Session 1: Scene Setting

CH2203 Physical Chemistry

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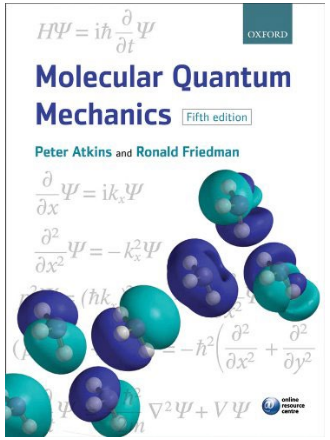
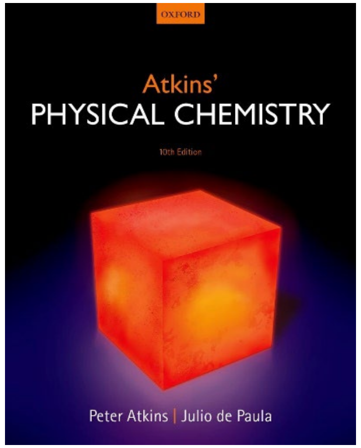
Course Plan

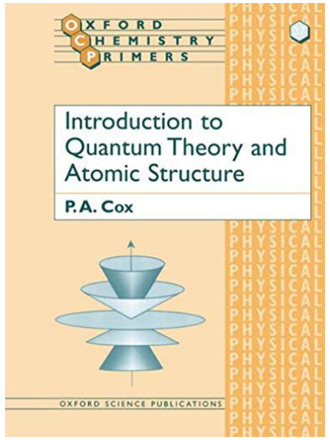
- To understand **atomic and molecular structure**.
- To understand **valence – the theory of chemical bonding.**
- To see where **everything you've learnt already** originates from.

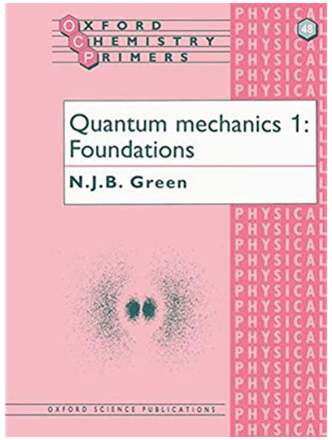
Course Plan

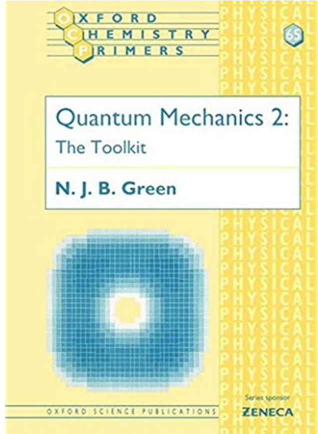
- Begin at the beginning: **fundamental quantum mechanics.**
- Moving into understanding **atomic structure.**
- Finally into understanding **chemical bonding.**











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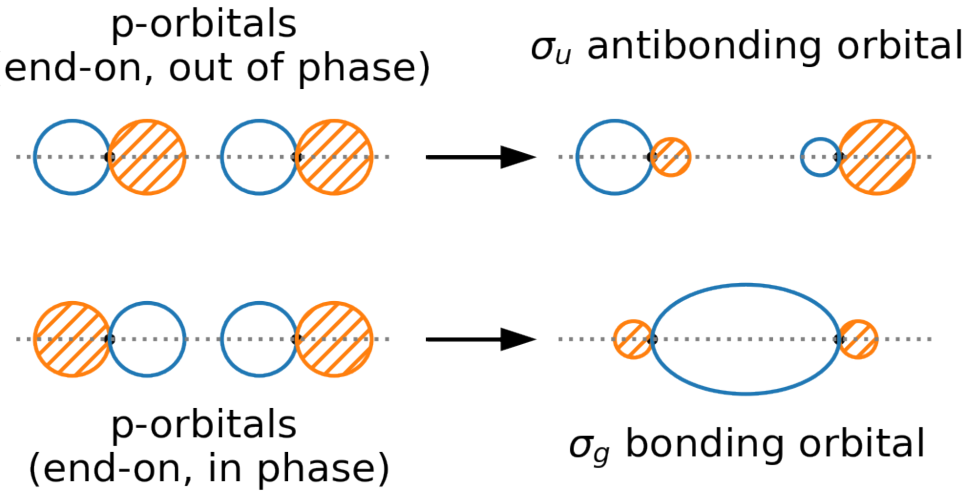
Questions we will answer



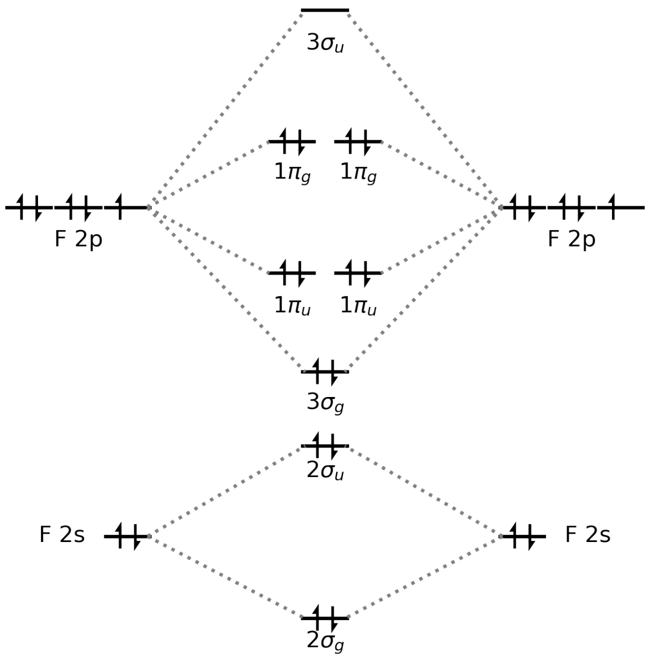
p-orbitals (end-on, out of phase)

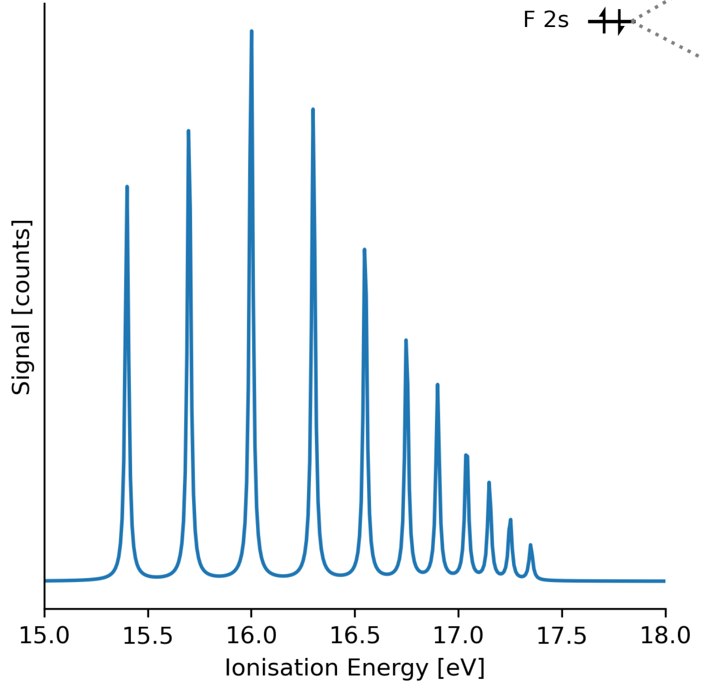
σ_u antibonding orbital

p-orbitals (end-on, in phase)

σ_g bonding orbital

...but rigorously, with fundamental **maths** and **physics.**





By the end of the course...

- You’ll understand how all the beautiful complexity of chemistry ultimately stems from some (relatively) simple quantum mechanics.

- You’ll see the ”other side” of physical chemistry....
  - Solutions/colloids is the **macroscopic** side.
  - Quantum/spectroscopy is the **microscopic** side.

- Hopefully, we will just put what you already know on a firmer footing.
  - We will mostly be drawing things together. It’ll be fun.

What we need to know...

- Most importantly: **maths from CH1204**, **especially calculus**.
  - There was a reason we learnt all of this!
  - Quantum mechanics is often unintuitive – we need mathematics to guide us.

- Also some of the basic QM learnt in CH1200 and CH2200.

- We can organise a session revising differentiation and integration if there's popular demand ☺

Today

- To understand why we need **quantum mechanics.**

- To recap some basics from previous modules.

- To set the scene for the rest of this module.

Motivation

”If we were to name the most powerful assumption of all, which leads one on and on in an attempt to understand life, ***it is that all things are made of atoms,*** *and that* ***everything that living things do can be understood in terms of the jigglings and wigglings of atoms****.”*

- Richard P. Feynman

Motivation (chemistry)

- Chemistry is all about **molecules** doing stuff.
  - Reacting, moving, having certain structures.

- **Molecules** are made of **atoms.**
  - The rich variety of chemistry comes from different atoms being different.

- Different atoms are different because of **electrons**.
  - So we're going to **start with electrons.**

The electron

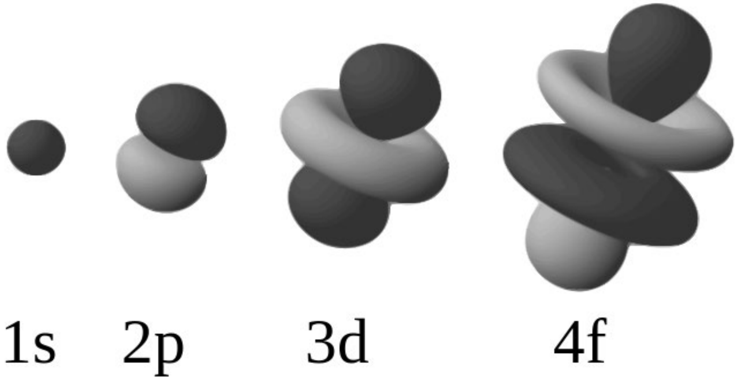
- Subatomic particle:
  - Mass = 9.1×10^{-31} kg (~1/2000 of the proton mass).
  - Charge = -1e (1e = 1.6×10^{-19}C)
  - **Fermion** – has half integer spin, s = ½.

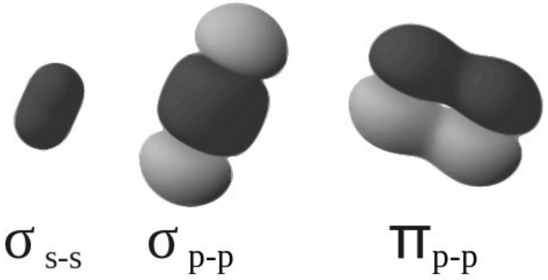
- A neutral atom contains equal numbers of **protons** and **electrons**.
  - Remember Year 8 science?

- Electrons can exhibit wave-like behaviour: **wavefunctions.**

Wavefunctions

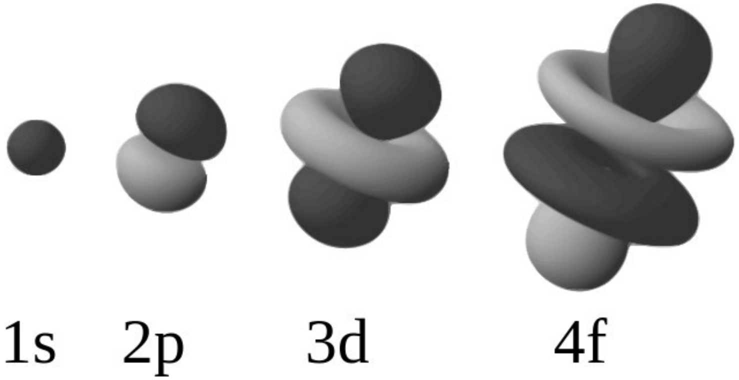
- Recall the de Broglie wavelength.
  - Relating particle and wave pictures.
- **Wavefunctions** describe particles.
  - A more general de Broglie wavelength.
  - Generally given symbol Ψ (Psi).
- Contains all **dynamical** info about system.
  - Where it is/how it’s moving.
  - A particle is **completely described** by its wavefunction.

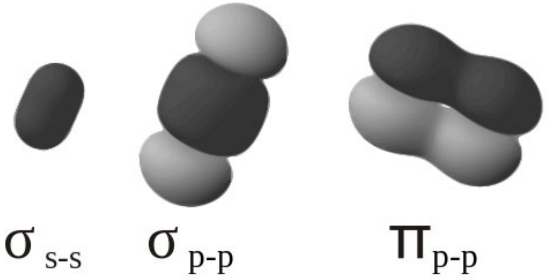




Wavefunctions

- Finding a wavefunction for a system means that we know **everything we can know** about it.
  - It’s energy, for instance.
- This is powerful for us as chemists:
  - We want to know about the energies of different molecules – ultimately this dictates everything: structure, reactivity, spectra...
- To find a wavefunction, we need to solve the **Schrödinger Equation.**





The Equation….

Wavefunction (of atom/molecule)

We will understand this soon! Basics first… What *is* quantum mechanics? What even *is* mechanics?!

Hamiltonian Operator (”*Hamiltonian*”)

Total Energy (of atom/molecule)

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Classical Mechanics

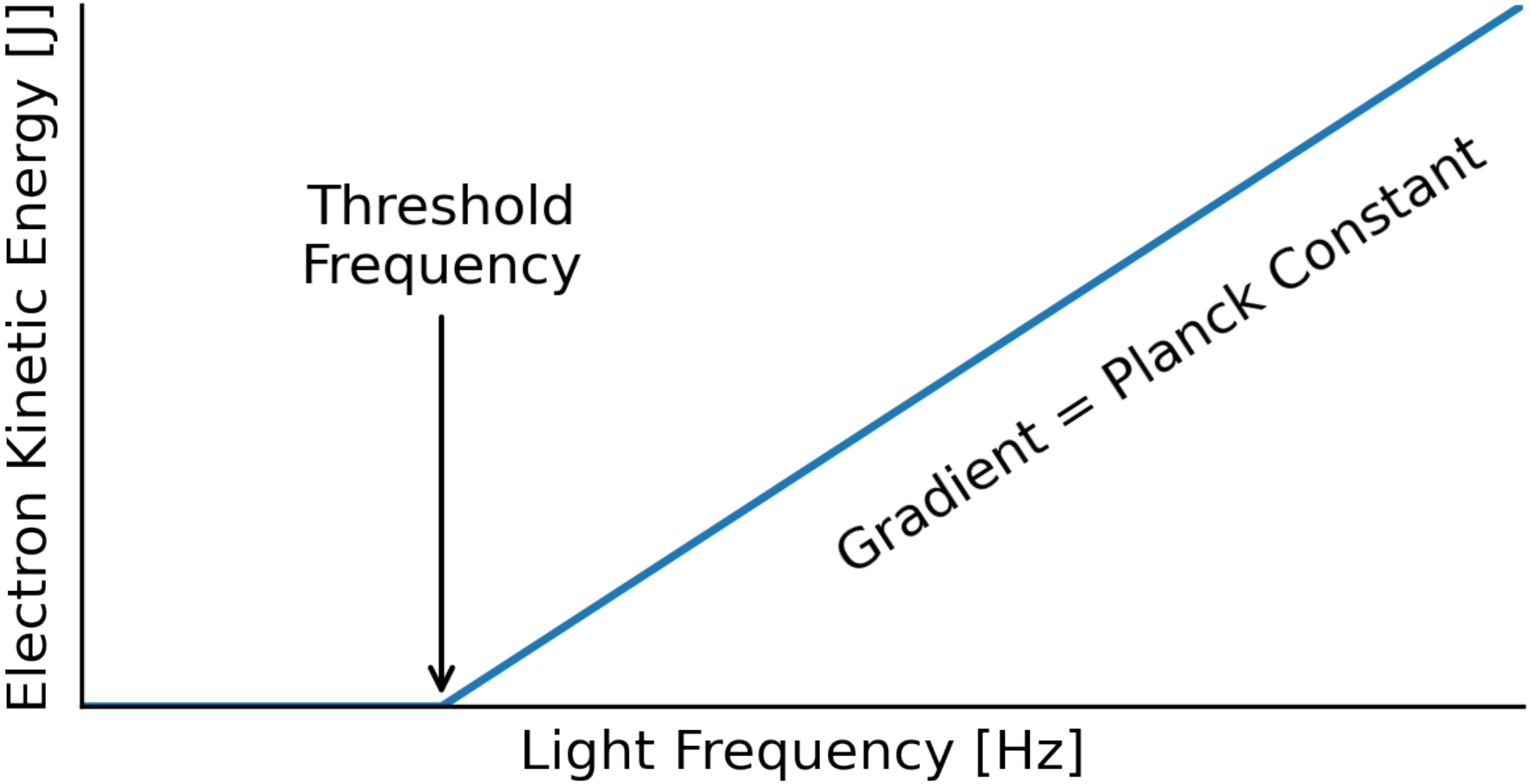
- **Mechanics** is the science that deals with motion of objects.

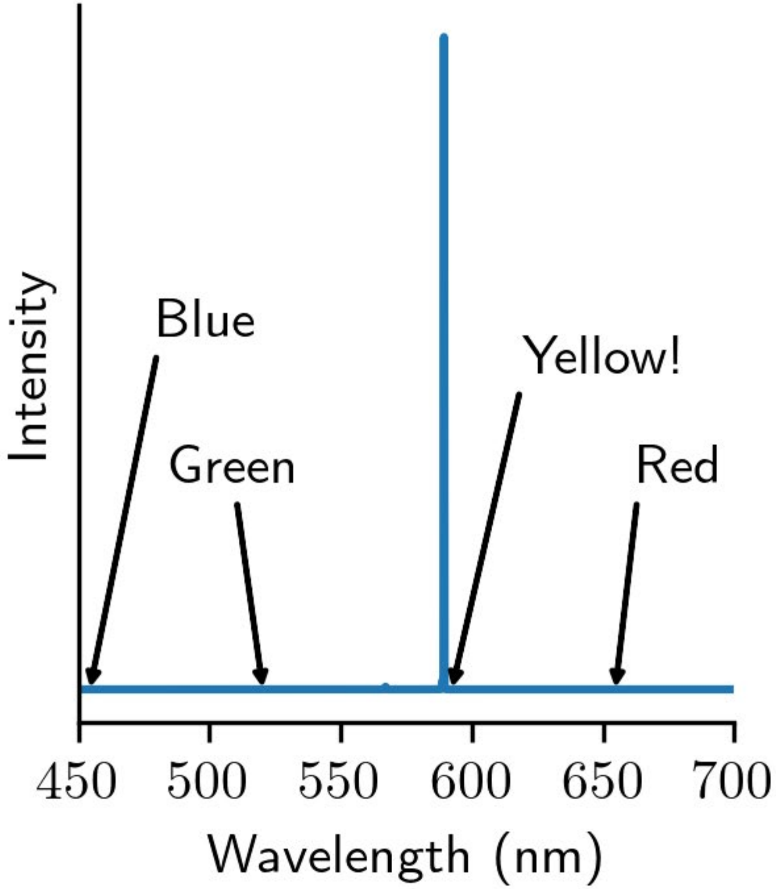
- **Classical mechanics** is already familiar:
  - Newton’s laws, F = ma, p = mv, etc… from CH1200, high school.

- Classical mechanics is great at describing **macroscopic things**.
  - Things we can see – cars, planets, bacteria….

New Experiments...

- Early 20th century – advances in experimental apparatus.
- Scientists were measuring lots of new things.
- Discoveries that couldn’t be explained classically.
  - Photoelectric effect – CH1200
  - Spectra of atoms and molecules- CH2200


Electron Kinetic Energy [J]
Threshold Frequency
Gradient = Planck Constant
Light Frequency [Hz]


Intensity
Blue
Green
Yellow!
Red
450
500
550
600
650
700
Wavelength (nm)

Quantum Mechanics

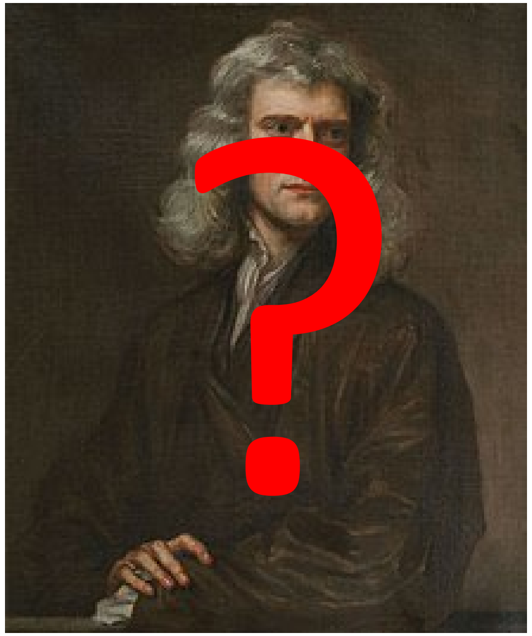
- A new theory was needed to explain things like:
  - Energy quantisation.
  - Wave-particle duality.

- Enter **quantum mechanics.**

- This theory was developed from the 1900s onwards.
  - Max **Planck**, Werner **Heisenberg**, Niels **Bohr**, Erwin **Schrödinger**, Wolfgang **Pauli**, Paul **Dirac**, Max **Born**, Albert **Einstein**, Louis **de Broglie**, Marie **Curie**, Paul **Ehrenfest**, Friedrich **Hund**...

Was Newton Wrong?

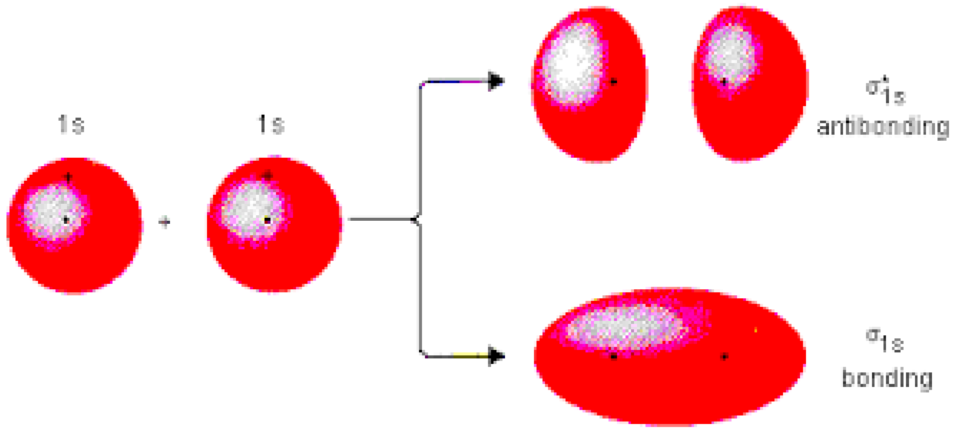
- No! Classical mechanics was never meant to describe atoms and molecules.
- New observations lead to new theories.
  - *The Scientific Method*
- Newton’s laws are still great, provided things aren’t too small or too fast.



Quantum Mechanics

- As chemists, *quantum mechanics* is the most important theory.

- This theory allows us to explain the existence of atoms, and molecules, and their interactions. In short: **chemistry**.



Quantum Mechanics

- Revolves around the **Schrödinger Equation**

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

- Easy to write down. **Almost impossible to solve.**

- We're going to break it into parts over the next few lectures.

