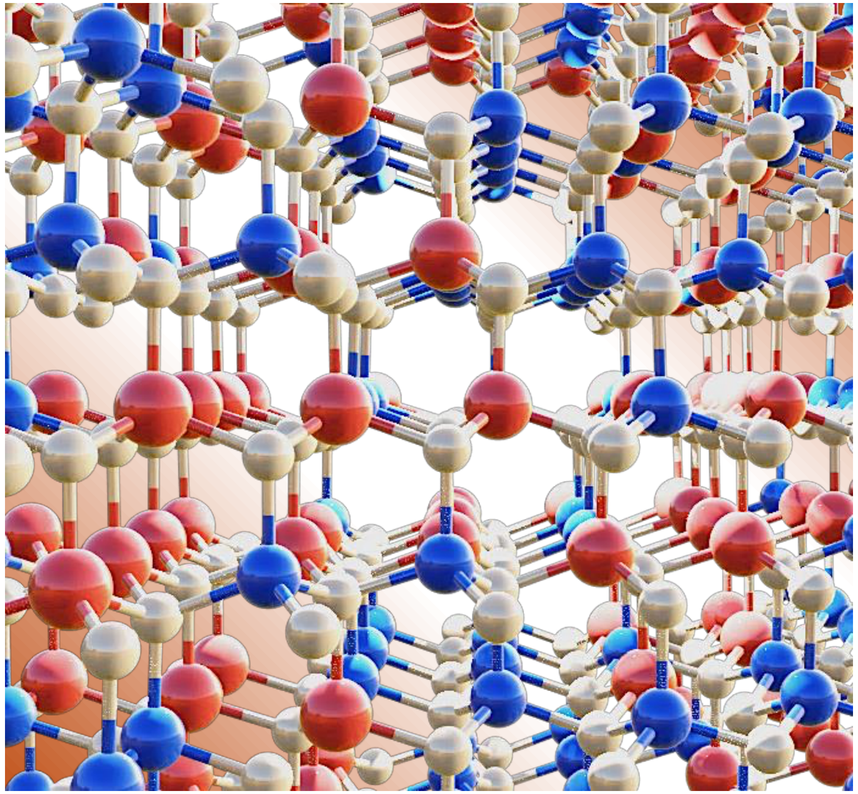
The physics of nitride semiconductors

Lecture 1: Overview of quantum mechanics, and introduction to band theory



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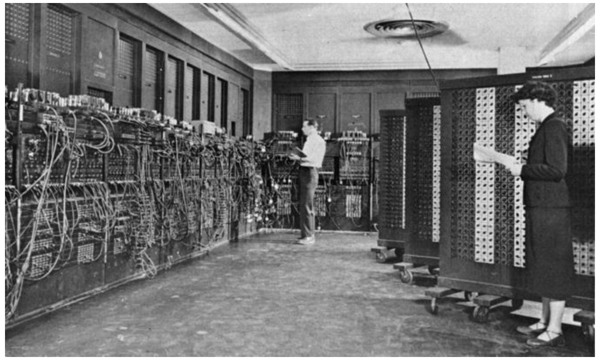
Semiconductors and their applications



ENIAC: first programmable, electronic, general-purpose digital computer, 1945-1955. Based on vacuum tubes. ~ 500 floating-point operations per second (Flops)

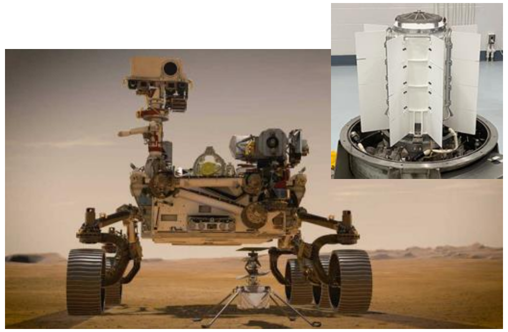
Today's smartphones: ~ 100 **G**Flops

Today's state of the art supercomputers:
~4 **P**Flops

Solar cells

Efficient light emitters

Indoor agriculture



Thermoelectric electricity production from heat

Nitrides: important for energy efficient lighting

Incandescent

Fluorescent

LED

- To **manufacture modern nitride electronic and optoelectronic devices**, we need to understand the behavior of electrons in nitrides and how they interact with external inputs (voltage, light, heat, pressure).
- Also, we need to **understand the interactions of light and electrons with materials** in order to develop modern characterization tools to study materials at the atomic scale.
- The behavior of electrons at the atomic scale and the interactions of light with materials <u>cannot</u> be described with the laws of classical mechanics (i.e., Newton's laws).
- To understand the electrons in electronic materials and devices, we need to apply the principles of **quantum mechanics**

Wave properties of matter

Classical physics:

Particles: localized, indivisible
Waves: extended, divisible

	Particle	Wave
Electron	✓	✗
Light	✗	✓

Quantum Physics:

	Particle	Wave
Electron	✓	?
Light	?	✓

Wave properties of matter

Classical physics:

Particles: localized, indivisible
Waves: extended, divisible

	Particle	**Wave**
Electron	✓	✗
Light	✗	✓

Quantum Physics:

	Particle	**Wave**
Electron	✓	**?**
Light	✓	✓

Evidence: Photoelectric effect, blackbody radiation, Compton scattering, X-rays

Photon energy $E = hf$ Photon momentum $p = h/\lambda$

h = Planck’s constant = 6.626×10^{-34} J s

Wave properties of matter

Classical physics:

Particles: localized, indivisible
Waves: extended, divisible

	Particle	Wave
Electron	✓	✗
Light	✗	✓

Electrons also have wave-like properties!
Wavelength λ = h/p, frequency f = E/h

Quantum Physics:

	Particle	Wave
Electron	✓	✓
Light	✓	✓

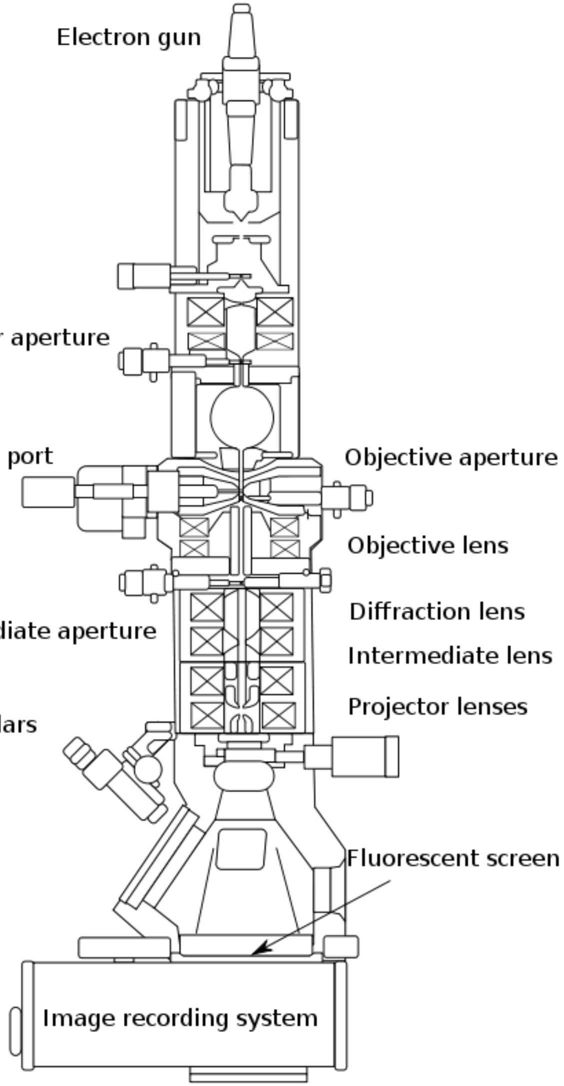
Evidence: Photoelectric effect, blackbody radiation, Compton scattering, X-rays
Photon energy $E = hf$ Photon momentum $p = h/\lambda$
h = Planck's constant = 6.626×10^{-34} J s

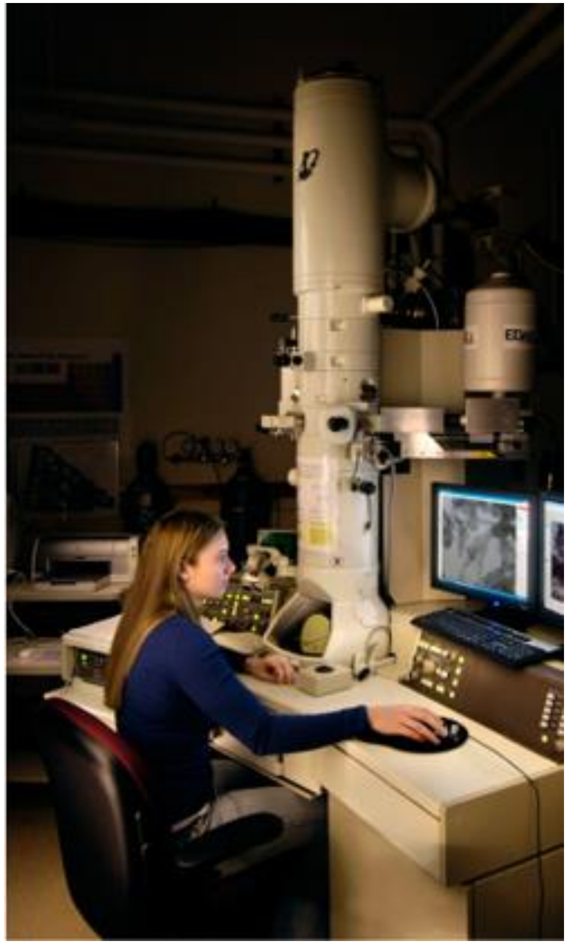
Proof and application: the electron microscope

Transmission electron microscope (TEM)

Uses electron waves to image materials

Wavelength of electrons shorter than wavelength of light, can image materials with sub-atomic resolution





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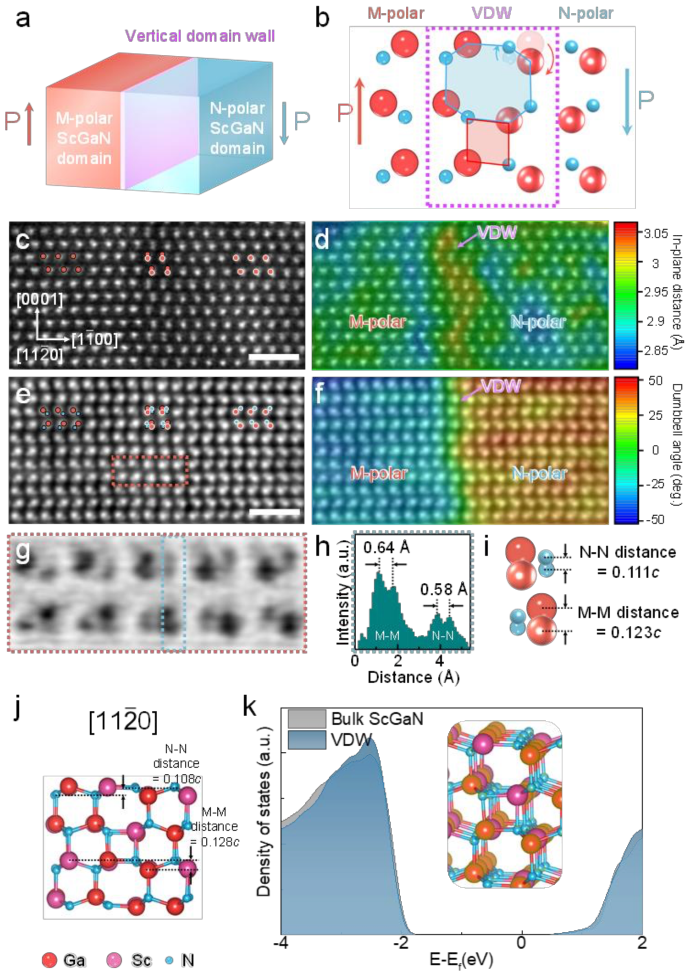
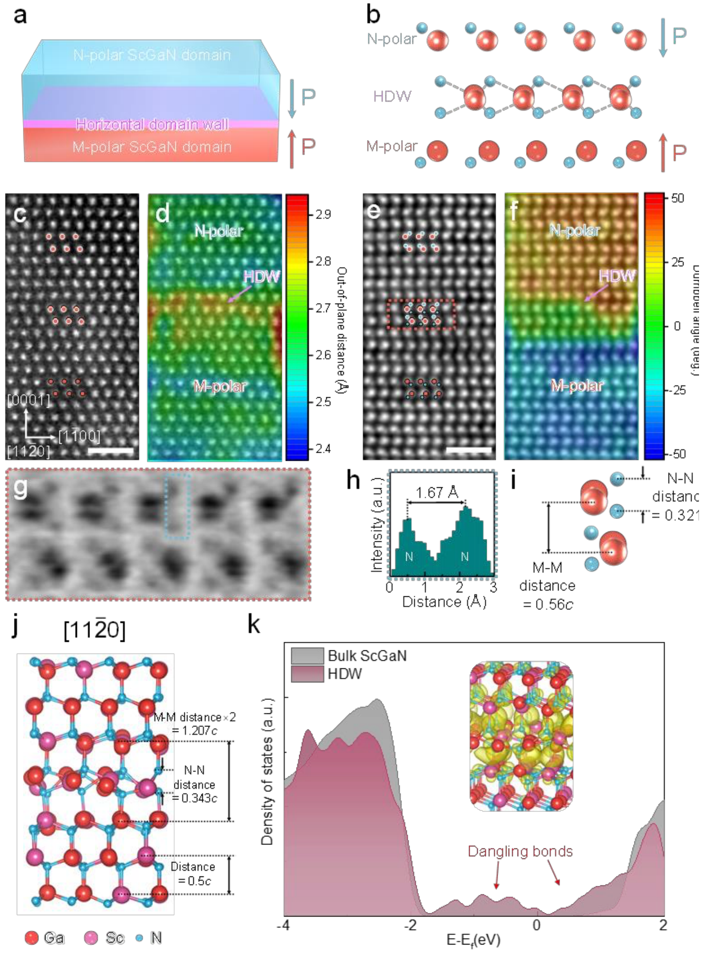
Application: seeing domain walls in ferroelectric ScGaN

Vertical charge-neutral domain walls



Horizontal charged domain walls, stabilized by dangling bonds



Images from D. Wang, ..., E. Kioupakis, Z. Mi, “Electric-Field-Induced Domain Walls in Wurtzite Ferroelectrics”, in press (https://arxiv.org/abs/2312.08645v2)

Particle waves

The electron has energy *E* and momentum *p*. Its wavelength *λ* and frequency *f* are given by:

$$E = hf \rightarrow f = E/h$$

$$p = \frac{h}{\lambda} \rightarrow \lambda = \frac{h}{p}$$

Ψ = **wave function** = wave associated with motion of electron

(just like the electric field is for photons)

$$P(x,t) = |\Psi(x,t)|^2$$

= probability of finding an electron at (x,t)

→ Quantum mechanics describes probabilities

$$\int_{-\infty}^{\infty} P(x,t)dx = \int_{-\infty}^{\infty} |\Psi(x,t)|^2 \, dx = 1$$

Normalization condition

Quantum Mechanics

It is a rigorous formalism to describe the motion of probability waves (wave functions) associated with the motion of particles (e.g., electrons) under the influence of an external potential (e.g., atomic nuclei or other electrons).

Also, it is a recipe of how to derive all measurable quantities of a particle (position, momentum, energy, interaction with light, etc.) from the knowledge of the wave function.

Key finding (1926): **Schrödinger’s equation**, the equation that determines the wave function given the external potential.

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t) + V(x,t)\Psi(x,t)$$

Schrödinger’s equation

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t) + V(x,t)\Psi(x,t)$$

What is V(x,t)? A: the potential energy that electrons experience (e.g., attraction by the nuclei, electric field in electronic devices, oscillating electric field in optical devices)

What is i ? A: imaginary number $i^2 = -1$. Wave functions are complex! Cannot be measured

To fully determine Ψ(x,t) we also need:

- *Boundary conditions*: Value of Ψ at boundary (determined by the problem we need to solve)
- *Initial condition*: Value of Ψ at t=0

Once we find Ψ(x,t), we can determine all measurable properties of the system.

Time-independent Schrödinger equation

If V(x,t)=V(x) only (independent of t) then write Ψ as:

$$\Psi(x,t) = \psi(x) f(t)$$

Separate time-*dependent* Schrödinger into two equations:

$$\begin{cases} f(t) = e^{-i\omega t} \\ \boxed{-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi(x) = E\psi(x)} \end{cases}$$

Time-*independent* Schrödinger equation (+ boundary conditions).
Energy eigenvalue problem, solve to find energy and ψ(x).

Example 1: particle in an infinite square well

$$V(x) = \begin{cases} \infty & x \leq 0,\ x \geq L \\ 0 & 0 < x < L \end{cases}$$

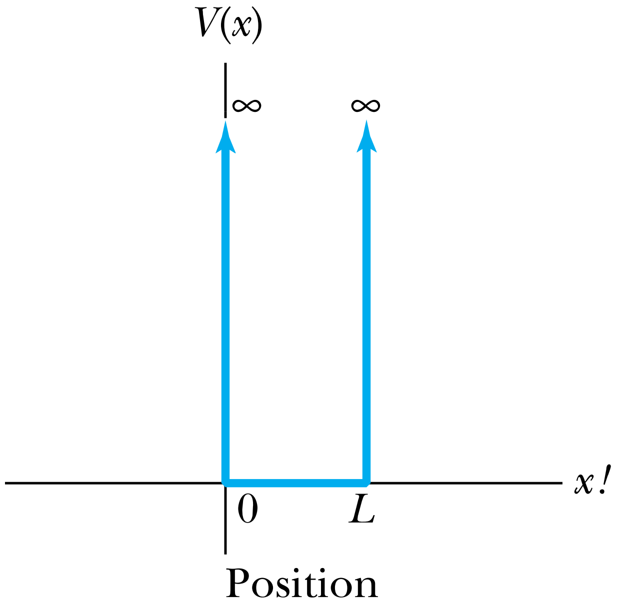
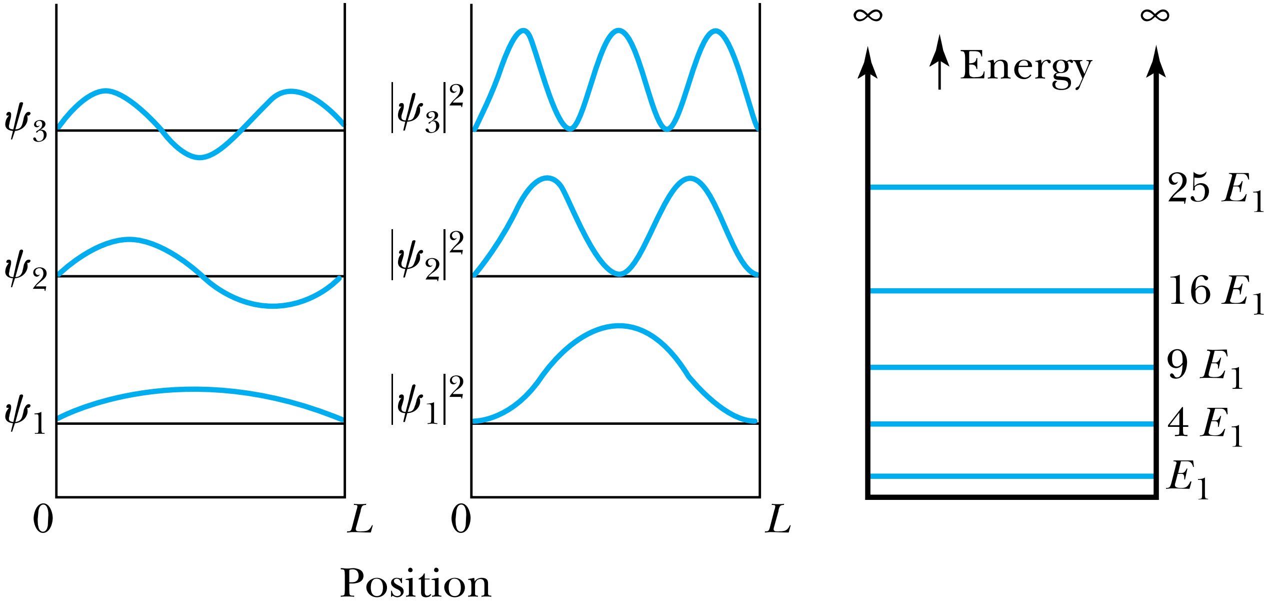


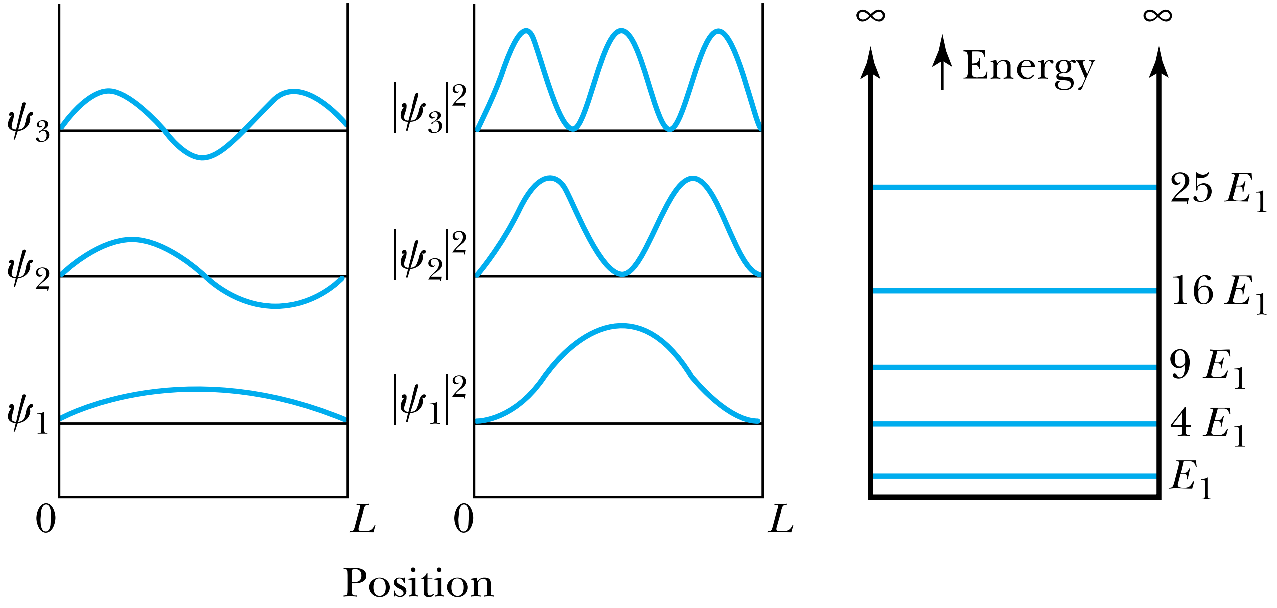
Figure 6.2 Infinite square-well potential. The potential is $V = \infty$ everywhere except the region $0 < x < L$, where $V = 0$.



$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad (n = 1, 2, 3, \ldots)$$

$$E_n = n^2 \frac{\pi^2 \hbar^2}{2mL^2} \quad (n = 1, 2, 3, \ldots)$$

Some key observations:



$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) \quad (n = 1, 2, 3, \ldots)$$

$$E_n = n^2\frac{\pi^2\hbar^2}{2mL^2} \quad (n = 1, 2, 3, \ldots)$$

- Ground state energy (n=1) is not zero → **zero point motion**. Electron is not at rest even at T = 0 K.
- Ground-state energy (which is kinetic energy only) increases as +1/L^2 with decreasing L → Increases more than attraction by the nucleus in atoms (~–1/L), therefore **electrons cannot fall into the nucleus**.
- Wave functions are oscillatory**. Ground state has no nodes** (no zeros). One more node (zero of wave function) for each increasing value of *n*.
- Wave functions are **orthogonal** to each other:

$$\int_{-\infty}^{\infty}\psi_m^*(x)\psi_n(x)dx$$

If m=n → Integral = 1
If m≠n → Integral = 0

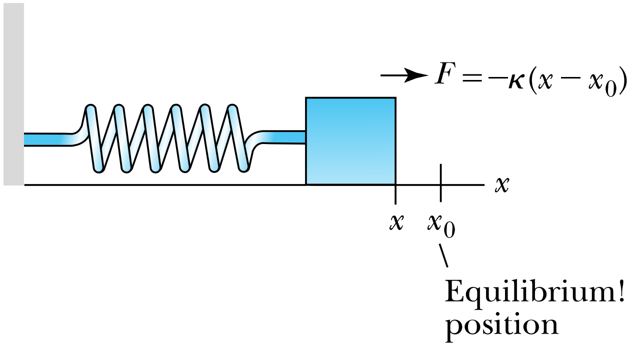
- Wave functions are **complete**: any wave function can be written as a linear combination of solutions to Schrödinger.

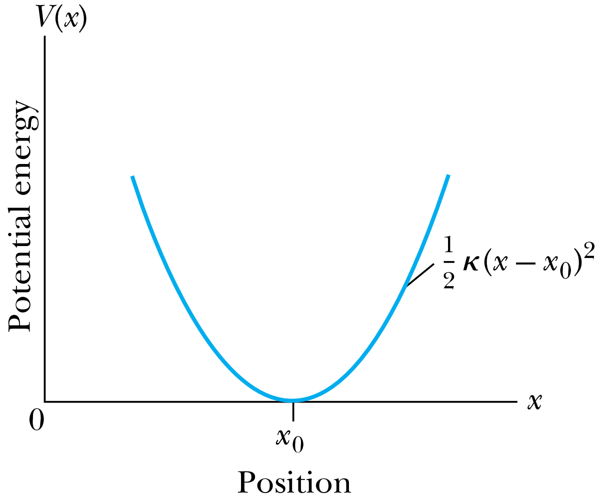
$$f(x) = \sum_{n=1}^{\infty} c_n\psi_n(x)$$

$$c_n = \int_{-\infty}^{\infty}\psi_n^*(x)f(x)dx$$

Example 2: Quantum harmonic oscillator

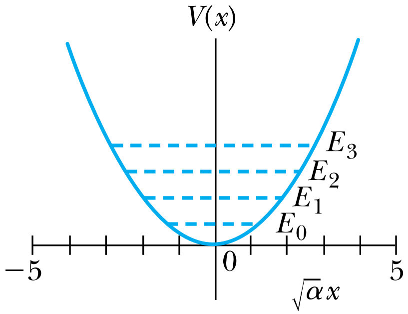
$$V(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2x^2,\ \omega = \sqrt{\frac{k}{m}}$$





Solution:

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega$$
$$= \left(n + \frac{1}{2}\right)\hbar\sqrt{\frac{k}{m}},\ n = 0, 1, 2, 3, \ldots$$

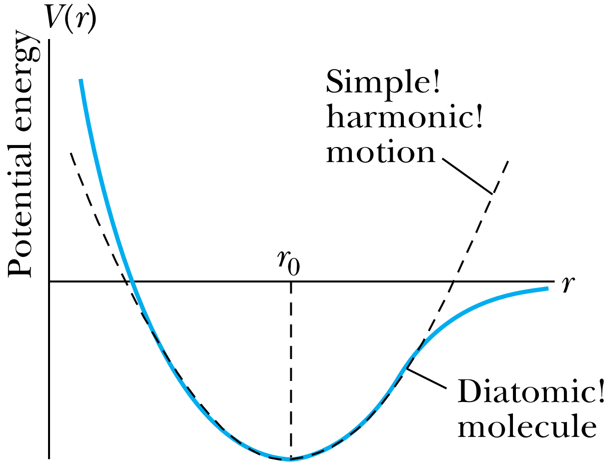


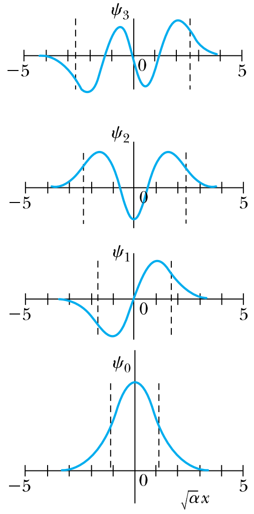
Wave functions

$$\psi_3(x) = \left(\frac{\alpha}{\pi}\right)^{1/4}\frac{1}{\sqrt{3}}\left(\sqrt{\alpha}x\right)\left(2\alpha x^2 - 3\right)e^{-\alpha x^2/2}$$
$$\psi_2(x) = \left(\frac{\alpha}{\pi}\right)^{1/4}\frac{1}{\sqrt{2}}\left(2\alpha x^2 - 1\right)e^{-\alpha x^2/2}$$
$$\psi_1(x) = \left(\frac{\alpha}{\pi}\right)^{1/4}\sqrt{2\alpha}\ xe^{-\alpha x^2/2}$$
$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4}e^{-\alpha x^2/2}$$

Why is it important?
Every potential is harmonic near a minimum.

