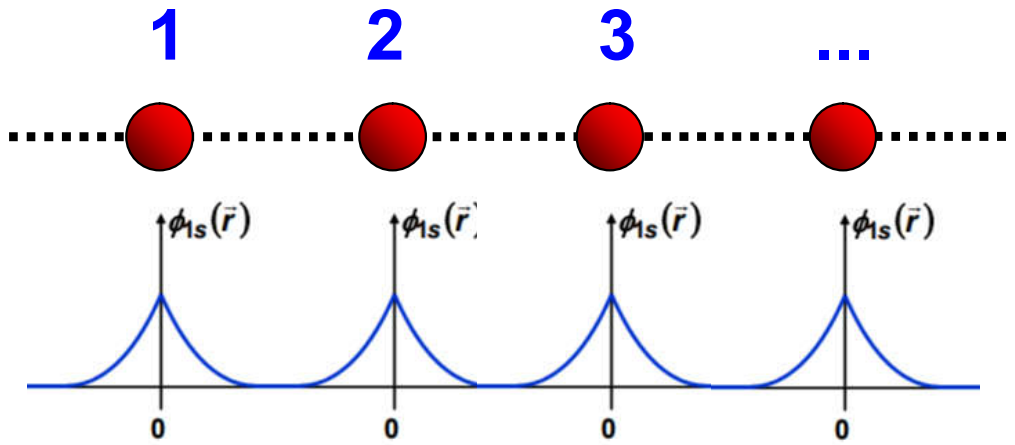


Chemical Bonding 化学键

- Metallic Bonding 金属键
- Ionic Bonding 离子键
- Covalent Bonding 共价键
- Van der Waals Bonding 范德华键
- Hydrogen Bonding 氢键
- ...

Chemical bonding originates from the electron wave functions distributed in multiple atoms

1D Chain of Atoms



Linear Combination of Atomic Orbitals (LCAO)