Take Home Messages

- New experiments around 100 years ago forced scientists to develop new theories to explain what they saw.
- **Energy quantisation** and **wave-particle duality** are key concepts.
- Central to it all is the **Schrödinger Equation.**

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

Next time: Unpacking the Schrödinger Equation

Session 2: Operators and Wavefunctions

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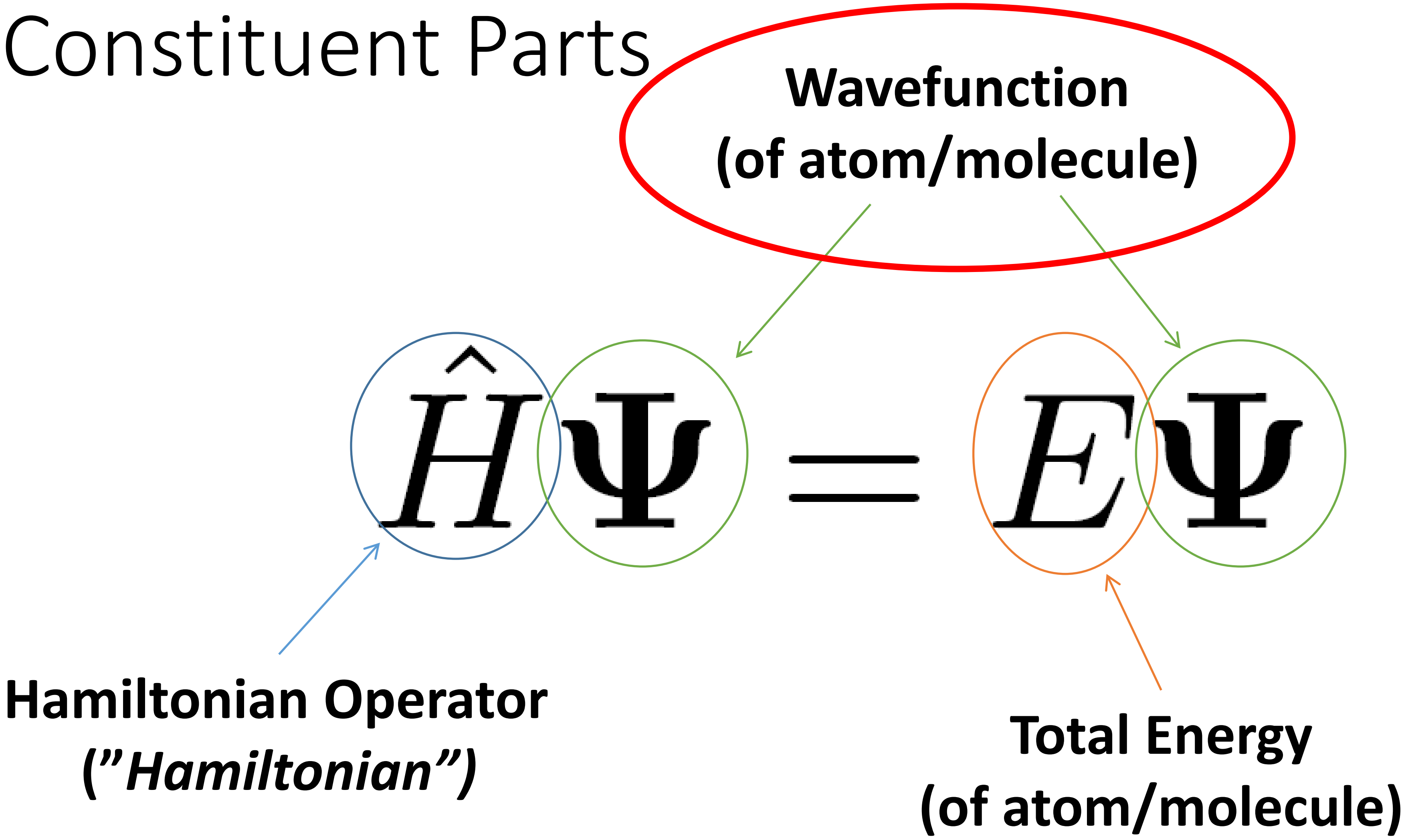
Today

- To understand *wavefunctions* in more detail.
- To understand how to think about wavefunctions.
- To start thinking about *operators*.

Constituent Parts



Wavefunction
(of atom/molecule)

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

Hamiltonian Operator
(*"Hamiltonian"*)

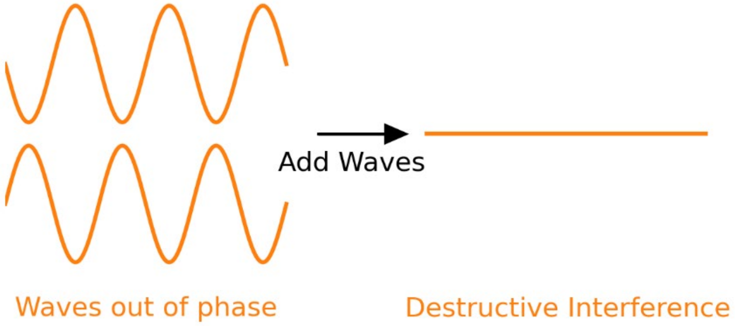
Total Energy
(of atom/molecule)

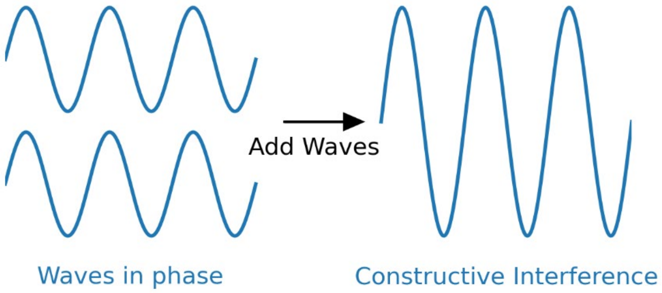
Wavefunctions

- The name hints at the meaning:
  - **Wave** = wave-y
  - **Function** = maths-y

- A mathematical **function** that can explain the **wave-like** behaviour of particles.

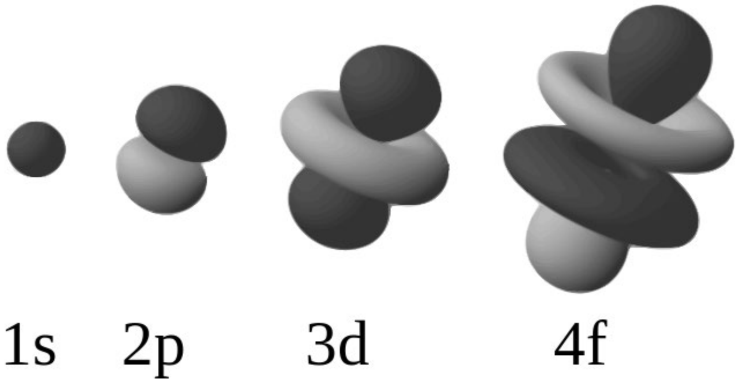
- Like **interference**, most crucially.

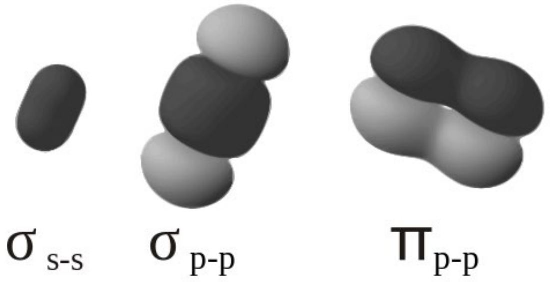




Wavefunctions

- A familiar set of wavefunctions are the **atomic orbitals** (depicted here).
- These are the **wavefunctions** of an **electron** in an **atom**.
- A wavefunction contains **all dynamical information** about a system.





Describing Wavefunctions

- Described using **quantum numbers** – for atoms (CH1200):
  - $n = 1, 2, 3 \ldots$ - the **principal quantum number**.
  - $l = 0, 1, 2 \ldots n$ – the **orbital angular momentum** quantum number.
  - $m_l = -l, -l+1, \ldots l-1, l$ – the **magnetic** quantum number.
  - $m_s = -\frac{1}{2}, \frac{1}{2}$ - the **spin** quantum number (strictly the **projection**... later).

- These numbers only apply for **single electrons in atoms**.
  - But we make approximations that mean it's OK to talk about them like this in molecules – we'll get into it later.
  - Different systems have different numbers.

Describing Wavefunctions

- The key is that **any wavefunction** is described using one or more quantum numbers.

- These numbers define a **set of functions** that will solve our SE.

- Recall from CH2200:
  - $\boldsymbol{E_{rot} = BJ(J+1)}$
    - The J quantum number describes the wavefunction of a rotating molecule.
  - $\boldsymbol{E_{vib} = \left(\mathrm{v} + \frac{1}{2}\right) h\nu}$
    - The v quantum number describes the wavefunction of a vibrating molecule.

- Wavefunctions don’t only describe electrons!

Thinking about Wavefunctions

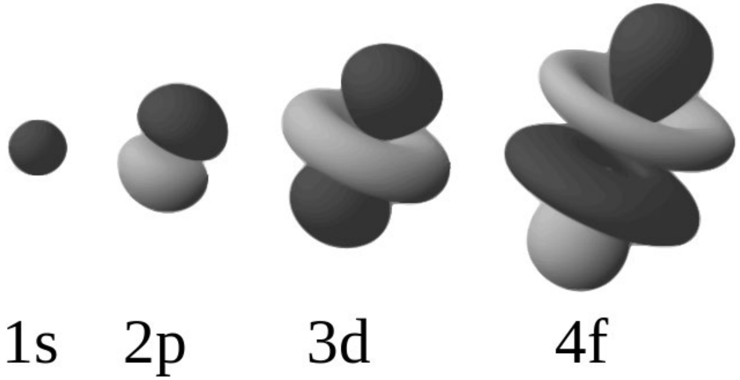
- Wavefunctions describe **anything** at the atomic scale.

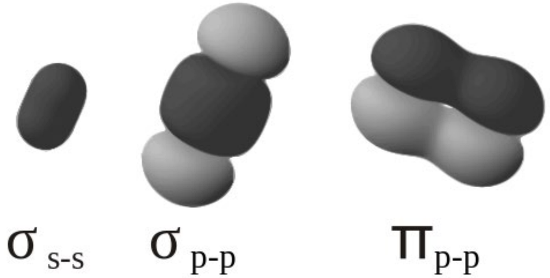
- Not just electrons – whole molecules:
  - Rotational and vibrational wavefunctions lead to the energy expressions from CH2200.

- Any system can be described with a wavefunction.
  - But for chemical bonding we mostly care about the wavefunctions of electrons in atoms and molecules.

Thinking about Wavefunctions

- How should you visualise a wavefunction?
- We do this with atomic orbitals – what does the orbital shape mean?
- Links the wavefunction to the **chance of finding an electron**.
    - i.e. probability
- The **Born Interpretation** (from CH1200).





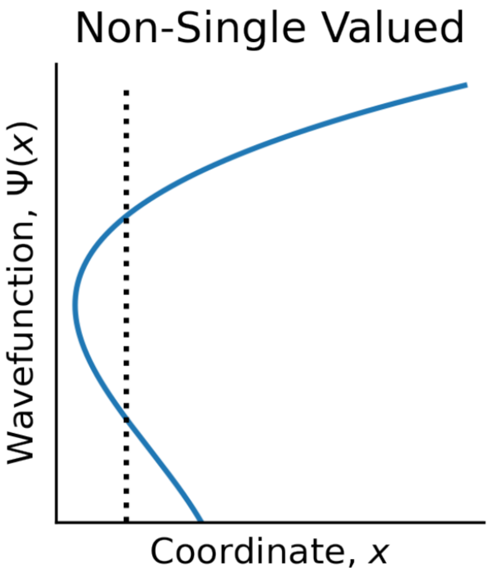
The Born Interpretation (recap)

- Wavefunctions are probability distributions.
  - Probability of finding particle at a location is proportional to the square of the wavefunction at that location.

$$P(x) \propto \mathbf{\Psi}^2(x)$$

- This means:
  - The wavefunction cannot be infinite **anywhere**.
  - The wavefunction cannot be zero **everywhere.**
  - The wavefunction must be **single-valued.**
  - The particle has to be found **somewhere**.

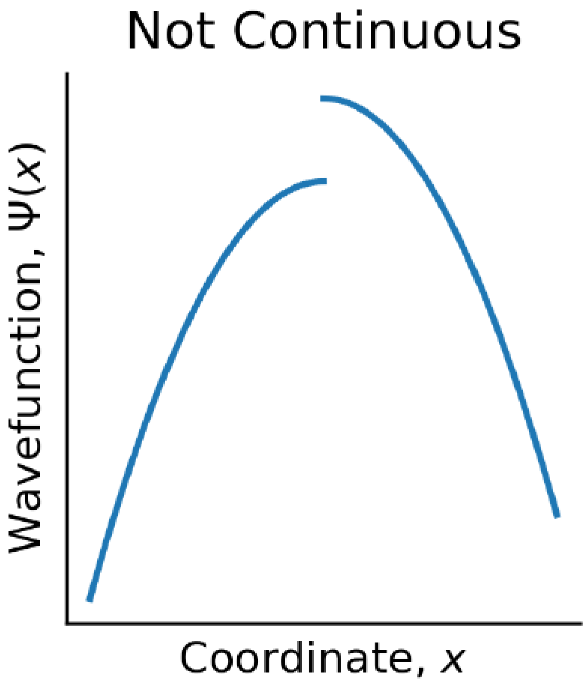
$$P(\text{all space}) = \int_{\text{all space}} \mathbf{\Psi}^2(x)\mathrm{d}x = 1$$



Wavefunction Constraints

- We have all the constraints from the previous slide, and two others:
  - The wavefunction must be **continuous.**
  - The wavefunction must **solve the SE!**

- Satisfying all of these constraints at once is almost impossible.
  - Only a few wavefunctions work.
  - Which is why we have **quantisation.**



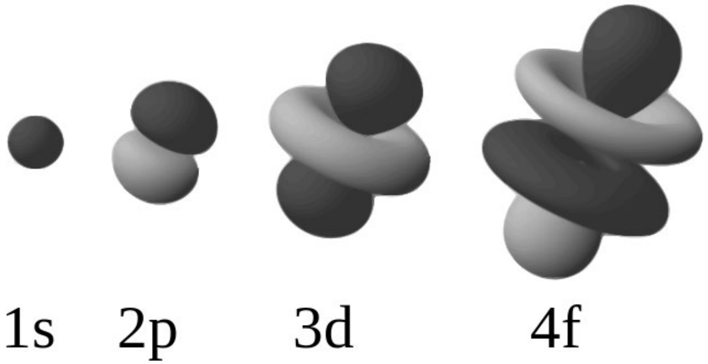
Quantisation

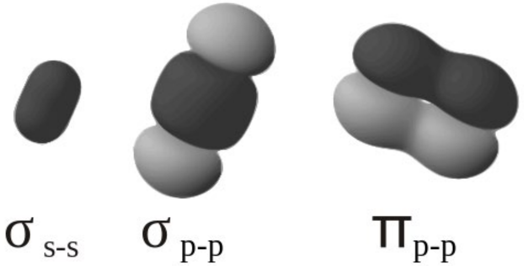
$$\hat{H}\Psi = E\Psi$$

- Only specific wavefunctions solve the SE.

- So only specific energies of the system are allowed.

- The quantum numbers tell you the allowed wavefunctions, and hence the allowed energies.

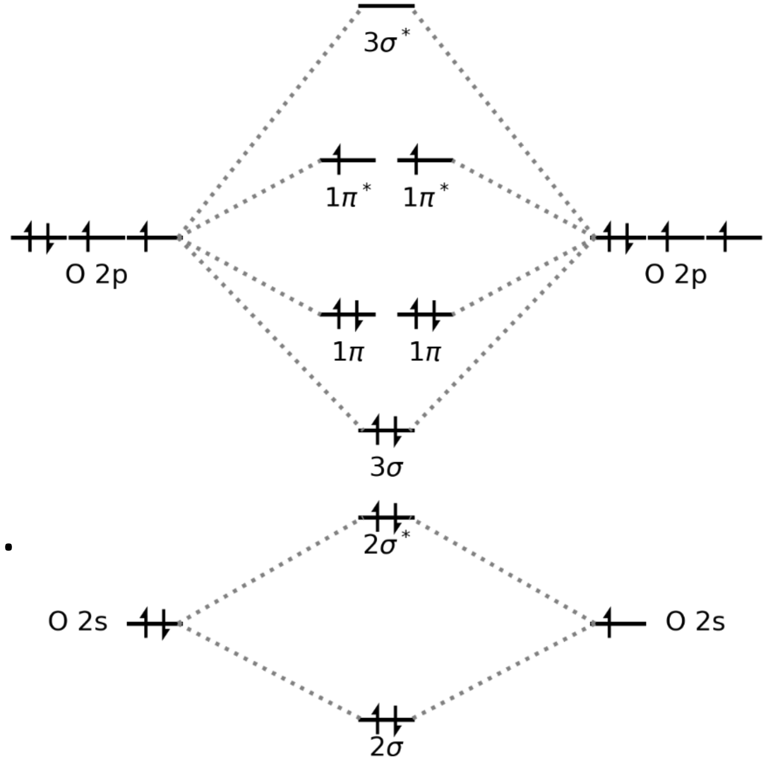




Energies

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

- **E** represents the **total energy** of the system described by the wavefunction.
- Examples:
  - Orbital energy – energy of a 1s wavefunction.
  - HOMO energy – energy of the HOMO (wavefunction).
- How do we actually get this **out** of the wavefunction?
  - Use the **Hamiltonian**...



Hamiltonians (1)

- The Hamiltonian ($\widehat{H}$) is an **operator.**
- **Operating** on the wavefunction with the Hamiltonian makes it spit out the energy.
- **What's an operator??**

$$\hat{H}\mathbf{\Psi} = E\mathbf{\Psi}$$

Interlude: Operator Algebra (1)

- An operator is a **mathematical instruction set.**
- For example, the operator $\hat{A} = \dfrac{d}{dx}$.
    - Operating with $\hat{A}$ on something is equivalent to ”take the derivative of that something wrt x”.
- For example, if we have a wavefunction $\psi = e^{ax}$:
    - $\hat{A}\psi = \dfrac{d}{dx}\psi = \dfrac{d\psi}{dx} = ae^{ax} = a\psi$

The ”hat” symbol means ”operator”

Advanced note: we got the wavefunction back after using this operator – so it’s an **eigenfunction** of the operator

Interlude: Operator Algebra (2)

- In QM, **operators** always correspond to **observables**.

- An observable is **something physical and measurable.**
  - Energy, position, momentum, angular momentum...

- Operating on a wavefunction with the operator that corresponds to an observable makes the wavefunction give you that observable*.
  - **Hamiltonian operator** -> Energy
  - **Momentum operator** -> Momentum
  - And so on.

*If the wavefunction is an eigenfunction of the operator – not always true, but will be for all of our cases.

Operator Practice

- Apply the operator $\hat{O} = \frac{d^2}{dx^2}$ to the wavefunction $\Psi = sin(ax)$.

What is the value of the corresponding observable?

Complex Numbers

- When we talk about wavefunctions and operators, or get into any more advanced maths later, we inevitably encounter **complex numbers.**

- These are numbers which involve a constant denoted i, defined such that $i^2 = -1$ (note: this is *not* the same as saying $i = \sqrt{-1}$, can you figure out why?)

- There is a lot we could discuss here, but for our purposes in this course as long as we know that $i^2 = -1$ it is sufficient.

Operator Practice

$i^2 = -1$

- The linear momentum operator is defined as: $\hat{p} = -i\hbar \frac{d}{dx}$
- What is the momentum of a particle with a wavefunction:
  - $\Psi = e^{ix}$
  - $\Psi = e^{2ix}$
  - $\Psi = e^{-ilx}$

Hamiltonian Operators

- Coming back, if we can find the Hamiltonian and wavefunction, we can use the SE to find energy!

$$\hat{H}\mathbf{\Psi} = E\mathbf{\Psi}$$

- Easy to find Hamiltonians – we'll do this next time.

Take Home Messages

- Wavefunctions describe the behaviour of particles.
- Think of them as probabilities.
- Use operators to get useful observables from wavefunctions.

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

Session 3: The Schrödinger Equation

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Today

- Construct a simple Hamiltonian operator.
- Apply this to a simple system: **particle in a box.**
- See quantum mechanics in action!

Recall

- Operators let us extract useful observables from wavefunctions.

- In chemistry, we overwhelmingly care about one observable: **energy, E**. To see why, consider:
  - The most stable **structure** of a molecule will have the lowest **energy.**
  - The **reactivity** will be determined by the **HOMO** and **LUMO** – their **energies** will tell us how the molecule reacts.
  - The **spectrum** of a molecule is linked to **structure**, and directly measures the **energy** of different states in the molecule (CH2200).
  - ..... **energy** is what we care about!

Hamiltonian Operator

- The operator that corresponds to **total energy** is the **Hamiltonian**.
- This is what the SE tells us! $\hat{H}\mathbf{\Psi} = E\mathbf{\Psi}$
- How to find the Hamiltonian? Think about contributions to energy.
  - **Kinetic** energy (motion of nuclei/electrons) – symbol **T**.
  - **Potential** energy (attraction/repulsion between nuclei/electrons) – symbol **V**.

Constructing Hamiltonians

- Total energy = sum of kinetic (T) and potential (V) energies.
  - So total energy operator ($\hat{H}$) = sum of kinetic ($\hat{T}$) and potential ($\hat{V}$) energy operators.

- How do we find $\hat{V}$ or $\hat{T}$?

- Start with operators for **momentum** and **position:**

$$\hat{p} = -i\hbar \frac{d}{dx}$$

$$\hat{x} = x$$

Philosophy note: that these are the operators for momentum and position is one of the **postulates** of QM. We assume it is true and every experiment we've ever done confirms it, but we can't prove it. Like how we assume without proof that 1+1 = 2, or that 2^0 = 1.

Constructing Hamiltonians

- Make analogy with classical mechanics.

- For example: kinetic energy, $T = \frac{1}{2}mv^2 = \frac{p^2}{2m}$

- To turn T into $\hat{T}$, simply replace every p with a $\hat{p}$!

$$\hat{T} = \frac{\hat{p}^2}{2m} = \frac{\left(-i\hbar\frac{d}{dx}\right)^2}{2m} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

Constructing Hamiltonians

- Similar ideas for potential energy – we will see it later.
- For now, let’s use our KE operator to construct and solve a real SE...

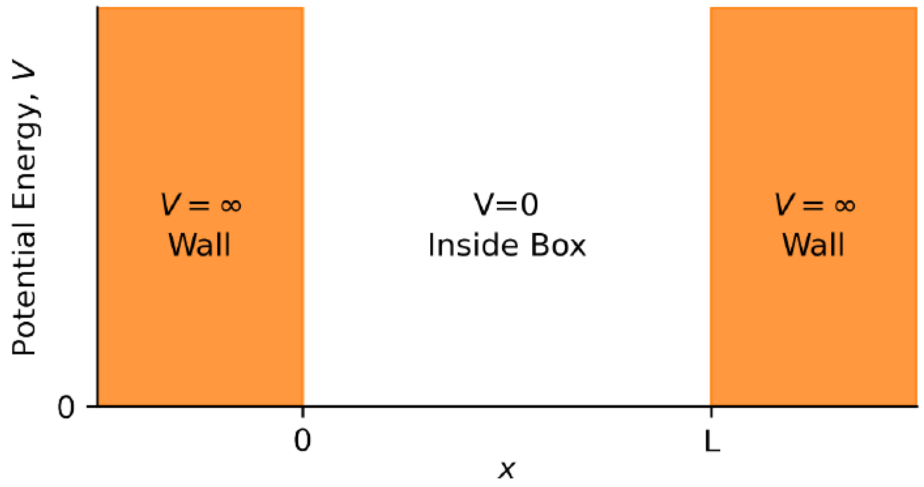
$$\hat{T} = \frac{\hat{p}^2}{2m} = \frac{\left(-i\hbar \frac{d}{dx}\right)^2}{2m} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

Particle in a Box

- Particle, mass *m,* in 1D box.

- Approach:
    - Construct Hamiltonian, write down SE.
    - Find a wavefunction that solves.
    - Apply **boundary conditions** to make it acceptable.

- Let’s go...



Solving the SE

$$\hat{H}\,\Psi(\mathrm{x}) = E\,\Psi(\mathrm{x})$$

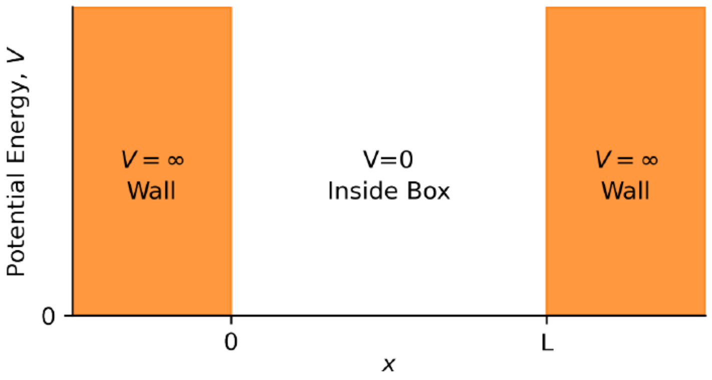
$$-\frac{\hbar^2}{2m}\frac{d^2\Psi(x)}{dx^2} = E\,\Psi(x)$$

$$\Psi(x) = N\sin(ax)$$

$$E = \frac{\hbar^2 a^2}{2m}$$

Applying Boundary Conditions

$\Psi(x) = N\sin(ax)$



- $\Psi(0) = \Psi(L) = 0$
- Leads to $a = \frac{n\pi}{L}$
  - Where $n = 1, 2, 3 \ldots$

Acceptable wavefunctions generally come in "sets" like this – for integer/half integer values of a quantum number.