E.g., atomic vibrations around equilibrium position.





Energy levels are equally spaced.

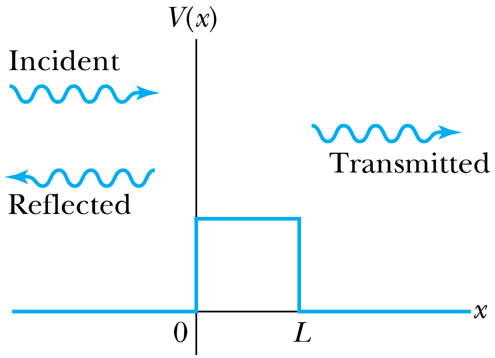
Quantum of vibrational energy = **phonon**

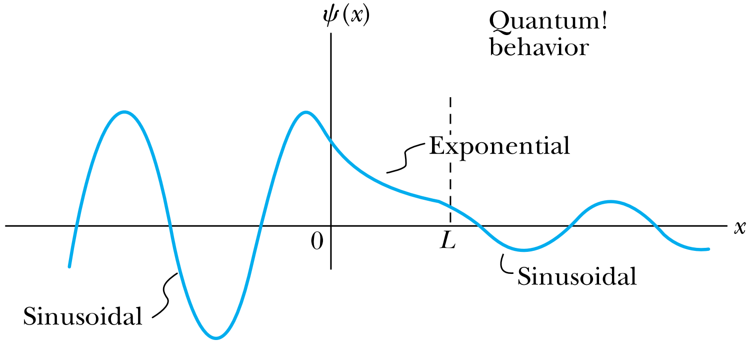
$$\Delta E = \hbar\omega = hf$$

Energy is absorbed and emitted by vibrating atoms in discrete amounts.

Example 3: Quantum tunneling

- Even if $E < V_0$, there is a probability that the particle can make it across the barrier → **Tunneling (transmission probability $T \neq 0$)**
- Even if $E > V_0$, there is a probability that the particle will be reflected at the barrier **(transmission probability $T \neq 1$)**





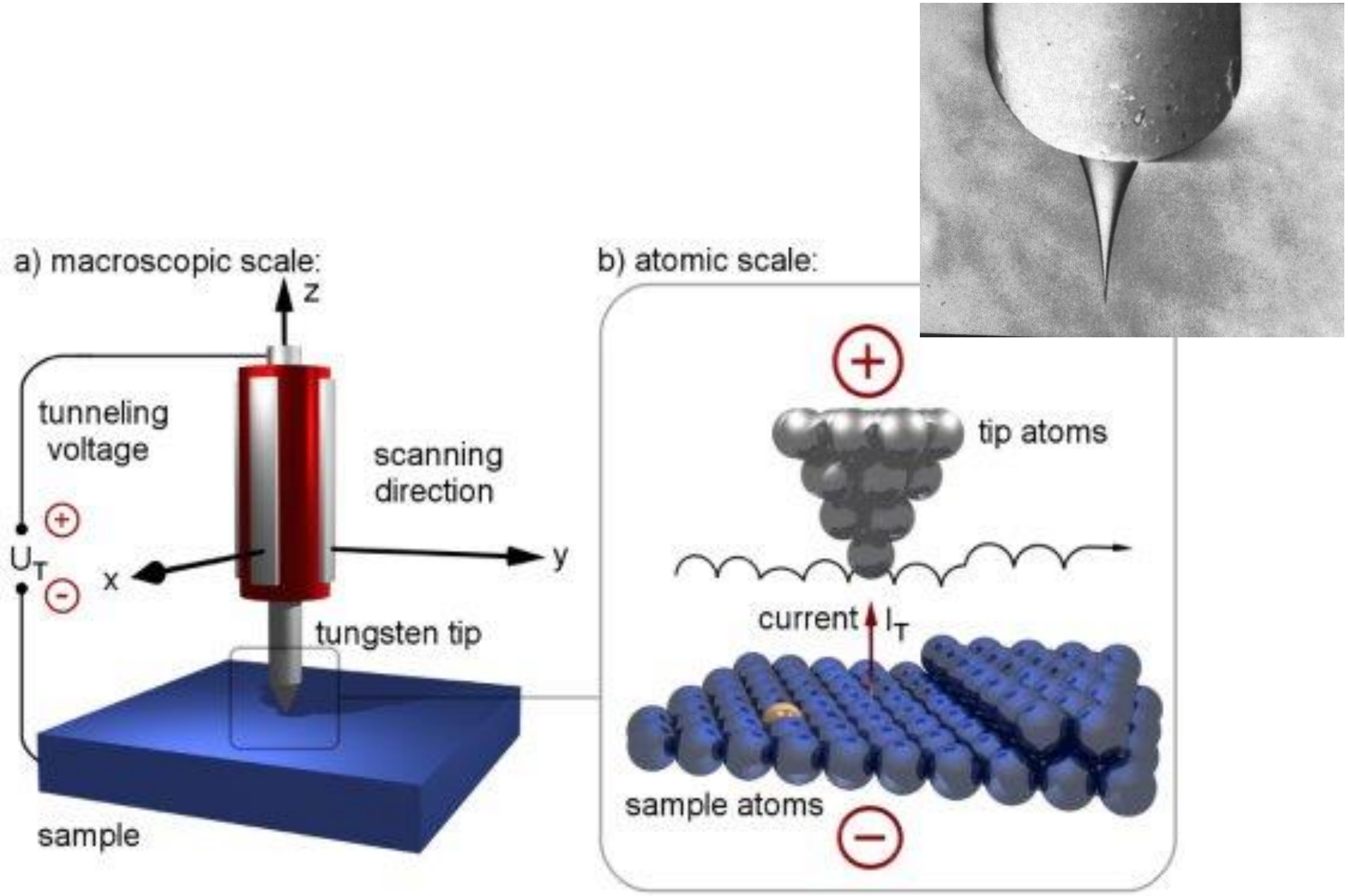
What is the probability T that a particle with energy E will be transmitted across a barrier of width L and height V_0?

Answer:

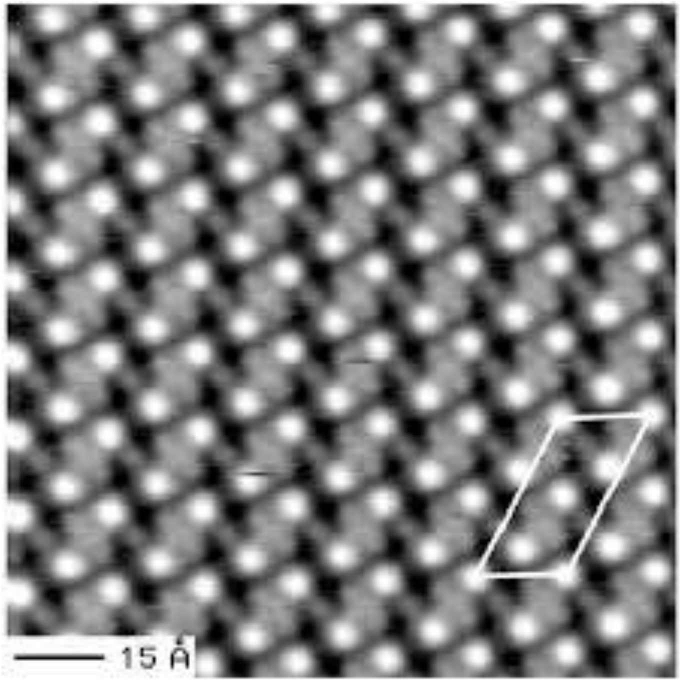
$$\text{For } E < V_0 \text{: } T = \left[1 + \frac{V_0^2 \sinh^2(\kappa L)}{4E(V_0 - E)}\right]^{-1}, \quad \kappa \equiv \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$$

$$\text{For } E > V_0 \text{: } T = \left[1 + \frac{V_0^2 \sin^2(k_2 L)}{4E(E - V_0)}\right]^{-1}, \quad k_2 \equiv \sqrt{\frac{2m(E - V_0)}{\hbar^2}}$$

Application: scanning tunneling microscope



Surface reconstruction of GaN



Smith et al., MRS Online Proceedings Library, **482**, 363 (1997)

Schrödinger’s equation for the hydrogen atom

Electron under the influence of the attractive potential by the proton:

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

3D Schrödinger’s equation:

$$\psi = \psi(x, y, z)$$

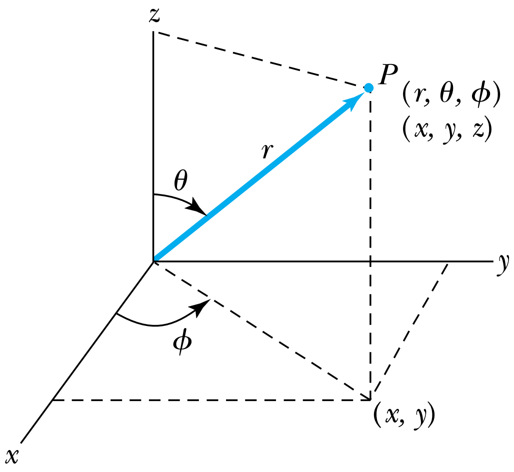
$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + V\psi = E\psi$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi}$$

Schrödinger's equation in spherical coordinates

$$\psi = \psi(r, \theta, \phi)$$



$$r = \sqrt{x^2 + y^2 + z^2}$$

$$\theta = \cos^{-1} \frac{z}{r} \quad \text{(Polar angle)}$$

$$\phi = \tan^{-1} \frac{y}{x} \quad \text{(Azimuthal angle)}$$

$$x = r \sin\theta \cos\phi$$
$$y = r \sin\theta \sin\phi$$
$$z = r \cos\theta$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial \psi}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 \psi}{\partial \phi^2} + \frac{2\mu}{\hbar^2}(E - V)\psi = 0 \qquad (7.3)$$

Three equations, one for each coordinate

$$\psi(r, \theta, \phi) = R(r) f(\theta) g(\phi)$$

Radial equation

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu}{\hbar^2}\left[E - V - \frac{\hbar^2}{2\mu}\frac{\ell(\ell+1)}{r^2}\right]R = 0$$

$$n = 1, 2, 3, 4, ...$$

$$l = 0, 1, 2, 3, ..., n-1$$

$$m_l = -l, -l+1, ..., -1, 0, 1, ..., l-1, l$$

Also: spin quantum number $m_s = +1/2, -1/2$

Angular equation

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{df}{d\theta}\right) + \left[\ell(\ell+1) - \frac{m_\ell^2}{\sin^2\theta}\right]f = 0$$

Azimuthal equation

$$\frac{d^2g}{d\phi^2} = -m_\ell^2 g$$

Only radial equation depends on the potential $V(r)$

→ Angular and azimuthal equations same for all atoms

Solutions to radial equation

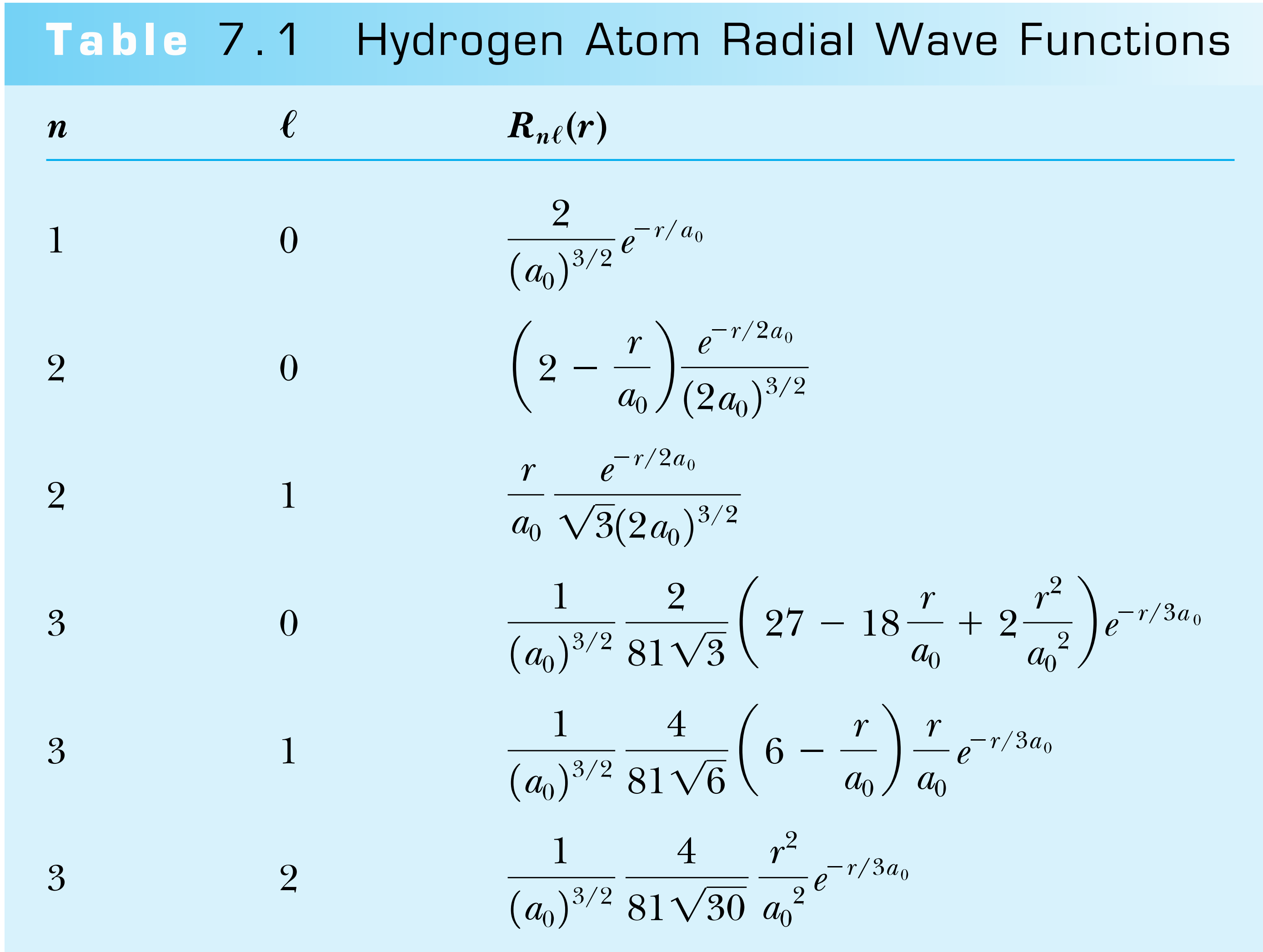
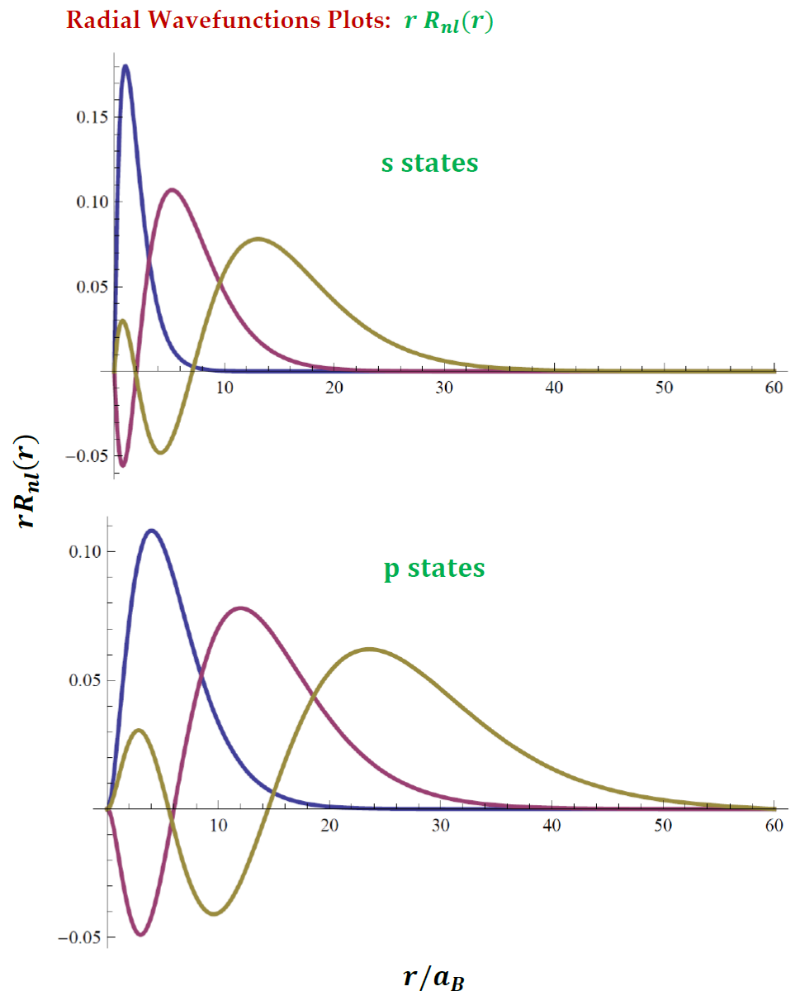


Table 7.1 Hydrogen Atom Radial Wave Functions

n	ℓ	$R_{n\ell}(r)$
1	0	$\dfrac{2}{(a_0)^{3/2}}e^{-r/a_0}$
2	0	$\left(2-\dfrac{r}{a_0}\right)\dfrac{e^{-r/2a_0}}{(2a_0)^{3/2}}$
2	1	$\dfrac{r}{a_0}\dfrac{e^{-r/2a_0}}{\sqrt{3}(2a_0)^{3/2}}$
3	0	$\dfrac{1}{(a_0)^{3/2}}\dfrac{2}{81\sqrt{3}}\left(27-18\dfrac{r}{a_0}+2\dfrac{r^2}{{a_0}^2}\right)e^{-r/3a_0}$
3	1	$\dfrac{1}{(a_0)^{3/2}}\dfrac{4}{81\sqrt{6}}\left(6-\dfrac{r}{a_0}\right)\dfrac{r}{a_0}e^{-r/3a_0}$
3	2	$\dfrac{1}{(a_0)^{3/2}}\dfrac{4}{81\sqrt{30}}\dfrac{r^2}{{a_0}^2}e^{-r/3a_0}$



https://medium.com/modern-physics/hydrogen-atom-4ca1599e94a8

Solutions to angular equation

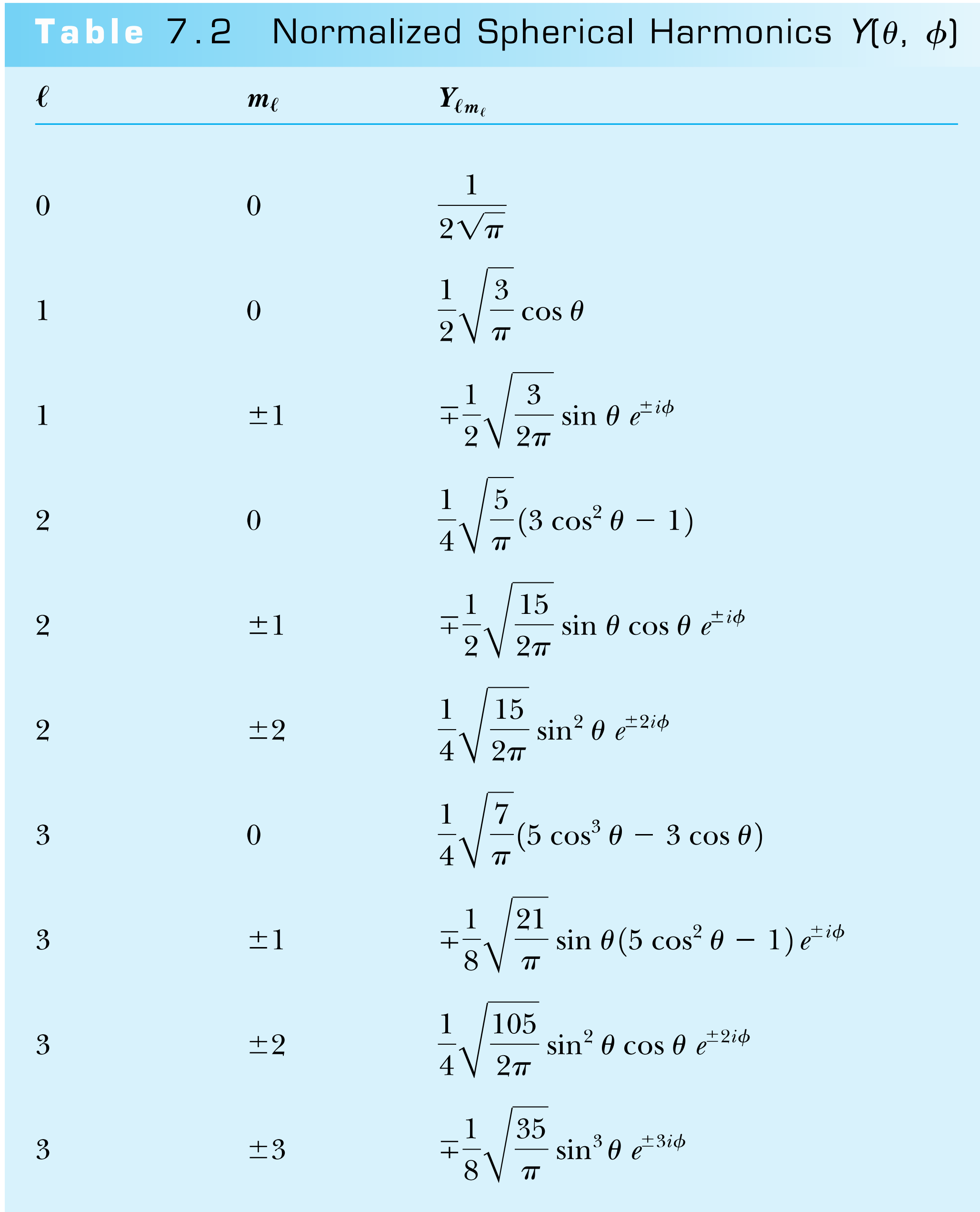
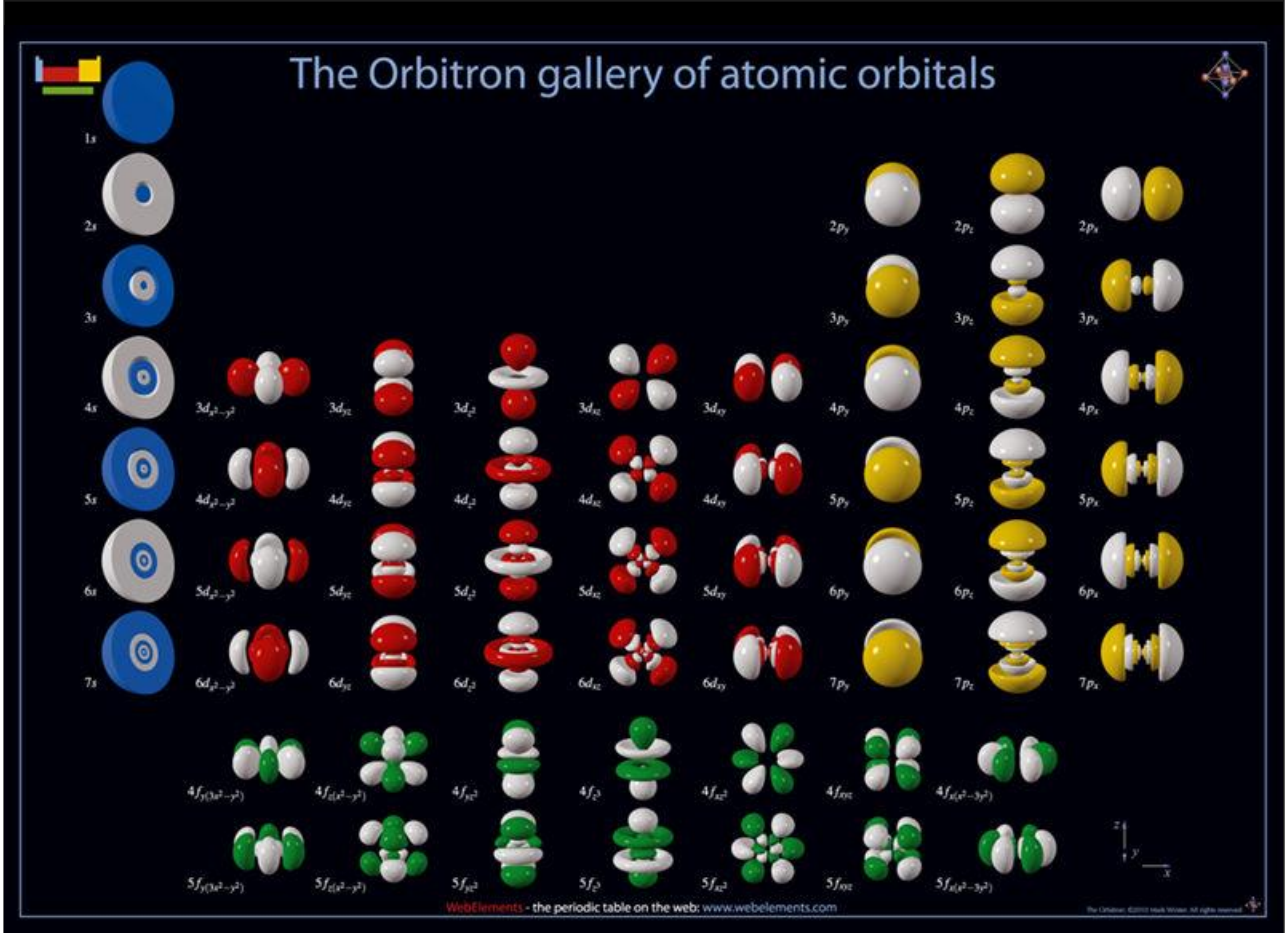


Table 7.2 Normalized Spherical Harmonics $Y(\theta, \phi)$

ℓ	m_ℓ	$Y_{\ell m_\ell}$
0	0	$\frac{1}{2\sqrt{\pi}}$
1	0	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$
1	± 1	$\mp\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta\, e^{\pm i\phi}$
2	0	$\frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$
2	± 1	$\mp\frac{1}{2}\sqrt{\frac{15}{2\pi}}\sin\theta\cos\theta\, e^{\pm i\phi}$
2	± 2	$\frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta\, e^{\pm 2i\phi}$
3	0	$\frac{1}{4}\sqrt{\frac{7}{\pi}}(5\cos^3\theta - 3\cos\theta)$
3	± 1	$\mp\frac{1}{8}\sqrt{\frac{21}{\pi}}\sin\theta(5\cos^2\theta - 1)\, e^{\pm i\phi}$
3	± 2	$\frac{1}{4}\sqrt{\frac{105}{2\pi}}\sin^2\theta\cos\theta\, e^{\pm 2i\phi}$
3	± 3	$\mp\frac{1}{8}\sqrt{\frac{35}{\pi}}\sin^3\theta\, e^{\pm 3i\phi}$



http://www.webelements.com/shop/product/orbitron-atomic-orbitals-poster/

Quantum mechanics of multi-electron atoms

Schrödinger’s equation for Helium atom:

2 electrons, one set of coordinates (r_1, r_2) for each electron

$$\psi = \psi(\vec{r}_1, \vec{r}_2)$$

Wave function of 2 electrons

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

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{1}{4\pi\varepsilon_0}\frac{2e^2}{r_1} - \frac{1}{4\pi\varepsilon_0}\frac{2e^2}{r_2} + \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

K.E. of e #1 K.E. of e #2 P.E. of e #1 P.E. of e #2 e–e interaction

Impossible to solve analytically due to interaction term.
We can solve it numerically using computers.
However, we can learn a lot by analyzing the wave functions of H

Wave functions of multielectron atoms

The wave functions of multielectron atoms have the same functional form as the wave functions of the hydrogen atom:

$$\psi_{n,l,m_l}(r,\theta,\phi) = R_{n,l}(r)Y_{l,m_l}(\theta,\phi)$$

The possible values of the integers n,l,m_l are **exactly the same**.

The spherical harmonics Y_{lml} are **exactly the same** as in the case of hydrogen (and in general for any spherically symmetric potential).

The radial wave functions R(r) and the energies of the orbitals differ from H. They depend on the atomic number of each element and they are determined by the interplay of electron-nucleus and electron-electron interactions. (we will see examples later)

Pauli exclusion principle

To understand multielectron atoms, we need one more quantum principle: **Pauli exclusion principle**.

