The Hydrogen Atom

Schrodinger Equation:

We consider the Hamiltonian for a single electron...

$$\Psi(r,\theta,\phi) = \psi_r \; \psi_\theta \; \psi_\phi$$

"Schrödinger $\implies$ 3 ODEs $\implies$ 3 Quantum Numbers"

$$E_n = -\frac{\mu Z^2 e^4}{2k^2 h^2 n^2} \qquad r_{\text{bohr}} = \frac{n^2 a_0}{Z}$$

$$a_0 \approx 0.529 \text{ Å}$$

Quantum Numbers:

Principle: n Azimuthal: ℓ Magnetic: m_ℓ

$n = 1, \; 2, \; \ldots$ $0 \leqslant \ell < n$ $-\ell \leqslant m_\ell \leqslant +\ell$

"m_ℓ from ϕ with periodic boundaries, ℓ from θ with ℓ^{th} derivative, and n from r with a factorial restriction"

Reduced Mass:

To treat the nucleus as stationary we use reduced mass...

$$\frac{1}{\mu} = \frac{1}{m} + \frac{1}{M}$$

Degenerate States:

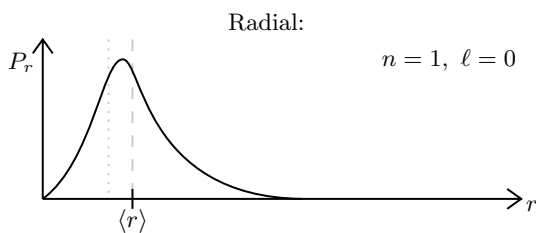*"Multiple states with the same energy"*

$$||\ell|| = n \qquad ||m_\ell|| = 2\ell + 1$$

Probability Density Distributions: *"Shape"*
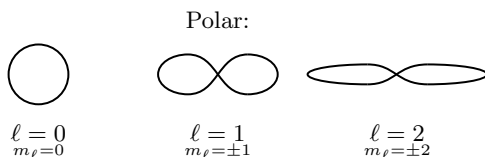
Radial:

$n = 1, \; \ell = 0$

$$\langle r \rangle = \int_0^\infty r P_n^\ell(r)\, dr = \frac{n^2 a_0}{Z}\left[1 + \frac{1}{2}\left(1 - \frac{\ell(\ell+1)}{n^2}\right)\right]$$

"n increases the radius and energy, with ℓ changing the shape"

Azimuthal:

$$P(\phi)\, d\phi \equiv A^2\, d\phi$$

"Rotationally symmetric about the z-axis"

Polar:

$\ell = 0$ $\ell = 1$ $\ell = 2$
$m_\ell = 0$ $m_\ell = \pm 1$ $m_\ell = \pm 2$

"m_ℓ changes the shape in θ and squishes the curve to x-y"

Angular Momentum:

$$\langle \ell_z \rangle = m_\ell \hbar \qquad \langle \underline{\ell}^2 \rangle = \ell(\ell+1)\hbar^2$$

$$\ell_z = m_\ell \hbar \qquad |\underline{\ell}| = \sqrt{\ell(\ell+1)}\,\hbar$$

Commutator Relations:

$$[\ell_x, \ell_y] = i\hbar \ell_z \qquad [\ell_z, \underline{\ell}^2] = 0$$

Electron Spin:

We introduce a generalised spin operator $\underline{\mathbf{j}}$, which has quantum numbers...

$$2j \in \mathbb{Z} \qquad -j \leqslant m_j \leqslant +j$$

j can be integer or 1/2-integer

From this we introduce spin $\underline{\mathbf{s}}$, where an electron has...

$$s = \frac{1}{2} \qquad m_s = \pm \frac{1}{2}$$

Spin

"Spin s is fixed for a given particle, however, m_s can vary"

Spin-Orbit Interactions: *"LS Coupling"*

The electron has an innate magnetic dipole due to the spin which interacts with the internal magnetic field generated by orbiting the charged nucleus. This changes the energy...