$$\psi(\mathbf{r}) = \sum_n c_n \phi_n(\mathbf{r})$$

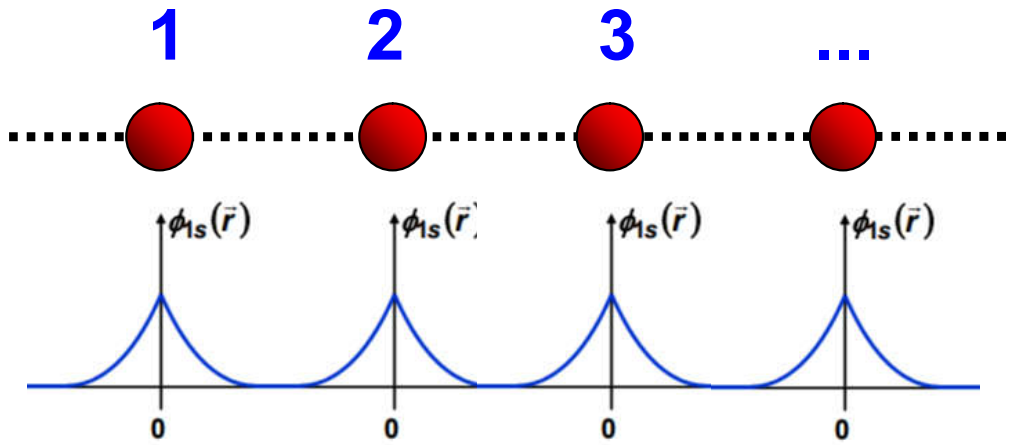
use Bloch's Theorem

$$\rightarrow \quad E(k) = E_{1s} - B - 2t\cos(ka)$$

$$k = \frac{2\pi}{a}\frac{n}{N} \qquad n = 0, \pm 1, \pm 2, \ldots$$

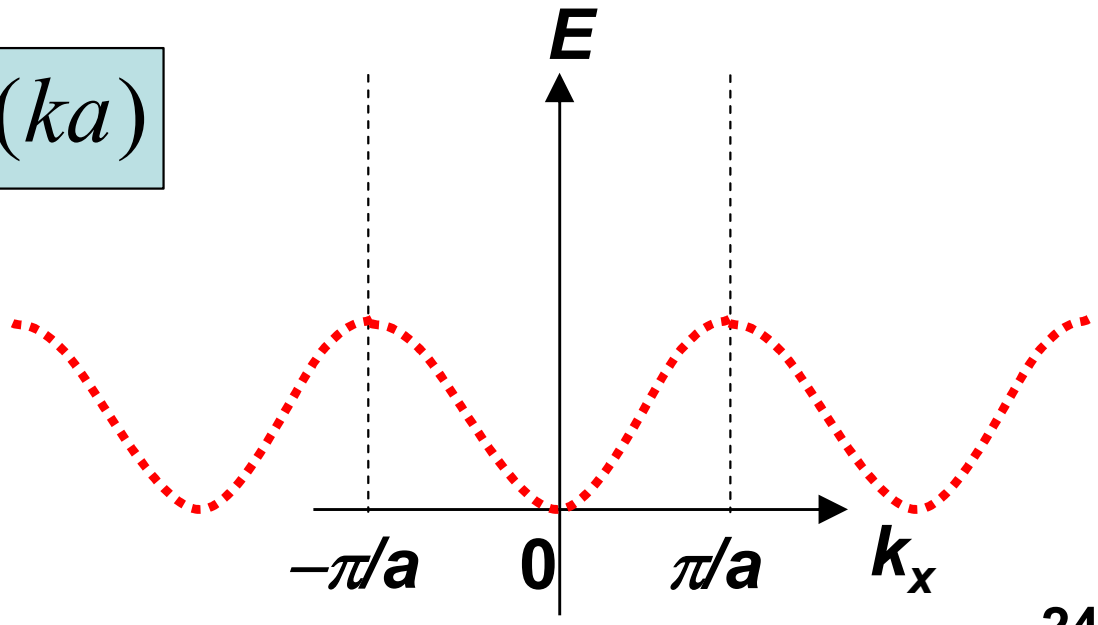
Homework 5.6

1D Chain of Atoms



$$E(k) = E_{1s} - B - 2t\cos(ka)$$