No two electrons can have the same set of quantum numbers.

For atoms, **no two electrons can have the same set of** (n, l, m_l, m_s)

→Explains organization of electrons in the energy levels of atoms.

The principle is more general: applies to all particles with **half-integer spin** = **fermions.**

As opposed to particles with **integer spin** = **bosons** (not subject to Pauli exclusion).

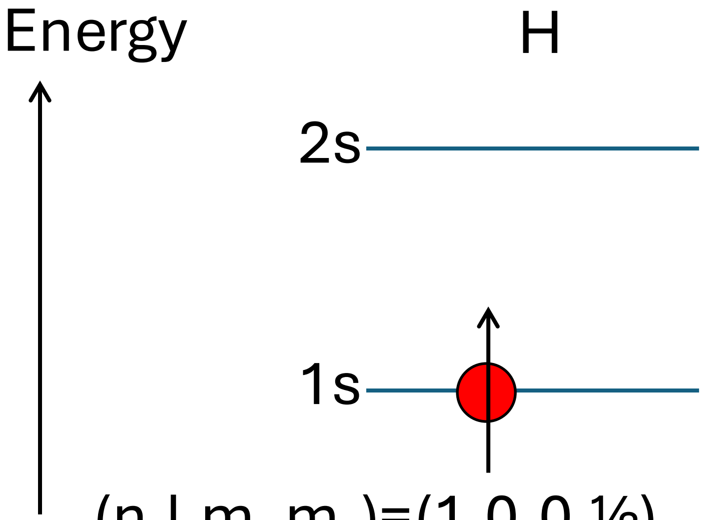
Examples of fermions and bosons?

Fermions: electron, proton, neutron, …

Bosons: photon, He^4 nucleus, Higgs, …

Origin: **indistinguishability** of quantum particles (see Gibbs paradox)

Electronic structure of H and He



(n,l,m_l,m_s)=(1,0,0,½)

Electronic structure: **$1s^1$**

Labeling atomic shells:

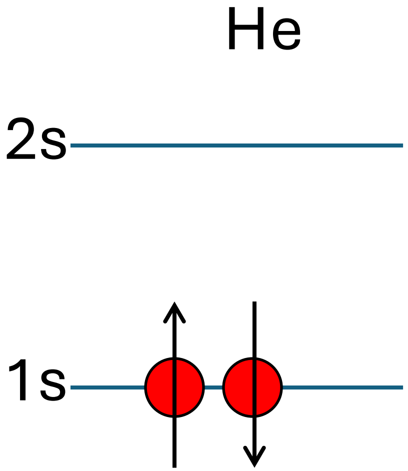
n=1 → K

n=2 → L

n=3 → M

n=4 → N

…



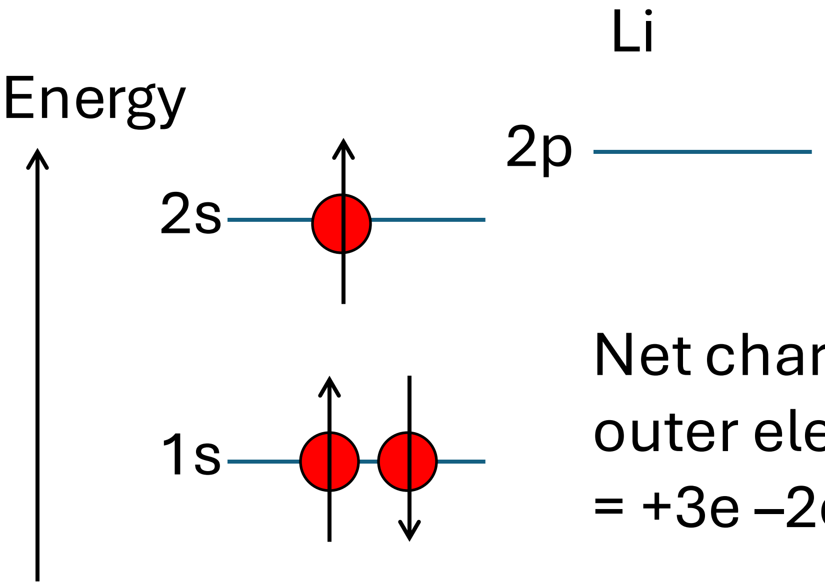
Electrons pair with opposite spins due to Pauli exclusion

1st electron: (n,l,m_l,m_s)=(1,0,0,½)

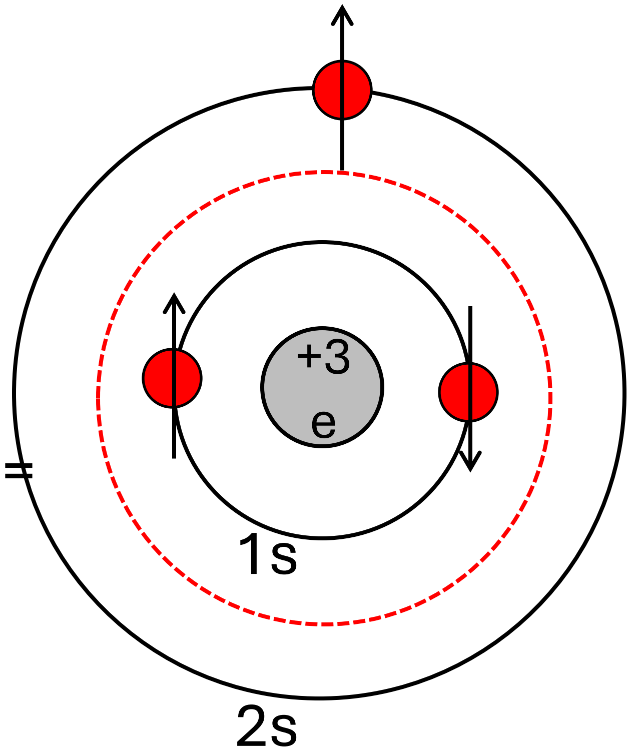
2nd electron: (n,l,m_l,m_s)=(1,0,0,–½)

Electronic structure: **$1s^2$**

Electronic structure of Li



Net charge that the outer electrons feel = = +3e –2e=+1e



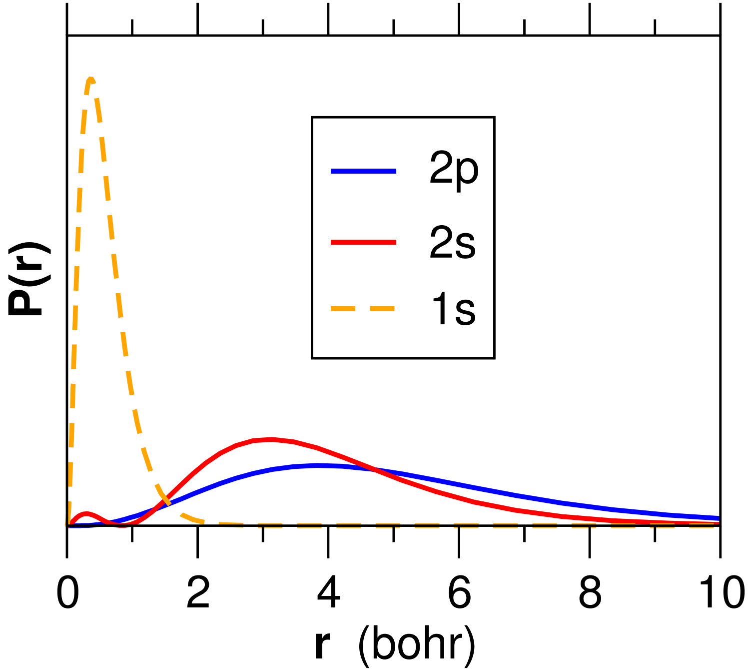
In H, the 2s and 2p states have the same energy

An electron in H is attracted by the bare Coulomb potential of the nucleus.

An outer electron in Li (or other multi-electron atoms) feels a reduced (“screened”) attractive potential due to the repulsion by the inner electrons.

Radial distribution function in Li

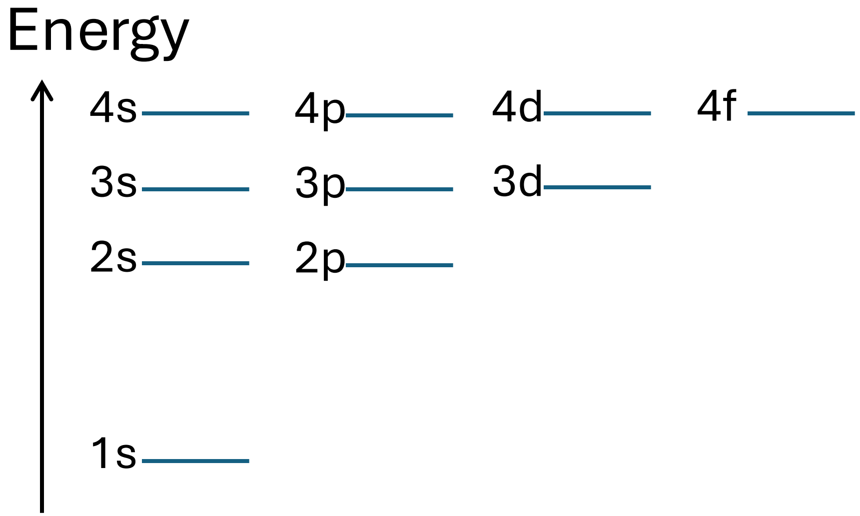
Calculated data for the radial probability distribution function P(r):



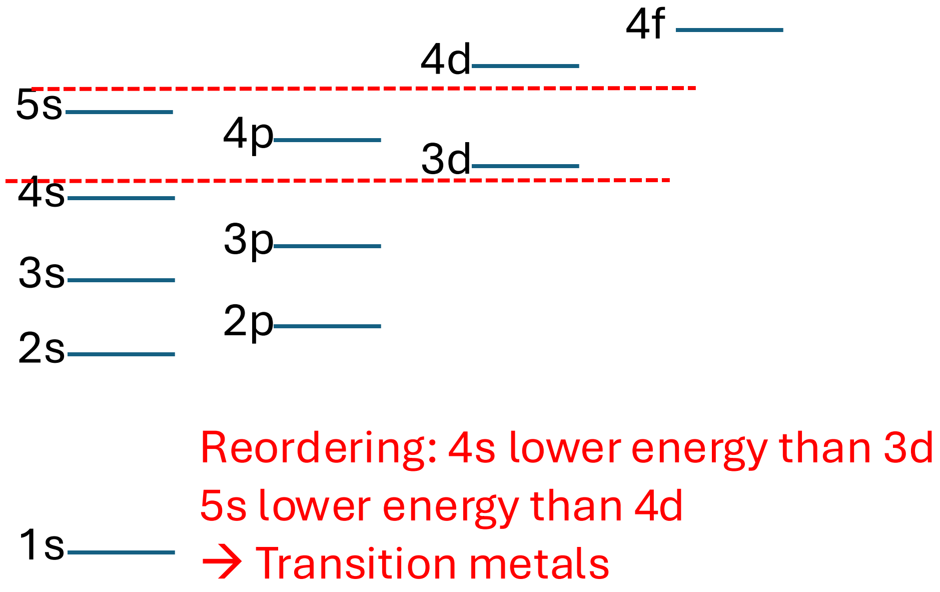
The electron in the 2*s* state penetrates more through the cloud of 1*s* electrons and feels a stronger attraction by the nucleus. 2*s* electrons have lower potential energy.

Orbital energies in multielectron atoms

Orbital energies in H



Orbital energies in multielectron atoms



Reordering: 4s lower energy than 3d

5s lower energy than 4d

→ Transition metals

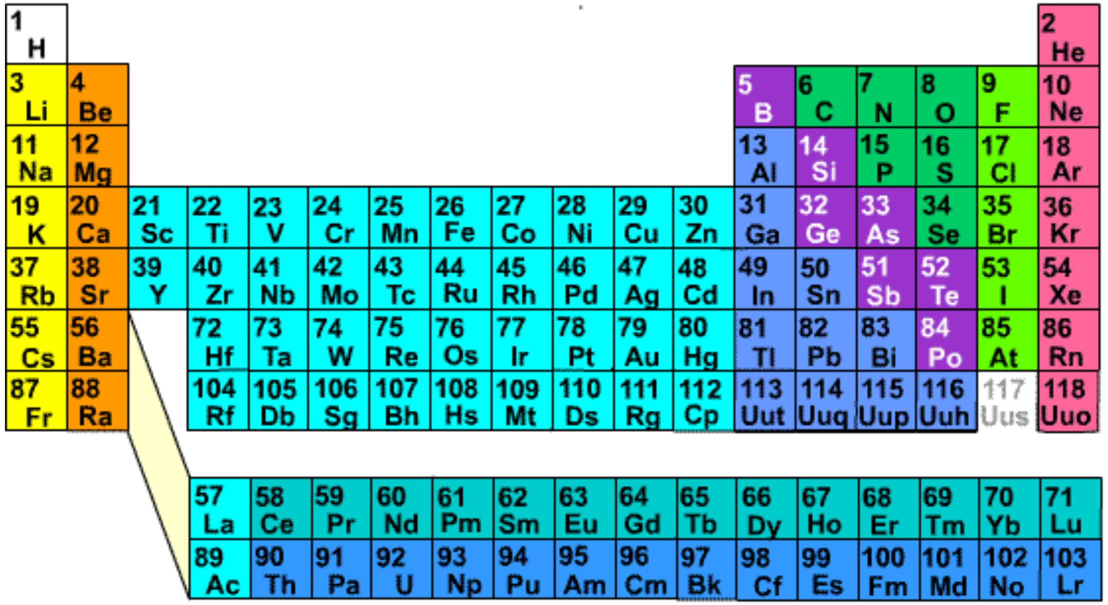
Filling the states: How many electrons in each subshell?

s: l=0 → $m_l = \{0\} \times 2$ (for spin) → 2 electrons

p: l=1 → $m_l = \{-1,0,+1\} \times 2$ (for spin) → 6 electrons

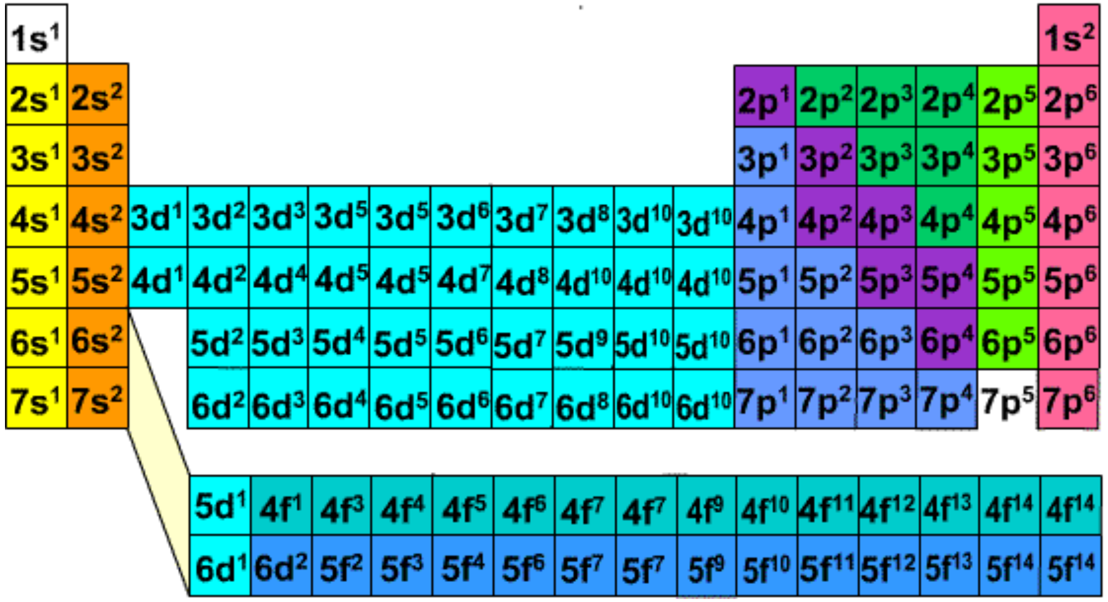
d: l=2 → $m_l = \{-2,-1,0,+1,+2\} \times 2$ (for spin) → 10 electrons

f: l=3 → $m_l = \{-3,-2,-1,0,+1,+2,+3\} \times 2$ (for spin) → 14 electrons



1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cp	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr



$1s^1$																	$1s^2$
$2s^1$	$2s^2$											$2p^1$	$2p^2$	$2p^3$	$2p^4$	$2p^5$	$2p^6$
$3s^1$	$3s^2$											$3p^1$	$3p^2$	$3p^3$	$3p^4$	$3p^5$	$3p^6$
$4s^1$	$4s^2$	$3d^1$	$3d^2$	$3d^3$	$3d^5$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^{10}$	$3d^{10}$	$4p^1$	$4p^2$	$4p^3$	$4p^4$	$4p^5$	$4p^6$
$5s^1$	$5s^2$	$4d^1$	$4d^2$	$4d^4$	$4d^5$	$4d^5$	$4d^7$	$4d^8$	$4d^{10}$	$4d^{10}$	$4d^{10}$	$5p^1$	$5p^2$	$5p^3$	$5p^4$	$5p^5$	$5p^6$
$6s^1$	$6s^2$		$5d^2$	$5d^3$	$5d^4$	$5d^5$	$5d^6$	$5d^7$	$5d^9$	$5d^{10}$	$5d^{10}$	$6p^1$	$6p^2$	$6p^3$	$6p^4$	$6p^5$	$6p^6$
$7s^1$	$7s^2$		$6d^2$	$6d^3$	$6d^4$	$6d^5$	$6d^6$	$6d^7$	$6d^8$	$6d^{10}$	$6d^{10}$	$7p^1$	$7p^2$	$7p^3$	$7p^4$	$7p^5$	$7p^6$

$5d^1$	$4f^1$	$4f^3$	$4f^4$	$4f^5$	$4f^6$	$4f^7$	$4f^7$	$4f^9$	$4f^{10}$	$4f^{11}$	$4f^{12}$	$4f^{13}$	$4f^{14}$	$4f^{14}$
$6d^1$	$6d^2$	$5f^2$	$5f^3$	$5f^4$	$5f^6$	$5f^7$	$5f^7$	$5f^9$	$5f^{10}$	$5f^{11}$	$5f^{12}$	$5f^{13}$	$5f^{14}$	$5f^{14}$

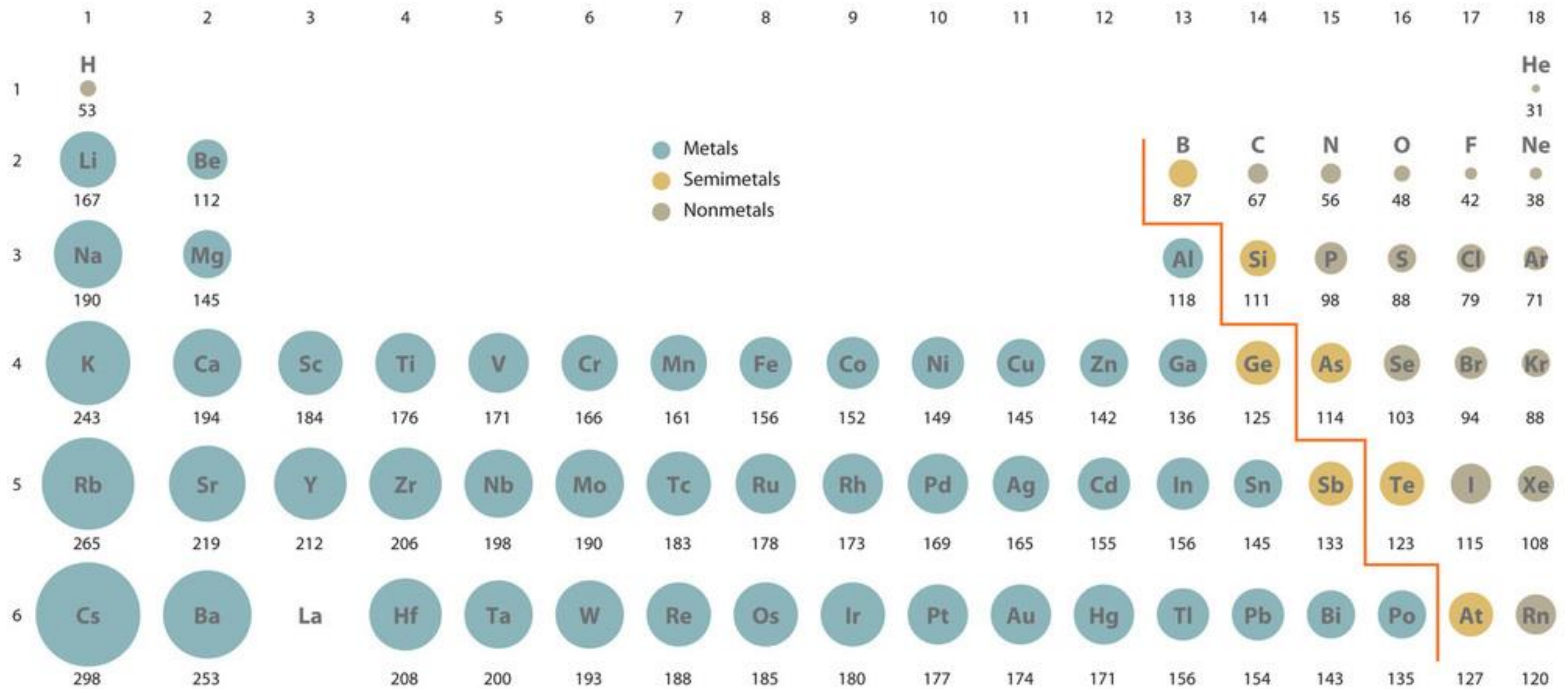
Periodic table

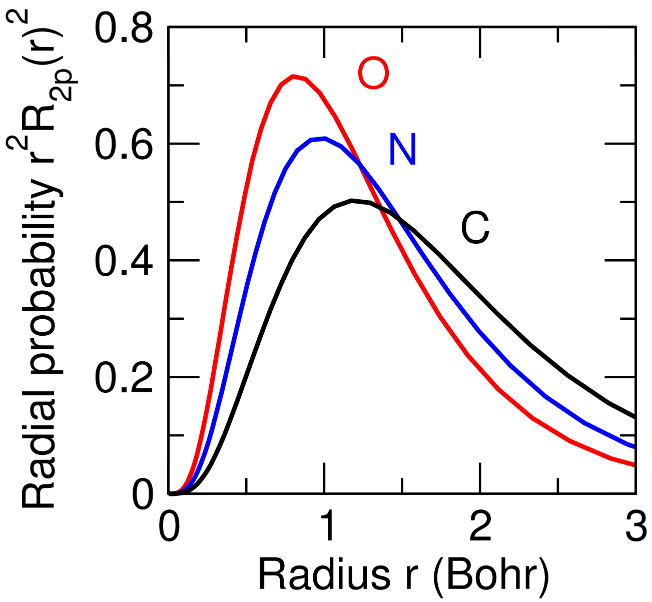
Grouping of elements based on filling of subshells.

Vertical columns = **groups**, elements with similar chemical and physical properties.

Horizontal rows = **periods**, due to repetition in filling of subshells

Size of the atoms





Why does the size of the atoms decrease from left to right?

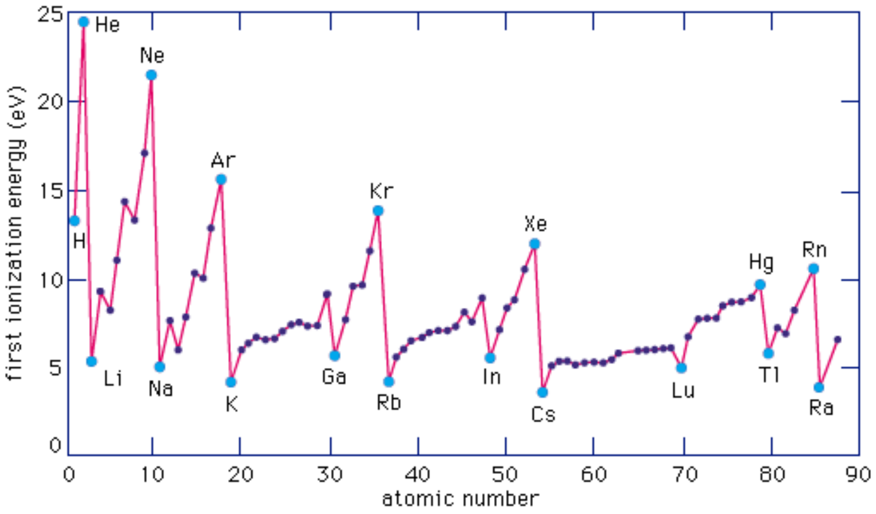
A: increasing Z → stronger attraction to nucleus.

Why does the size increase from top to bottom?

A: outer shells are more weakly bound to nucleus (screening by inner electrons)

https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/07._Periodic_Properties_of_the_Elements/7.3%3A_Sizes_of_Atoms_and_Ions

Ionization energy



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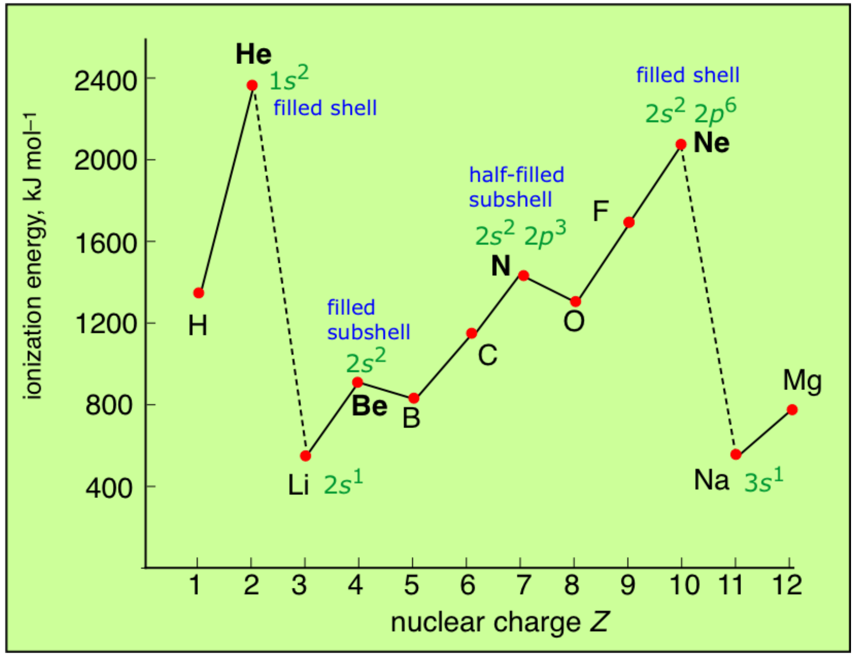
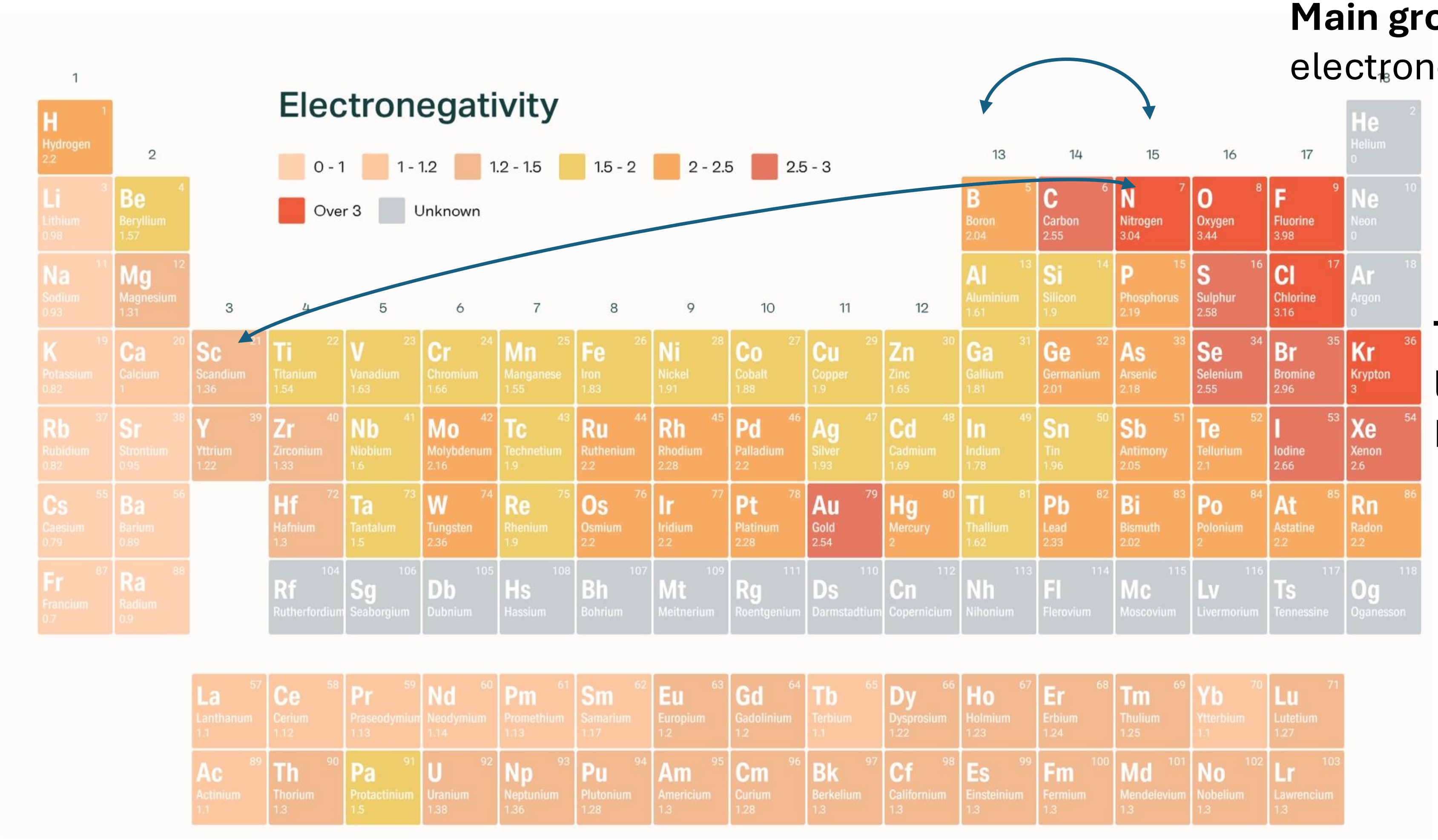


Ionization energy = energy needed to remove outermost electron
= measure of stability of e in atoms.
What trends do you see?