$$E_n^j = -\frac{\mu Z^2 e^4}{2k^2 h^2 n^2}\left[1 + \frac{\alpha^2}{n}\left(\frac{1}{j+1/2} - \frac{3}{4n}\right)\right]$$

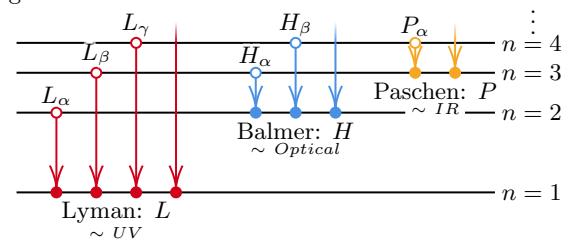*"ℓ and s are now coupled and no longer quantised in z"*

Total Angular Momentum:

$$\underline{\mathbf{j}} = \underline{\boldsymbol{\ell}} + \underline{\mathbf{s}} \qquad j = \begin{cases} \ell \pm 1/2, \; \ell > 0 \\ 1/2, \qquad \ell = 0 \end{cases}$$

Atomic State Transitions

"Electrons emit photons when transitioning between levels"

Hydrogen Transitions:

Selection Rules:

$$\Delta n \text{ is unrestricted}$$

$$\Delta \ell = \pm 1 \qquad\qquad \Delta j = 0, \pm 1$$

$$\Delta m_\ell = 0, \pm 1 \qquad\qquad \Delta m_j = 0$$

Multi-Electron Atoms

Pauli's Exclusion Principle:

"No two fermions can occupy the same quantum state"

Element Notation:

$$^A_Z \mathrm{X}$$

Z : *Atomic Number* (Protons) A : *Mass Number* (Protons+Neutrons)

Spectroscopic Notation:

$$n\ell^e$$

ℓ : s^2 p^6 d^{10} f^{14} $\cdots$
     0   1   2   3

Madelung's Rule:

$1s$
$2s$ $2p$
$3s$ $3p$ $3d$
$4s$ $4p$ $4d$ $4f$
$5s$ $5p$ $5d$ $5f$ $5g$

"This applies well to weak ions"

System Angular Momentum:

The system momentum is the sum of the individual...

$$\underline{\ell}' = \left|\sum \underline{\ell}\right| \qquad \underline{s}' = \left|\sum \underline{s}\right| \qquad \underline{j}' = \underline{l}' + \underline{s}'$$

The system quantum numbers are...

$$\ell' = \left|\sum m_\ell\right| \qquad s' = \left|\sum m_s\right| \qquad |\ell' - s'| \leqslant j' \leqslant \ell' + s'$$

Multiplicity: $2s' + 1$

Groundstate Term:

$$^{(2s'+1)}L'_{j'}$$

Hund's Rules:

"Hund's rules find the groundstate term"

> 1 - Madelung's Rules
> 2 - Distribute electrons
> 3 - Calculate the system quantum numbers ℓ' and s'
> 4 - Find j' for less $(|\ell' - s'|)$ or more $(\ell' + s')$ half full

Nobel Gases:

"Nobel Gases are stable points in electron configurations where all subshell $n \leqslant N$ are filled. Except for Helium, they end in the p subshell being full."

L'S' and J'J' Coupling:

"L'S' are simple interactions between the whole system, however, in some cases, there is a more complex interaction between individual momenta known as J'J'."

The Zeeman Effect:

Under the presence of an external magnetic field, the system's angular momentum can change the energy of quantum states...

$$\Delta E = \mu_B B g m'_j$$

Bohr Magneton: $\mu_B = \dfrac{e\hbar}{2m_e}$ *Landé g-factor*

$$g = 1 + \frac{j'(j'+1) + s'(s'+1) - \ell'(\ell'+1)}{2j'(j'+1)}$$

The Born-Oppenheimer Approximation

Born-Oppenheimer Approximation:

As Nuclei are much heavier than electrons...

