[CH932]

Quantum Chemistry

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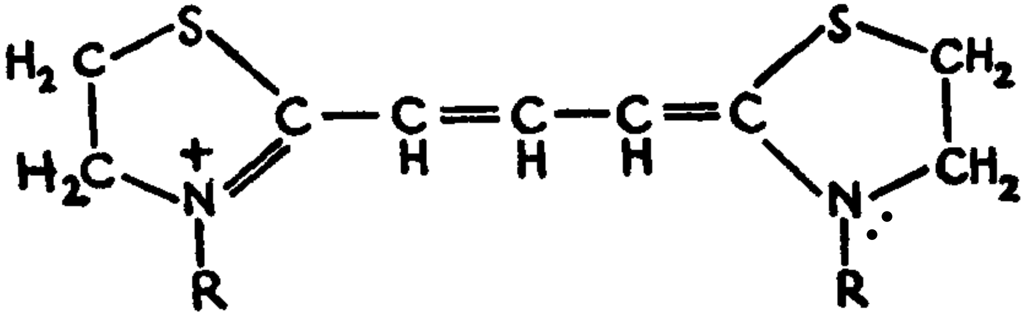
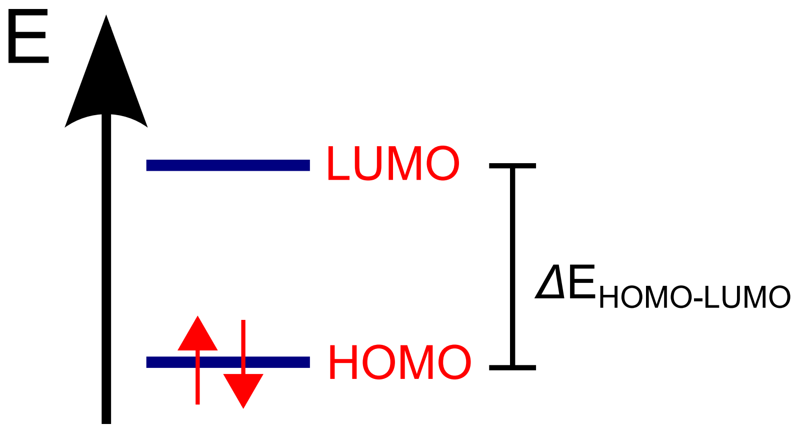
Term I, 2017/2018

Why should I care?

- Spectroscopy - e.g. UV/Vis spectroscopy





$$E = h\nu = \frac{hc}{\nu}$$

$$\lambda_{\text{HOMO-LUMO}} = \frac{hc}{\Delta E_{\text{HOMO-LUMO}}}$$

Why should I care?

- Charge transfer in biological systems

Biological electron-transfer (ET) reactions are typically described in the framework of coherent two-state electron tunneling or multistep hopping. However, these ET reactions may involve multiple redox cofactors in van der Waals contact with each other and with vibronic broadenings on the same scale as the energy gaps among the species.

Zhang, Y., Liu, C., Balaeff, A., Skourtis, S.S., and Beratan, D.N. (2014).
Biological charge transfer via flickering resonance. PNAS 111, 10049–10054.

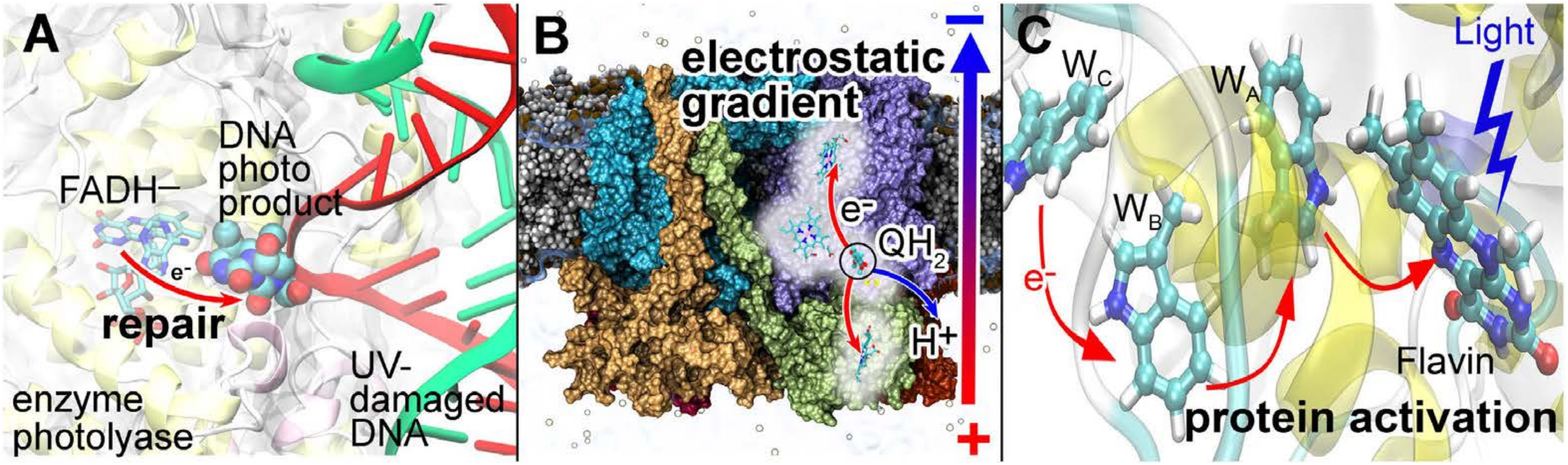


Figure 1. Examples of biological systems where electron transfer play a key role. (**A**) electron transfer initiating DNA UV-lesion repair by enzyme photolyase. (**B**) electron transfer triggering a cascade of charge transfer reactions in the cytochrome bc1 complex that lead to a formation of an electrostatic gradient through the plasma membrane. (**C**) Activation of cryptochrome protein initiated by blue light excitation of the FAD cofactor leading to a formation of a radical pair.

Sjulstok, E., Olsen, J.M.H., and Solov'yov, I.A. (2015).
Quantifying electron transfer reactions in biological systems: what interactions play the major role? Scientific Reports 5, srep18446.

Why should I care?

- Computational chemistry

$$\mathcal{H}|\psi\rangle = E|\psi\rangle$$

↓

- Post-Hartree-Fock methods (CI, CC, MP2…)
- Density Functional Theory
- […]

↓

hb_1.mp4

Outline

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Assessment:
Workshop (pass/fail)

Course resources

Books:

- Reading list on Moodle
- Remember: *nothing is essential, everything is useful*

Moodle:

- Lecture notes [plus Lecture Capture]

Myself:

- Via email: G.Sosso@warwick.ac.uk [anytime]
- In person: G Block, Office 4. Office hours for CH932: Thursday, 2-3 PM. [A 24h notice via email would be highly appreciated]

Intro

Learning Objectives

By the end of this lectures you should…

- … be familiar with the basic concepts of quantum mechanics
- … be able to deal with a few model systems (free particle, particle in a box, hydrogen atom…)
- … be confident about the notion of chemical bonds and intermolecular interactions

Assumptions

At this stage you should be familiar with …

- Nothing - we shall start from scratch!

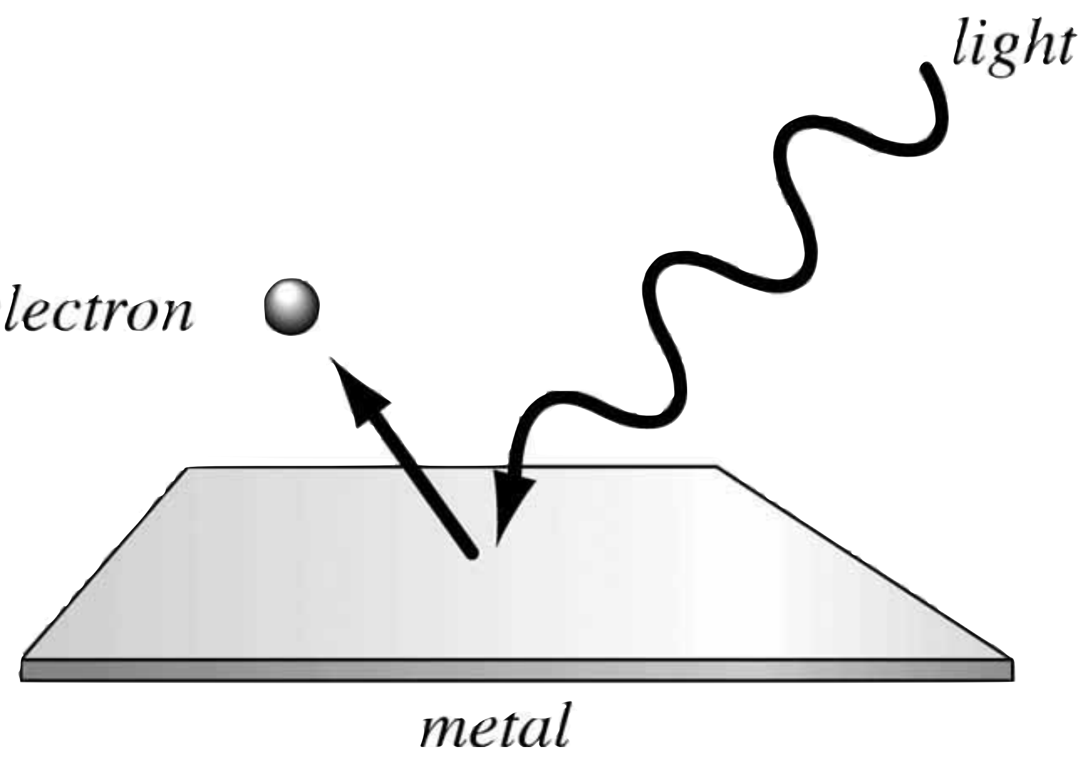
The need for quantum mechanics

- Early birds: Ludwig Boltzmann (1877) [discrete energy levels]
- Old quantum theory:
  - Max Planck (1900) [black-body radiation]
  - Albert Einstein (1905) [photoelectric effect]
  - Niels Bohr (~1910)[hydrogen line spectrum]
  - […]
- Unified & Formalised (~1930)
  - David Hilbert
  - Paul Dirac
  - […]

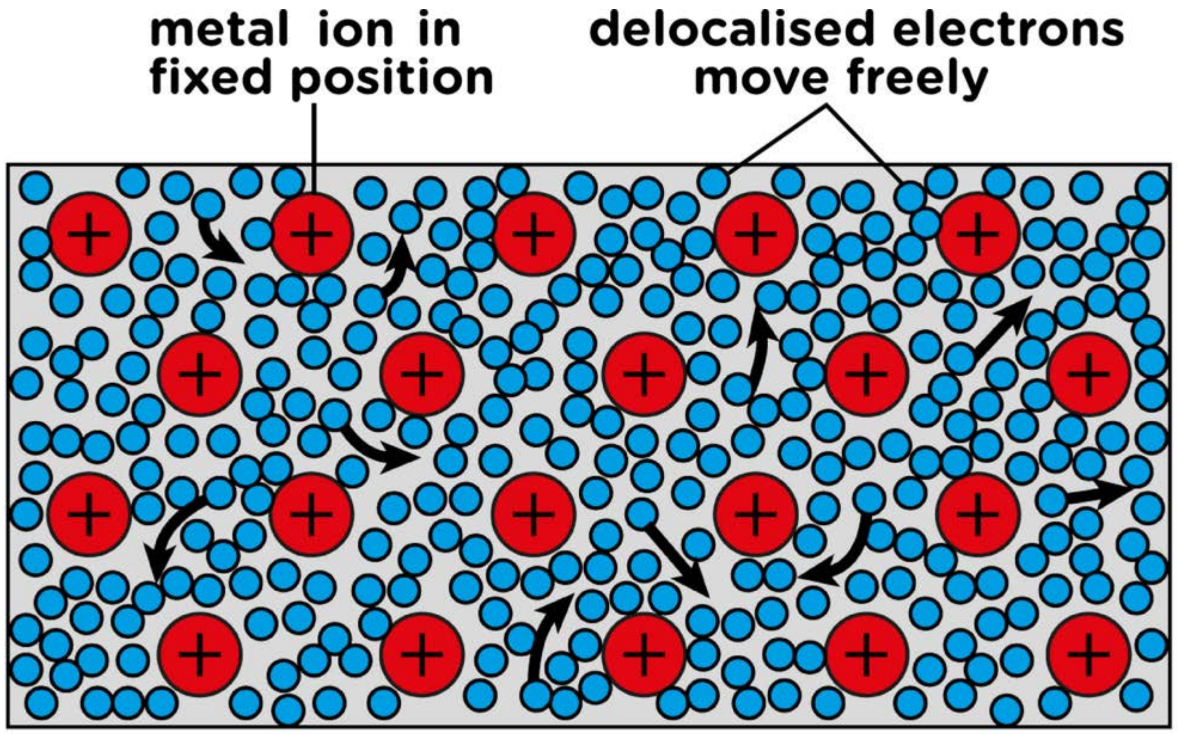
Photoelectric effect

- Energy quantisation
- Wave-particle duality

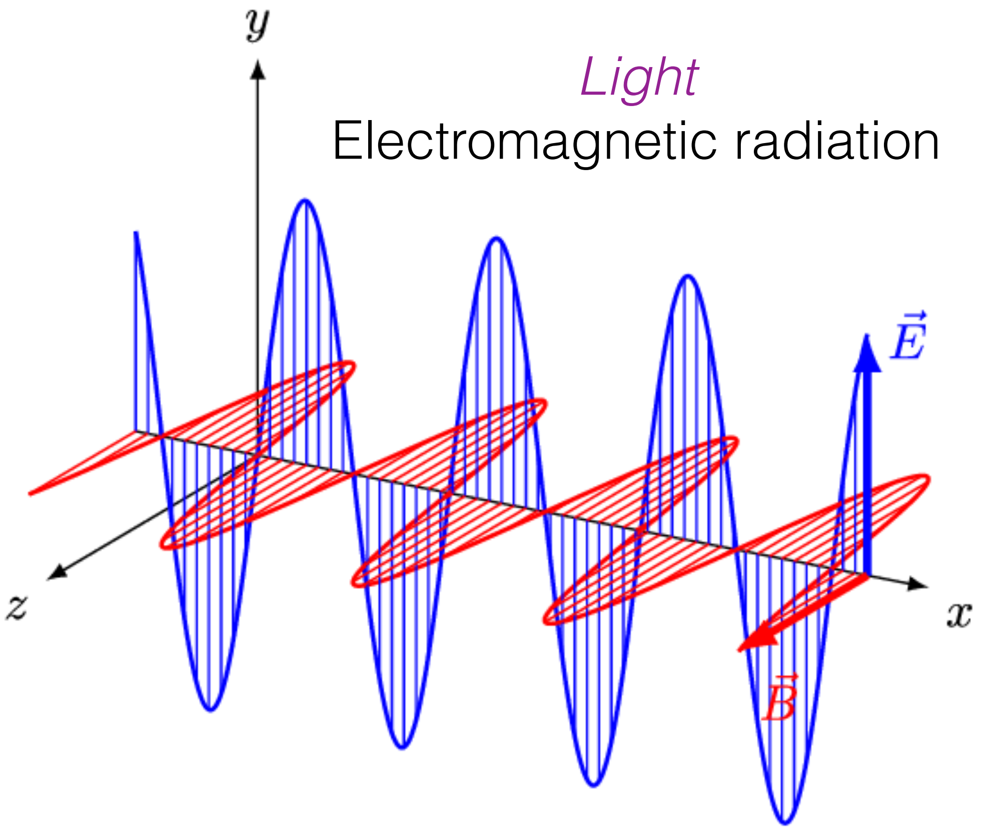
Photoelectric effect



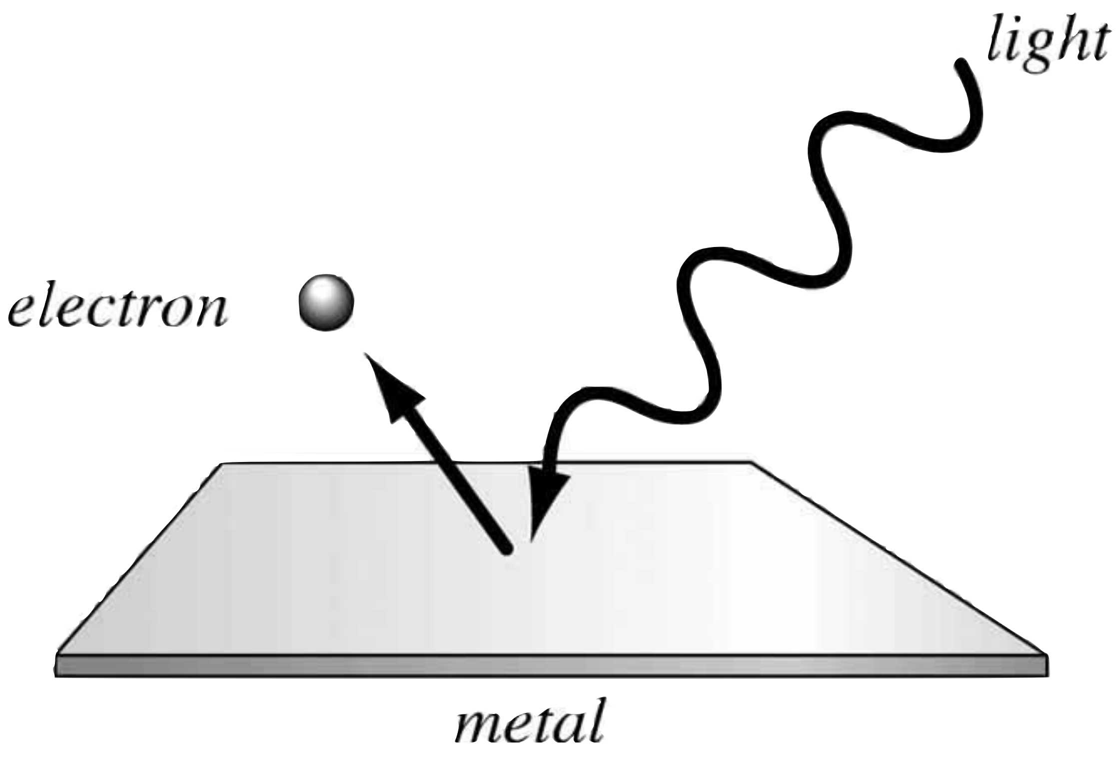
Metal
Free electron model



Light
Electromagnetic radiation



Photoelectric effect



Classical electromagnetic theory

Energy transfer from the light to the electron

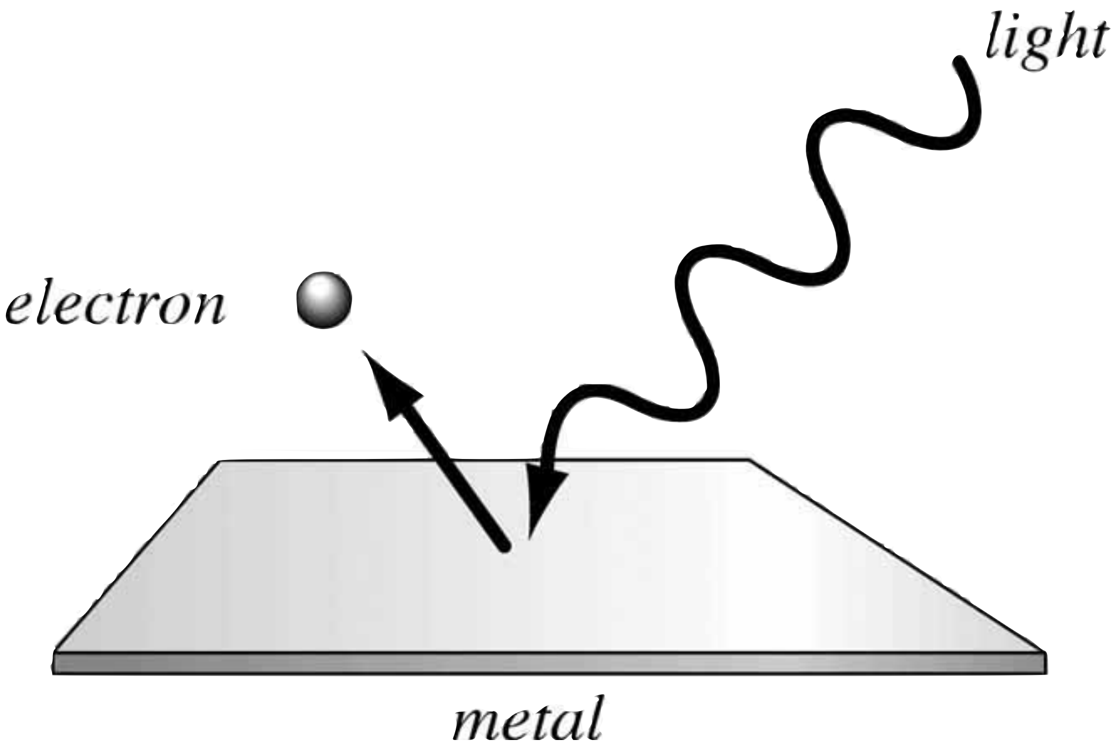
↓

The more intense the light, the strongest the force applied to the electron
(eventually, for a sufficiently intense light, the electron *will* leave the metal)

NOPE

For each metal, there exist a characteristic cutoff frequency below which no electrons are emitted,
no matter how intense the light

Photoelectric effect



Einstein interpretation

Light is *quantised* into “bundles of energy” (*particles!*) called photons, each with energy

$$E = h\nu$$

Increasing the intensity of the light increase the number of photons,
but not their frequency, hence their individual energy is the same

What we need instead is photons with:

$$\nu > \frac{w_0}{h}$$

Wave-particle duality

Classical physics

Radiation
(Waves)

Matter
(Particles)

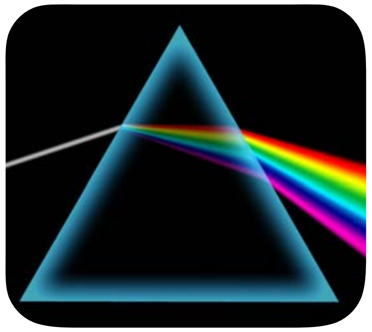
Quantum physics

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

de Broglie relation:
the wavelength λ of the *wave* associated with the motion of the *particle* having a momentum p

Atomic spectra

The spectra emitted by macroscopic objects
upon the interaction with electromagnetic radiation are continuous



HOWEVER

The spectra emitted by free atoms
display a number of discrete wavelengths

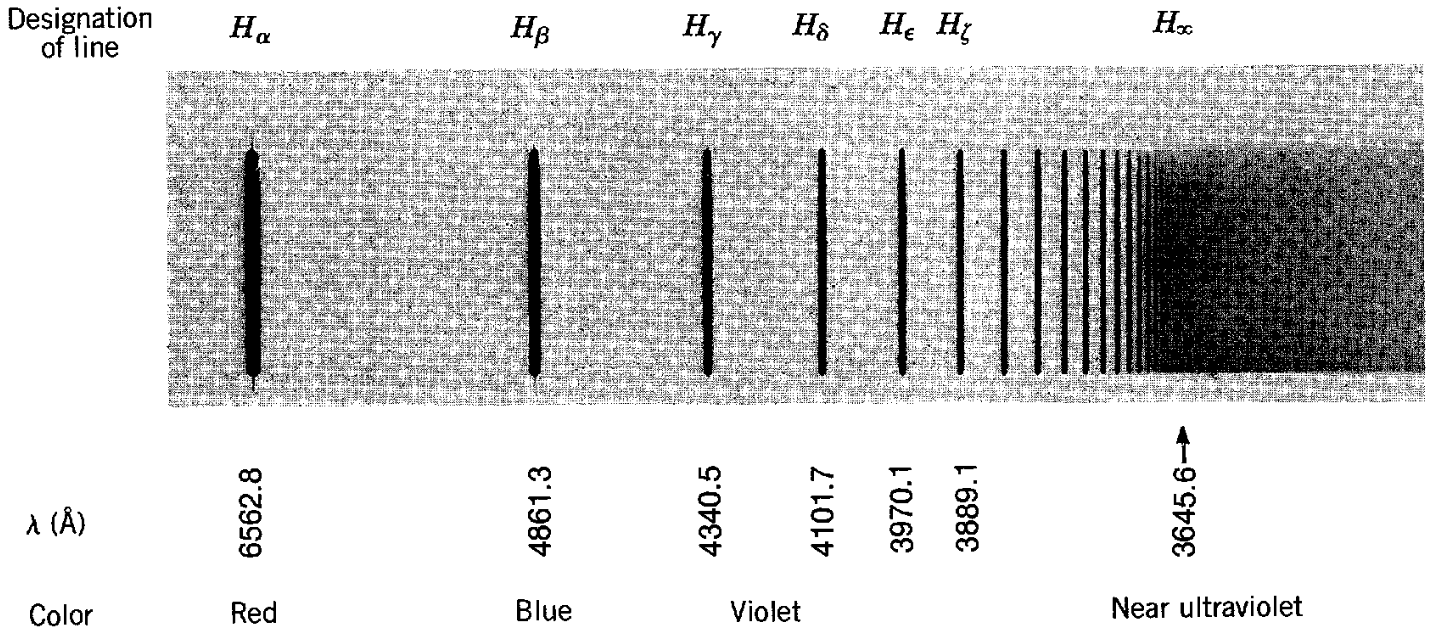


Figure 4-10 A photograph of the visible part of the hydrogen spectrum. (*Spectrum from W. Finkelnburg, Structure of Matter, Springer-Verlag, Heidelberg, 1964.*)

The electronic structure of atoms is quantised

The Schrödinger equation

How do we calculate these discrete energy levels
e.g. for the hydrogen atom?

The Schrödinger equation

$$\mathcal{H}|\psi(\bar{r},t)\rangle = i\hbar\frac{\partial}{\partial t}|\psi(\bar{r},t)\rangle$$

$$H\psi = E\psi$$

- Operators
- *Wave function*
- Time dependency

Classical mechanics:
A system (say, a free particle) is described by positions and momenta

Quantum mechanics
A system (say, a free particle) is described by its wave function ψ

The wave function

All the information about the state of a quantum system are contained in the wave function ψ

It has to be:

- Continuous
- Single valued
- Finite
- Smooth
- *Square integrable*

It *can*:

- be time dependent
- include an imaginary part

Born’s interpretation of ψ

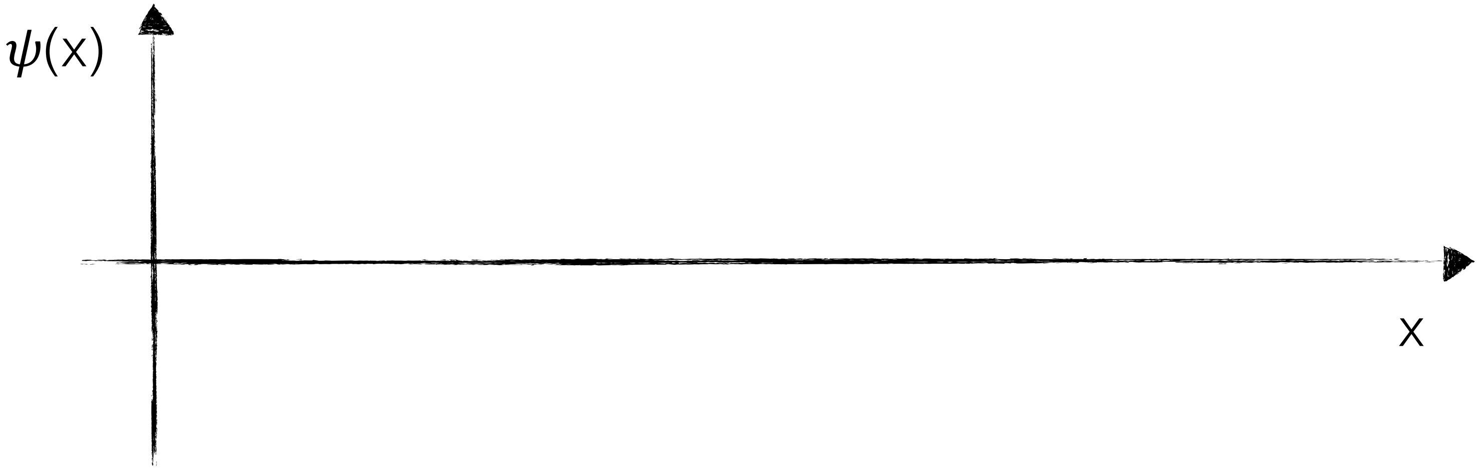
The connection between ψ and the actual behaviour of the associated system (e.g. a particle) is given by The Born Rule:

$$P(x,t) = \psi^*(\bar{r},t) \cdot \psi(\bar{r},t)$$

The probability of finding e.g. a particle at the position *r(+dr)* and at time *t(+dt)* is equal to the square of the particle's wave function at that point

- This is a probability density
- It is always real and non-negative
- It makes sense: the particle is likely to be found where/when ψ has a decent amplitude

No time dependence, one dimension (x)…



$$P(a < x < b) = \int_a^b |\psi(x)|^2 dx$$

The Schrödinger equation -II

How do we calculate these discrete energy levels
e.g. for the hydrogen atom?