- Our solution: $\Psi(x) = N\sin(\frac{n\pi x}{L})$ for $n = 1, 2, 3 \ldots$
- With energy: $E = \frac{n^2h^2}{8mL^2}$ where $n = 1, 2, 3 \ldots$

Take Home Messages

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

- We can construct any operator starting from the two operators for **position** and **momentum**.

- We saw how to set up and solve the SE for the **particle in a 1D box.**

- **Do the problems in problem sheet 1 now.**
  - Doing problems are the **only** way to get the hang of this stuff.

Session 4: Problems 1

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Session 5: Extended Problems 1

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Session 6: The Hydrogen Atom

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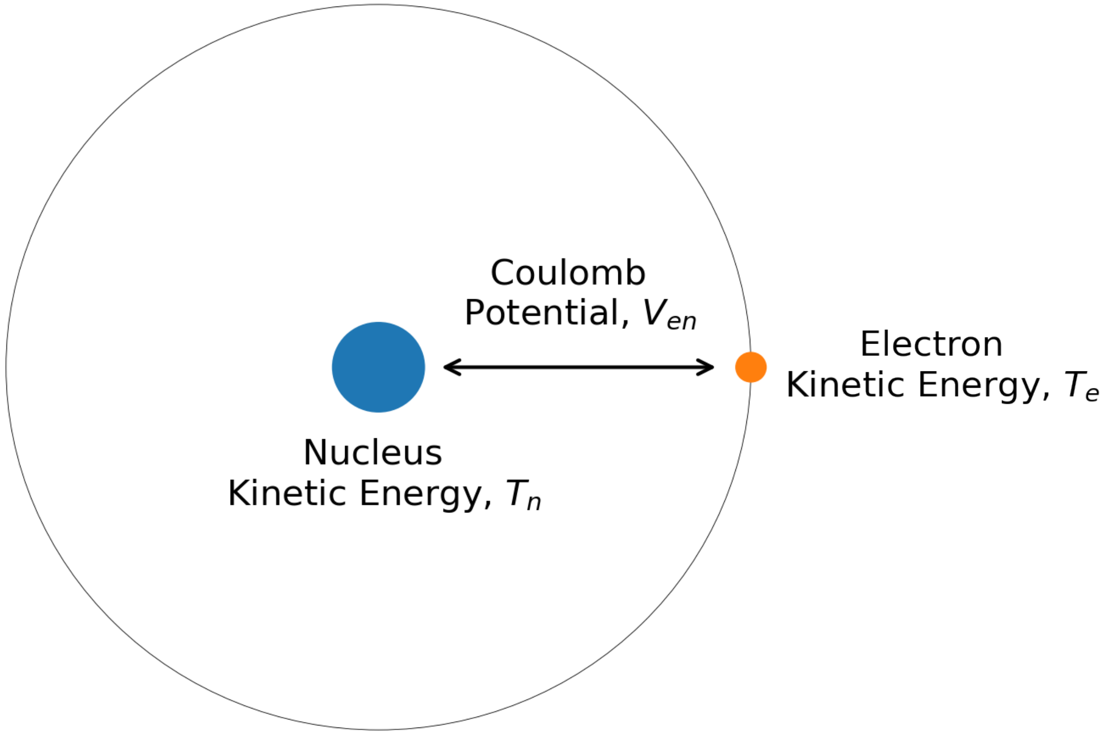
Today

- To understand the SE for the H atom.

- To understand radial and angular wavefunctions for the H atom.

- To see that familiar behaviour actually comes from somewhere!

Hydrogen

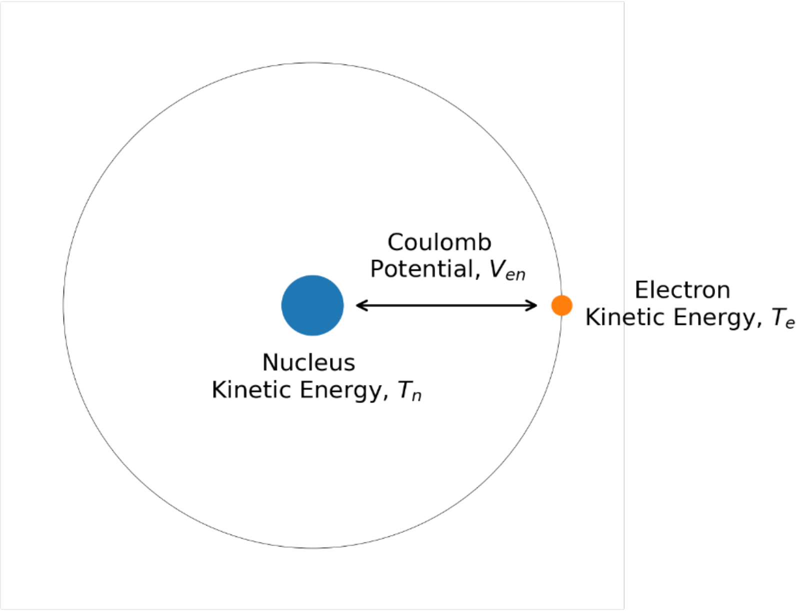

Coulomb
Potential, V_{en}
Electron
Kinetic Energy, T_e
Nucleus
Kinetic Energy, T_n

Hamiltonian

- $\hat{H} = \hat{T}_n + \hat{T}_e + \hat{V}_{en}$
- Actual equation? Recall:

$$\hat{T} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

- However, atoms are 3D...



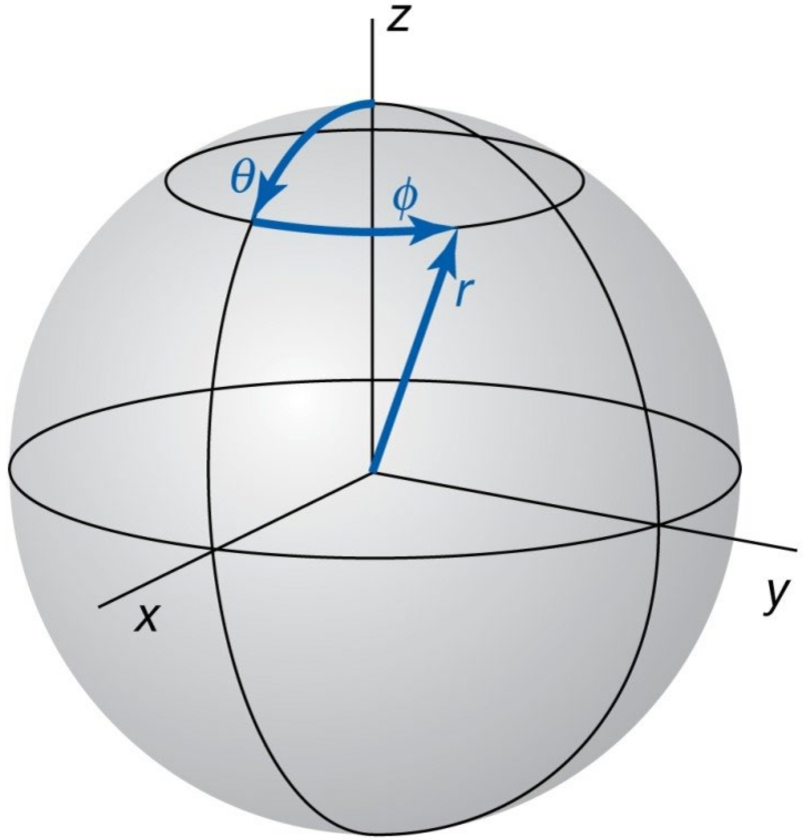
1D to 3D

- $(x) \rightarrow (x, y, z)$
- $\hat{T}_{1D} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \rightarrow \hat{T}_{3D} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$
- This set of derivatives is called the *Laplacian*, ∇^2

$$\nabla^2 = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

Coordinate Transformations

- Atoms are spherically symmetric:
  - Spherical Polar coordinates: (r, θ, ϕ)



- Can convert between systems:

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

$$\theta = \arctan\left(\frac{\sqrt{x^2 + y^2}}{z}\right) = \arccos\left(\frac{z}{\sqrt{x^2 + y^2 + z^2}}\right)$$

$$\varphi = \arctan\left(\frac{y}{x}\right) = \arccos\left(\frac{x}{\sqrt{x^2 + y^2}}\right) = \arcsin\left(\frac{y}{\sqrt{x^2 + y^2}}\right)$$

$$x = \rho \sin\theta \cos\varphi$$

$$y = \rho \sin\theta \sin\varphi$$

$$z = \rho \cos\theta$$

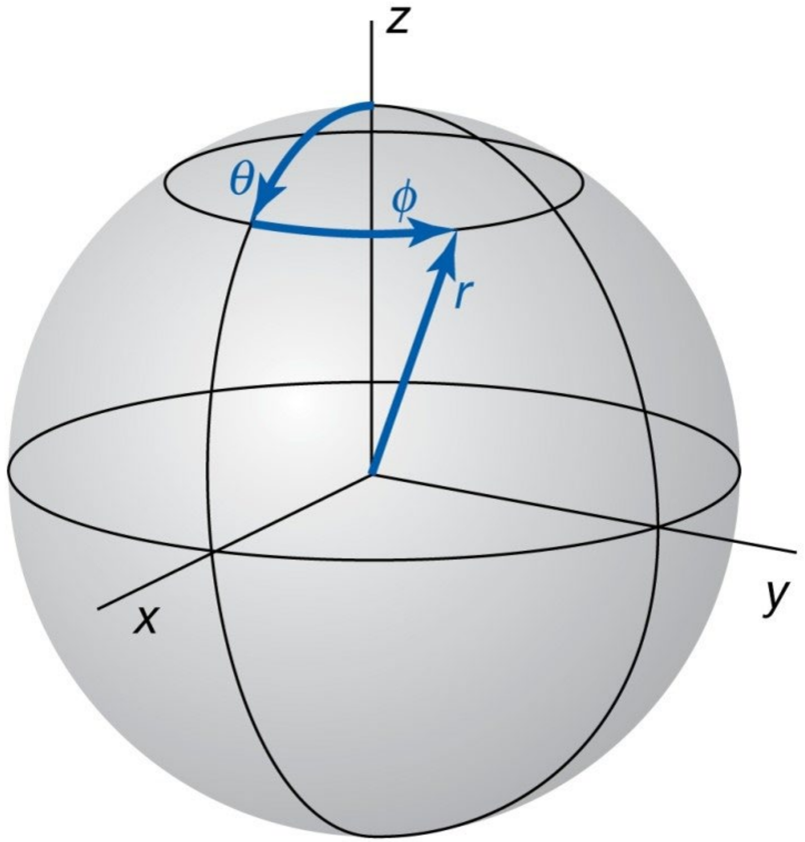
Wiki uses different notation

Coordinate Transformations

- System conversion is more tedious than hard.
- Laplacian in spherical coords:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial f}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2 f}{\partial\varphi^2}$$

- For interest!



Potential Energy

- Coulomb energy: $V = k\frac{q_1 q_2}{r}$

- Charges are the electron and the nucleus. Express in terms of the elementary charge, e (1e = 1.6x10^{-19}C).
  - $q_1 = -e$
  - $q_2 = +Ze$ where Z is the number of protons. $Z = 1$ for hydrogen.

- Coulomb attraction: $V = -\frac{Ze^2}{\mathrm{r}}$
  - To make the operator, note r is just position.
  - So simply replace with the position **operator**, $\hat{r} = r$
  - ... So it looks the same as an operator ☺

Potential Energy

- Can now write down $\hat{H}$:

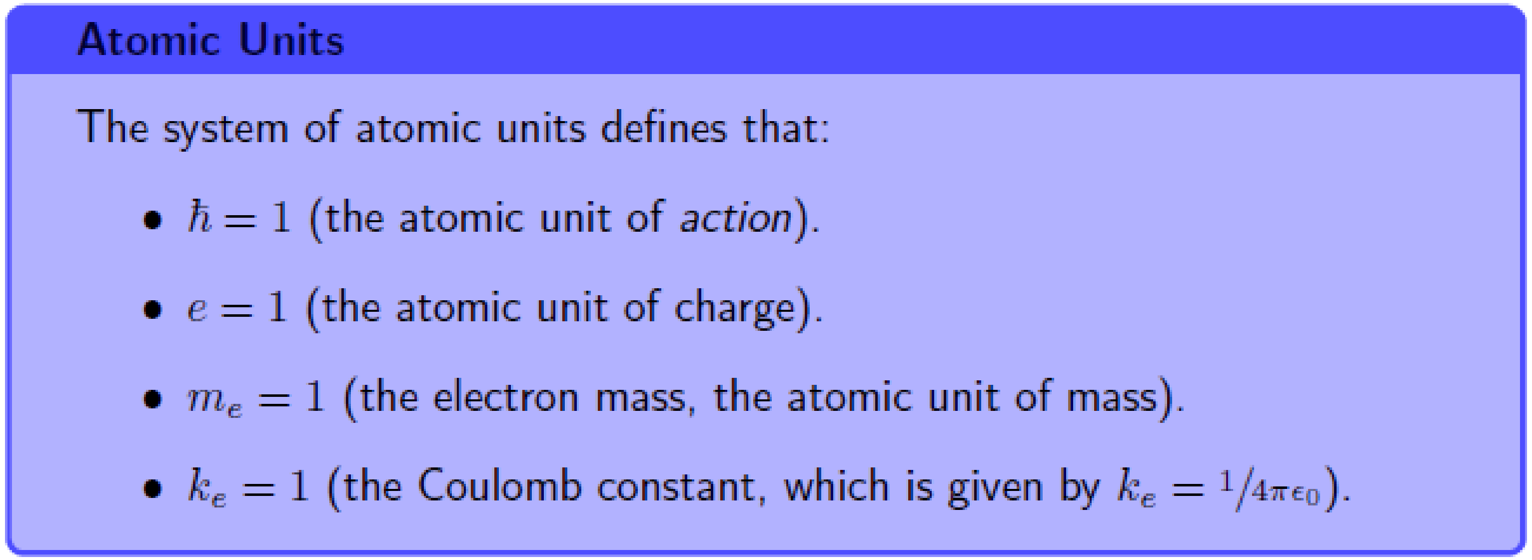
$$\hat{H} = \hat{T}_n + \hat{T}_e + \hat{V}_{en}$$

$$\hat{H} = -\frac{\hbar^2}{2m_n}\nabla_n^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - k_e\frac{1}{r}$$

All these constants are going to get cumbersome for bigger systems!

Atomic Units

- Define a system of **atomic units**, as proposed by Douglas Hartree:



Atomic Units

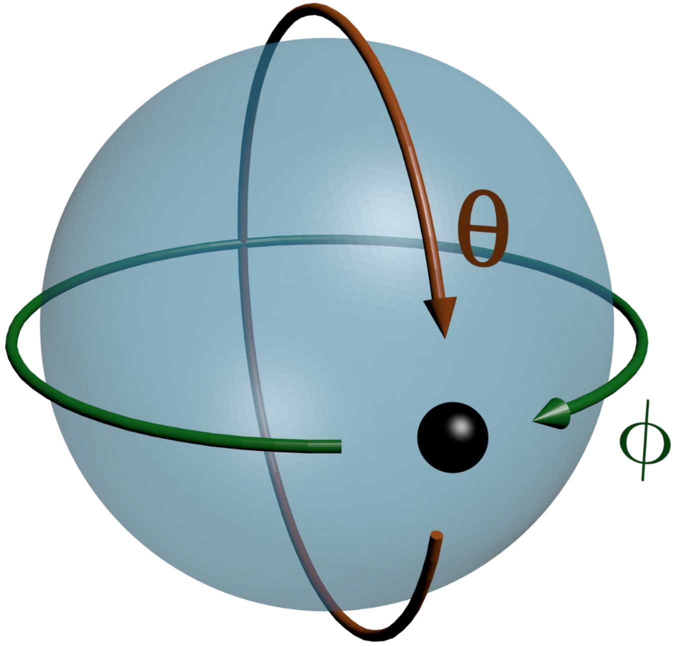
The system of atomic units defines that:

- $\hbar = 1$ (the atomic unit of *action*).
- $e = 1$ (the atomic unit of charge).
- $m_e = 1$ (the electron mass, the atomic unit of mass).
- $k_e = 1$ (the Coulomb constant, which is given by $k_e = {}^1/_{4\pi\epsilon_0}$).

Atomic Units

- Why is this allowed?
- Any choice of units is arbitrary – why is a metre ”one metre”?
- For small things, these are more convenient than using tiny fractions of SI units.
  - Smart idea Prof Hartree.

Hydrogen SE



- In atomic units:

$$\hat{H} = -\frac{1}{2m}\nabla_n^2 - \frac{1}{2}\nabla_e^2 - \frac{1}{r}$$

- Full SE:

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

$$\left[-\frac{1}{2m}\nabla_n^2 - \frac{1}{2}\nabla_e^2 - \frac{1}{r}\right]\Psi(r,\theta,\phi) = E\,\Psi(r,\theta,\phi)$$

- This can be solved – exactly, using *separation of variables*:

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

Radial part

Angular part

Radial Wavefunctions

- Radial part of $\Psi(r, \theta, \phi)$:

Laguerre polynomial (results in radial nodes).

$$R(r) = N_{n,l} \times L(r) \times e^{-r}$$

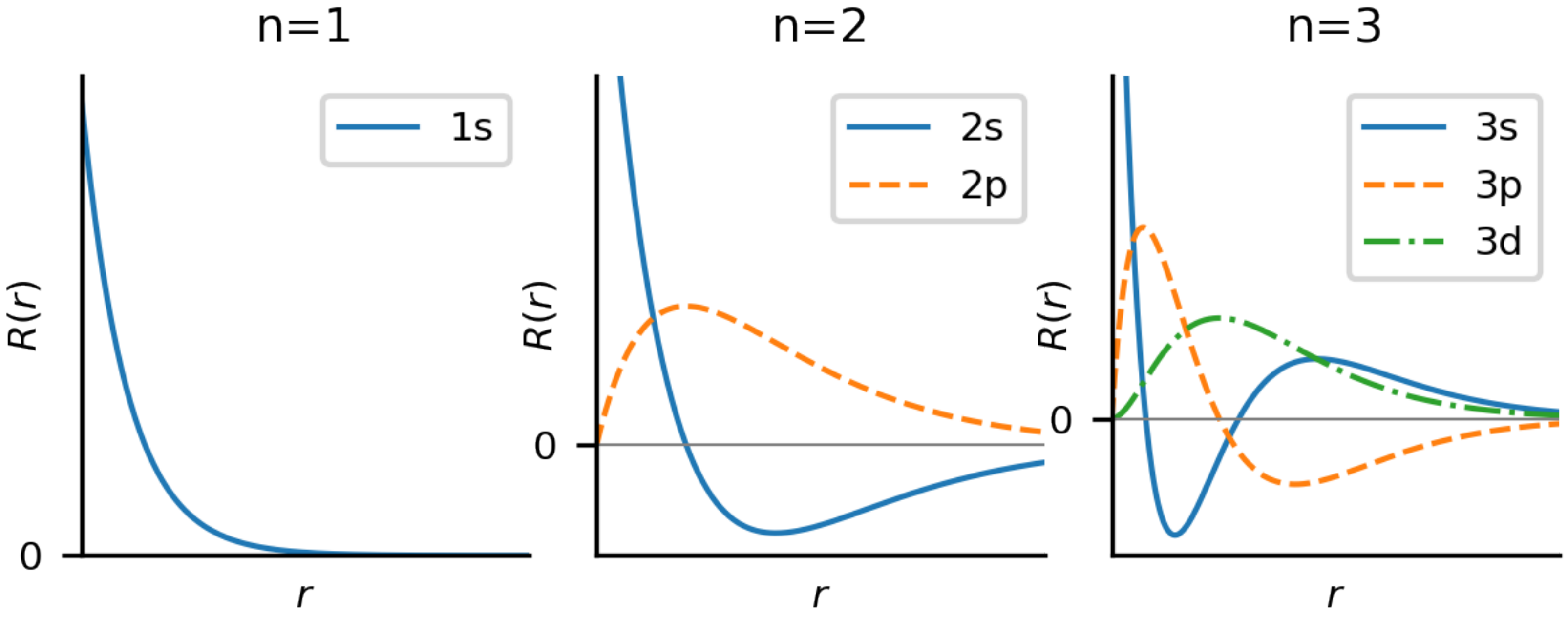
Normalisation constant – ensures R(r) is normalised.

Exponential decay – ensures wavefunction goes to zero at large distances

Note the quantum numbers! These functions depend on the quantum numbers, n and l.

Radial Wavefunctions

$$R(r) = N_{n,l} \times L(r) \times e^{-r}$$



Radial Wavefunctions (Summary)

- Radial parts determine the *size* of the wavefunction (orbital).

- For hydrogenic atoms, the radial parts determine the energy, via the *n* quantum number (see later).

- We can work out the most probable distance of an electron from the nucleus from the radial parts – radial distribution function.

Angular Wavefunctions (for info!)

- Angular part of $\Psi(r, \theta, \phi)$:

Legendre polynomial – gives the θ dependence (and angular nodes)

$$Y_{l,m_l}(r) = N_{l,m_l} \times P_{l,m_l}(\cos\theta) \times e^{im_l\phi}$$

Normalisation constant – ensures R(r) is normalised.

Gives the ϕ dependence.

Note the quantum numbers! These functions depend on the quantum numbers, l and m_l - <u>not</u> n.

Spherical Harmonics

- These equations are known as **spherical harmonics.**

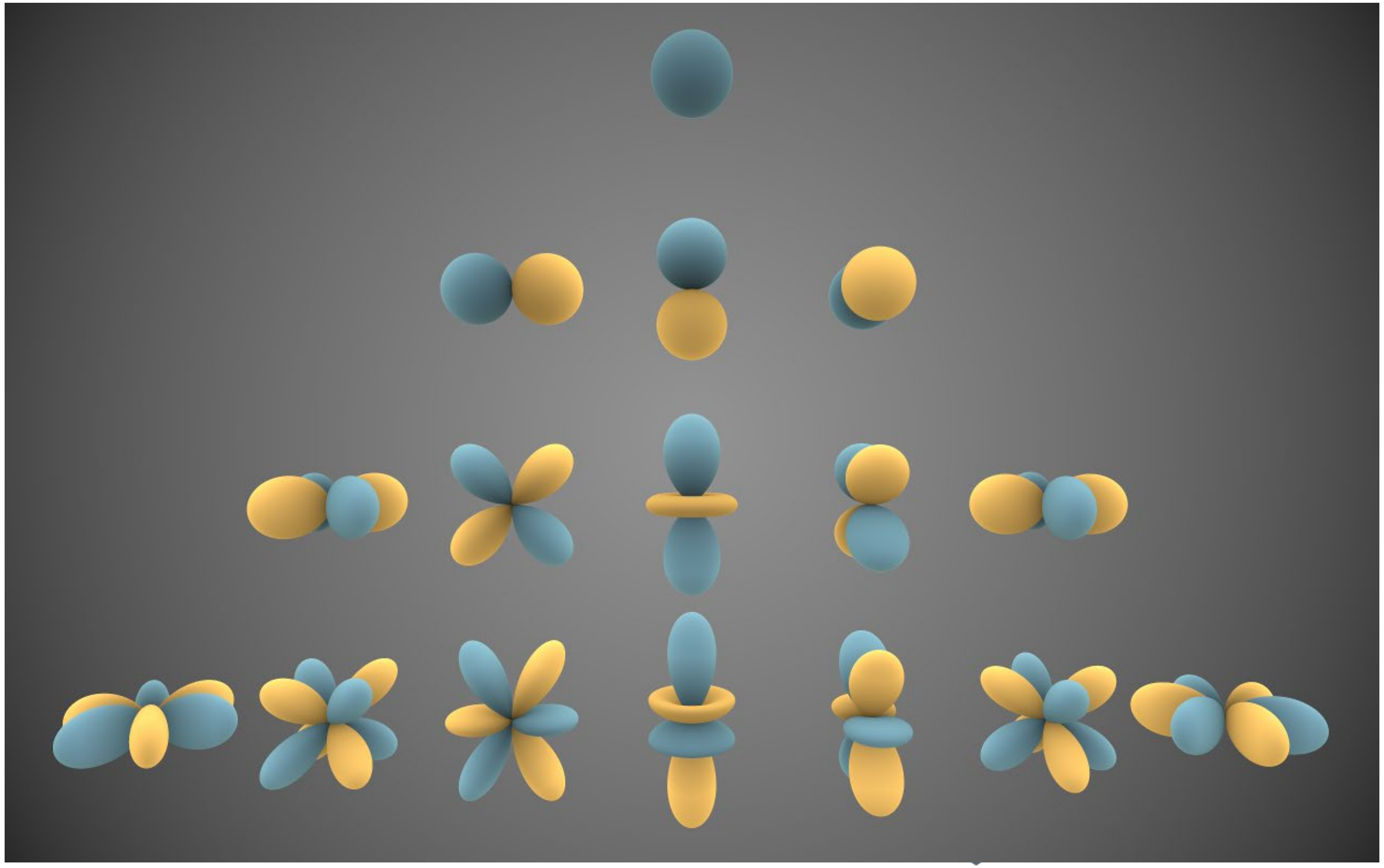
$$Y_{l,m_l}(r) = N_{l,m_l} \times P_{l,m_l}(\cos\theta) \times e^{im_l\phi}$$

- Very common set of functions that solve differential equations.
  - And the SE is just a differential equation!