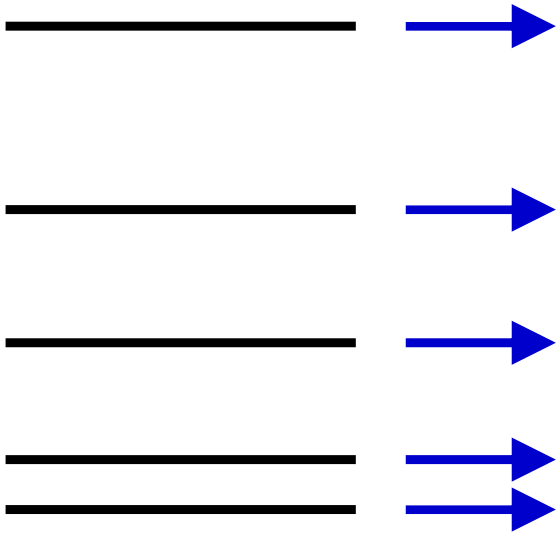
1s orbital ⟶

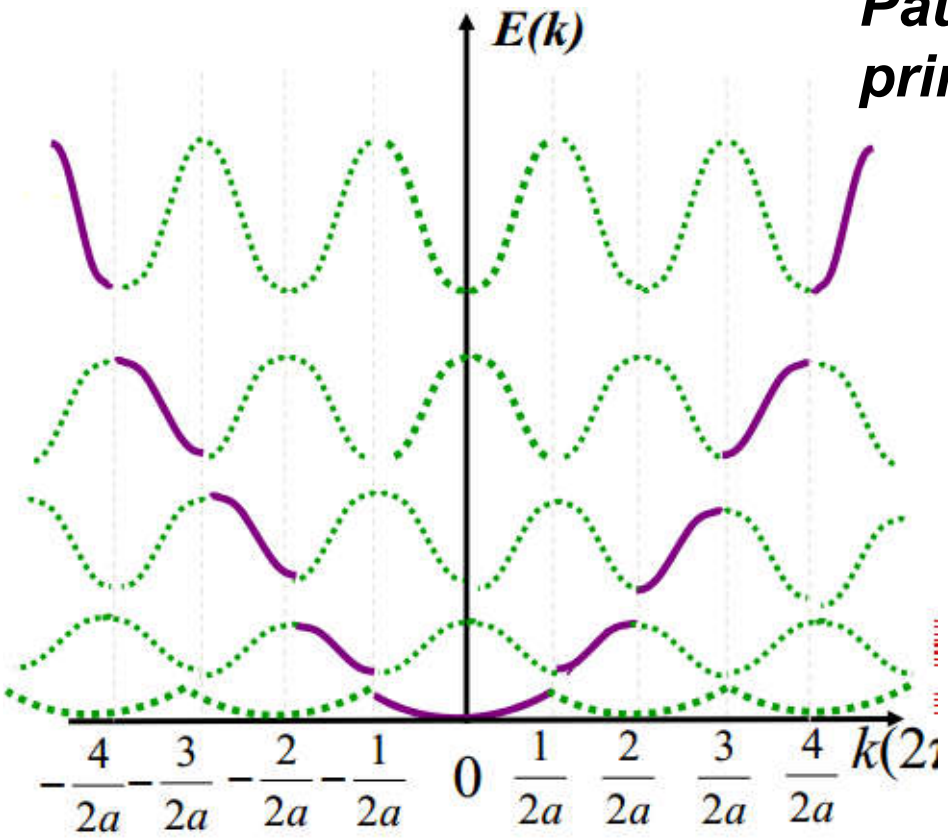


Pauli exclusion principle

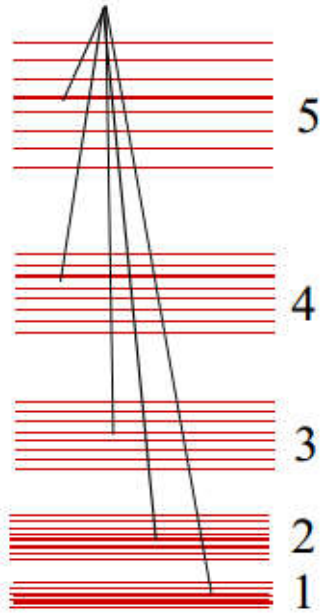
1D Chain of Atoms

orbitals





Pauli exclusion principle



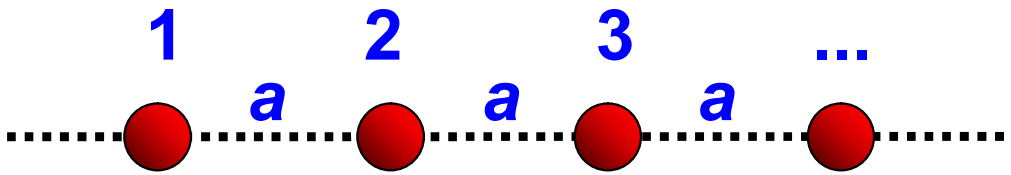
$$E(k) = E_{1s} - B - 2t\cos(ka)$$

$$k = \frac{2\pi}{a}\frac{n}{N}$$