The Schrödinger equation

$$\mathcal{H}|\psi(\bar{r},t)\rangle = i\hbar\frac{\partial}{\partial t}|\psi(\bar{r},t)\rangle$$

$$H\psi = E\psi$$

- *Operators*
- Wave function
- Time dependency

Operators

Objects that act on the wave function
Mathematics makes it easier [matrixes and vectors]

$$\mathcal{H} \Rightarrow \text{ Hamiltonian operator}$$

$$i\hbar\frac{\partial}{\partial t} \Rightarrow \text{ energy operator}$$

Operators

The Hamiltonian operator

In analogy with classical mechanics:

$$\mathcal{H} = V + K$$

$$K_{\text{one dim.}} = -\frac{\hbar^2}{2m} \cdot \frac{\partial^2}{\partial x^2}$$

The Energy operator

We “get rid of this” via *separation of variables*

$$\mathcal{H}|\psi(\bar{r},t)\rangle = i\hbar\frac{\partial}{\partial t}|\psi(\bar{r},t)\rangle$$

We look for wave functions that can be written as:

$$\psi(\bar{r},t) = \psi(\bar{r}) \cdot \psi(t)$$

$$\psi(t) = e^{-\frac{iEt}{\hbar}}$$

↓

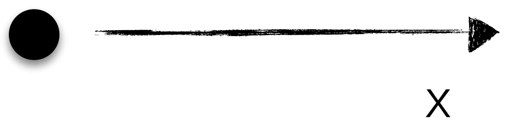
Time-independent Schrödinger equation:

$$H\psi(\bar{r}) = E\psi(\bar{r})$$

The free particle

The free particle:

- The zero potential
- Just the kinetic term
- One dimension (x)



We have to solve the Schrödinger equation:

$$H\psi(\bar{r}) = E\psi(\bar{r})$$

↓

$$-\frac{\hbar^2}{2m} \cdot \frac{\partial^2 \psi(x)}{\partial x^2} = E\psi(x)$$

Remember the time dependence!

$$\psi(\bar{r}, t) = \psi(\bar{r}) \cdot e^{-\frac{iEt}{\hbar}}$$

The free particle - wave function

$$-\frac{\hbar^2}{2m}\cdot\frac{\partial^2\psi(x)}{\partial x^2} = E\psi(x)$$

$$\frac{\partial^2\psi(x)}{\partial x^2} = -\frac{2mE}{\hbar^2}\psi(x)$$

$$\psi\text{''} = -k^2\psi, \text{ with } k = \frac{\sqrt{2mE}}{\hbar}$$

$$\psi(x) = \sin(kx)\ ,\ \text{or}\ \ \cos(kx)\ ,\ \text{or}\ e^{ikx}$$

$$\psi(x) = \alpha\cos(kx) + \beta\sin(kx)$$

$$e^{ix} = \cos(x) + i\sin(x)$$

⬇

$$\psi(x) = e^{ikx}$$

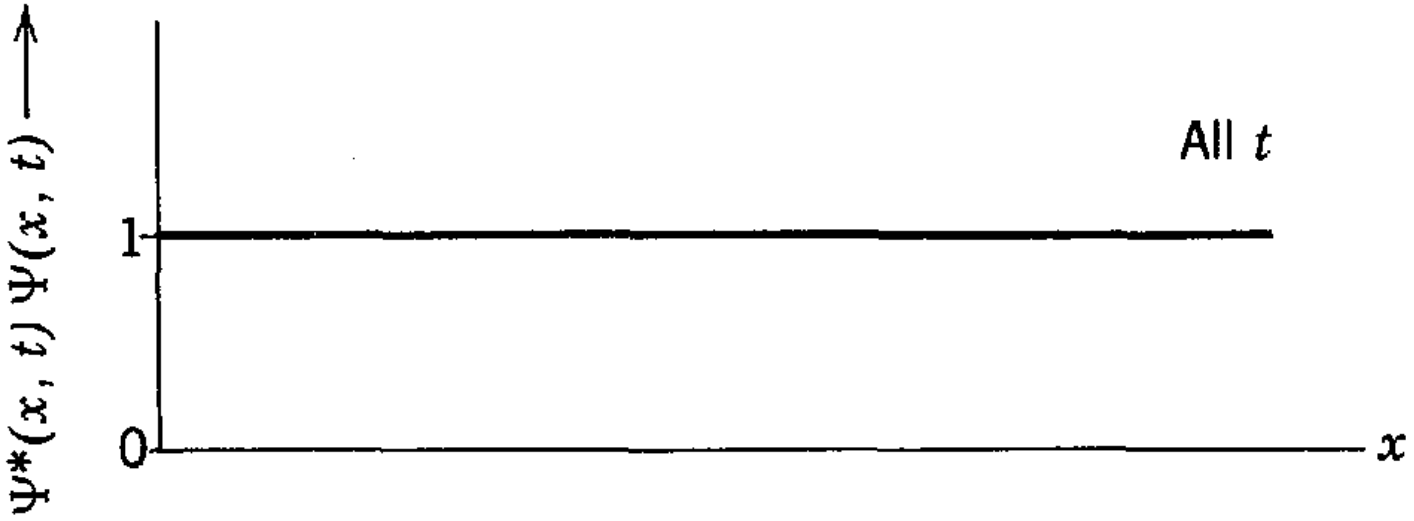
$$\psi(x,t) = e^{ikx}\cdot e^{-\frac{iEt}{\hbar}} = e^{i\cdot(kx-\frac{Et}{\hbar})}$$

$P(x,t)$??

①

The free particle - wave function

$$P(x,t) = 1 \quad \forall t$$



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

NOPE

Group of traveling waves…

$$\psi_{\text{group}}(x,t) = \sum_{i=1}^{N} A_i \cdot e^{i(k_i x - \frac{E_i t}{\hbar})}$$

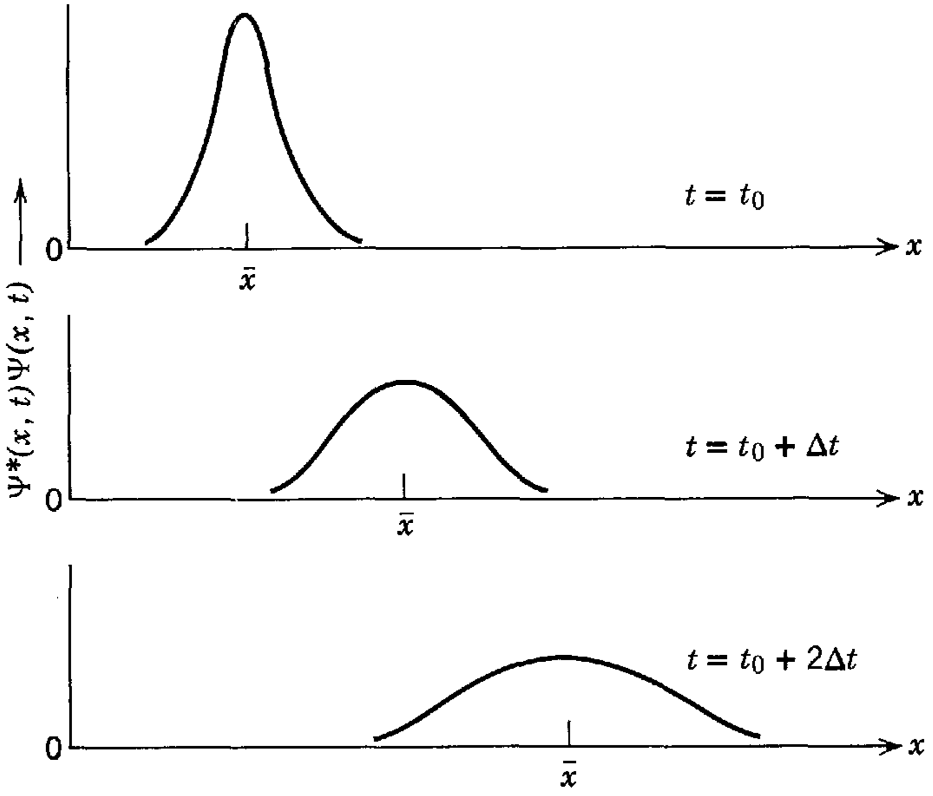


Figure 6-2 The probability density $\Psi^*\Psi$ for a group traveling wave function of a free particle. With increasing time the group moves in the direction of increasing *x*, and also spreads.

The free particle - energy levels

There are no restrictions on the value of *k*…

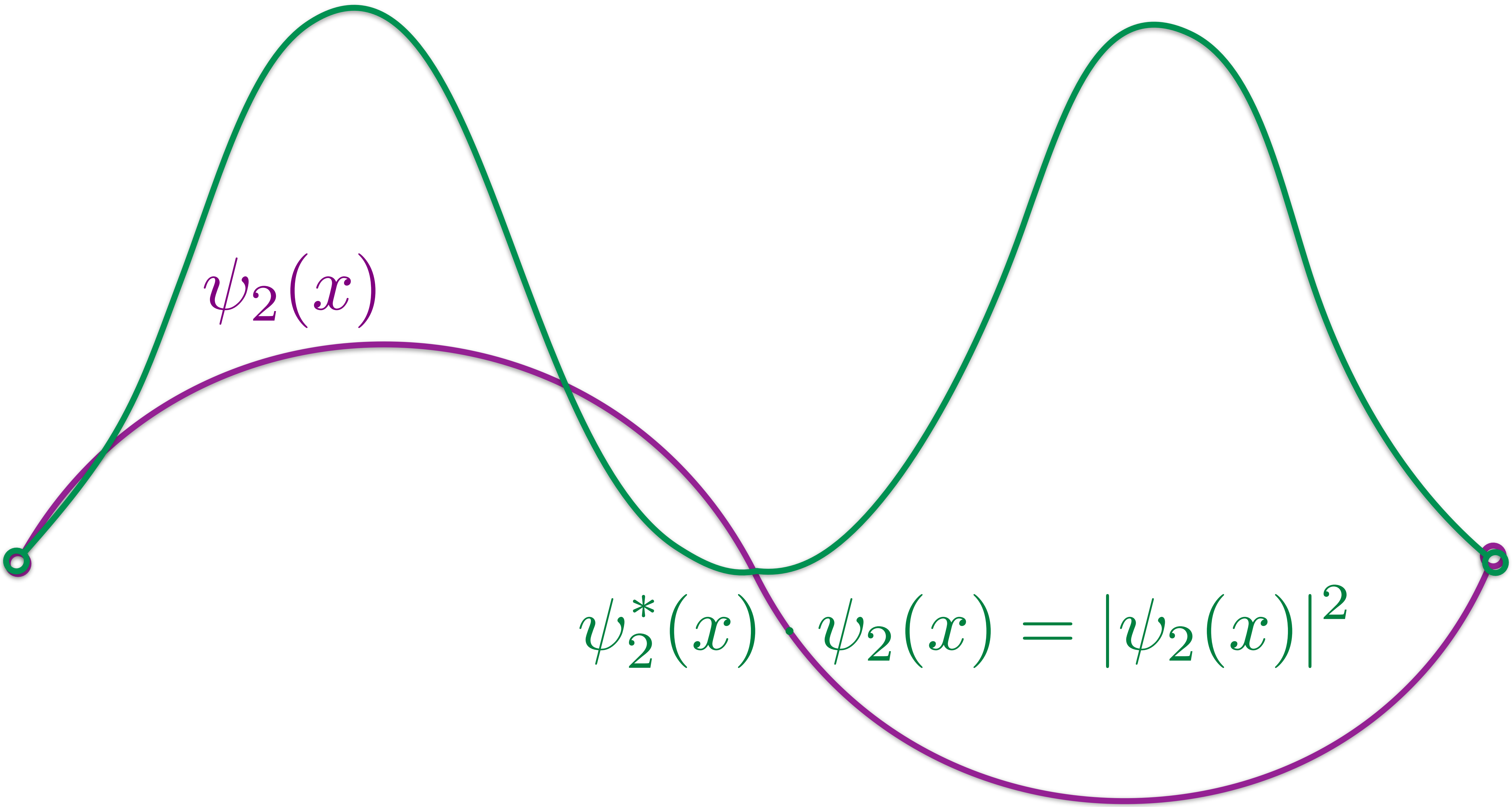
$$E = \frac{k^2\hbar^2}{2m} \quad \forall E \geq 0$$

- Energy levels are *not* quantised
- This is identical to the classical case

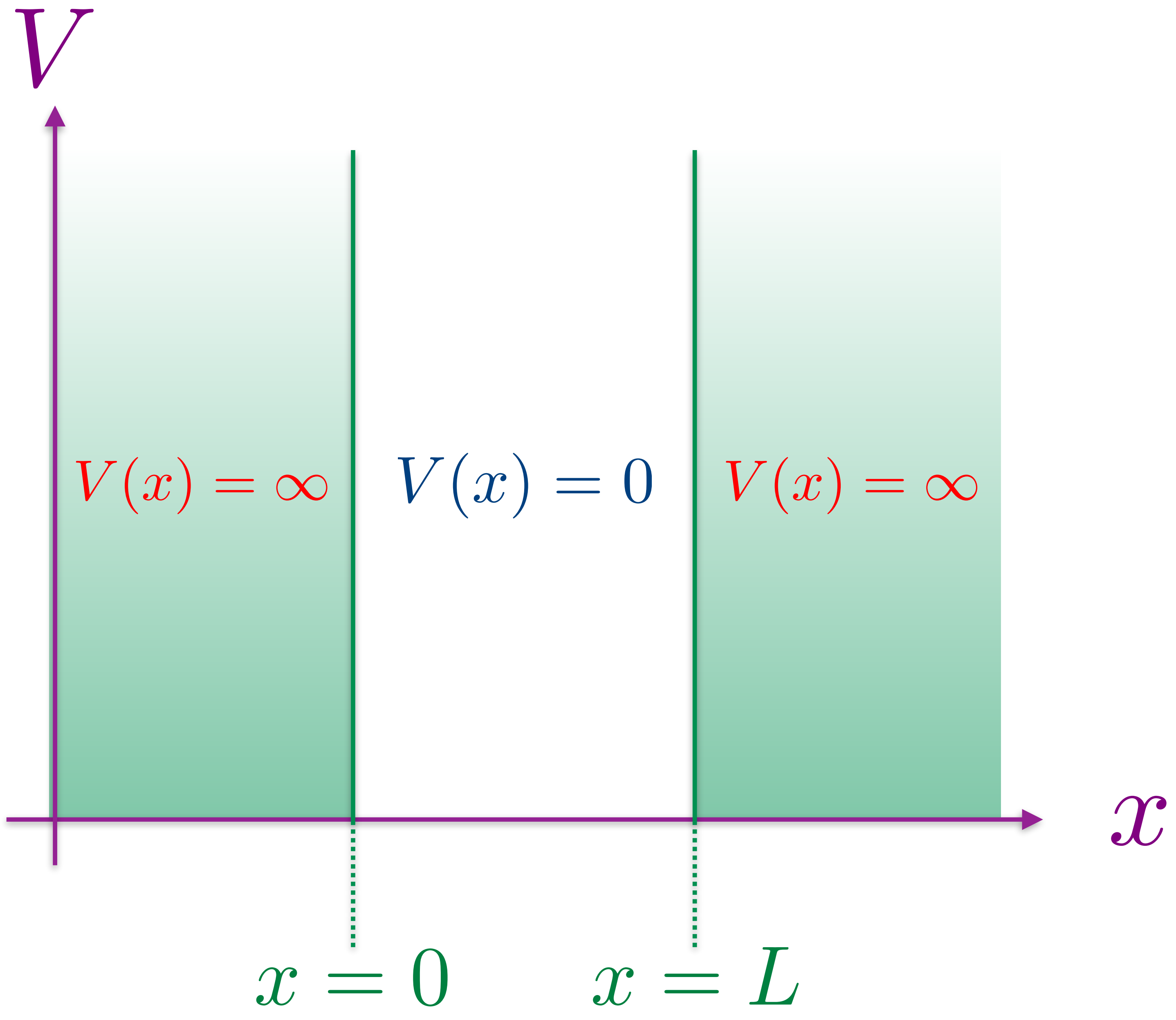
HOWEVER

What happens if instead of *V(x)=0*…

The particle in the box

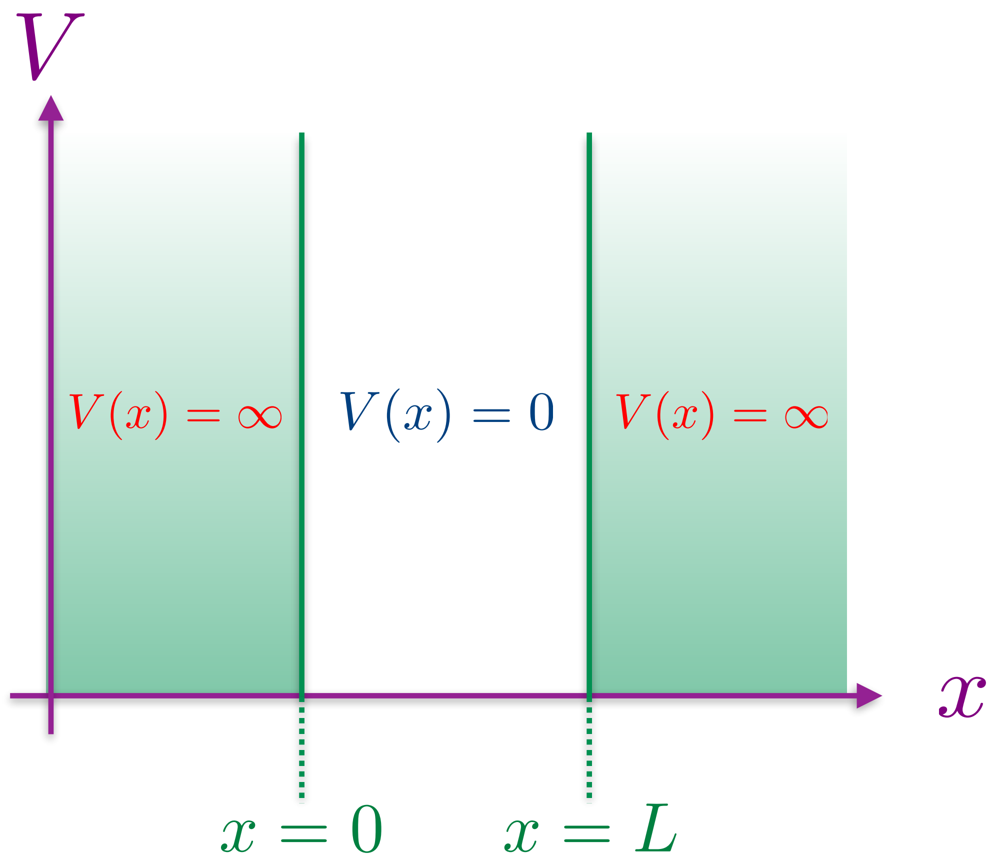


The box



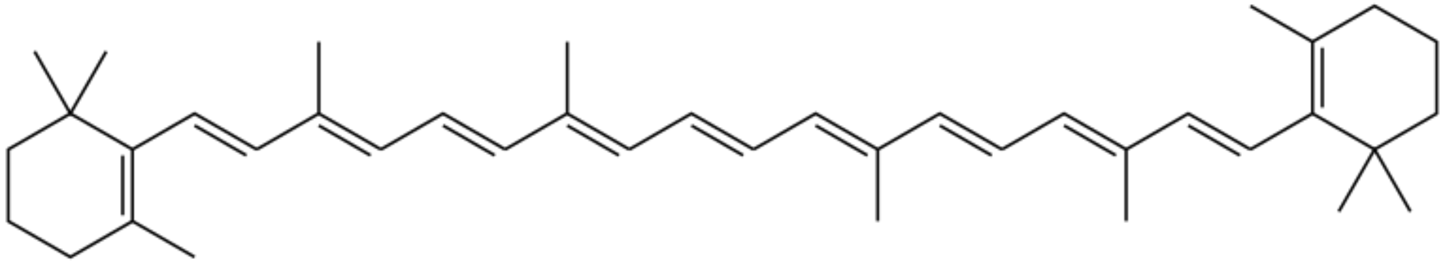
$$V(x) = \begin{cases} 0, & \text{for } 0 \leq x \leq L \\ \infty, & \text{for } x < 0 \text{ or } x > L \end{cases}$$

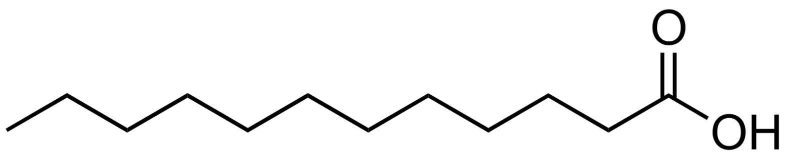
Not so boring!



$$V(x) = \begin{cases} 0, & \text{for } 0 \leq x \leq L \\ \infty, & \text{for } x < 0 \text{ or } x > L \end{cases}$$

Beta-Carotene



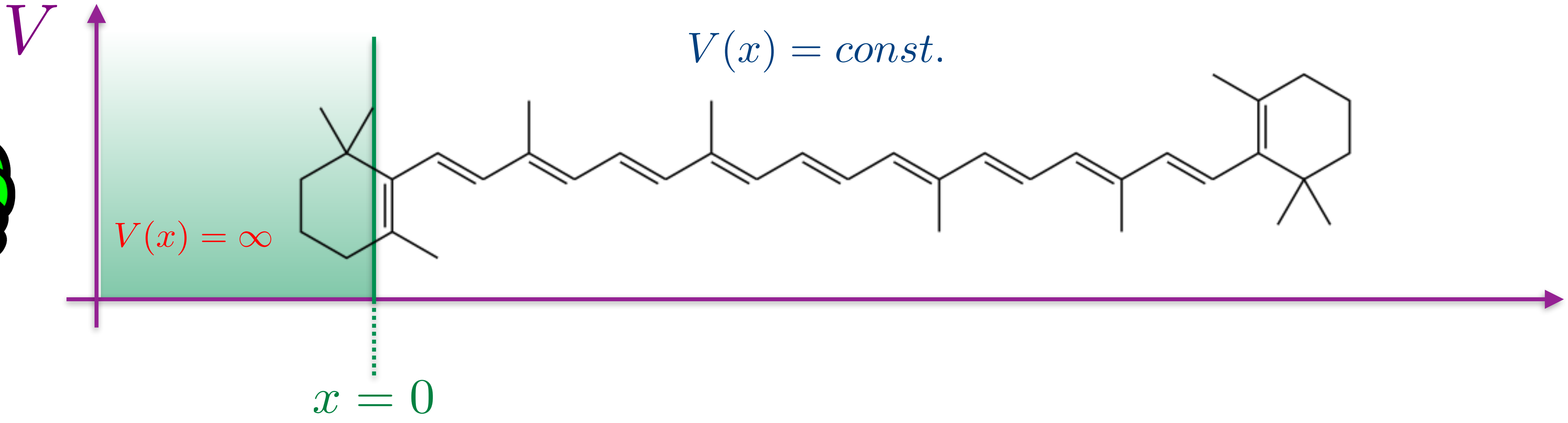


Lauric Acid

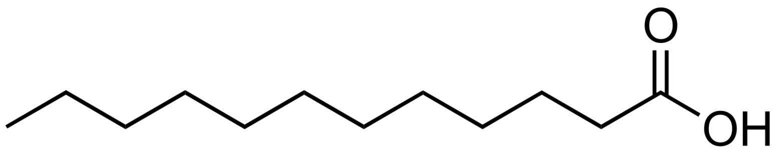
② ③

Particle in a box ~ conjugated systems

Beta-Carotene



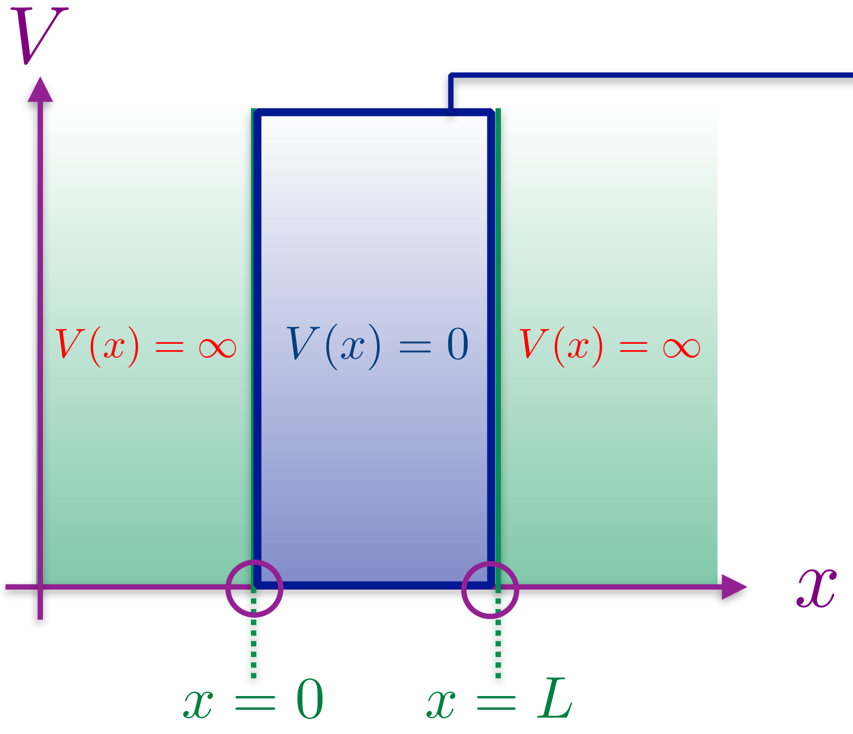
- Conjugated system (22 conjugated C-C bonds)
- The (22) conjugated electrons are delocalised across the whole chain
- They are (more or less) free to move across the chain
- They (roughly) feel the same potential at each point



Lauric Acid

- Saturated bonds
- Localised states - electrons are mostly bound
- Functional (polar!) group unbalance the potential across the chain

Particle in a box - the wave function



Within the box $\Rightarrow V(x)=0$

The wave function if that of the free particle in one dimension!

$$\psi(x)=\alpha\cos(kx)+\beta\sin(kx)\ ,\ k=\frac{\sqrt{2mE}}{\hbar}$$

Particle in a Box:
The wave function has to be continuous everywhere

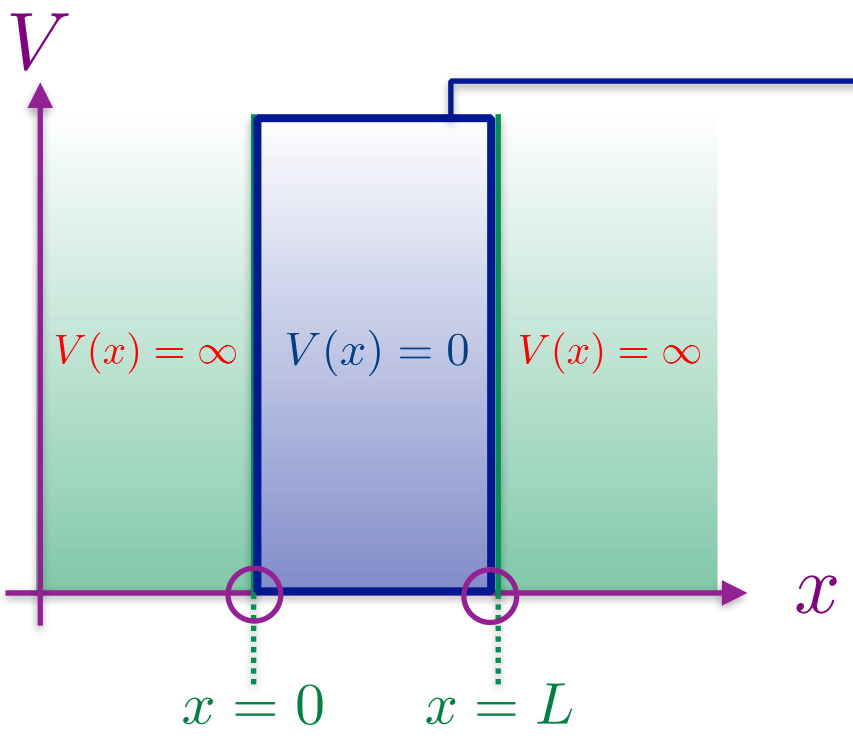
$$\psi(x=0)=\psi(x=L)=0$$

1. $\psi(x=0)=\alpha\cos(0)+\beta\sin(0)=0\ \Rightarrow\ \alpha=0$

2. $\psi(x=L)=\alpha\cos(kL)+\beta\sin(kL)=0\ \Rightarrow\ \beta\sin(kL)=0$

$$\Rightarrow\ kL=n\pi\ ,\ 1,2\ldots\ \Rightarrow\ k=\frac{n\pi}{L}\ ,\ 1,2\ldots$$