- They are defined in terms of the l and m_l quantum numbers:
  - Each value of l has $2l + 1$ different possible values of m_l
  - Due to **quantisation of the angular momentum** (see extra).

Spherical Harmonics

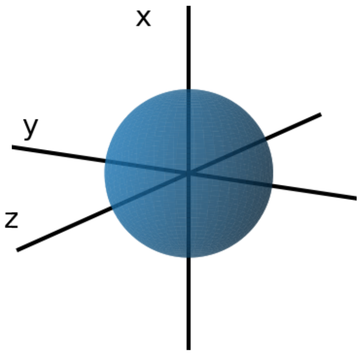
- There are $2l + 1$ different orientations of m_l:
  - $l = 0 \rightarrow 1\, m_l$ (s orbital)
  - $l = 1 \rightarrow 3\, m_l$ (p orbitals)
  - $l = 2 \rightarrow 5\, m_l$ (d orbitals)
  - And so on



Angular Wavefunctions

- Get **angular nodes (nodal planes)** due to the Legendre polynomials.

$$Y_{l,m_l}(r) = N_{l,m_l} \times P_{l,m_l}(\cos\theta) \times e^{im_l\phi}$$

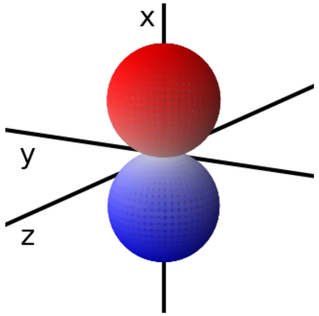


$Y_{0,0}$
s-orbital

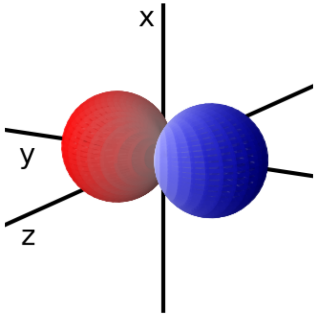
- Wavefunction changes sign (phase) at nodes.

Important for chemical bonding - interference

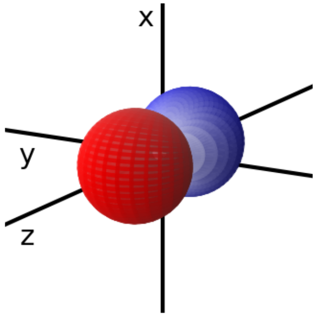
- Get l angular nodes.



$Y_{1,0}$
p_x orbital



$\frac{1}{\sqrt{2}}(Y_{1,-1} + Y_{1,1})$
p_y orbital



$\frac{1}{\sqrt{2}}(Y_{1,-1} - Y_{1,1})$
p_z orbital

Energies

- We have all our wavefunctions - what about energies?

- Simple for hydrogen:

Higher n = higher energy, further from nucleus

$$E_n = -\frac{1}{n^2}$$

Negative – energy of the bound electron is lower than free electron.

- Leads to the **Rydberg Equation** (exercise).

Note! No dependence on l or m_l if hydrogenic -> s, p, d, all same energy.

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

Take Home Messages

- We construct the SE for H using atomic units, and in spherical coordinates (and in 3D). Can be solved exactly.
- Solutions are split into radial and angular solutions – resulting in familiar orbitals.
- Energies are determined by n for hydrogenic – no penetration/shielding.

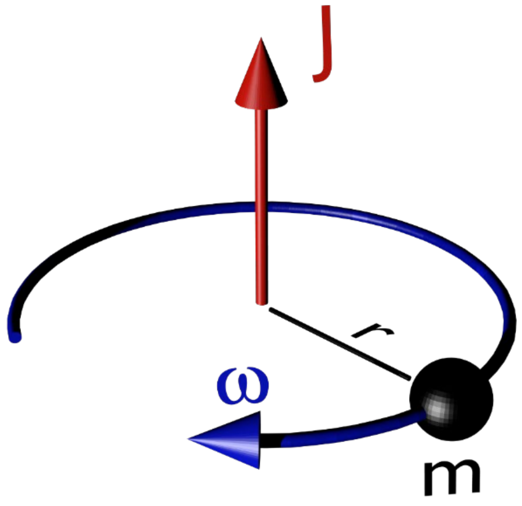
BONUS EXTRA: Angular Momentum

CH2203 Physical Chemistry

(if you want more understanding – this is not critical if you are happy to just accept that there are three p-orbitals, and five d-orbitals, and so on..)

EXTRA MATERIAL – NOT EXAMINED DIRECTLY

Angular Momentum



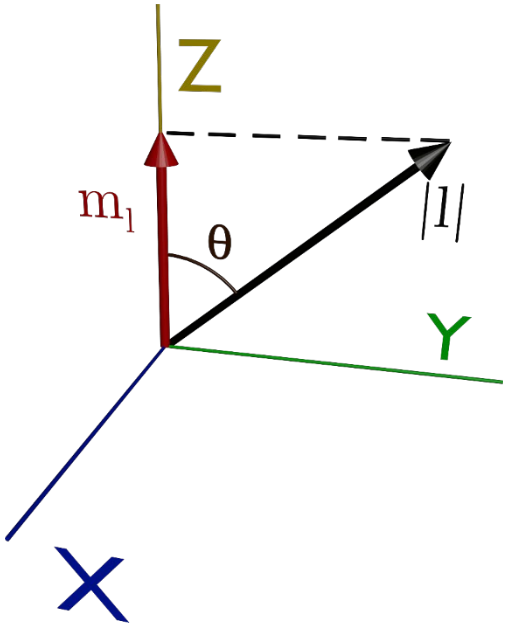
- Classically: momentum of a rotating thing.
  - A **vector** – with magnitude and direction. Symbol: J
  - Rotational analogue of linear momentum, p.

- Lots of things rotate in the quantum world:
  - Electrons **orbiting** around atoms.
  - Particles **spin** on their own axis*
    - Leads to **electron spin.**
    - Also to **nuclear spin** (remember CH2200 and NMR?)

*Yeah, alright, this doesn't really happen. But its a useful way to picture it in your head.

EXTRA MATERIAL – NOT EXAMINED DIRECTLY

Angular Momentum in Chemistry



- We can talk about lots of kinds of angular momenta:
  - **Orbital** angular momentum: l, m_l
  - **Electron spin** angular momentum: s, m_s
  - **Nuclear spin** angular momentum: I, m_I
  - **Total** (orbital + spin) angular momentum: j, m_j
- We talk about both the **length** (l, s, I, j) of the angular momentum vector, and it's **projection** (m_l, m_s, m_I, m_j) onto an axis.
- Angular momentum is **quantised.**

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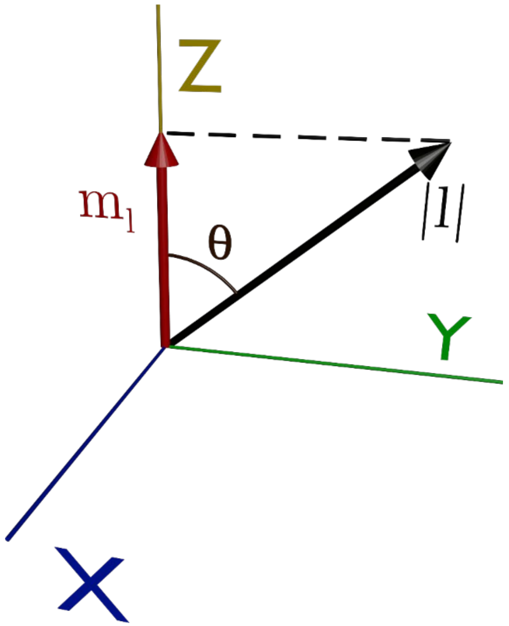
EXTRA MATERIAL – NOT EXAMINED DIRECTLY

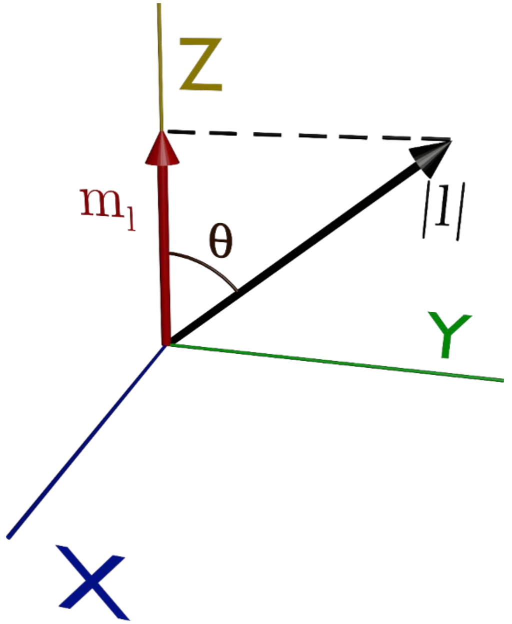
Angular Momentum in Chemistry



- For an angular momentum vector with length l, there are $2l + 1$ possible orientations of m_l
    - Due to the quantisation – see Atkins MQM for more.
- **Applies to every angular momentum:**
    - Electron spin, $s = \frac{1}{2}$, so $2s + 1 = 2$ -> two orientations
        - Spin ”up” and spin ”down”.
    - Orbital, if $l = 1$ (p orbital), $2l + 1 = 3$ -> three p orbitals
        - p_x, p_y, p_z

EXTRA MATERIAL – NOT EXAMINED DIRECTLY

Angular Momentum Practice

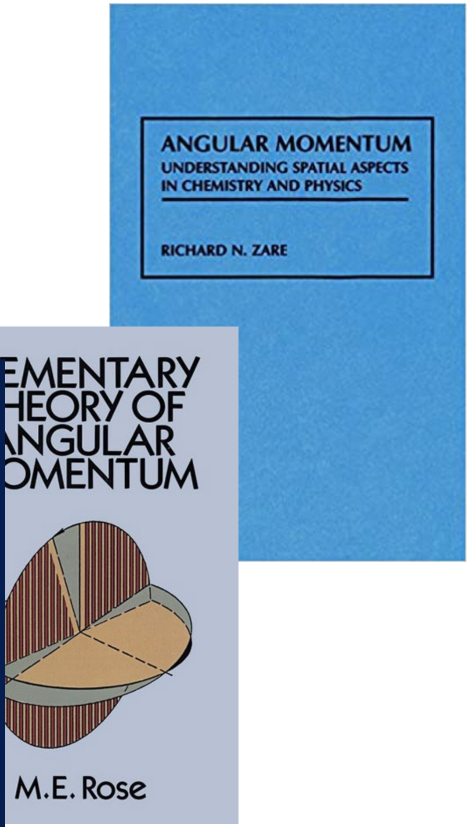


- An electron is in a level where $l = 2$
    - What are the possible values of m_l?

- A ^{1}H nucleus has a nuclear spin quantum number $I = \frac{1}{2}$
    - What are the possible values of m_I?

EXTRA MATERIAL – NOT EXAMINED DIRECTLY

Angular Momentum



- Next ye
  produce
  describ
- For now
  - There
  - There
  - There's a reason 1H NMR involves transitions between two spin states.

Session 7: More Electrons

CH2203 Physical Chemistry

Today

- To extend our model to bigger atoms.
- To understand why electrons ruin everything.
- Dealing with repulsions: approximate methods.

Hydrogenic Atoms

- Extending our previous treatment to other hydrogenics (He^+, Li^{2+}, etc..) is trivially easy.
- Account for the increased nuclear charge, Z, in the attraction:

$$\hat{H} = -\frac{1}{2m}\nabla_n^2 - \frac{1}{2}\nabla_e^2 - \frac{Z}{r}$$

- Leads to a slightly modified expression for energy...

Energies

- Including the effect of the nuclear charge:

Higher Z = lower energy, held more tightly.

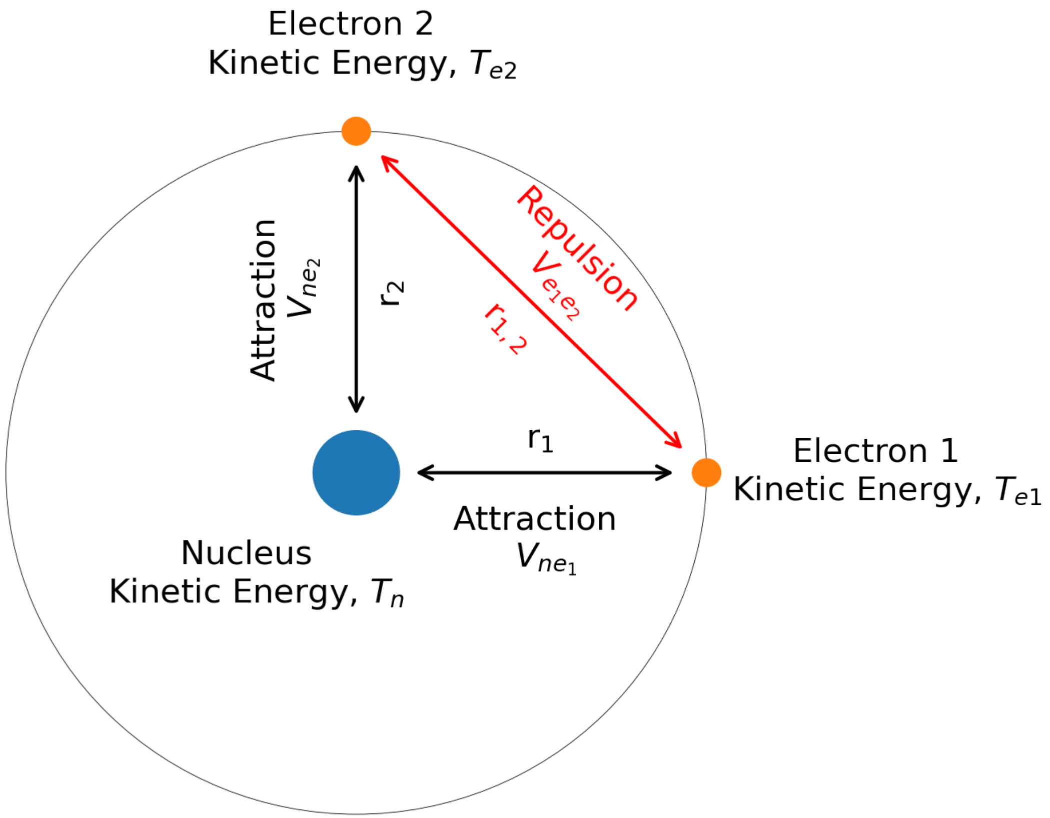
$$E_n = -\frac{Z^2}{n^2}$$

Negative – energy of the bound electron is lower than free electron.

Higher n = higher energy, further from nucleus

- Still no dependence on l or m_l if hydrogenic -> s, p, d, all same energy.
  - What if we add another electron though?

Hydrogen

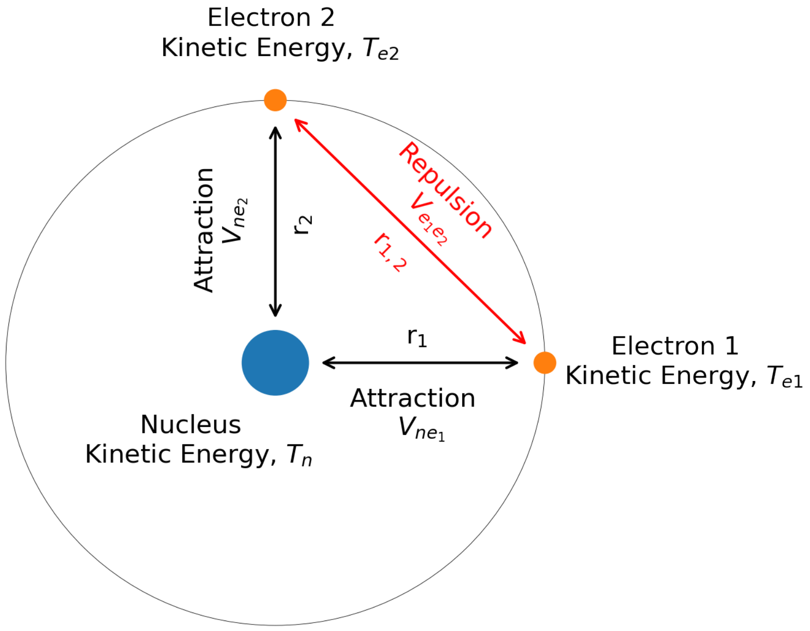


Electron 2
Kinetic Energy, T_{e2}
Attraction
V_{ne_2}
r_2
Repulsion
$V_{e_1e_2}$
$r_{1,2}$
r_1
Electron 1
Kinetic Energy, T_{e1}
Attraction
V_{ne_1}
Nucleus
Kinetic Energy, T_n

Hamiltonian

- $\hat{H} = \hat{T}_n + \hat{T}_{e1} + \hat{T}_{e2} + \hat{V}_{ne1} + \hat{V}_{ne2} + {\color{red}\hat{V}_{e1e2}}$
- $\hat{H} = -\frac{1}{2m}\nabla_n^2 - \frac{1}{2}\nabla_{e1}^2 - \frac{1}{2}\nabla_{e1}^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + {\color{red}\frac{1}{r_{12}}}$
- Easy enough to construct, can we solve?

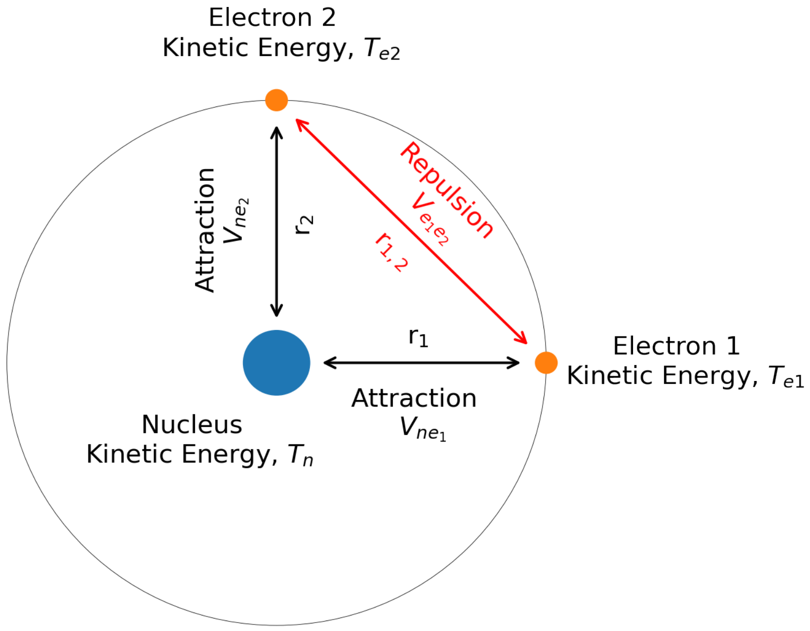
$$\hat{H}\Psi = E\Psi$$



The Problem

$$\hat{H} = -\frac{1}{2m}\nabla_n^2 - \frac{1}{2}\nabla_{e1}^2 - \frac{1}{2}\nabla_{e1}^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}$$

- To solve, need to know r_{12}
- Need positions of both electrons.
- To find the positions, need to solve SE.
  - To get the wavefunction, and then $P(x) \propto \Psi(x)^2$
- But to solve, need to know r_{12}
- Damn.



The Problem

$$\hat{H} = -\frac{1}{2m}\nabla_n^2 - \frac{1}{2}\nabla_{e1}^2 - \frac{1}{2}\nabla_{e1}^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}$$

- If more than 1 electron: the SE **depends on its own solutions.**
- Because electron positions are **correlated.**
  - The positions affect each other – if one moves, the other moves.
- So can’t solve **analytically** (with a pen and paper).
- Can solve it **numerically** (using a computer to get the best approximation).
- Need to make some assumptions...

The Orbital Approximation (1)

- Each electron exists in its own one-electron orbital.
  - Call this an **atomic orbital (AO)**.

- Each AO feels attraction to nucleus, and an **average repulsion** from other nuclei.

- Average repulsion: don’t need to know *exact* position.
  - Just the *average* position.

The Orbital Approximation (2)

- Then write the total (many electron) wavefunction:

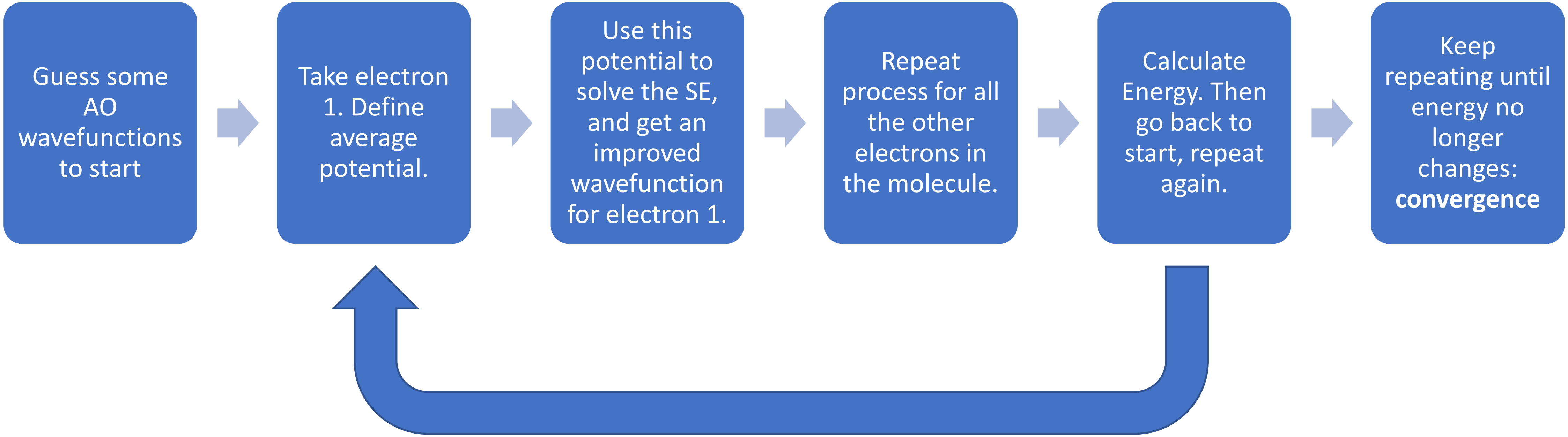
$$\Psi_{He}(r_1, r_2) = \phi_1(r_1) \times \phi_2(r_2)$$ (ϕ is the atomic orbital).

- Generally:

$$\Psi_{atom}(r_1, \ldots, r_n) = \prod_{i=1}^{n} \phi_i(r_i)$$

- How do we find each ϕ?

