# Lecture 10: Quantum mechanics and molecular structure-1

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**Classroom: Teaching Center 401**

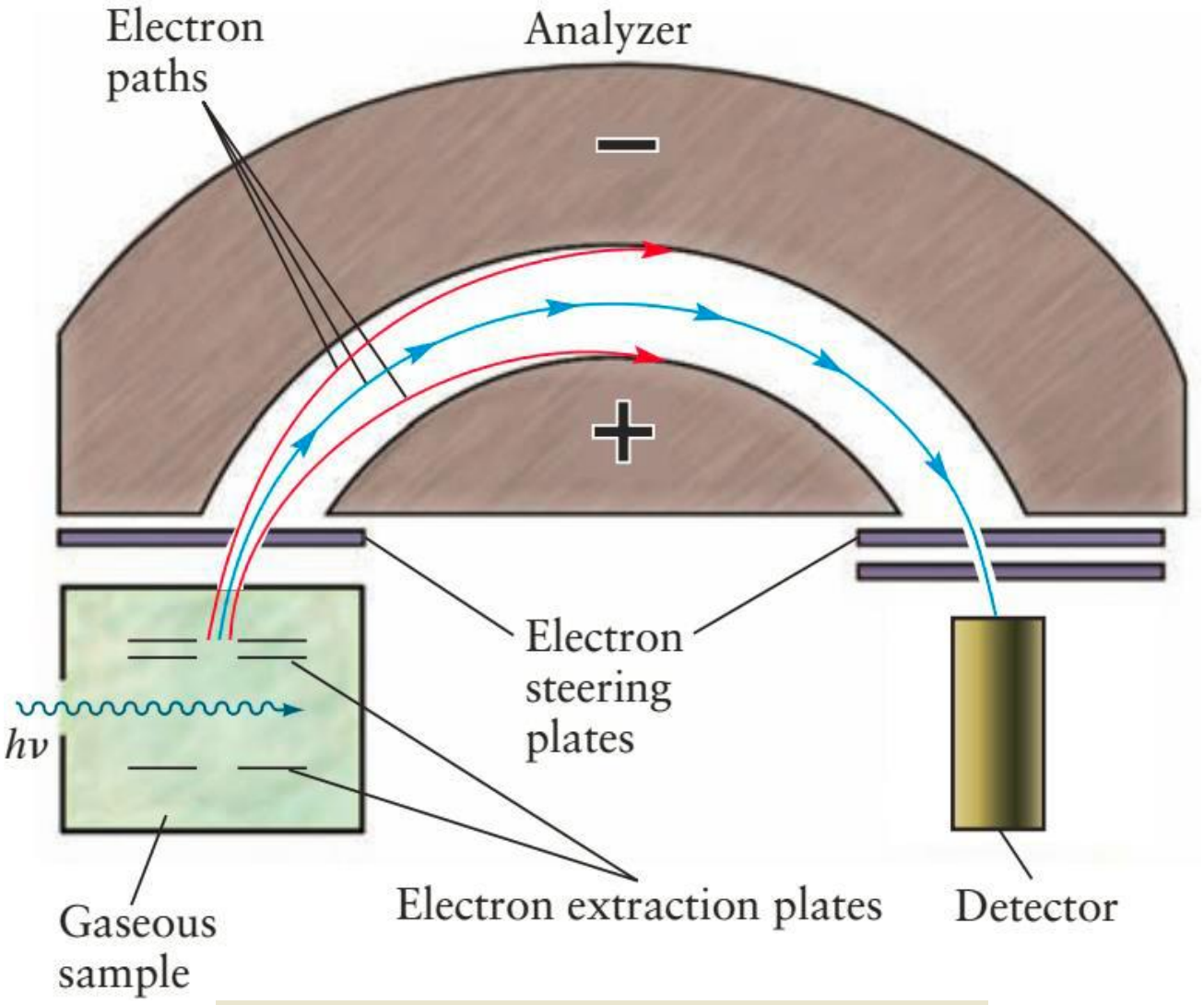
**Wednesday/Friday: 10:15-11:00; 11:10-11:55**

**2025/11/12**

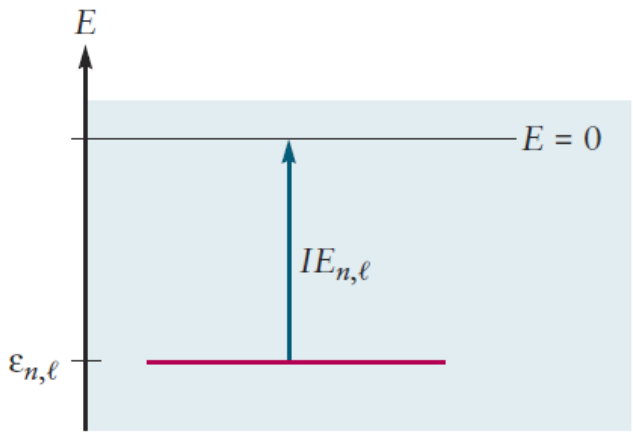
# Major points of last lecture

- **Quantum mechanics and atomic structure**
  1. **The hydrogen atom**
  2. **Shell model for many-electron atoms**
  3. **Aufbau principle and electron configuration**
  4. **Shells and the periodic table: photoelectron spectroscopy**
  5. **Periodic properties and electronic structure**

# Photoelectron Spectroscopy (PES)




$$IE = h\nu_{\text{photon}} - \frac{1}{2}\, m_e v^2_{\text{electron}}$$

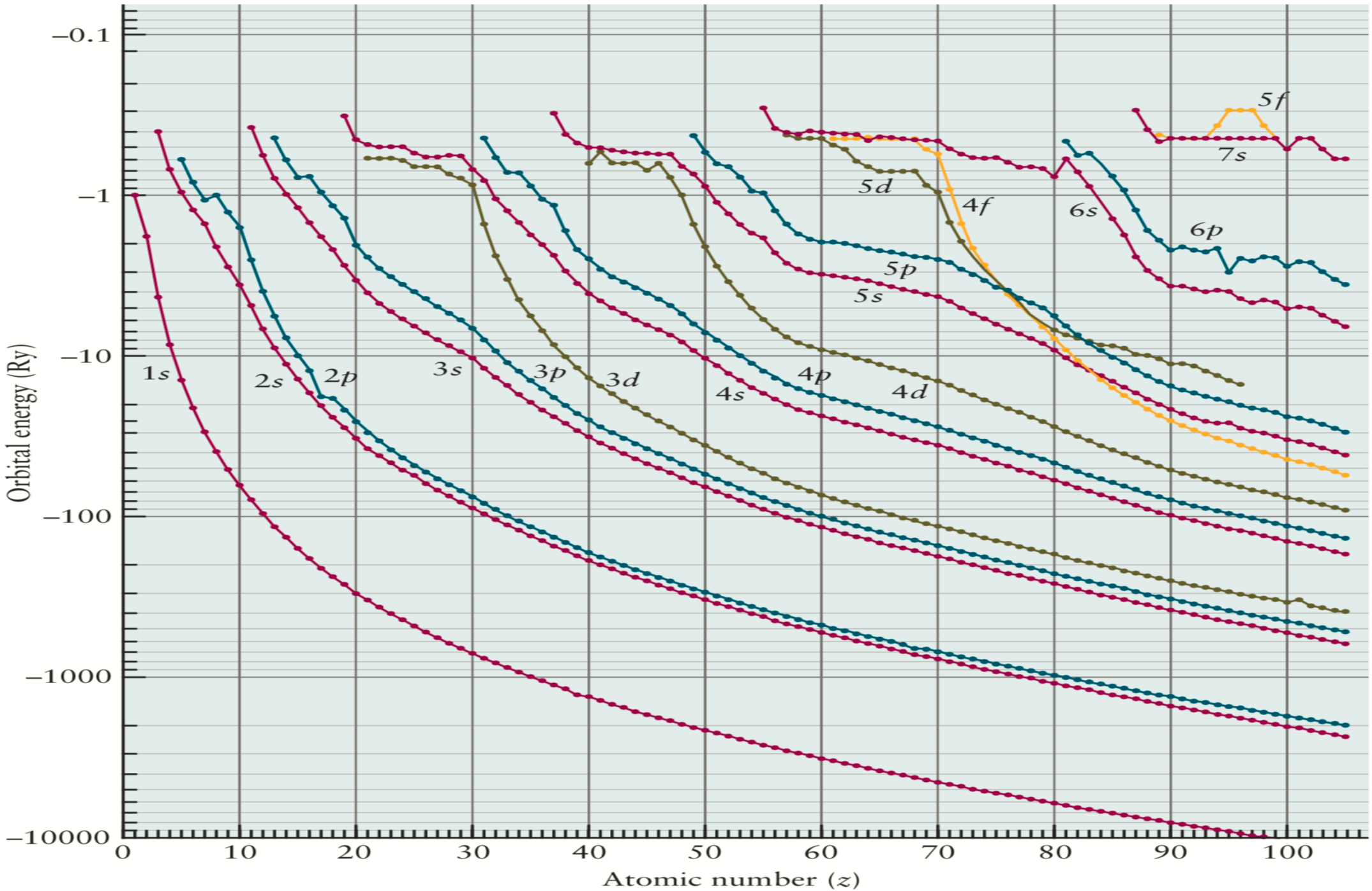


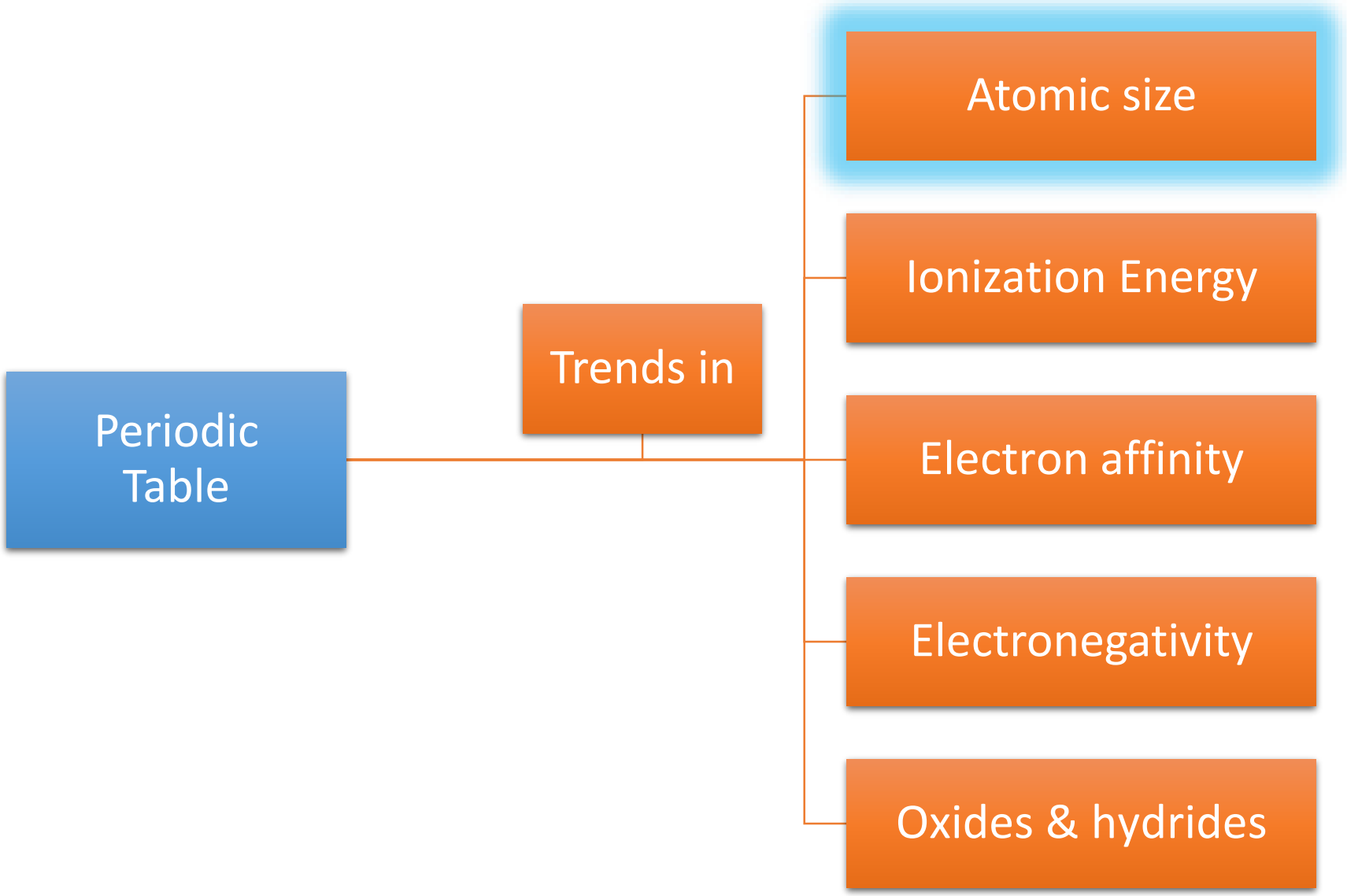

The ionization energy $IE_{n,\ell}$ is the energy required to remove an electron from this atomic state and set it free from the atom.

$$IE_\alpha = -\varepsilon_\alpha$$

**Koopmans's（科普曼斯）approximation: the ionization energy of an electron is the negative of the energy of the Hartree orbital of the electron.**

**It is not strictly valid because it assumes the orbital energies are the same in the ion as in the parent atom, despite the loss of an electron.**

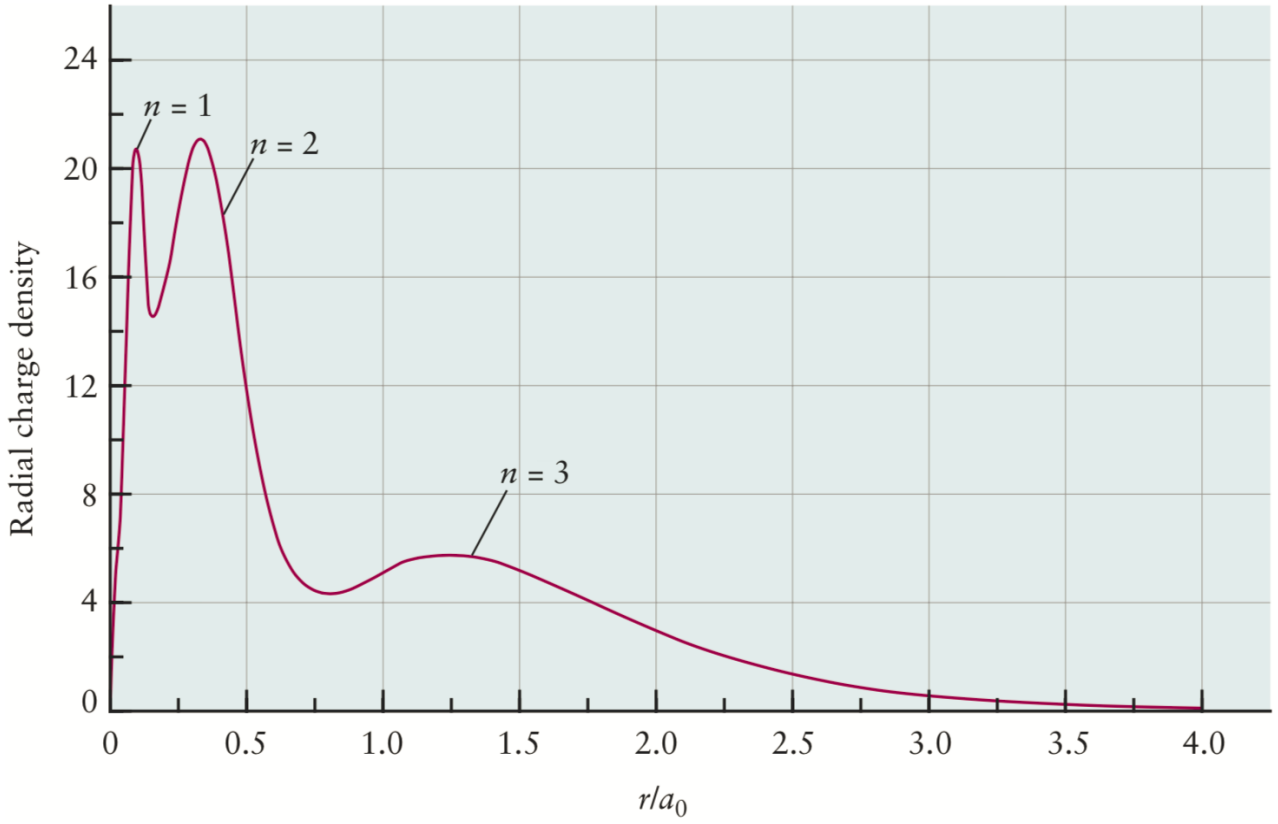

Orbital energy (Ry)
−0.1
−1
−10
−100
−1000
−10000
0
10
20
30
40
50
60
70
80
90
100
Atomic number (z)
1s
2s
2p
3s
3p
3d
4s
4p
4d
4f
5s
5p
5d
5f
6s
6p
7s


Periodic Table
Trends in
Atomic size
Ionization Energy
Electron affinity
Electronegativity
Oxides & hydrides

# Sizes of atoms and ions

**Atomic Radius (原子半径): not a precisely defined concept, these sizes can be estimated in several ways**

**根据不同的标度和测量方法，原子半径的定义不同：范德华半径，共价半径，金属半径等。同一原子依不同定义得到的原子半径差别可能很大。**




**原子半径：主要受电子层数和核电荷数两个因素影响。一般来说，电子层数越多，核电荷数越小，原子半径越大**

# Radii of Atoms with Same n

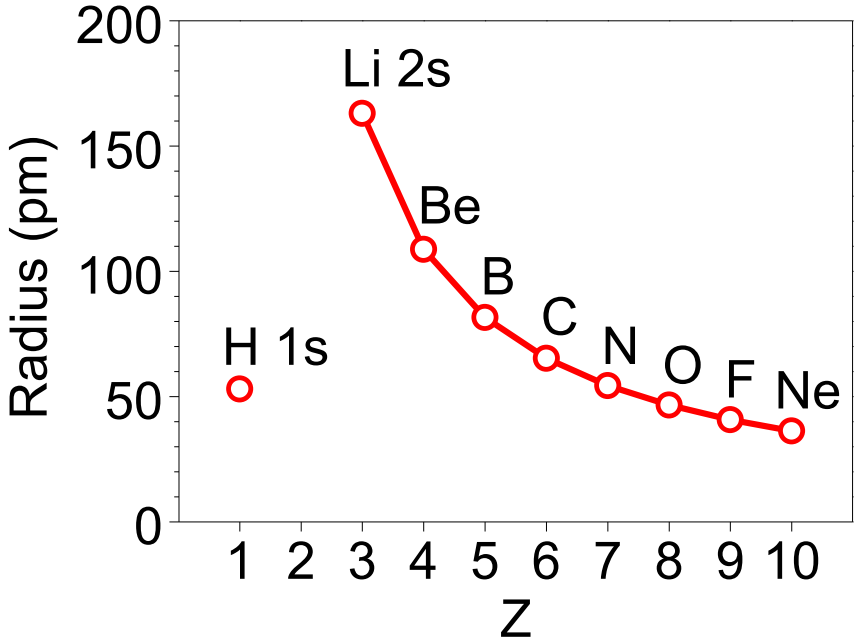
| Atom | $Z$ | $Z_{eff}(2s)$ | Valence shell |
|---|---|---|---|
| Li | 3 | ~1.30 | $2s^1$ |
| Be | 4 | ~1.95 | $2s^2$ |
| B | 5 | ~2.60 | $2s^2 2p^1$ |
| C | 6 | ~3.25 | $2s^2 2p^2$ |