Particle in a box - the wave function



Within the box $\Rightarrow V(x) = 0$

The wave function if that of the free particle in one dimension!

$$\psi(x) = \alpha \cos(kx) + \beta \sin(kx)\ ,\, k = \frac{\sqrt{2mE}}{\hbar}$$

Particle in a Box:
The wave function has to be continuous everywhere

$$\psi(x) = \alpha \cos(kx) + \beta \sin(kx)$$

$$\downarrow$$

1. $\alpha = 0$ and $k = \frac{n\pi}{L}\ ,\ 1, 2 \ldots$ **2.**

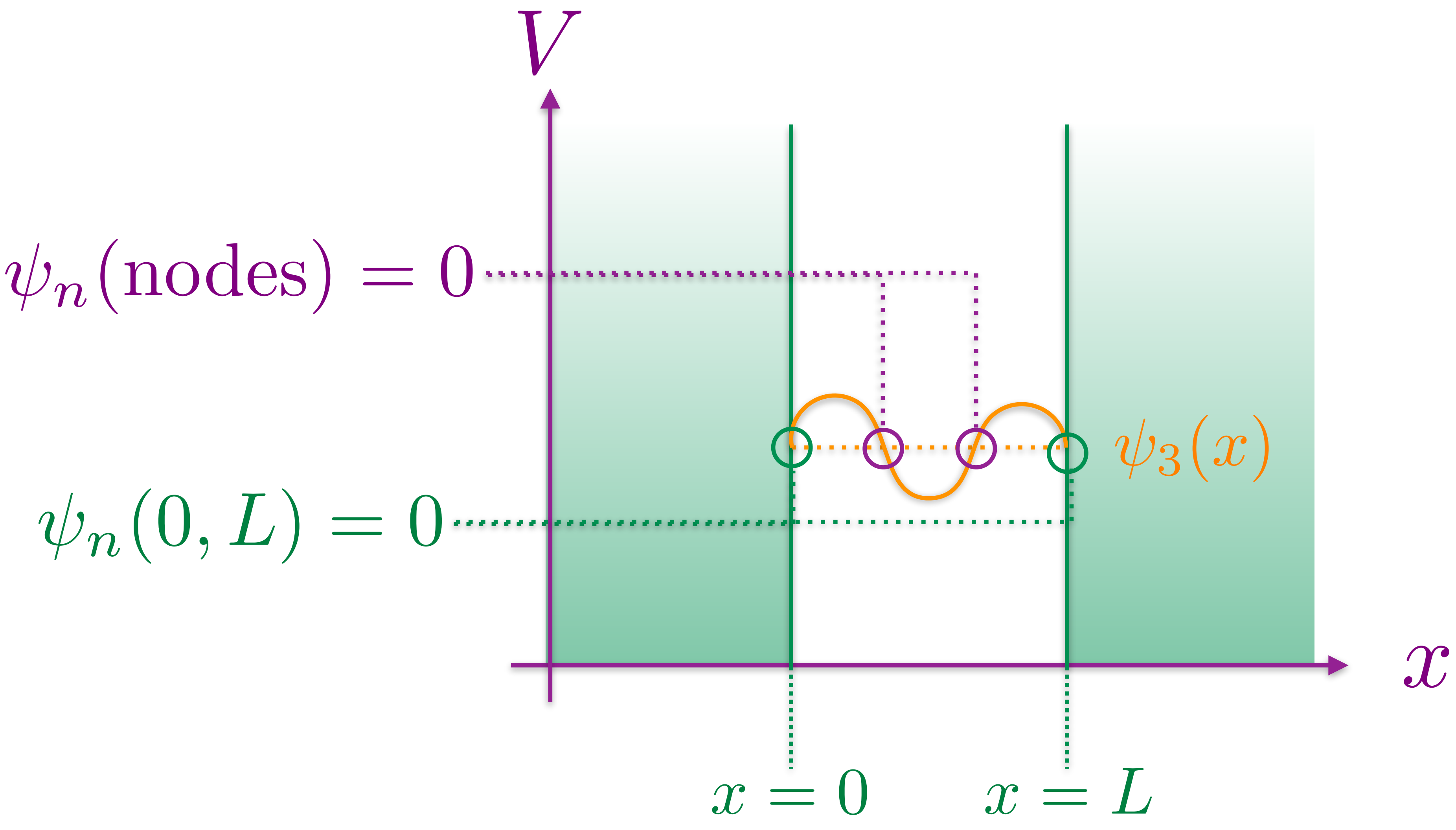
$$\downarrow$$

Particle in a Box Wave Function

$$\psi_n(x) = \beta \sin\left(\frac{n\pi}{L} x\right)$$

Particle in a box - the wave function

$\psi_n(x)$ has $n-1$ nodes (points other than $x=0$ and $x=L$ for which $\psi_n(x)=0$)



Particle in a box - probability density

Where is the particle?

$$\text{Probability density}$$

$$\psi_n^*(x) \cdot \psi_n(x) = |\psi_n(x)|^2$$

For (infinitely) large values of n the particle can be found anywhere in the box with the same probability

4

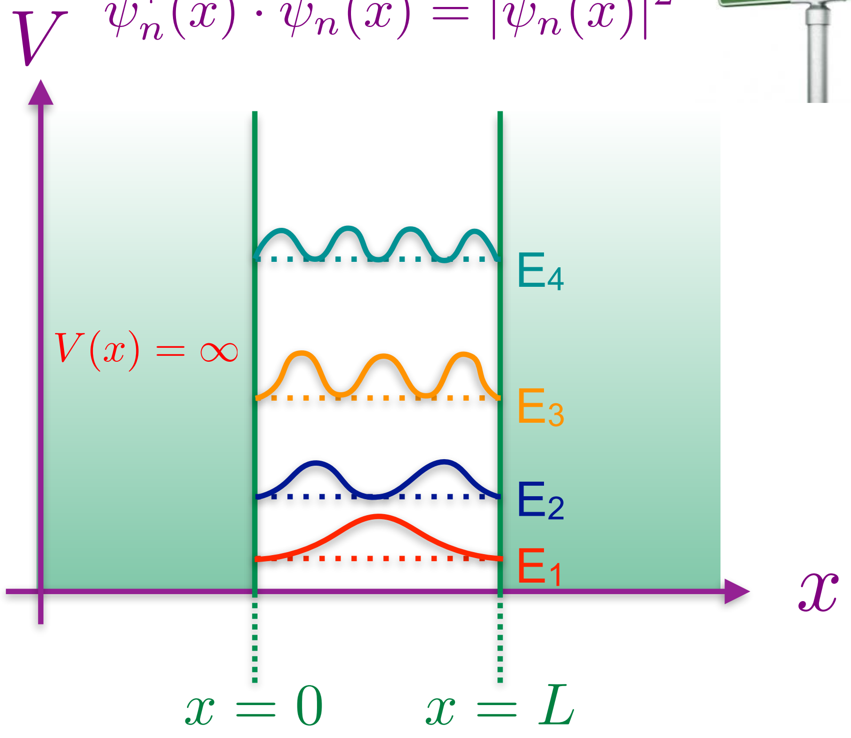
Correspondence principle

For (infinitely) large values of n the particle can be found anywhere in the box with the same probability

Probability density

$$\psi_n^*(x) \cdot \psi_n(x) = |\psi_n(x)|^2$$

True!



Correspondence Principle

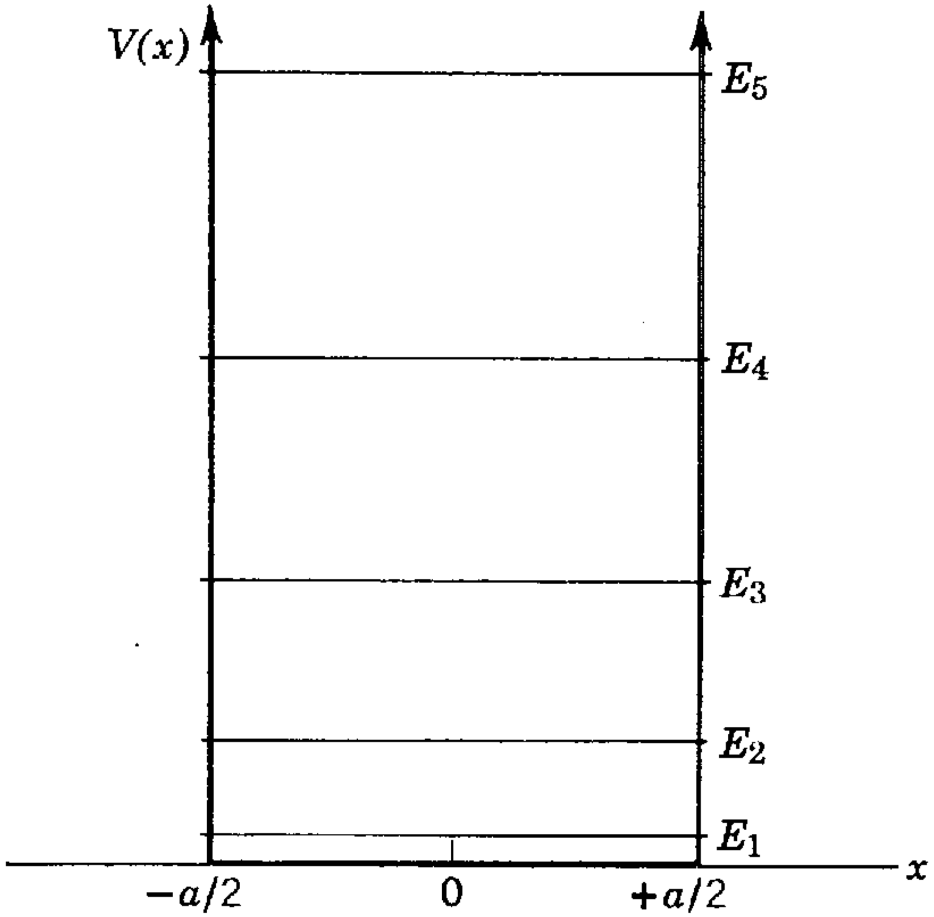
In the limit of large quantum numbers, we recover classical mechanics

Particle in a box - energy levels

$$k = \frac{\sqrt{2mE}}{\hbar} \text{ and } k = \frac{n\pi}{L}$$

$$\Downarrow$$

$$E_n = \frac{\hbar^2 n^2 \pi^2}{2mL^2}, \text{ with } n = 1, 2, \ldots$$



- Energy levels *are* quantised
- There exist a zero point energy
- 2D box introduces *degeneracy*

$$E_{n_x,n_y} = \frac{\hbar^2 \pi^2}{2mL^2} \cdot (n_x^2 + n_y^2),$$
$$\text{with } n_x = 1, 2, \ldots \text{ and } n_y = 1, 2, \ldots$$

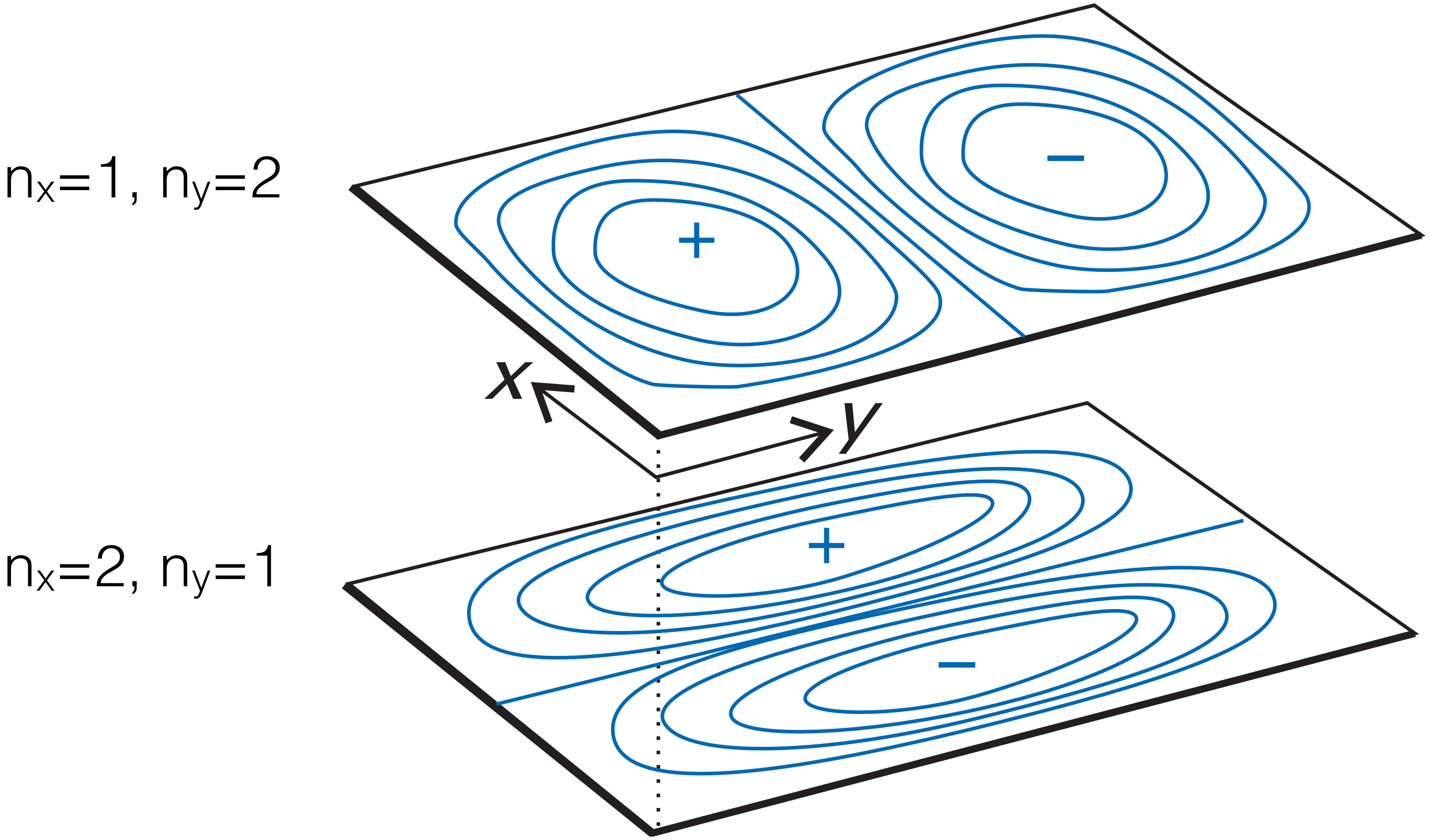
5

Particle in a box - degenerate states

$$\text{If } A[n_x = 1, n_y = 2] \text{ and } B[n_x = 2, n_y = 1]$$

$$E(A) = \frac{\hbar^2 \pi^2}{2mL^2} \cdot 5 = E(B)$$

$$\psi(A) = \sqrt{\frac{2}{L}} \cdot \sin\left(\frac{\pi x}{L}\right) \cdot \sqrt{\frac{2}{L}} \cdot \sin\left(\frac{2\pi y}{L}\right) \neq \sqrt{\frac{2}{L}} \cdot \sin\left(\frac{2\pi x}{L}\right) \cdot \sqrt{\frac{2}{L}} \cdot \sin\left(\frac{\pi y}{L}\right)$$



Coffee!

The hydrogen atom

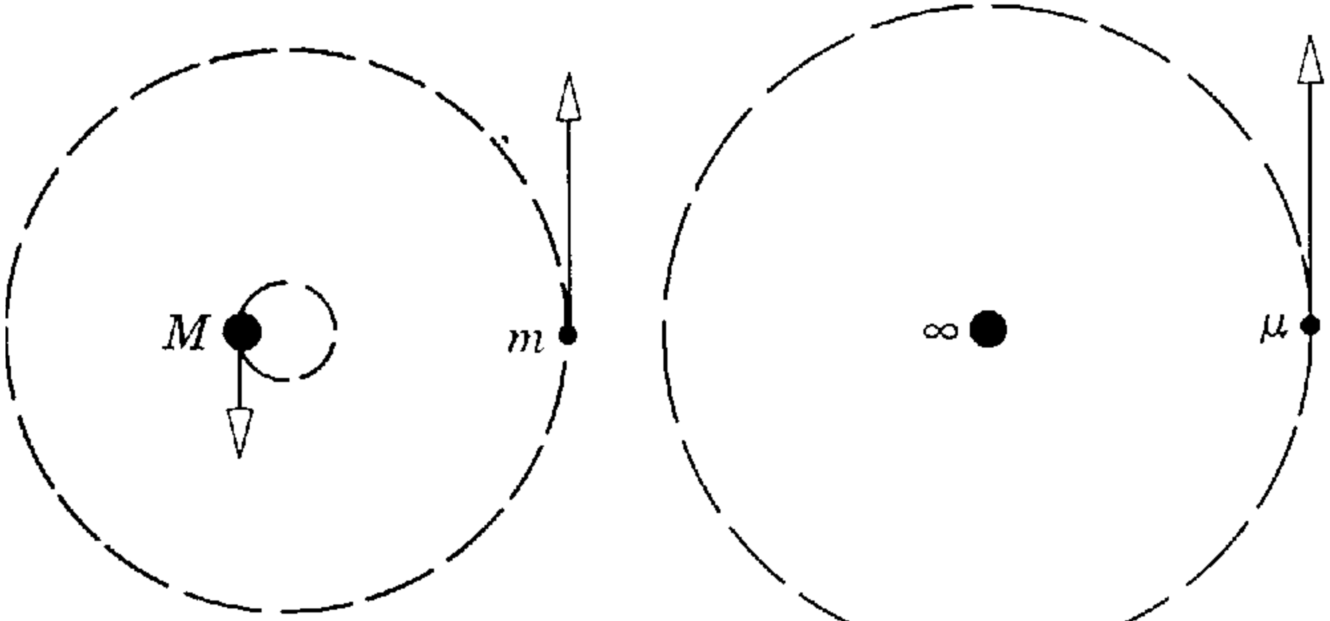
This is one of the *very* few cases where we can solve Schrödinger equation analytically
As in the case of e.g. the free particle and the particle in the box

HOWEVER

Even just for the helium atom, no closed-form solution can be found

The Schrödinger equation for the hydrogen atom

1. Reduced mass μ



Actual system

Model system

$$\mu = \left(\frac{M_{\text{nucleus}}}{m_{\text{electron}} + M_{\text{nucleus}}} \right) \cdot m_{\text{electron}} = 0.995\ m_{\text{electron}}$$

The hydrogen atom

So that we have an electron with reduced mass μ
interacting with the nucleus via the Coulomb potential

$$V = \frac{q_{\text{nucleus}} \cdot q_{\text{electron}}}{4\pi\epsilon_0 \bar{r}_{\text{nucleus-electron}}} = \frac{Ze \cdot -e}{4\pi\epsilon_0 \cdot \bar{r}} = -\frac{e^2}{4\pi\epsilon_0 \cdot \bar{r}}$$

The Hamiltonian of the system is thus:

$$\mathcal{H} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 \cdot \bar{r}}$$

⬇

(Spherical) polar coordinates & separation of variables (radial and angular [polar + azimuth] parts)…

⬇

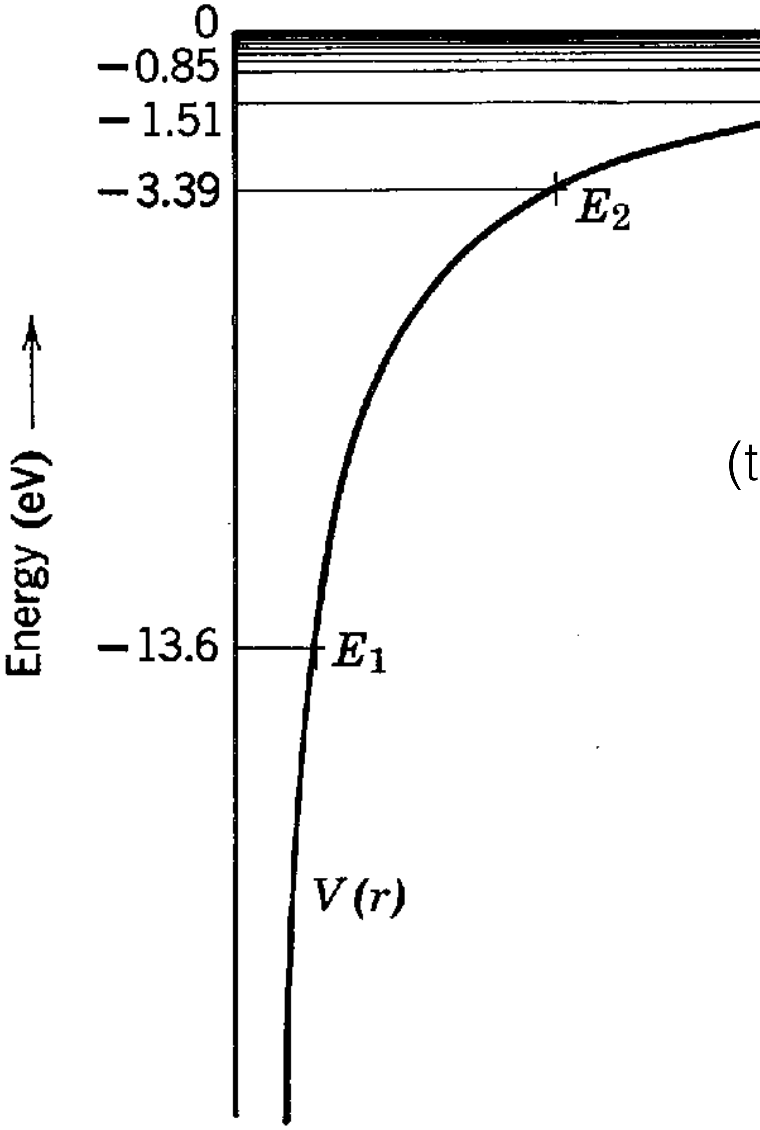
Energy levels

$$E_n = -\frac{\mu Z^2 e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2}$$

The hydrogen atom - energy levels

$$E_n = -\frac{\mu Z^2 e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2}$$

$n = 1, 2, \ldots, \infty$
Principal quantum number



Energy levels are quantised
(the Coulomb potential is a *binding* potential)

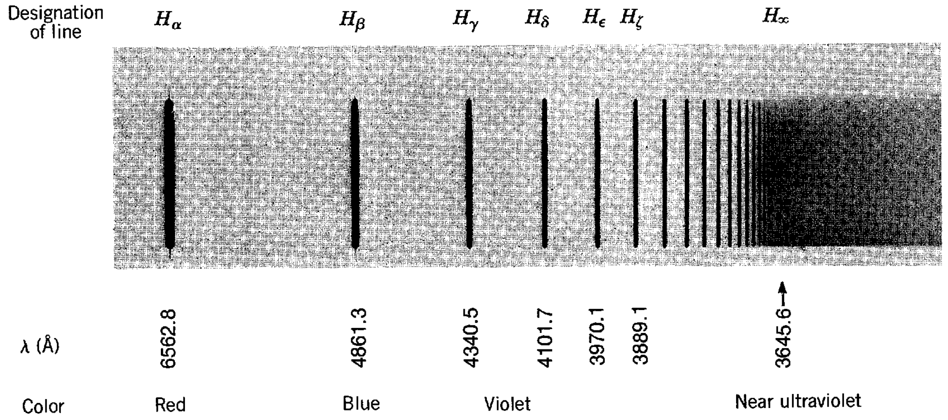


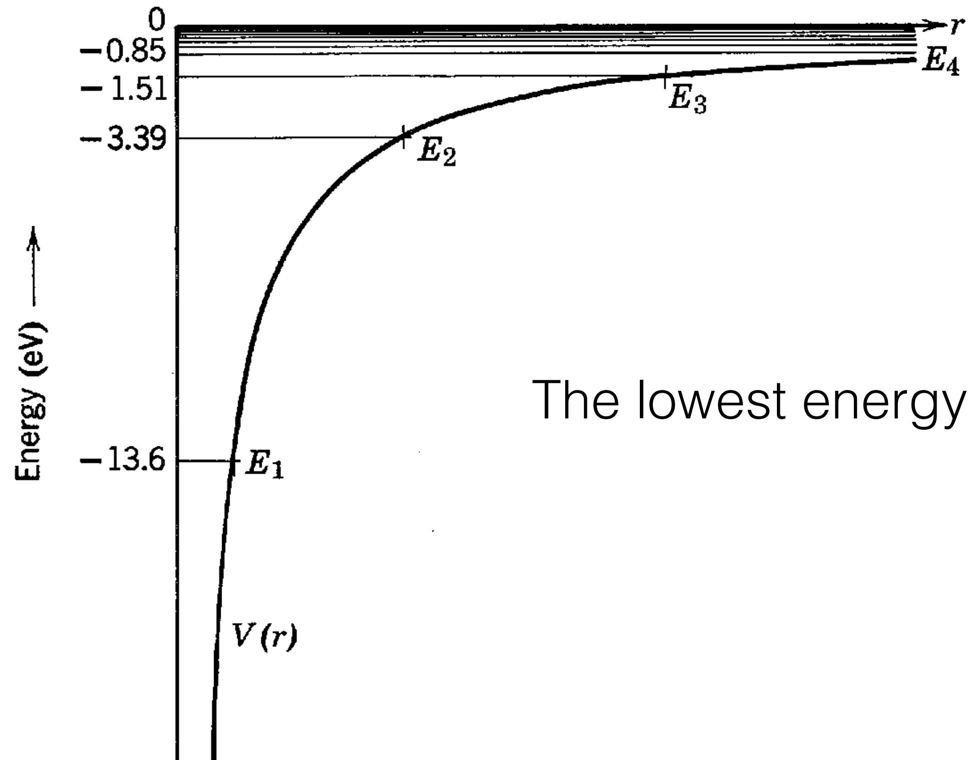
Figure 4-10 A photograph of the visible part of the hydrogen spectrum. (*Spectrum from W. Finkelnburg, Structure of Matter, Springer-Verlag, Heidelberg, 1964.*)

Quantitative agreement with the experimental spectrum

The hydrogen atom - zero point energy

$$E_n = -\frac{\mu Z^2 e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2}$$

$n = 1, 2, \ldots, \infty$
Principal quantum number



The lowest energy level lies *above* the minimum of the potential:
Zero-point energy

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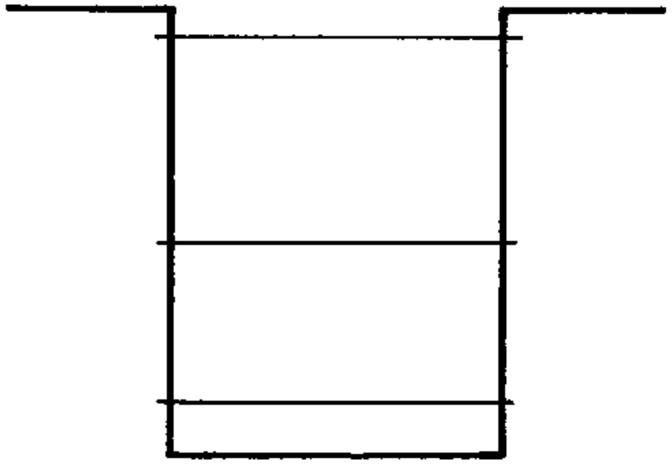
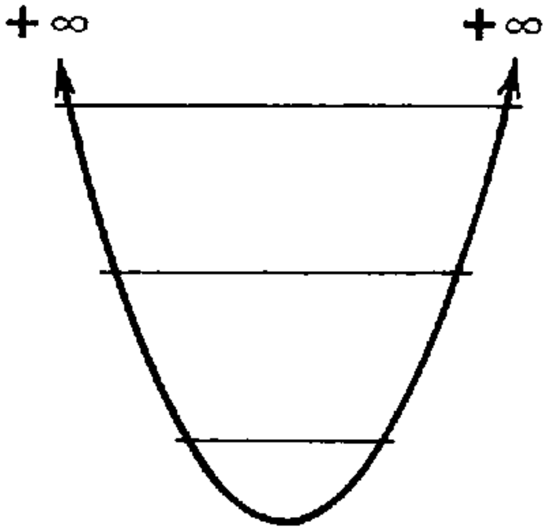
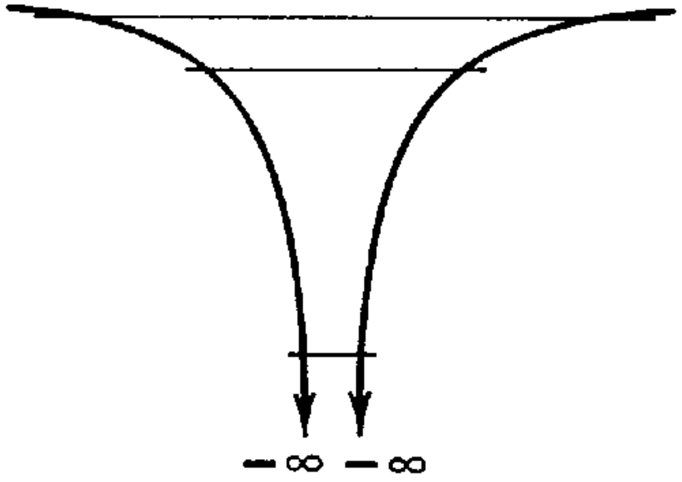