- Large for inert gases, low for alkalis and alkaline earths
- Li→ Ne: overall increase for increasing Z
- Be→B: occupation of p orbitals. N→O: double occupation of p orbital

Electronegativity = tendency to attract shared electrons

B, Ga, Al, In, Sc, Y, La: metals, electropositive, tend to give electrons (cations).
N: nonmetal, electronegative, tends to attract electrons (anion).



Electronegativity

🟧 0 - 1
🟧 1 - 1.2
🟧 1.2 - 1.5
🟨 1.5 - 2
🟧 2 - 2.5
🟥 2.5 - 3
🟥 Over 3
⬜ Unknown

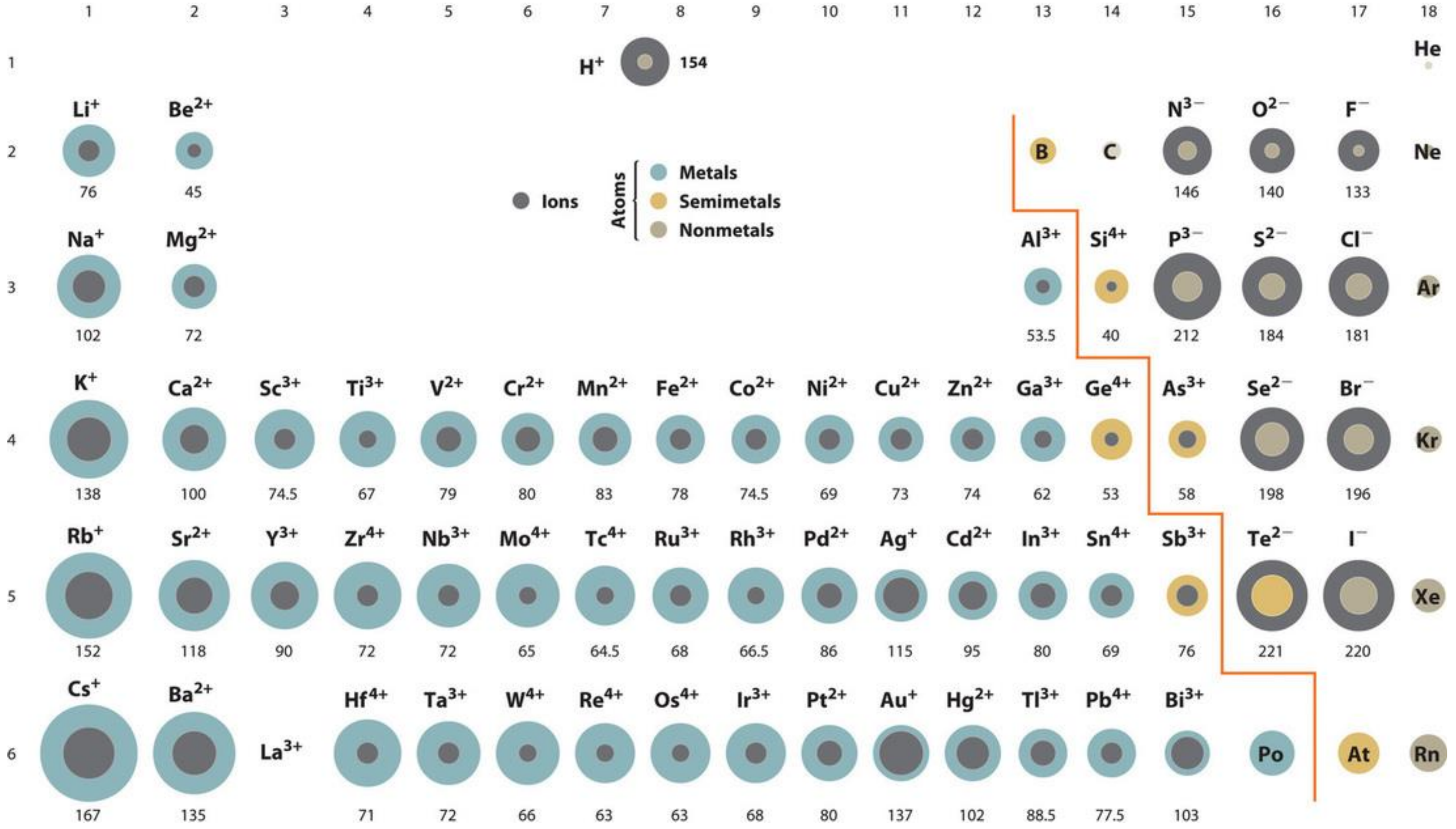
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H 1 Hydrogen 2.2																	He 2 Helium 0
Li 3 Lithium 0.98	Be 4 Beryllium 1.57											B 5 Boron 2.04	C 6 Carbon 2.55	N 7 Nitrogen 3.04	O 8 Oxygen 3.44	F 9 Fluorine 3.98	Ne 10 Neon 0
Na 11 Sodium 0.93	Mg 12 Magnesium 1.31											Al 13 Aluminium 1.61	Si 14 Silicon 1.9	P 15 Phosphorus 2.19	S 16 Sulphur 2.58	Cl 17 Chlorine 3.16	Ar 18 Argon 0
K 19 Potassium 0.82	Ca 20 Calcium 1	Sc 21 Scandium 1.36	Ti 22 Titanium 1.54	V 23 Vanadium 1.63	Cr 24 Chromium 1.66	Mn 25 Manganese 1.55	Fe 26 Iron 1.83	Ni 28 Nickel 1.91	Co 27 Cobalt 1.88	Cu 29 Copper 1.9	Zn 30 Zinc 1.65	Ga 31 Gallium 1.81	Ge 32 Germanium 2.01	As 33 Arsenic 2.18	Se 34 Selenium 2.55	Br 35 Bromine 2.96	Kr 36 Krypton 3
Rb 37 Rubidium 0.82	Sr 38 Strontium 0.95	Y 39 Yttrium 1.22	Zr 40 Zirconium 1.33	Nb 41 Niobium 1.6	Mo 42 Molybdenum 2.16	Tc 43 Technetium 1.9	Ru 44 Ruthenium 2.2	Rh 45 Rhodium 2.28	Pd 46 Palladium 2.2	Ag 47 Silver 1.93	Cd 48 Cadmium 1.69	In 49 Indium 1.78	Sn 50 Tin 1.96	Sb 51 Antimony 2.05	Te 52 Tellurium 2.1	I 53 Iodine 2.66	Xe 54 Xenon 2.6
Cs 55 Caesium 0.79	Ba 56 Barium 0.89		Hf 72 Hafnium 1.3	Ta 73 Tantalum 1.5	W 74 Tungsten 2.36	Re 75 Rhenium 1.9	Os 76 Osmium 2.2	Ir 77 Iridium 2.2	Pt 78 Platinum 2.28	Au 79 Gold 2.54	Hg 80 Mercury 2	Tl 81 Thallium 1.62	Pb 82 Lead 2.33	Bi 83 Bismuth 2.02	Po 84 Polonium 2	At 85 Astatine 2.2	Rn 86 Radon 2.2
Fr 87 Francium 0.7	Ra 88 Radium 0.9		Rf 104 Rutherfordium	Sg 106 Seaborgium	Db 105 Dubnium	Hs 108 Hassium	Bh 107 Bohrium	Mt 109 Meitnerium	Rg 111 Roentgenium	Ds 110 Darmstadtium	Cn 112 Copernicium	Nh 113 Nihonium	Fl 114 Flerovium	Mc 115 Moscovium	Lv 116 Livermorium	Ts 117 Tennessine	Og 118 Oganesson
		La 57 Lanthanum 1.1	Ce 58 Cerium 1.12	Pr 59 Praseodymium 1.13	Nd 60 Neodymium 1.14	Pm 61 Promethium 1.13	Sm 62 Samarium 1.17	Eu 63 Europium 1.2	Gd 64 Gadolinium 1.2	Tb 65 Terbium 1.1	Dy 66 Dysprosium 1.22	Ho 67 Holmium 1.23	Er 68 Erbium 1.24	Tm 69 Thulium 1.25	Yb 70 Ytterbium 1.1	Lu 71 Lutetium 1.27	
		Ac 89 Actinium 1.1	Th 90 Thorium 1.3	Pa 91 Protactinium 1.5	U 92 Uranium 1.38	Np 93 Neptunium 1.36	Pu 94 Plutonium 1.28	Am 95 Americium 1.3	Cm 96 Curium 1.28	Bk 97 Berkelium 1.3	Cf 98 Californium 1.3	Es 99 Einsteinium 1.3	Fm 100 Fermium 1.3	Md 101 Mendelevium 1.3	No 102 Nobelium 1.3	Lr 103 Lawrencium 1.3	

Main group-III elements: small electronegativity difference with Nitrogen
→ Primarily **covalent** bonding

Transition metal group-III elements: large electronegativity difference with Nitrogen → **Ionic** bonding

https://www.breakingatom.com/learn-the-periodic-table/electronegativity-of-the-elements

Size of ions



In ceramic materials (e.g., compound semiconductors) the elements have a partial ionic character (e.g., $Ga^{3+}N^{3-}$). Need to consider size of ions when electrons are removed from (cations) or added to (anions) the outer shell.

E.g., Ga^{3+}: large size difference between size of atom and size of ion. Dense packing of atoms enables strong orbital overlap. Explains high mobility of Ga-based semiconductors.

https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/07._Periodic_Properties_of_the_Elements/7.3%3A_Sizes_of_Atoms_and_Ions

Molecules and Chemical Bonding

Molecule = collection of nuclei + electrons. Need to describe coupled motion of electrons and nuclei.

Two basic approximations:

1) **Born-Oppenheimer** or **Adiabatic** approximation: since electrons are much lighter and move much faster than nuclei ($m_e/Mp \sim 1/1836$), they respond instantaneously to the nuclear motion.
   - Solve electronic motion assuming that the nuclei are static
   - Solve nuclear motion assuming that electrons are always in their ground state

   Good approximation in general, corrections needed for lightest elements.

2) **Classical Nuclei** approximation: electrons need quantum mechanics, but the motion of the nuclei can be described by classical physics.

Molecules and Chemical Bonding

In molecules, the valence electrons do not stay in their atomic orbitals. Instead, they join together to form bonds.

Quantum principles still apply: discrete energy levels, electrons described by wave functions.

Wave functions in atoms =
atomic orbitals (e.g., 1s, $2p_x$, …)

Wave functions in molecules =
molecular orbitals (e.g., σ, π, …)

Need to solve Schrödinger's equation for molecule. Hard to do, need approximations.

http://magneticcarpet.deviantart.com
/art/Molecular-orbital-102480755

Linear Combination of Atomic Orbitals

Near an atom, molecular wave functions look like the atomic wave functions of the atom.

Assumption: the molecular wave function can be approximated by a **Linear Combination of Atomic Orbitals** (**LCAO method**)

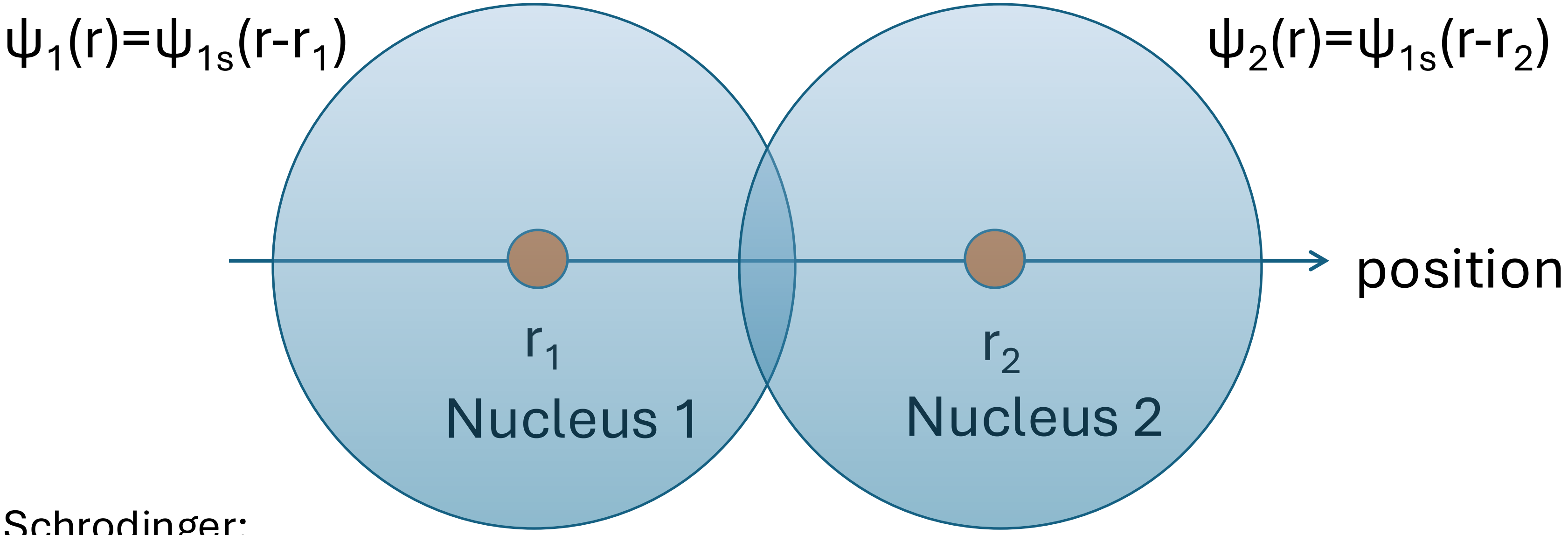
$$\psi_{\mathrm{molecule}}(\vec{r}) = c_1\psi_{\mathrm{atom1}}(\vec{r}-\vec{r}_1) + c_2\psi_{\mathrm{atom2}}(\vec{r}-\vec{r}_2)$$

c_1, c_2 = numerical prefactors, chosen to satisfy Schrodinger’s equation.

Physical meaning of c_1, c_2: Measure how much each of ψ1, ψ2 contribute to the molecular wave function, depend on the electronegativity of the atoms.

$|c_1|^2$ = probability that the electron in the molecular orbital is found in state ψ_1

Example: LCAO for the H_2 molecule



Schrodinger:

$$H\psi_{\text{molecule}}(\vec{r}) = E_{\text{molecule}}\psi_{\text{molecule}}(\vec{r})$$

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V_{\text{molecule}}(\vec{r})$$

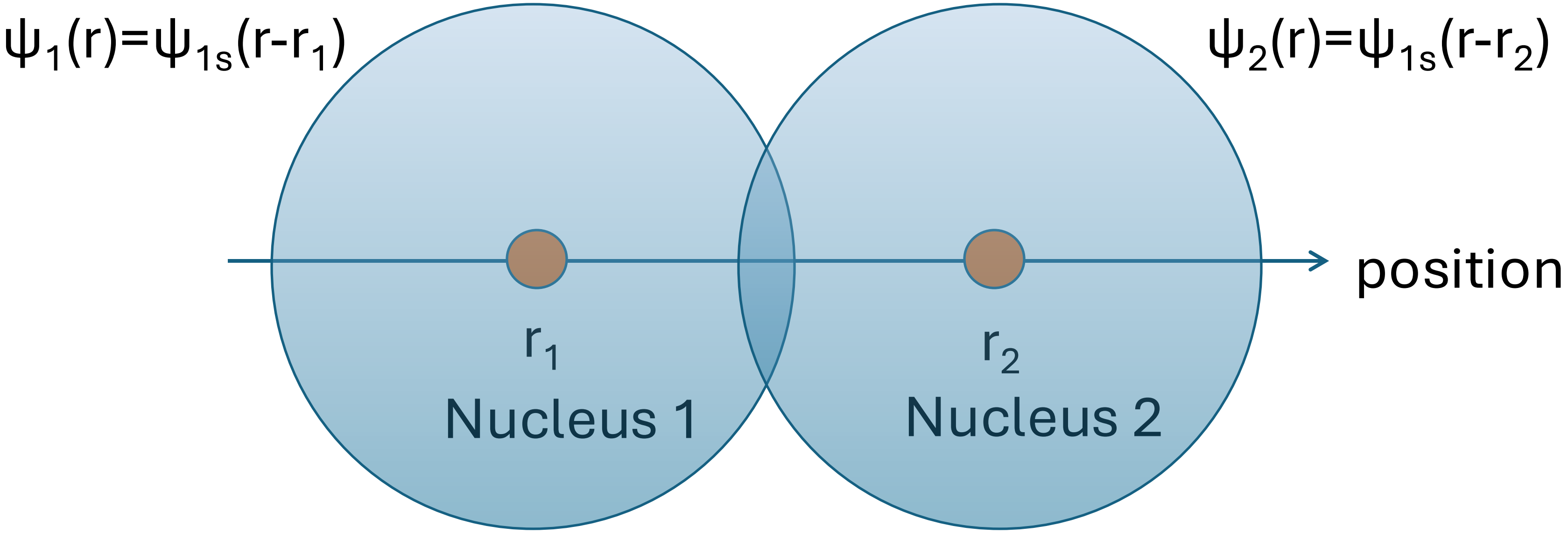
Potential:

$$V_{\text{molecule}}(\vec{r}) = V_{\text{atom1}}(\vec{r}-\vec{r}_1) + V_{\text{atom2}}(\vec{r}-\vec{r}_2)$$

Wave function:

$$\begin{aligned}\psi_{\text{molecule}}(\vec{r}) &= c_1\psi_{\text{atom1}}(\vec{r}-\vec{r}_1) + c_2\psi_{\text{atom2}}(\vec{r}-\vec{r}_2)\\ &= c_1\psi_1(\vec{r}) + c_2\psi_2(\vec{r})\end{aligned}$$

Example: LCAO for the H_2 molecule



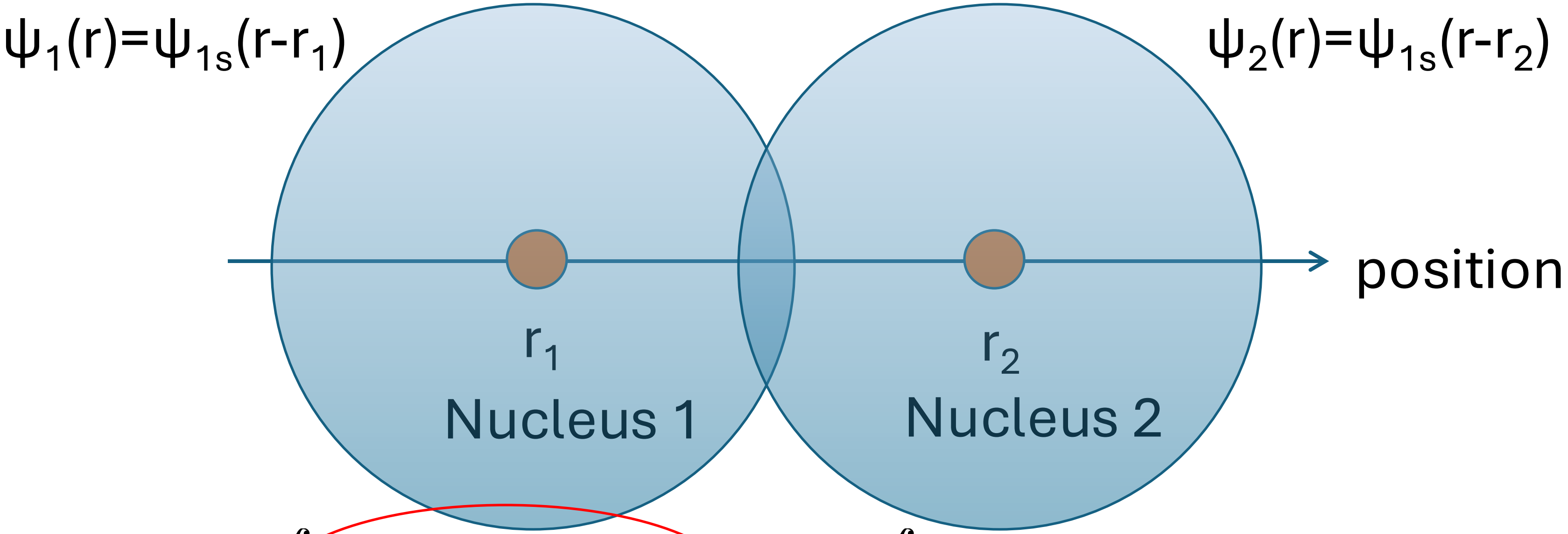
$$c_1(H\psi_1) + c_2(H\psi_2) = Ec_1\psi_1 + Ec_2\psi_2$$

Multiply both sides by ψ_1* and integrate over r:

$$c_1 \int \psi_1^*(\vec{r}) H \psi_1(\vec{r}) d\vec{r} + c_2 \int \psi_1^*(\vec{r}) H \psi_2(\vec{r}) d\vec{r} =$$

$$= Ec_1 \int \psi_1^*(\vec{r}) \psi_1(\vec{r}) d\vec{r} + Ec_2 \int \psi_1^*(\vec{r}) \psi_2(\vec{r}) d\vec{r}$$

Physical meaning of the integrals



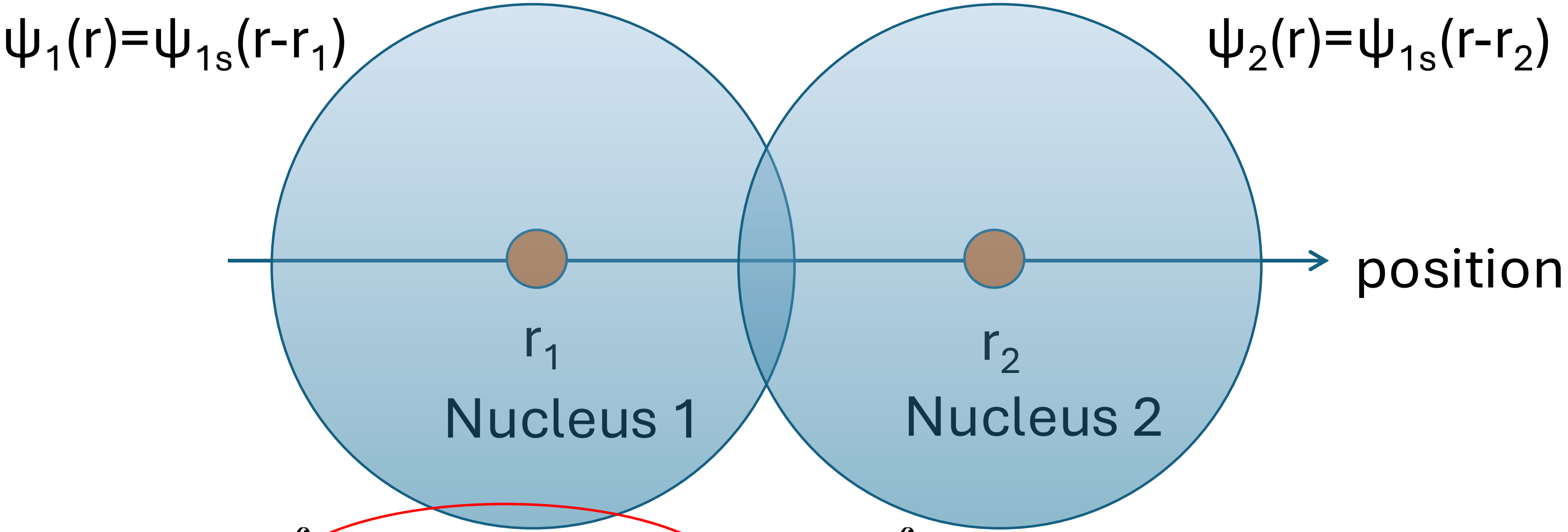
$$c_1 \boxed{\int \psi_1^*(\vec{r}) H \psi_1(\vec{r}) d\vec{r}} + c_2 \int \psi_1^*(\vec{r}) H \psi_2(\vec{r}) d\vec{r} =$$

$$= Ec_1 \int \psi_1^*(\vec{r}) \psi_1(\vec{r}) d\vec{r} + Ec_2 \int \psi_1^*(\vec{r}) \psi_2(\vec{r}) d\vec{r}$$

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V_{\text{molecule}}(\vec{r})$$

$$V_{\text{molecule}}(\vec{r}) = V_{\text{atom1}}(\vec{r}-\vec{r}_1) + V_{\text{atom2}}(\vec{r}-\vec{r}_2)$$

Physical meaning of the integrals



$$c_1 \boxed{\int \psi_1^*(\vec{r}) H \psi_1(\vec{r}) d\vec{r}} + c_2 \int \psi_1^*(\vec{r}) H \psi_2(\vec{r}) d\vec{r} =$$

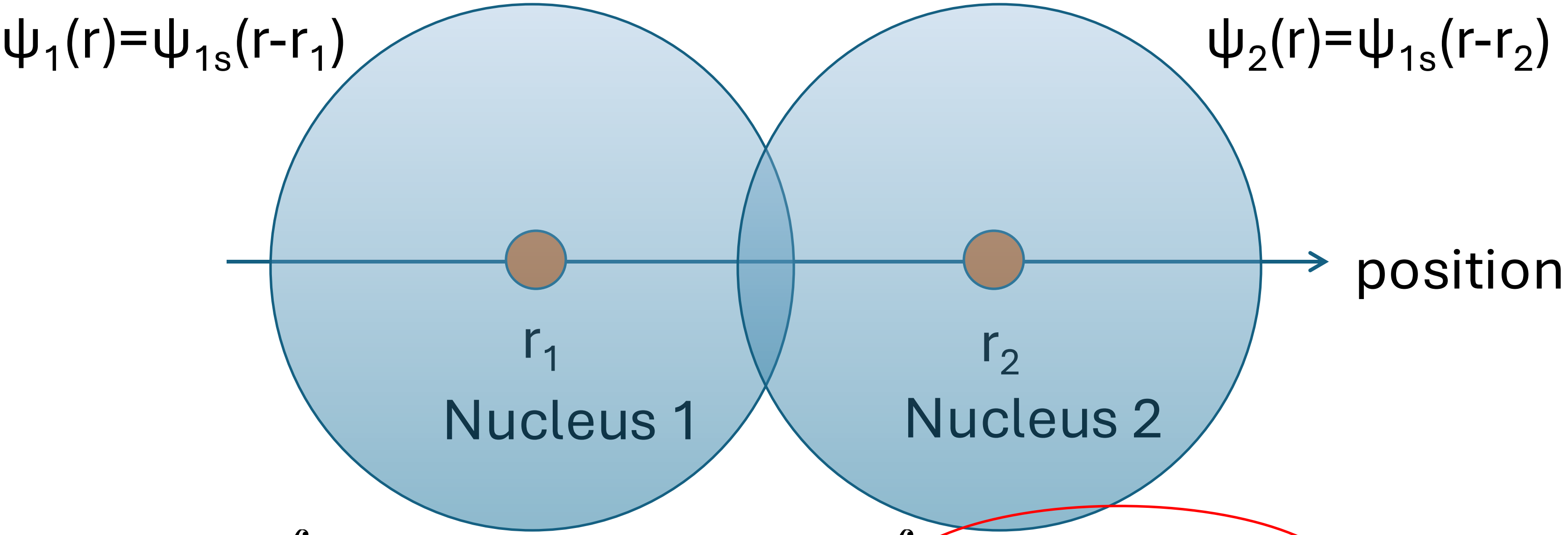
$$= E c_1 \int \psi_1^*(\vec{r}) \psi_1(\vec{r}) d\vec{r} + E c_2 \int \psi_1^*(\vec{r}) \psi_2(\vec{r}) d\vec{r}$$