For *s* and *p* subshells,

$\Delta Z_{eff}(ns) \approx 0.65\ \Delta Z$

For 2*s* and 2*p*,

$Z_{eff} \approx 0.65(Z - 1)$



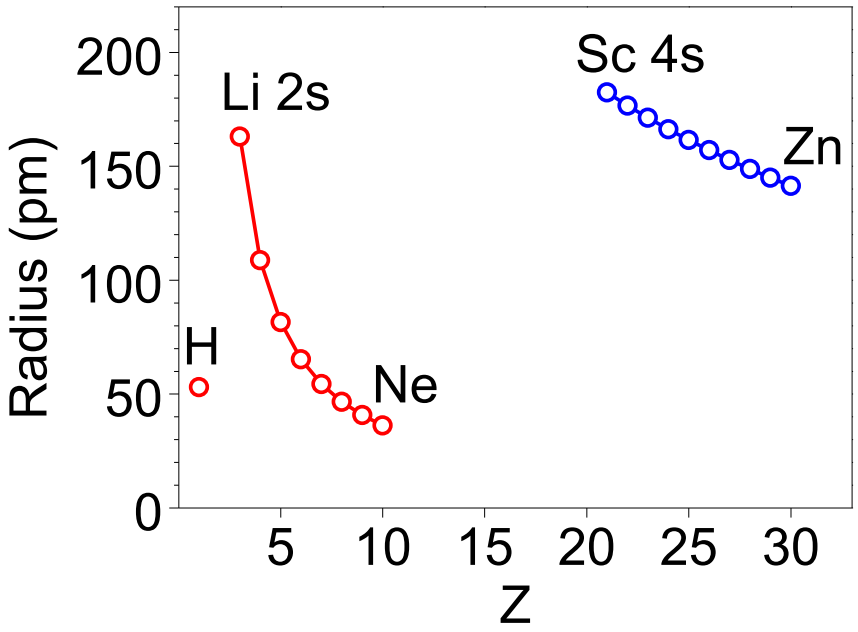
John C. Slater
(MIT, 1900–1976)

# Radii of Atoms with Same n

| Atom | $Z$ | $Z_{eff}(4s)$ | Valence shell |
|---|---|---|---|
| Mn | 25 | 5.28 | $3d^5 4s^2$ |
| Fe | 26 | 5.43 | $3d^6 4s^2$ |
| Co | 27 | 5.58 | $3d^7 4s^2$ |
| Ni | 28 | 5.71 | $3d^8 4s^2$ |

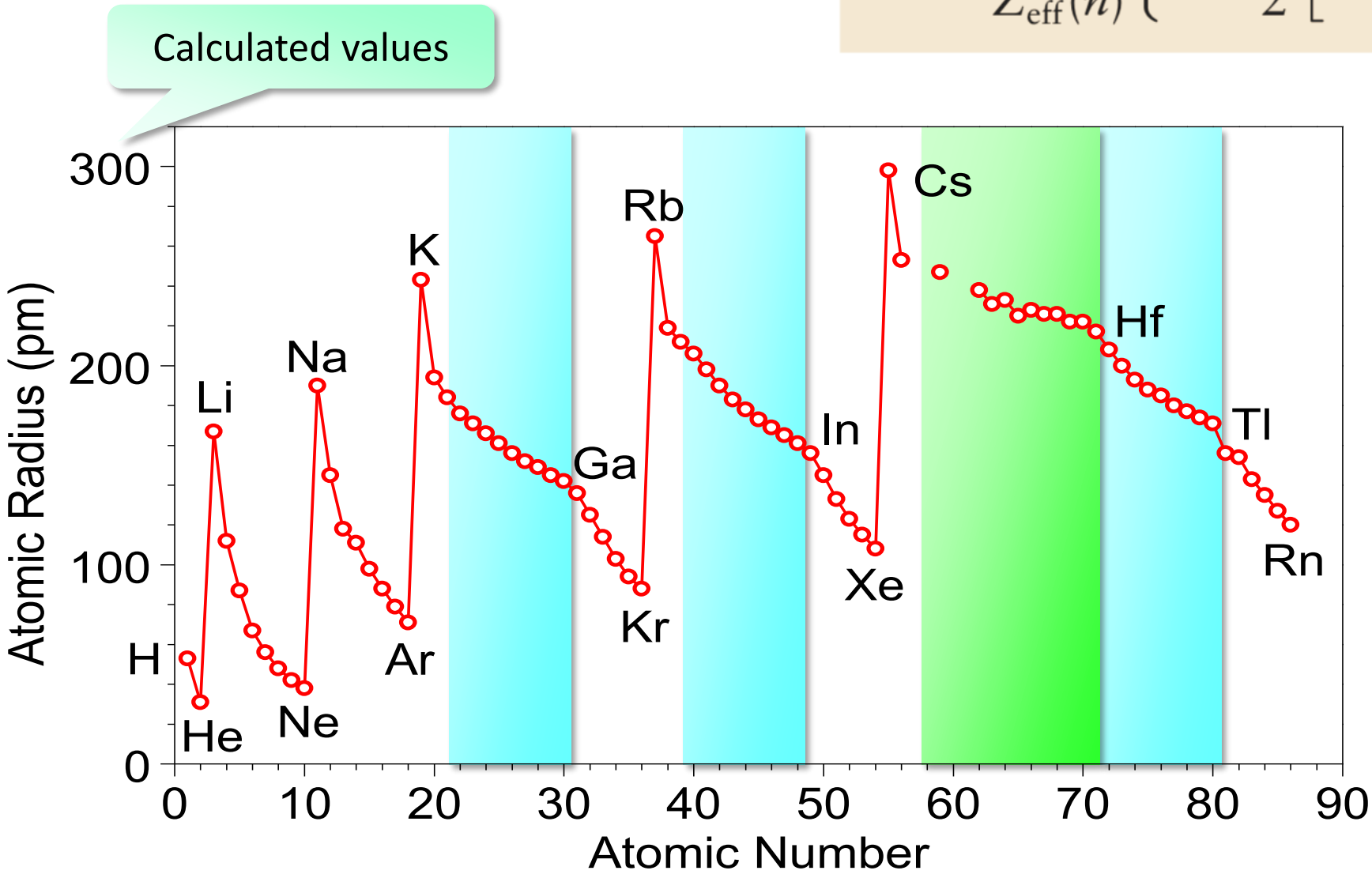
Slater's Rules
(1930)
OGC7 p.214

For *d* subshells, $\Delta Z_{eff}(ns) \approx 0.15\ \Delta Z$;

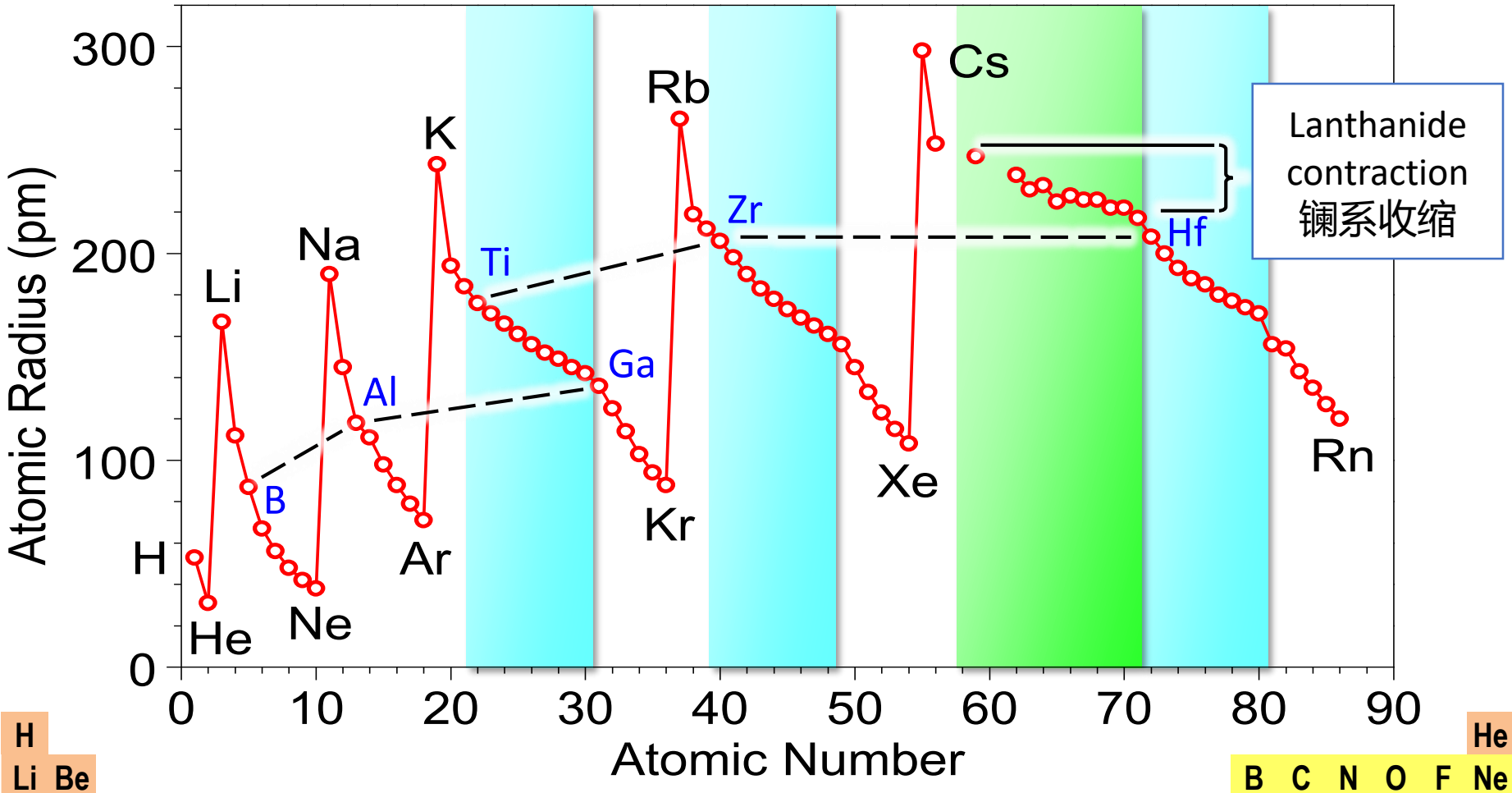


# Trends in Atomic Radii (1)

$$\bar{r}_{n\ell} \approx \frac{n^2 a_0}{Z_{\text{eff}}(n)}\left\{1 + \frac{1}{2}\left[1 - \frac{\ell(\ell+1)}{n^2}\right]\right\}$$

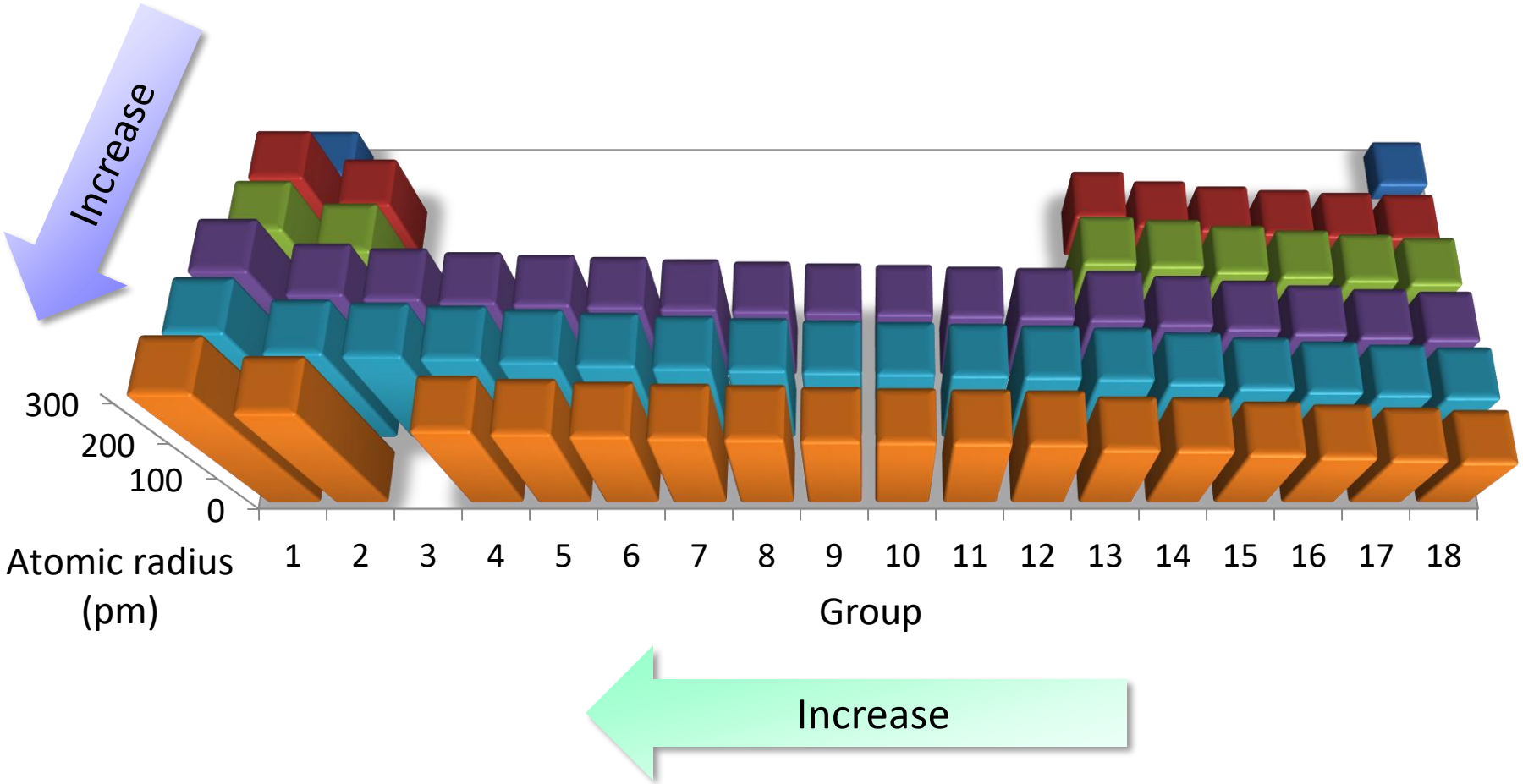


# Trends in Atomic Radii (2)

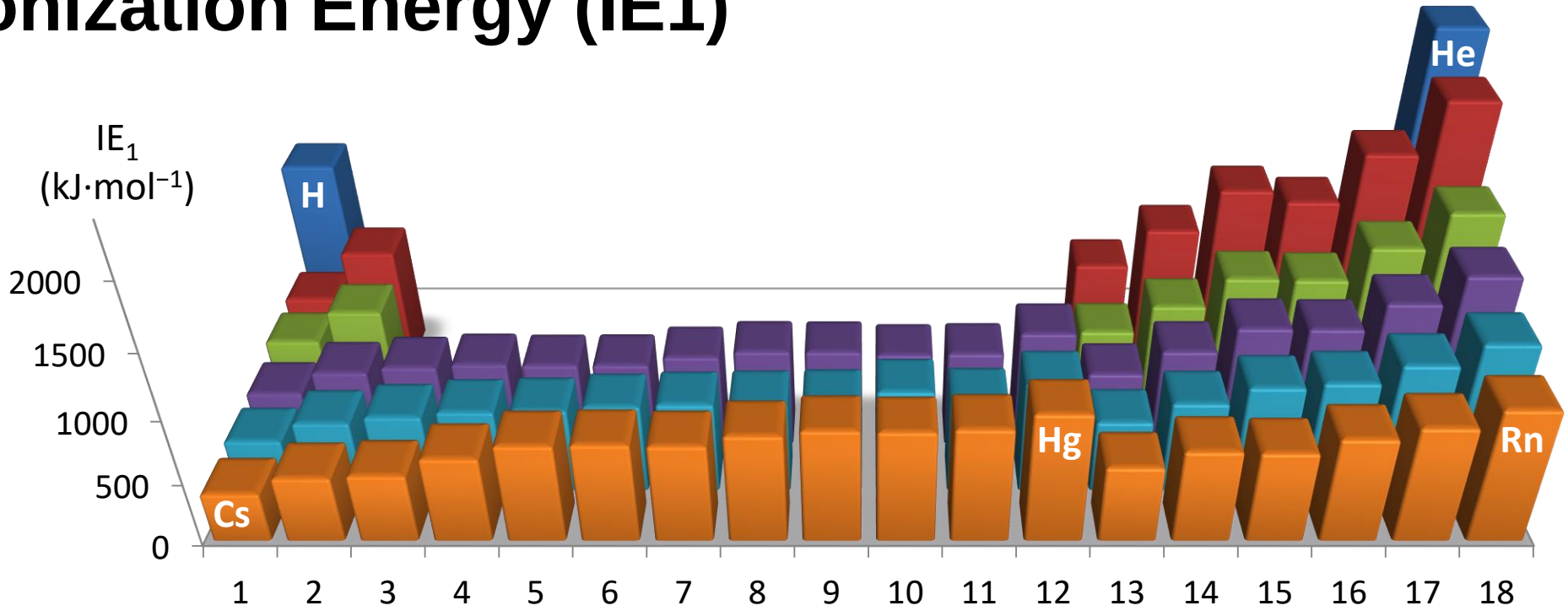


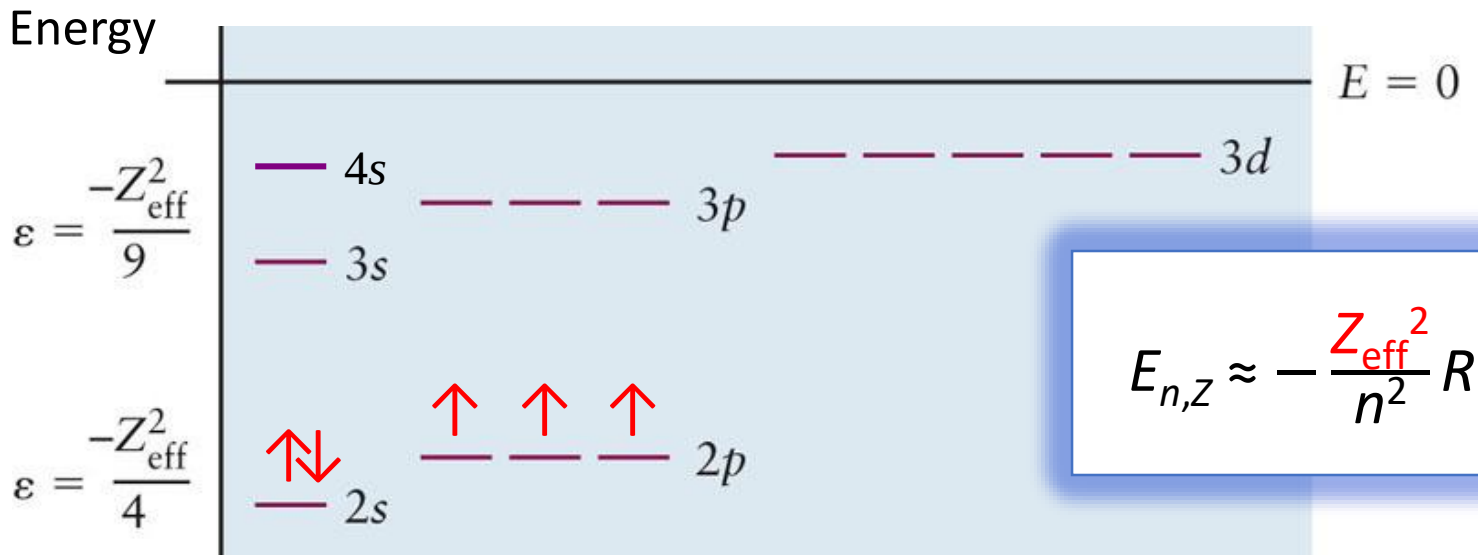

| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | H | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | He |
| 2 | Li | Be | | | | | | | | | | | | | | | | | | | | | | | | | B | C | N | O | F | Ne |
| 3 | Na | Mg | | | | | | | | | | | | | | | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| 4 | K | Ca | | | | | | | | | | | | | | | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| 5 | Rb | Sr | | | | | | | | | | | | | | | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe |
| 6 | Cs | Ba | La | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |

# Periodic Trends in Atomic Radii



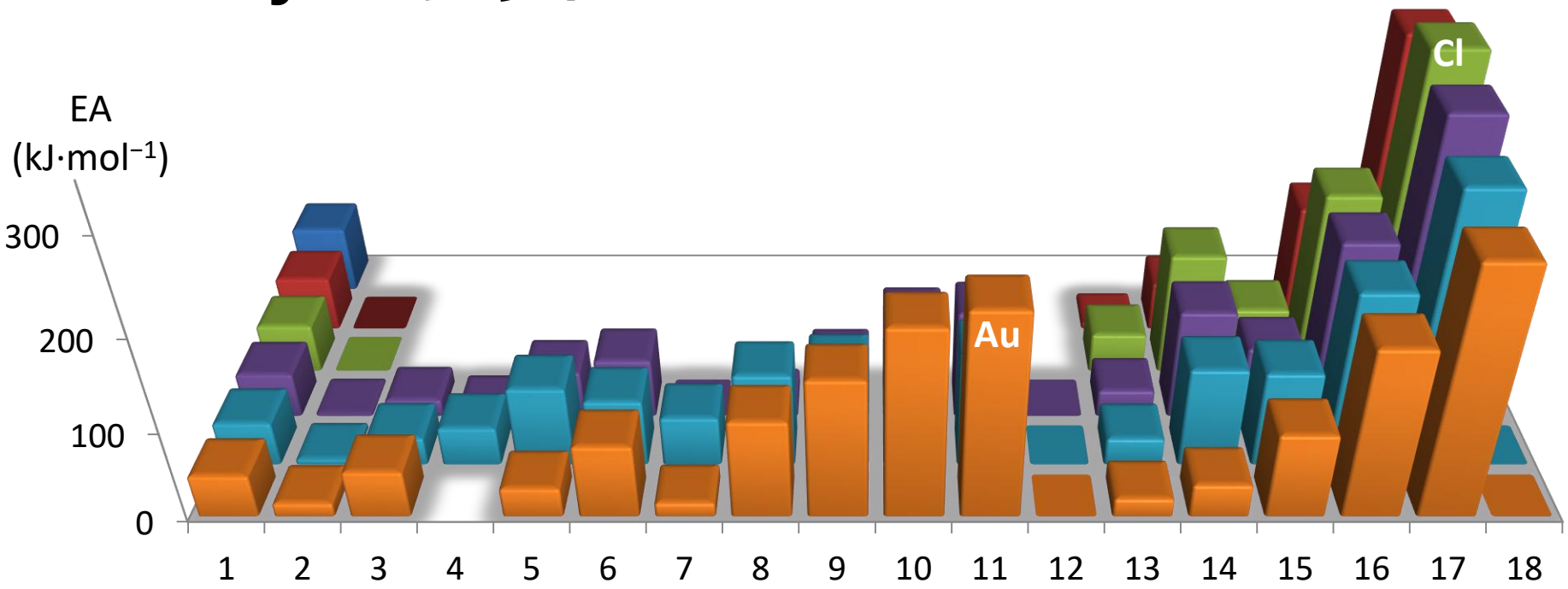
# First Ionization Energy (IE1)

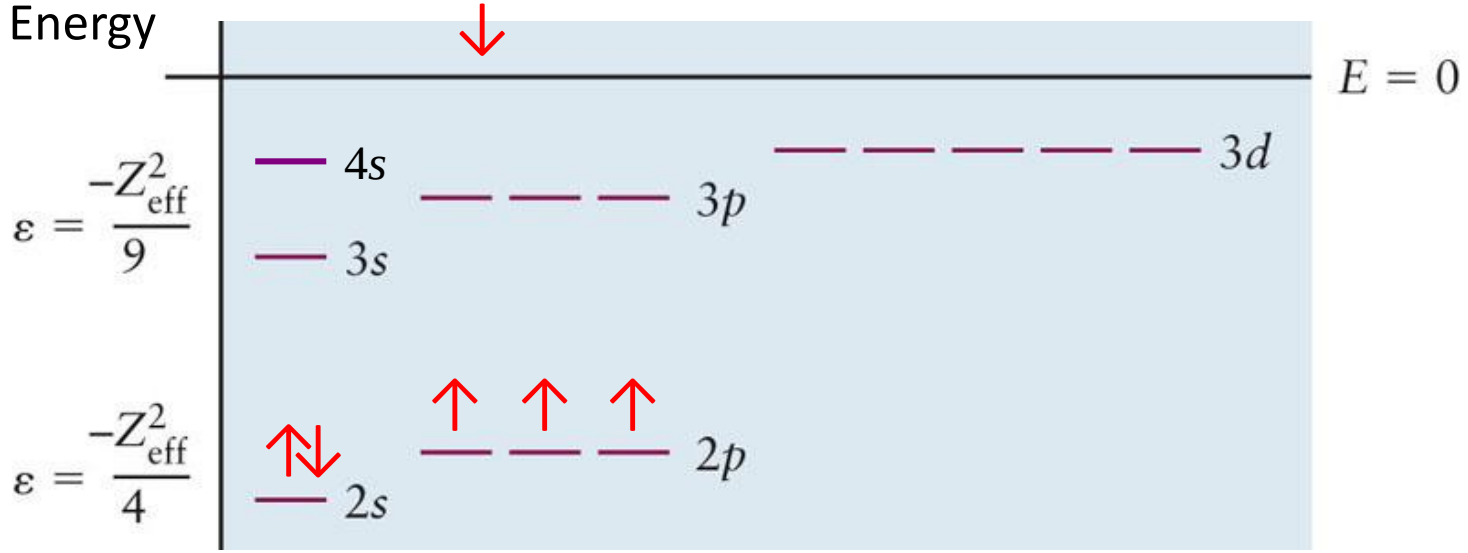


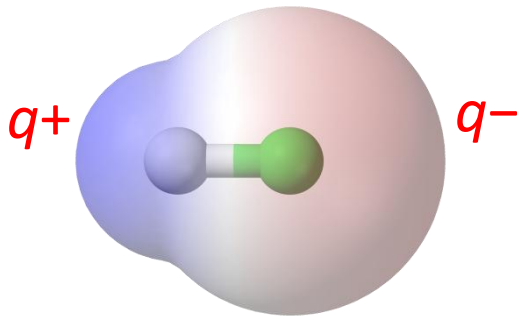

$$E_{n,Z} \approx -\frac{Z_{\text{eff}}^2}{n^2} R_{\text{H}}$$

# Electron Affinity 电子亲和能



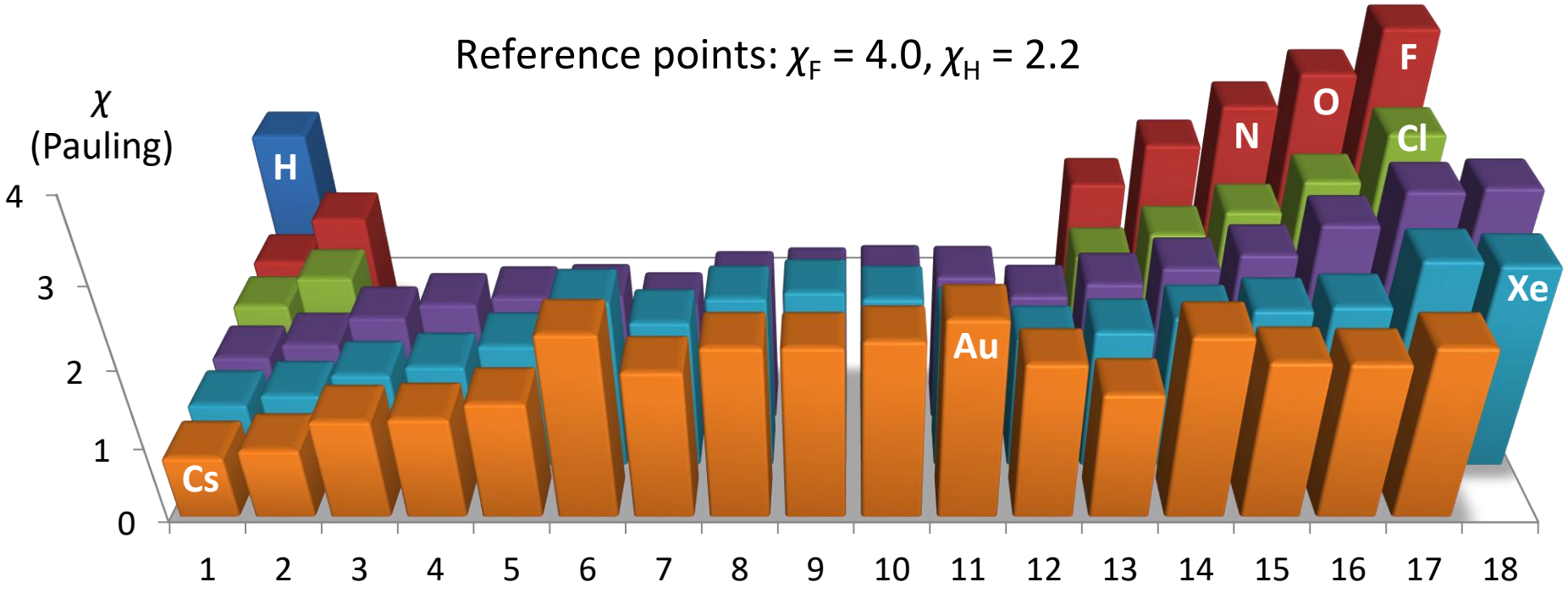
# Calculating Electronegativities




$H^{q+}—Cl^{q-}$

$$(\chi_A - \chi_B)^2 \propto q^2 \propto \Delta E$$

Reference points: $\chi_F = 4.0$, $\chi_H = 2.2$



# Periodic Trends in Forming Hydrides

| | | | | | | |
|---|---|---|---|---|---|---|
| $LiH$ | $BeH_2$ | $\overset{\delta-}{BH_3}$ | $\overset{\delta+}{CH_4}$ | $NH_3$ | $H_2O$ | $HF$ |
| $NaH$ | $MgH_2$ | $AlH_3$ | $SiH_4$ | $PH_3$ | $H_2S$ | $HCl$ |

Ionic ← Covalent → Polar

$\chi = 2.20$

$\chi = 2.55$

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | | | | | | | | | | | | | | | | | He |
| Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe |
| Cs | Ba | * | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |
| Fr | Ra | ** | | | | | | | | | | | | | | | |

# Periodic Trends in Forming Oxides

| | | | | | | |
|---|---|---|---|---|---|---|
| $Li_2O$ | $BeO$ | $B_2O_3$ | $CO_2$ | $\overset{\delta-}{N_2O_5}$ | | $\overset{\delta+}{OF_2}$ |
| $Na_2O$ | $MgO$ | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | $SO_3$ | $Cl_2O_7$ |

Ionic ⟷ Covalent

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | | | | | | | | | | | | | | | | | He |
| Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe |
| Cs | Ba | * | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |
| Fr | Ra | ** | | | | | | | | | | | | | | | |

# Acid/Base Properties of Oxides

**Basic:**

$$Na_2O + H_2O \rightarrow Na^+(aq) + OH^-(aq)$$

**Acidic:**

$$Cl_2O_7 + H_2O \rightarrow ClO_4^-(aq) + H^+(aq)$$

**Amphoteric 两性的:**

$$Al_2O_3 + H^+(aq) \rightarrow Al^{3+}(aq) + H_2O$$

$$Al_2O_3 + OH^-(aq) + H_2O \rightarrow Al(OH)_4^-(aq)$$

aq: aqueous 水合

Most acidic: $HClO_4$
Most basic: CsOH

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | | | | | | | | | | | | | | | | | He |
| Li | Be | *Basic* | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | *Amphoteric* | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe |
| Cs | Ba | * | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |

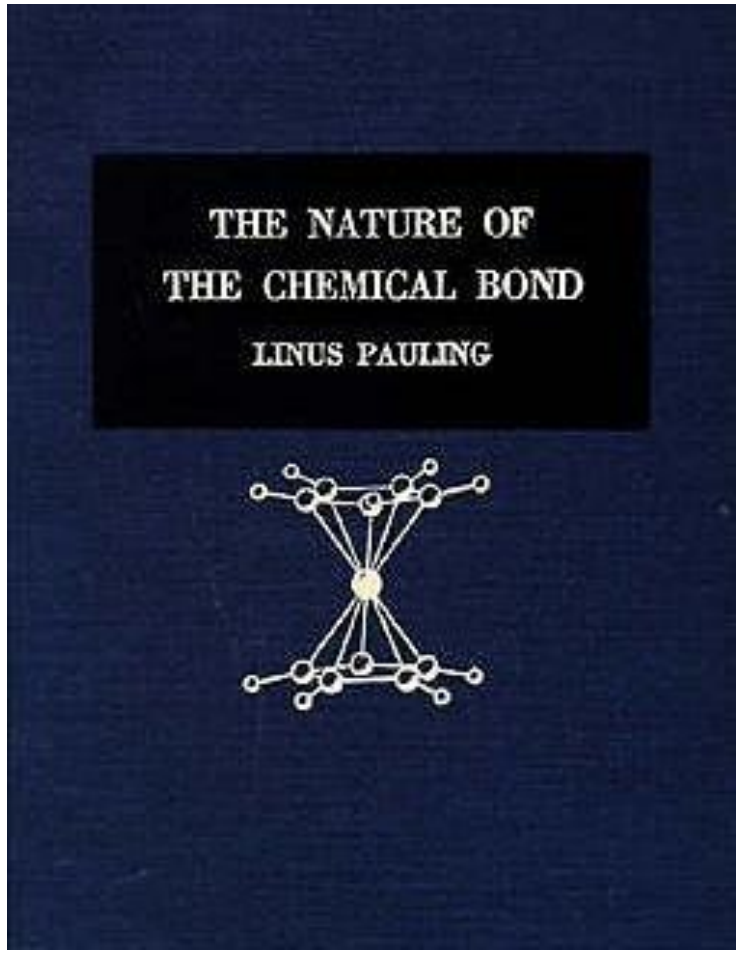
*Acidic*

# Major points of today's lecture

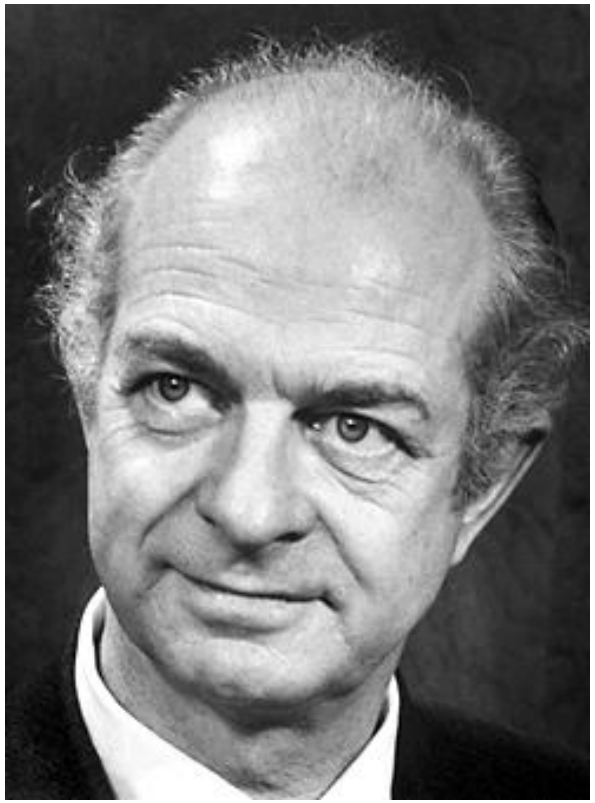
- **Quantum mechanics and molecular structure**

  1. **Quantum Picture of the Chemical Bond**
  2. **Exact Molecular Orbitals (MO) for the Simplest Molecule $H_2^+$**

# Chemistry in the 20th Century



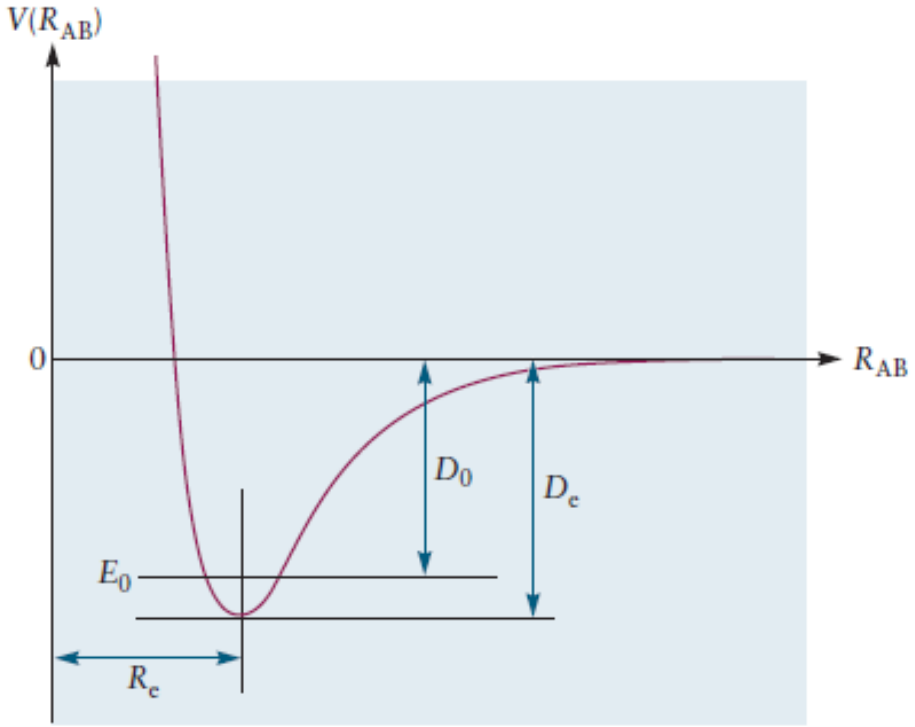

*The Nature of the Chemical Bond*
(1939)



Linus Pauling
(1901–1994)

# Quantum Picture of the Chemical Bond

**FIGURE 6.1** Schematic representation of the potential energy of two hydrogen atoms as a function of the distance between them. As distance decreases, the potential energy reaches a minimum value of $-458$ kJ mol$^{-1}$ at a distance of 0.74 Å. The value of $D_0$ for $H_2$ is 432 kJ mol$^{-1}$ or 4.48 eV molecule$^{-1}$.