Finite
square well



Simple harmonic
oscillator



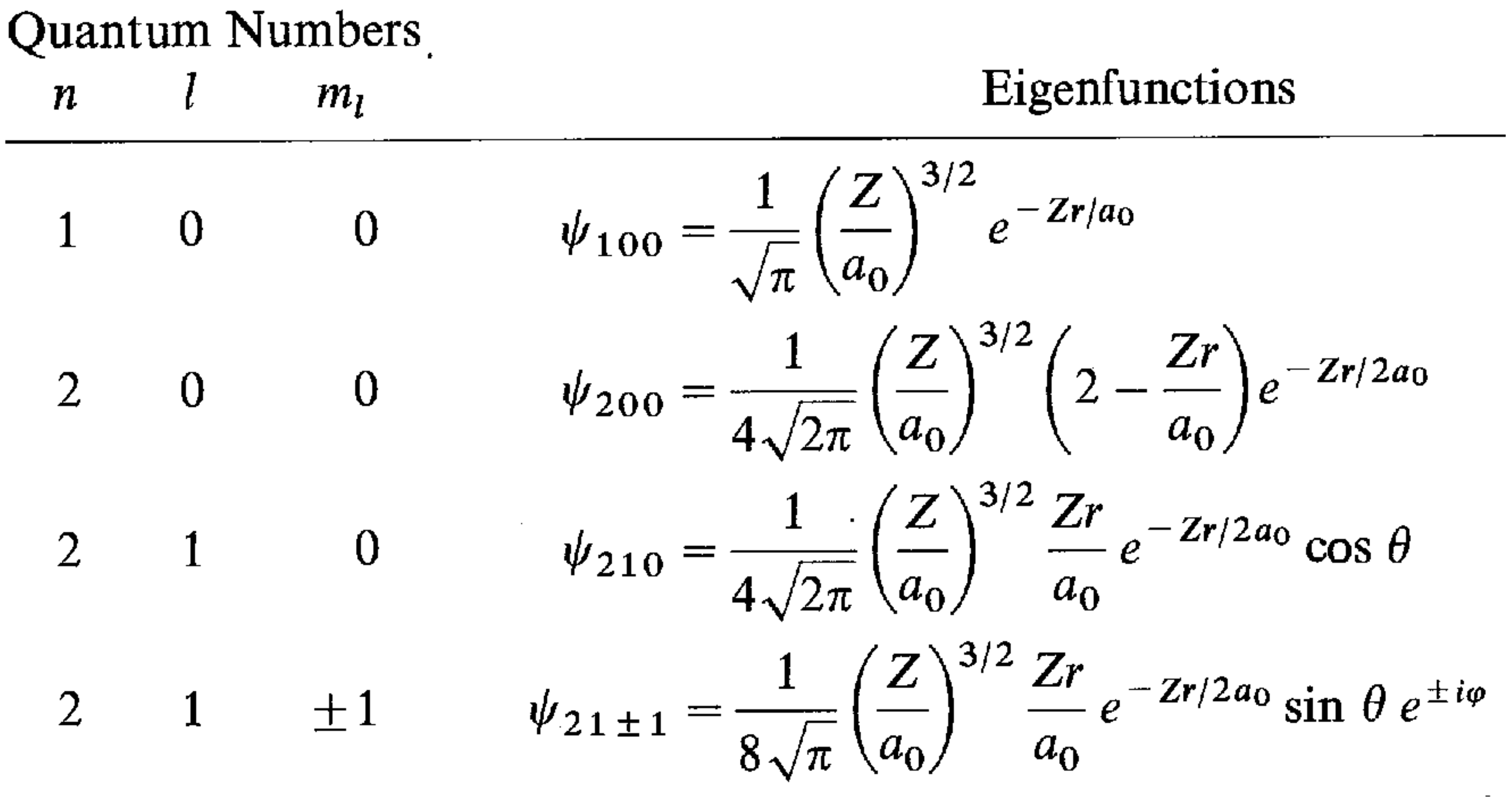
Coulomb

The hydrogen atom - wave functions

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

$$R_{n,l}(r) = e^{-\frac{\text{constant}\cdot r}{n}}\cdot r^l \Rightarrow \text{ polynomial in } r \text{ [Radial part]}$$

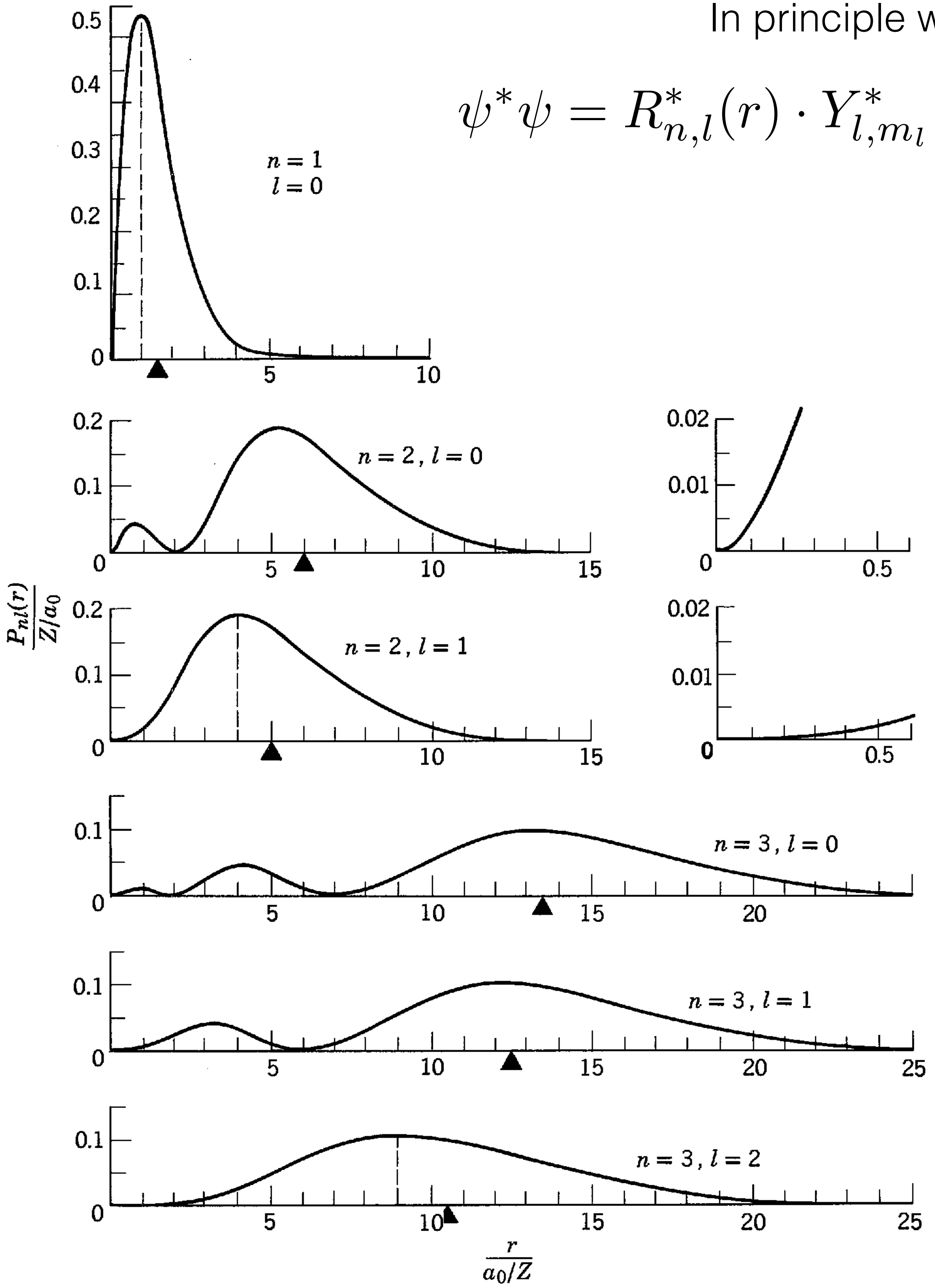
$$Y_{l,m_l}(\theta,\phi) = e^{im_l\phi}\cdot \sin^{|m_l|}\theta \Rightarrow \text{ spherical harmonics \quad [Angular part]}$$



Quantum Numbers n	l	m_l	Eigenfunctions
1	0	0	$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
2	0	0	$\psi_{200} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$
2	1	0	$\psi_{210} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Zr}{a_0}e^{-Zr/2a_0}\cos\theta$
2	1	± 1	$\psi_{21\pm1} = \frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Zr}{a_0}e^{-Zr/2a_0}\sin\theta\, e^{\pm i\varphi}$

- The principal quantum number *n* is related to energy *[n > 0]*
- The orbital quantum number *l* is related to angular momentum *[0 < l < n-1]*
- The magnetic quantum number m_l is related to direction of the angular momentum of the electron *[-l <* m_l *< +l]*

The hydrogen atom - probability densities



In principle we should look at…

$$\psi^*\psi = R^*_{n,l}(r) \cdot Y^*_{l,m_l}(\theta,\phi) \cdot R_{n,l}(r) \cdot Y_{l,m_l}(\theta,\phi)$$

Radial probability density

$$P_{n,l}(r)dr = R^*_{n,l}(r) \cdot R_{n,l}(r) 4\pi r^2 dr$$

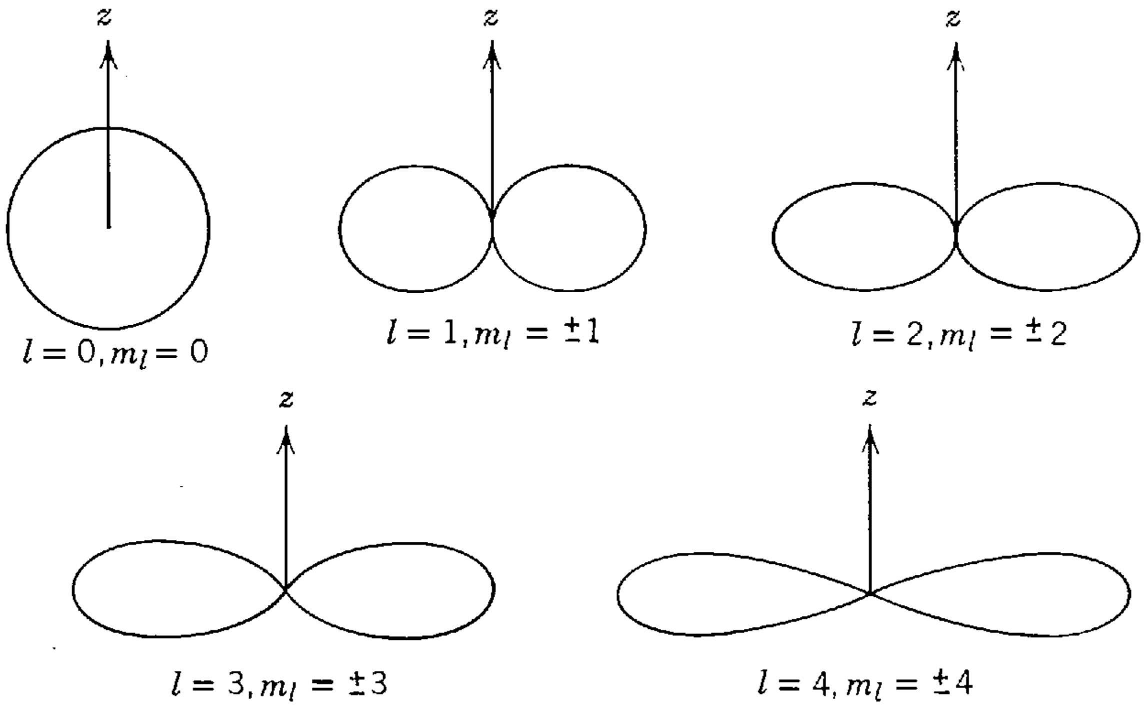
- *n* determines:
  - the *extent* (r) of the probability
  - the *number of nodes* N_N in ψ (and thus P(r) as well) [N_N=n-1]
- *l* determines the *shape* of the probability

- *P(r)* decays quite rapidly
- *P(r)* is *not* homogeneous

The hydrogen atom - probability densities

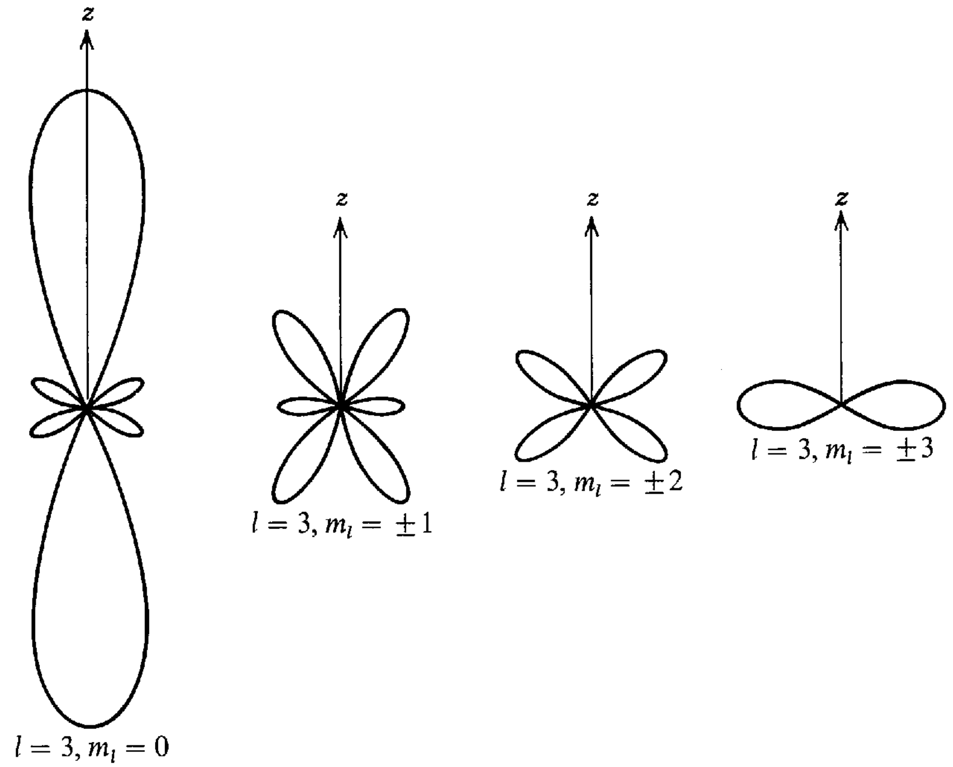
Angular probability density

$$P_{l,m_l}(\theta) = Y^*_{l,m_l}(\theta,\phi) \cdot Y_{l,m_l}(\theta,\phi)$$



l determines
the *shape* of the probability

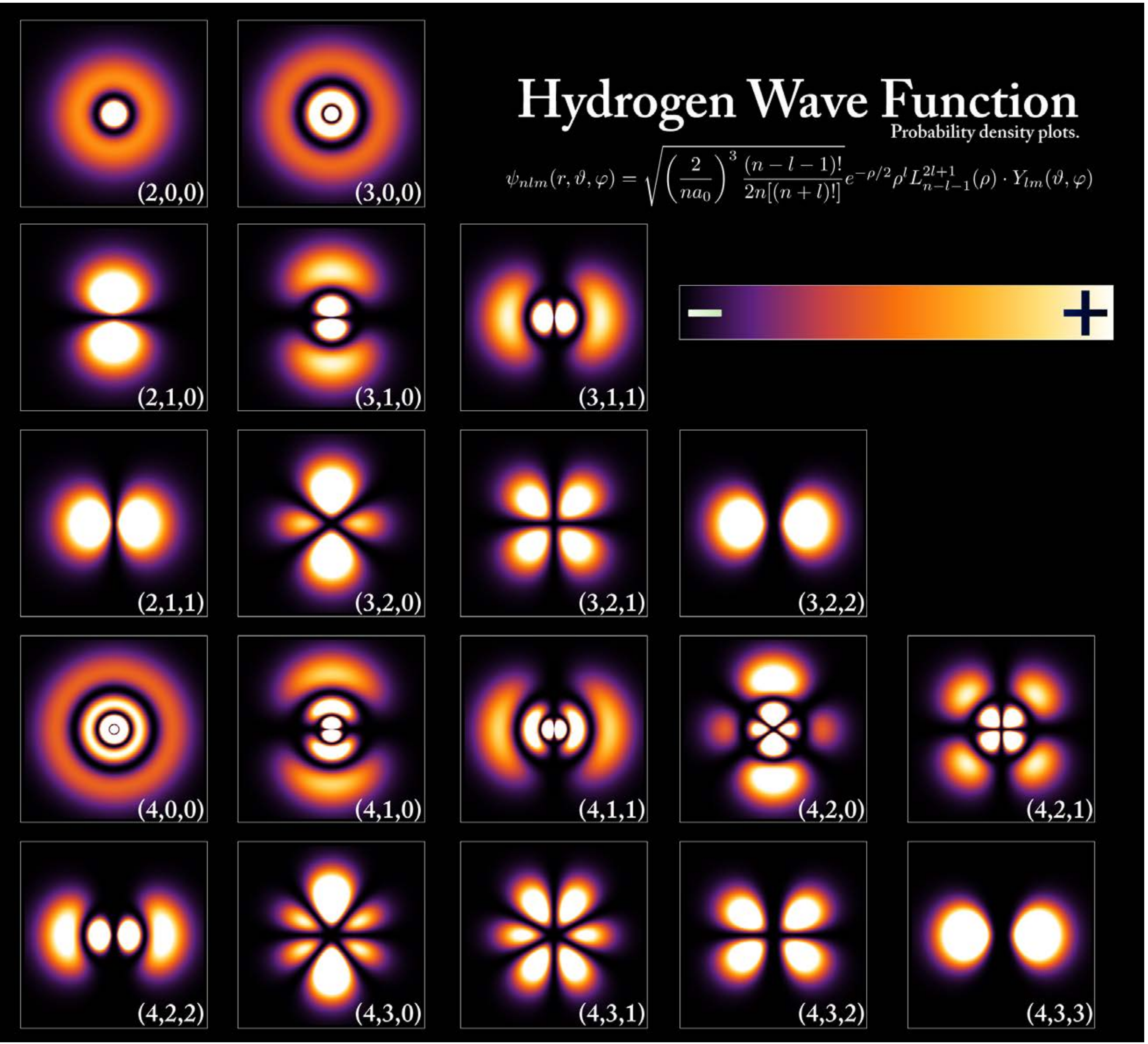
ml determines the *orientational dependence* of the probability



The hydrogen atom - atomic orbitals

Radial and angular results together…

Atomic (hydrogen-like) orbitals



- n → size
- l → shape
- m_l → orientation

Labelling:

$$nl(s,p,d...)^{\text{n. electrons}} \quad \text{e.g. } 3d^2$$

Each atomic orbital can host
up to two electrons
Spin quantum number m_S
from Dirac equation

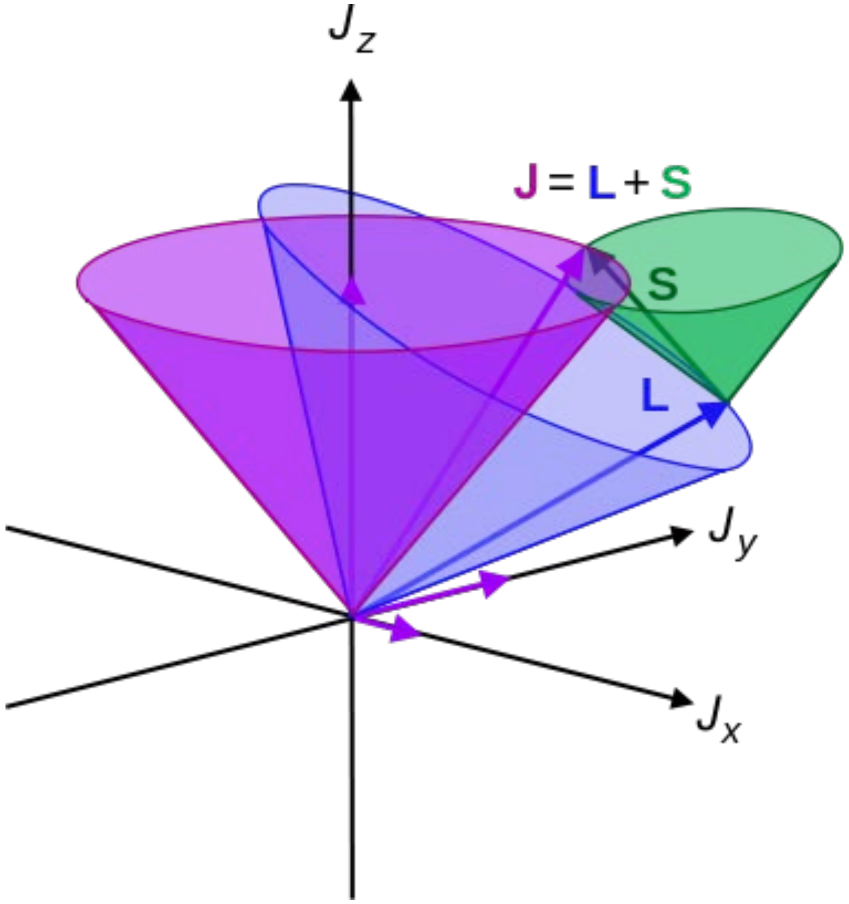
Orbital angular momentum (L)

The quantum number *l* is related to
the orbital angular momentum *L* of the electron

The two quantities are related by the following equation:

$$\mathcal{L}^2|\psi\rangle = \hbar^2 l(l+1)|\psi\rangle$$

L describes the "orbital" motion of the electron about the center of the atom



This motion can be described in terms of spherical harmonics

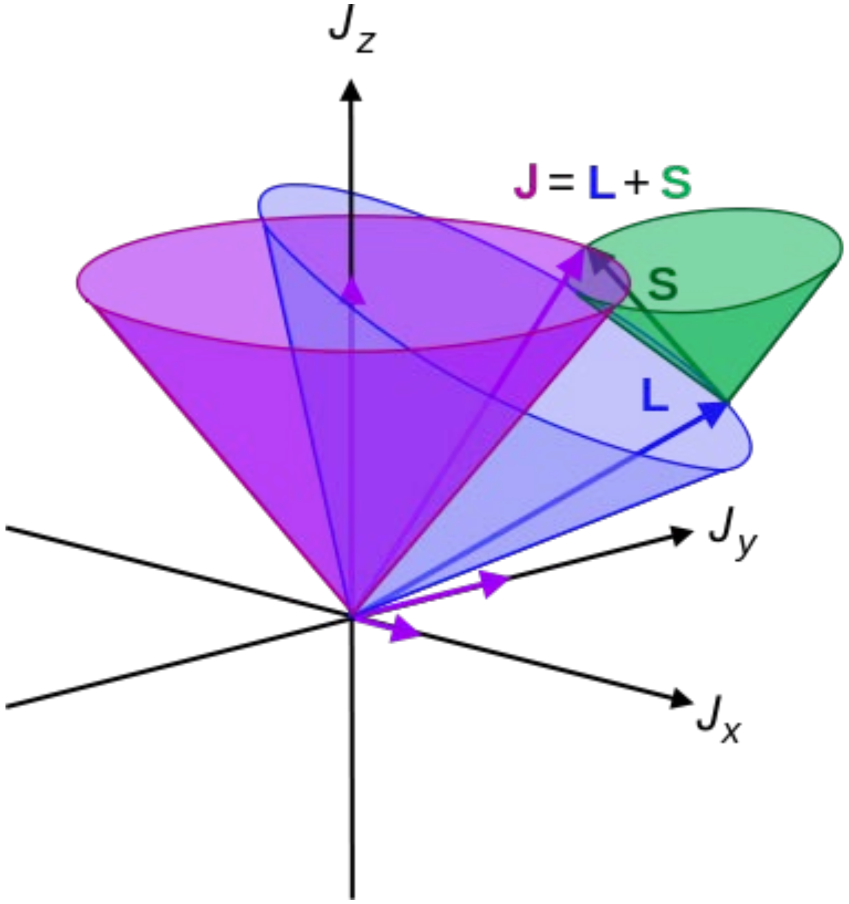
Spin (S)

Electrons (well, in fact *any* elementary particle!) have an *intrinsic angular momentum* as well, *S*

Exactly as in the case of *L*…

$$\mathcal{S}^2|\psi\rangle = \hbar^2 s(s+1)|\psi\rangle$$

~~*S* describes the "intrinsic" motion of the electron about its center of mass…~~



- There is *no* direct analogy with classical mechanics
- *s* is *not* related to positions and/or angles
- It is something so fundamental that every particle has its own spin - its own value os *s*

Spin - electrons

"Ordinary" matter has s=1/2

The Higgs boson has s=0

Integral or zero spin:
bosons

↓

The wave function is
symmetric
under particle interchange

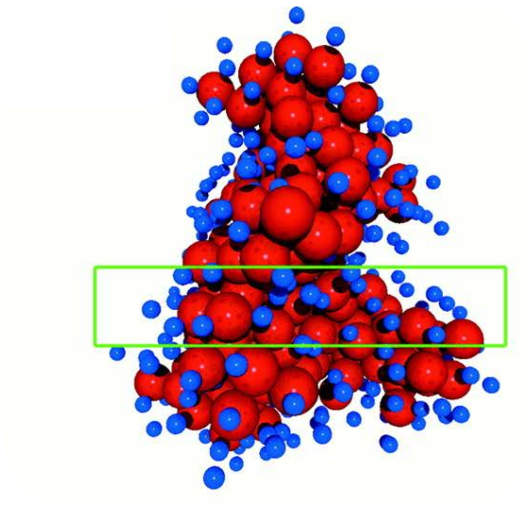
Half-integral spin:
fermions

↓

The wave function is
antisymmetric
under particle interchange

??

In classical mechanics we can *label* particles:



Gasser, U., et al. (2001).
Real-Space Imaging of Nucleation and Growth in Colloidal Crystallization.
Science 292, 258–262.

Spin - electrons

In quantum mechanics, usually we cannot:
particles are *indistinguishable*

Suppose we have two particles (say, two electrons), 1 and 2
and two states, A and B (four quantum number included in one letter!)