In the neighborhood of atom 1 (where ψ_1 is large): $V_{\text{molecule}} \cong V_{\text{atom1}}$

$$\Rightarrow \int \psi_1^*(\vec{r}) H \psi_1(\vec{r}) d\vec{r} \simeq \int \psi_1^*(\vec{r}) H_{\text{atom1}} \psi_1(\vec{r}) d\vec{r} = E_{1s} \equiv \epsilon_1$$

= Energy of the atomic orbital ψ_1 of atom 1 = energy of 1s orbital of Hydrogen atom

Physical meaning of the integrals



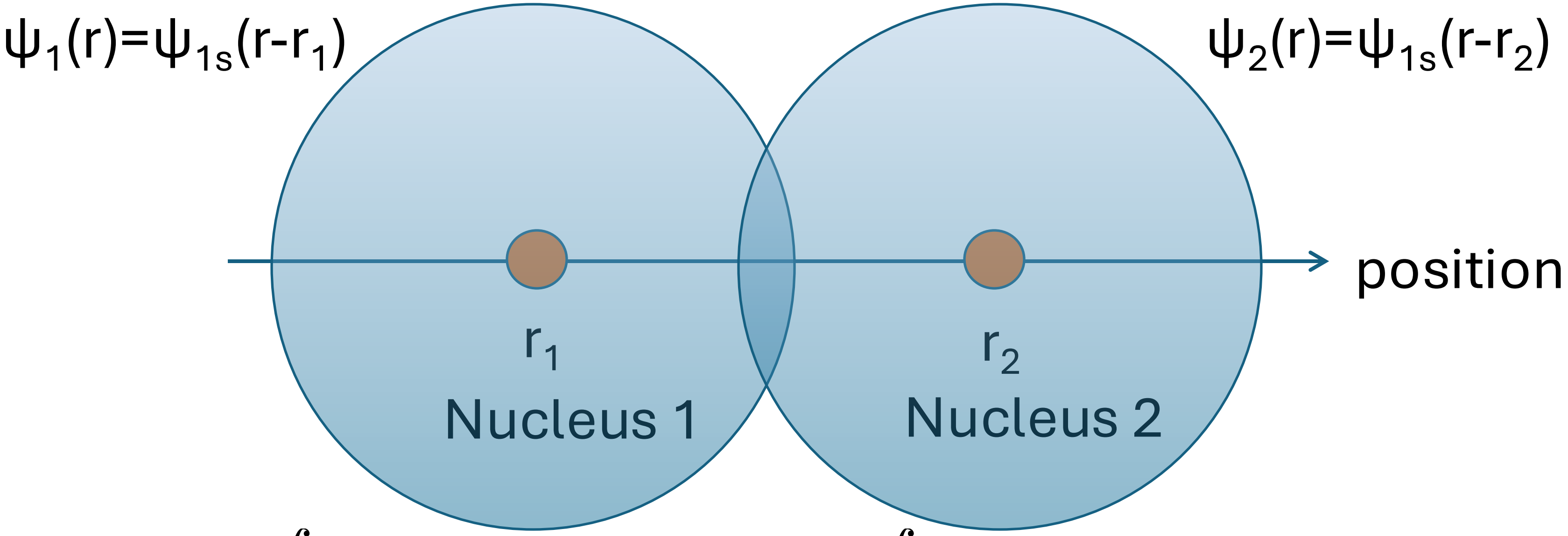
$$c_1 \int \psi_1^*(\vec{r}) H \psi_1(\vec{r}) d\vec{r} + c_2 \int \psi_1^*(\vec{r}) H \psi_2(\vec{r}) d\vec{r} =$$

$$= E c_1 \int \psi_1^*(\vec{r}) \psi_1(\vec{r}) d\vec{r} + E c_2 \int \psi_1^*(\vec{r}) \psi_2(\vec{r}) d\vec{r}$$

Interatomic matrix element: $$\int \psi_1^*(\vec{r}) H \psi_2(\vec{r}) d\vec{r} = -V_s$$

= a negative number. It is related to the probability that an electron can transition from atomic orbital ψ_1 to ψ_2 = relates to **sharing** of electrons between atoms.

Physical meaning of the integrals



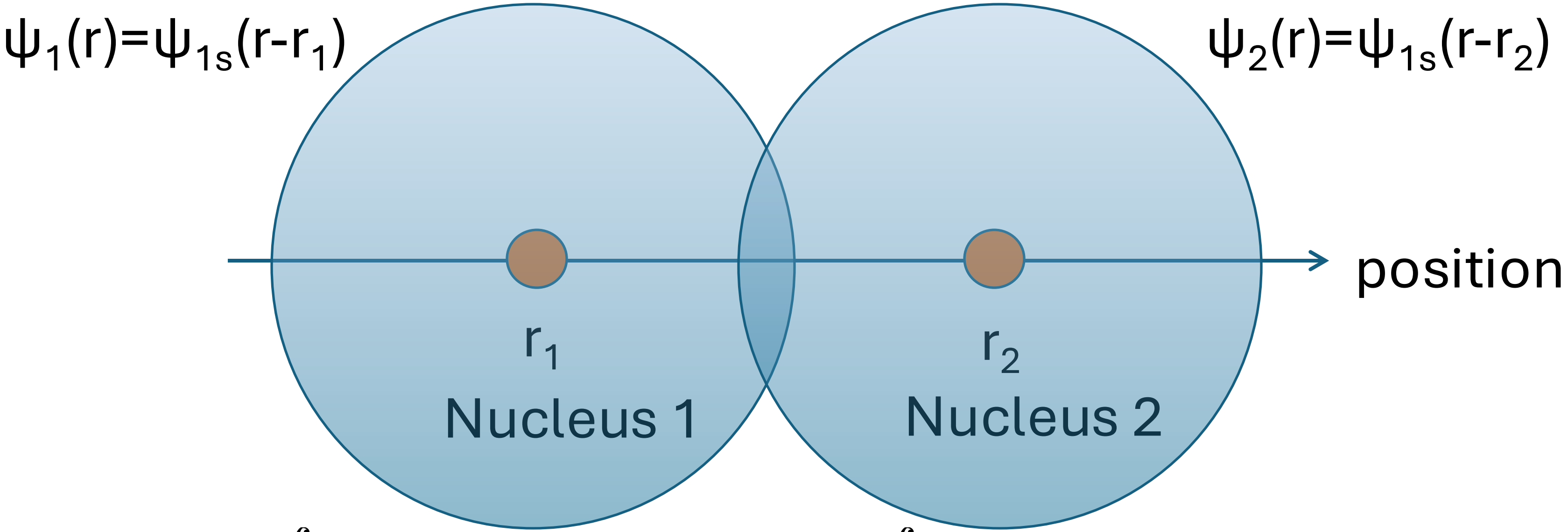
$$c_1 \int \psi_1^*(\vec{r}) H \psi_1(\vec{r}) d\vec{r} + c_2 \int \psi_1^*(\vec{r}) H \psi_2(\vec{r}) d\vec{r} =$$

$$= E c_1 \boxed{\int \psi_1^*(\vec{r}) \psi_1(\vec{r}) d\vec{r}} + E c_2 \int \psi_1^*(\vec{r}) \psi_2(\vec{r}) d\vec{r}$$

Question: what is the value of this integral?

Answer: = 1

Physical meaning of the integrals



$$c_1 \int \psi_1^*(\vec{r}) H \psi_1(\vec{r}) d\vec{r} + c_2 \int \psi_1^*(\vec{r}) H \psi_2(\vec{r}) d\vec{r} =$$

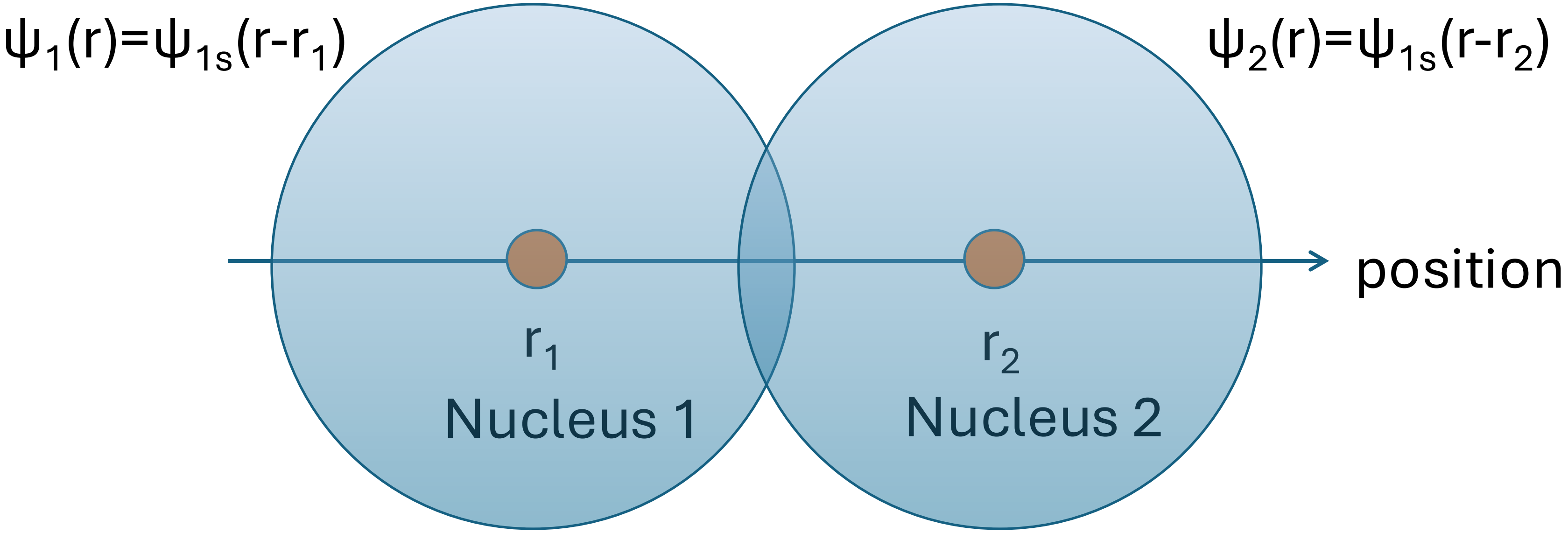
$$= E c_1 \int \psi_1^*(\vec{r}) \psi_1(\vec{r}) d\vec{r} + E c_2 \int \psi_1^*(\vec{r}) \psi_2(\vec{r}) d\vec{r}$$

Question: what is the value of this integral?

Answer: overlap integral

$$\int \psi_1^*(\vec{r}) \psi_2(\vec{r}) d\vec{r} = S \simeq 0$$

Physical meaning of the integrals



$$\boxed{\Rightarrow c_1\epsilon_1 - c_2V_s = Ec_1}$$

One equation with 3 unknowns. Question: What to do next?

Answer: go back to Schrodinger equation, multiply by ψ_2 and integrate

Question: and now what?

$$\boxed{\begin{aligned} c_1\epsilon_1 - c_2V_s &= Ec_1 \\ -c_1Vs + c_2\epsilon_2 &= Ec_2 \end{aligned}}$$

$$\text{For H}_2: \epsilon_1 = \epsilon_2 = E_{1s}$$

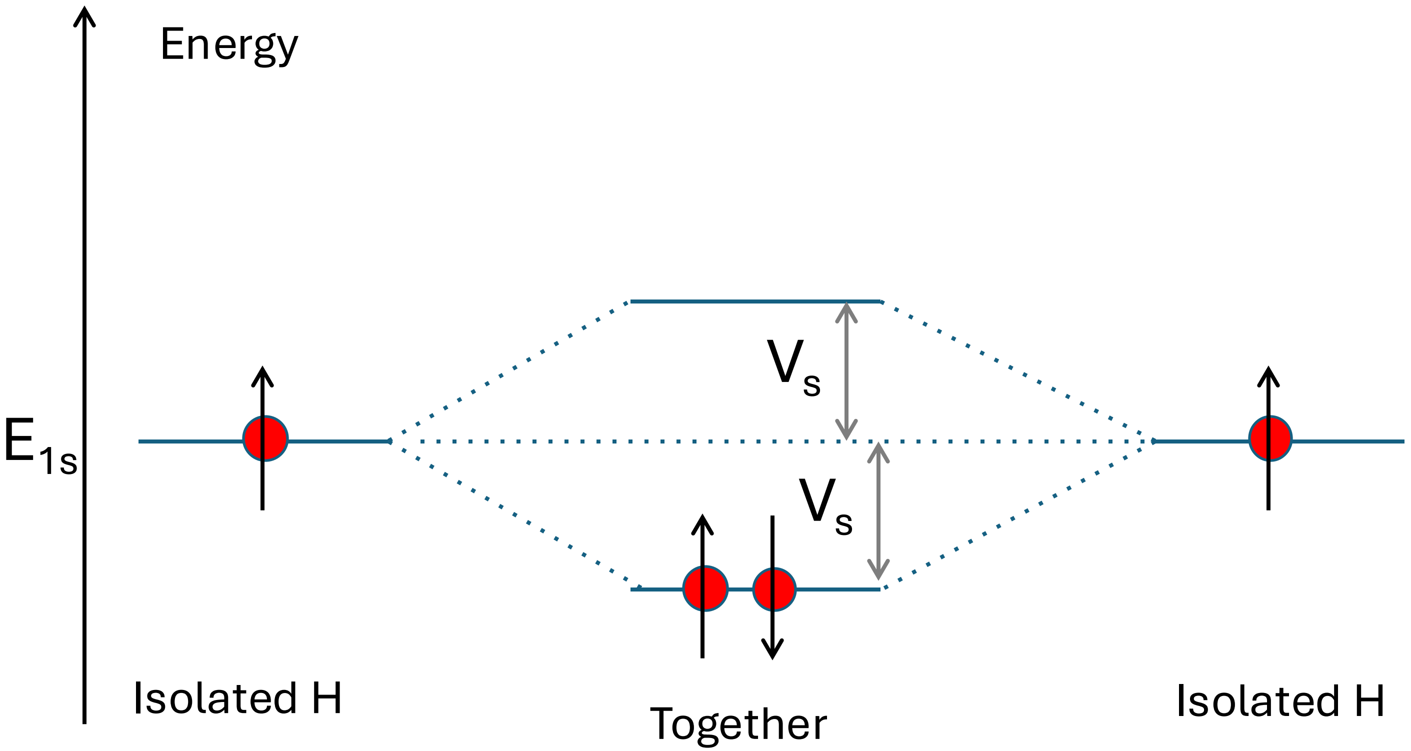
Hint: how many unknowns and how many equations?

Answer: determinant of coefficients must be zero. Otherwise, the system of the two equations has a unique trivial solution: $c_1=c_2=0$

$$\boxed{\begin{aligned} c_1(\epsilon_1 - E) - c_2V_s &= 0 \\ -c_1Vs + c_2(\epsilon_2 - E) &= 0 \end{aligned}}$$

Algebra …

Energy levels of H_2 molecular orbitals



Question: Does the energy increase or decrease when the two H atoms are brought together? What can you say about bond formation?

Answer: Energy is lowered by $2V_s$, the molecule has a lower energy than individual atoms → **chemical bond** forms between H atoms.

The wave functions of the H_2 molecule (molecular orbitals)

What is the wave function for $E_{bonding} = E_{1s} - V_s$?

And what is the wave function for $E_{antibonding} = E_{1s} + V_s$?

Answer: go back to the set of equations and set the energy equal to the bonding or the antibonding orbital energy, find the ratio of c_1/c_2. Then, impose normalization $c_1^2 + c_2^2 = 1$

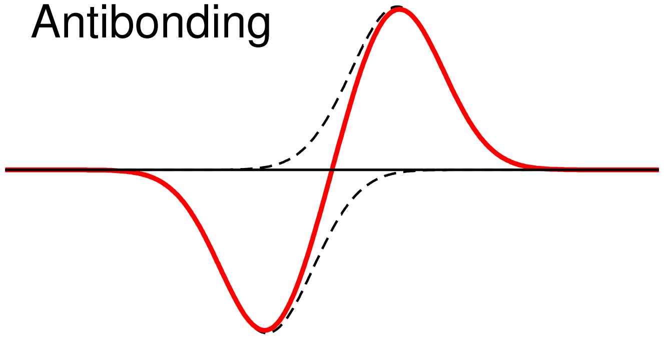
For the **bonding** orbital:
(σ orbital, no node)

$$\boxed{c_1 = c_2 = \frac{1}{\sqrt{2}}}$$

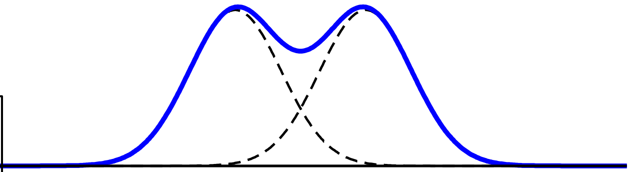
For the **antibonding** orbital:
(σ* orbital, with node)

$$\boxed{c_1 = -c_2 = \frac{1}{\sqrt{2}}}$$

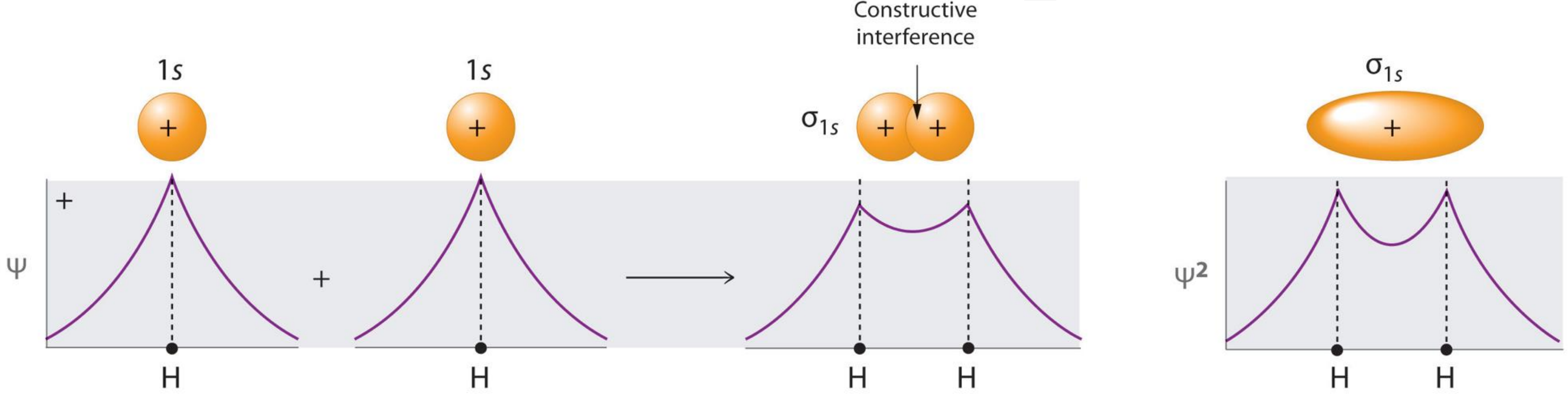
Antibonding



Bonding

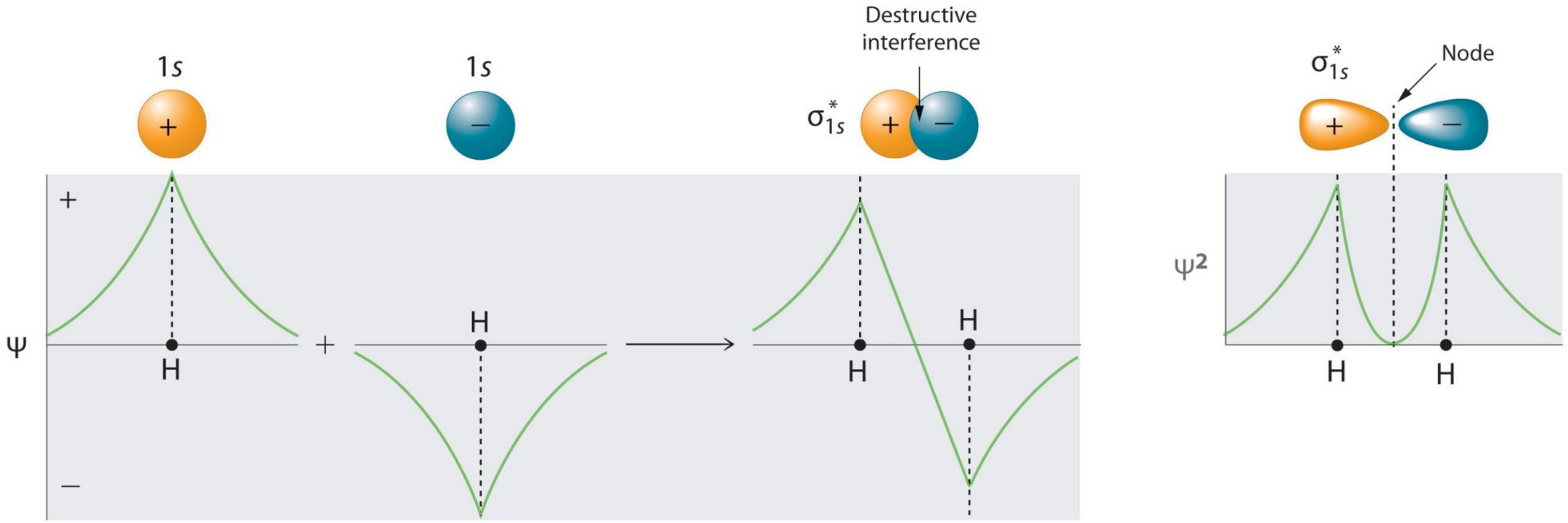


Molecular orbitals of H_2 molecule



(a) Wave functions combined for σ_{1s}

(b) Bonding probability density



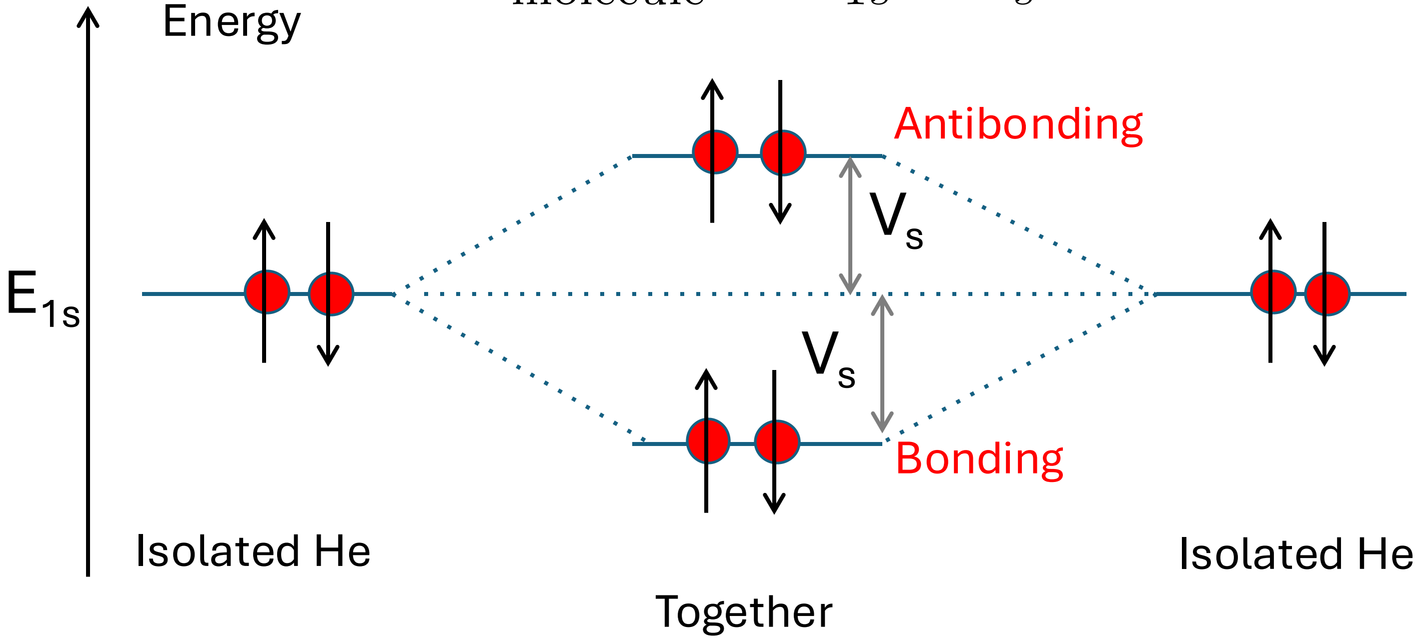
(c) Wave functions combined for σ^*_{1s}

(d) Antibonding probability density

http://chemwiki.ucdavis.edu/Textbook_Maps/General_Chemistry_Textbook_Maps/Map%3A_Chemistry%3A_The_Central_Science_(Brown_et_al.)/09._Molecular_Geometry_and_Bonding_Theories/9.7%3A_Molecular_Orbitals

Follow the same steps for the He_2 molecule. Does the He_2 molecule bind? Why or why not?

$$E_{\text{molecule}} = E_{1s} \pm V_s$$

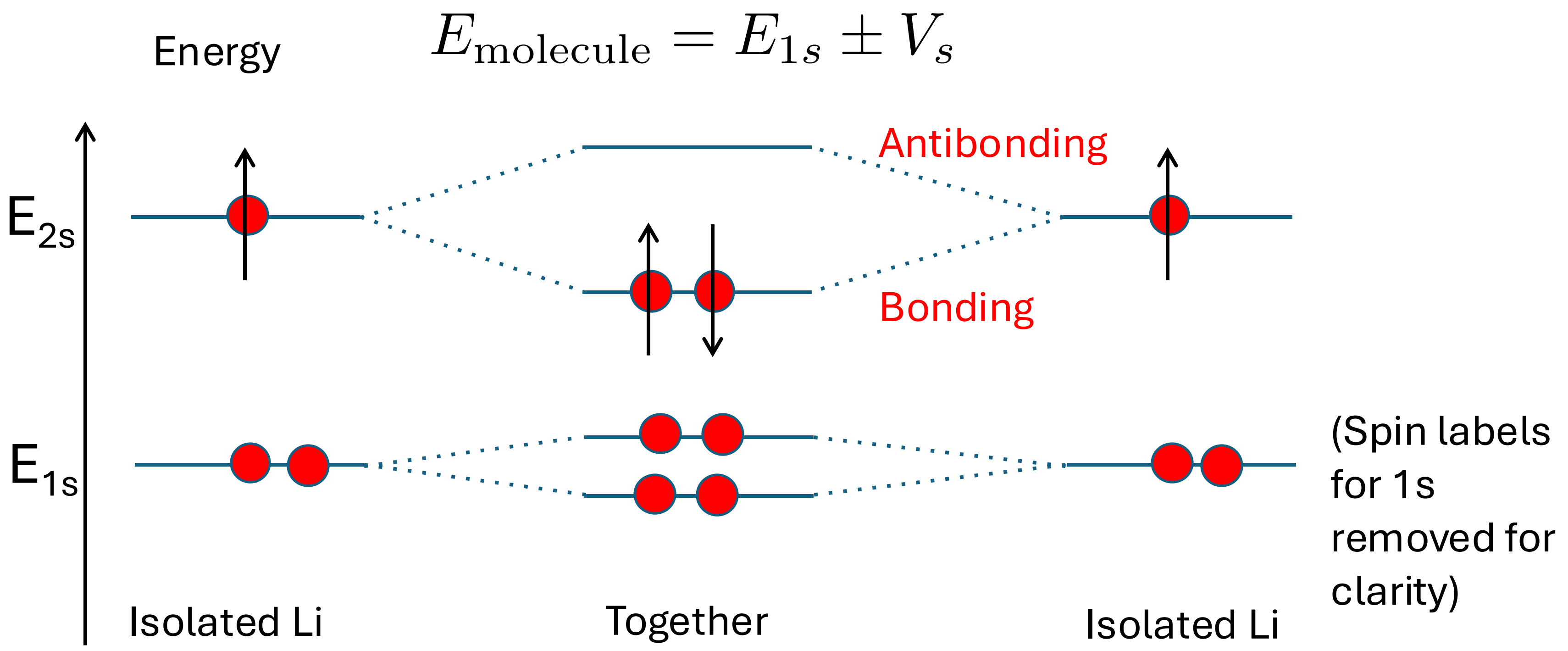


Answer: The four electrons occupy both the bonding and the antibonding orbitals. The net energy gain is zero. → No bond formation.