- *From the perspective of the electrons, nuclei are stationary*
- *To the nuclei, the electrons react instantaneously*

Diabatic and Adiabatic Processes in Quantum Mechanics:

> *In a diabatic process, the Hamiltonian changes too rapidly for the wavefunction to react...*
>
> $$H_i \to H_f \ : \ H_i|\psi_i\rangle = E_i|\psi_i\rangle \to H_f|\psi_i\rangle \neq E_f|\psi_i\rangle$$
>
> *In an adiabatic process, the wavefunction can adjust and remains in the same eigenstate...*
>
> $$\psi_i \to \psi_f \ : \ H_i|\psi_i\rangle = E_i|\psi_i\rangle \to H_f|\psi_f\rangle = E_f|\psi_f\rangle$$

*"The electrons follow nuclei motion **adiabatically**"*

Hamiltonian:

$$H(\underline{\mathbf{r}}, \underline{\mathbf{R}}) = \sum_\mu \frac{\hbar^2}{2m_\mu}\nabla_\mu^2 - \sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 + V_{\mathrm{ne}}(\underline{\mathbf{r}}, \underline{\mathbf{R}}) + V_{\mathrm{ee}}(\underline{\mathbf{r}}) + V_{\mathrm{nn}}(\underline{\mathbf{R}})$$

"BOA: decouple the electronic and nuclear wavefunctions"

Let's simplify solving the electronic wavefunction...

Core and Valence Electrons

Core Electrons:

"Innermost energy level electrons which are tightly bound and do not significantly interact with external fields or particles. They do contribute potential but are constant."

Valence Electrons:

"Outermost energy level electrons which actively interact with external fields and particles. They can be excited to higher energy states and participate in bonding."

> *Take all electrons from highest n orbital then add on electrons from remaining not-full orbitals*

Nobel Gases:

"Nobel gases have no valence electrons"

Ionisation Energy:

"Energy required to remove an electron from the atom in its groundstate. The atom must be isolated and gaseous."

Electron Affinity:

"Energy released when an electron is added to the atom in its groundstate. The atom must be isolated and gaseous."

Molecular Bonding

Ionic Bounding:

When a low ionisation atom and a high electron affinity atom come close, the transfer of valence electrons occurs to minimise the energy, forming an ionic bond between the ions due to coulomb attraction and Fermi repulsion...
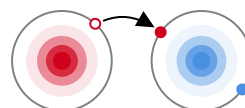
Covalent Bonding:

The superposition of nuclei potentials can cause a symmetric wavefunction where electrons have less energy (more stable) when between both nuclei. Due to Pauli's exclusion principle, the shared electrons have anti-parallel spins and thus form a covalent bonding pair...
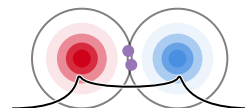
Bond Shapes:

$$1 : \sigma \qquad 2 : \sigma + \pi \qquad 3 : \sigma + 2\pi$$

Hydrised Orbits:

Superpositions of eigenstates can reduce the overall energy in certain covalent bonds, forming orientated hybridised orbits...

$$sp : 2 : Linear \qquad sp^2 : 3 : Tri\text{-}Planar \qquad sp^3 : 4 : Tetrahedral$$

Electronegativity:

"The tendency of an atom to attract electrons"

Vibrational Modes

Harmonic Potential:

The minimum energy of a bonded system can be approximated as parabolic...

$$V(x) = \frac{1}{2}k(x - x_e)^2$$

x_e: *Equilibrium Bond Length*

$$E_\nu = \left(\nu + \frac{1}{2}\right)\hbar\omega \qquad \Delta\nu = \pm 1 \qquad \omega = \sqrt{k/\mu}$$

Vibrational Quantum Number: $\nu = 0, 1, 2\ldots$

"Even in the lowest vibrational state, the system has energy $\hbar\omega/2$ and still vibrates"

Morse Potential:

An asymmetric approximation is...

$$V(x) = D_e\left(1 - e^{-\alpha(x - x_e)}\right)^2$$

$$E_\nu = \left(\nu + \frac{1}{2}\right)\hbar\omega - \chi\left(\nu + \frac{1}{2}\right)^2\hbar\omega \qquad \Delta\nu = \pm 1, \pm 2$$

Triatomic Molecule Modes:

The bonds can symmetrically/asymmetrically stretch, or bend in two planes

Rotational Modes

Rotational Inertia:

For a rigid diatomic molecule, the Rotational Inertia is...

$$I = \mu R_0^2 \implies E_\rho = \frac{\hbar^2}{2I}\rho(\rho + 1)$$

Vibrational Quantum Number: $\rho = 0, 1, 2, \ldots$

Rotational Transitions:

The transition wavelength from ρ to $(\rho - 1)$ is...