The combined wave functions of the system are:

$$\psi_{\text{Combined}} = \psi_A(1)\psi_B(2) \text{ or } \psi_B(1)\psi_A(2)$$

This does not work, though!
The probability density is not the same if I swap 1 with 2!

$$\psi_A^*(1)\psi_B^*(2)\cdot\psi_A(1)\psi_B(2) \neq \psi_A^*(2)\psi_B^*(1)\cdot\psi_A(2)\psi_B(1)$$

However, we can construct linear combinations in order to make things right:

$$\psi_{\text{Combined}}^{\text{Symmetric}} = \frac{1}{2}[\psi_A(1)\psi_B(2) + \psi_B(1)\psi_A(2)]$$

Integral or zero spin: bosons

$$\psi_{\text{Combined}}^{\text{Antisymmetric}} = \frac{1}{2}[\psi_A(1)\psi_B(2) - \psi_B(1)\psi_A(2)]$$

Half-integral spin: fermions

The exclusion principle

$$\psi^{\text{Antisymmetric}}_{\text{Combined}} = \frac{1}{2}[\psi_A(1)\psi_B(2) - \psi_B(1)\psi_A(2)]$$

Consider two electrons in *exactly* the same state A:

↓

$$\psi^{\text{Antisymmetric}}_{\text{Combined}} = \frac{1}{2}[\psi_A(1)\psi_A(2) - \psi_A(1)\psi_A(2)]$$

NOPE

Pauli expulsion principle:
Two electrons *cannot* occupy *exactly* the same state

Singlet and Triplet states

Note that for fermions/bosons
the *total* wave function has to be antisymmetric/symmetric

$$\psi = \psi_{\text{Spatial}} \cdot \psi_{\text{Spin}}$$

For fermions (e.g. electrons):

$$\psi = \psi_{\text{Spatial}}^{\text{Antisymmetric}} \cdot \psi_{\text{Spin}}^{\text{Symmetric}} \text{ or } \psi_{\text{Spatial}}^{\text{Symmetric}} \cdot \psi_{\text{Spin}}^{\text{Antisymmetric}}$$

antisymmetric spin eigenfunction:

$$\frac{1}{\sqrt{2}}[(+1/2,-1/2)-(-1/2,+1/2)] \quad \text{(singlet)}$$

symmetric spin eigenfunctions:

$$(+1/2,+1/2)$$

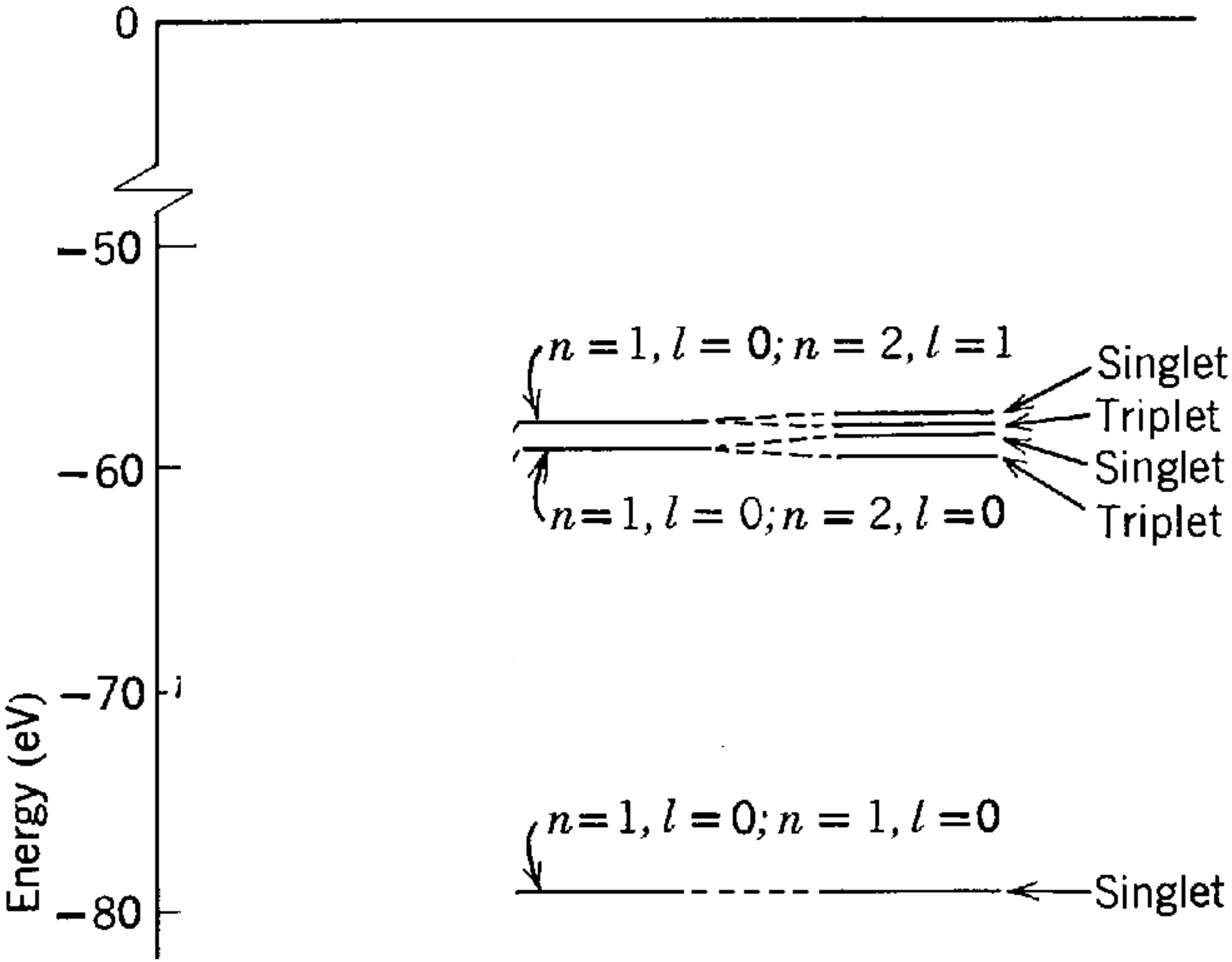
$$\frac{1}{\sqrt{2}}[(+1/2,-1/2)+(-1/2,+1/2) \quad \text{(triplet)}$$

$$(-1/2,-1/2)$$

Singlet and Triplet states

Singlet and triplet states have different energies!

e.g. energy levels of the helium atom



Wait, no triplet state?

H_2^+ and the Born-Oppenheimer approx.

Even in the case of the H_2^+ molecule (2 protons, 1 electron),
it is impossible to solve the Schrödinger equation analytically

$$\mathcal{H} = -\frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial z^2} - \frac{\hbar^2}{2M_1}\frac{\partial^2}{\partial Z_1^2} - \frac{\hbar^2}{2M_2}\frac{\partial^2}{\partial Z_2^2} + V(z, Z_1, Z_2)$$

$$\mathcal{H}\psi(z, Z_1, Z_2) = E\psi(z, Z_1, Z_2)$$

$$\Downarrow$$

The Born-Oppenheimer approximation:

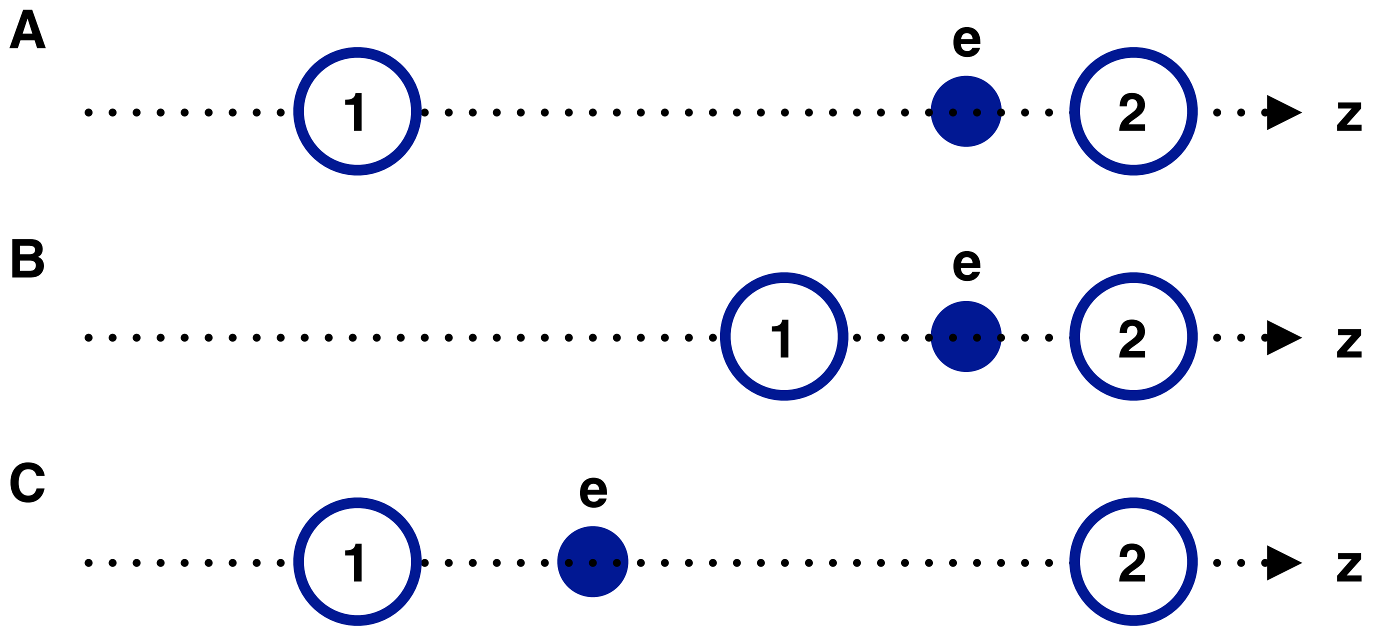
$$\psi(z, Z_1, Z_2) = \psi(z, \{Z_1, Z_2\}) \cdot \psi(Z_1, Z_2)$$
$$\psi(\bar{r}_e, \bar{R}_N) = \psi(\bar{r}_e, \{\bar{R}_N\}) \cdot \psi(\bar{R}_N)$$

The Born-Oppenheimer approximation

$$\psi(\bar{r}_e, \bar{R}_N) = \psi(\bar{r}_e, \{\bar{R}_N\}) \cdot \psi(\bar{R}_N)$$

The wave function for the electrons depend on the position of the electrons and, *parametrically*, on the position of the nuclei

For each nuclear configuration {**R**N}, we have a different electronic wave function



The Born-Oppenheimer approximation

Electrons are *much* (~$10^{3\text{-}4}$) lighter than the nuclei, so
for each movement of the nuclei, the electrons follows *immediately*

Electrons are *immobile* on the timescale of nuclear motion

The electron-nuclei interaction *is still there*

HOWEVER

We discard the kinetic terms for the nuclei (*and* the mixed electron-nuclei terms) in the Hamiltonian

$$\mathcal{H} = -\frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial z^2} - \frac{\hbar^2}{2M_1}\frac{\partial^2}{\partial Z_1^2} - \frac{\hbar^2}{2M_2}\frac{\partial^2}{\partial Z_2^2} + V(z, Z_1, Z_2)$$

$$\Downarrow$$

$$\mathcal{H} = -\frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial z^2} + V(z, \{Z_1, Z_2\})$$

$$\mathcal{H} = -\frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial z^2} - \frac{e^2}{4\pi\epsilon_0 z_{e-1}} - \frac{e^2}{4\pi\epsilon_0 z_{e-2}} + \frac{e^2}{4\pi\epsilon_0 Z_{1-2}}$$

The Born-Oppenheimer approximation

$$\mathcal{H} = -\frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial z^2} - \frac{e^2}{4\pi\epsilon_0 z_{e-1}} - \frac{e^2}{4\pi\epsilon_0 z_{e-2}} + \frac{e^2}{4\pi\epsilon_0 Z_{1-2}}$$

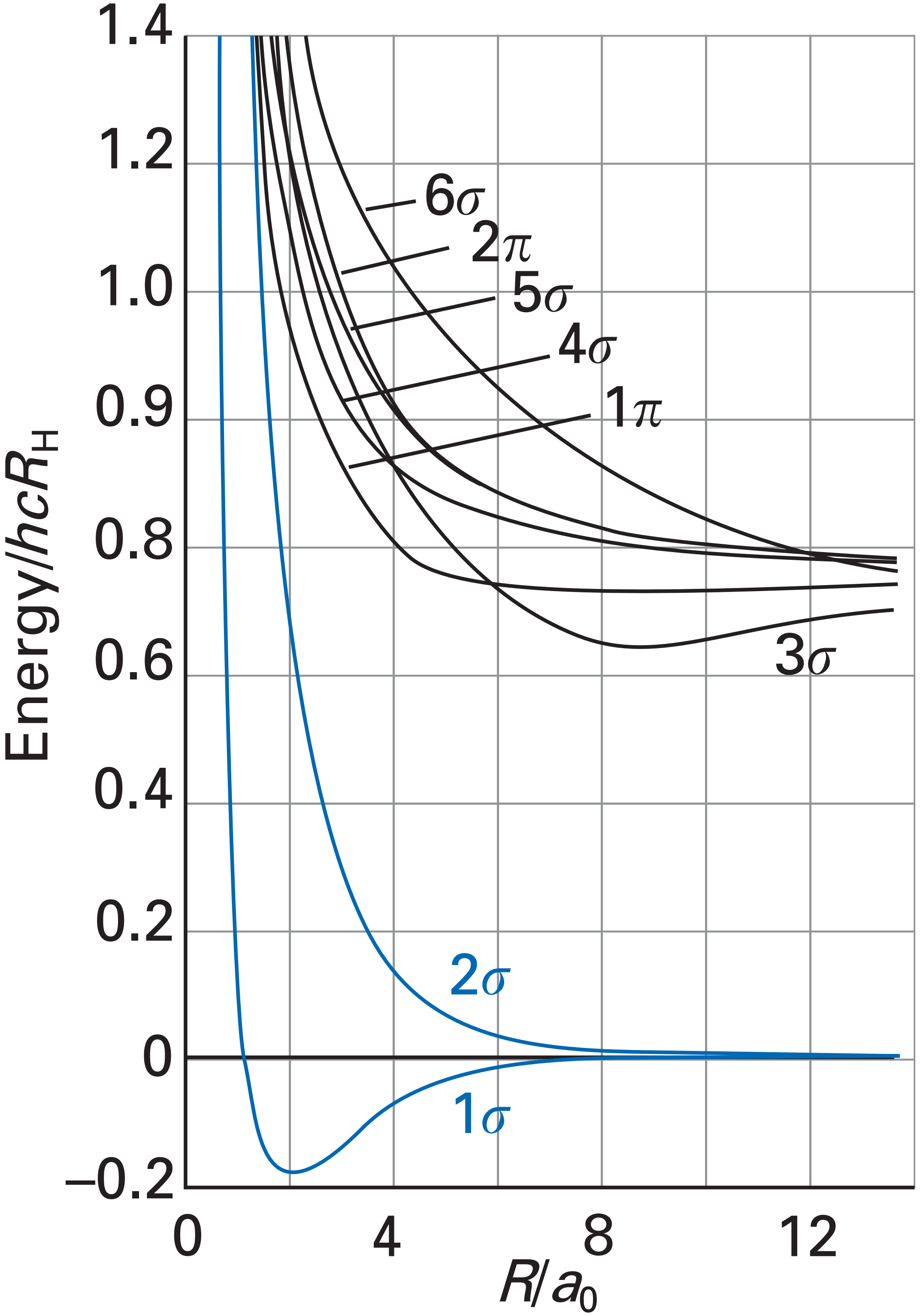
Comparison with the Hamiltonian for the hydrogen atom:

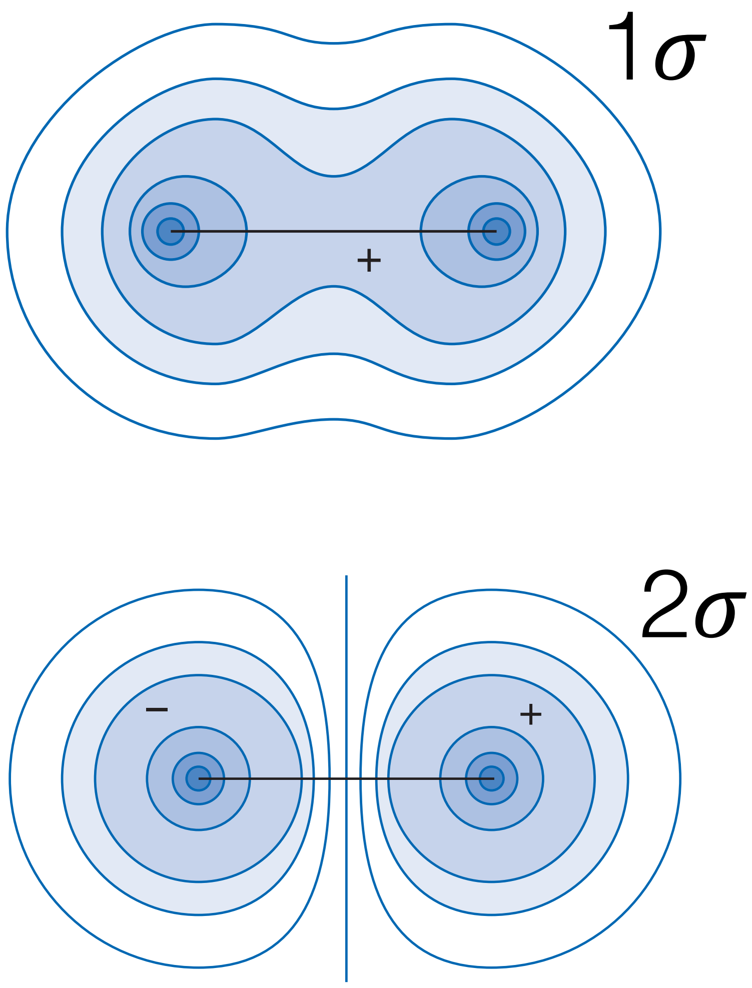
$$\mathcal{H} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 \cdot \bar{r}}$$

We can do this - analytically!
(*ellipsoidal instead of spherical polar coordinates*)

H_2^+ - molecular orbitals

Solving the Schrödinger equation for H_2^+
in the Born-Oppenheimer approximation leads to…





H_2^+ - molecular orbitals

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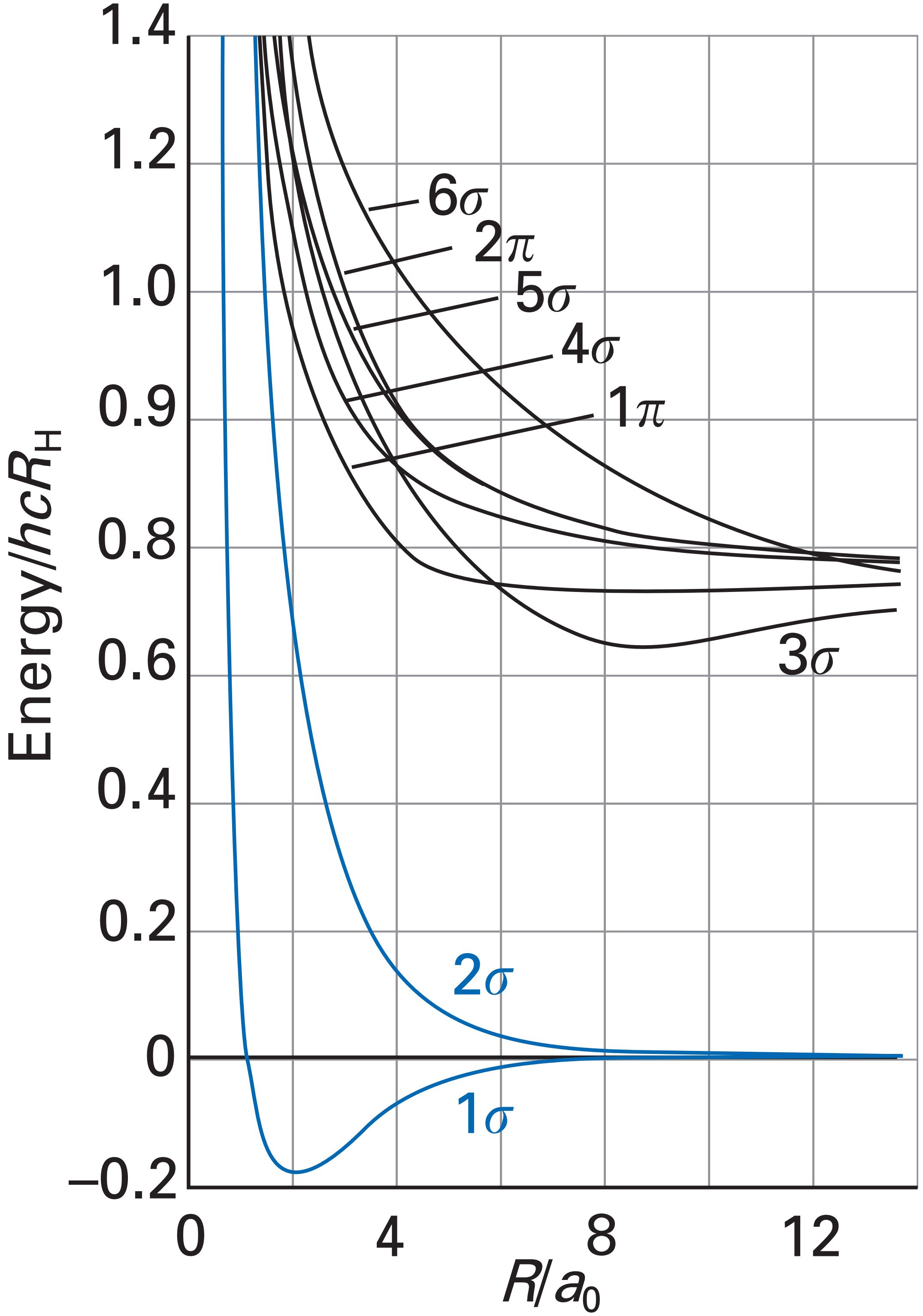
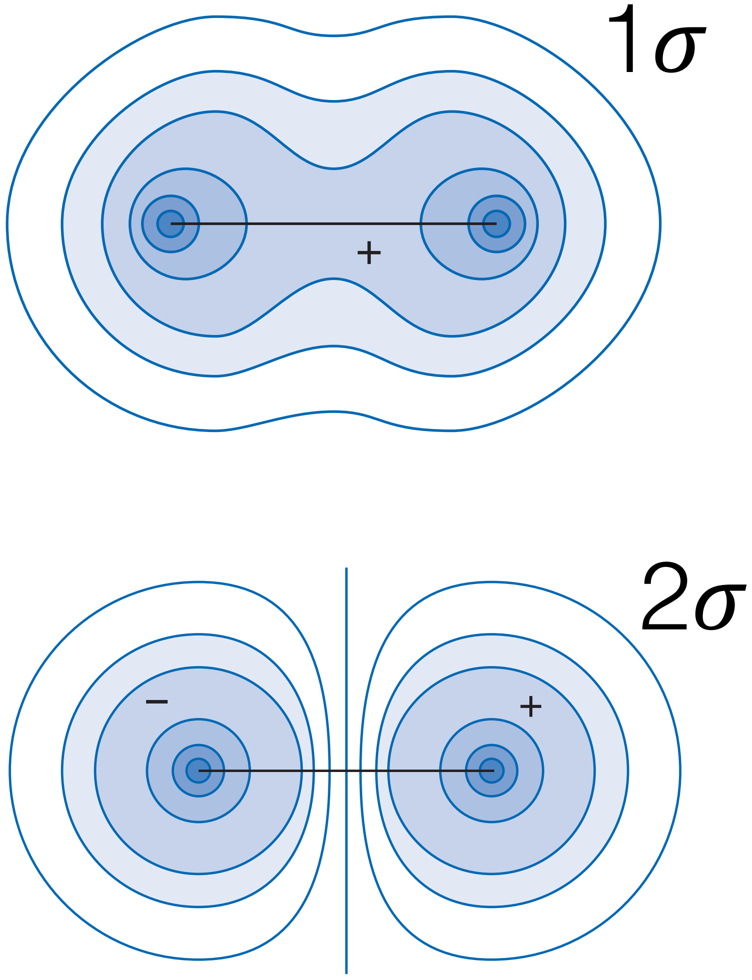




Molecular Orbitals (MO)
Look at the probability density!

- 1σ ➠ Bonding orbital
- 2σ ➠ Antibonding orbital

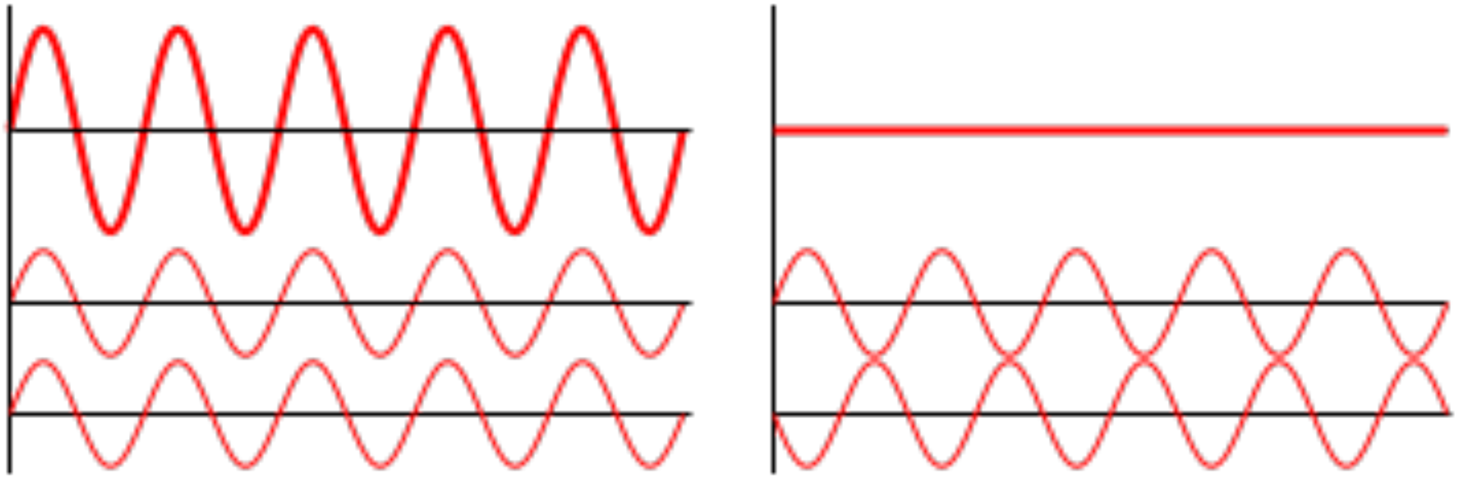
LCAO

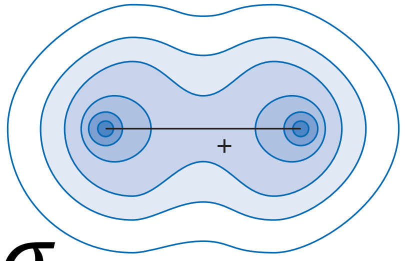
Actually, we cannot solve the Schrödinger equation for anything more complicated than H_2^+
- *even when using the Born-Oppenheimer approximation*

HOWEVER

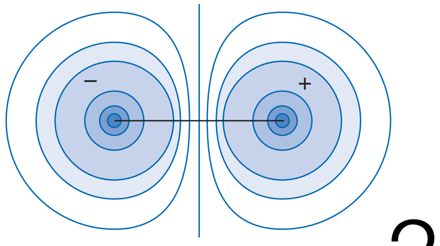
Inspired by the H_2^+ MO, we can think that
building MO is a matter of constructive/destructive interference

In the case of H_2^+ constructive/destructive interference between
the two atomic (σ) orbitals of the hydrogen atom





1σ



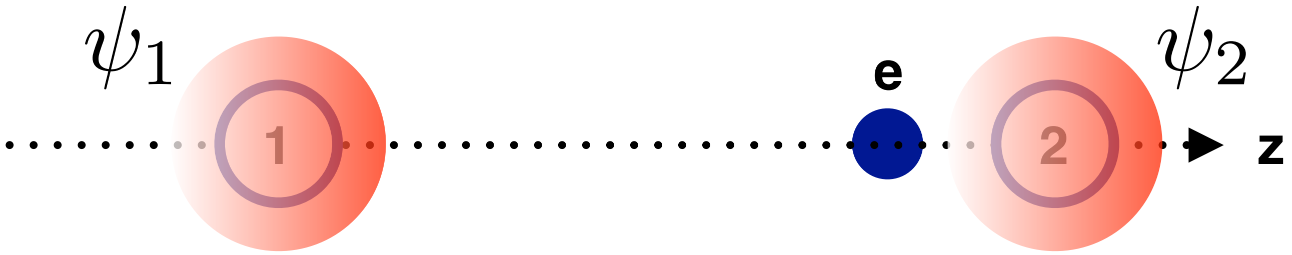
2σ

LCAO

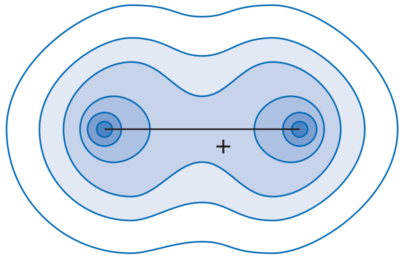
Linear Combination of Atomic Orbitals
LCAO

$$\psi_{\text{Molecular Orbital}} = \sum_i c_i \psi_{\text{Atomic Orbital}}$$

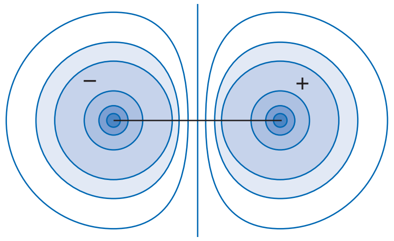
The case of H_2^+ again:



$$\psi^{1\sigma}_{\mathrm{H}_2^+} \approx \psi_1 + \psi_2$$



$$\psi^{2\sigma}_{\mathrm{H}_2^+} \approx \psi_1 - \psi_2$$



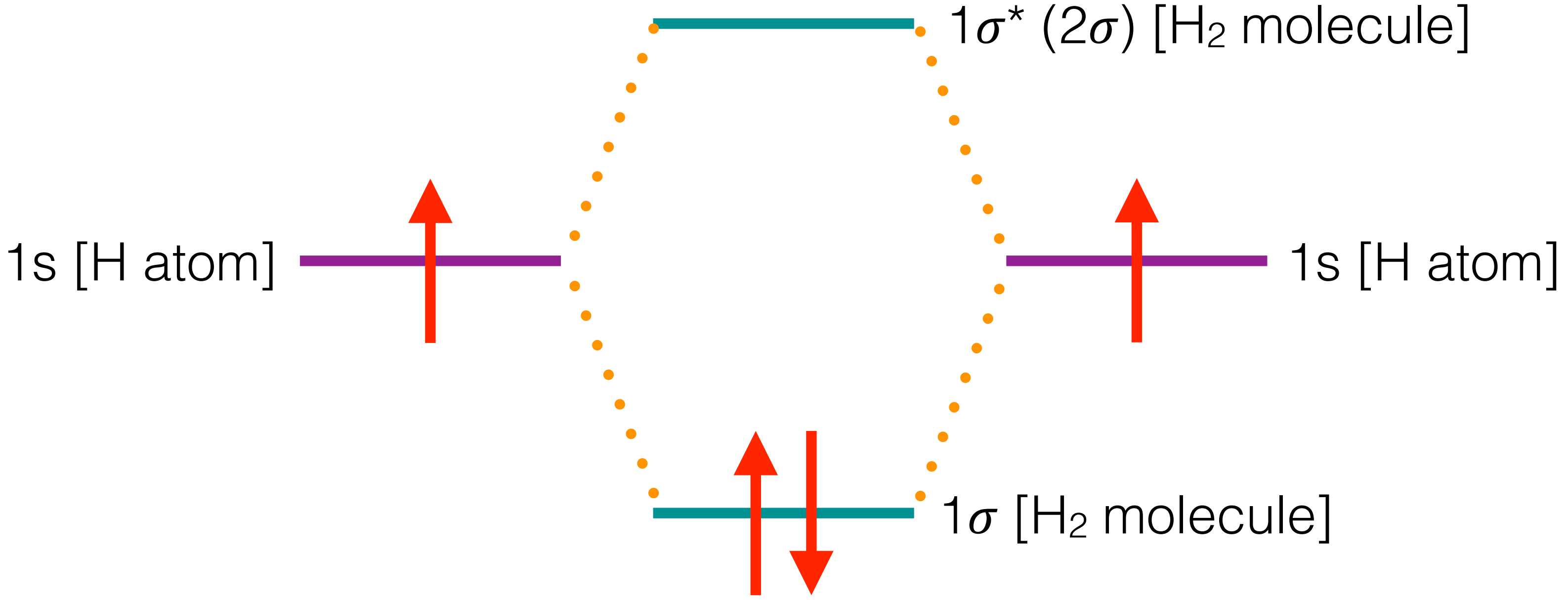
Symmetry

Are the MO invariant upon inversion of electronic coordinates?