Self-Consistent Field Methods



Guess some AO wavefunctions to start

Take electron 1. Define average potential.

Use this potential to solve the SE, and get an improved wavefunction for electron 1.

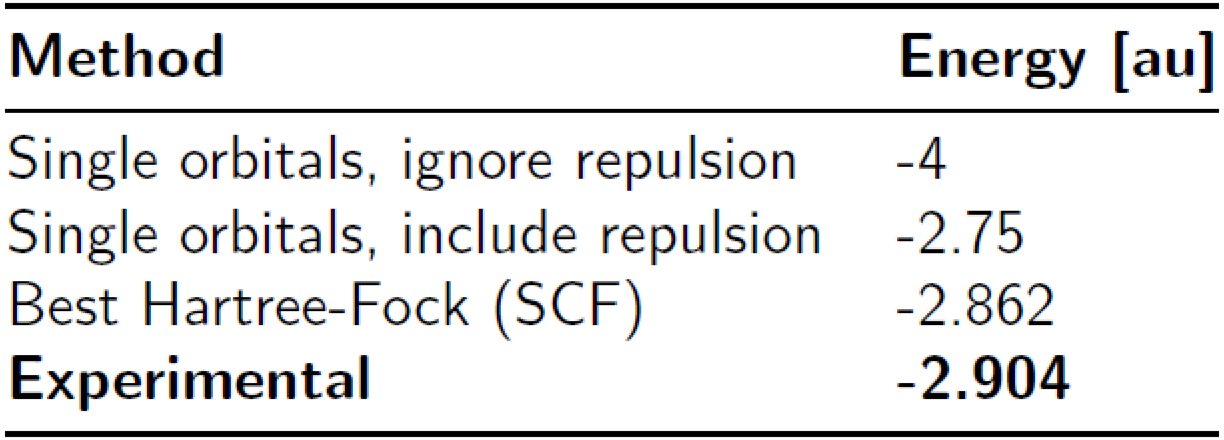
Repeat process for all the other electrons in the molecule.

Calculate Energy. Then go back to start, repeat again.

Keep repeating until energy no longer changes: **convergence**

Self-Consistent Field Methods

- Approximate solution – but can be very accurate (0.001%).
- Examples are **Hartree-Fock Theory** and **Kohn-Sham DFT.**



Method	**Energy [au]**
Single orbitals, ignore repulsion	-4
Single orbitals, include repulsion	-2.75
Best Hartree-Fock (SCF)	-2.862
Experimental	**-2.904**

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Take Home Messages

- Electrons stop us being able to exactly solve the SE.
- We have to make a series of approximations to continue to be able to learn about atomic and molecular structure.
- **Do the problems in problem sheet 2 now.**

Session 8: Problems 2

CH2203 Physical Chemistry

Session 9: The Simplest Molecule

CH2203 Physical Chemistry

Aims

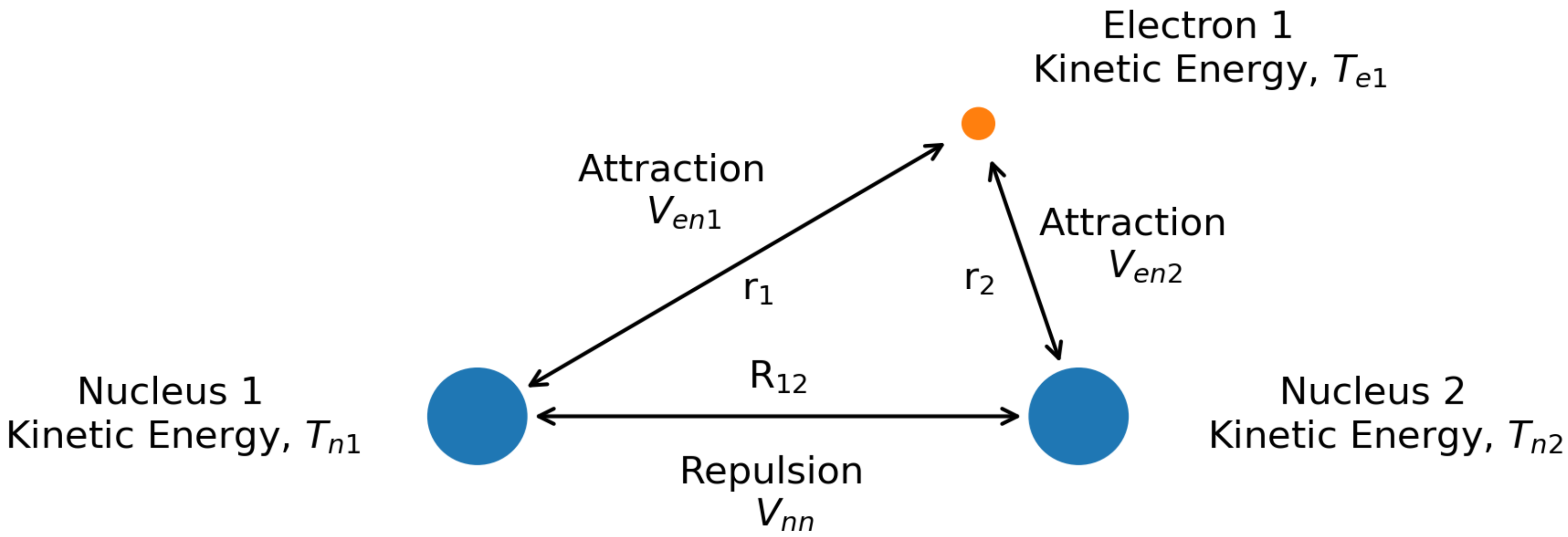
- To understand the **Born-Oppenheimer Approximation**.

- (there is only one aim today).

Previous Approach

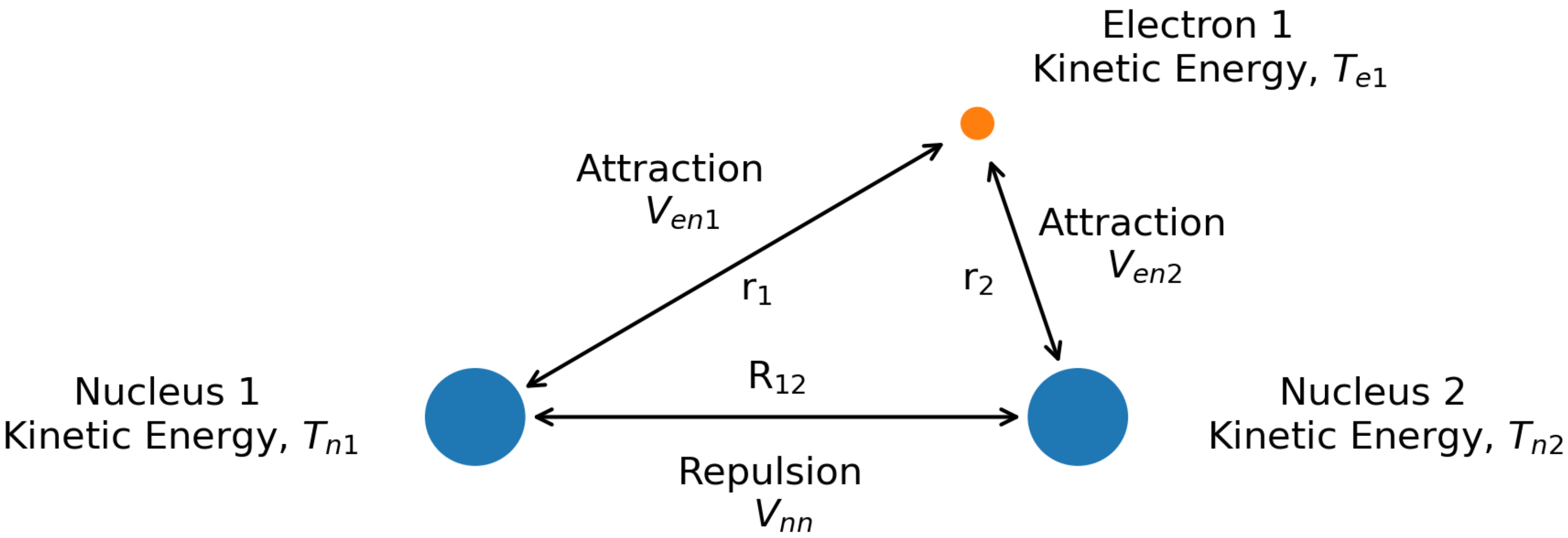
- One-electron systems – exactly solvable.
- Use the exact solutions to develop *approximate* solutions for unsolvable systems.
- Refine the approximate solutions to describe more complex systems.
  - Let’s try the **hydrogen molecular ion**.

Hydrogen Molecular Ion



Hamiltonian

- $\hat{H} = -\frac{1}{2m}\nabla_{n1}^2 - \frac{1}{2}\nabla_{n2}^2 - \frac{1}{2}\nabla_e^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{R_{12}}$



Electron 1
Kinetic Energy, T_{e1}

Attraction
V_{en1}

Attraction
V_{en2}

Nucleus 1
Kinetic Energy, T_{n1}

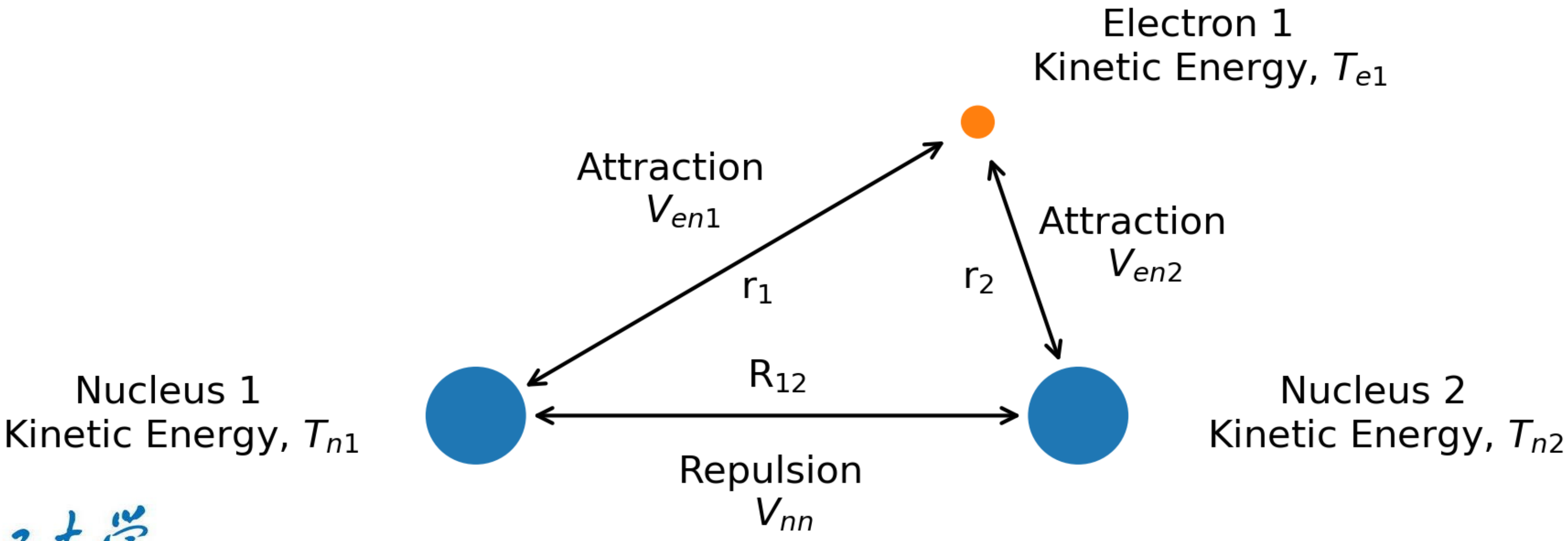
Nucleus 2
Kinetic Energy, T_{n2}

Repulsion
V_{nn}

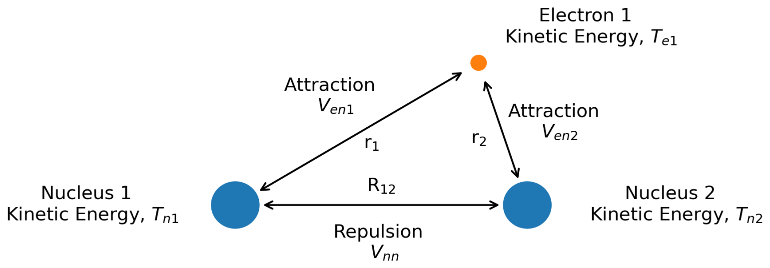
Hmm...

- We’re stuck, right? Same problem as before, but with nuclei.

- We need another approximation:
  - **The Born-Oppenheimer Approximation**



Born-Oppenheimer Approximation



- Electrons are very light compared to nuclei.
- For the same force, they move much faster.
- We can **separate the electronic and nuclear motion.**
  - Split the wavefunction into an electronic and nuclear part:

$$\Psi_{total}(R,r) = \Psi_{elec}(r) \times \phi_{nuc}(\mathrm{R})$$

  - Leads to two equations – the **electronic** and **nuclear** SE.

Applying BOA to H_2^+

- $\hat{H} = \hat{T}_{Nuc.} + \hat{H}_{elec.} = -\frac{1}{2m}\nabla^2_{n1} - \frac{1}{2m}\nabla^2_{n2} - \frac{1}{2}\nabla^2_e - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{R_{12}}$

- Assume R_{12} is constant on the timescale of electron motion (stationary nuclei), and thus set up the **electronic SE**:

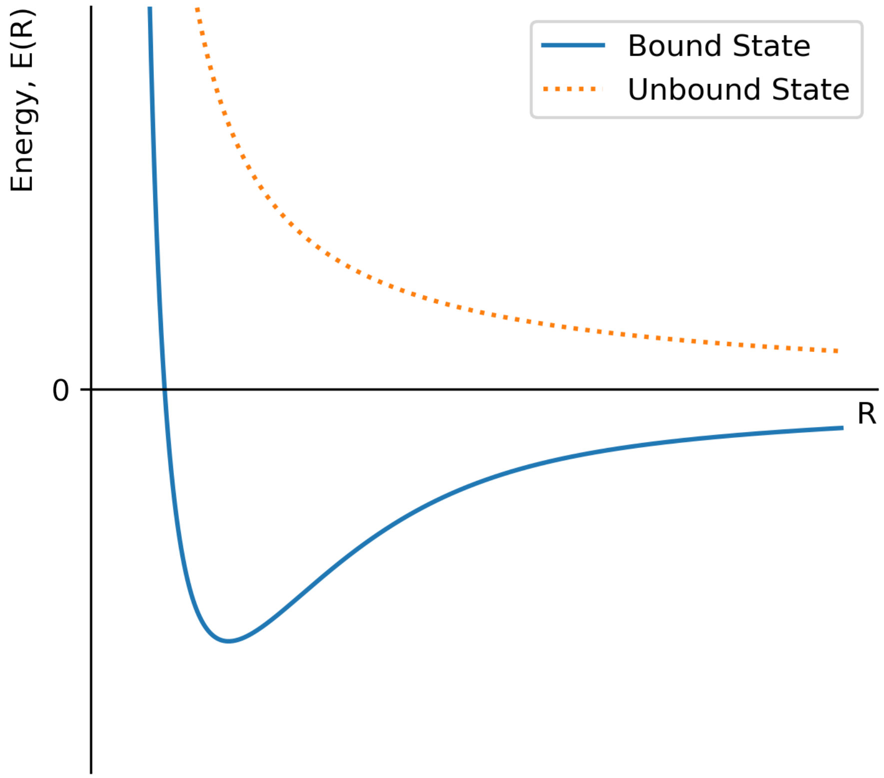
$$\hat{H}_{elec.}\Psi_{elec}(r|R) = E_{elec}(r|R)\Psi_{elec}(r|R)$$

- This equation gives rise to **electronic states**, $E_{elec}(r|R)$, which still depend on the given (fixed) nuclear separation.

$$\hat{H}_{elec.}\Psi_{elec}(r|R) = E_{elec}(r|R)\Psi_{elec}(r|R)$$

The Electronic SE

- The BOA gives us a SE for the energies of the electrons, producing the electronic states, $E_{elec}(r|R)$.
- Solving this equation at different values of R produces the (maybe) familiar **potential energy curves.**
  - How the electronic energy varies as a function of nuclear position.



The Nuclear SE

- The electronic energies $E_{elec}(r|R)$represent the **potential energy** the nuclei feel at a given separation.
  - Can write down a SE for the **motion of the nuclei:**

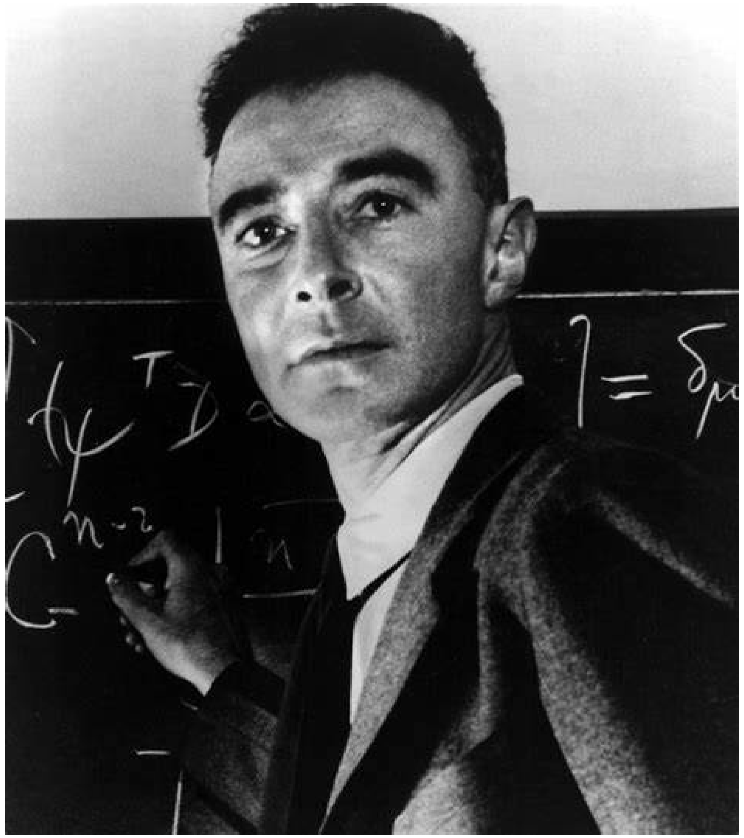
$$\underset{\text{Nuclear Hamiltonian}}{\hat{H}_{nuc}}\phi_{nuc}(R) = [\underset{\text{Nuclear KE}}{\hat{T}_{nuc}} + \underset{\text{"Nuclear PE"}}{E_{elec}(r|R)}]\phi_{nuc}(R) = \mathrm{E}_{nuc}\phi_{nuc}(R)$$

- Results in energies (E_{nuc}) and wavefunctions (ϕ_{nuc}) for nuclear motion – i.e. rotations and vibrations of the molecule.

- This equation ultimately leads to familiar expressions from CH2200 for rotational and vibrational energy levels.

BOA Summary

- Separating the electronic and nuclear motion gives us an electronic and a nuclear SE:
  - Electronic SE = gives us electronic wavefunctions (MOs) and energies
  - Nuclear SE = gives us rotational/vibrational wavefunctions and energies.
- Breaks down when nuclei move fast.
  - When bonds break/form.



<u>Historical perspective:</u> Oppenheimer is remembered mostly for developing the atomic bomb, but the Born-Oppenheimer Approximation has, I think, had a much greater impact on society and the world. We wouldn't know any chemistry today without it.

Great, but this doesn’t actually help...

- Our aim is to develop a theory that can explain bonding.
  - We need to be able to explain multi-electron systems.

- The BOA helps us by separating out the nuclear and electronic motion, but we still have the problem of e-e repulsion.
  - For anything more complex than H_2^+, at least.

- Solution? As before – other approximate methods.
  - Need to find an approximate electronic wavefunction to refine.
  - Call this a **molecular orbital.**
  - **How do we make a molecular orbital?**

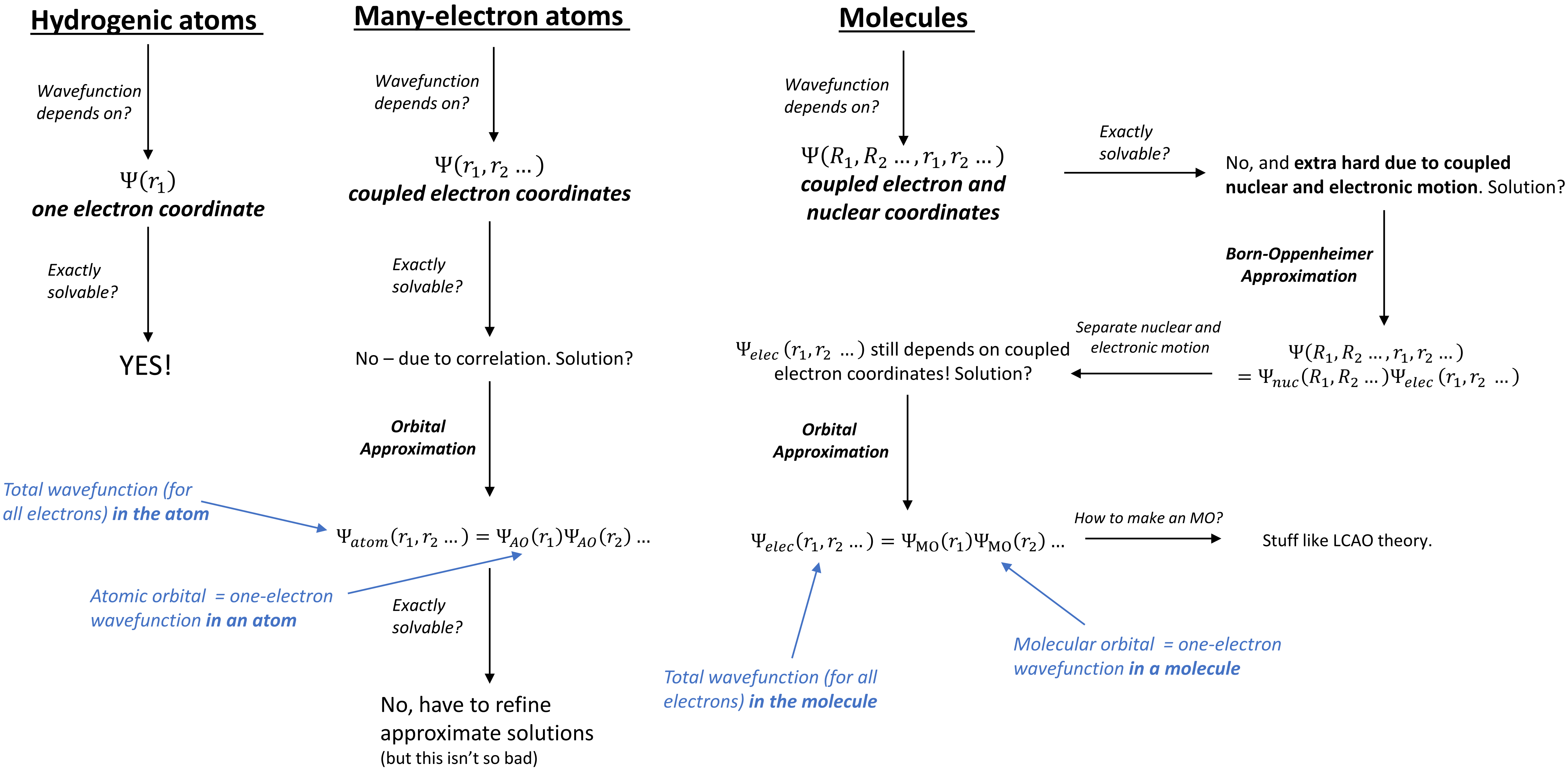
Next time: Molecular Orbitals

Session 10: Molecular Orbitals

CH2203 Physical Chemistry

The story so far....

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



Hydrogenic atoms

Wavefunction depends on?

$\Psi(r_1)$

one electron coordinate

Exactly solvable?

YES!

Many-electron atoms

Wavefunction depends on?

$\Psi(r_1, r_2 \ldots)$

coupled electron coordinates

Exactly solvable?

No – due to correlation. Solution?