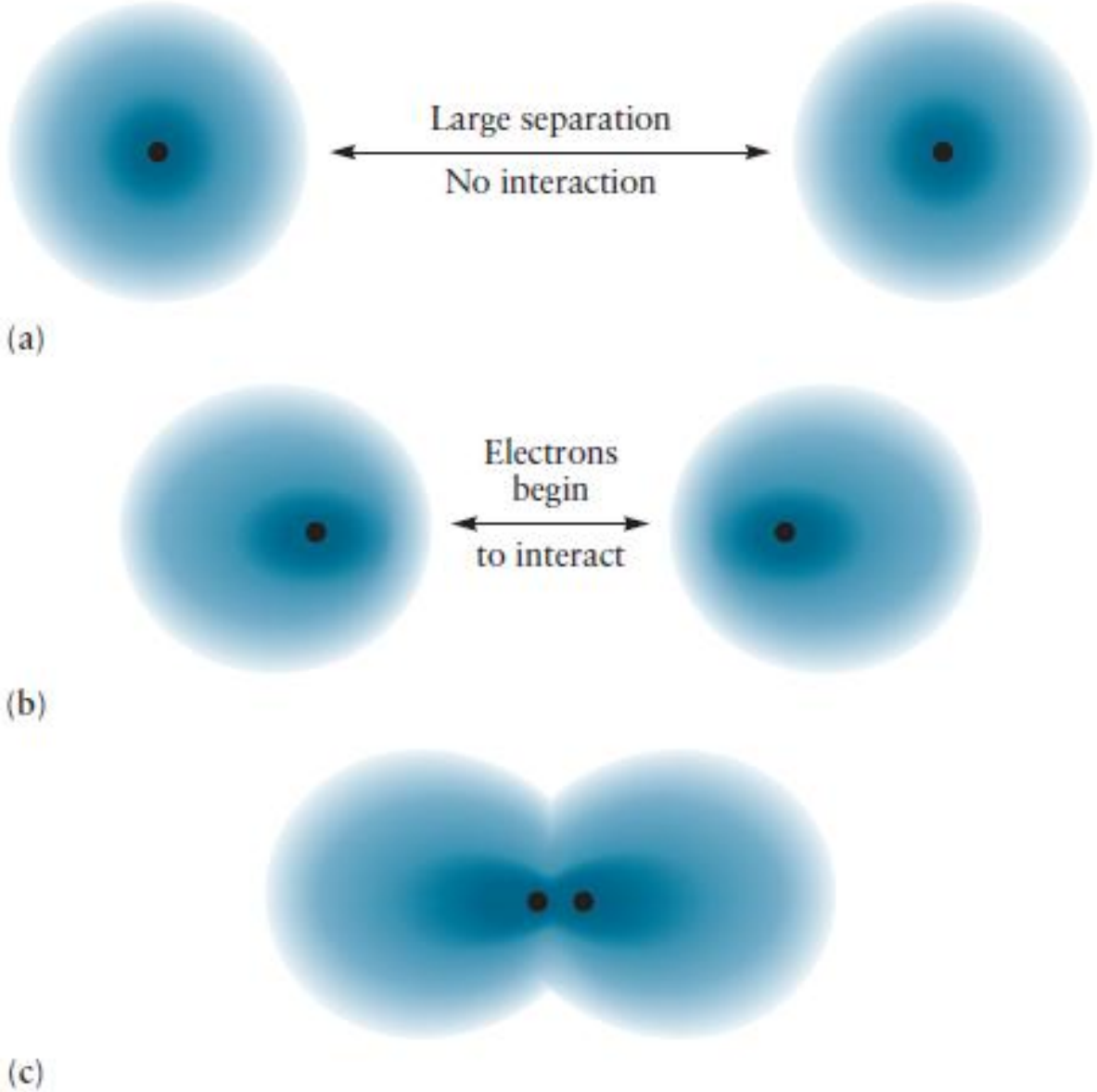



**The uncertainty principle requires that there is a zero-point energy for the molecule. This is the lowest allowed value of the total energy, and is represented by the line $E_0$.**

**Relative to the zero-point energy, the dissociation energy is defined as $D_0$, it is measurable experimentally as the energy needed to dissociate the molecule.**

**Both $D_0$ and $D_e$ are called dissociation energies. $D_e$ is useful as a parameter to construct model potentials and optimize geometry in calculations.**

# The Nature of the Chemical Bond




$$H + H \longrightarrow H{-}H$$

$$He + He \not\longrightarrow He{-}He \quad \text{or} \quad He{=}He$$

**FIGURE 6.2** At very large distances the electron densities of the two H atoms are independent. As the distance becomes sufficiently small, the two densities interpenetrate to form a new pattern of electron density characteristic of the $H_2$ molecule.

# From Classical to Modern Chemistry

- The way of thinking

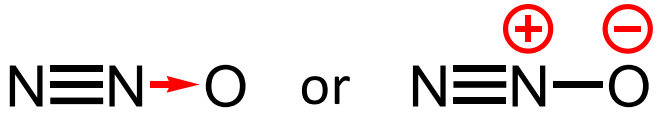
Valence
化合价

→

Orbital 轨道
Bonding 成键

- The language

$\overset{+1\ -2}{N_2O}$ →




- Capability to analyze unfamiliar systems under theoretical guidance

# Quantum Picture of the Chemical Bond

- **Chemists seek to understand the atomic interactions that form molecules and extended solid structures, to understand intermolecular interactions, and most importantly, to understand chemical reactivity.**

- **Set up the Schrödinger equation for a molecule and solve it to find molecular wave functions, energy levels, and electron probability densities.**

- **Molecular orbitals (MOs), wave functions that describe the electronic structure of molecules.**

- **Two powerful ways to construct approximate wave functions from atomic orbitals (AOs): the linear combination of atomic orbitals (LCAO) method and the valence bond (VB) method.**

# Major points of today's lecture

- **Quantum mechanics and molecular structure**

  1. **Quantum Picture of the Chemical Bond**
  2. **Exact Molecular Orbitals (MO) for the Simplest Molecule $H_2^+$**

# Exact Molecular Orbitals (MO) for the Simplest Molecule $H_2^+$

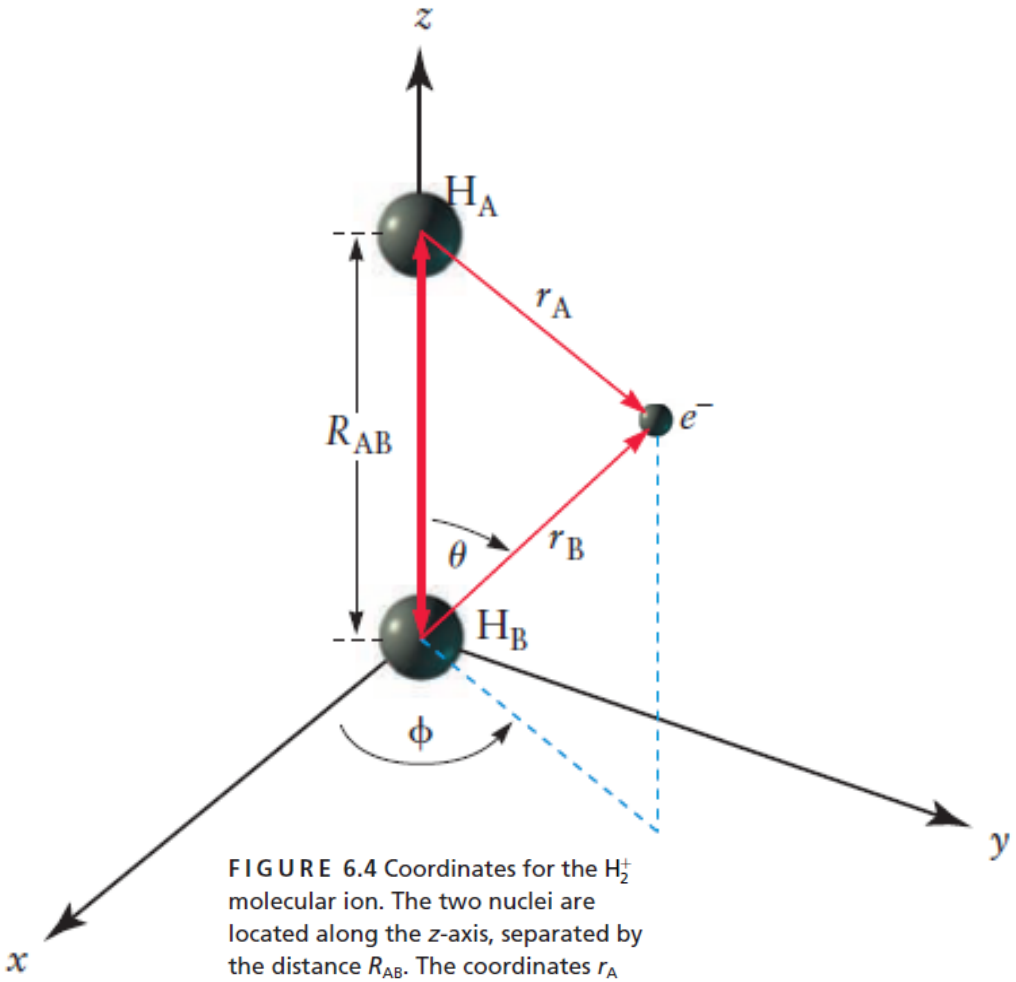



**FIGURE 6.4** Coordinates for the $H_2^+$ molecular ion. The two nuclei are located along the *z*-axis, separated by the distance $R_{AB}$. The coordinates $r_A$ and $r_B$ are the distances of the electron from nuclei A and B, respectively; $r_A$ and $r_B$ range from 0 to $\infty$. The angle $\theta$ is determined from $r_A$, $r_B$, and $R_{AB}$ by the law of cosines; it does not appear explicitly in the calculation. The angle $\phi$ varies from 0 to $2\pi$.

**The potential energy of the system**

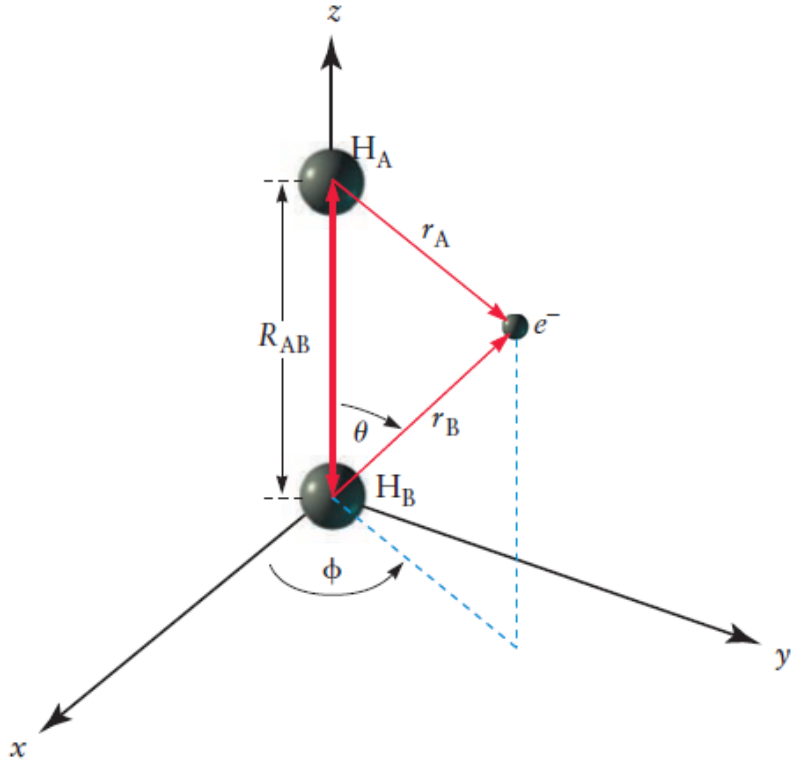
$$V = -\frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_A} + \frac{1}{r_B}\right) + \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{R_{AB}}\right) = V_{en} + V_{nn}$$

**attractions between the electron and the two nuclei**

**repulsion between the pair of protons**

# Exact Molecular Orbitals (MO) for the Simplest Molecule $H_2^+$

**Solution of Schrödinger equation: $\psi_{mol}(R_{AB}, r_A, r_B, \phi)$, a function of all four of these coordinates.**




- **symmetry of the system has changed from spherical to ellipsoidal.**
- **converted the system into the so-called three-body problem, for which there is no exact solution.**
- **Born-Oppenheimer approximation that treats the nuclear and electronic motions almost as if they were independent.**
- **This method allows us to solve the Schrödinger equation exactly and provides an solution $\psi_{el}(r_A, r_B, \phi; R_{AB})$**

# Exact Molecular Orbitals (MO) for the Simplest Molecule $H_2^+$

$$\psi_{\mathrm{mol}}(R_{\mathrm{AB}}, r_{\mathrm{A}}, r_{\mathrm{B}}, \phi) \approx \psi_{\mathrm{el}}(r_{\mathrm{A}}, r_{\mathrm{B}}, \phi; R_{\mathrm{AB}}) \times \psi_{\mathrm{nuc}}(R_{\mathrm{AB}})$$

the ***electronic wave function*** for the electrons around the fixed nuclei:

$\boldsymbol{\psi}_{el}(r_{\mathrm{A}}, r_{\mathrm{B}}, \phi; R_{\mathrm{AB}})$

the ***nuclear wave function***:

$\boldsymbol{\psi}_{\mathrm{nuc}}(R_{\mathrm{AB}})$

# Born-Oppenheimer Approximation

**The basic idea of the Born-Oppenheimer approximation (玻恩-奥本海默近似): because the nuclei are so much more massive than the electrons. Slow Nuclei, Fast Electrons.**

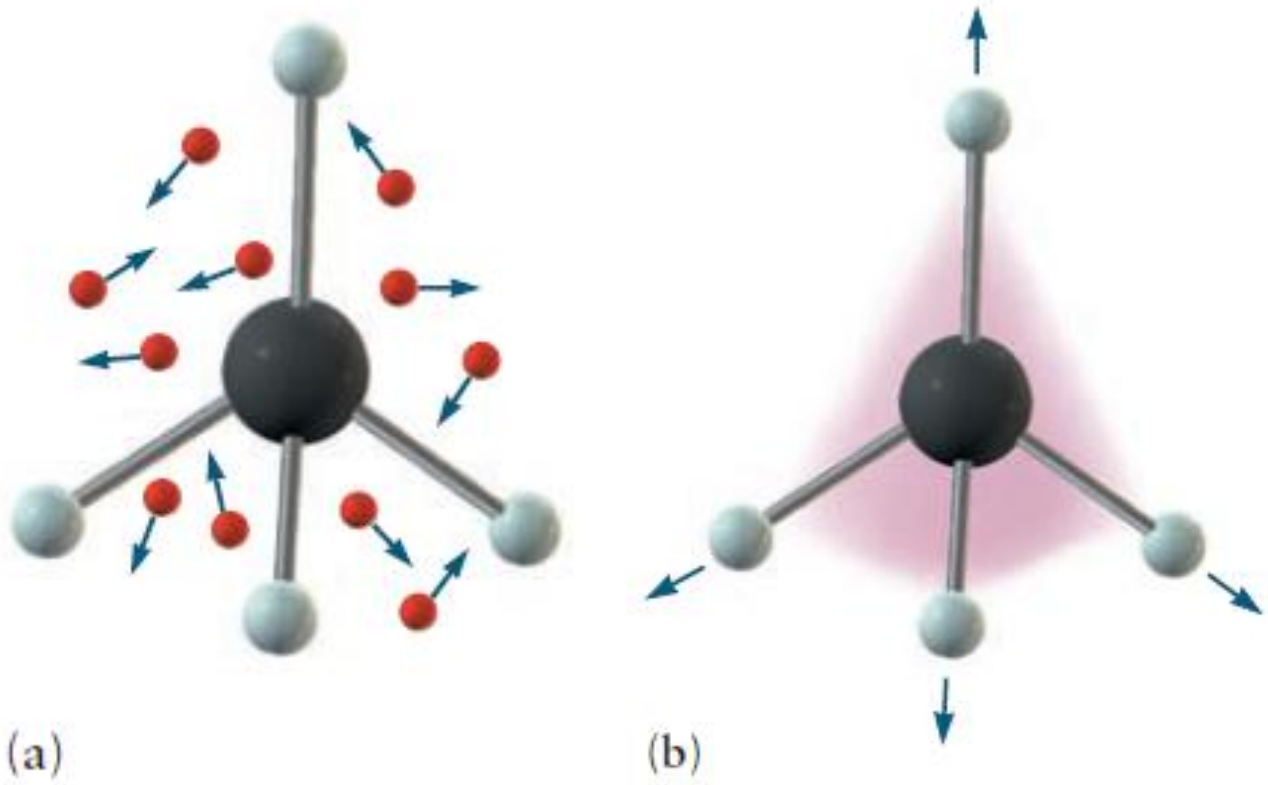
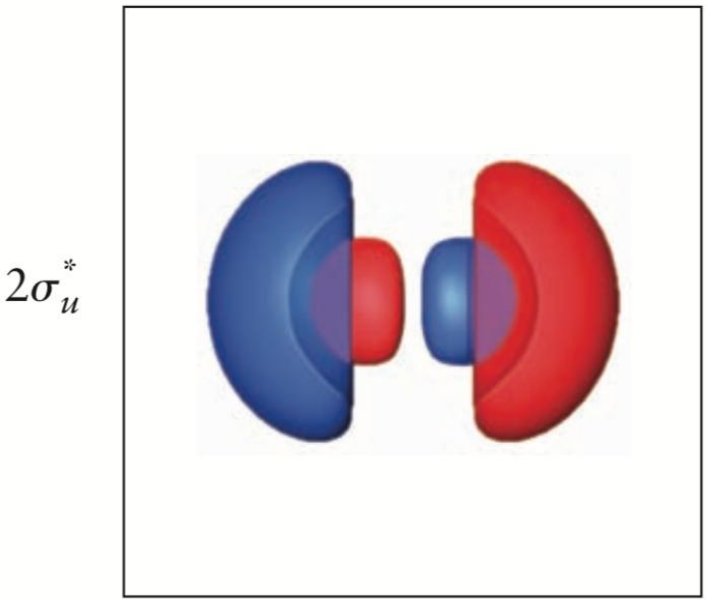
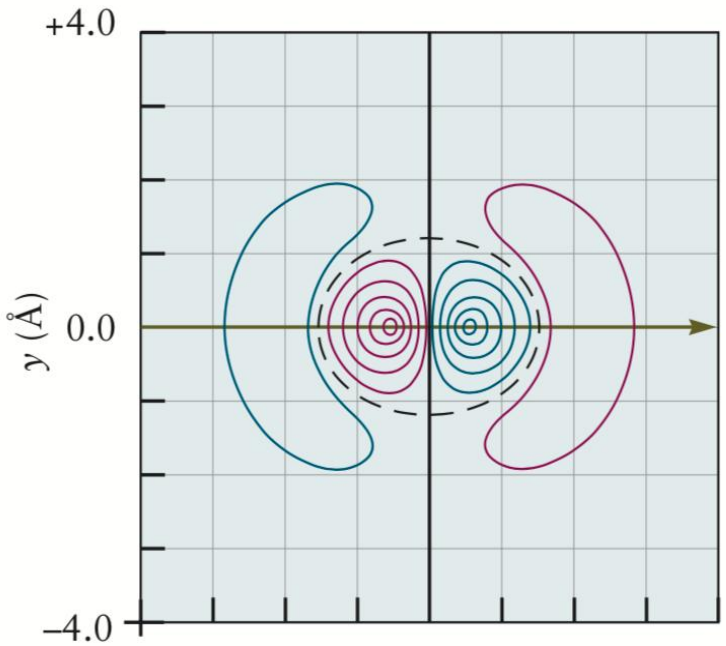


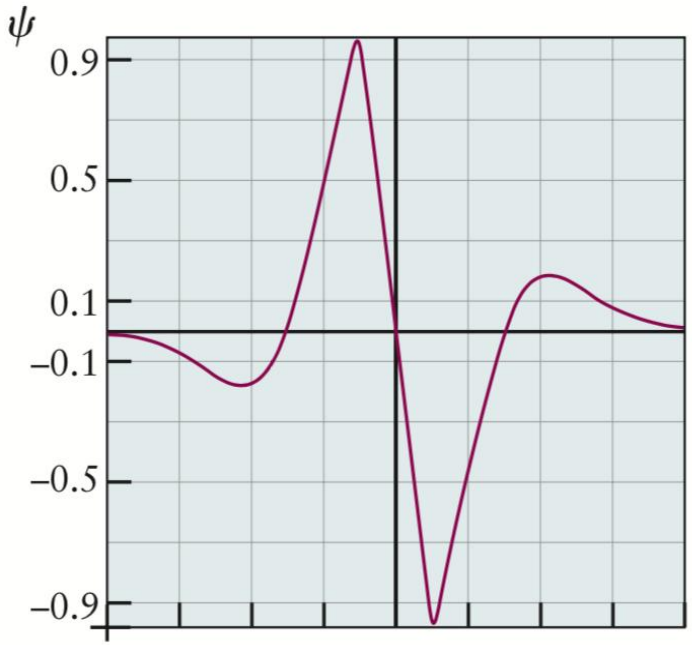

**FIGURE 6.3** Schematic representation of the Born–Oppenheimer approximation for methane. (a) The nuclei are assumed to be fixed at positions corresponding to the equilibrium bond distances, while the electrons move rapidly around them. The wave functions and allowed energy values are calculated for the electrons at many different positions of the nuclei. (b) The allowed energy values calculated in (a), with the internuclear repulsions added in, are viewed as the effective potential energy functions that govern the relative motions of the nuclei in the molecule, as occurs in vibrations. The multidimensional effective potential energy function is suggested here as a cloud.