(in reality: weak van der Waals bond, but broken by zero point motion: Helium remains liquid even at 0 K.

In-class exercise: Li_2

Follow the same steps for the Li_2 molecule. Does the Li_2 molecule bind or not? If yes, which electrons contribute to bonding?



(Spin labels for 1s removed for clarity)

Answer: the filled 1s electrons (**core electrons**) do not contribute to bonding. The **valence** 2s **electrons** lower the energy and bind Li_2. V_s is larger for 2s electrons than 1s electrons. Why?

Answer: 2s orbital is larger, 2s electrons more easily shared than 1s.

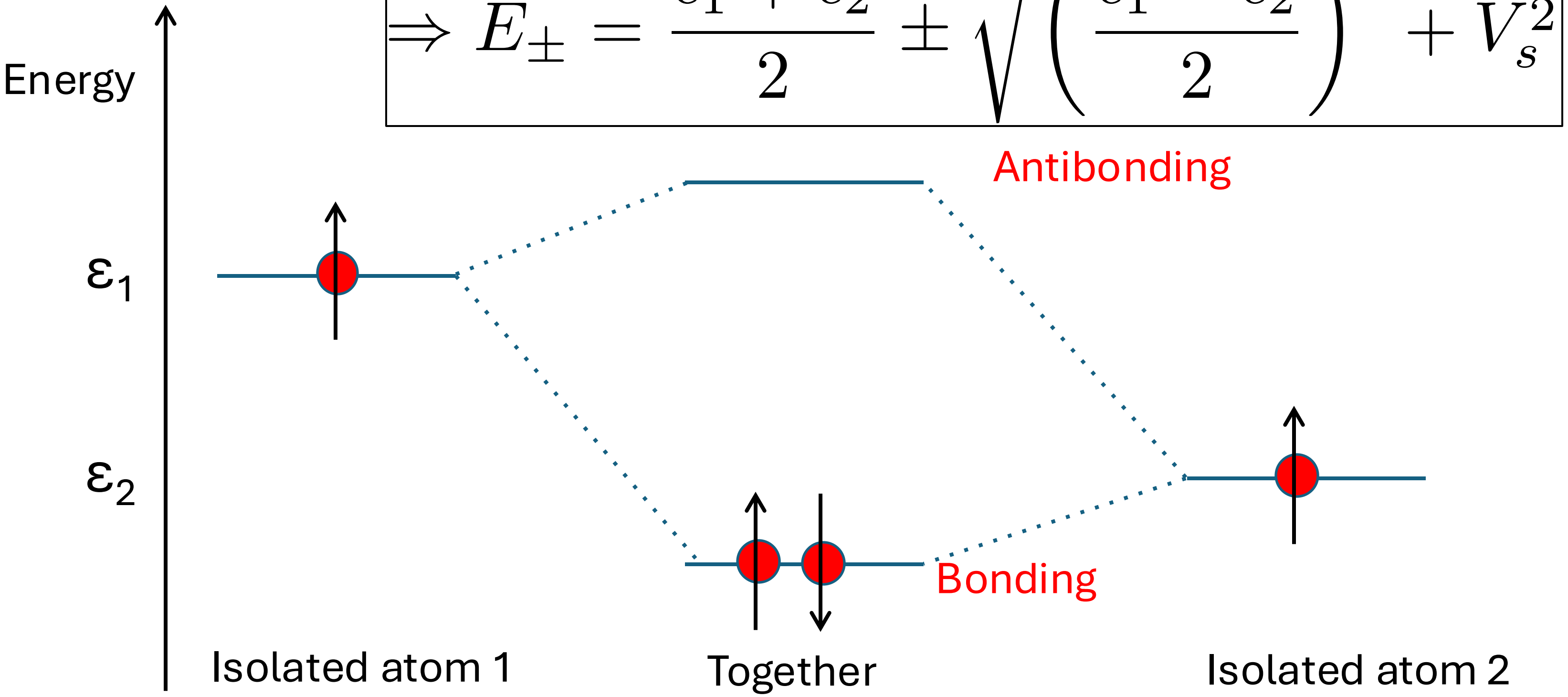
What if the two atoms are different?

In-class: what are the energies of the molecular orbitals if $\varepsilon_1 \neq \varepsilon_2$?

Answer: go back to the eigenvalue problem (determinant) and solve for $\varepsilon_1 \neq \varepsilon_2$.

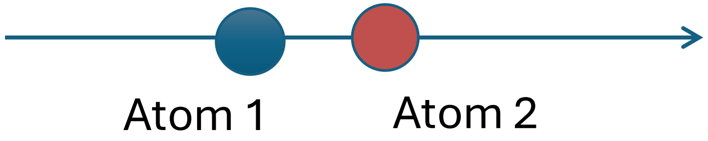
$$\mathrm{Det} = 0 \Rightarrow (\epsilon_1 - E)(\epsilon_2 - E) - V_s^2 = 0$$

$$\boxed{\Rightarrow E_\pm = \frac{\epsilon_1 + \epsilon_2}{2} \pm \sqrt{\left(\frac{\epsilon_1 - \epsilon_2}{2}\right)^2 + V_s^2}}$$

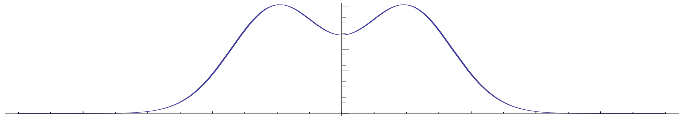


Question

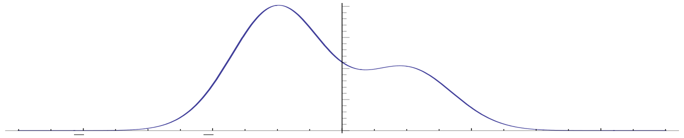
If $\varepsilon_1 > \varepsilon_2$, what is the shape of the bonding molecular orbital?



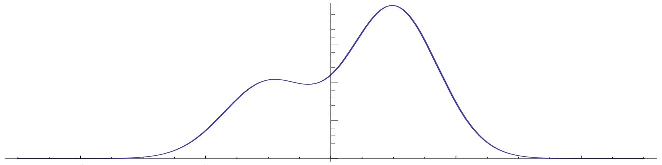
A.



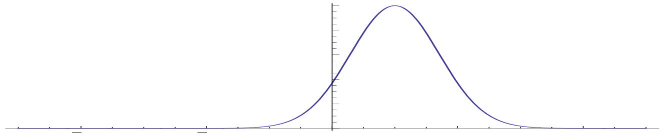
B.



C.



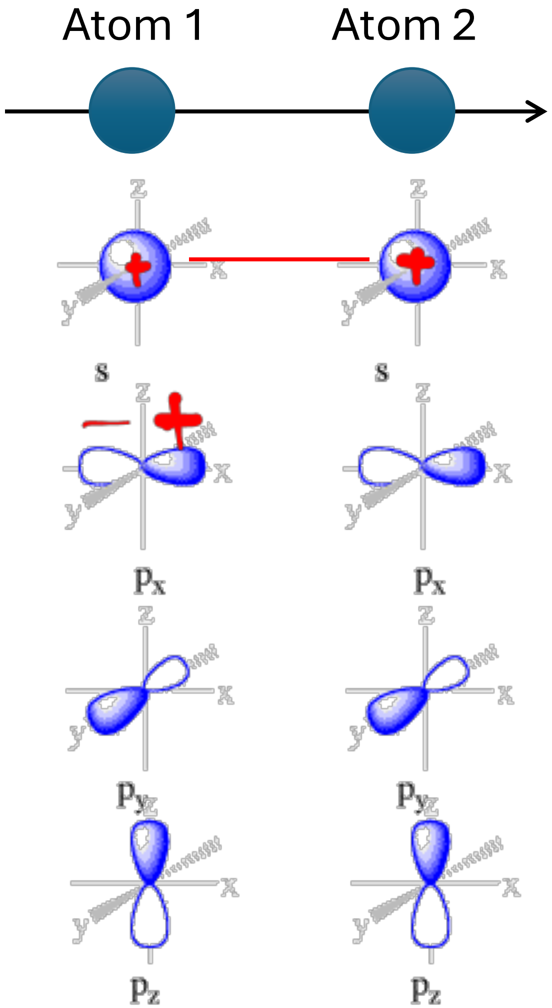
D.



Answer: **C**: Atom 2 is more electronegative ($\varepsilon_2<\varepsilon_1$, therefore the potential well is deeper). There is a higher probability that the electron will be nearer atom 2. However, there is still some probability that the electron will be shared between both atoms.

Diatomic molecules with p orbitals

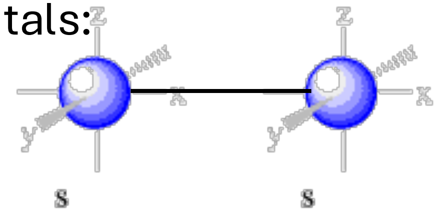
The p valence electrons (e.g., C, N, O) also participate in bonding



Key quantities**: interatomic matrix elements** for each pair of atomic orbitals

$$\int \psi_1^*(\vec{r}) H \psi_2(\vec{r}) d\vec{r}$$

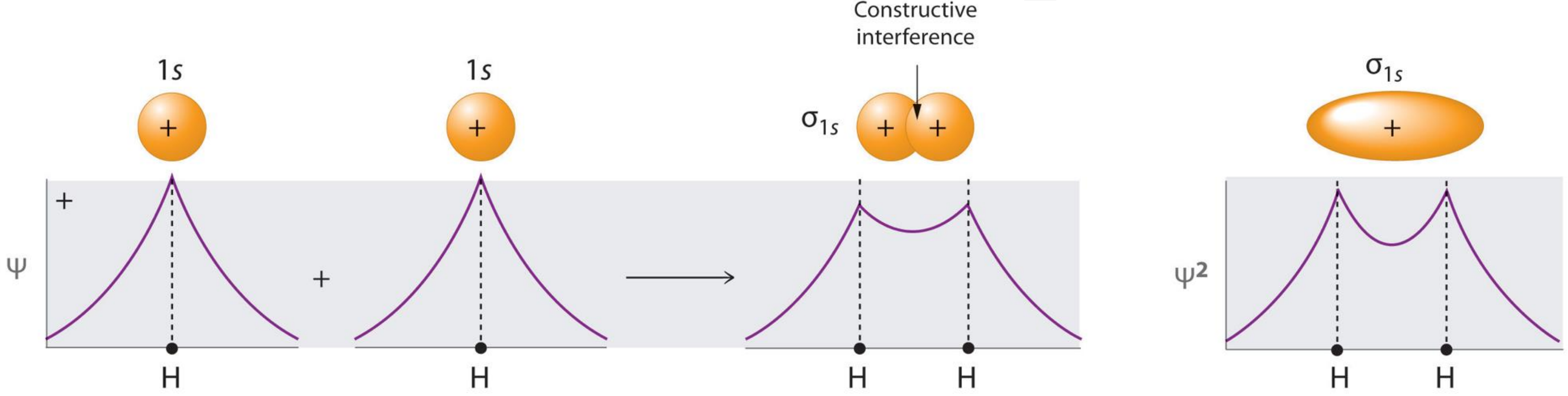
For a pair of s orbitals:



$$\int \psi_1^*(\vec{r}) H \psi_2(\vec{r}) d\vec{r} = -V_s = V_{ss\sigma}$$

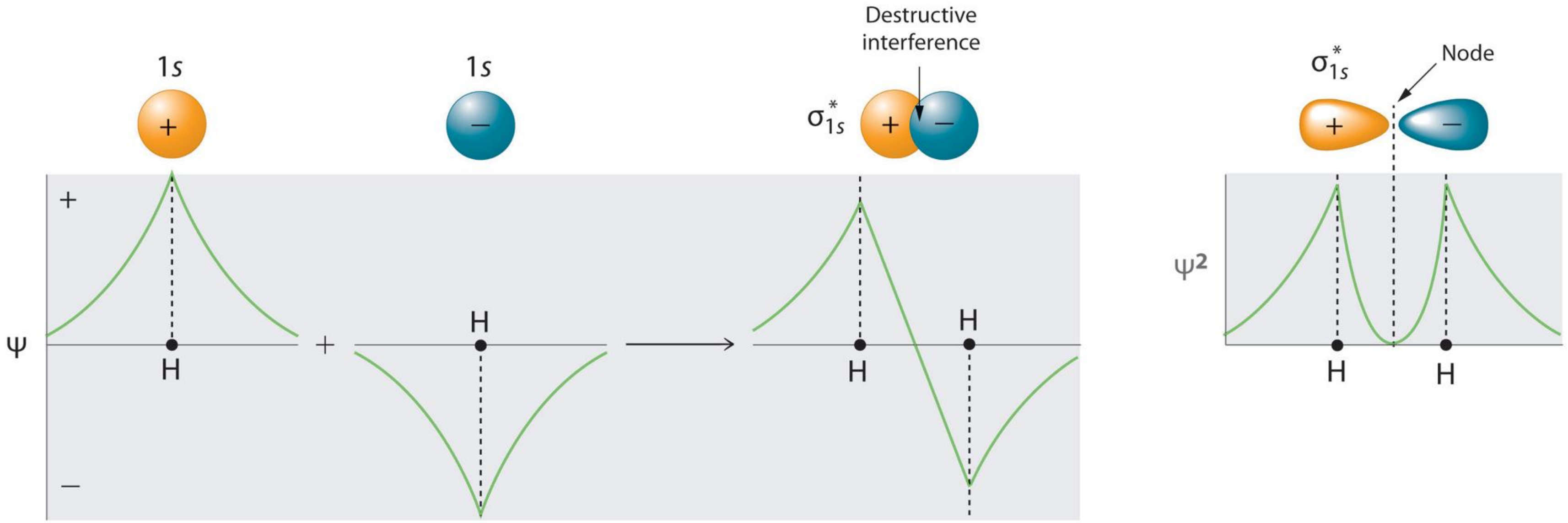
Two atomic s orbitals combine to form σ and σ* molecular orbitals

Molecular orbitals of H_2 molecule



(a) Wave functions combined for σ_{1s}

(b) Bonding probability density



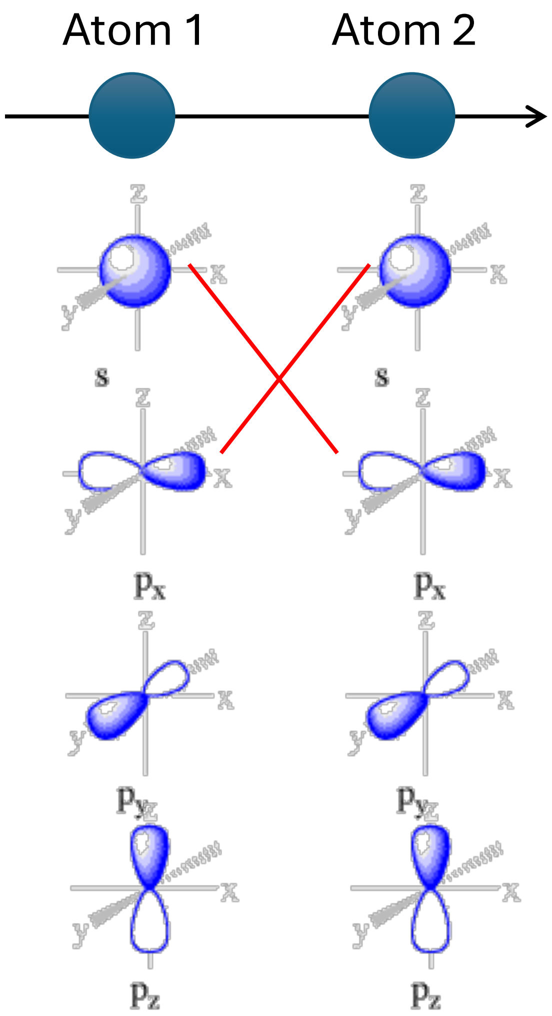
(c) Wave functions combined for σ^*_{1s}

(d) Antibonding probability density

http://chemwiki.ucdavis.edu/Textbook_Maps/General_Chemistry_Textbook_Maps/Map%3A_Chemistry%3A_The_Central_Science_(Brown_et_al.)/09._Molecular_Geometry_and_Bonding_Theories/9.7%3A_Molecular_Orbitals

Diatomic molecules with p orbitals

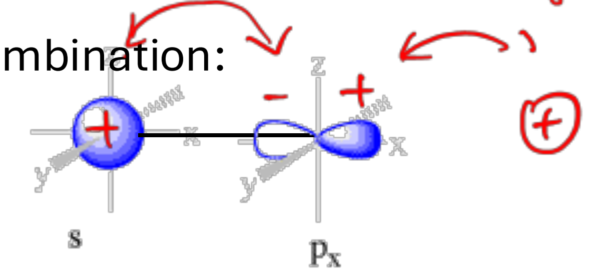
The p valence electrons (e.g., C, N, O) also participate in bonding



For the p_x–s combination:

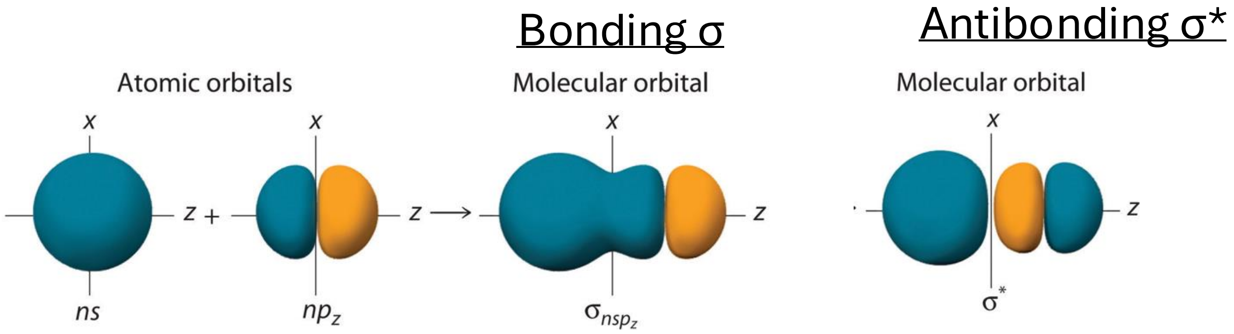
$V_{sp\sigma} > 0$

$V_{sp\sigma} < 0$



$$\int \psi_1^*(\vec{r}) H \psi_2(\vec{r}) d\vec{r} = V_{sp\sigma}$$

One s and one p orbitals combine to form σ and σ* orbitals:

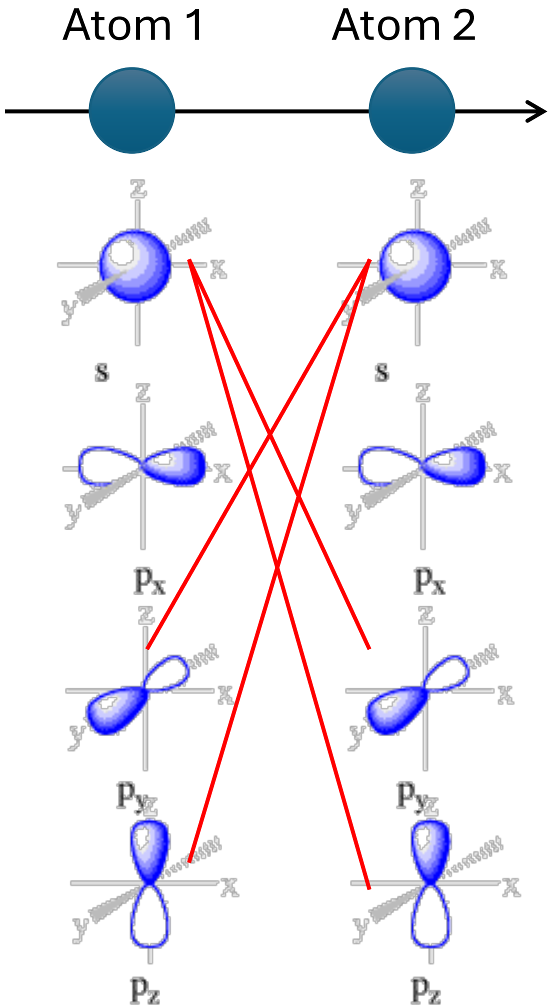


Bonding σ

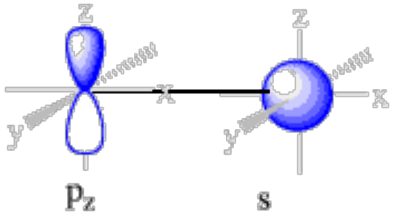
Antibonding σ*

Diatomic molecules with p orbitals

The p valence electrons (e.g., C, N, O) also participate in bonding



For the p_y–s or p_z–s combinations:

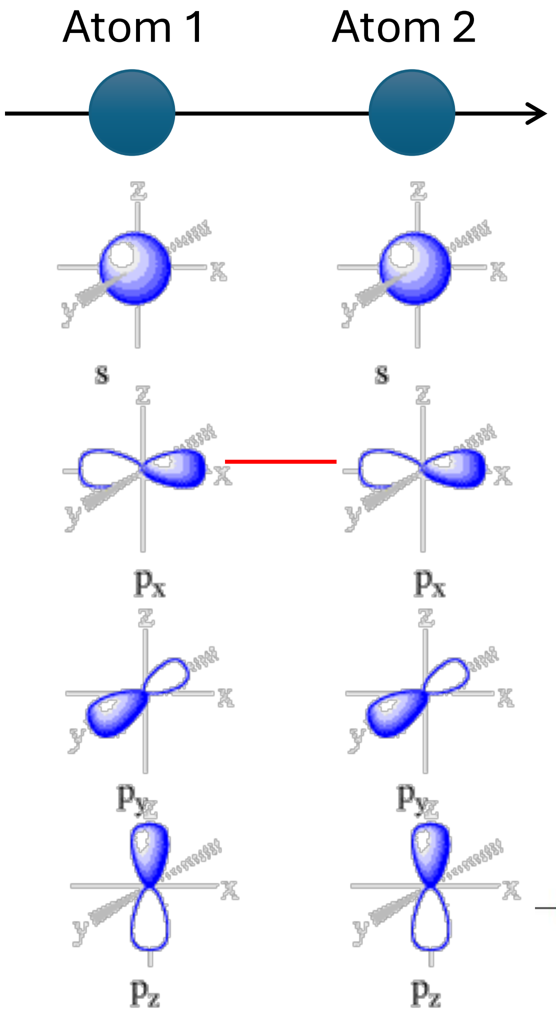


$$\int \psi_1^*(\vec{r}) H \psi_2(\vec{r}) d\vec{r} = 0$$

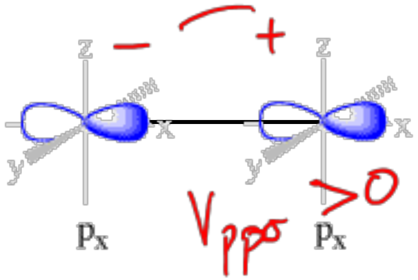
The product of the two orbitals is an odd function with respect to z axis, integral is zero

Diatomic molecules with p orbitals

The p valence electrons (e.g., C, N, O) also participate in bonding



For a pair of p orbitals that interact tip-to-tip :



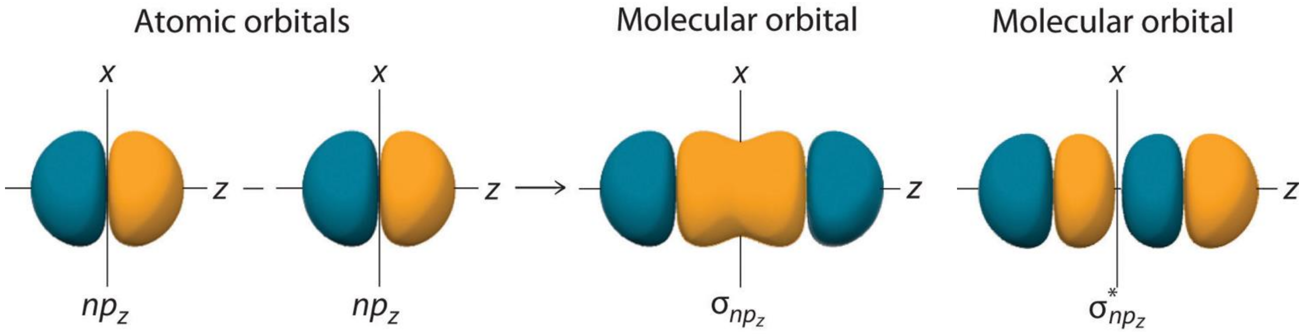
$V_{pp\sigma} > 0$

$$\int \psi_1^*(\vec{r}) H \psi_2(\vec{r}) d\vec{r} = V_{\underline{pp\sigma}}$$

Two p orbitals combine to form σ and σ* orbitals

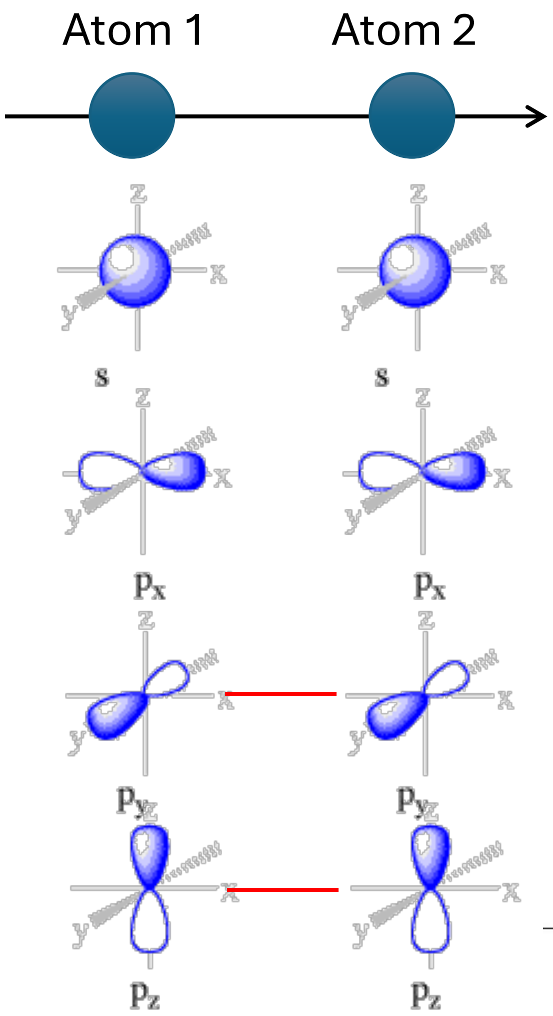
Bonding σ

Antibonding σ*

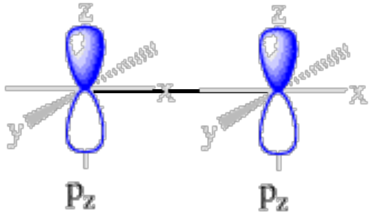


Diatomic molecules with p orbitals

The p valence electrons (e.g., C, N, O) also participate in bonding



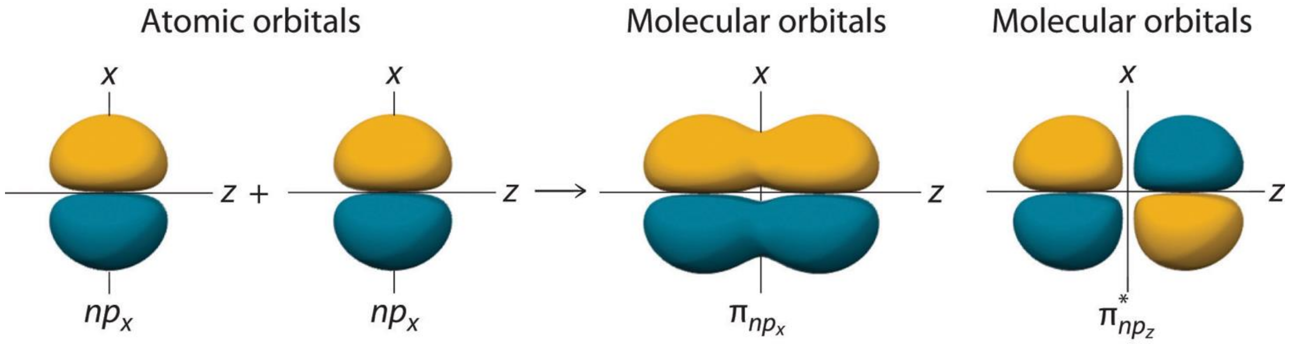
For a pair of p orbitals that interact side-to-side :



$$\int \psi_1^*(\vec{r}) H \psi_2(\vec{r}) d\vec{r} = V_{pp\pi}$$

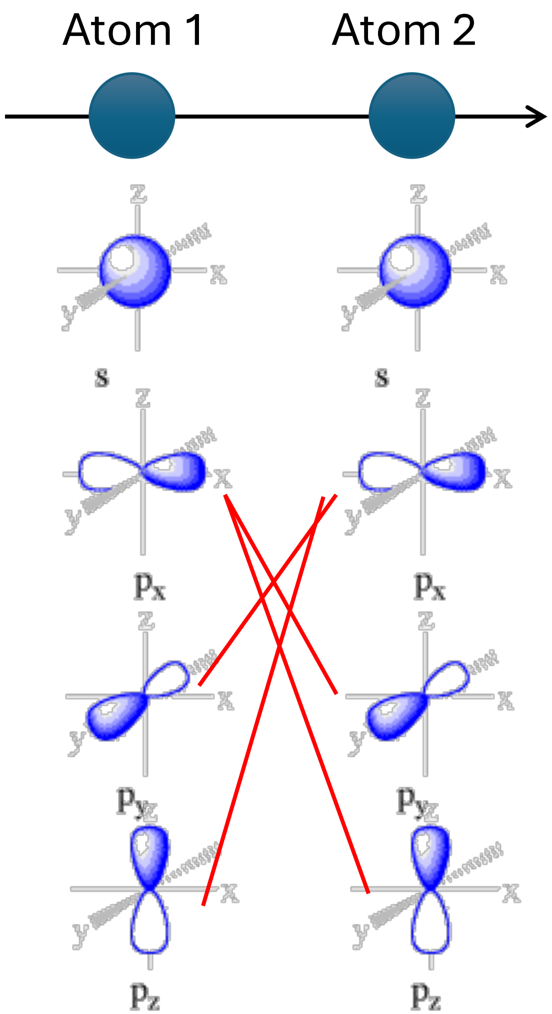
Two p orbitals combine to form π and π* molecular orbitals:

<u>Bonding π</u> <u>Antibonding π*</u>

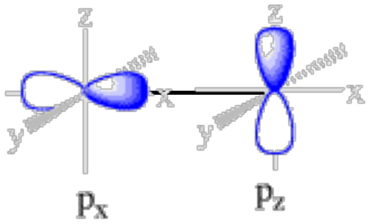


Diatomic molecules with p orbitals

The p valence electrons (e.g., C, N, O) also participate in bonding



For the tip-to-side p-orbital combination:

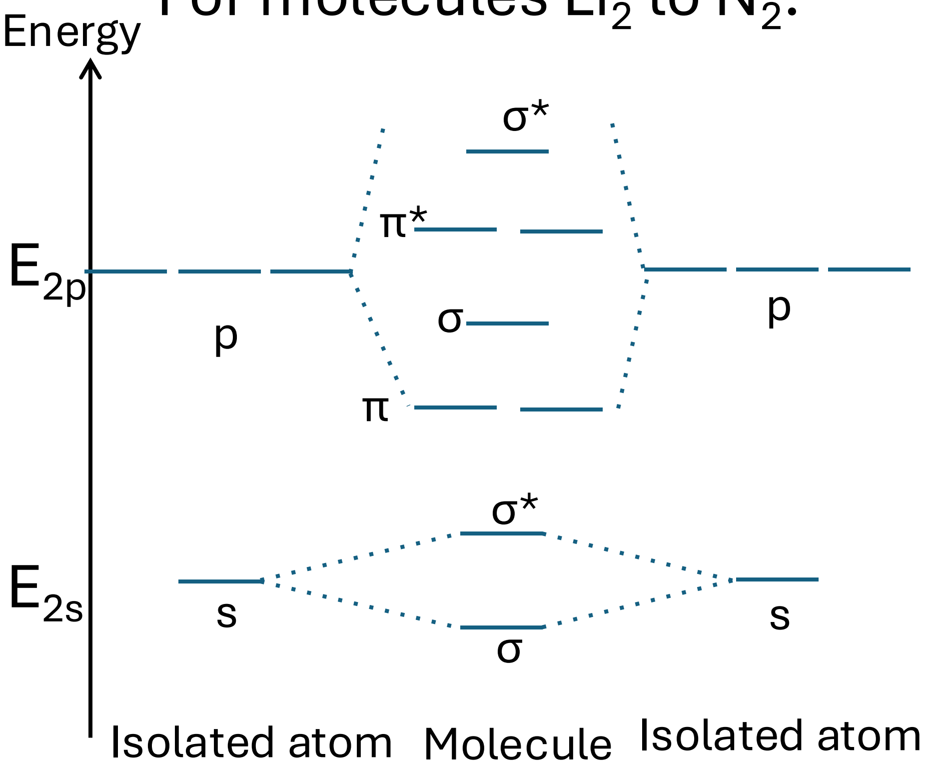


$$\int \psi_1^*(\vec{r}) H \psi_2(\vec{r}) d\vec{r} = 0$$

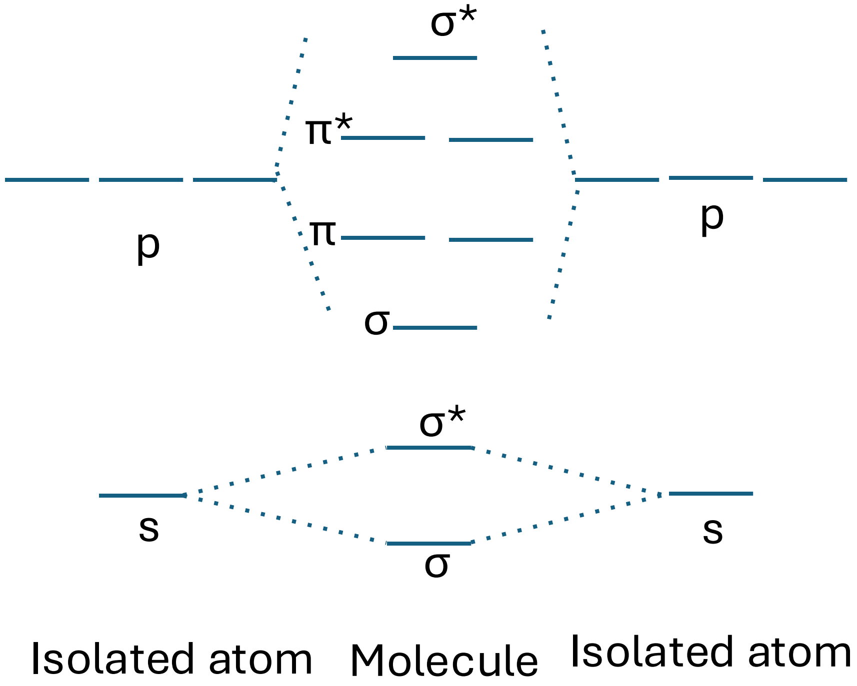
The product of the two orbitals is an odd function with respect to z, integral is zero

Energies of molecular orbitals

For molecules Li_2 to N_2:

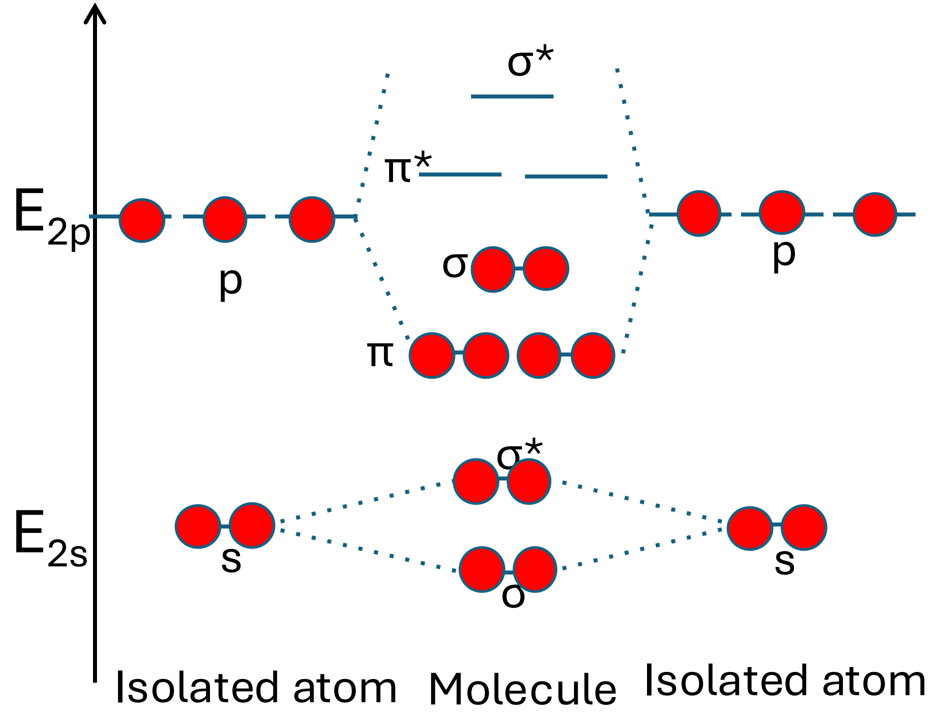


For O_2 and F_2:



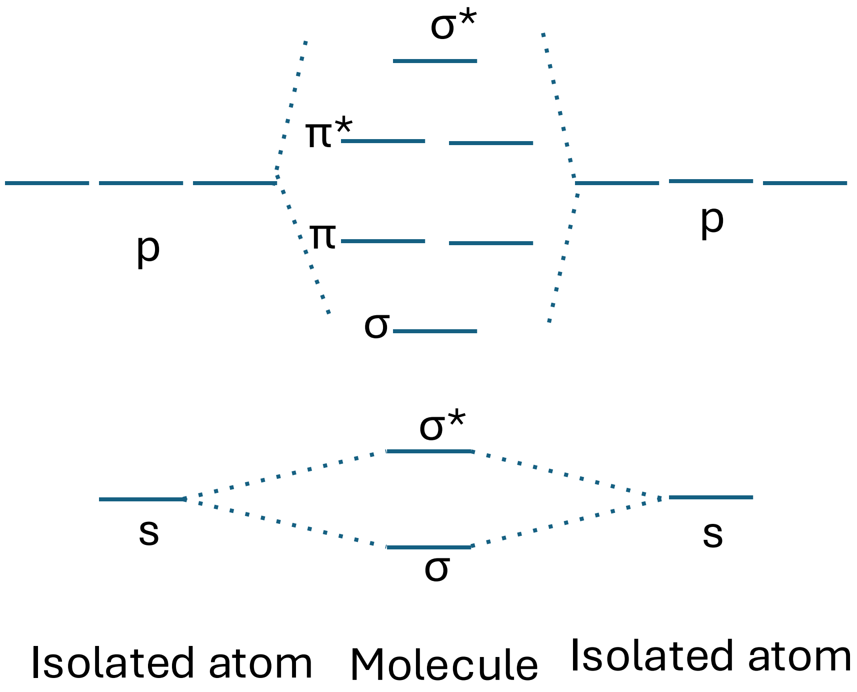
Exercise: occupations of the molecular orbitals of N_2

For molecules Li_2 to N_2:



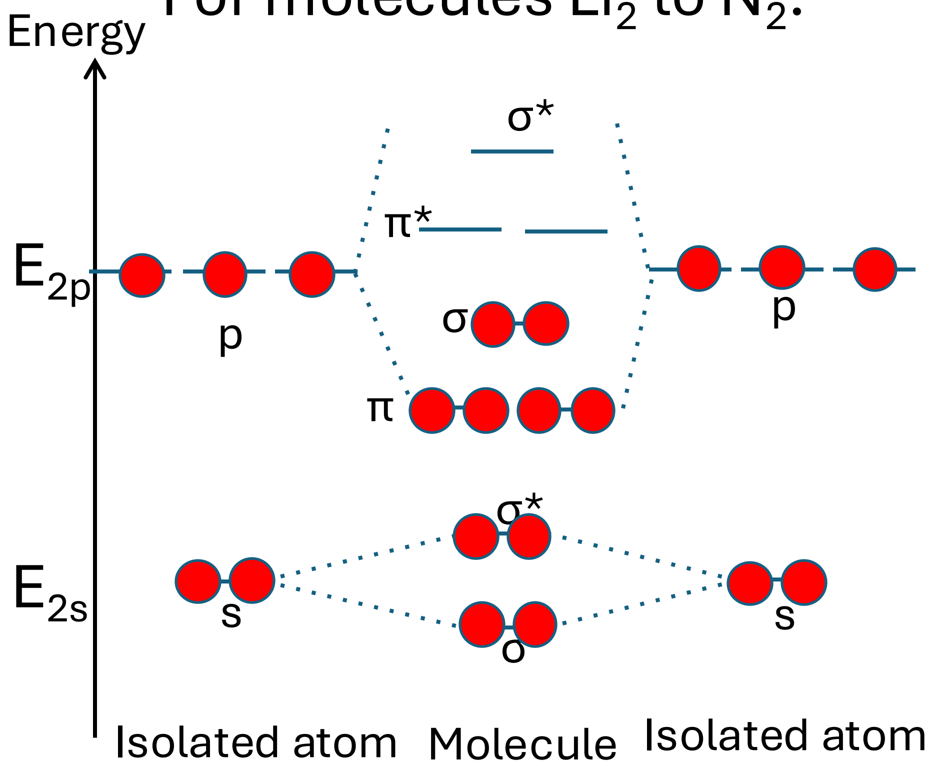
Answer

For O_2 and F_2:



Question

For molecules Li_2 to N_2:



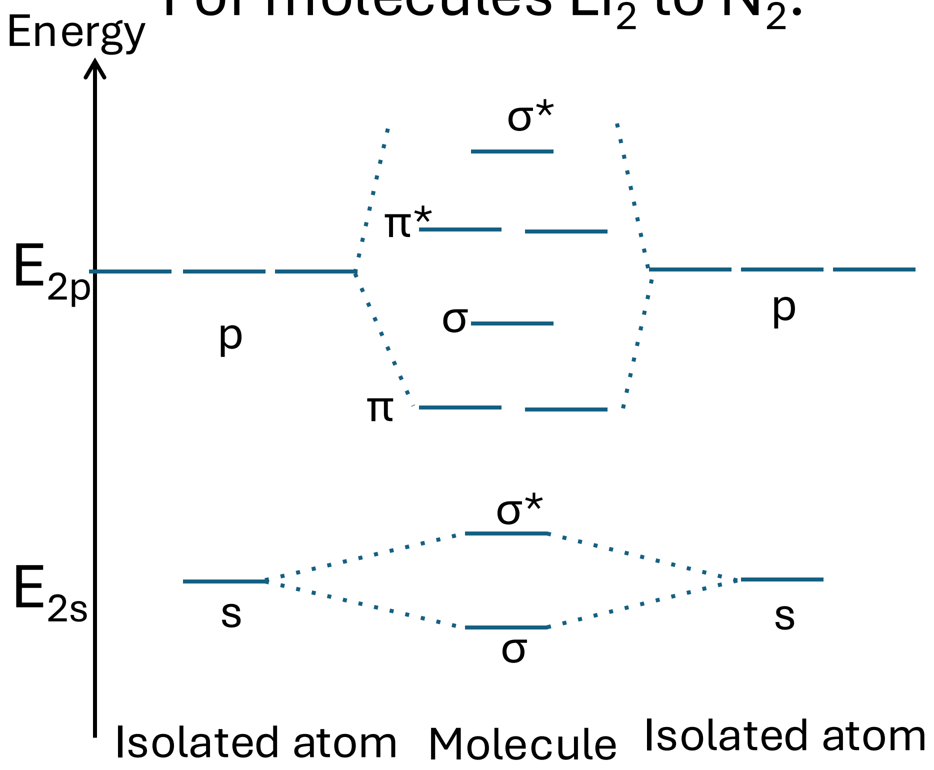
What is the nature of the bond of N_2?

A. Single
B. Double
C. Triple
D. Quadruple

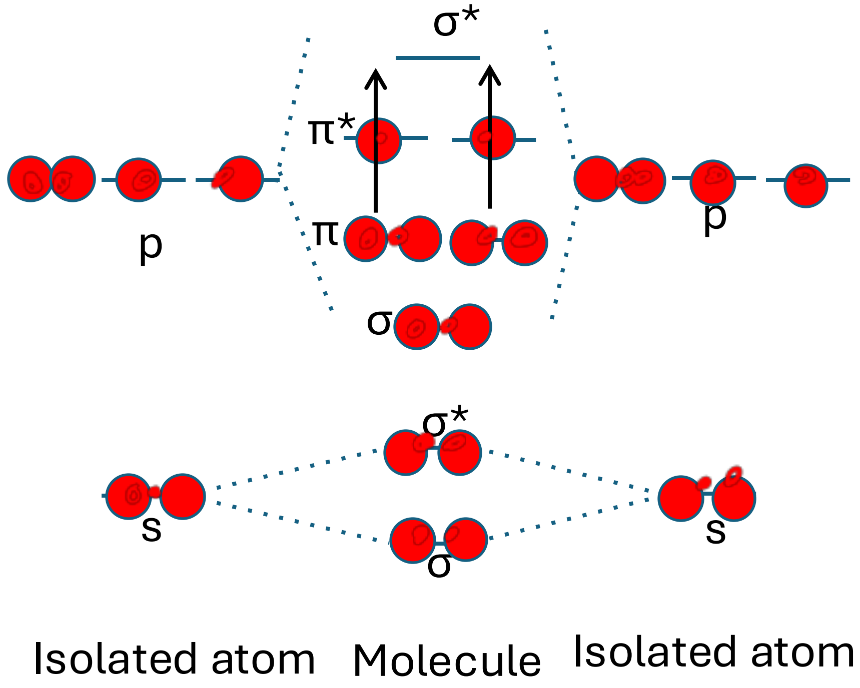
Answer: C. Three pairs of electrons lower their energy by occupying molecular orbitals

In-class exercise: find the occupations of the molecular orbitals of O_2

For molecules Li_2 to N_2:



For O_2 and F_2:



Answer

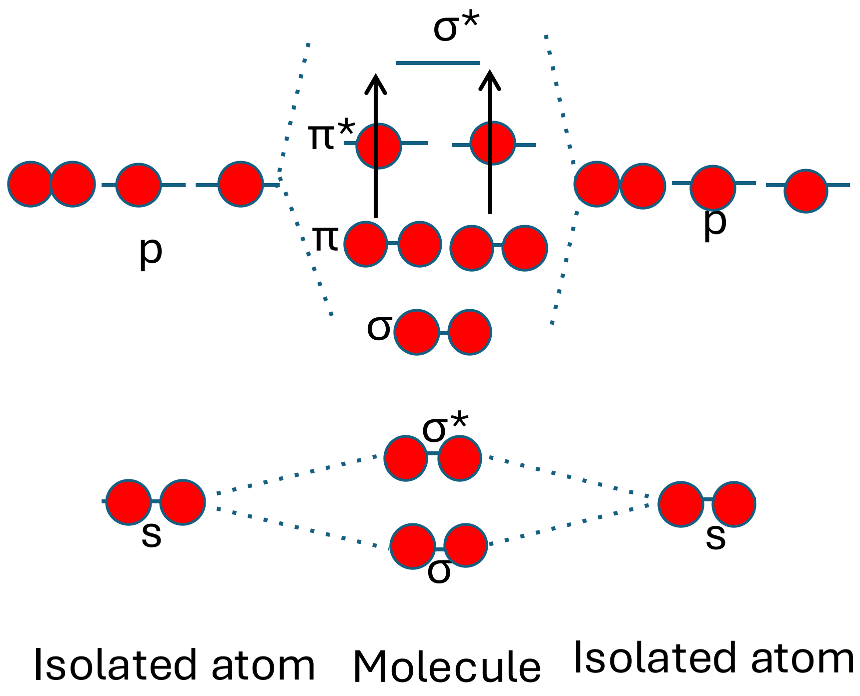
Question:

What is the nature of the bond of O_2?

A. Single
B. Double
C. Triple
D. Quadruple

Answer: B. The pair of electrons occupying π* cancel out the energy gain by one of the π pairs

For O_2 and F_2:

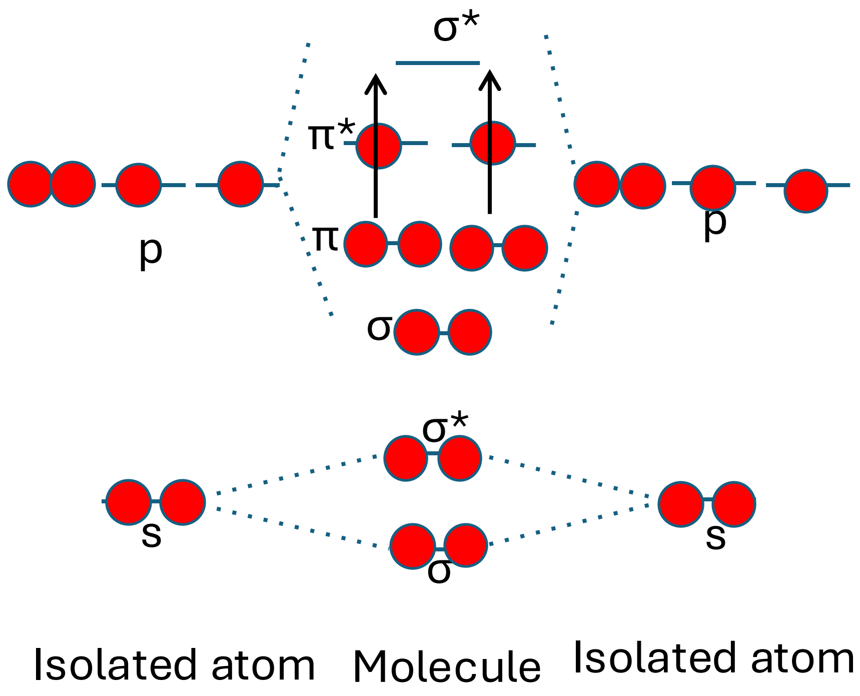


Question:

Is O_2 really magnetic?

Answer:
https://www.youtube.com/watch?v=Lt4P6ctf06Q

For O_2 and F_2:



Hybridization

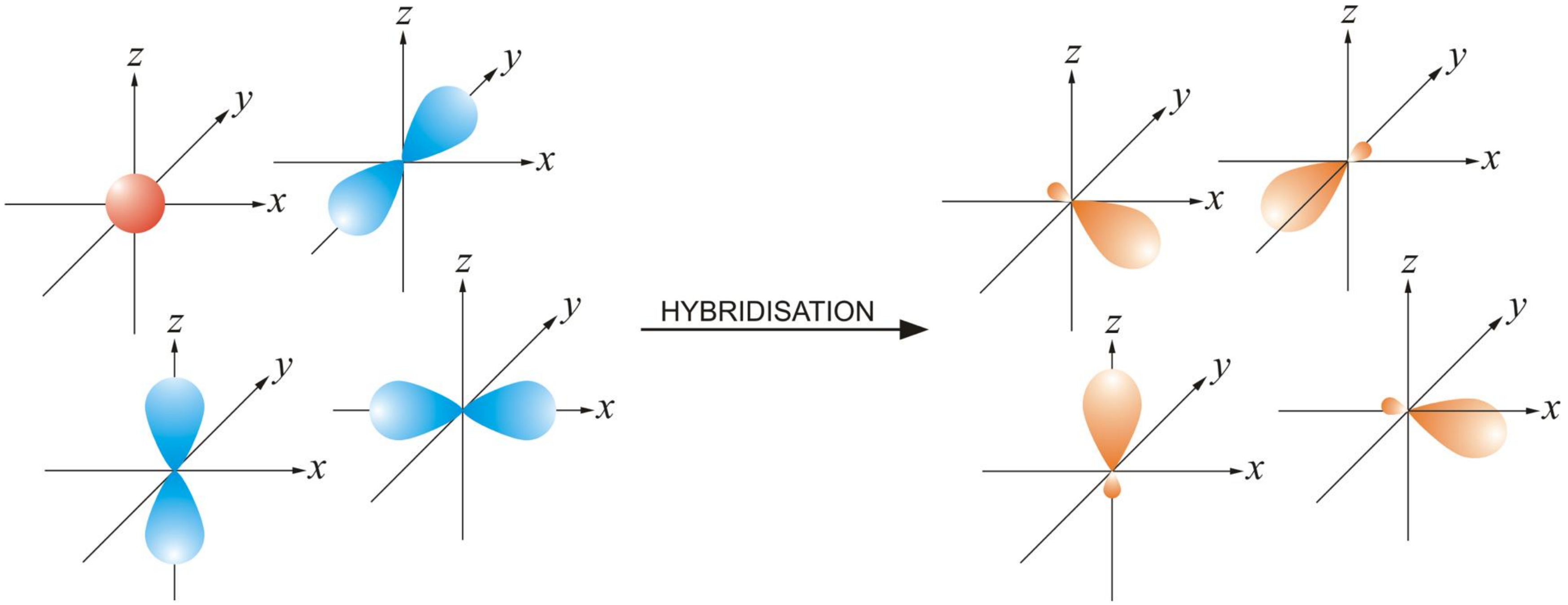
Mix s and p orbitals of the same atom to create new types of hybrid orbitals. More directional, stronger bonding.

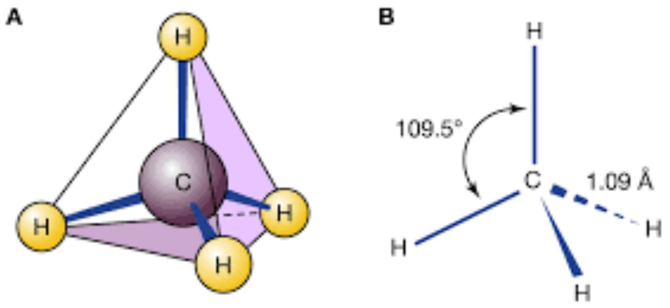
http://glossary.periodni.com/glossary.php?en=sp3+hybrid+orbital

sp^3 hybridization: mix all 3 p orbitals with s.

Directional orbitals: more overlap, larger interatomic matrix element, stronger bonds.