- 1σ is! g (*gerade*)
- 2σ is not! u (*ungerade*)

LCAO diagrams

The *hydrogen* molecule



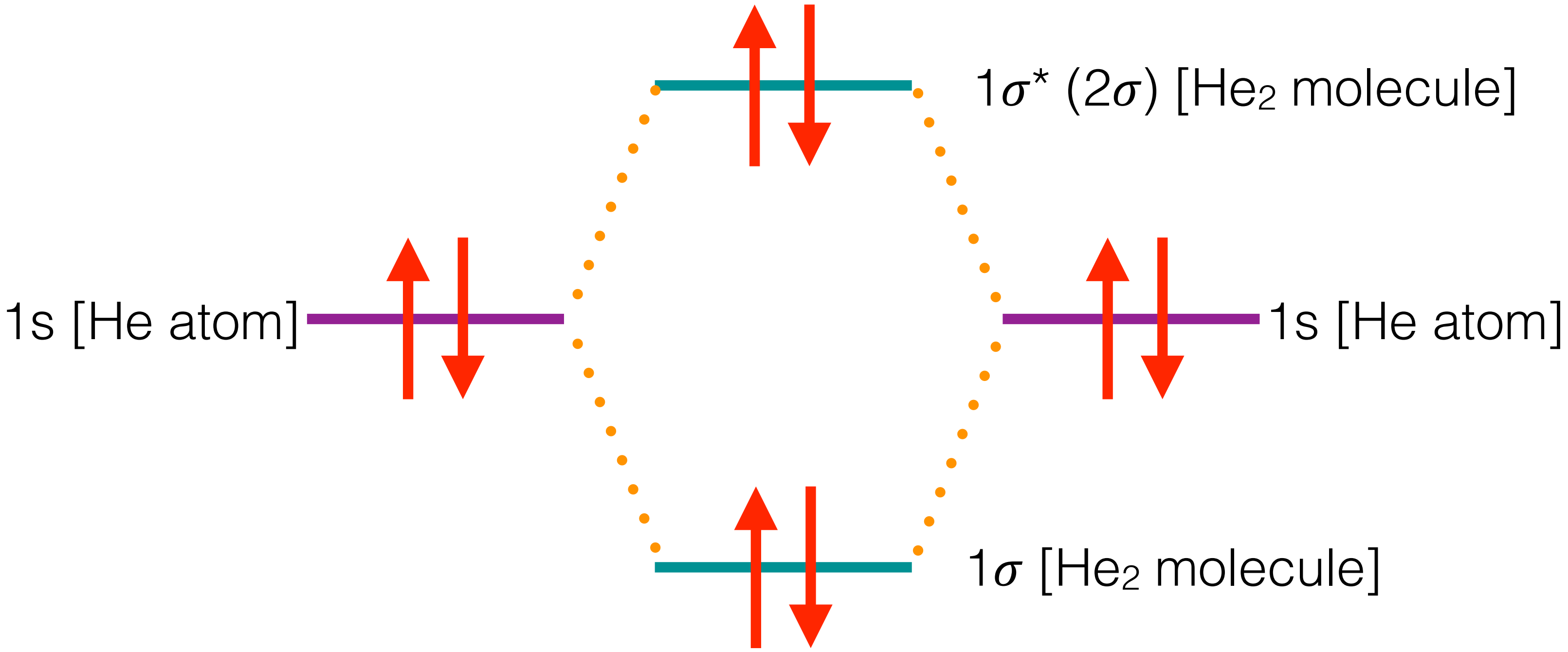
$1\sigma^*$ (2σ) [H_2 molecule]

1s [H atom]

1s [H atom]

1σ [H_2 molecule]

The *helium* molecule



$1\sigma^*$ (2σ) [He_2 molecule]

1s [He atom]

1s [He atom]

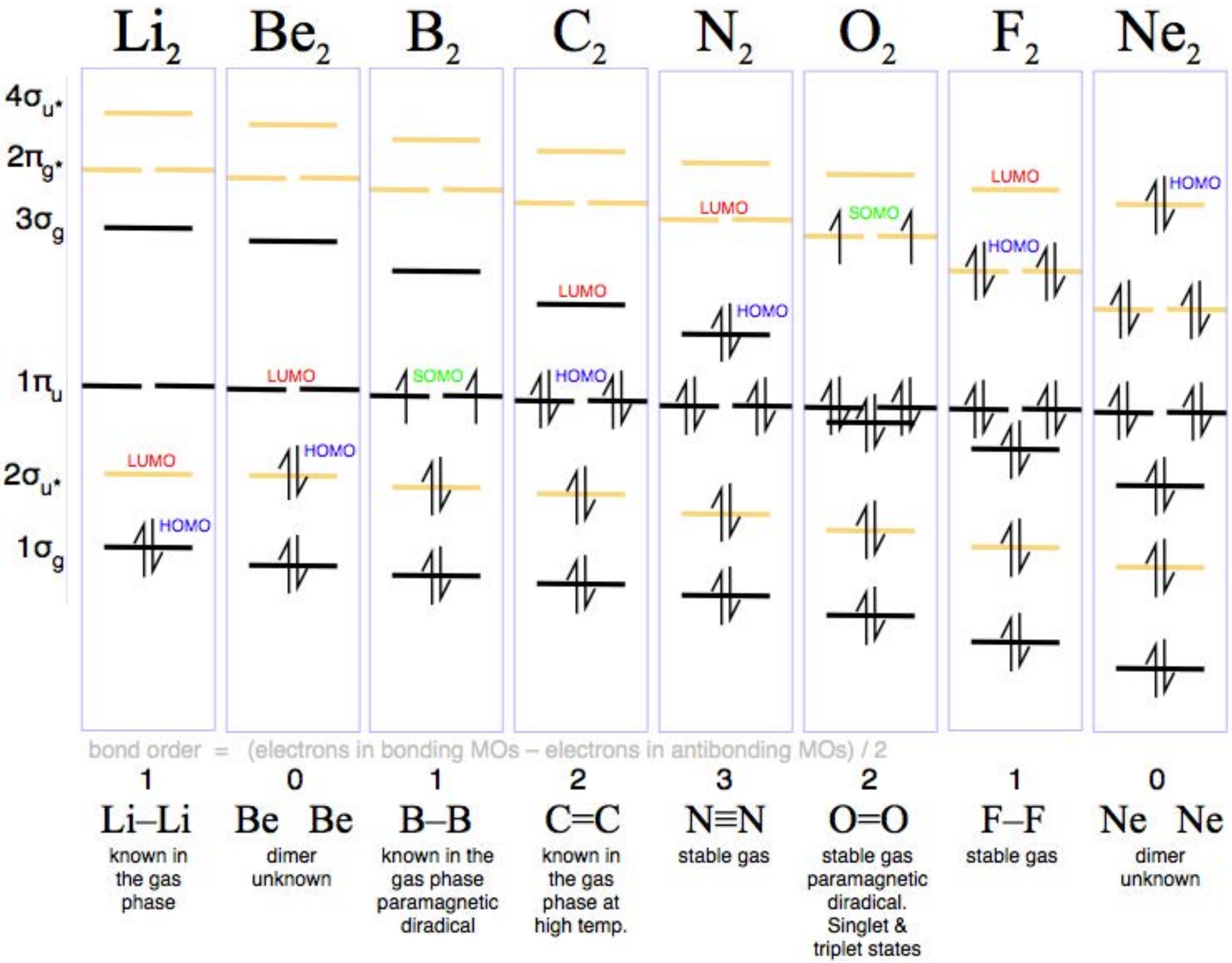
1σ [He_2 molecule]

Bond order

$$\text{Bond order: } \frac{\text{N. of bonding } e - \text{ N. of antibonding } e}{2}$$

The higher the bond order (BO), the stronger the bond [length, enthalpy]

- Hydrogen molecule: BO=1
- Helium *molecule*: BO=0



LCAO diagrams

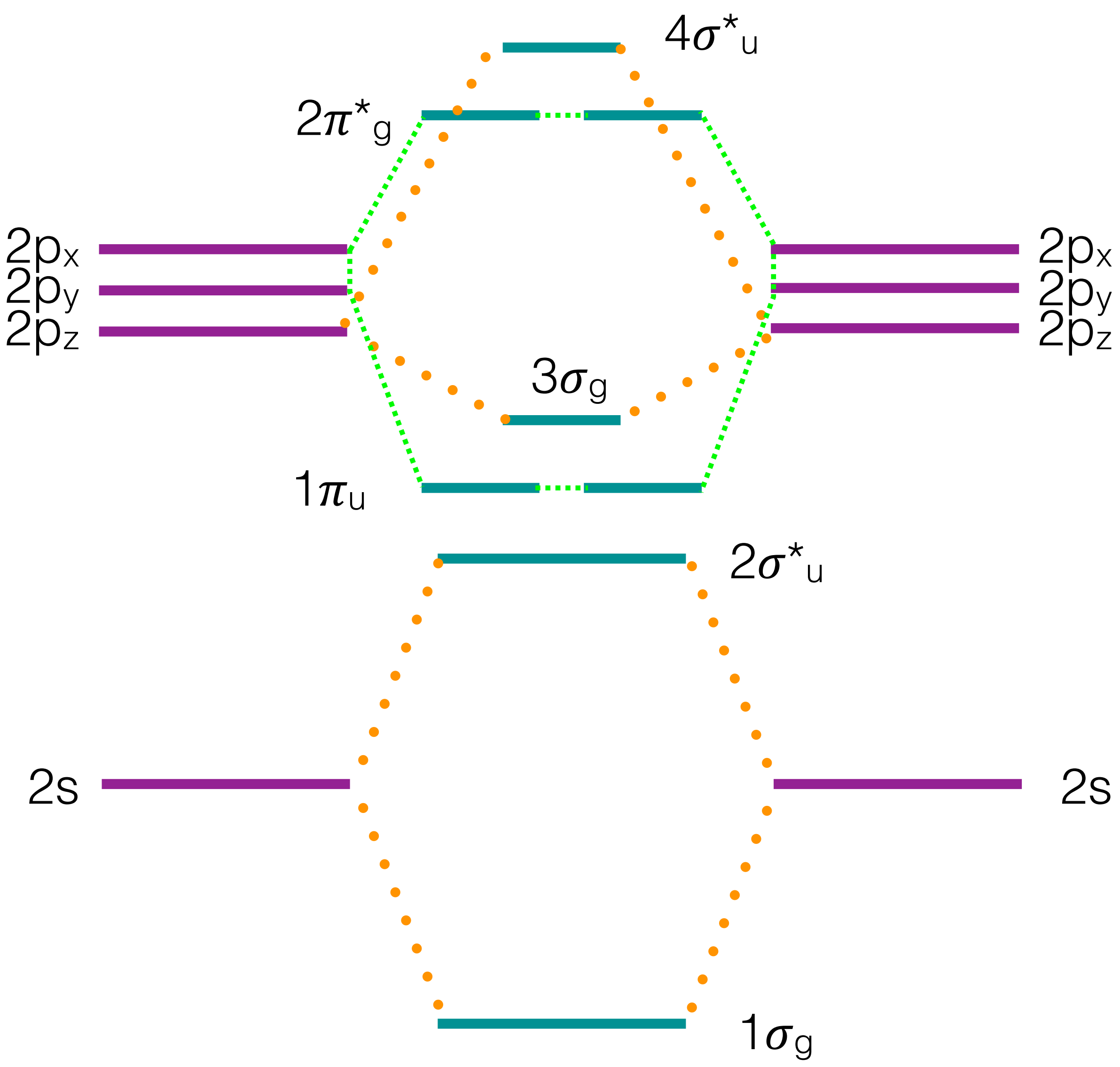
LCAO how to:

1. Find the *valence electrons* for each atom in the molecule
2. Homo- vs hetero- nuclear molecule (the more electronegative atom will be placed lower on the diagram)
3. Build the MOs, keeping in mind that:
    - More nodes = higher MOs
    - Sigma orbitals are stronger than pi bonds
    - Antibonding MOs are higher in energy than bonding MOs
    - Constructive overlap = fewer nodes = more stable (less energetic)
    - Destructive overlap = more nodes = less stable (more energetic)
4. Double check: the number of individual atomic orbitals should equal the number of MOs

LCAO diagrams

The *nitrogen* molecule

Electronic configuration of the nitrogen atom:
[He] $2s^2 2p^3$



Bond order?

Molecular orbitals

The *HF* molecule

Electronic configuration of the fluorine atom:
[He] $2s^2 2p^5$

The σ atomic orbital of F cannot interact with the σ atomic orbital of H

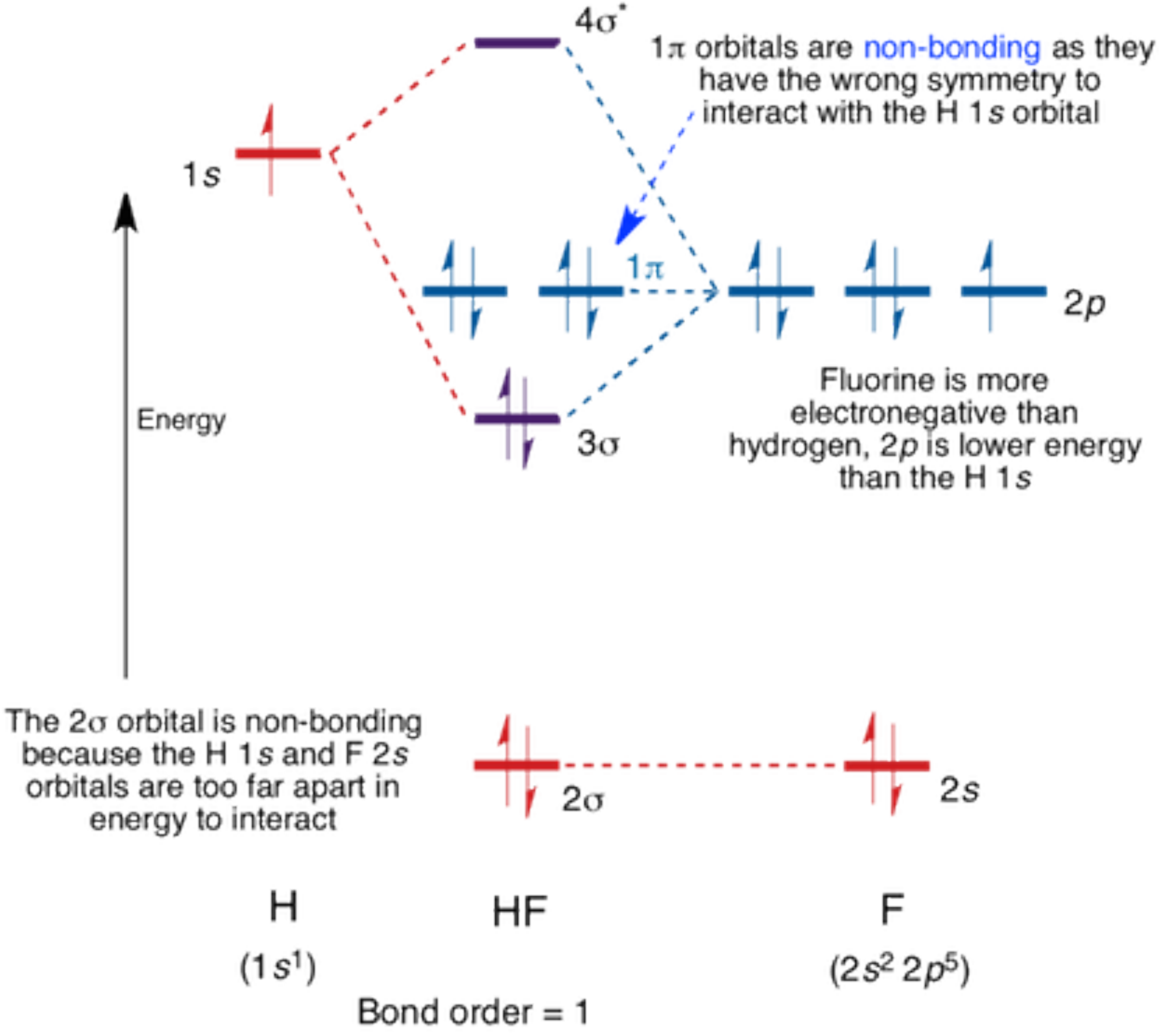
10

Molecular orbitals

The *HF* molecule

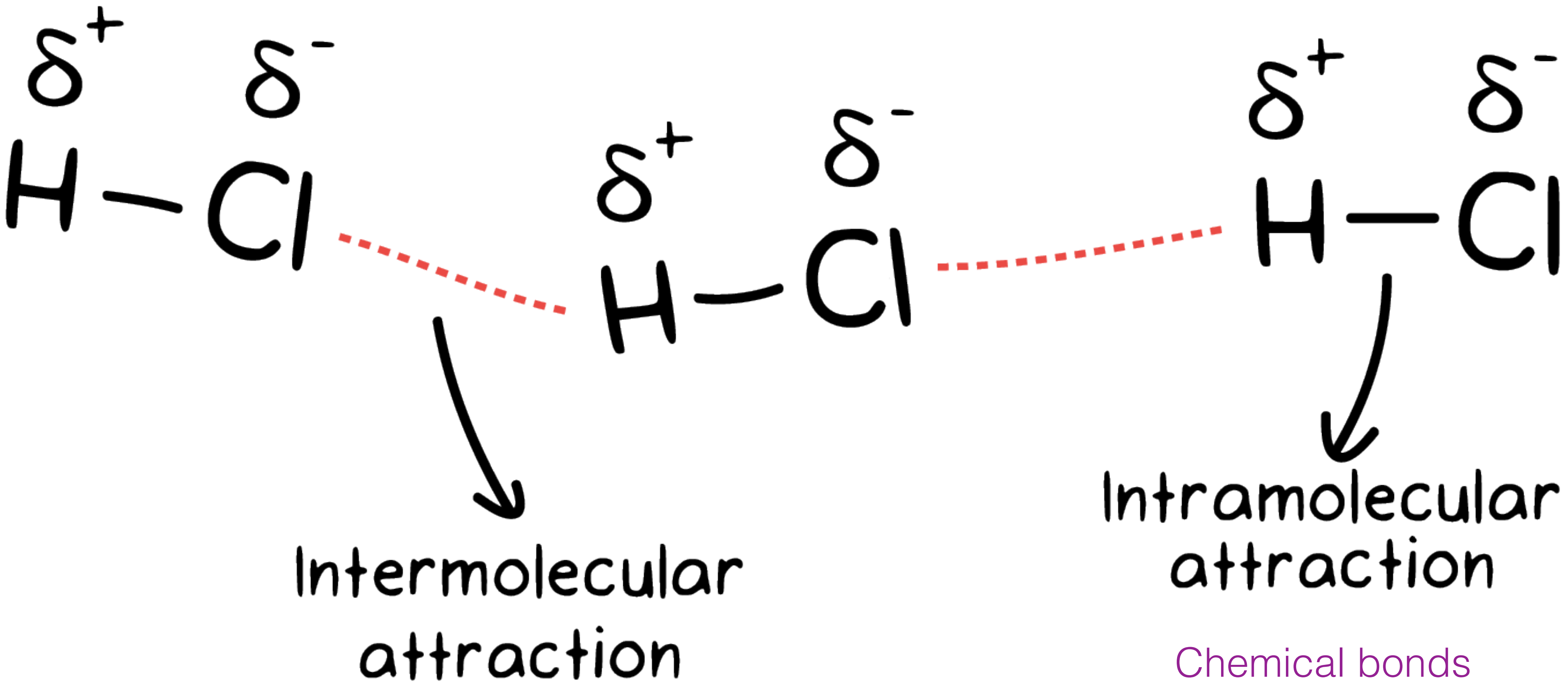
Electronic configuration of the fluorine atom:
[He] $2s^22p^5$

The σ atomic orbital of F cannot interact with the σ atomic orbital of H



Coffee!

Intra- & Inter- molecular interactions



Chemical bonds

You have to do chemistry to break/form them

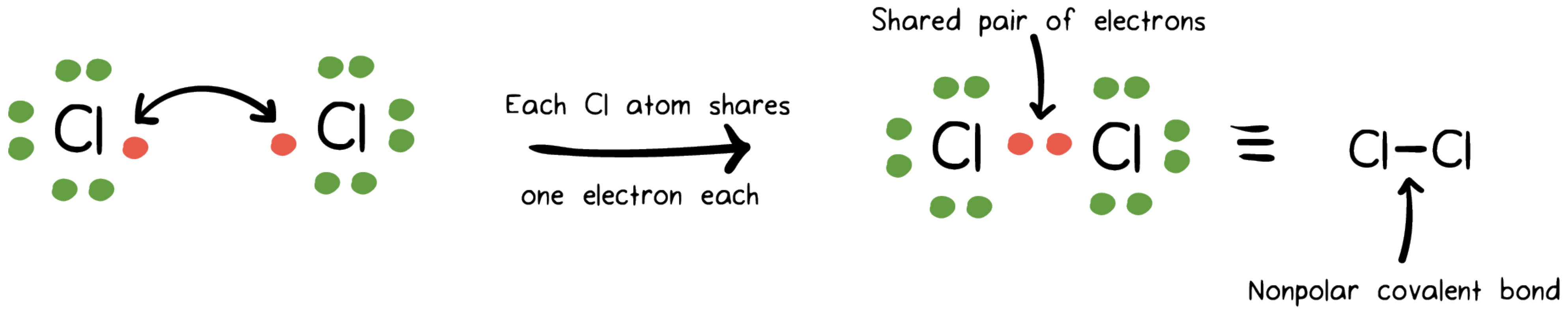
Typically much weaker

No need to do chemistry, electrostatic is usually enough…

Covalent bond

Covalent bonds are the realm of LCAO

Non polar



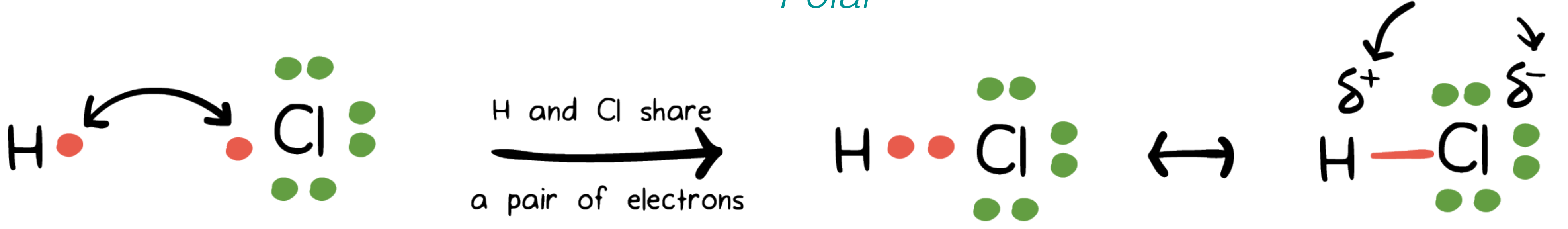
Each Cl atom shares one electron each

Shared pair of electrons

Nonpolar covalent bond

Cl pulls the shared pair
of electrons towards itself,
developing a partial - charge
and as a result H gets
a partial + charge

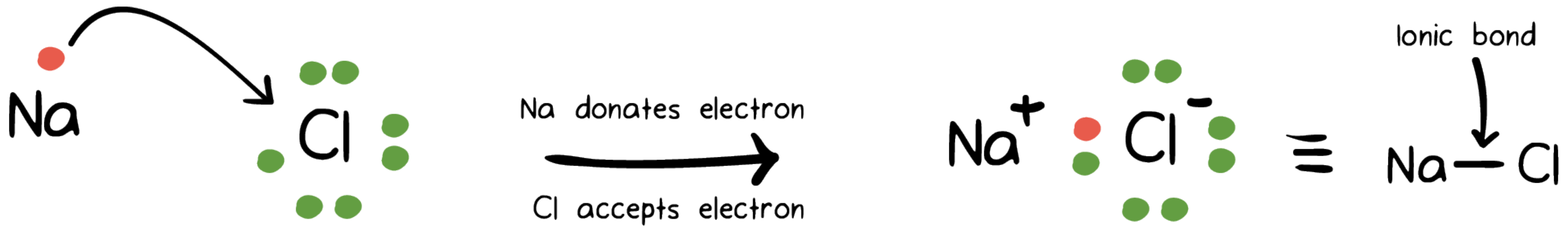
Polar



H and Cl share a pair of electrons

Cl is more electronegative
than H (H = 2.1 and Cl = 3
on the electronegativity scale)