# Electronic wave functions for $H_2^+$

- The solutions for $\psi_{el}$ are mathematically exact.
- Because of their ellipsoidal symmetry, they cannot be written as simple exponential and polynomial functions, as were the hydrogen atom solutions



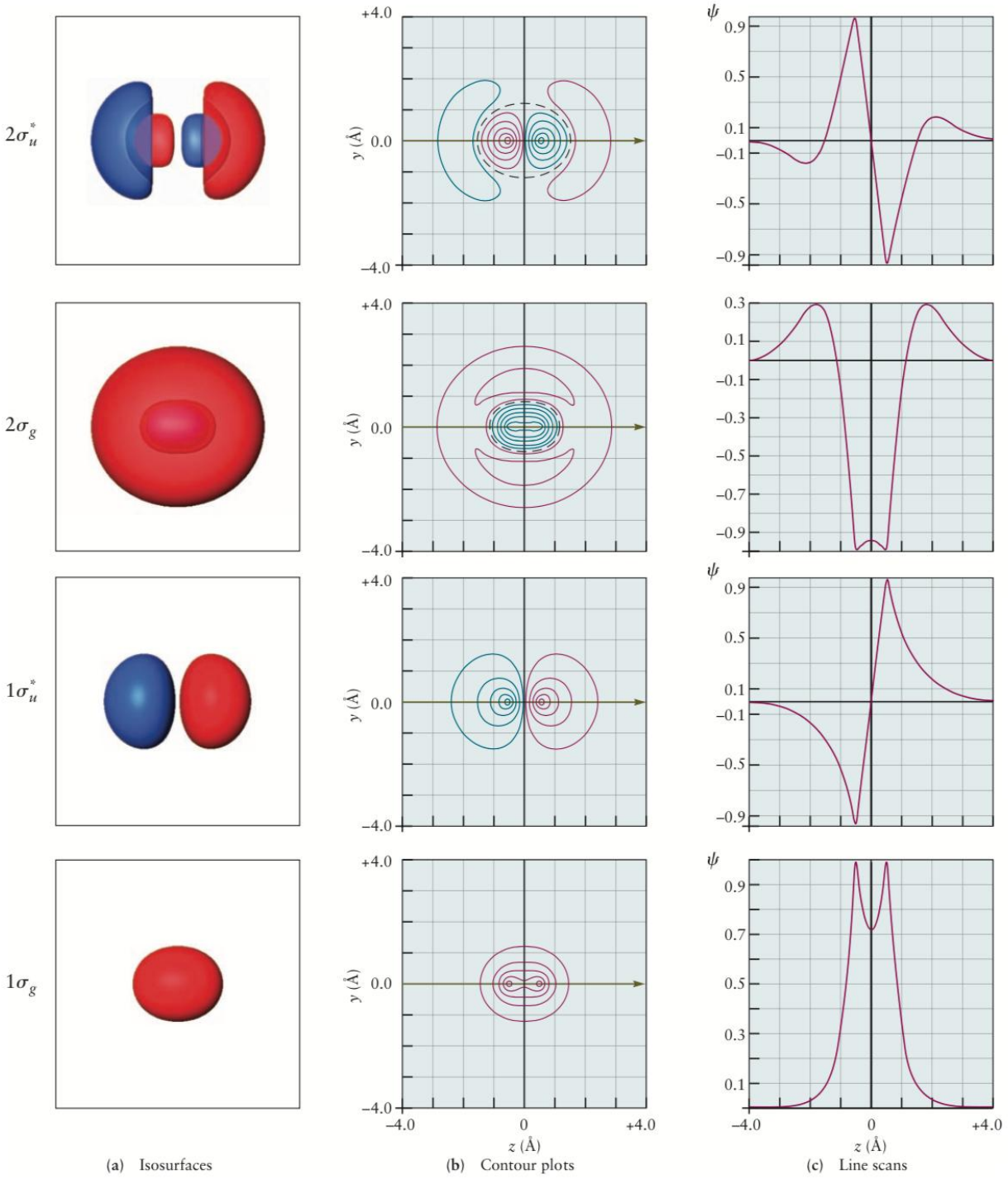




Isosurfaces 等值面 corresponding to contours at 0.1 of the maximum amplitude.

Contours 等高线 of constant amplitude in the x-z plane, at values 0.1, 0.3, 0.5, 0.7, and 0.9 of the maximum amplitude.

amplitude along z-axis (“line scan”) along the direction indicated by the green arrow in (b).




$$1\sigma_g < 1\sigma_u^* < 2\sigma_g < 2\sigma_u^*$$

- **The energy index integer: tracks the relative energies of the wave functions of each symmetry type. (analogous to the principal quantum number n for atomic orbitals)**
- **As the index increases within each symmetry type, the number of nodes along the internuclear axis increases.**
- **The subscript g or u describes how the wave function changes as we invert our point of observation through the center of the molecule.**
- **The sign of the wave function is the same at the point (x, y, z) and at the point (-x, -y, -z), it is called symmetric and labeled g**
- **If the sign of the wave function is opposite at these two points, it is called antisymmetric and labeled u**

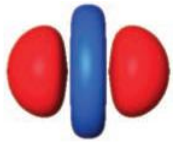
- The **energy index integer**: tracks the relative energies of the wave functions of **each symmetry type**. (analogous to the principal quantum number n for atomic orbitals)

As the index increases within each symmetry type, the **number of nodes along the internuclear axis increases**.

- $1\sigma_g$ is the first (lowest on the energy scale) of the $\sigma_g$ wave functions

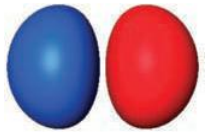
$1\sigma_g$

$2\sigma_g$

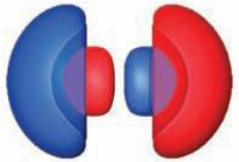


$3\sigma_g$

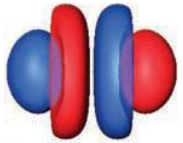
- $2\sigma_u^*$ is the second lowest energy of the $\sigma_u^*$ wave functions



$1\sigma_u^*$



$2\sigma_u^*$



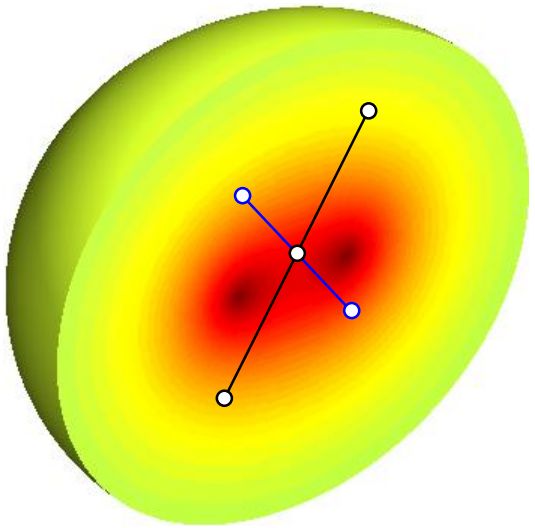
$3\sigma_u^*$

- $1\pi_u$ is the lowest energy of the $\pi_u$ wave functions

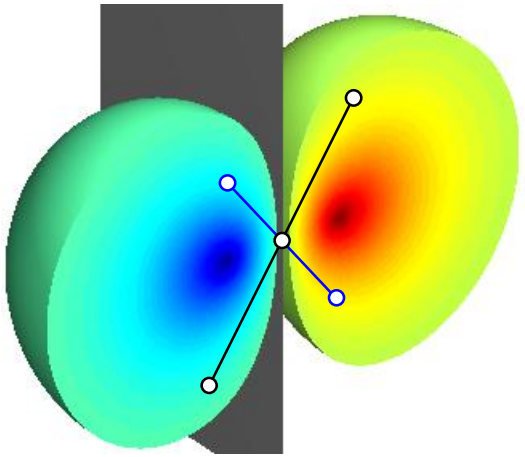
$1\pi_u$

- The subscript g or u describes how the wave function changes as we invert our point of observation through the center of the molecule.
- The sign of the wave function is the same at the point (x, y, z) and at the point (-x, -y, -z), it is called symmetric and labeled g
- If the sign of the wave function is opposite at these two points, it is called antisymmetric and labeled u

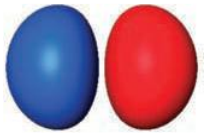
$1\sigma_g$



Centrosymmetric (*g*)

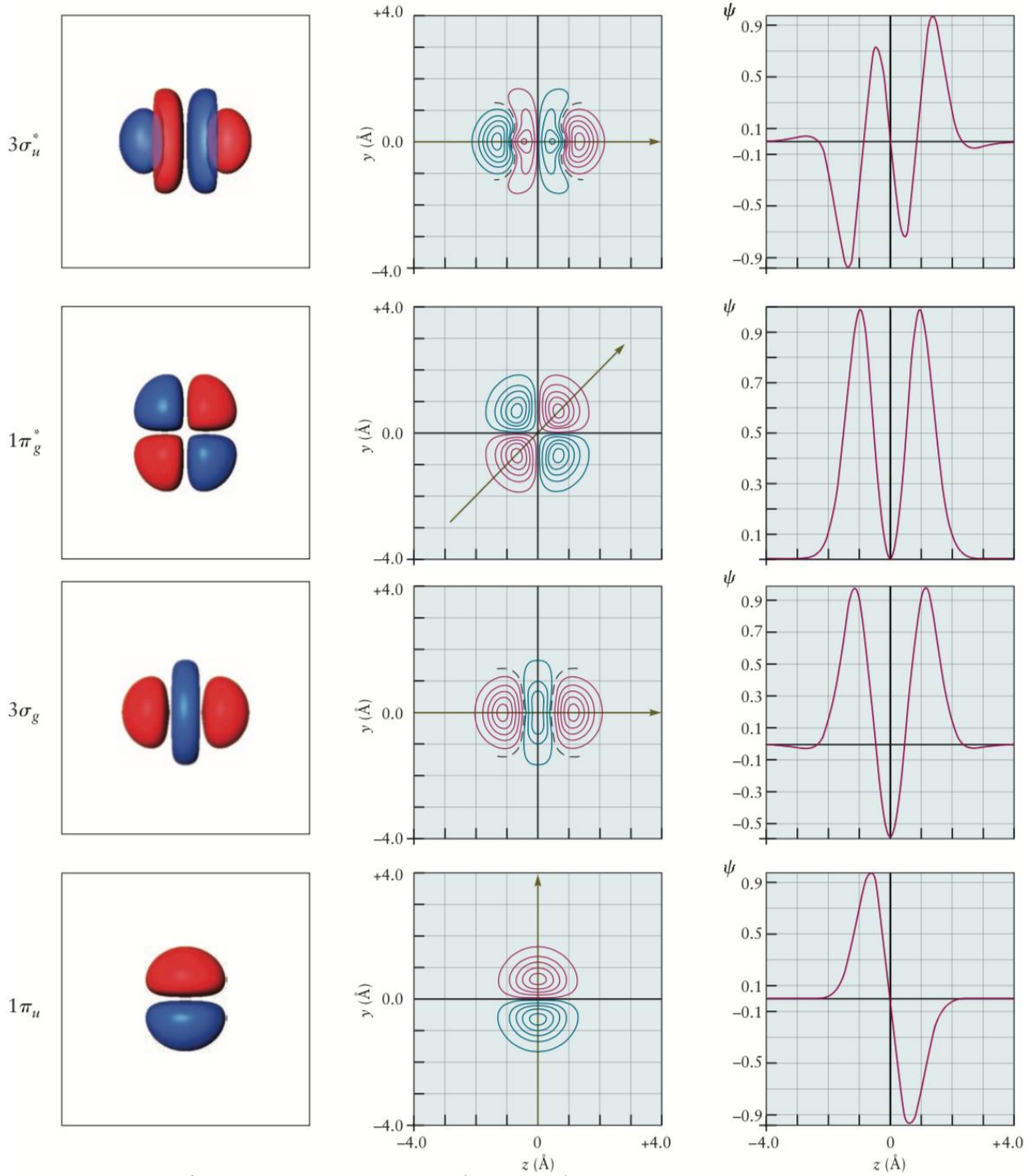


Antisymmetric (*u*)



$1\sigma_u^*$

| CN | EN | DE | Label |
|---|---|---|---|
| 中心对称 | Centrosymmetric | gerade | *g* |
| （中心）反对称 | Antisymmetric | ungerade | *u* |

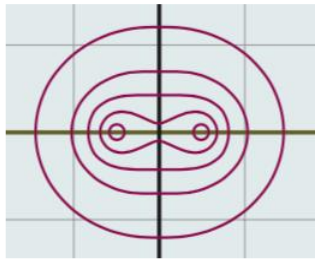



$$1\pi_u < 3\sigma_g < 1\pi_g^* < 3\sigma_u^*$$

- **The Greek letter: how the amplitude of the wave function is distributed around the internuclear axis.**
- **The letter σ: the amplitude has cylindrical symmetry around the axis.**
- **The letter π: the wave function has a nodal plane that contains the internuclear axis.**

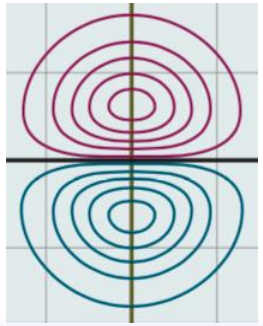
- **The Greek letter: how the amplitude of the wave function is distributed around the internuclear axis.**
- **The letter σ: the amplitude has cylindrical symmetry around the axis.**
- **The letter π: the wave function has a nodal plane that contains the internuclear axis.**

**$1\sigma_g$**



**No nodal plane that contains the bond axis.**

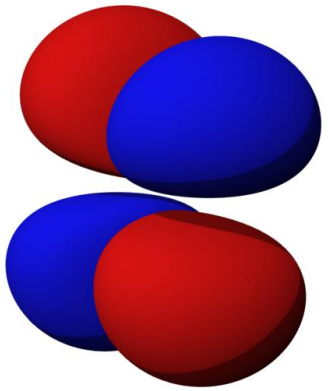
**$1\pi_u$**



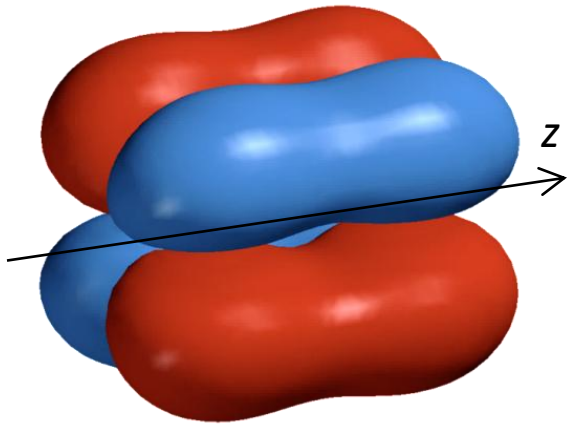
**1 nodal plane that contains the bond axis.**

$$\sigma \longrightarrow \text{angular momentum component} = 0$$
$$\pi \longrightarrow \text{angular momentum component} = \pm h/2\pi$$
$$\delta \longrightarrow \text{angular momentum component} = \pm 2h/2\pi$$
$$\varphi \longrightarrow \text{angular momentum component} = \pm 3h/2\pi$$

| Nodal planes | Atomic orbital | $L_z$ | Molecular orbital | $L_z$ |
|---|---|---|---|---|
| 0 | *s* | 0 | $\sigma$ | 0 |
| 1 | *p* | $-\hbar, 0, \hbar$ | $\pi$ | $\pm\hbar$ |
| 2 | *d* | $-2\hbar, -\hbar, 0, \hbar, 2\hbar$ | $\delta$ | $\pm 2\hbar$ |



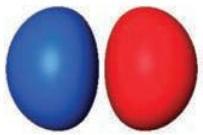
*d* orbital




$\delta$ orbital

- **asterisk " * " denotes an antibonding orbital.**
- **If the wave function changes sign upon reflection, it receives the superscript *. Each wave function labeled * has a node on the internuclear axis at the center of the molecule.**

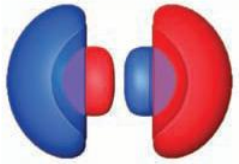
**$1\sigma_g$**



**$1\sigma_u^*$**

1 nodal plane in the middle of the bond.

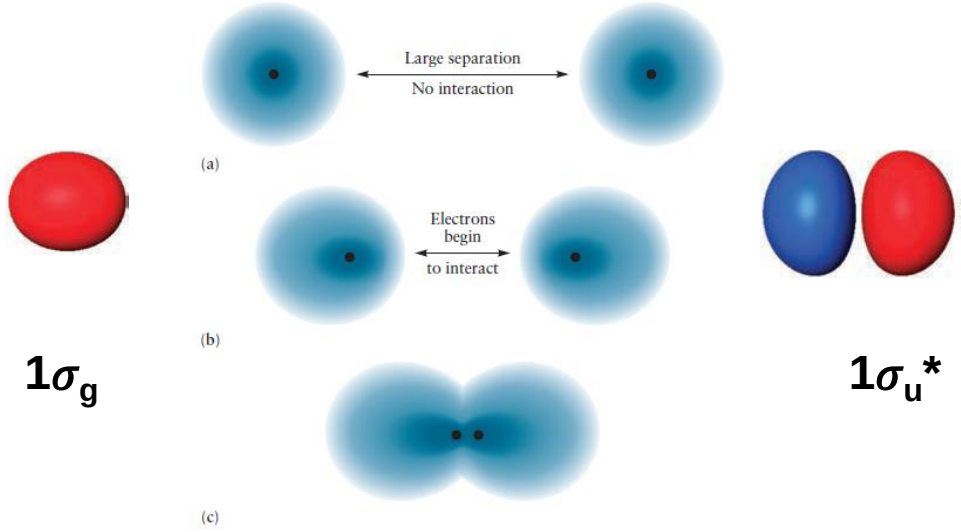
**$2\sigma_g$**



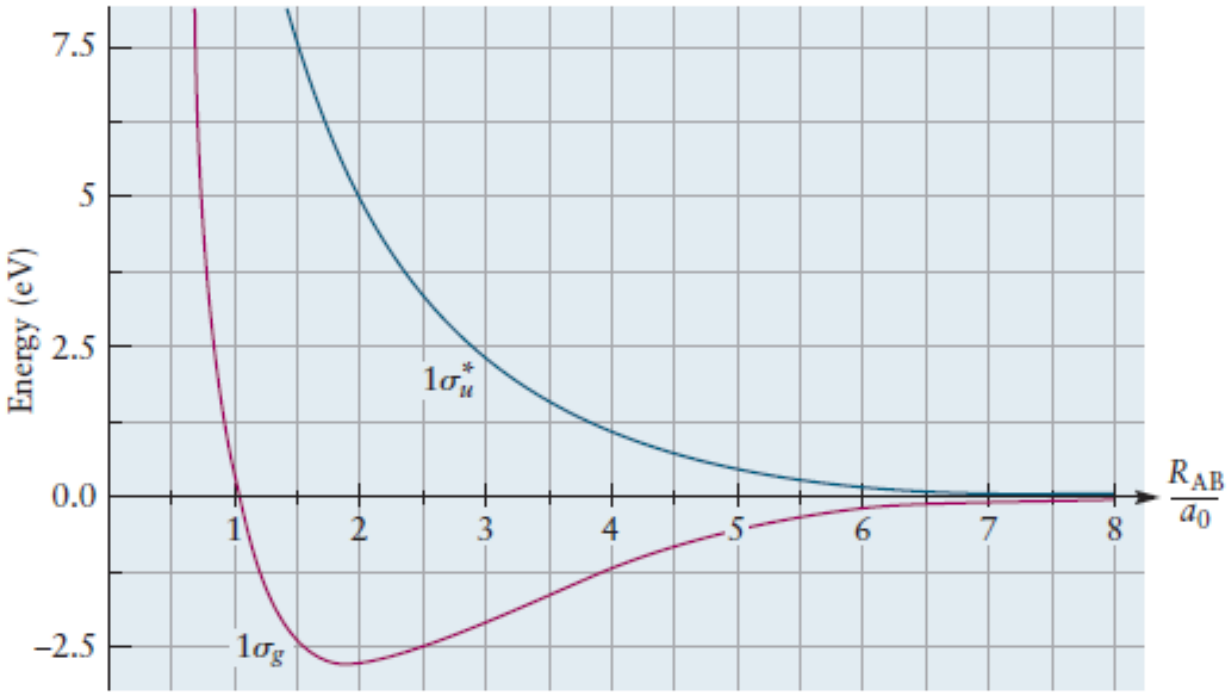
**$2\sigma_u^*$**

# Nature of the chemical bond in $H_2^+$

- $1\sigma_g$ is called a bonding molecular orbital.
- $1\sigma_u^*$ is called a antibonding molecular orbital.
- The $1\sigma_u^*$ orbital shows zero electron density halfway between the nuclei and increased energy.




$$\psi_{mol}(R_{AB}, r_A, r_B, \phi) \approx \psi_{el}(r_A, r_B, \phi; R_{AB}) \times \psi_{nuc}(R_{AB})$$



In Section 5.1 we classified the atomic orbitals of H according to their number of angular nodes (each defined by a plane) and their radial nodes (each defined by a spherical surface). How do we extend this analysis to the molecular orbitals of $H_2^+$?