Example: CH_4





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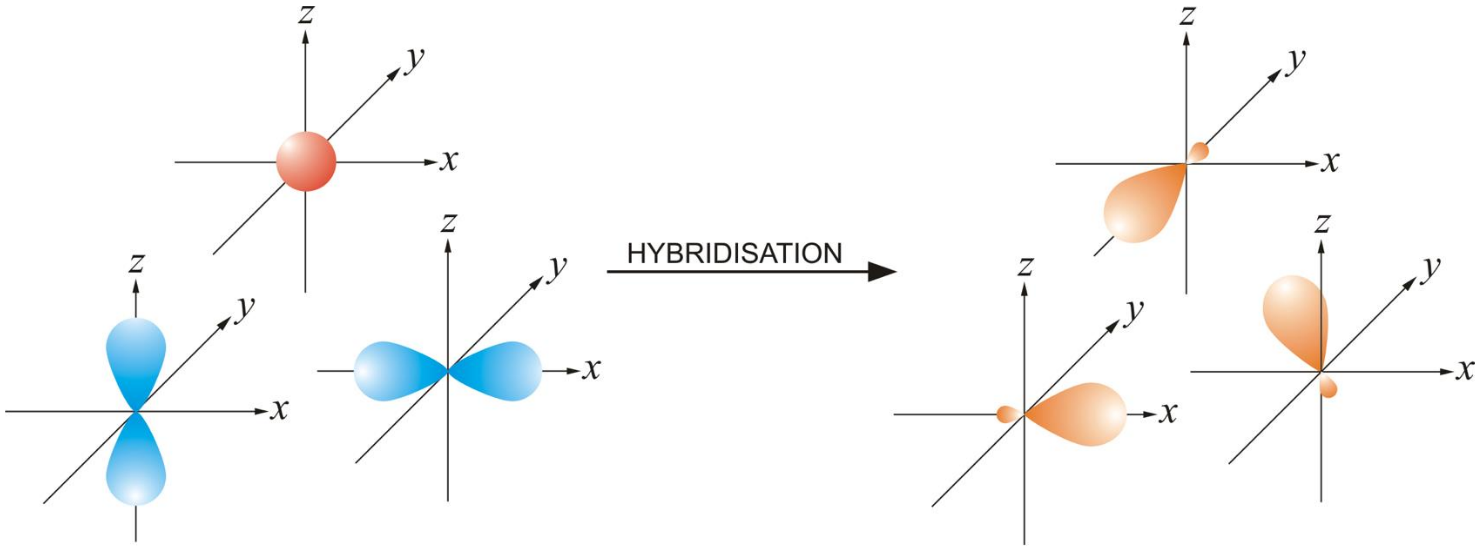
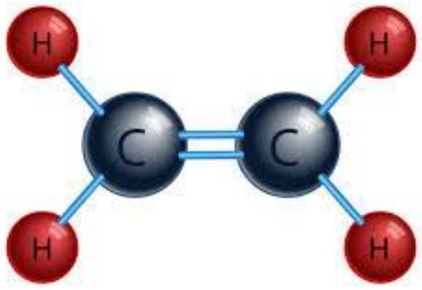
sp2 hybridization

Mix s with only two of the three p orbitals, create planar directional molecules.

http://glossary.periodni.com/glossary.php?en=sp2+hybrid+orbital

Example: ethene C_2H_4



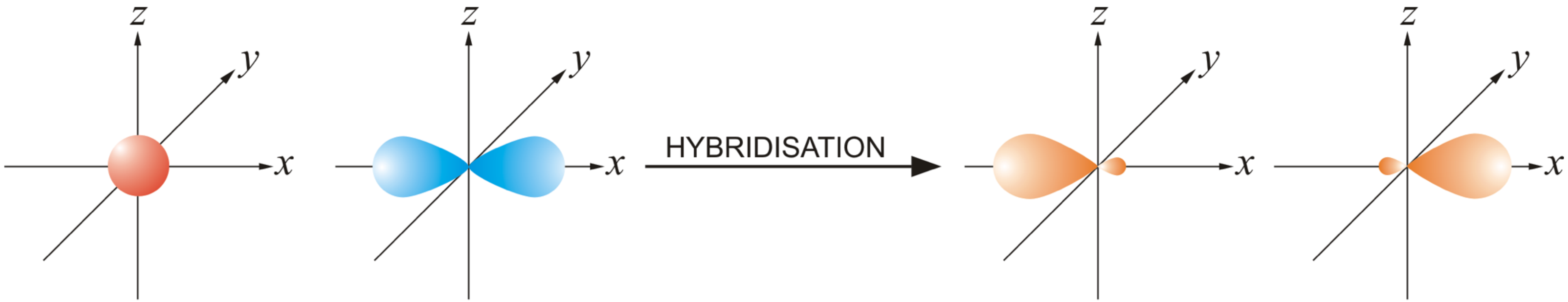


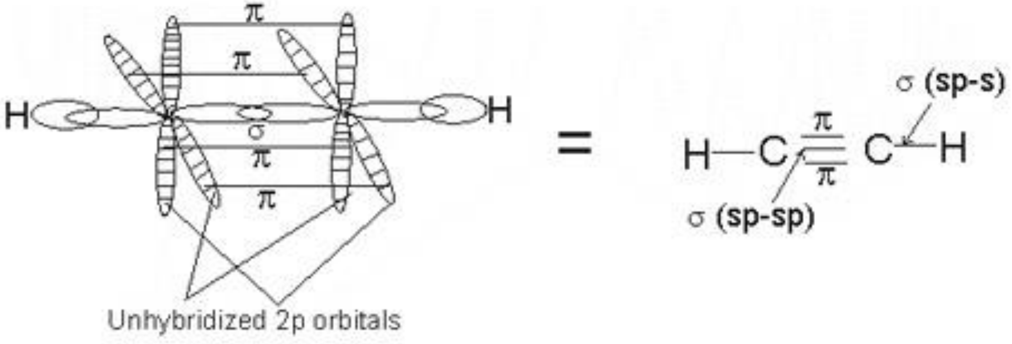
sp hybridization

Mix s with only one p orbital, create linear bonds.

http://glossary.periodni.com/glossary.php?en=sp+hybrid+orbital

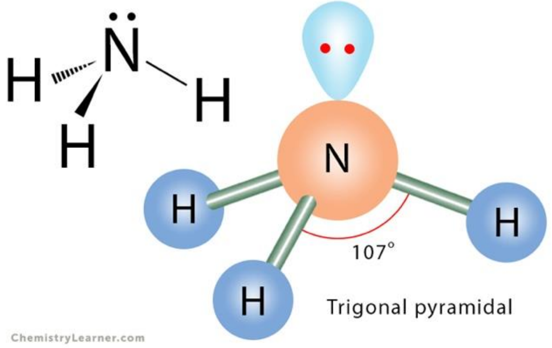
Example: acetyline (ethyne) C_2H_2



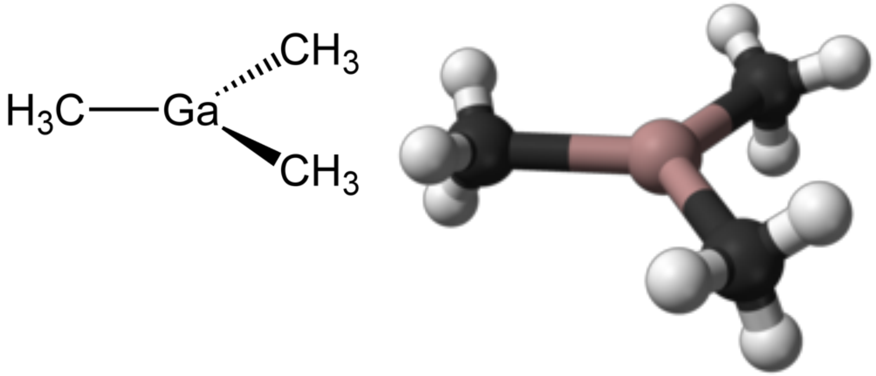


Precursors for the MOCVD synthesis of nitrides

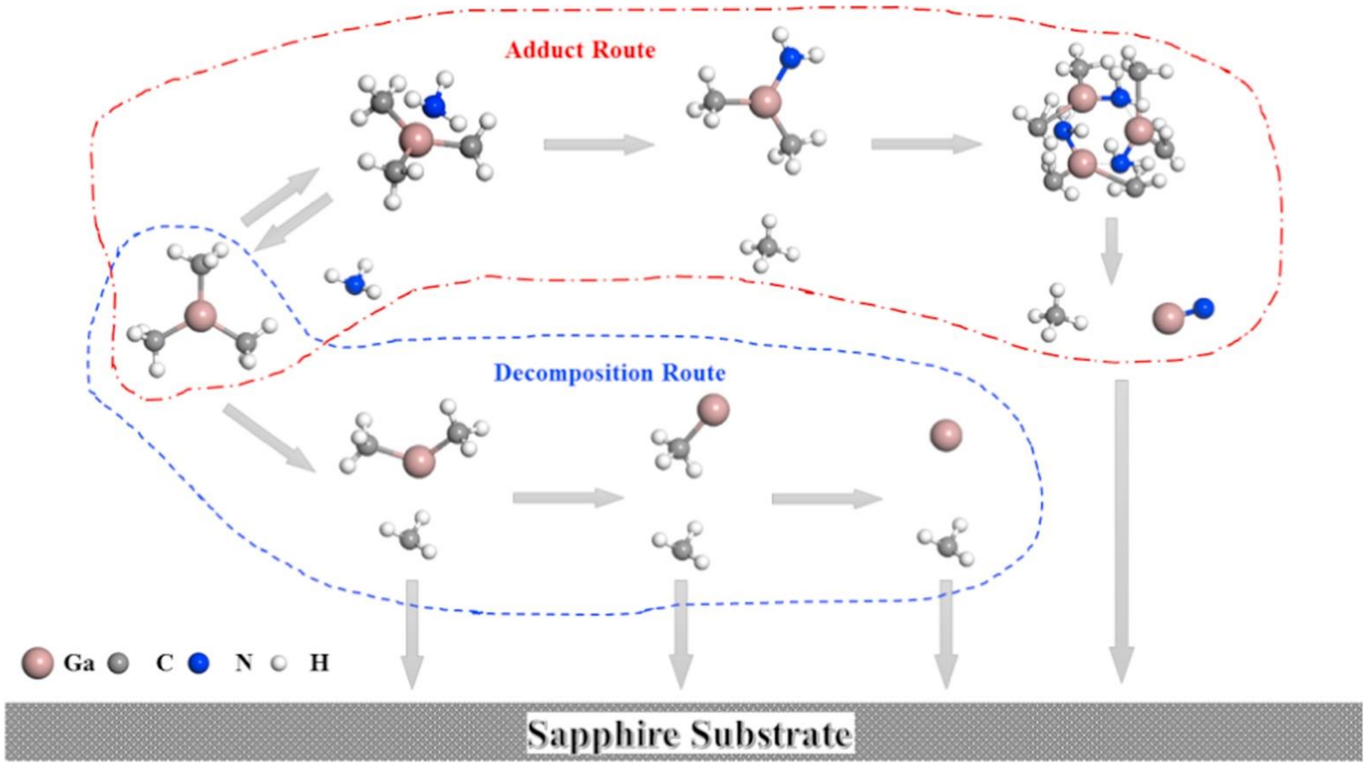
Ammonia: NH_3



Trimethylgallium: $Ga(CH_3)_3$



$NH_3 + Ga(CH_3)_3 \rightarrow GaN(s) + 3CH_4$



https://doi.org/10.1016/j.jcrysgro.2016.09.010

Conjugation

Alternate single-double bonds

Example: $CH_2{=}CH{-}CH{=}CH_2$

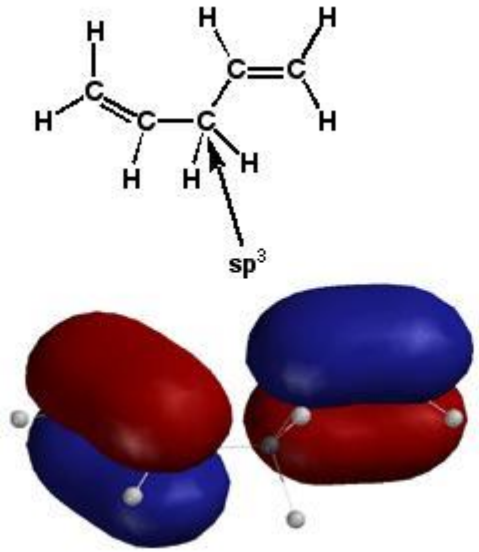
Example: benzene

Conjugated wave functions extend over the entire volume of the molecule.

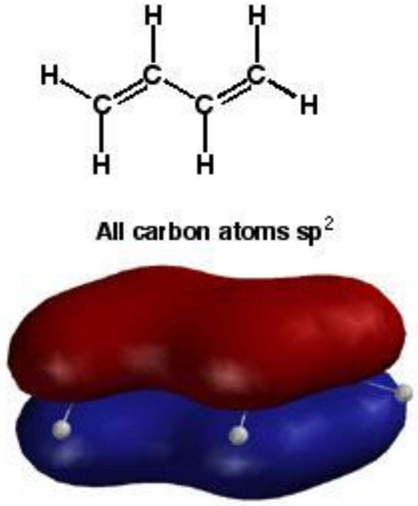
Applications: organic electronics.

Wave functions of extended systems (e.g., nitrides) are also extended over the entire volume of the material.

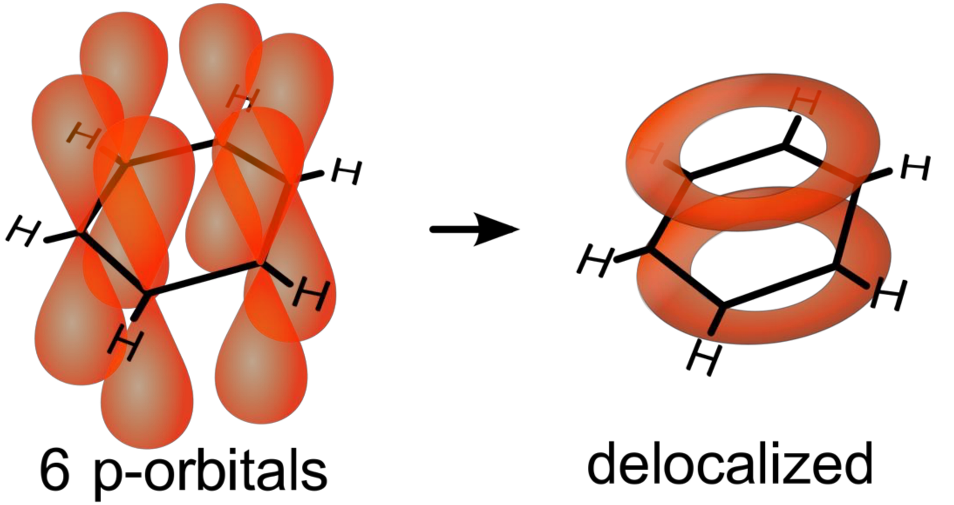
https://instruct.uwo.ca/chemistry/373f/Nifty%20Stuff/ethylene.htm



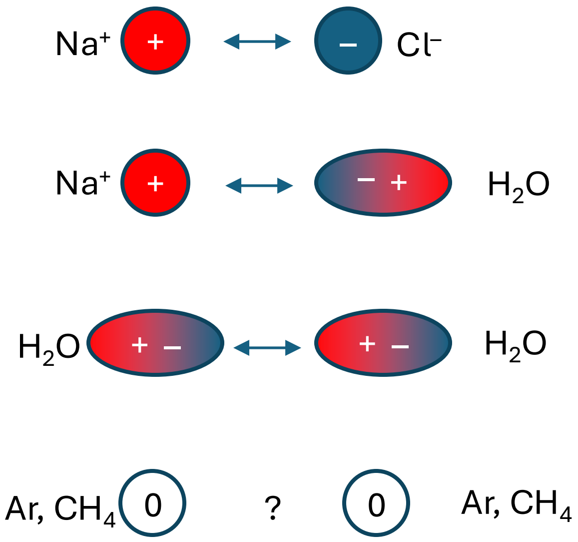
Non-conjugated π system
(π bonds do not interact)

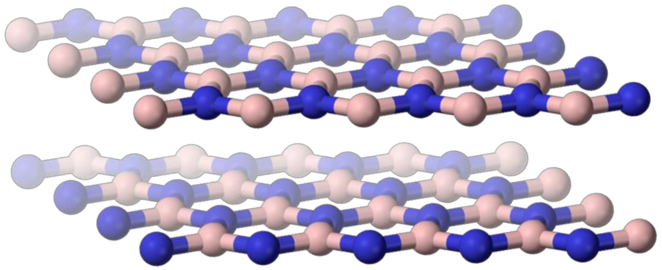


Conjugated π system
(Electron density
delocalized over all
four carbon atoms)



Van der Waals interaction





For neutral, non-polar objects (Ar, CH_4):

Expectation value of electric dipole moment:
$\langle \overrightarrow{d_1} \rangle = \langle \overrightarrow{d_2} \rangle = 0$

→No static dipole-dipole interaction

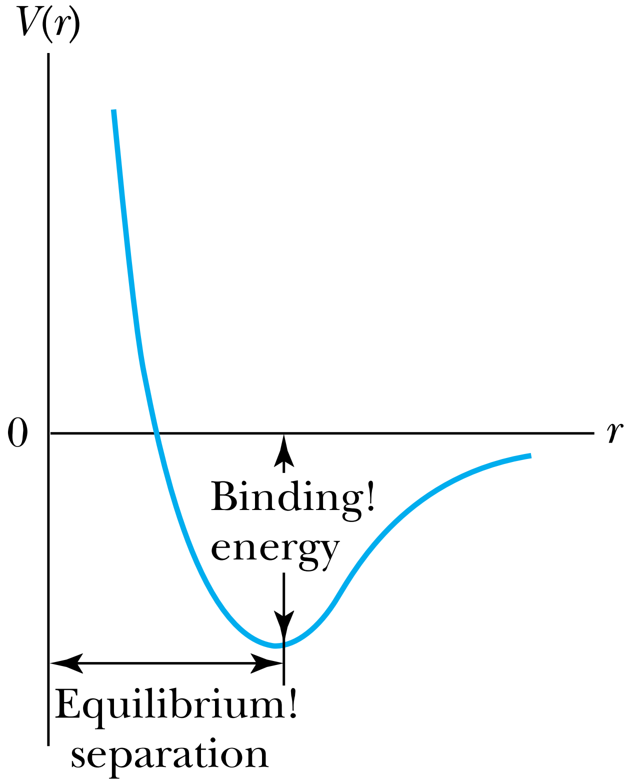
But: from quantum mechanics: $\langle \overrightarrow{d_1} \cdot \overrightarrow{d_2} \rangle \neq 0$
→Dynamic dipole-dipole interaction

The van der Waals interaction is a purely quantum mechanical interaction. Always attractive.

$$V(r) = -\frac{A}{r^6}$$

E.g., van der Waals bonding in 2D materials (graphite, hexagonal BN, etc.)

Binding energy and equilibrium separation



Typical values for the equilibrium distance and for the binding energy: $R_0 \cong 10^{-10}$ m, $E_0 \cong 1$ eV

Vibrational spectra of molecules

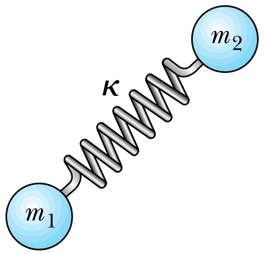
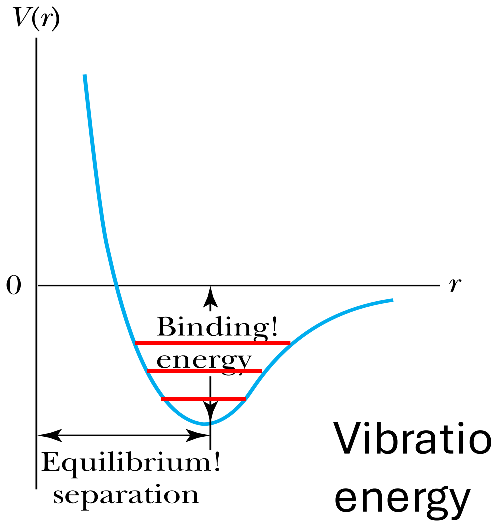


Figure 10.5 A model of a diatomic molecule with the two masses m_1 and m_2 connected by a massless spring with force constant κ.

$$E_{\text{vibr}} = \left(n + \tfrac{1}{2}\right)\hbar\omega$$

$$\omega = \sqrt{\frac{\kappa}{\mu}}$$

$$\mu = m_1 m_2 / (m_1 + m_2)$$



Vibrational energy levels

Exercise: what is the vibrational frequency of HCl if k = 480 N/m?

m_H = 1 u, m_{Cl} = 35.5 u, u = 1.66054×10^{-27} kgr

Answer:

$\mu = m_H m_{Cl}/(m_H + m_{Cl}) = 1.63\times10^{-27}$ kgr

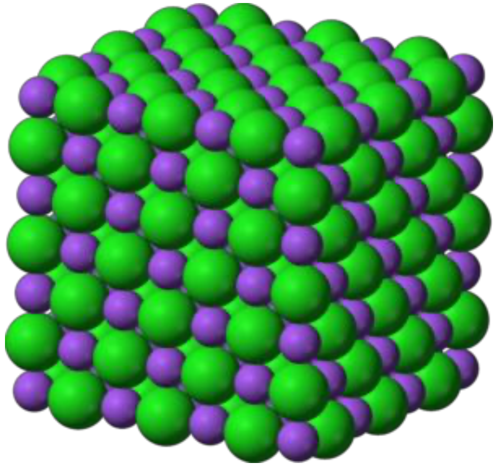
$\omega = 5.43\times10^{14}$ rad/s, $\hbar\omega = 0.36$ eV

$f = \omega/2\pi = 8.64\times10^{13}$ Hz

Crystals

Crystal = regular periodic arrangement of atoms in a material

As opposed to **amorphous** materials: no long-range order



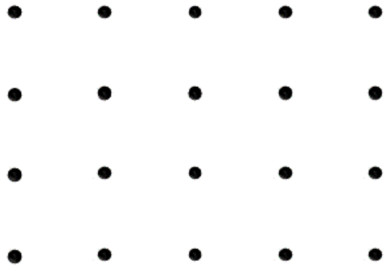
Question: give examples of crystalline materials: Answer: salt, sugar, metals, silicon, nitrides, all materials at low T

Question: what evidence do we have that materials are crystalline? Answer: X-ray and electron diffraction

Question: Why are materials crystalline? Answer: a crystal arrangement minimizes the energy

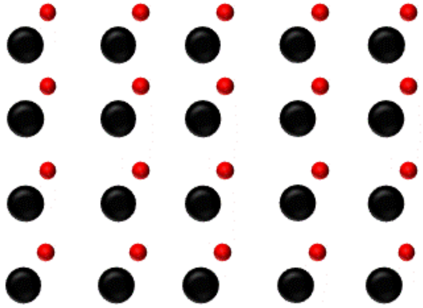
Question: Why? Answer: we do not know

Crystal structure = space lattice + atomic basis



Space Lattice

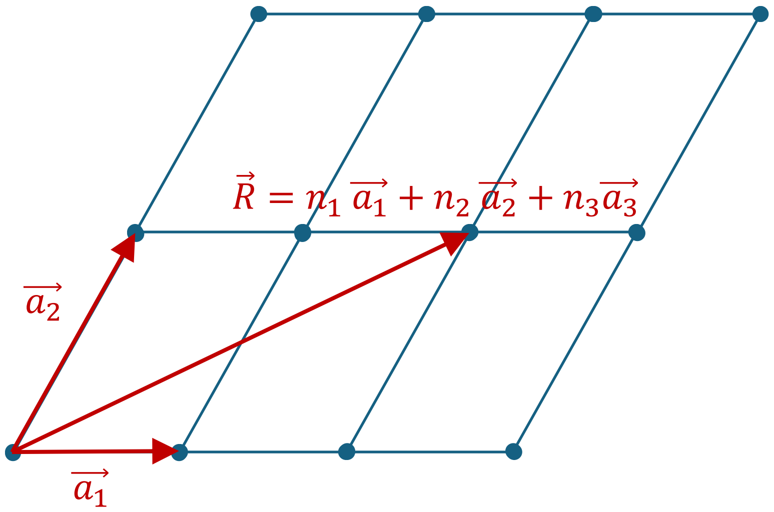
Basis (atoms)



Crystal structure

The crystal structure is formed by adding basis (atoms) to every lattice points of the lattice. The number of atoms in the basis may be one or more than one.

http://scienceline.ucsb.edu/getkey.php?key=4630



Space lattice = mathematical translation of the crystal that leaves the material unchanged.

A crystal has translational symmetry: if we perform a displacement by a vector R, the potential is identical

$$V(\vec{r} + \vec{R}) = V(\vec{r})$$

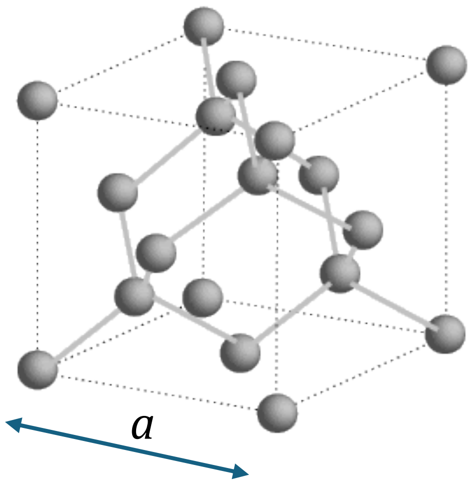
Lattice vectors $\vec{R} = n_1 \overrightarrow{a_1} + n_2 \overrightarrow{a_2} + n_3 \overrightarrow{a_3}$

n_1, n_2, n_3 are integers

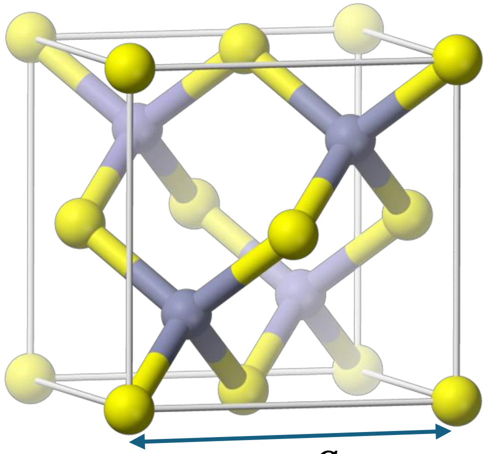
$\overrightarrow{a_1}, \overrightarrow{a_2}, \overrightarrow{a_3}$ are the basis vectors

Each point of the lattice is given by a set of integers, and each set of integers gives a point on the lattice.

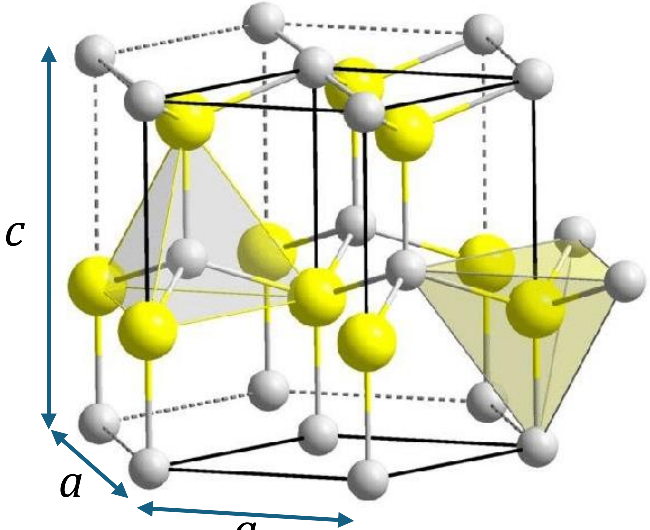
Crystal structures of semiconductors



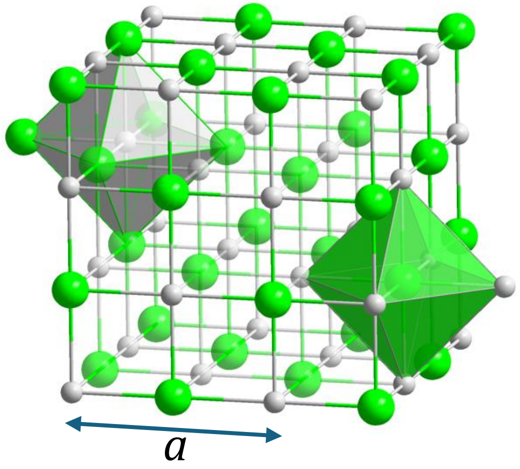
Silicon, germanium:
diamond structure



GaAs: zincblende (or
sphalerite) structure



GaN, AlN, InN:
wurtzite structure



ScN, YN, LaN:
rocksalt structure

Based on *fcc* lattice:

Lattice vectors:

$$\overrightarrow{a_1} = \frac{a}{2}(\hat{x} + \hat{y})$$
$$\overrightarrow{a_2} = \frac{a}{2}(\hat{y} + \hat{z})$$
$$\overrightarrow{a_3} = \frac{a}{2}(\hat{x} + \hat{z})$$

Basis:

$$\overrightarrow{\tau_1} = 0$$
$$\overrightarrow{\tau_2} = \frac{a}{4}(\hat{x} + \hat{y} + \hat{z})$$

Based on *hcp* lattice:

$$\overrightarrow{a_1} = a\hat{x}$$
$$\overrightarrow{a_2} = \left(\frac{a}{2}\hat{x} + \frac{\sqrt{3}a}{2}\hat{y}\right)$$
$$\overrightarrow{a_3} = c\hat{z}$$

Ga: $\overrightarrow{\tau_1} = 0$

Ga: $\overrightarrow{\tau_2} = \frac{1}{3}(\overrightarrow{a_1} + \overrightarrow{a_2}) + \frac{1}{2}\overrightarrow{a_3}$

N: $\overrightarrow{\tau_3} = u\,\hat{z}$

N: $\overrightarrow{\tau_4} = \frac{1}{3}(\overrightarrow{a_1} + \overrightarrow{a_2}) + (u + \frac{1}{2})\,\overrightarrow{a_3}$

Based on *fcc* lattice:

$$\overrightarrow{a_1} = \frac{a}{2}(\hat{x} + \hat{y})$$
$$\overrightarrow{a_2} = \frac{a}{2}(\hat{y} + \hat{z})$$
$$\overrightarrow{a_3} = \frac{a}{2}(\hat{x} + \hat{z})$$

$$\overrightarrow{\tau_1} = 0$$
$$\overrightarrow{\tau_2} = \frac{a}{2}\hat{x}\ [\text{or } \overrightarrow{\tau_2} = \frac{a}{2}(\hat{x} + \hat{y} + \hat{z})]$$