Orbital Approximation

$\Psi_{atom}(r_1, r_2 \ldots) = \Psi_{AO}(r_1)\Psi_{AO}(r_2) \ldots$

Total wavefunction (for all electrons) ***in the atom***

Atomic orbital = one-electron wavefunction ***in an atom***

Exactly solvable?

No, have to refine approximate solutions

(but this isn't so bad)

Molecules

Wavefunction depends on?

$\Psi(R_1, R_2 \ldots, r_1, r_2 \ldots)$

coupled electron and nuclear coordinates

Exactly solvable?

No, and **extra hard due to coupled nuclear and electronic motion**. Solution?

Born-Oppenheimer Approximation

$\Psi(R_1, R_2 \ldots, r_1, r_2 \ldots)$
$= \Psi_{nuc}(R_1, R_2 \ldots)\Psi_{elec}(r_1, r_2 \ldots)$

Separate nuclear and electronic motion

$\Psi_{elec}(r_1, r_2 \ldots)$ still depends on coupled electron coordinates! Solution?

Orbital Approximation

$\Psi_{elec}(r_1, r_2 \ldots) = \Psi_{MO}(r_1)\Psi_{MO}(r_2) \ldots$

Total wavefunction (for all electrons) ***in the molecule***

Molecular orbital = one-electron wavefunction ***in a molecule***

How to make an MO?

Stuff like LCAO theory.

Aims

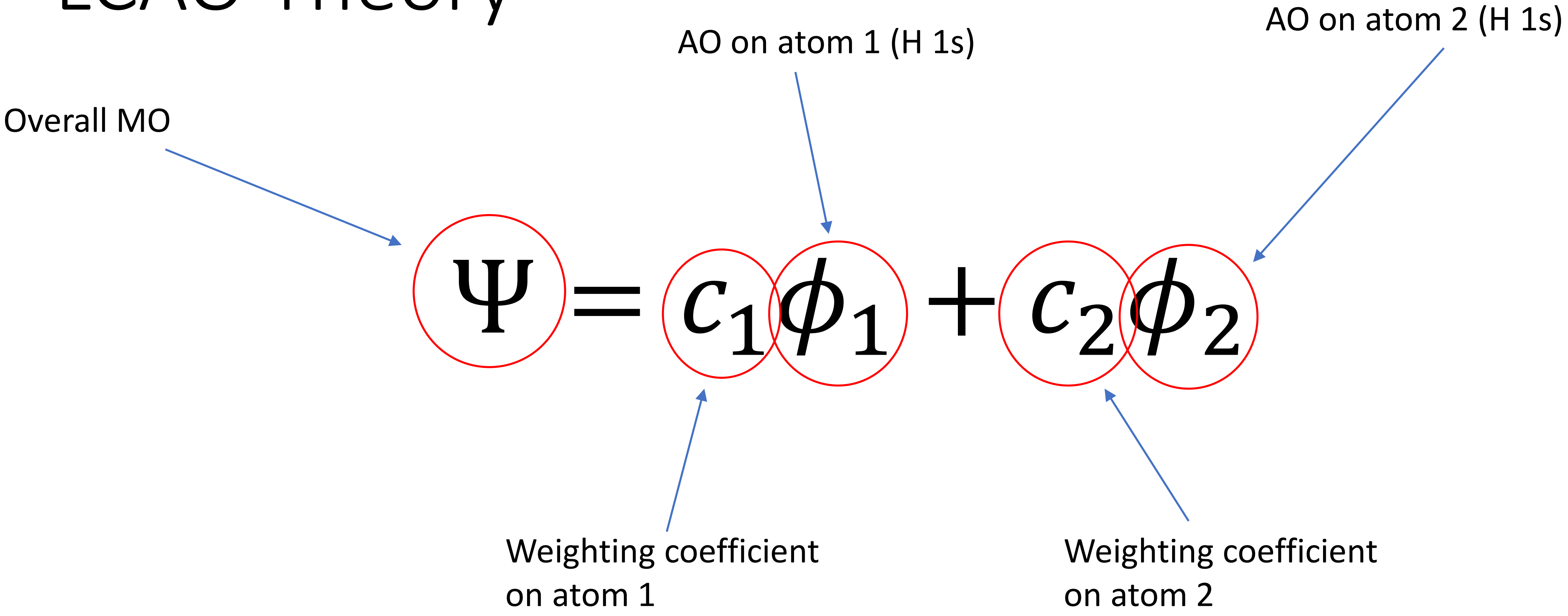
- To understand how we can make a molecular orbital.
- To understand the **LCAO method**.
- To make a molecule!

LCAO Theory

- Construct an MO (Ψ) as a linear combination of AOs (ϕ).
- We already know how to get AOs – hydrogenic wavefunctions.
- For H_2^+, two atoms, so:

$$\Psi = c_1\phi_1 + c_2\phi_2$$

LCAO Theory



$$\Psi = c_1\phi_1 + c_2\phi_2$$

Overall MO

AO on atom 1 (H 1s)

AO on atom 2 (H 1s)

Weighting coefficient
on atom 1

Weighting coefficient
on atom 2

Weighting coefficients tell you how much each AO contributes to the total MO. **What are the coefficients?**

LCAO Theory

$$\Psi = c_1\phi_1 + c_2\phi_2$$

- Electron density ρ is given by the square of the wavefunction.

$$\rho \propto \Psi^2$$

- H_2^+ and other homonuclear diatomics are symmetrical, so:

$$\rho_{atom\ 1} = \rho_{atom\ 2}$$ ← Otherwise the molecule would be polar

$$(c_1\phi_1)^2 = (c_2\phi_2)^2$$

$$c_1^2 = c_2^2$$ ← Because $\phi_1 = \phi_2$ (both are H 1s orbitals)

$$\boldsymbol{c_1 = \pm c_2}$$

i.e. $\boldsymbol{c_1 = c_2}$ **or** $\boldsymbol{c_1 = -c_2}$

LCAO Theory

$$\Psi = c_1\phi_1 + c_2\phi_2$$

- So two options for our overall MO:

$$\Psi^{+} = c\phi_1 + c\phi_2$$
$$\Psi^{-} = c\phi_1 - c\phi_2$$

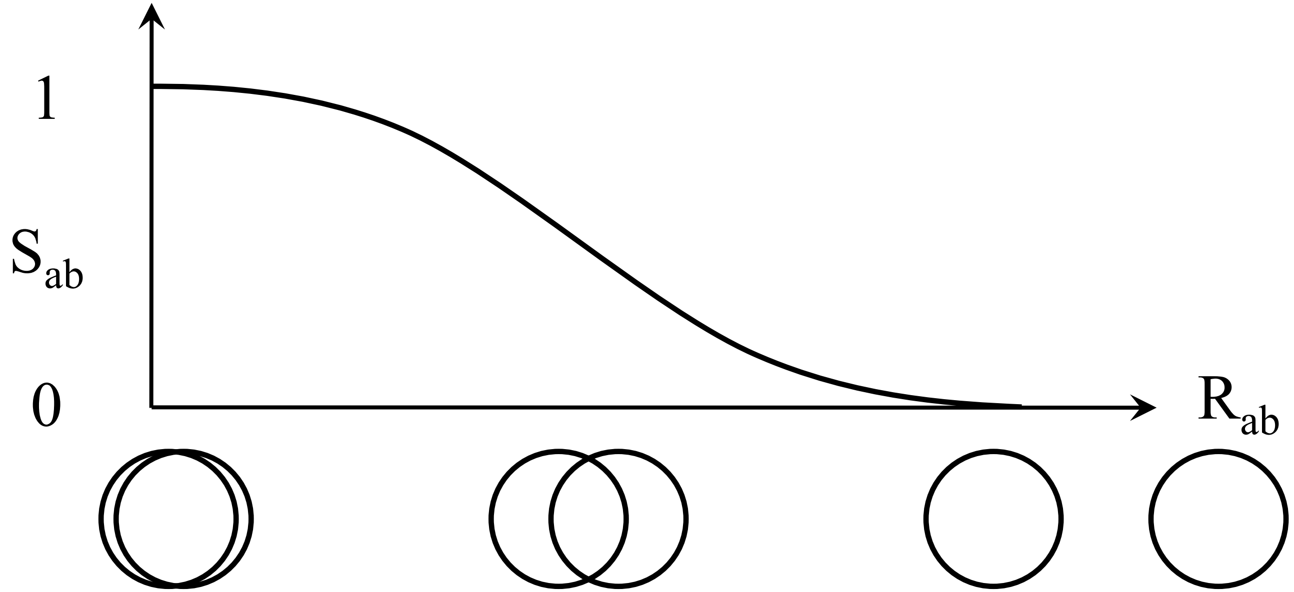
Dropping the subscripts because they are the same atom

- *<u>Nice</u>* – two AOs combine to give two different MOs.
  - Just like we learned in first year. **What is c?**

- Via normalisation, find: $c = \sqrt{\frac{1}{2(1 \pm S_{12})}}$

Overlap integral

Overlap Integral



R_{ab} = 0; S_{ab} = 1
perfect overlap
(but physically impossible due to repulsion between the nuclei)

R_{ab} = 106 pm; S_{ab} = 0.59

at H_2^+ bond length

R_{ab} = big; S_{ab} = 0

no overlap & no bond

LCAO Theory

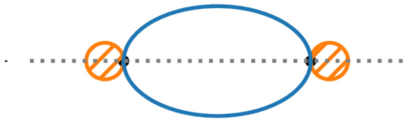
$$\Psi^{+} = \frac{\phi_1+\phi_2}{2(1+S_{12})}$$

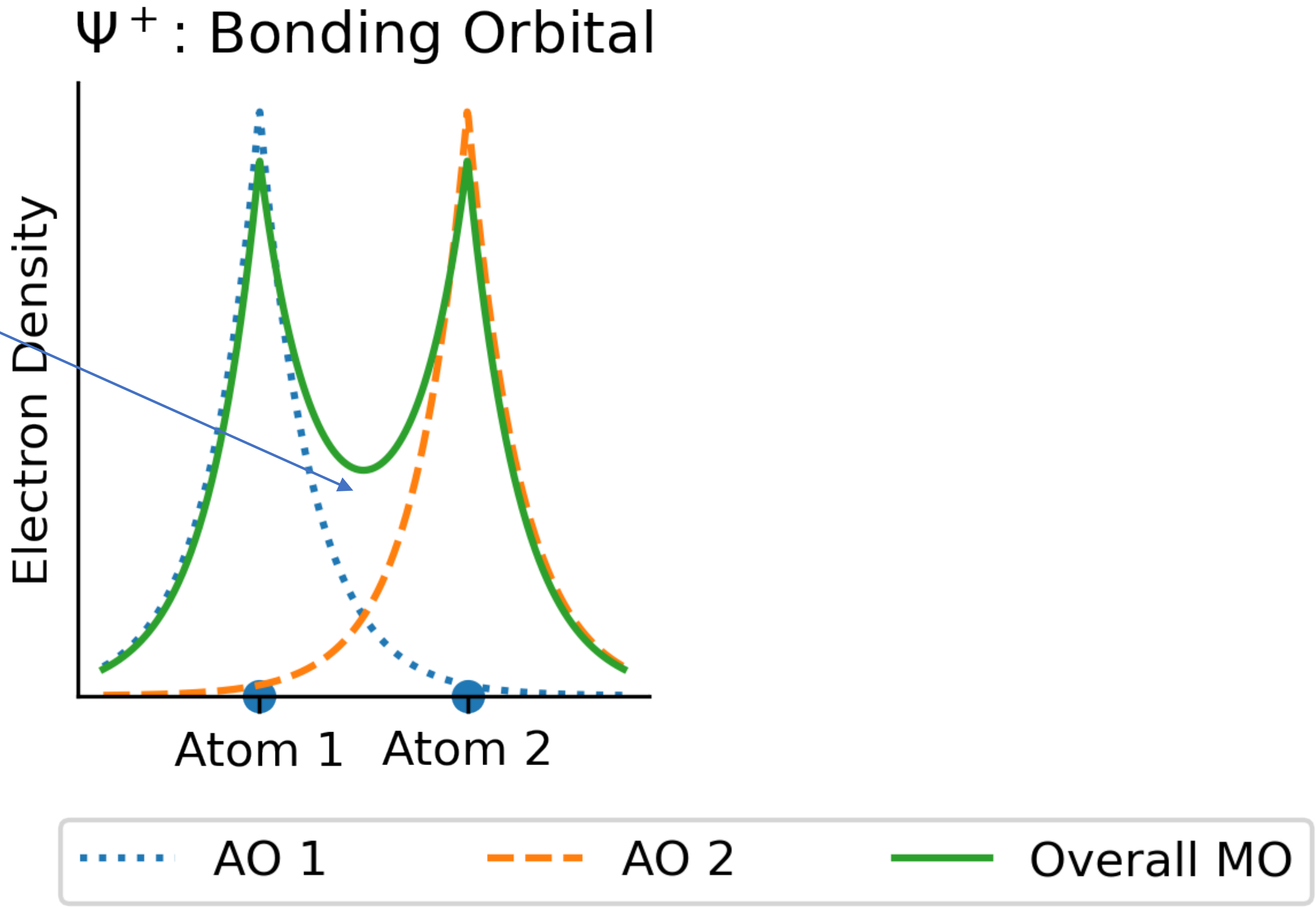
$$\Psi^{-} = \frac{\phi_1-\phi_2}{2(1-S_{12})}$$

This tells us nothing, let’s make a graph, taking a simple 1s orbital, with the form $\phi \propto e^{-r}$ as an example…

$$\Psi^{+} = \frac{\phi_1+\phi_2}{2(1+S_{12})}$$

Electron density
concentrated
between atoms
and reduced
outside them:
bonding orbital

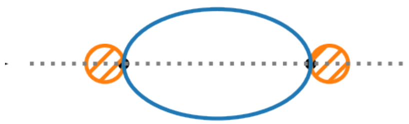


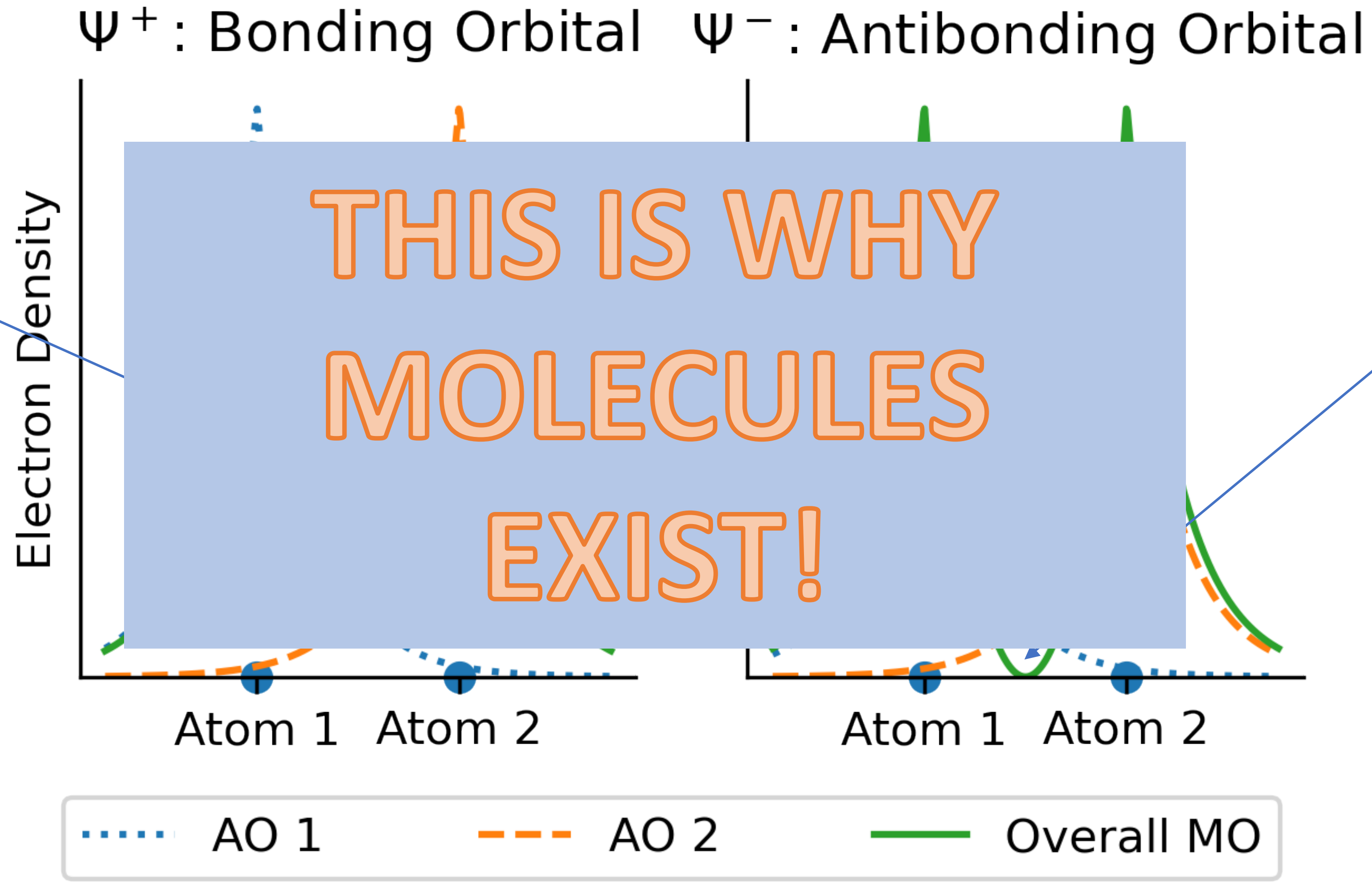


The concentration of electron density *between* nuclei is the <u>essence</u> of chemical bonding.

$$\Psi^{+} = \frac{\phi_1+\phi_2}{2(1+S_{12})} \qquad \Psi^{-} = \frac{\phi_1-\phi_2}{2(1-S_{12})}$$

Electron density concentrated between atoms and reduced outside them: **bonding orbital**





THIS IS WHY MOLECULES EXIST!

Electron density reduced between atoms and increased outside them: **antibonding orbital**

Mutual attraction of many nuclei to the electron density between them holds molecules together.

That was exciting! So what are the MO energies?

- Umm... LCAO wavefunctions don’t solve the SE.
  - Damn.

- But we can find the **expectation value** of the energy.
  - Like the value it has ”on average”.

- Doing the maths (ask for details):

$$E^{\pm} = \frac{\alpha \pm \beta}{1 \pm S_{12}}$$

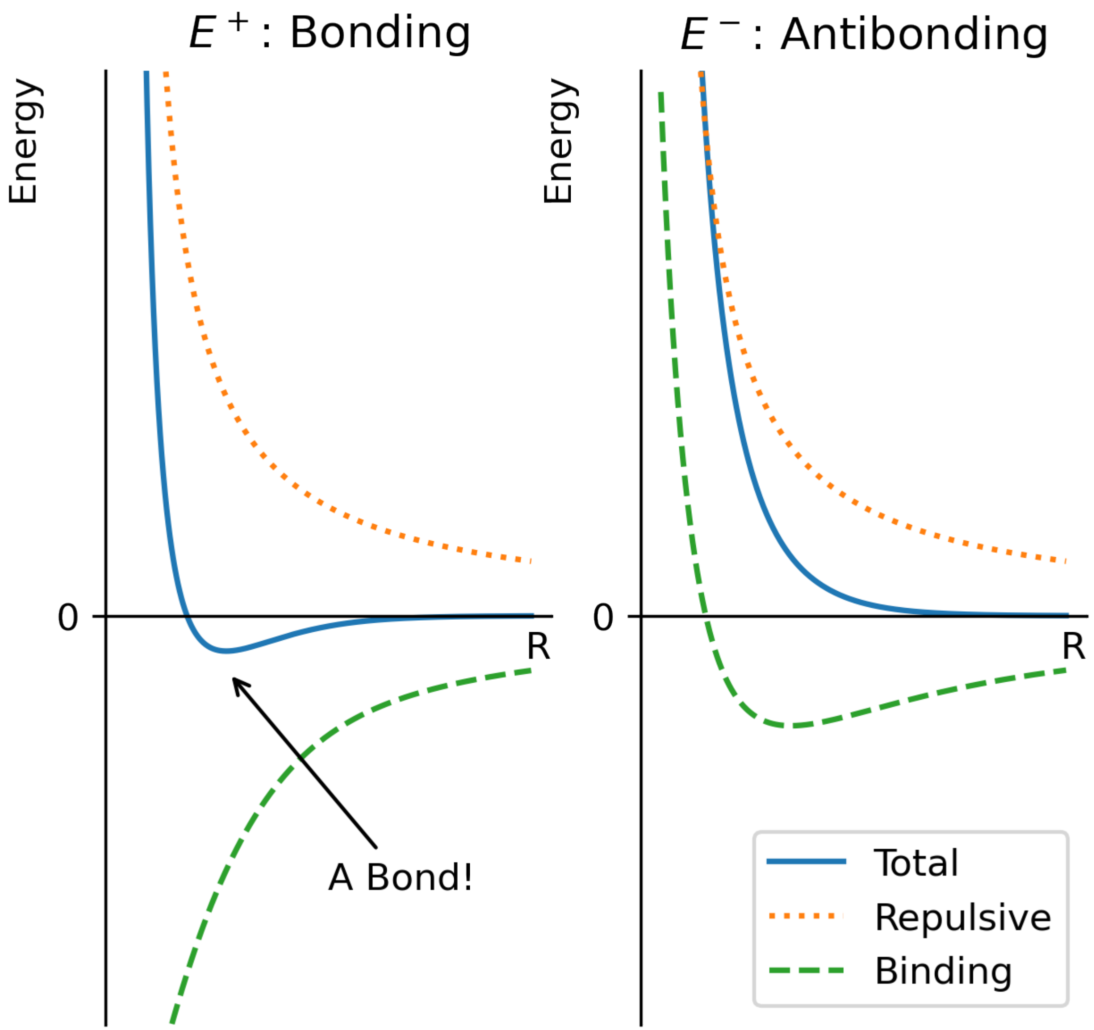
Energies

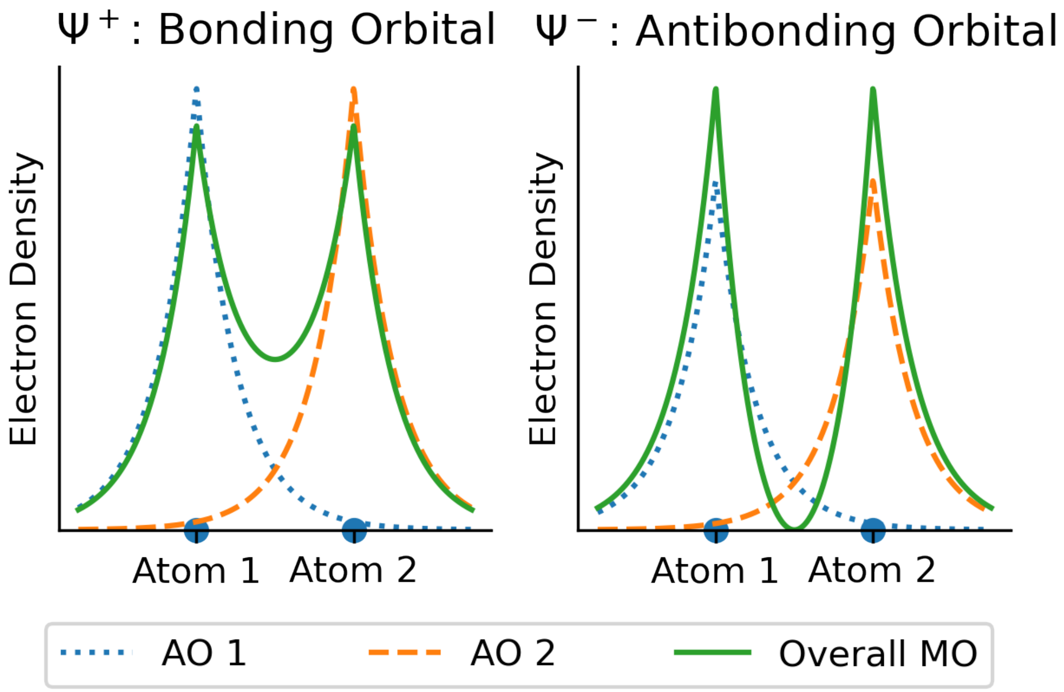
Coulomb integral: energy of electron on atom 1, but in the presence of atom 2

$$E^{\pm} = \frac{\alpha \pm \beta}{1 \pm S_{12}}$$

Resonance integral: interaction energy between the nuclei and the **overlap electron density.**