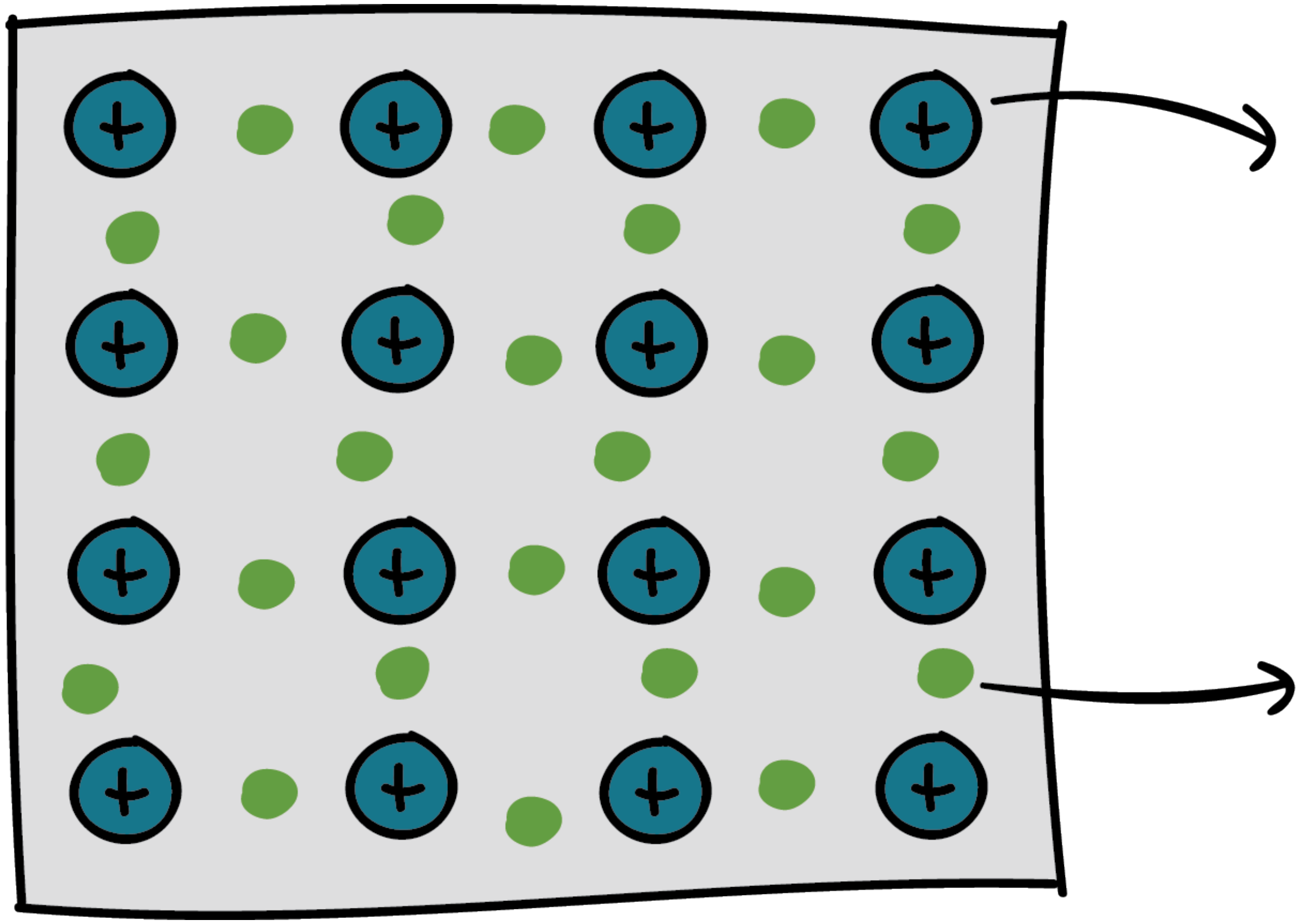
Ionic bond



Chemistry in solution

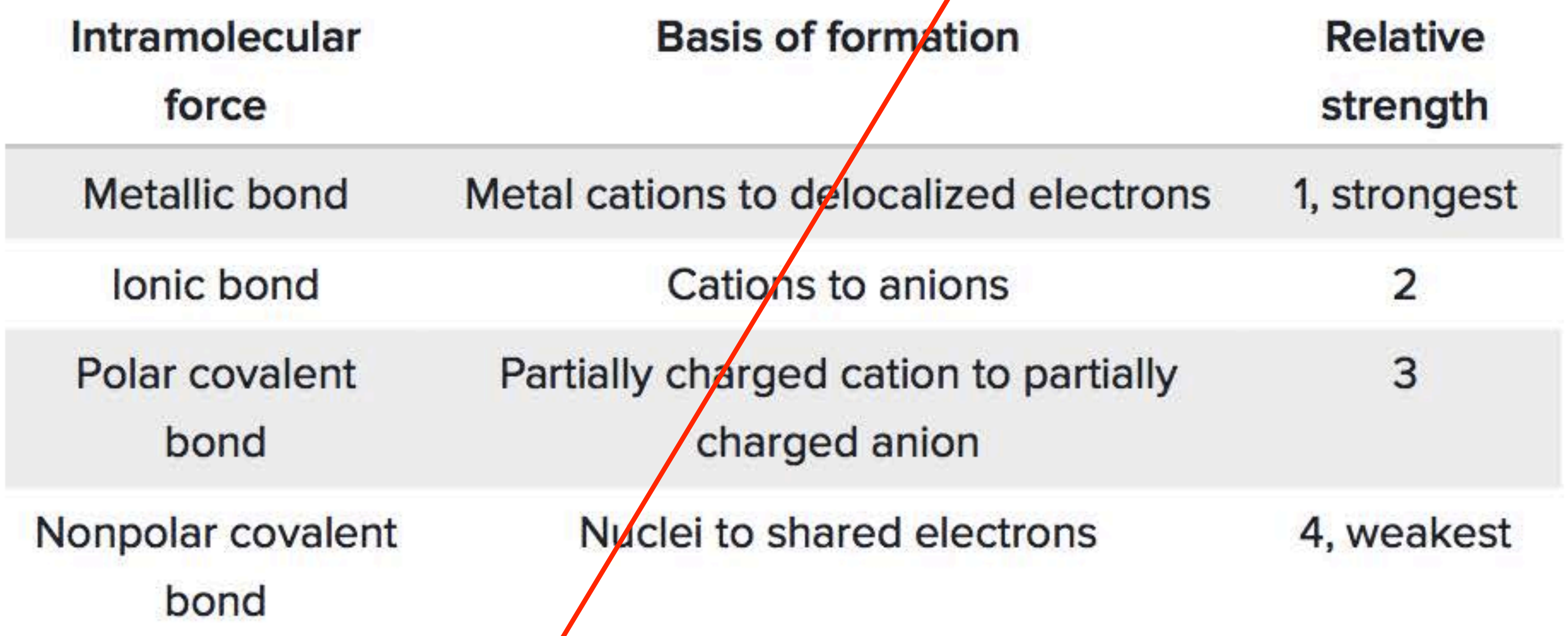
nacl_2.mp4

Metallic bond


positively charged atoms of the metal

mobile valence electrons

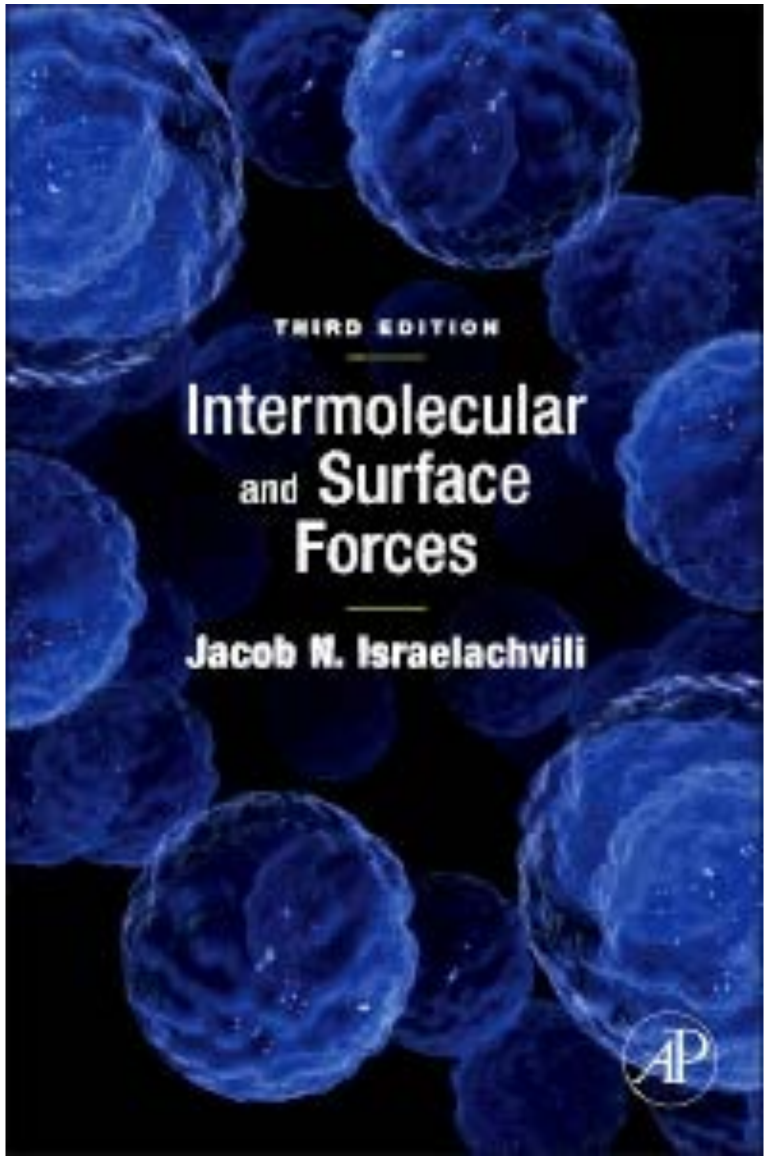
Ranking [?]



Intramolecular force	Basis of formation	Relative strength
Metallic bond	Metal cations to delocalized electrons	1, strongest
Ionic bond	Cations to anions	2
Polar covalent bond	Partially charged cation to partially charged anion	3
Nonpolar covalent bond	Nuclei to shared electrons	4, weakest

Intermolecular forces

Intermolecular forces according to Jacob Israelachvili,
commenting upon a corollary of the Hellmann-Feynman theorem…



THIRD EDITION

Intermolecular and Surface Forces

Jacob N. Israelachvili

"[…] all intermolecular forces are essentially electrostatic in origin […] once the spatial distribution of the electron clouds has been determined by solving the Schrödinger equation, the intermolecular forces may be calculated on the basis of straightforward classical electrostatic"

Intermolecular forces

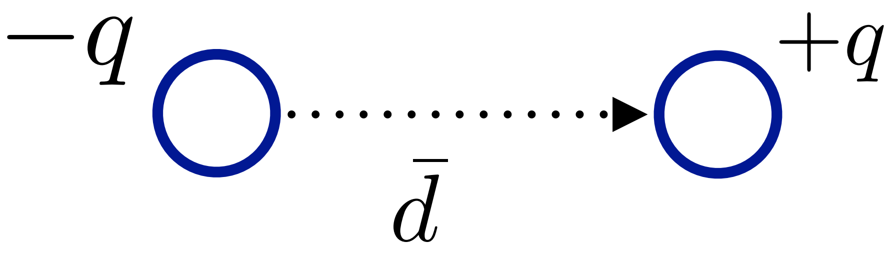
A rather subjective list:

- Van der Waals forces:
  - Keesom forces (permanent dipole-permanent dipole)
  - Debye forces (permanent dipole-induced dipole)
  - London dispersion forces (fluctuating dipole-induced dipole)
- Ion-(induced or permanent…) dipole
- Hydrogen bonding
- Halogen bonding […]

Molecular dipoles

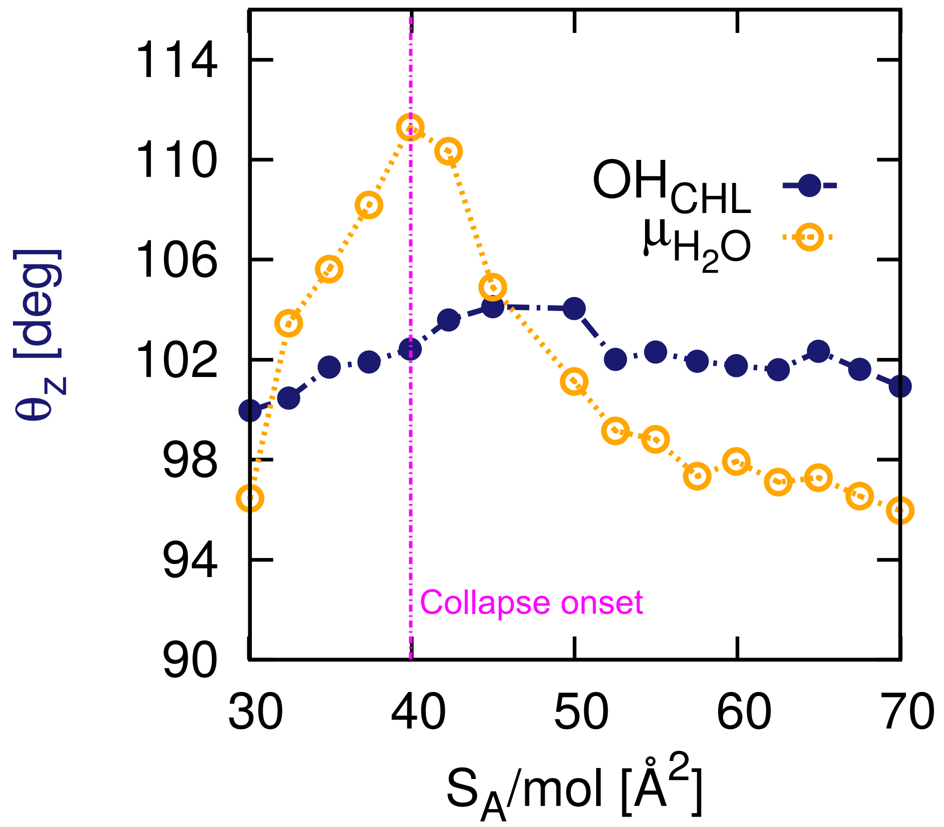
(electric) Dipole moment

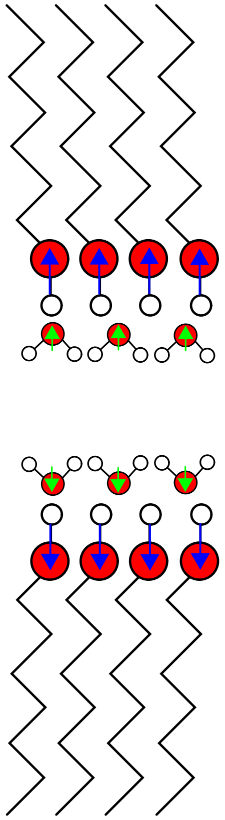
$$\bar{\mu} = q \cdot \bar{d}$$

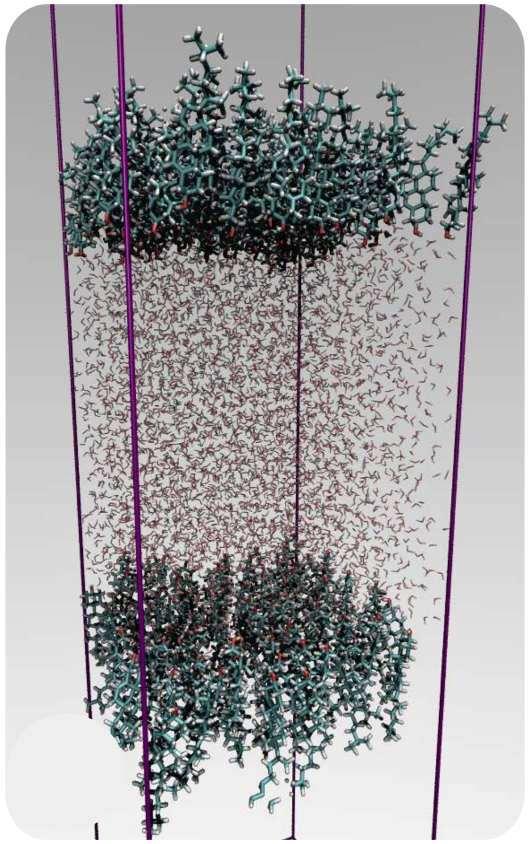


Beware the sign!

- Chemists: from + to -
- Physicists: from - to +





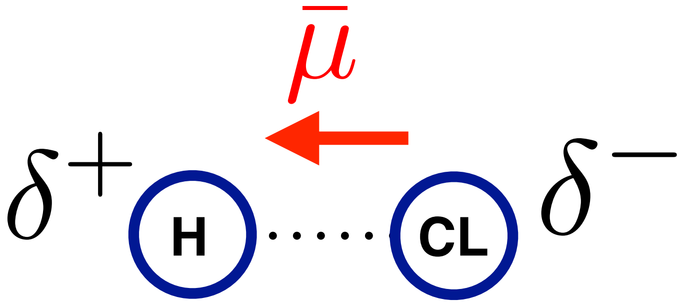


Molecular dipoles

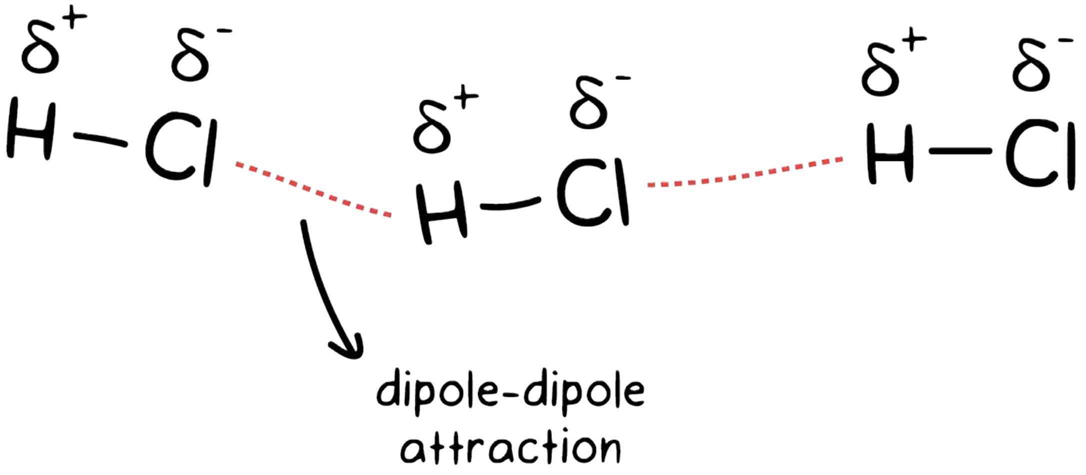
Molecular dipoles

- *Permanent* dipoles
- *Induced* dipoles
- *Fluctuating* dipoles

Permanent dipole



Keesom forces



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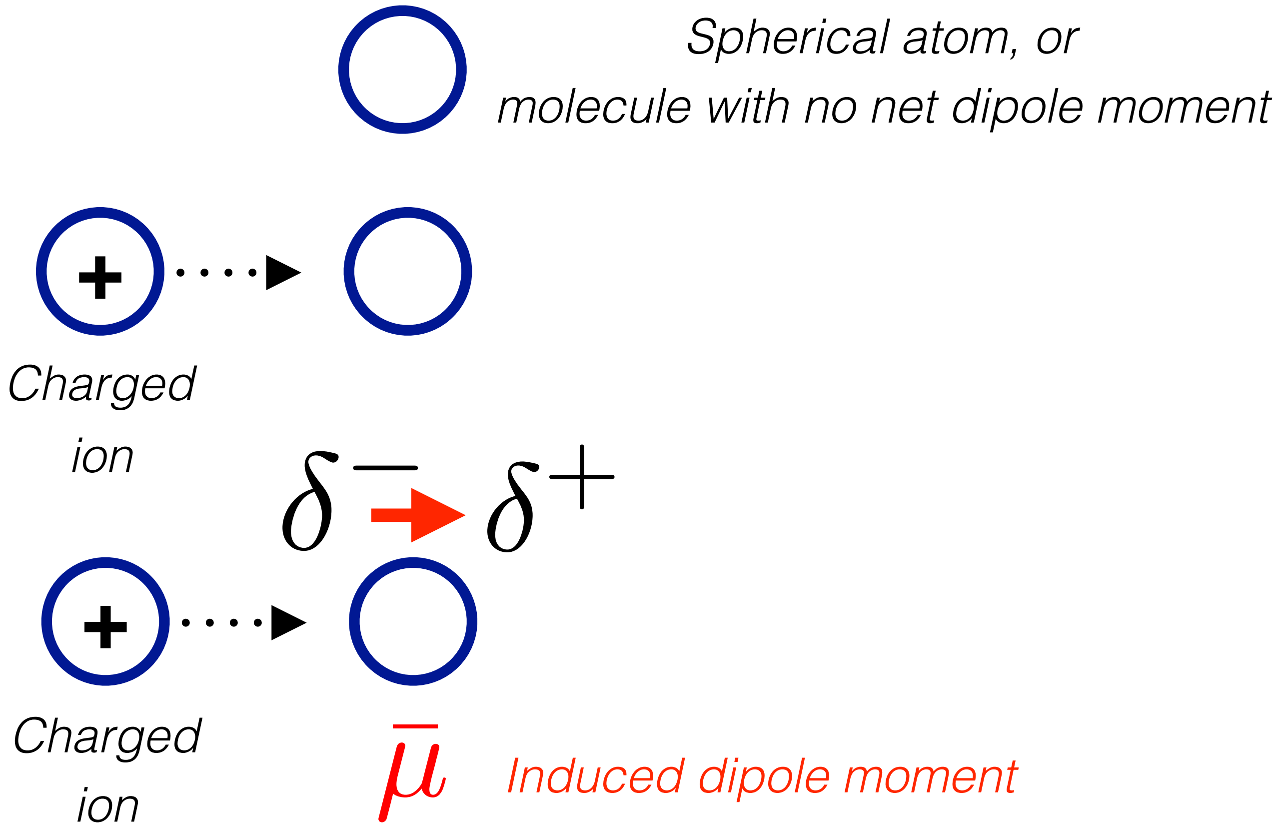
Molecular dipoles

Molecular dipoles

- *Permanent* dipoles
- *Induced* dipoles
- *Fluctuating* dipoles

Induced dipole



Spherical atom, or
molecule with no net dipole moment

Charged ion

δ^{-} δ^{+}

Charged ion

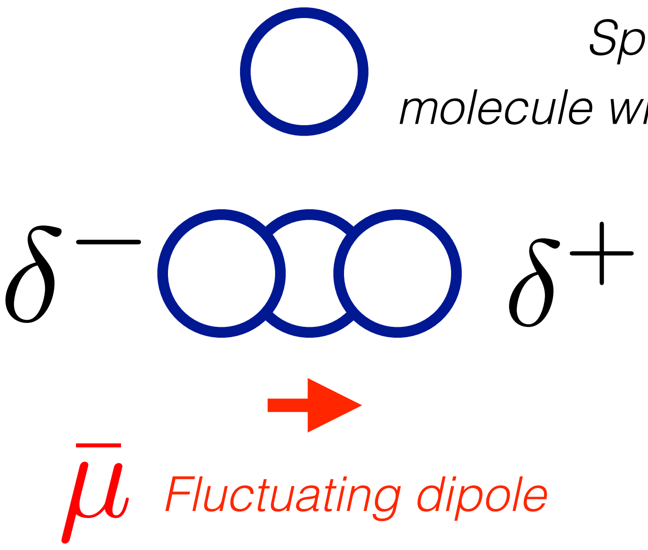
$\bar{\mu}$ *Induced dipole moment*

Molecular dipoles

Molecular dipoles

- *Permanent* dipoles
- *Induced* dipoles
- *Fluctuating* dipoles

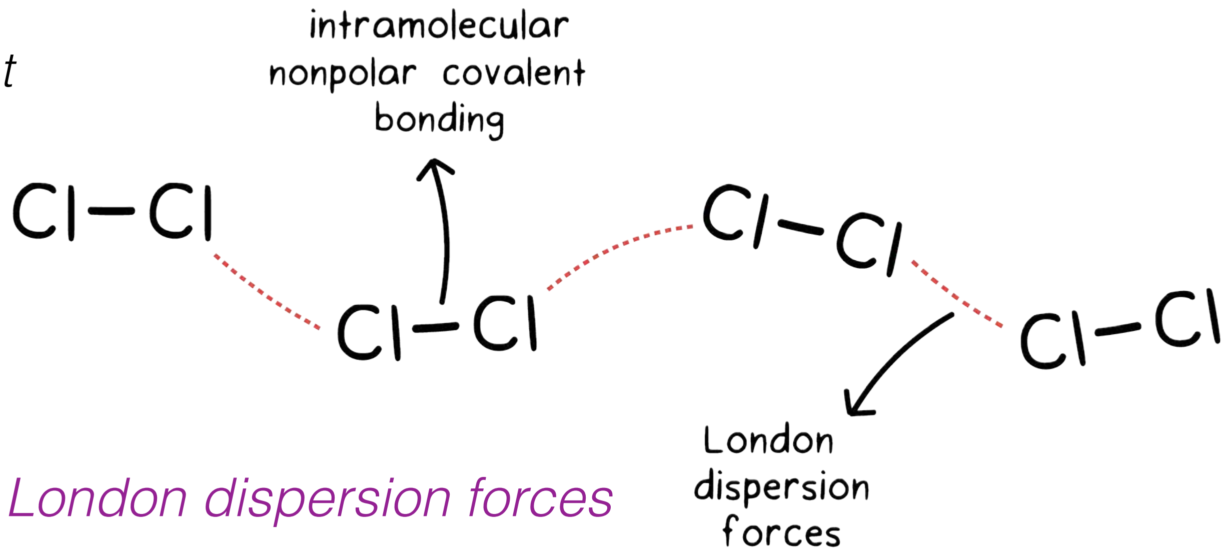
Fluctuating dipole



Spherical atom, or molecule with no net dipole moment

$\bar{\mu}$ *Fluctuating dipole*

They have a finite lifetime

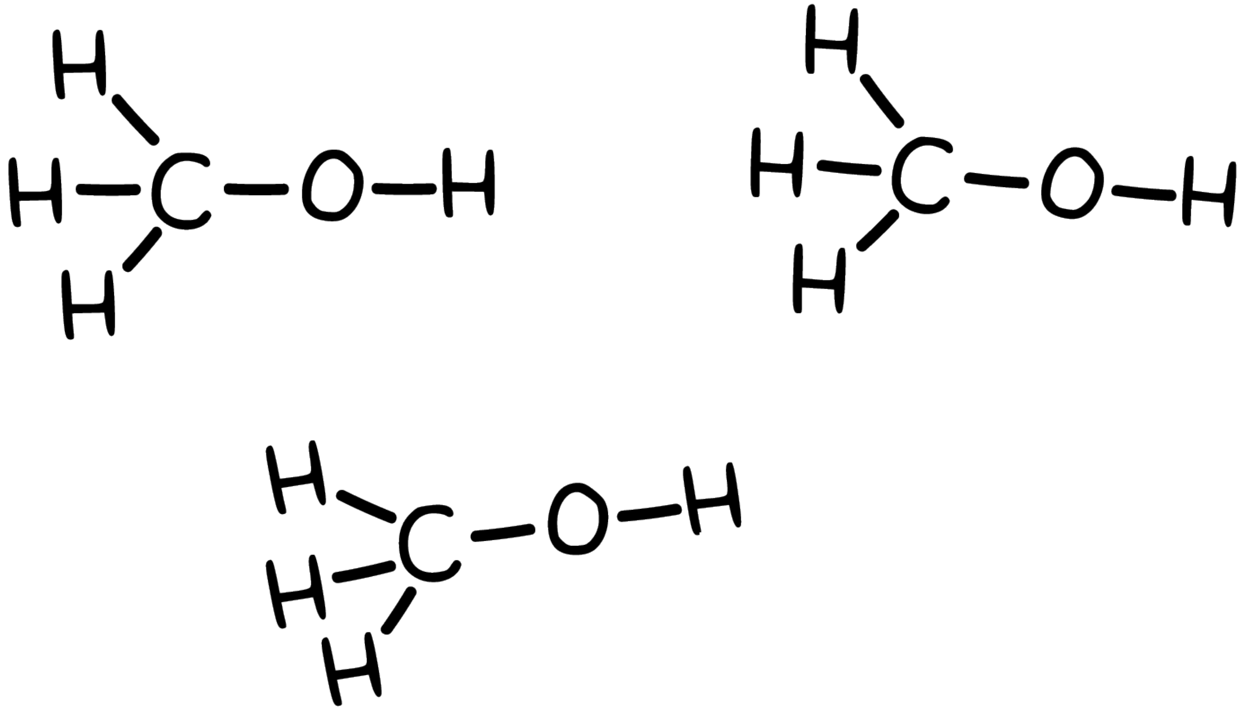


London dispersion forces

The strength of these dipoles depends upon the *polarizability* of the electrons involved
i.e. how electrons respond to an electric field

How many electrons?
How tightly are they bound to the nuclei?