# Summary

- **Nuclei to be fixed (more precisely, slowly vibrating around) at positions corresponding to the equilibrium bond length of the molecule while the electrons move rapidly around them (the Born–Oppenheimer approximation)**

- **A molecular orbital is a one-electron wave function whose square describes the distribution of electron density around the nuclei in their equilibrium positions.**

# Summary

- A **bonding molecular orbital** describes increased electron density in the region between the nuclei and decreased effective potential energy relative to that of the separated atoms.

- Each bonding molecular orbital is related to an **antibonding molecular orbital** which has zero amplitude on a surface between the nuclei and thus a node on the internuclear axis. An electron in an antibonding molecular orbital leads to effective potential energy higher than that of the separated atoms.

# Summary

- **$\sigma$ orbitals are those for which the electron density is distributed symmetrically about the internuclear axis. A $\sigma$ orbital has cylindrical symmetry; cross-sections perpendicular to the internuclear axis are discs.**

- **π orbitals are those for which the electron density has a nodal plane that contains the internuclear axis. Consequently, the amplitude is concentrated "off the axis" and the orbital does not have cylindrical symmetry about the internuclear axis.**

# Major points of today's lecture

- **Quantum mechanics and molecular structure**

1. **Quantum Picture of the Chemical Bond**
2. **Exact Molecular Orbitals (MO) for the Simplest Molecule $H_2^+$**
3. **Molecular Orbital Theory and the Linear Combination of Atomic Orbitals Approximation for $H_2^+$**
4. **Homonuclear Diatomic Molecules: First-Period Atoms**
5. **Homonuclear Diatomic Molecules: Second-Period Atoms**
6. **Heteronuclear Diatomic Molecules**
7. **Summary Comments for the LCAO Method and Diatomic Molecules**

# Linear Combination of Atomic Orbitals (LCAO) method

**Linear Combination of Atomic Orbitals (LCAO，原子轨道线性组合) :** selecting sums and differences (linear combinations) of atomic orbitals to generate the best **approximation** to each type of molecular orbital.

**Approximation for $H_2^+$**

- Electron is close to nucleus A: not very different from that in an isolated hydrogen atom. The ground-state wave function for the electron near A should therefore resemble a 1s atomic wave function $\varphi^A_{1s}$.
- Near B: the wave function should resemble $\varphi^B_{1s}$.

$$\psi_{MO} = C_A(R_{AB})\varphi^A_{1s} \pm C_B(R_{AB})\varphi^B_{1s}$$

- An **approximate MO** for $H_2^+$: a linear combination of two atomic orbitals, obtained by adding or subtracting the two: with coefficients whose values depend on $R_{AB}$:

# Linear Combination of Atomic Orbitals (LCAO) method

**New symbols $\sigma_{g1s}$ and $\sigma^*_{u1s}$ for the approximate MOs:**

**(1) distinguish them from the exact MOs;**

**(2) indicate explicitly the AOs from which they were constructed.**

$$1\sigma_g \approx \sigma_{g1s} = C_g[\varphi^A_{1s} + \varphi^B_{1s}]$$

$$1\sigma^*_u \approx \sigma^*_{u1s} = C_u[\varphi^A_{1s} - \varphi^B_{1s}]$$

**TABLE 6.1**

**Molecular Orbitals for Homonuclear Diatomic Molecules**

| Exact MO Notation | LCAO MO Notation |
|---|---|
| $1\sigma_g$ | $\sigma_{g1s}$ |
| $1\sigma^*_u$ | $\sigma^*_{u1s}$ |
| $2\sigma_g$ | $\sigma_{g2s}$ |
| $2\sigma^*_u$ | $\sigma^*_{u2s}$ |
| $1\pi_u$ | $\pi_{u2p_x}$, $\pi_{u2p_y}$ |
| $3\sigma_g$ | $\sigma_{g2p_z}$ |
| $1\pi^*_g$ | $\pi^*_{g2p_x}$, $\pi^*_{g2p_y}$ |
| $3\sigma^*_u$ | $\sigma^*_{u2p_z}$ |

# Linear Combination of Atomic Orbitals (LCAO) method

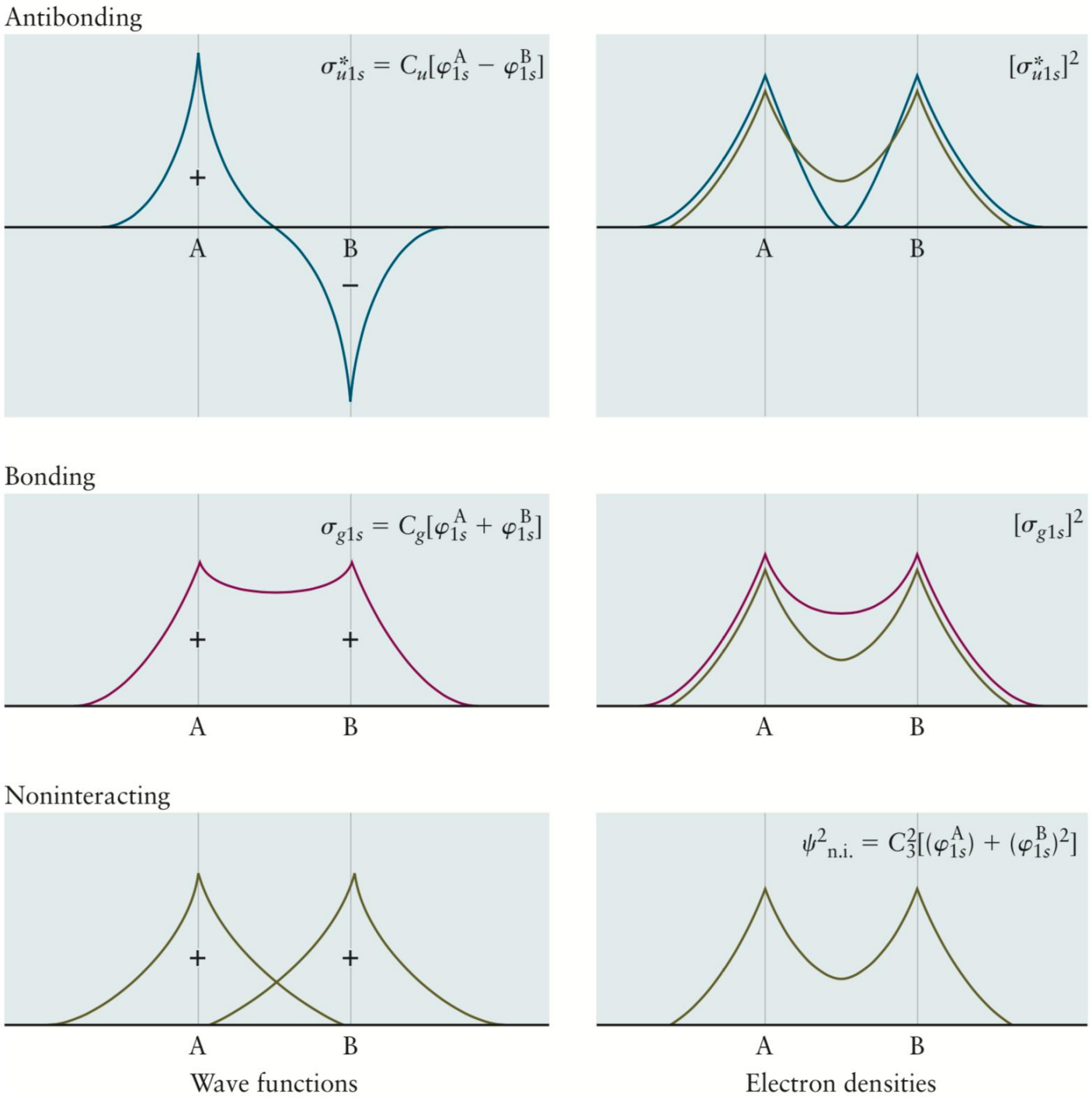
**The distribution of electron probability density: squaring each of the approximate MOs:**

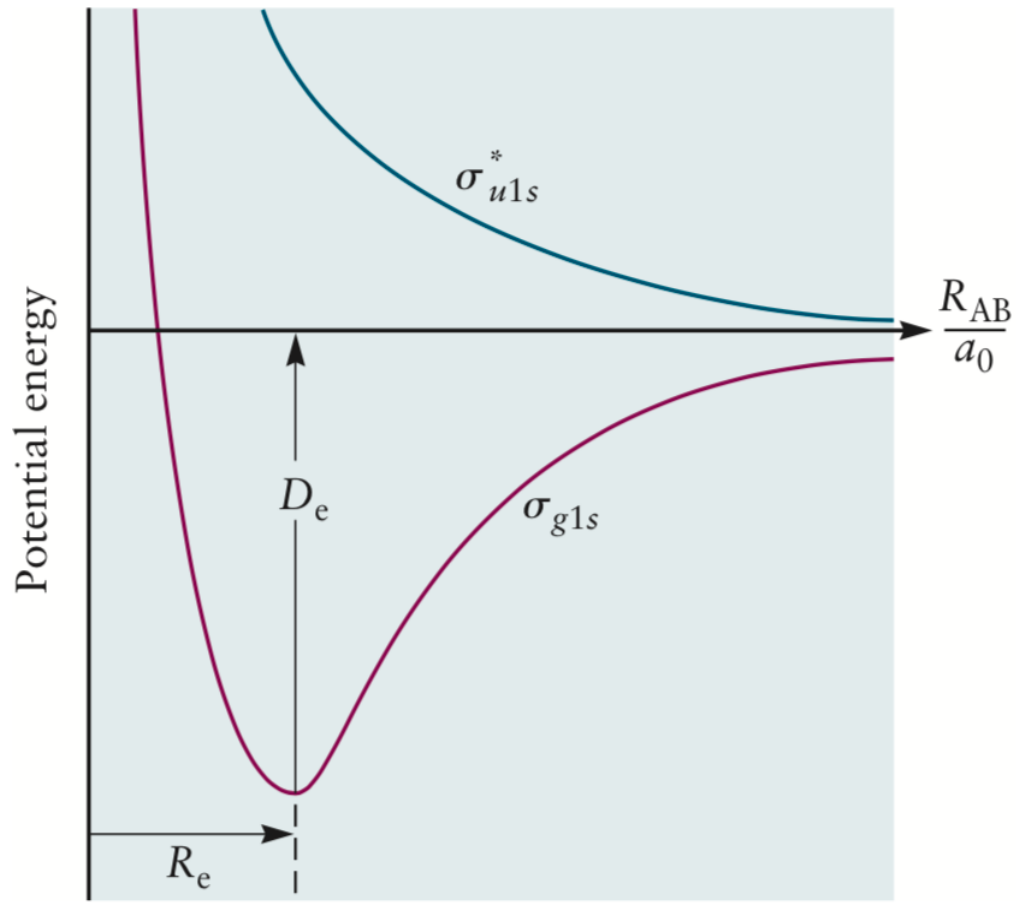
$$[\sigma_{g1s}]^2 = C_g^2[(\varphi_{1s}^{A})^2 + (\varphi_{1s}^{B})^2 + 2\varphi_{1s}^{A}\varphi_{1s}^{B}]$$

$$[\sigma_{u1s}^{*}]^2 = C_u^2[(\varphi_{1s}^{A})^2 + (\varphi_{1s}^{B})^2 - 2\varphi_{1s}^{A}\varphi_{1s}^{B}]$$

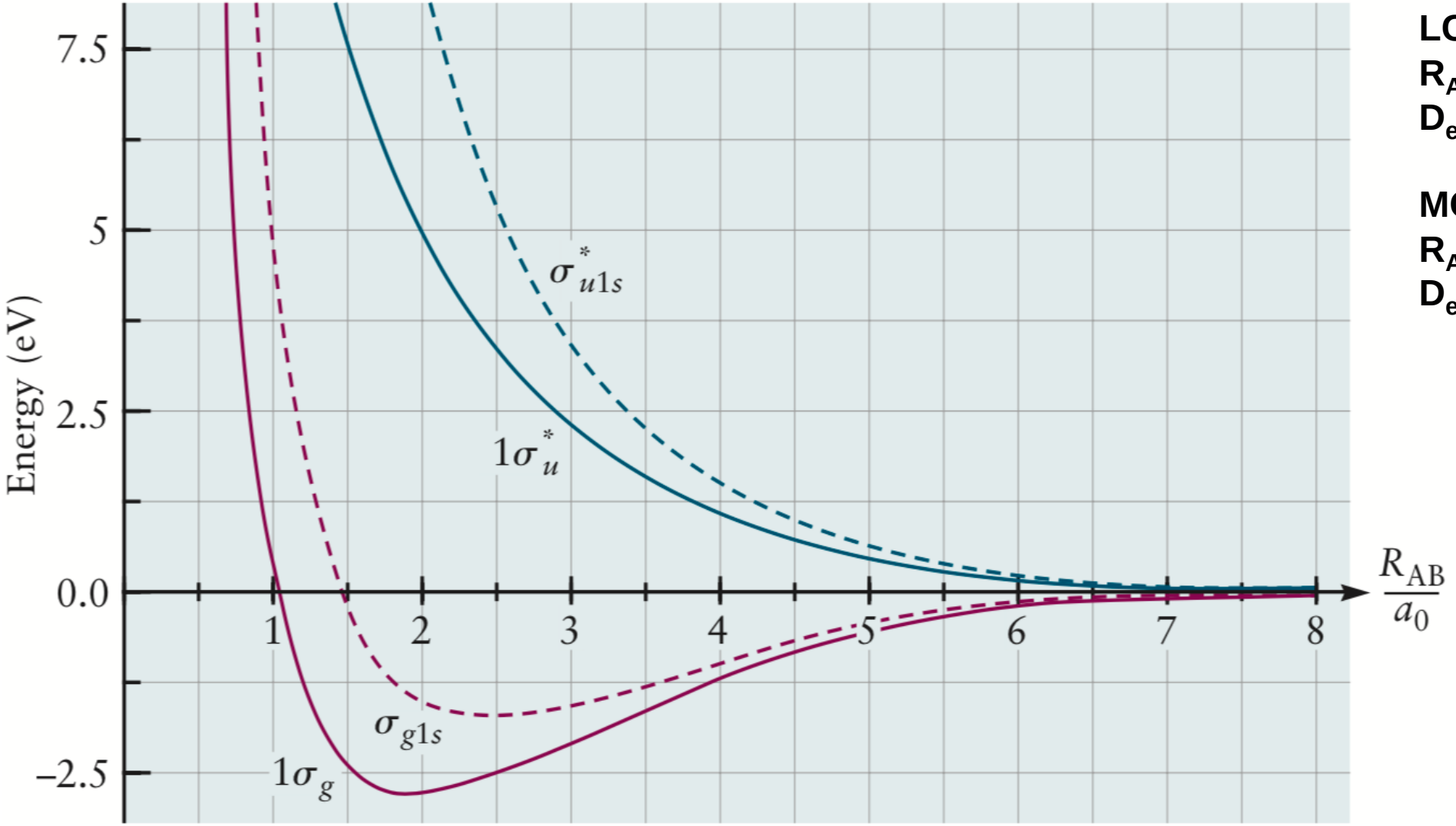
**The probability distribution for a non-interacting (n.i.) system (averaging the probabilities for $H_A^+ + H_B$ and $H_A + H_B^+$):**

$$\psi_{\text{n.i.}}^2 = C_3^2[(\varphi_{1s}^{A})^2 + (\varphi_{1s}^{B})^2]$$


Antibonding
$\sigma^*_{u1s} = C_u[\varphi^A_{1s} - \varphi^B_{1s}]$
$[\sigma^*_{u1s}]^2$
+
−
A
B
Bonding
$\sigma_{g1s} = C_g[\varphi^A_{1s} + \varphi^B_{1s}]$
$[\sigma_{g1s}]^2$
+
+
A
B
Noninteracting
$\psi^2_{\text{n.i.}} = C_3^2[(\varphi^A_{1s}) + (\varphi^B_{1s})^2]$
+
+
A
B
Wave functions
Electron densities


Potential energy
$\sigma^*_{u1s}$
$\sigma_{g1s}$
$D_e$
$R_e$
$\frac{R_{AB}}{a_0}$

# Linear Combination of Atomic Orbitals (LCAO) method




**LCAO 理论值：**
**$R_{AB}$ = 1.32 Å**
**$D_e$ = 1.76 eV**

**MO理论值：**
**$R_{AB}$ = 1.060 Å**
**$D_e$ = 2.791 eV**

**FIGURE 6.9** Comparison of the effective potential energy for the $\sigma_{g1s}$ and $\sigma^*_{u1s}$ orbitals of $H_2^+$ in the LCAO approximation (dashed lines) with the exact results (solid lines). The internuclear separation is plotted in units of the Bohr radius. (Adapted from R. S. Berry, S. A. Rice, and J. Ross, *Physical Chemistry*, 2nd ed., New York: Oxford, 2000, Figure 6.6, by permission.)