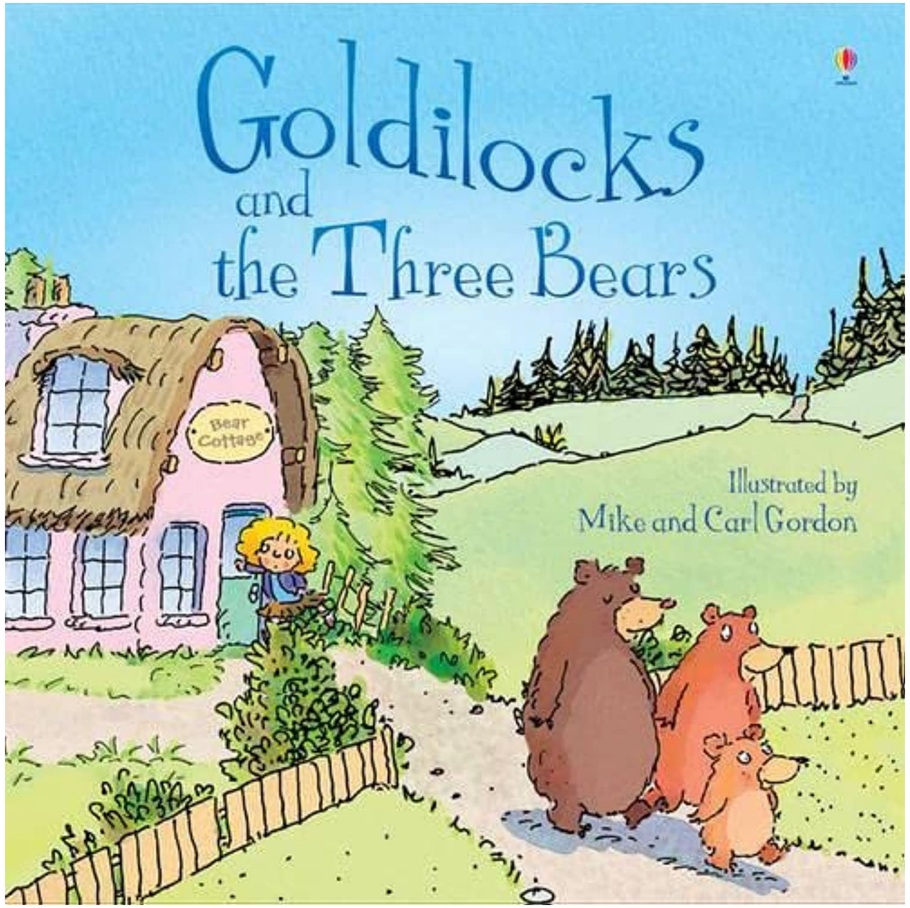
Overlap integral: degree of orbital overlap between atom 1 and 2


E^+: Bonding
E^-: Antibonding
Energy
Energy
0
0
R
R
A Bond!
Total
Repulsive
Binding

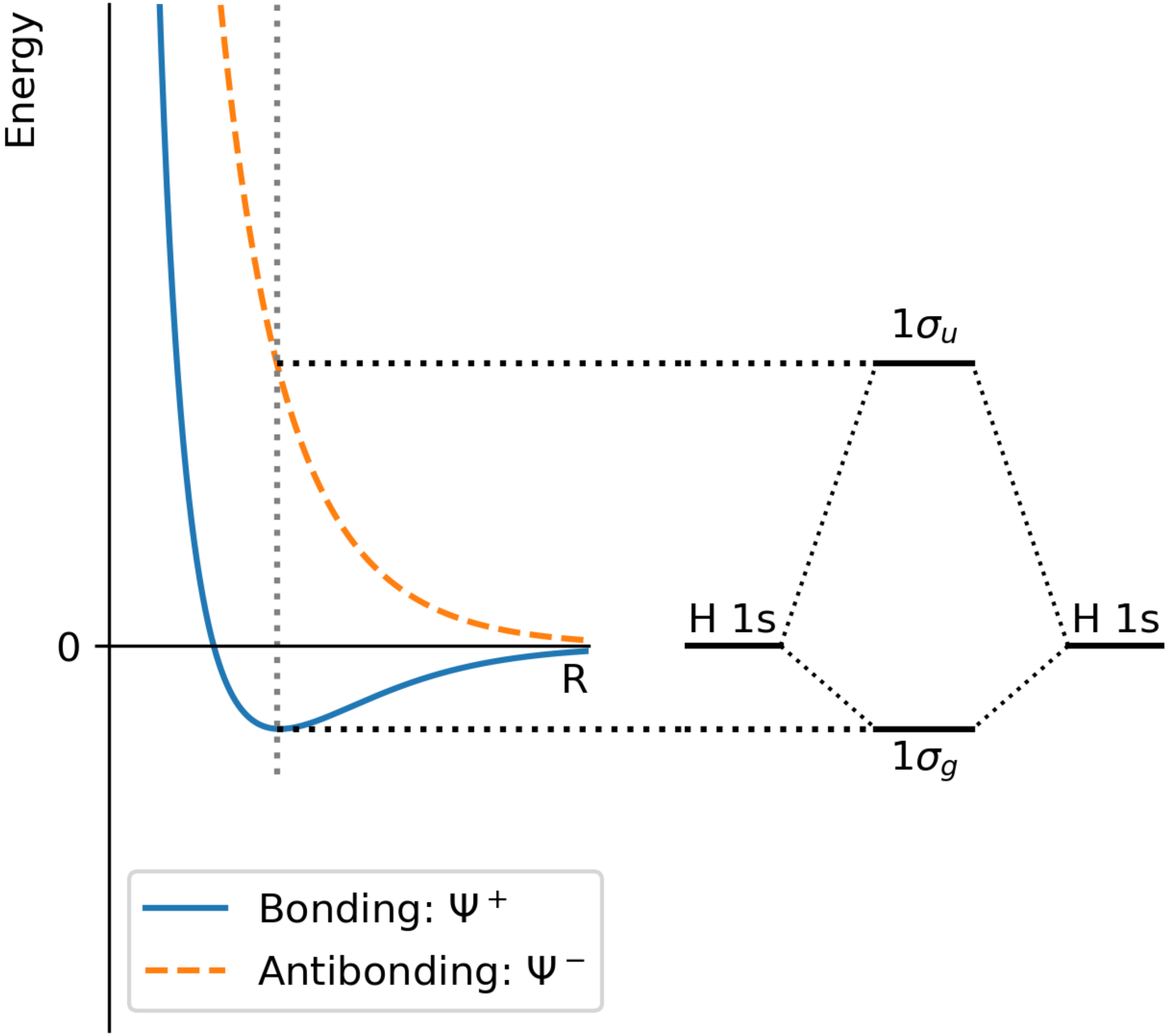

Ψ^+: Bonding Orbital
Ψ^-: Antibonding Orbital
Electron Density
Electron Density
Atom 1
Atom 2
Atom 1
Atom 2
AO 1
AO 2
Overall MO

Energies in Chemical Bonding

- Attraction of nuclei to overlap density: **good, stabilising.**
- Repulsion of nuclei from each other: **bad, destabilising.**
- Three regimes:
    - **Large internuclear separation**: low repulsion, and low attraction.
    - **Small internuclear separation**: high repulsion, high attraction (but repulsions dominate).
    - **”Just right” separation**: attractions outweigh repulsions.



MO Diagram for H_2^+

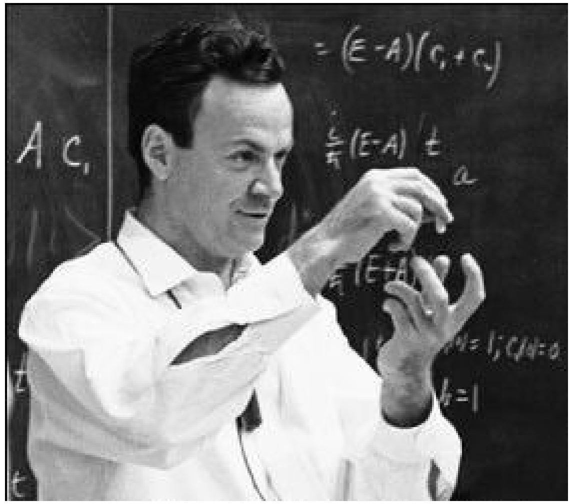


Summary

- Under the BOA, we can describe chemical bonding using LCAO methods.
- Wavefunctions interfere destructively and constructively to give bonding and antibonding MOs.
- **The existence of chemical bonds is a quantum mechanical phenomenon!**

‘Nature isn’t classical, dammit. If you want a make a simulation of nature, **you’d better make it quantum mechanical, and by golly it’s a wonderful problem,** because it doesn’t look so easy.’

– Richard P Feynman



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Next time: MO theory

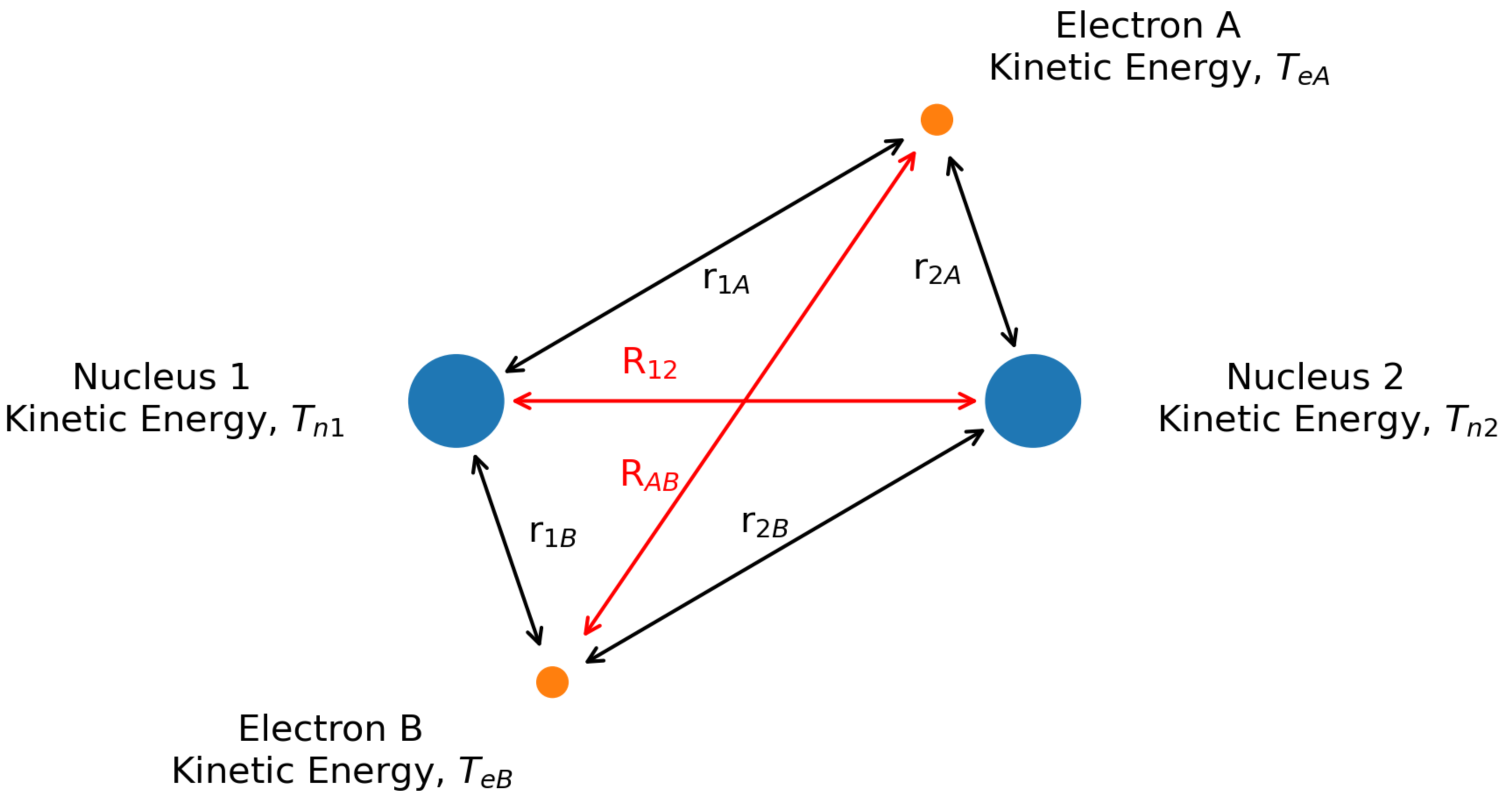
Session 11: MO Theory

CH2203 Physical Chemistry

Aims

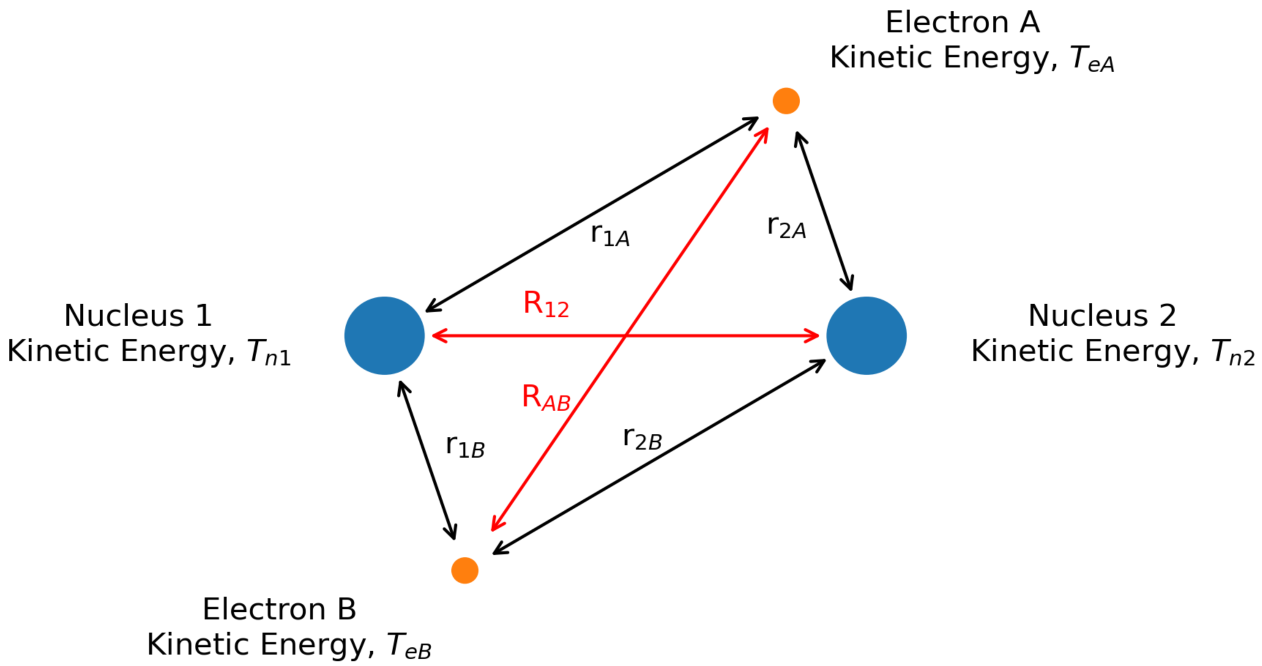
- LCAO theory for multi-electron systems.
- Construction of molecular orbitals.
- MO diagrams for simple diatomics.

Hydrogen


Electron A
Kinetic Energy, T_{eA}
r_{1A}
r_{2A}
R_{12}
Nucleus 1
Kinetic Energy, T_{n1}
Nucleus 2
Kinetic Energy, T_{n2}
R_{AB}
r_{1B}
r_{2B}
Electron B
Kinetic Energy, T_{eB}

(Electronic) Hamiltonian

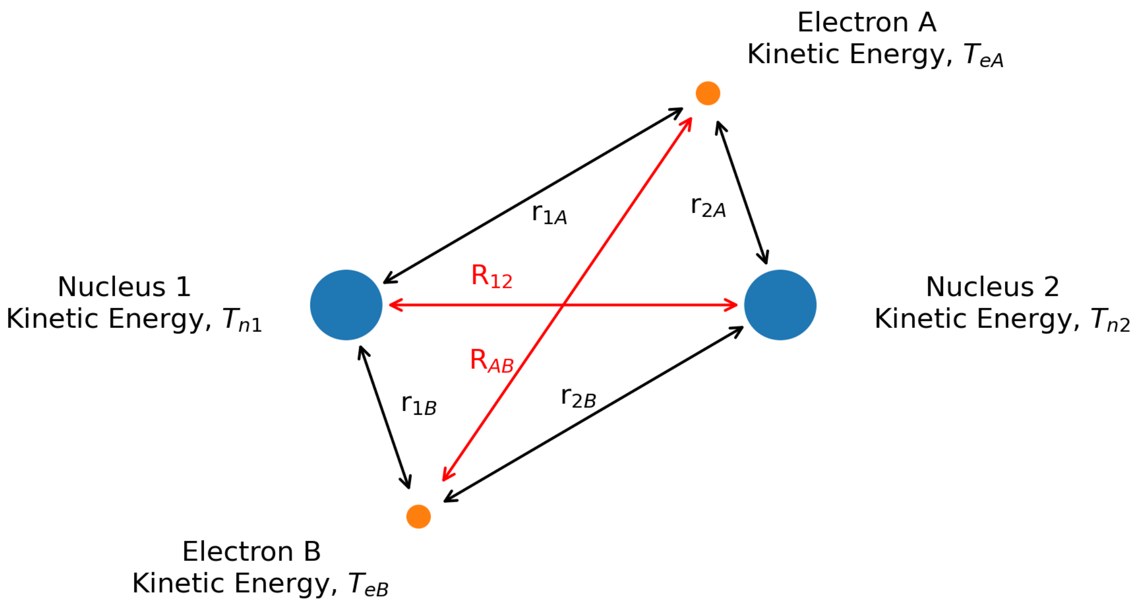
- $\hat{H} = -\frac{1}{2}\nabla_{e1}^2 - \frac{1}{2}\nabla_{e2}^2 - \frac{1}{r_{1A}} - \frac{1}{r_{2A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2B}} + \frac{1}{R_{12}} + \frac{1}{R_{AB}}$



$$\hat{H} = -\frac{1}{2}\nabla_{e1}^2 - \frac{1}{2}\nabla_{e2}^2 - \frac{1}{r_{1A}} - \frac{1}{r_{2A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2B}} + \frac{1}{R_{12}} + \frac{1}{R_{AB}}$$

What now?

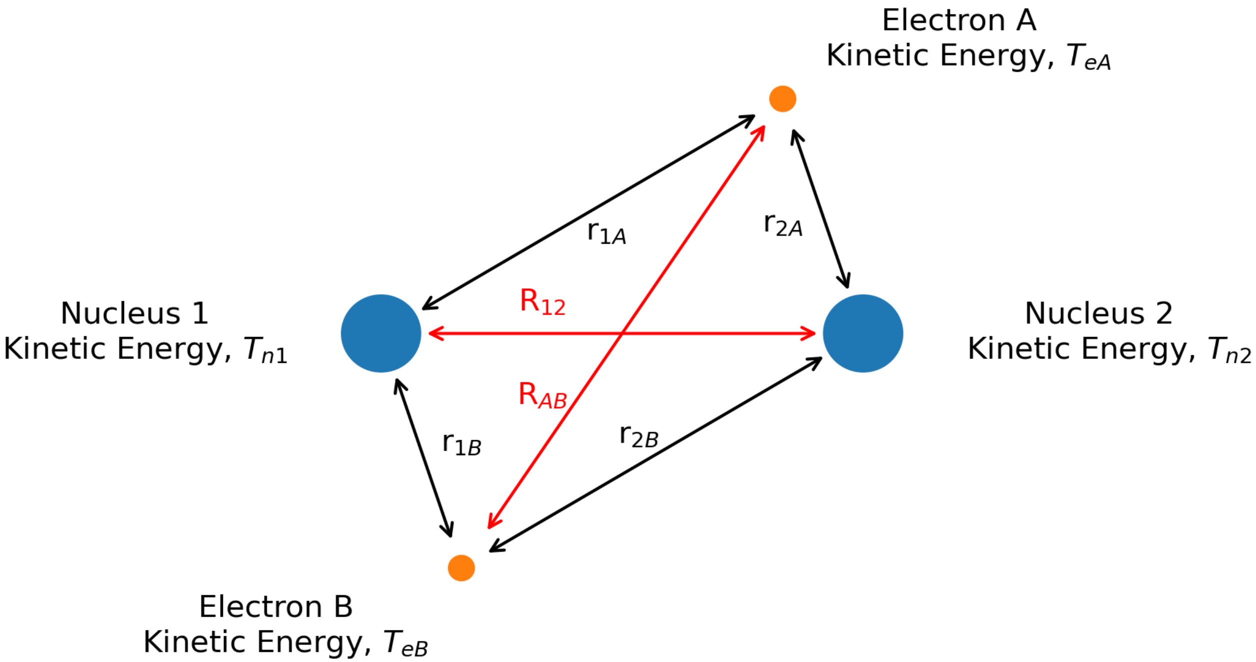
- Still got the electron repulsion issue. How can we progress?
  - Quantitatively - using computational methods.
  - Can we progress *qualitatively*? To get an intuitive feel for the chemistry?



$$\hat{H} = -\frac{1}{2}\nabla_{e1}^2 - \frac{1}{2}\nabla_{e2}^2 - \frac{1}{r_{1A}} - \frac{1}{r_{2A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2B}} + \frac{1}{R_{12}} + \frac{1}{R_{AB}}$$

What now?

- LCAO theory was nice, simple – gave some chemical insight.
  - How can we extend it to bigger molecules? **Basis sets**.



Basis Sets

- To describe H_2 – use two H 1s AOs.
  - This is our **basis set**.

$$\Psi = c_1\phi_1 + c_2\phi_2$$

- Build MOs by mixing together parts of the basis set.

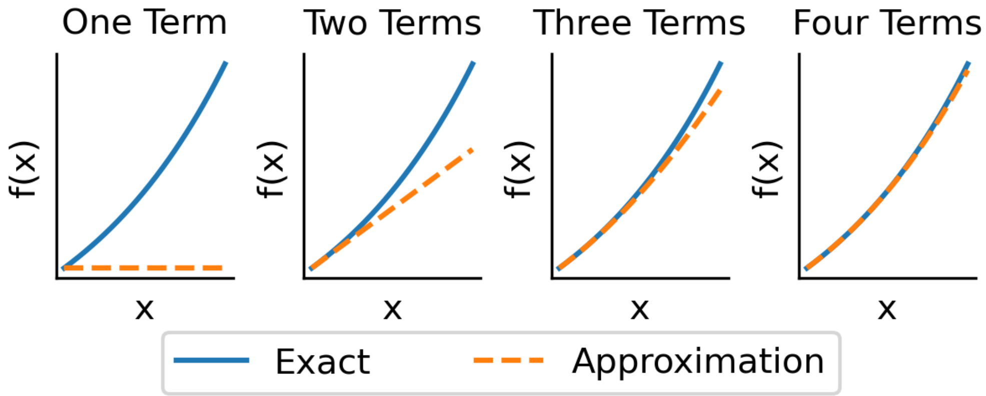
- We can get a more accurate MO by adding more functions to the basis set.

Basis Sets

- Familiar – think about co-ordinates.
    - 2D – need two. 3D – need three, etc..

- Common mathematical technique – expanding complex functions as a sum of simpler ones:

$$e^x = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots$$



Basis Sets for Bonding

- Take more AOs into our MO:

$$\Psi = c_1\phi_1 + c_2\phi_2 \xrightarrow{\hspace{4em}} \Psi = \sum_{i}^{n} c_i\phi_i$$

Basis Sets for Bonding

- More AOs = better. But expensive.
  - What’s the minimum number we need?
    - **Minimum basis set –** the smallest basis set that captures the key behaviour.