The case of methanol



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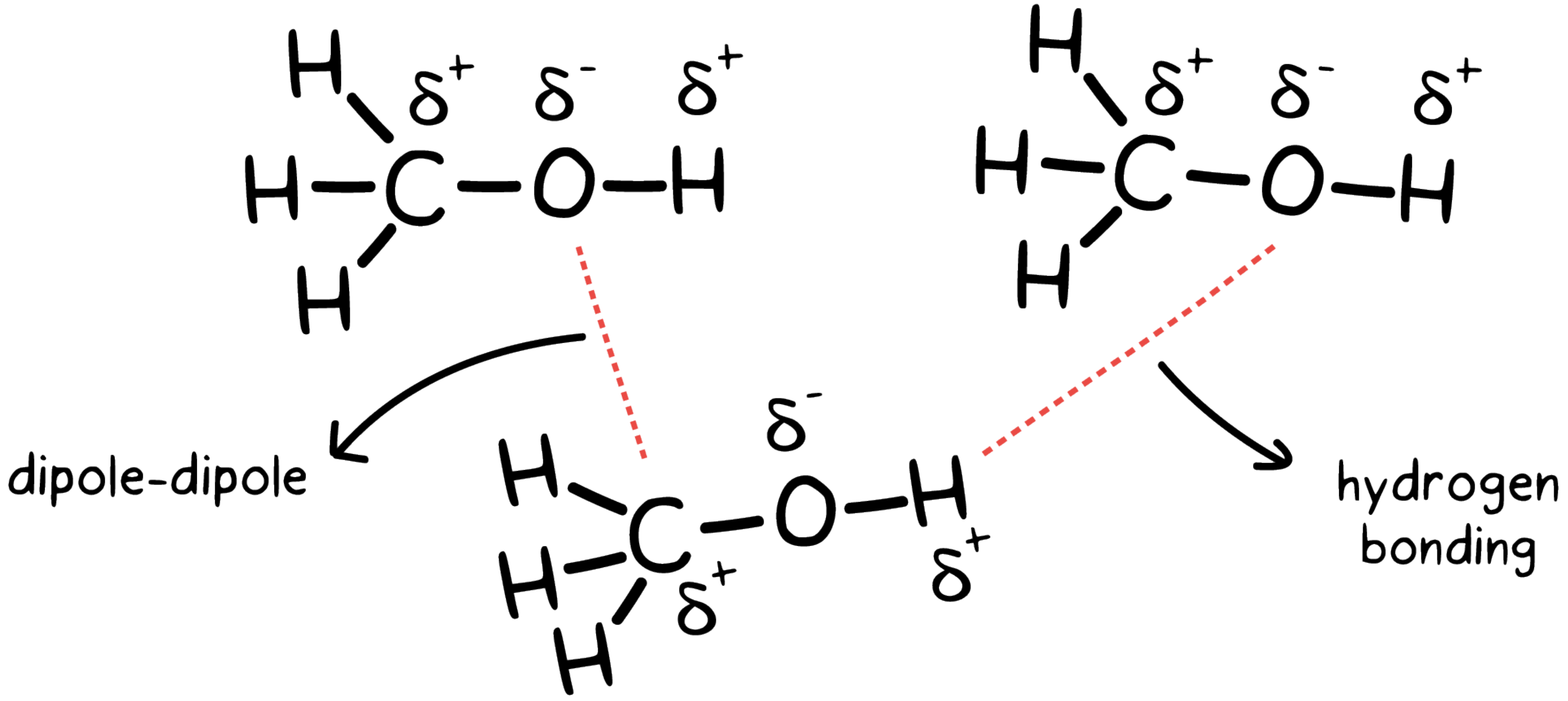
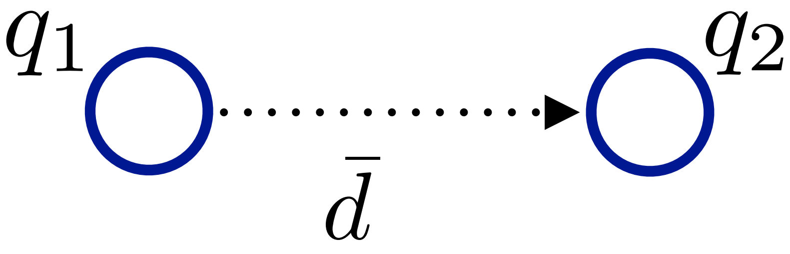
Something



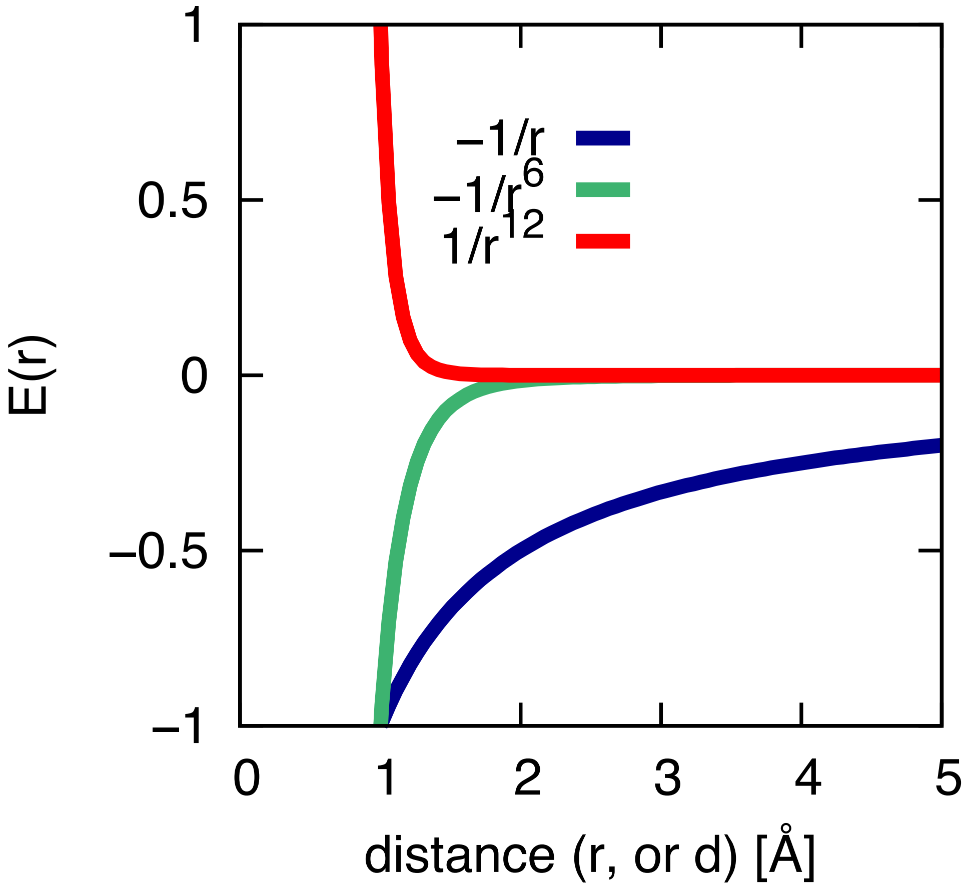
Electrostatic interactions

The electrostatic potential energy between two charges *q₁* and *q₂* is:

$$E_{\mathrm{Electrostatic}}(\bar{d}) = \pm \frac{q_1 \cdot q_2}{4\pi\epsilon_0 \bar{d}}$$



$$F_{\mathrm{Electrostatic}}(\bar{d}) = -\nabla E_{\mathrm{Electrostatic}}(\bar{d}) = \pm \frac{q_1 \cdot q_2}{4\pi\epsilon_0 \bar{d}^2}$$



Intra- & Inter- molecular forces

A long-standing challenge for molecular simulations

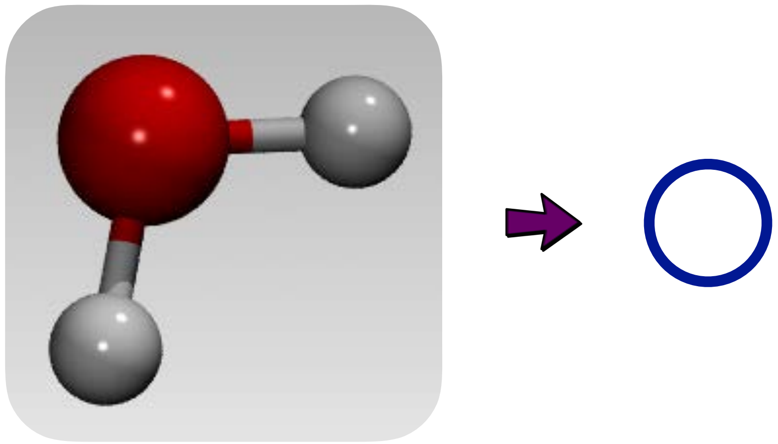
The energy (and thus the forces) of the system depends on both intra- and inter- molecular interactions

ab initio vs *classical* methods

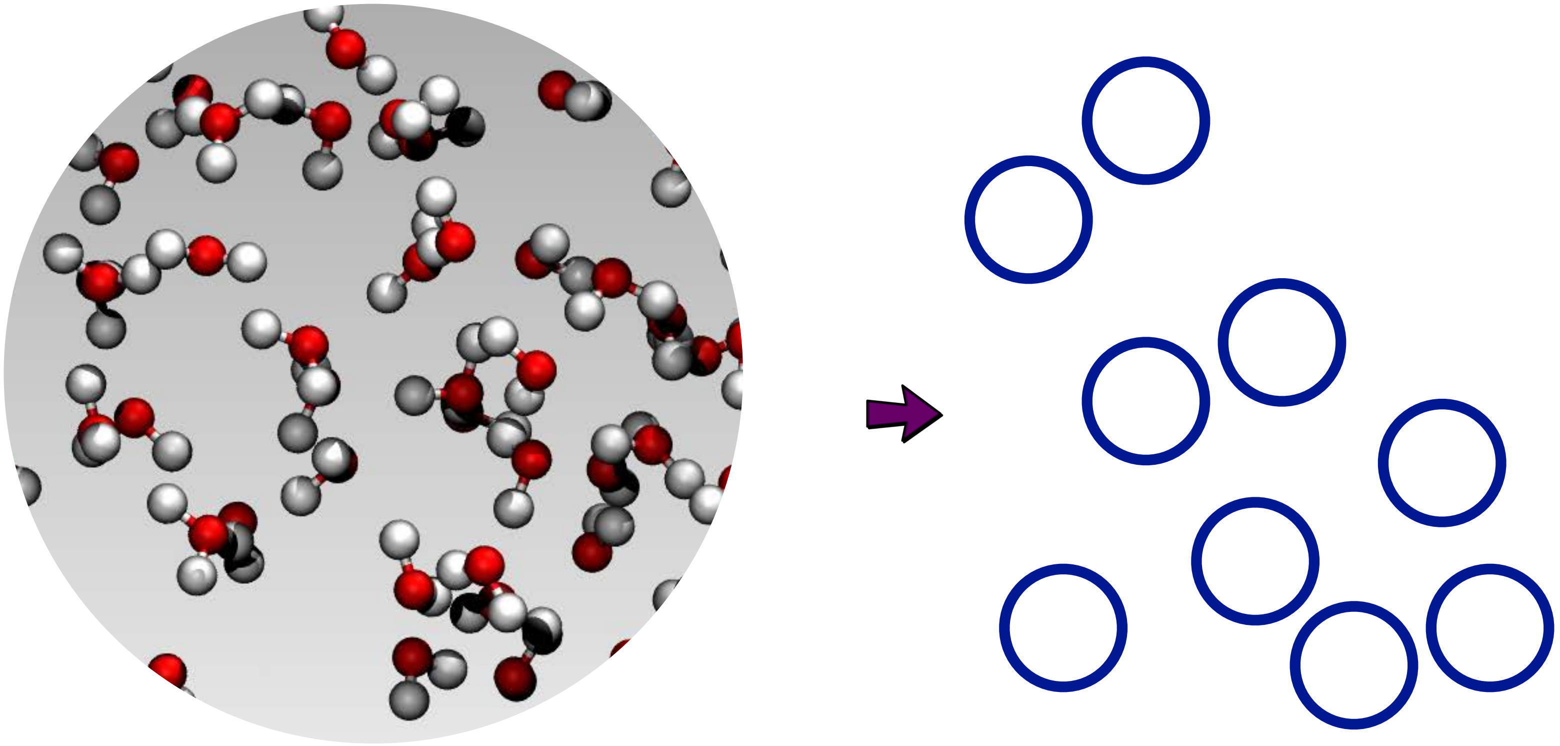
How do we represent intra- and inter- molecular interactions?

The case of water…

0. Keep it simple:

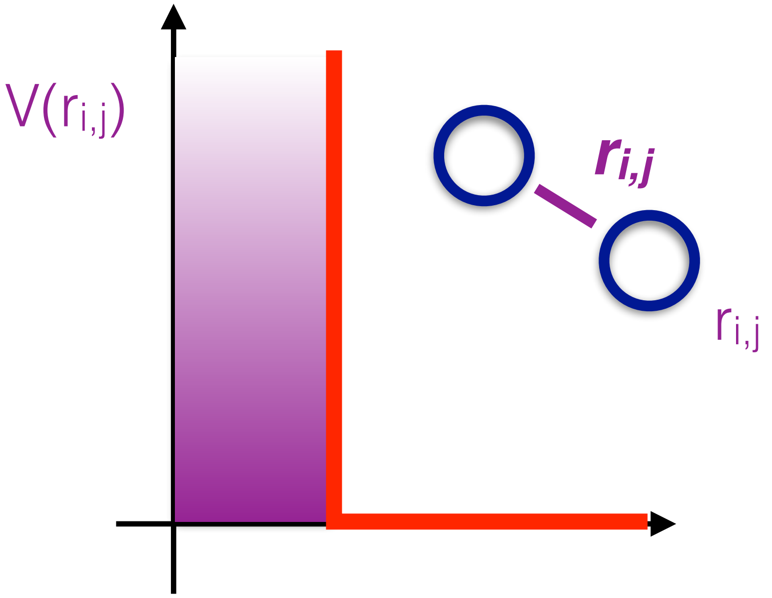


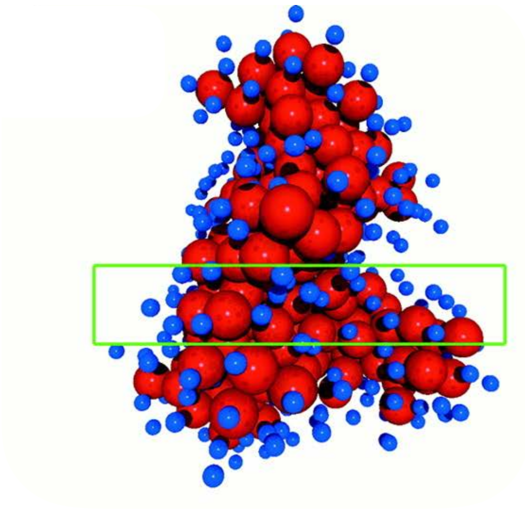
The case of water



1. Molecules cannot overlap

Hard spheres [colloidal particles]





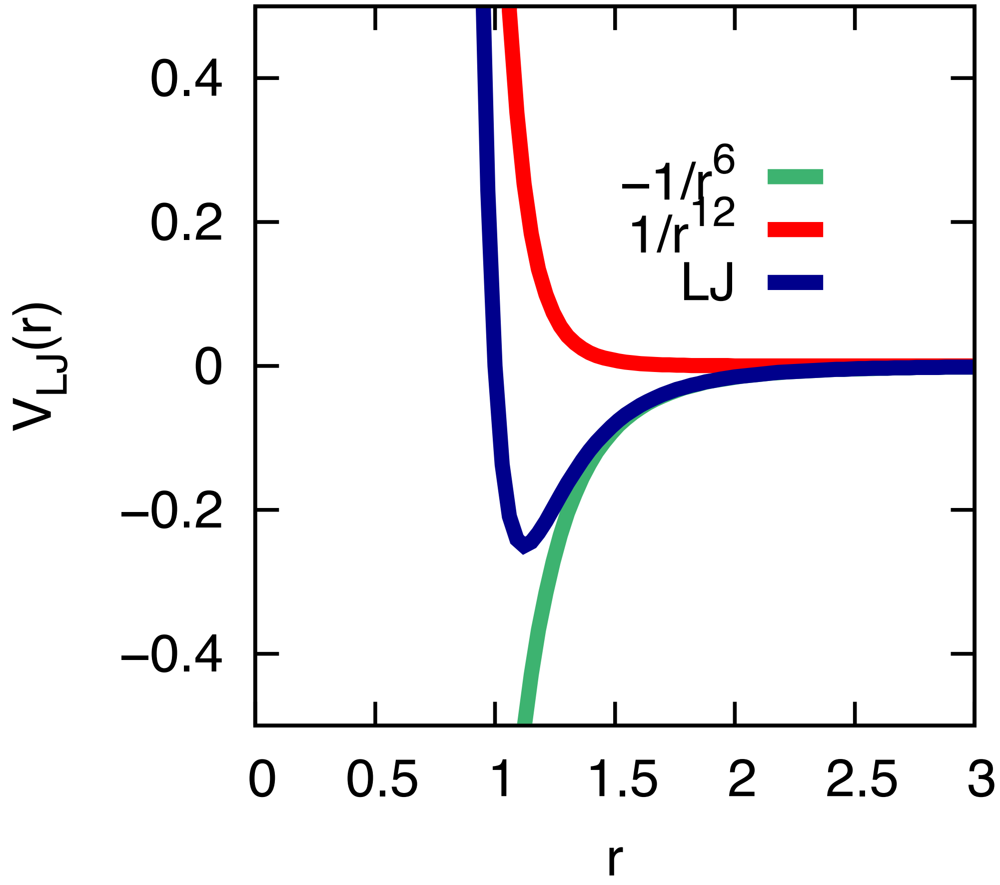
Gasser, U., et al. (2001).
Real-Space Imaging of Nucleation and Growth in Colloidal Crystallization.
Science 292, 258–262.

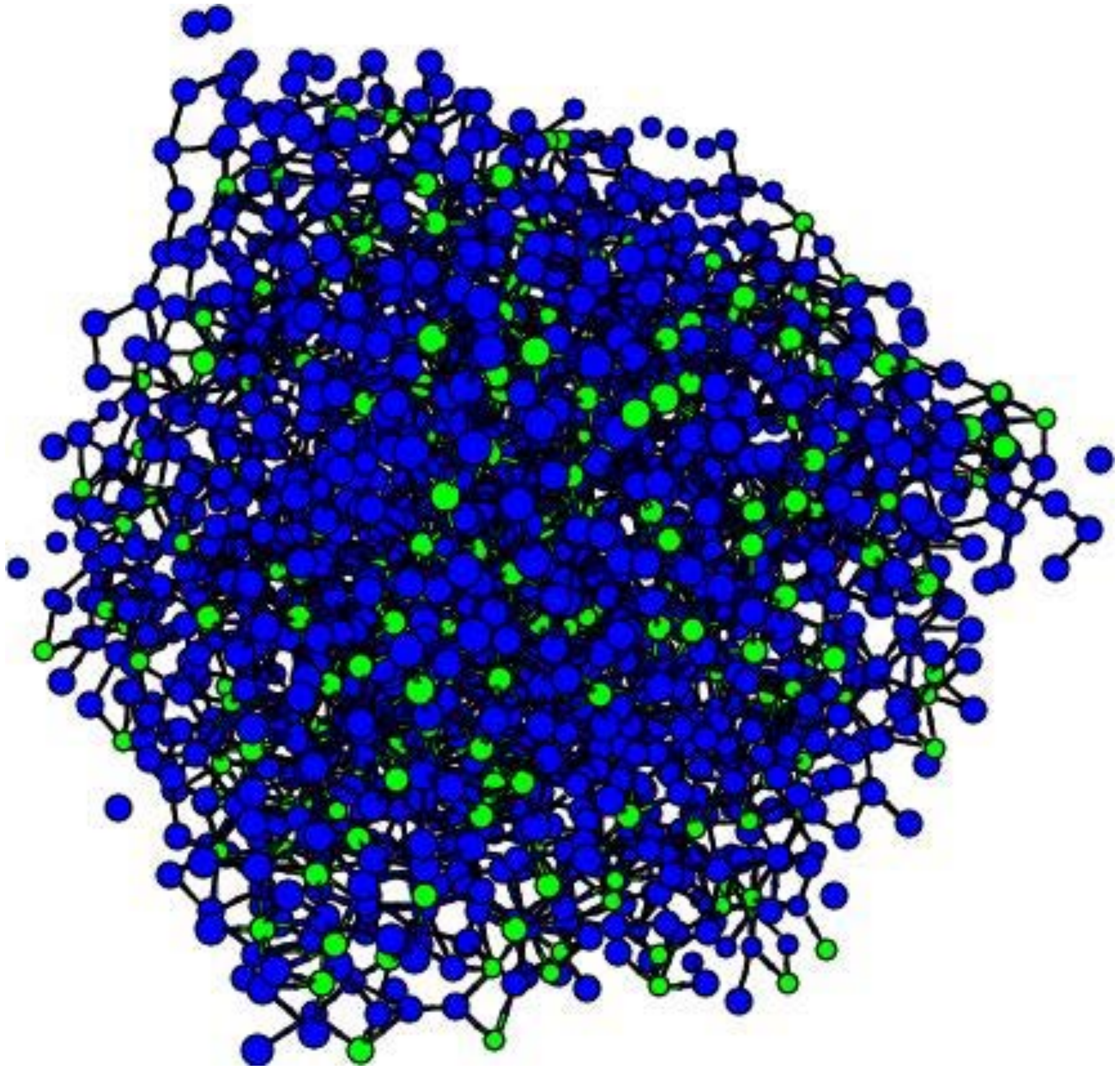
The case of water

2. Repulsive and attractive terms

Lennard-Jones potential [e.g. metallic liquids]

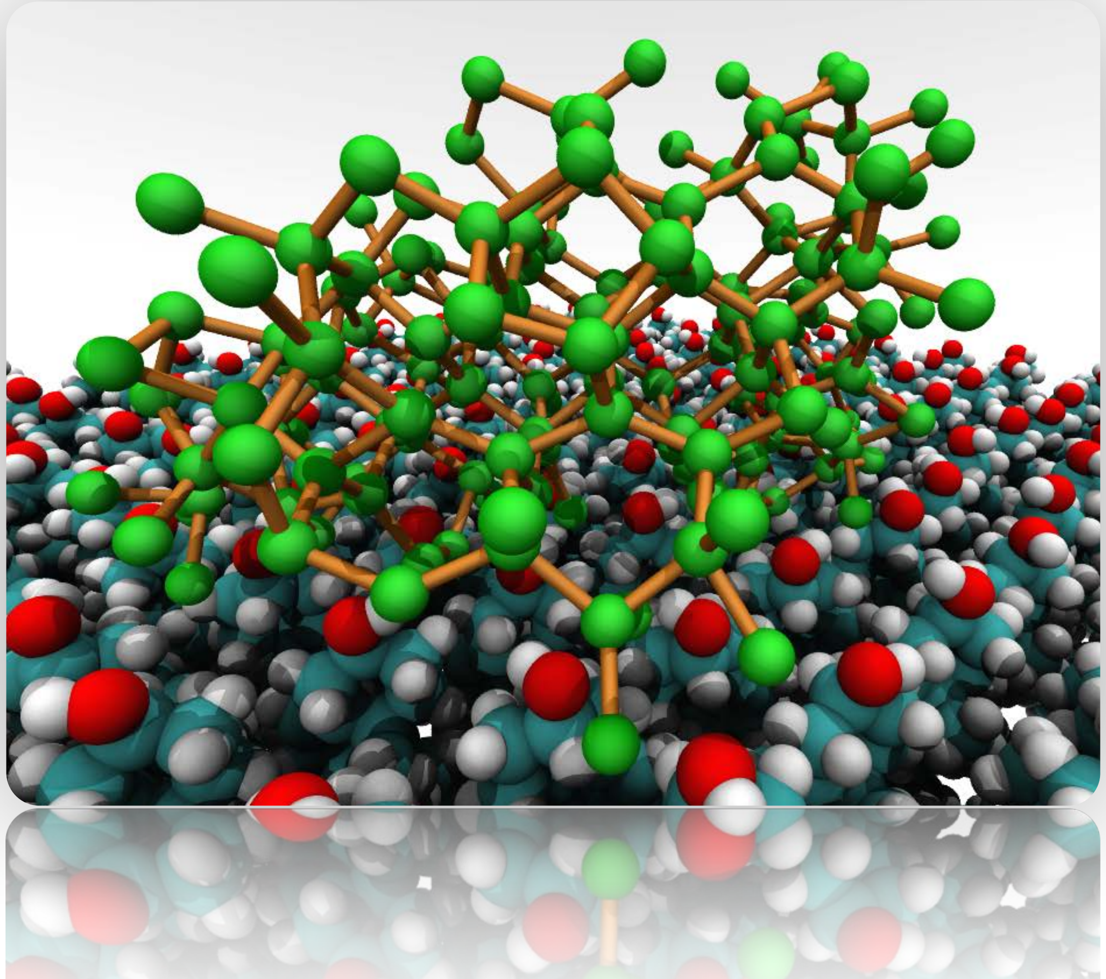
$$V_{LJ}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$





The case of water

3. Back to the water molecule - *Bond and angles*
4. What about the dipole moment? - *Point charges*
5. Liquid water - *LJ + point charges*
6. Polarisable liquid water - *LJ + point charges that can vary in time*
7. Proton transfer in water - *DFT (or machine-learning based potentials)*
8. Nuclear quantum effects in water - *Path Integral simulations*
9. Heterogeneous ice nucleation - *Different interactions for different components…*



Outro

Learning Objectives

By the end of this lectures you should…

- … be familiar with the basic concepts of quantum mechanics
- … be able to deal with a few model systems (free particle, particle in a box, hydrogen atom…)
- … be confident about the notion of chemical bonds and intermolecular interactions

⑬ ⑭ ⑮

Additional reading

CH932: Quantum Chemistry (2017/18)

View Online

Additional reading with respect to the Quantum Chemistry part of the CH932 module [Introduction to Chemistry and Biochemistry]

2 items

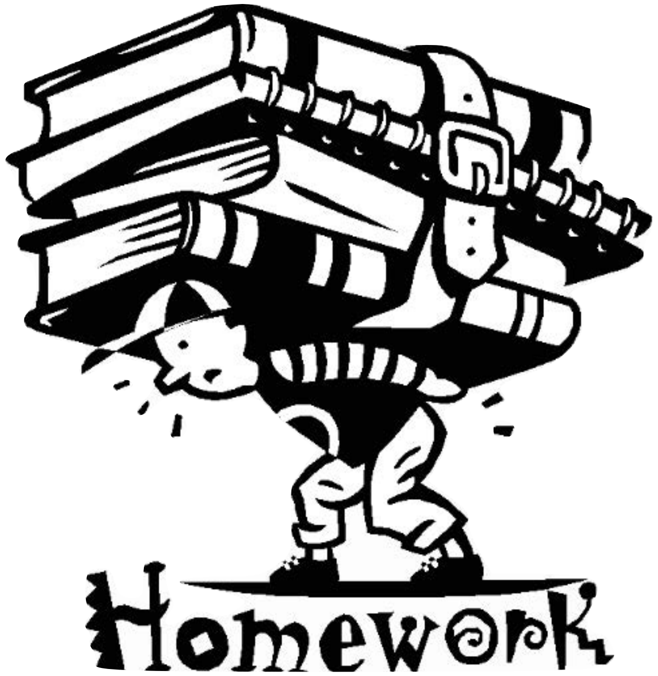
Quantum physics of atoms, molecules, solids, nuclei, and particles - Robert M. Eisberg, Robert Resnick, c1985

Book | **recommended** | This is a classic textbook, encompassing most of the basic concepts of quantum mechanics. It is amazingly clear, and avoids as much mathematics as possible in illustrating concepts and examples. It also contains a number of problems for which solutions are available (separate book). It can very well level the playfield when dealing with interdisciplinary content/research anytime quantum chemistry is involved.

Molecular Quantum Mechanics - Peter W. Atkins, Ronald S. Friedman, 2010

Book | **recommended** | This book cover an incredible collection of topics. While never entering into the very details, it offer a fairly rigorous treatment of many aspect of quantum chemistry. It also included several excellent examples plus a diverse array of problems - solutions to which can be easily found.

The workshop



Pen, paper & calculator
14:00, MOAC seminar room

Lunch