# Linear Combination of Atomic Orbitals (LCAO) method

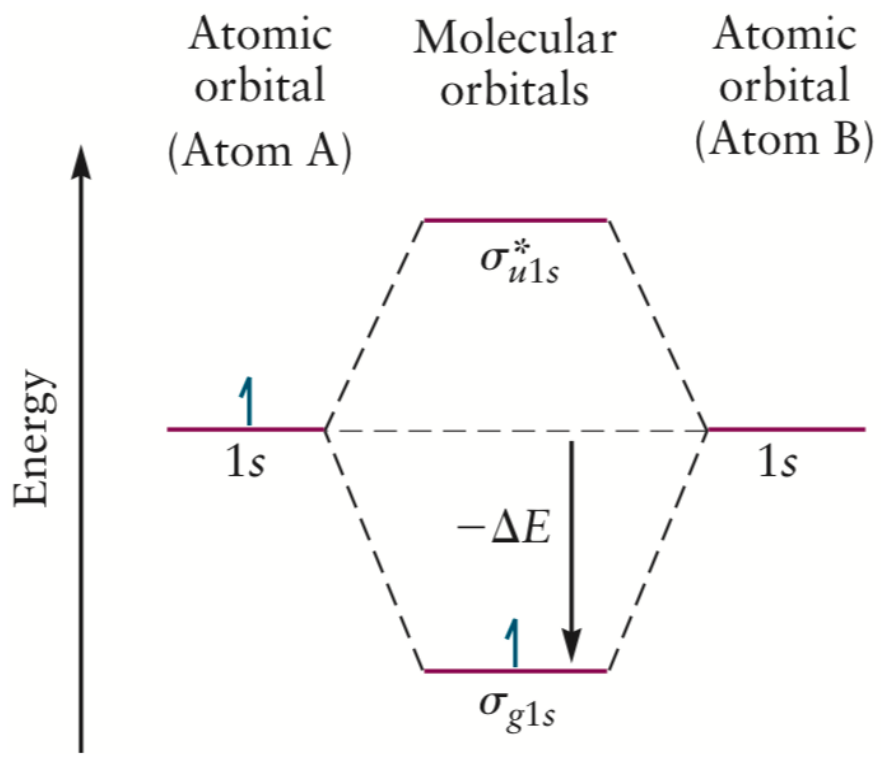
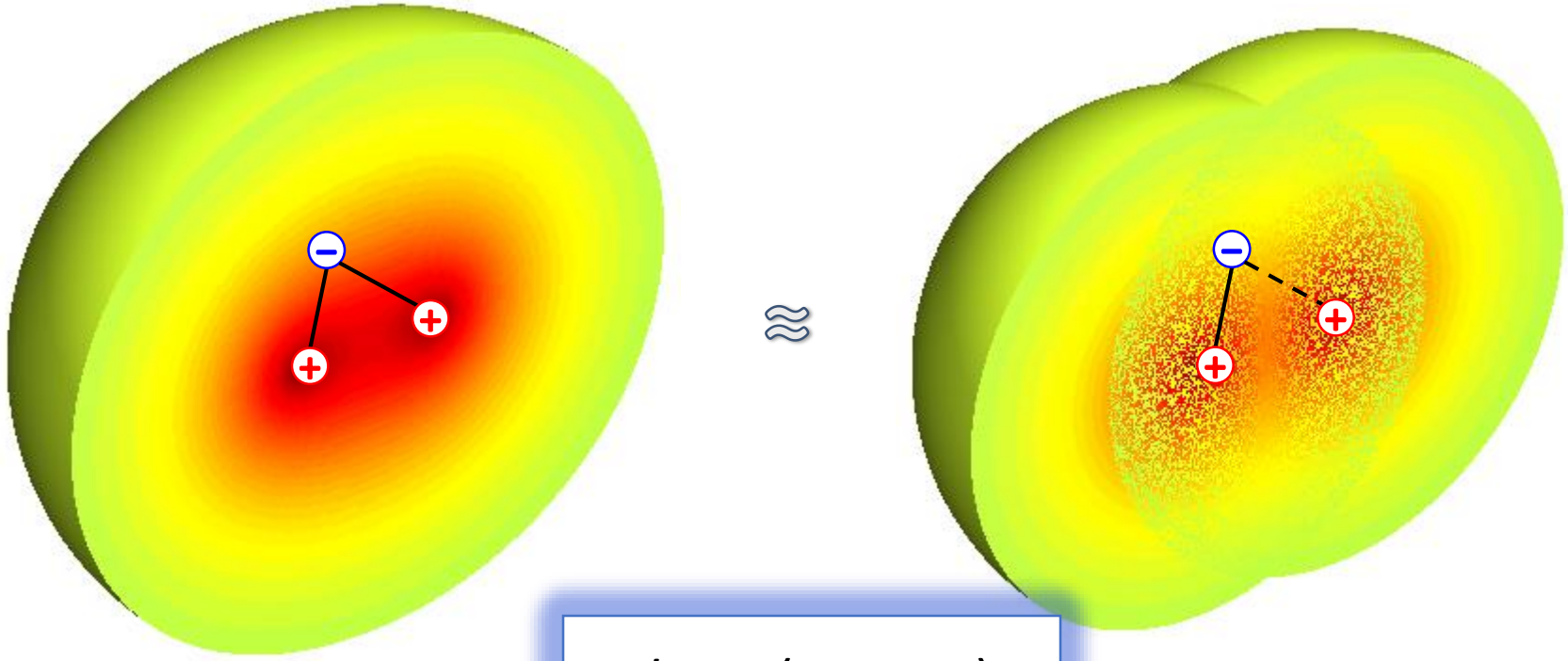



**FIGURE 6.10** Correlation diagram for $H_2^+$ in the linear combination of atomic orbitals (LCAO) approximation. The bonding orbital is stabilized relative to the noninteracting system by the energy difference $-\Delta E$.

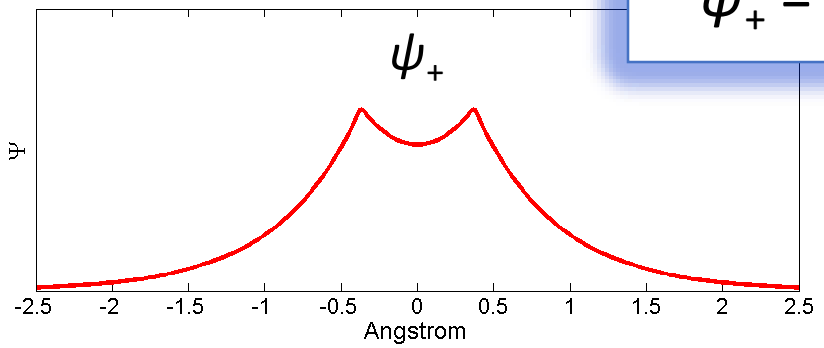
**Correlation diagram (轨道相关图):** **the energy-level diagram within the LCAO approximation**

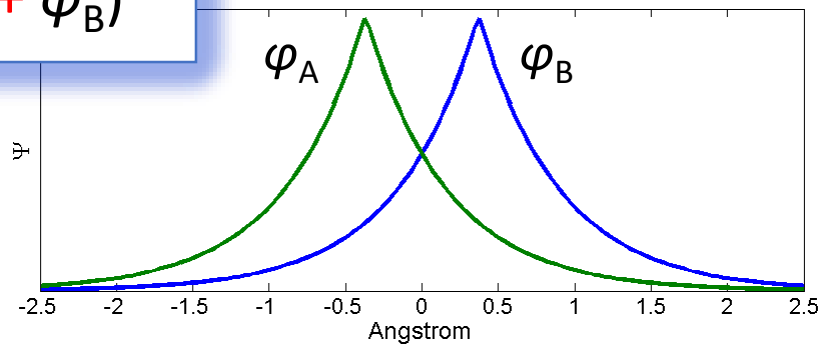
**Two 1s AOs have been combined to give a $\sigma_{g1s}$ MO with energy lower than the AOs and a $\sigma^*_{u1s}$ MO with energy higher than the AOs.**

# Summary: LCAO



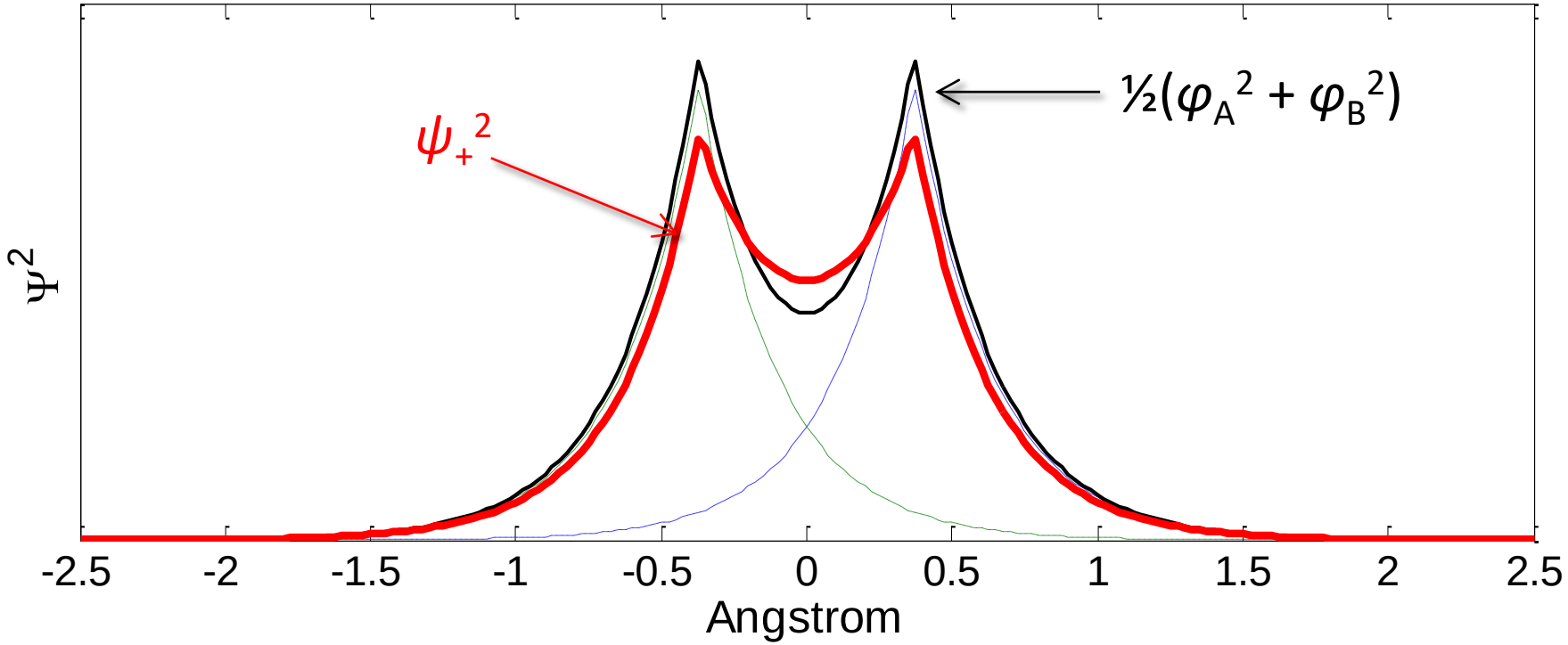
$$\psi_+ = c(\varphi_A + \varphi_B)$$



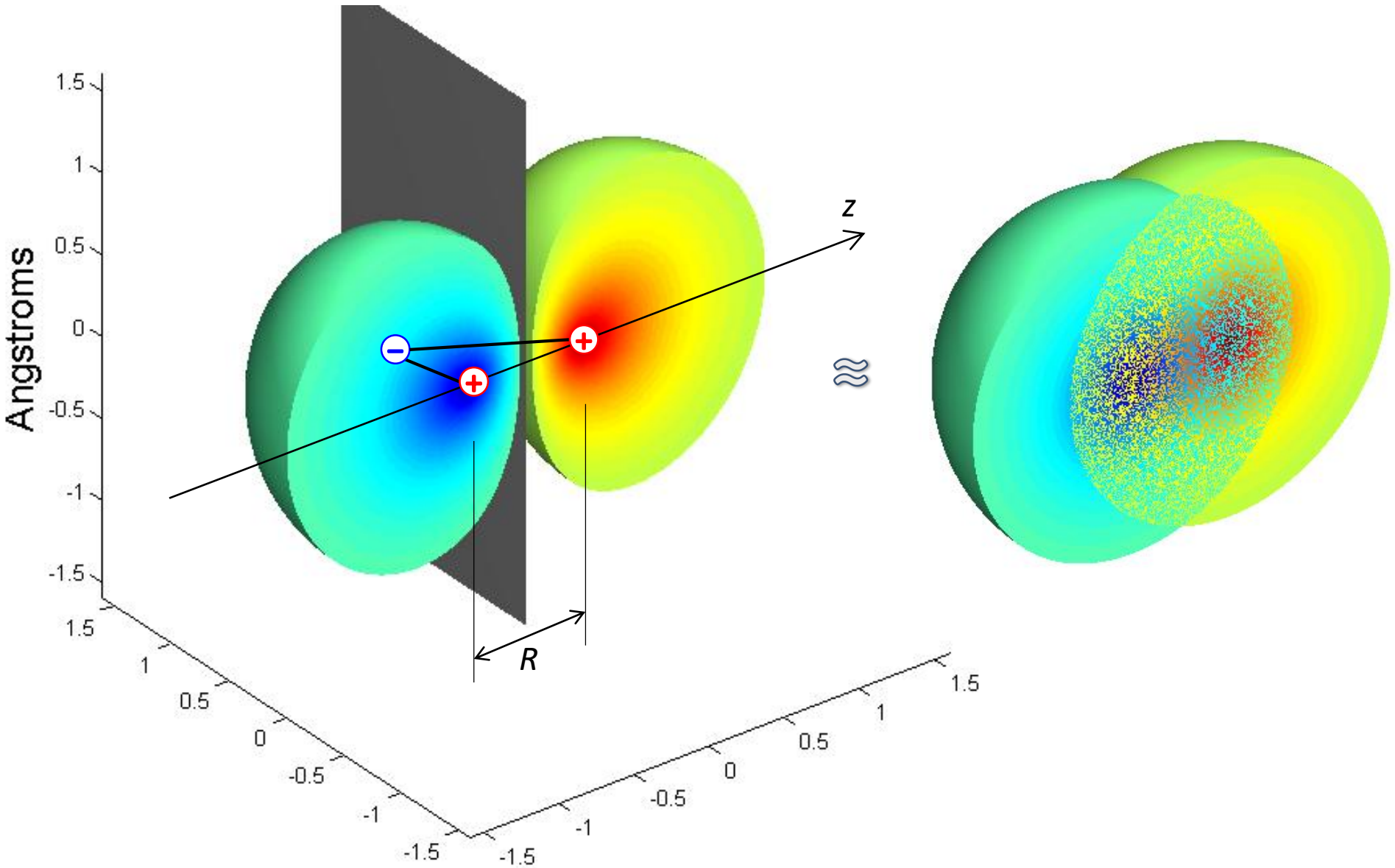



# Summary: Bonding from Constructive Interference

$$\psi_+^2 = c^2(\varphi_A + \varphi_B)^2 = c^2(\varphi_A^2 + \varphi_B^2 + 2\varphi_A\varphi_B)$$



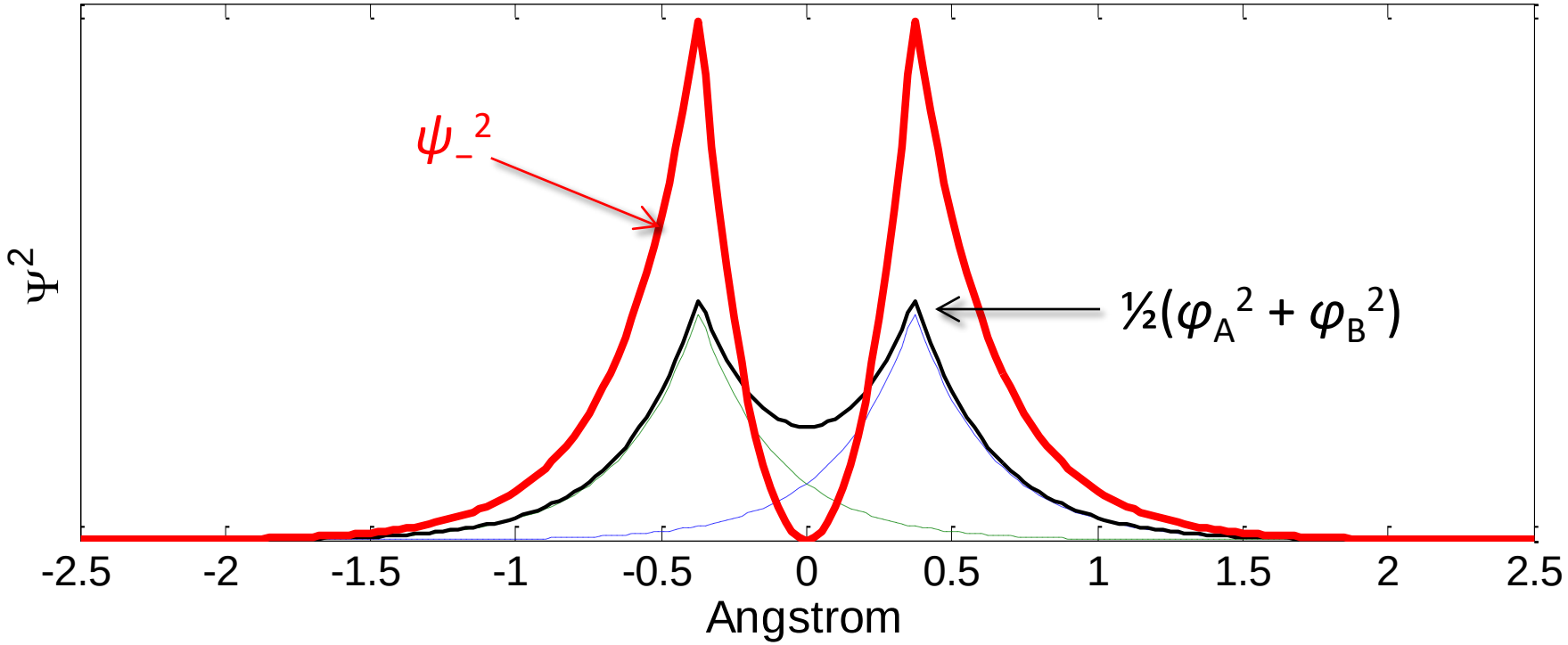
# Summary: Antibonding Orbital



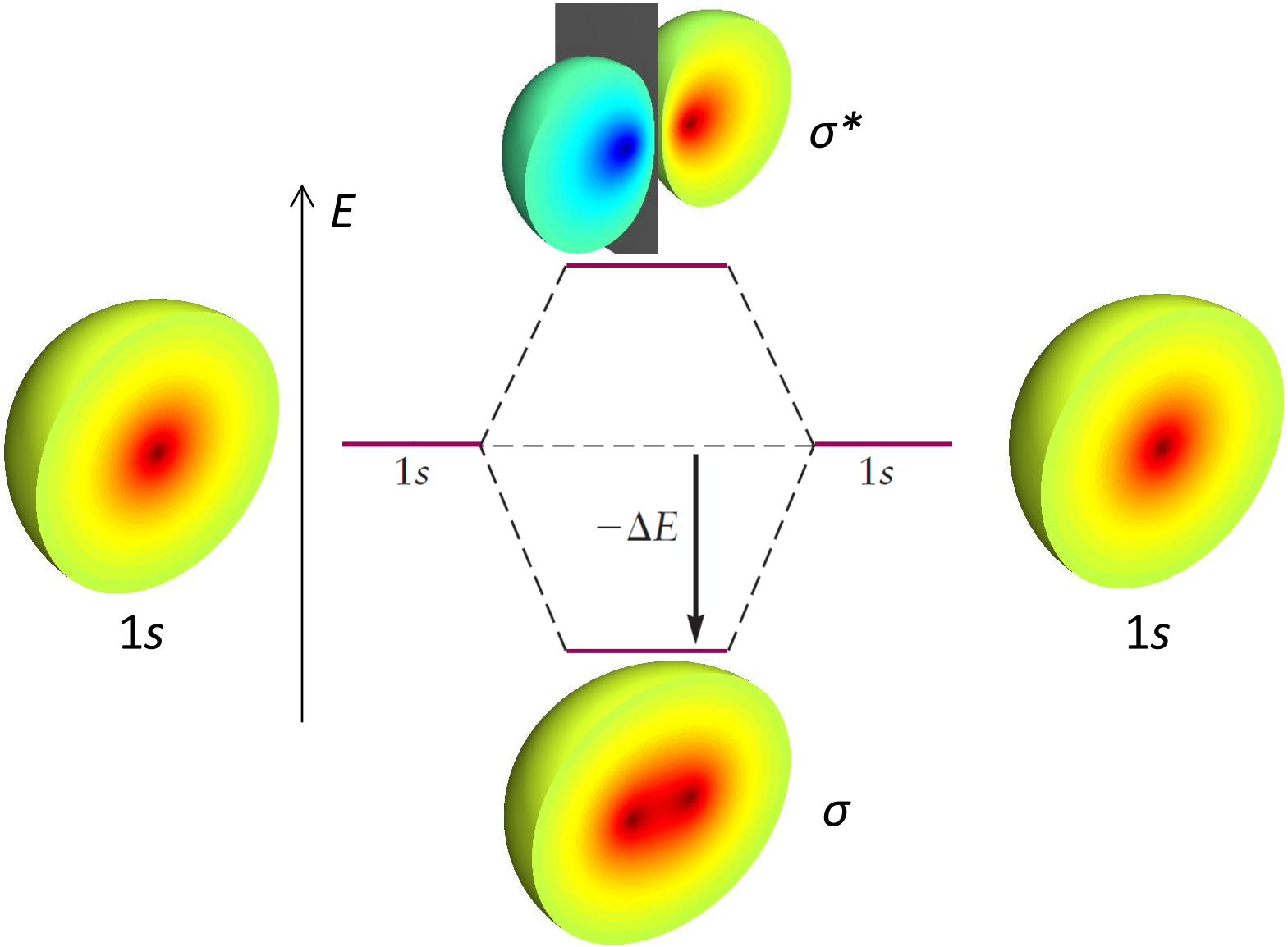
# Summary: Antibonding from Destructive Interference