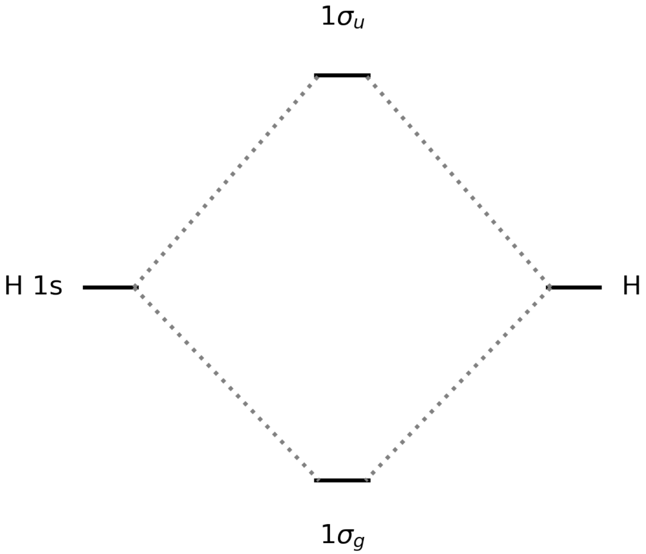
$$\Psi = c_1\phi_1 + c_2\phi_2 \longrightarrow \Psi = \sum_{i}^{n} c_i\phi_i$$

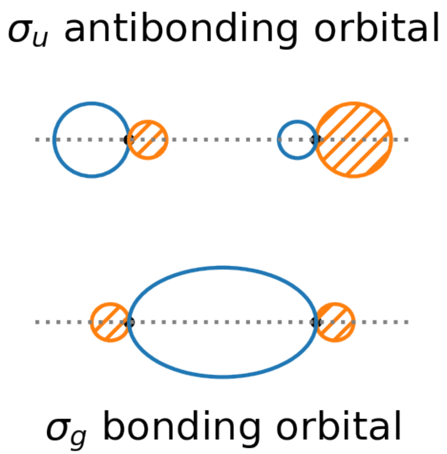
Minimum Basis Set

- For hydrogen/helium – H 1s AOs.
  - These are the orbitals that contain the electrons involved in bonding.

- How do we form the MOs given this basis set?
  - We saw this before – combining the two AOs into two MOs.

- Leads to:





Using MO Diagrams

- Why is H_2 found as a diatomic gas, but He found as a monatomic gas?
- Why is the bond length of the H_2^+ ion longer than that of the H_2 neutral?
- Would you expect He_2^+ to be bound or unbound?
- Would you expect the bond length of the hydrogen molecular anion to be longer or shorter than the neutral molecule?

You can answer all these questions using the MO diagrams, which are derived using QM ☺

Take Home Messages

- We can use LCAO theory to describe simple bonding.
- The basis set used determines how accurate the approximation is – minimum basis set lets us rationalise simple chemistry.
- **Do problem set 3!**

Next time: Problems 3

Session 12: Problems 3

CH2203 Physical Chemistry

Session 13: First Row Diatomics

CH2203 Physical Chemistry

Aims

- Apply LCAO/MO to the first row of the periodic table.

- Symmetries of molecular orbitals.

- MO diagrams for the first row.

Recap

- Build MOs out of AOs (LCAO approximation).

- More AOs in the MO improves the approximation.
  - And the difficulty of the calculation!

$$\Psi = c_1\phi_1 + c_2\phi_2 \longrightarrow \Psi = \sum_{i}^{n} c_i\phi_i$$

First Row Diatomics

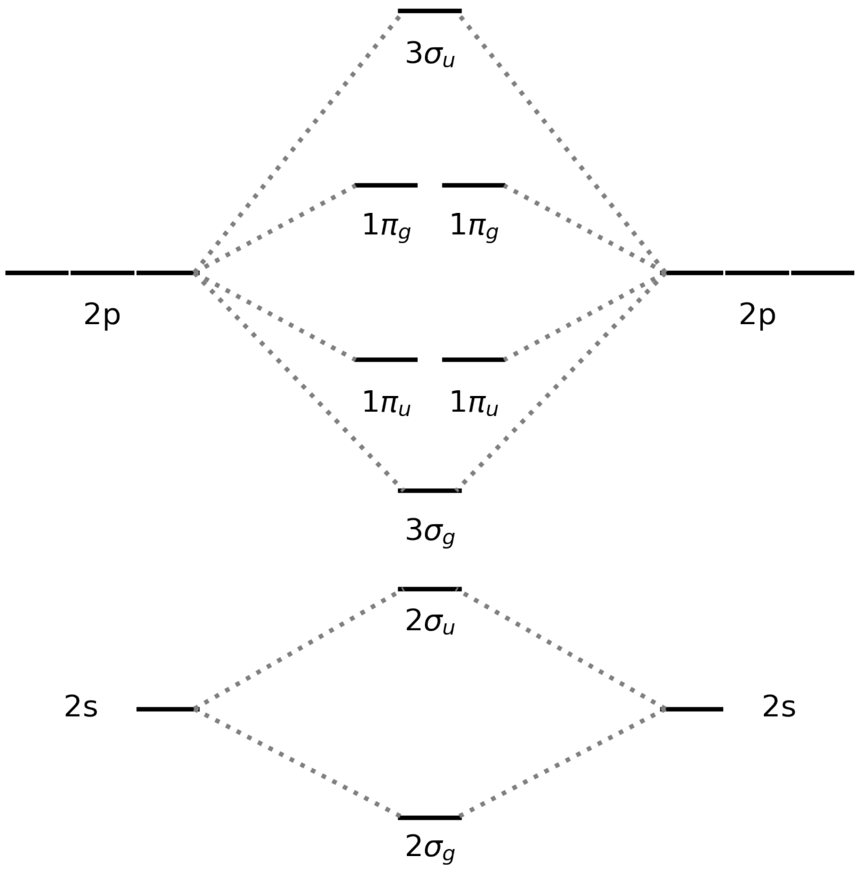
- Li_2 to F_2
- What is the minimum basis set?
  - **Valence orbitals**
- Core orbitals don’t really affect bonding and structure.
  - But you’d need to include them to accurately model the total energy of the molecule

Forming MOs

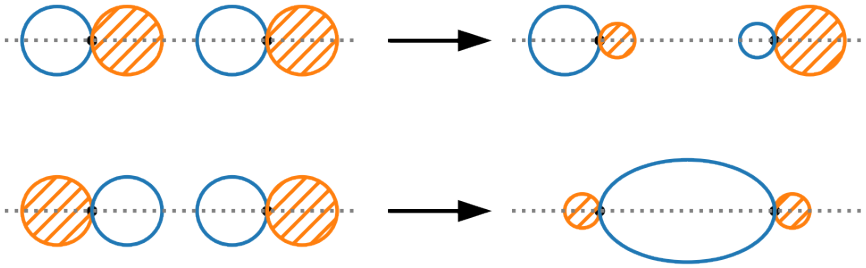
- Rule 1: Energy
  - AOs must be of similar energy to overlap and form bonding MOs.

- Rule 2: Symmetry
  - AOs must have the correct symmetry to overlap.

- Rule 3: Space
  - AOs need to actually be near each other in space to overlap.



Orbital Symmetry

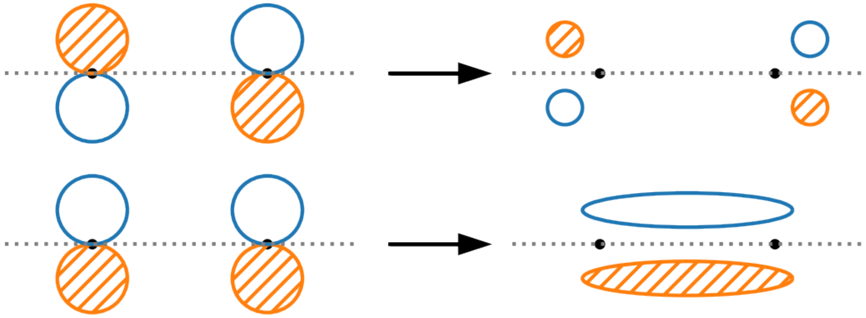


p-orbitals
(end-on, out of phase)

σ_u antibonding orbital

p-orbitals
(end-on, in phase)

σ_g bonding orbital



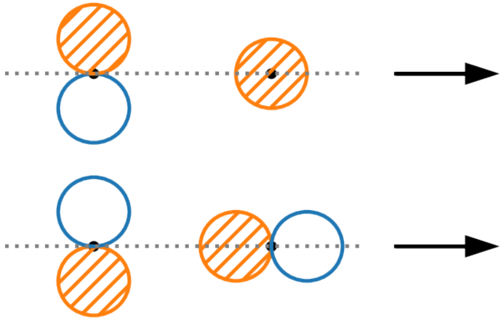
Two p-orbitals
(side-on, out of phase)

π_g antibonding orbital

Two p-orbitals
(side-on, in phase)

π_u bonding orbital

s- and p-orbital (side on)



$$\int \phi_A \phi_B \, d\tau = 0$$

$\therefore$ no bonding

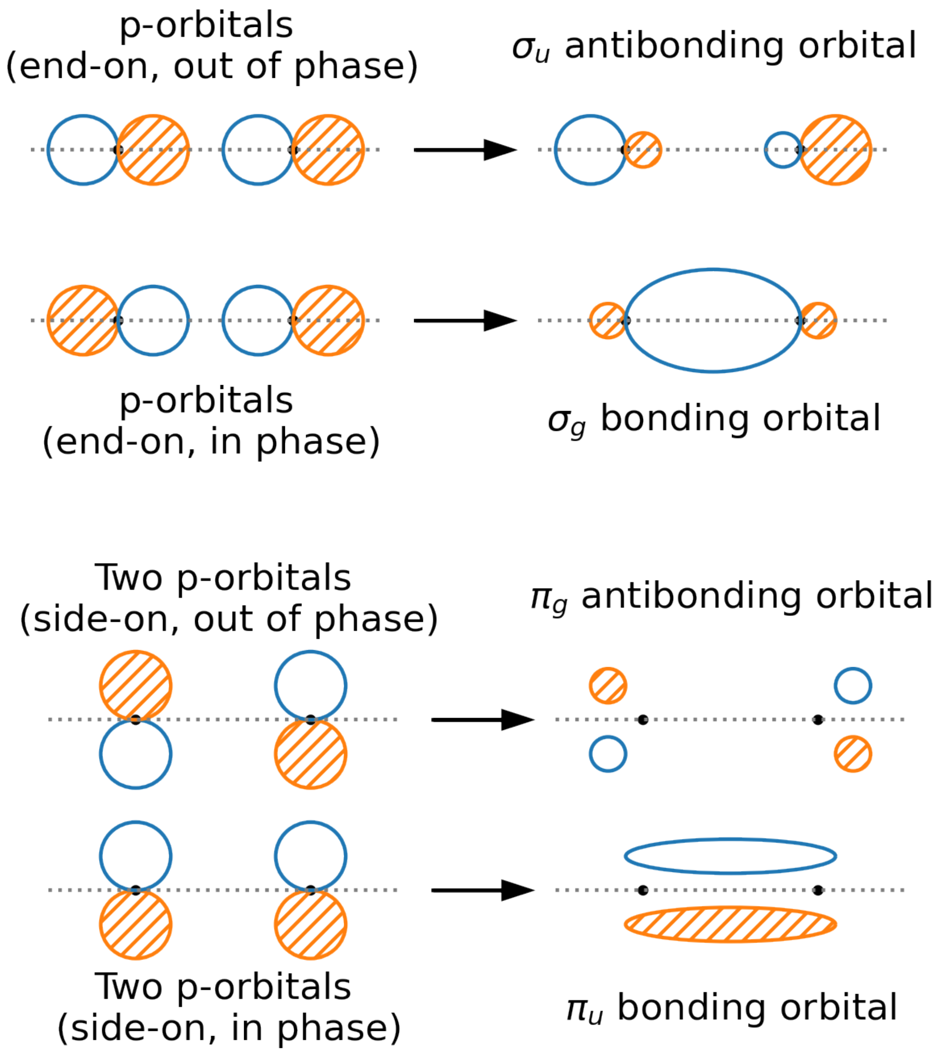
Orthogonal p-orbitals

Naming MOs (1)

- Symmetry around bond axis.

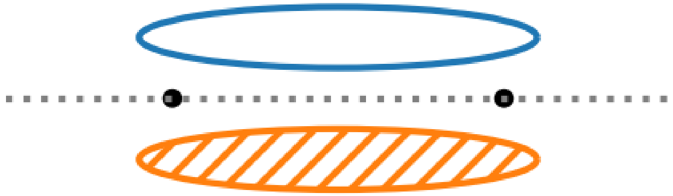
- Angular nodes:
  - 1 = σ (s)
  - 2 = π (p)
  - 3 = δ (d)
  - Etc

<ins>Group theory note</ins>: these are the same as the symmetries of irreps in the linear point groups. The label for the MO is just a symmetry label – telling you how the MO transforms under the operations of the point group.



Naming MOs (2)

- Inversion symmetry through centre of molecule.
- If there is inversion symmetry:
  - Label as ”g” (gerade – even)
- If there is not:
  - Label as ”u” (ungerade – odd)

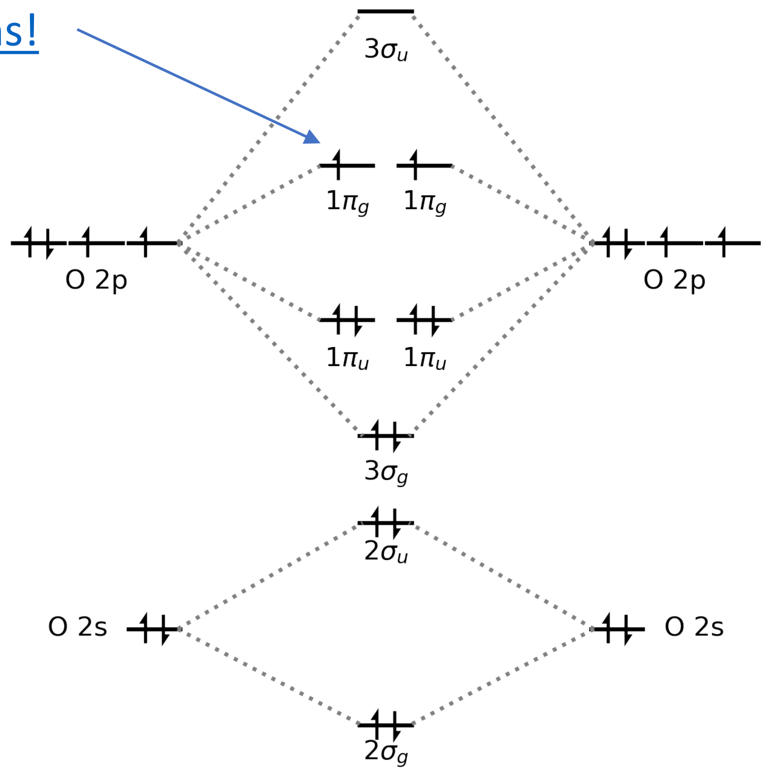

π_u orbital


π_g orbital

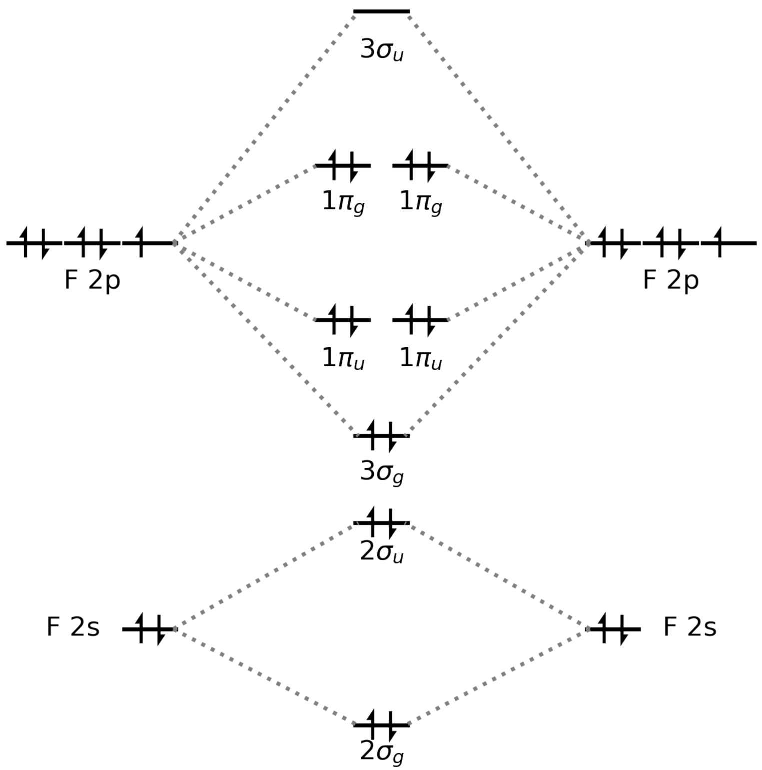
Important Point

- These labels **are just symmetry labels**.
- They do not tell you **anything** about the energy or bonding/antibonding character of the orbital.
- They tell you about the symmetry of the orbital in the point group of the molecule.
  - Strictly – the symmetry of the spatial part of the wavefunction (remember an MO is just a wavefunction of an electron in a molecule).

Oxygen and Fluorine

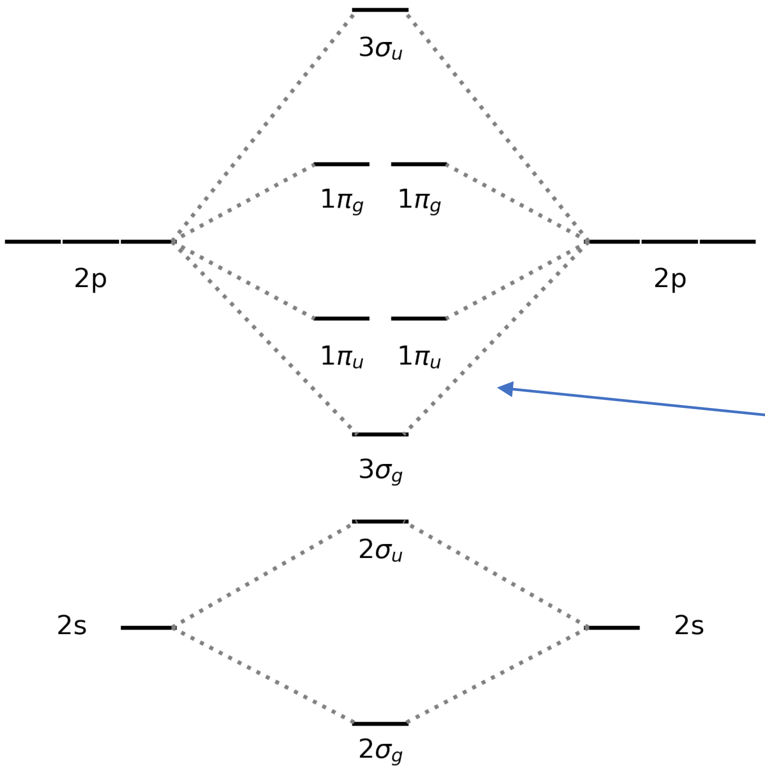


Unpaired Electrons!



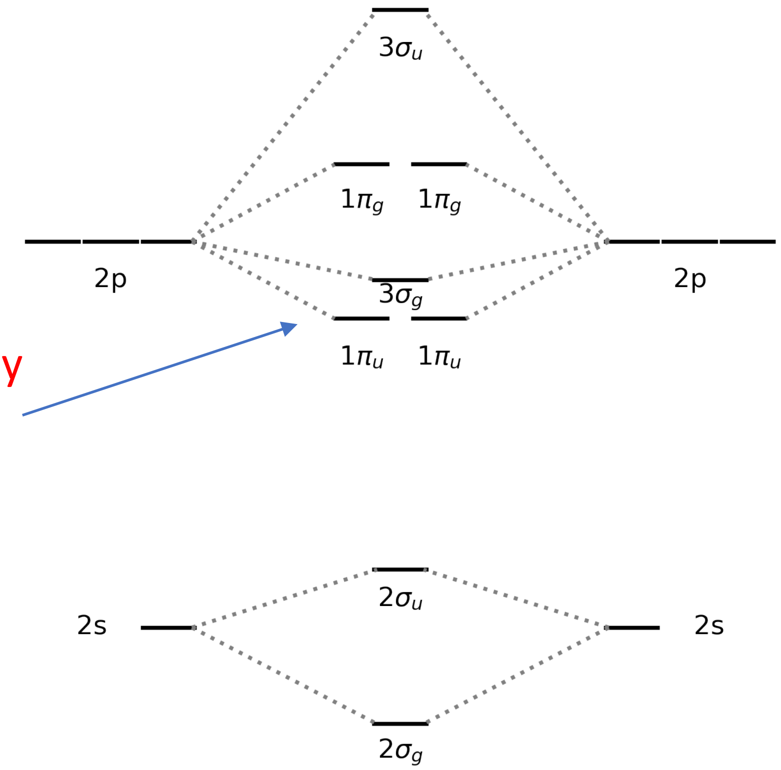
Bond order?

First Row Diatomics (heavy vs light)



Heavy diatomics
(oxygen, fluorine)

Note the energy ordering has changed!



Light diatomics
(everything else)

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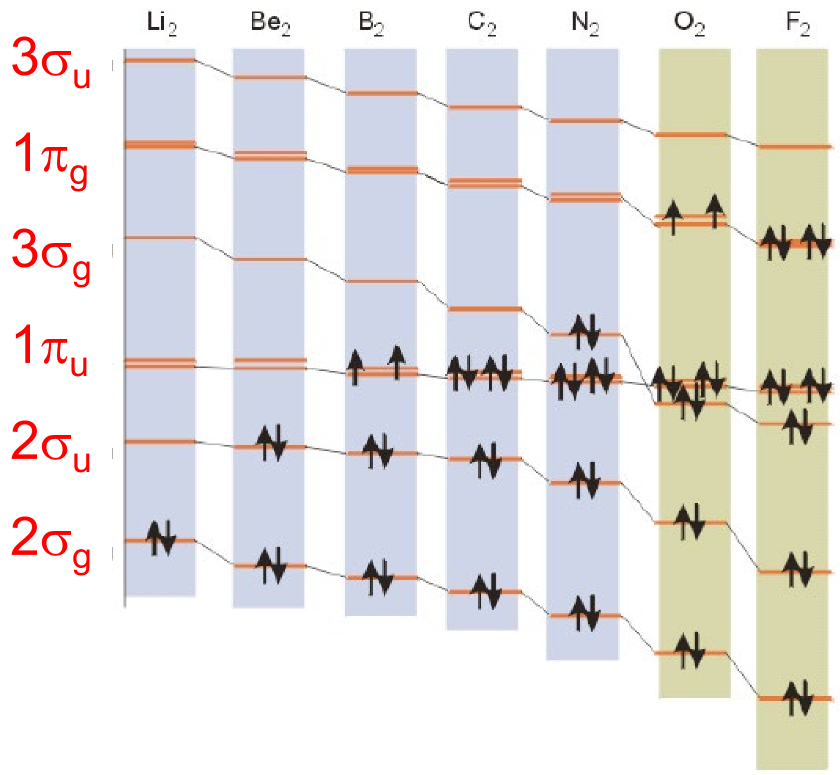
s-p Mixing

- Energy gap between 2s and 2p reduces from fluorine to lithium.
- So s and p can mix, contributing to the MOs with σ symmetry.
- This means: 3σ rise in energy, 2σ fall.
    - Relative to what they would do in absence of mixing.



Using MO diagrams

- Does nitrogen gas or fluorine gas have a higher bond enthalpy?
- Why is liquid oxygen blue, but liquid nitrogen colourless?
- Explain why diatomic boron is paramagnetic.
- Would the diatomic carbon anion have a larger or smaller bond length than the neutral? What about the cation?

Summary

- LCAO theory is improved by increasing the **basis set size**.

- To form MOs: Energy, Symmetry, Location (size).
  - A much more detailed description of bonding.

- s-p mixing is important for lighter diatomics.
  - It’s all just orbital overlap, nothing magical!

That’s It!

- For the lectures.

- Coming up – problem set 4 and extended problems 2, then revision.

- **Make sure you do the problems**. It is the only way to learn this stuff.
  - You can’t learn to ride a bike by watching someone else ride a bike.

Session 14: Problems 4

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Session 15: Extended Problems 2

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