$$n = 0, \pm 1, \pm 2, \ldots$$

discrete orbitals become quasi-continuous bands

1D Chain of Atoms



$$E(k) = E_{1s} - B - 2t\cos(ka)$$

when ka is large

$$E(k) = \text{constant}$$ → discrete orbitals

when ka is small

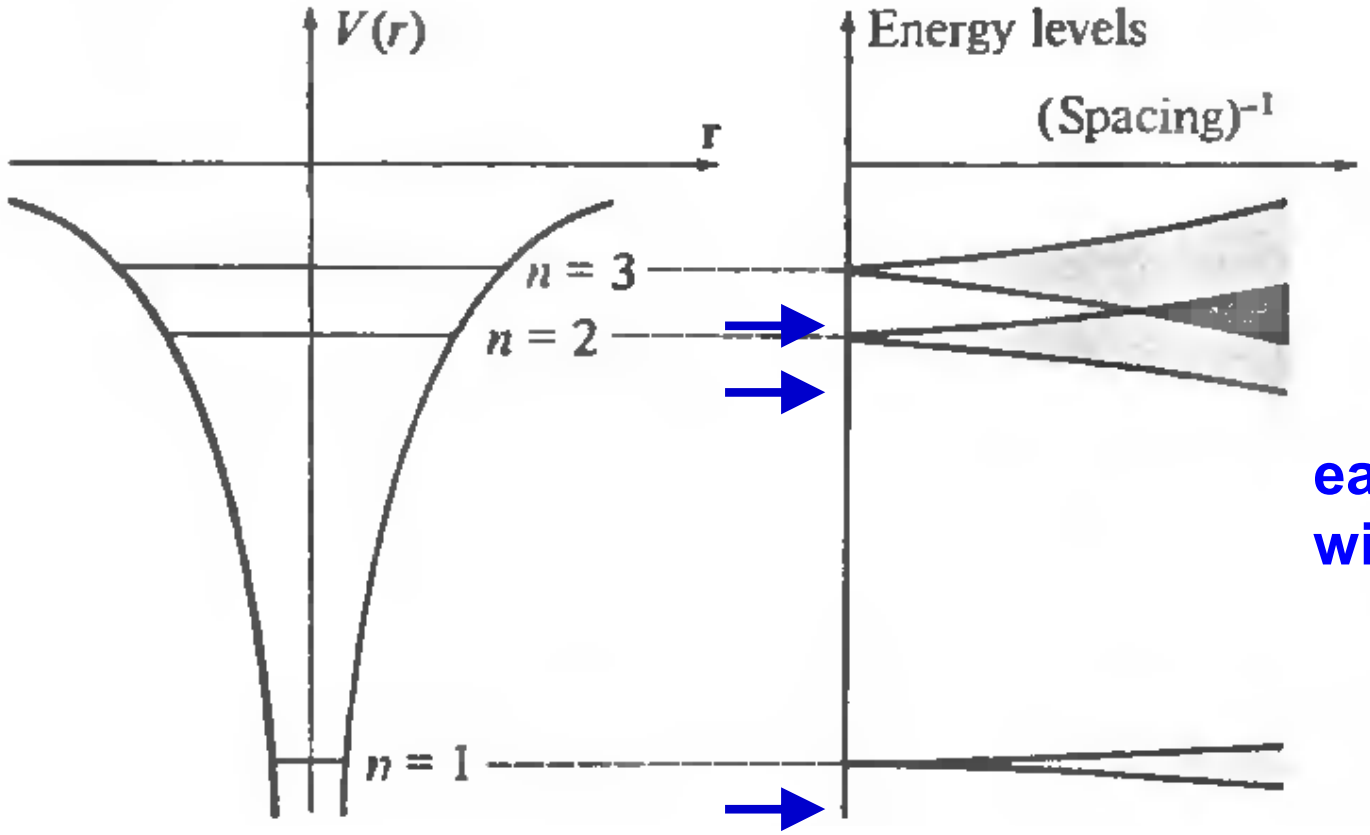
$$E(k) \approx E_{1s} - B - 2t + ta^2k^2 \propto k^2$$