反键

$$\psi_-^2 = c^2(\varphi_A - \varphi_B)^2 = c^2(\varphi_A^2 + \varphi_B^2 - 2\varphi_A\varphi_B)$$



# Summary: Orbital Correlation Diagram 轨道相关图



**In constructing MOs and predicting their behavior by the overlap argument: the relative phases of the two AOs are critical in determining whether the resulting MO is bonding or antibonding.**

**Bonding orbitals form through the overlap of wave functions with the same phase, by constructive interference of "electron waves".**

**Antibonding orbitals form through the overlap of wave functions with opposite phase, by destructive interference of "electron waves."**

# Major points of today's lecture

- **Quantum mechanics and molecular structure**

1. **Quantum Picture of the Chemical Bond**
2. **Exact Molecular Orbitals (MO) for the Simplest Molecule $H_2^+$**
3. **Molecular Orbital Theory and the Linear Combination of Atomic Orbitals Approximation for $H_2^+$**
4. **Homonuclear Diatomic Molecules: First-Period Atoms**
5. **Homonuclear Diatomic Molecules: Second-Period Atoms**
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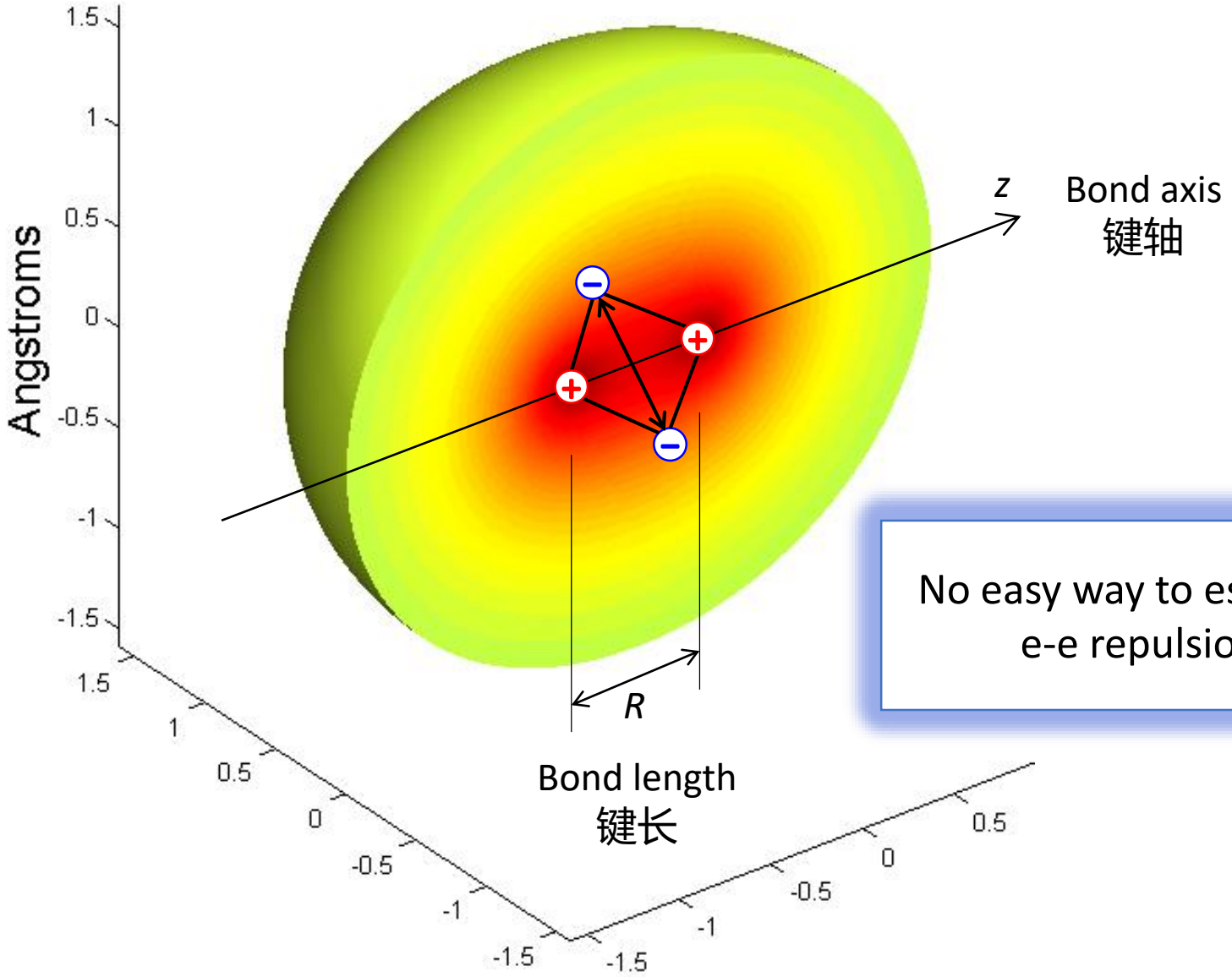
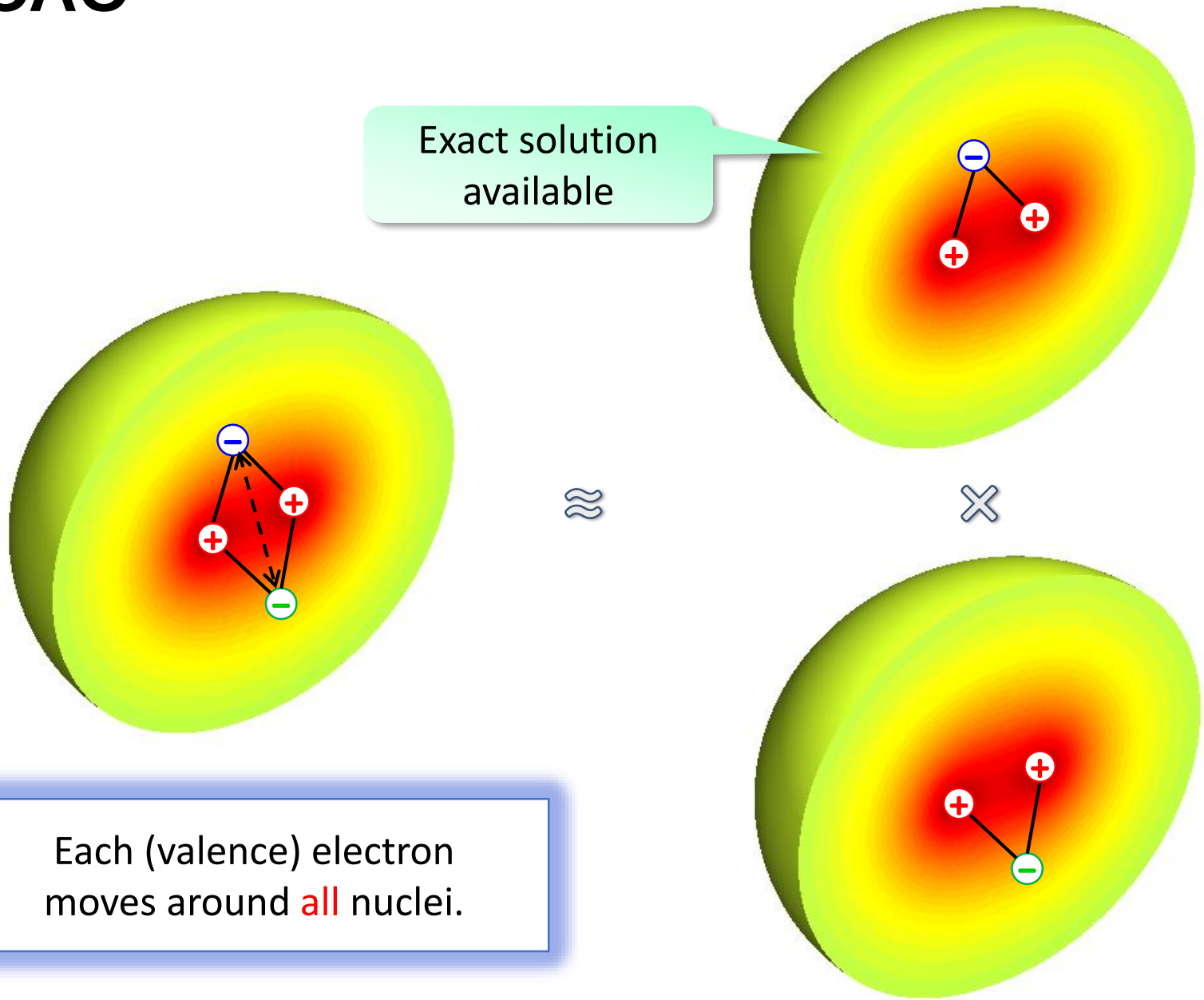
7. **Summary Comments for the LCAO Method and Diatomic Molecules**

# $H_2$: the Simplest Molecule




No easy way to estimate e-e repulsion

# Summary: LCAO




Each (valence) electron moves around all nuclei.

# Homonuclear Diatomic Molecules: First-Period Atoms

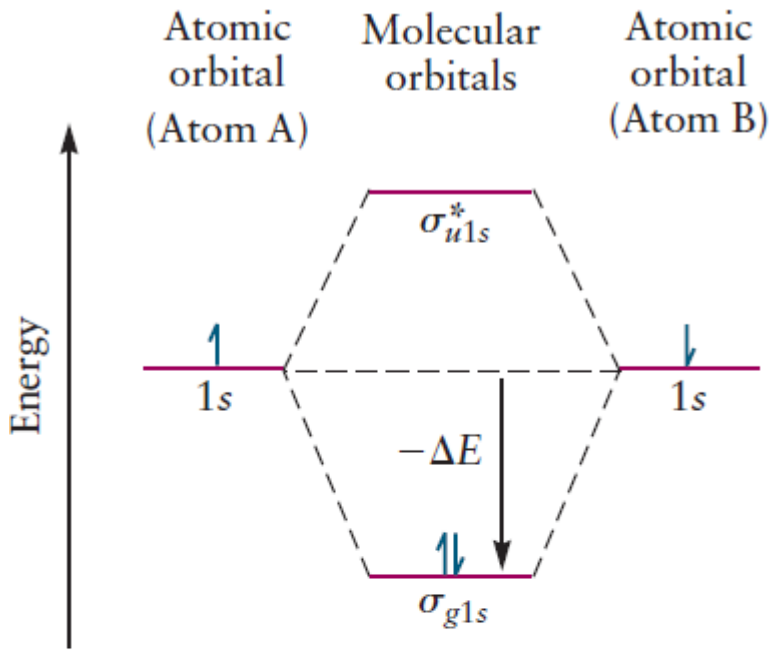



**FIGURE 6.11** Correlation diagram for first-period diatomic molecules. Blue arrows indicate the electron filling for the $H_2$ molecule. All of the atomic electrons are pooled and used to fill the molecular orbitals following the aufbau principle. In the molecules, electrons are no longer connected to any particular atom.

**Combine the LCAO method with an aufbau principle:**

**Electrons available from the two atoms are "fed" into the molecular orbitals, starting with the MO of lowest energy.**

# Homonuclear Diatomic Molecules: First-Period Atoms

**First-Period Atoms: the LCAO approximation can be applied in this same way to $He_2^+$ and $He_2$**

- **One change: the electrons in $He_2^+$ and $He_2$ experience a potential close to that in a He atom (Use He 1s AOs instead of H 1s AOs).**

**The equations for the MOs:**

$$\sigma_{g1s} = C_g[\varphi_{1s}^{A}(\mathrm{He}) + \varphi_{1s}^{B}(\mathrm{He})]$$

$$\sigma_{u1s}^{*} = C_u[\varphi_{1s}^{A}(\mathrm{He}) - \varphi_{1s}^{B}(\mathrm{He})]$$

**A simper notation:**

$$\sigma_{g1s} = C_g[1s^{A} + 1s^{B}]$$

$$\sigma_{u1s}^{*} = C_u[1s^{A} - 1s^{B}]$$

# Homonuclear Diatomic Molecules: First-Period Atoms

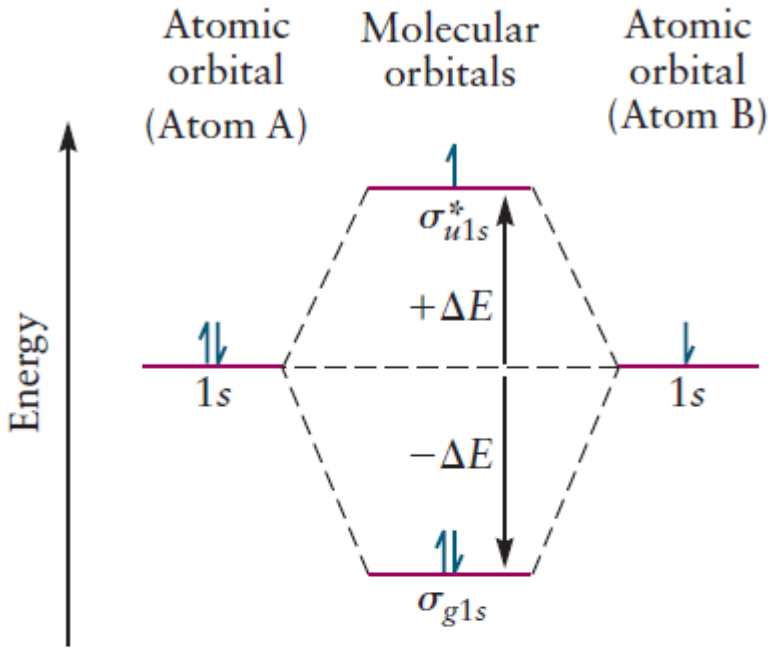



**FIGURE 6.12** Correlation diagram for first-period diatomic molecules. Blue arrows indicate the electron filling for the $He_2^+$ molecule. The aufbau principle fills the bonding orbital with two electrons, so the third electron must go into the antibonding orbital, thus reducing the bond order compared with that in $H_2$.

**$He_2^+$ and $He_2$ > 2 electrons: the aufbau principle requires them to have some electrons in the $\sigma^*_{u1s}$ antibonding orbital.**

- **Each of these electrons contributes a destabilization energy in the amount E relative to the separated helium atoms.**

- **This effect competes with the stabilization energy of E per electron in the $\sigma_{g1s}$ bonding orbital, giving a weak bond in $He_2^+$ and no stable bond in $He_2$.**

# Homonuclear Diatomic Molecules: First-Period Atoms

- **In bonding MOs: bond formation arises from the sharing of electrons. The average electron density is greatest between the nuclei and tends to pull them together.**
- **Electrons that are shared in an antibonding MO tend to force the nuclei apart, reducing the bond strength.**

$$\text{bond order} = \frac{1}{2}\,(\text{number of electrons in bonding molecular orbitals} - \text{number of electrons in antibonding molecular orbitals})$$

# Bond Order

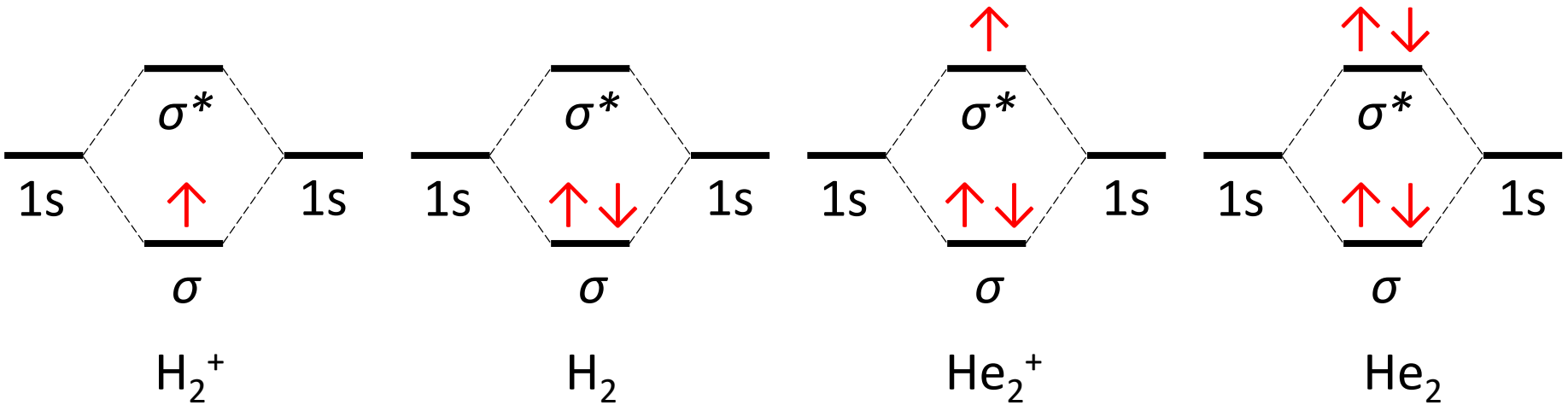



**TABLE 6.2**

**Electron Configurations and Bond Orders for First-Row Diatomic Molecules**

| Species | Electron Configuration | Bond Order | Bond Energy (kJ mol$^{-1}$) | Bond Length (Å) |
|---|---|---|---|---|
| $H_2^+$ | $(\sigma_{g1s})^1$ | $\frac{1}{2}$ | 255 | 1.06 |
| $H_2$ | $(\sigma_{g1s})^2$ | 1 | 431 | 0.74 |
| $He_2^+$ | $(\sigma_{g1s})^2(\sigma^*_{u1s})^1$ | $\frac{1}{2}$ | 251 | 1.08 |
| $He_2$ | $(\sigma_{g1s})^2(\sigma^*_{u1s})^2$ | 0 | ~0 | Large |

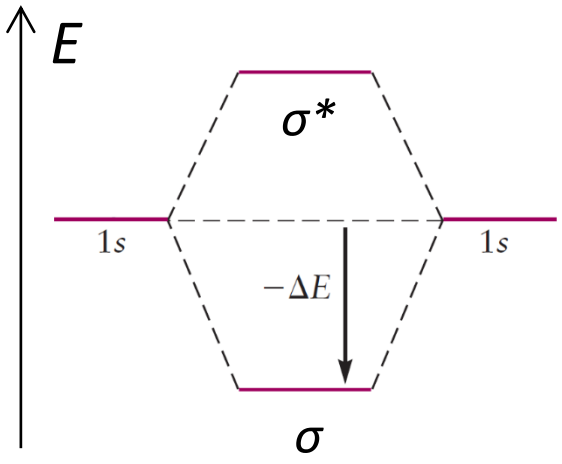
# Homonuclear Diatomic Molecules: First-Period Atoms

systematic procedure: three steps

1. Form linear combinations of the minimum basis set of AOs to generate MOs. The total number of MOs formed in this way must equal the number of AOs used.

2. Arrange the MOs in order from lowest to highest energy.

3. Put in electrons (at most two electrons per MO), starting from the orbital of lowest energy. Apply Hund's rules when appropriate.




Molecular orbitals *do not* change:

- Total number of orbitals
- Total energy of all orbitals
- Total number of electrons

Give the ground-state electron configuration and the bond order of the $He_2^+$ molecular ion.

**Homework: read “principle of modern chemistry”, chapter 6.1; 6.2; 6.3; 6.4;**