→ nearly free electrons

1D Chain of Atoms

1s orbital → $2N$ states

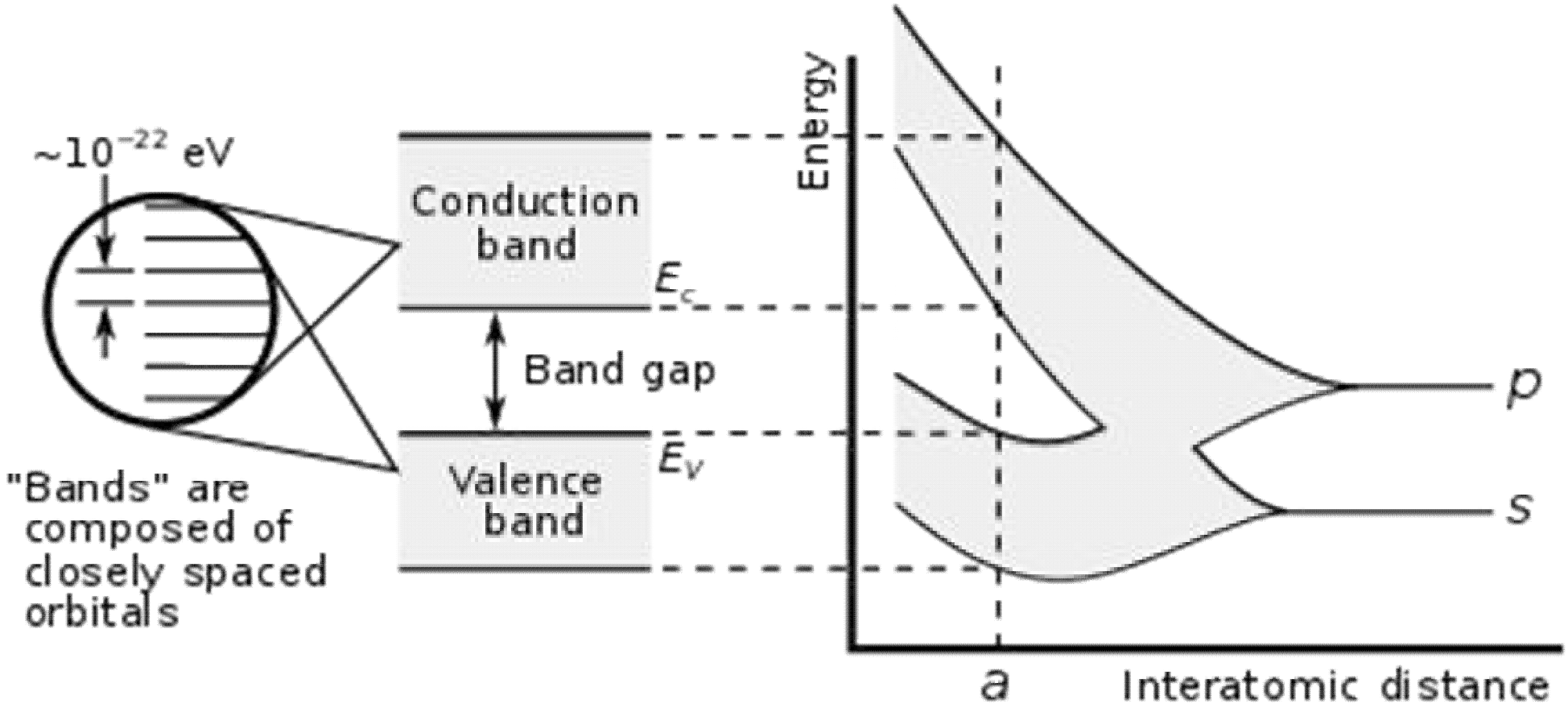
Pauli exclusion principle



each band with $2N$ states

There are N k-states, the factor of 2 is from the spin up and spin down

Formation of bands and gaps



Thank you for your attention