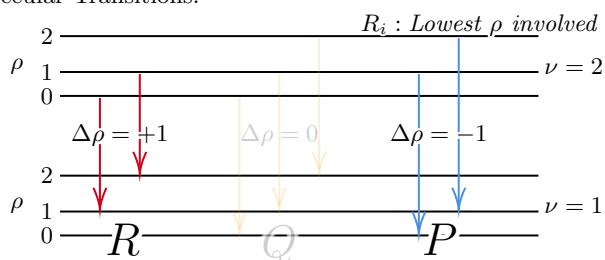$$\frac{1}{\lambda} = \frac{\hbar}{2\pi I c}\rho \qquad \Delta\rho = \pm 1$$

$\hbar^2/I \sim 10^{-4}\ eV \implies$ *Rotation Transitions require little energy*

"Vibrational energy is much higher than rotational energy"

Spectroscopy *"Rotational and Vibrational Spectra"*

Molecular Transitions:

R_i : *Lowest ρ involved*

ρ ... $\nu = 2$

$\Delta\rho = +1$ $\qquad \Delta\rho = 0 \qquad \Delta\rho = -1$

ρ ... $\nu = 1$

$R \qquad Q \qquad P$

"Rotational and Vibrational transitions in molecules are coupled, emitting or absorbing photons"

Observed Spectra:

Observed spectra don't have equally spaced $1/\lambda$ on the R-branch due to centrifugal distortion. This leads to a distribution of ρ...

$$\eta(\rho) = (2\rho + 1)\exp\left(-\frac{\rho(\rho + 1)\hbar^2}{2I k_B T}\right)$$

Electronic Spectra

Molecules also exist in excited electron states, but, these require much higher energies than vibrational-rotational transitions...

Vib-Rot: $\Delta E \sim$ meV $\qquad$ Elec: $\Delta E \sim$ eV

Franck-Condon Principle

Franck-Condon Principle:

Building on the Born-Oppenheimer Approximation...

- *Nuclei are stationary during electronic transitions*
- *Nuclei are stationary during vib-rot transitions*

Overlap Integral:

*The intensity of a transition is proportional to the overlap integral of their wavefunctions...*

$$I \propto \int_V \psi_i \psi_f^* \, d^3\underline{r}$$

Nuclear Properties

- *Nuclei are massive, containing most the mass of the atom*
- *Nuclei are small with a radius $\sim 10^{-14}$ m*
- *Nuclei contain a Coulomb force due to their protons*
- *There must be a strong attractive force that counteracts*
- *Nuclei have an internal magnetic dipole moment*

Nuclear Sizes

Plum Pudding Model:
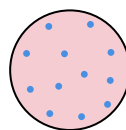
"An atom is a cloud of positive charge with full of negative electrons"

*The **Rutherford Scattering experiment** proved this was incorrect as alpha particles mostly passed through a foil of gold atoms, whilst some were strongly deflected, implying a smaller volume of positive charge.*

Size of the Nucleus:

"Using electron scattering, the radii of the nucleus is $\sim$ fm"

The charge density can be empirically approximated...

$$\rho^c(r) = \rho_0^c\left(1 + e^{(r - a)/b}\right)^{-1}$$

$a \approx 1.07 A^{1/3}$ fm $\qquad b \approx 0.55$ fm

"The radius at which the charge density halves is a, with a surface thickness of $2b$"

Nuclear Masses

Mass as Energy:

$$E = mc^2 \implies 1 \text{ MeV/c}^2 \approx 1.783 \times 10^{-30} \text{ kg}$$

"Smaller Mass $\to$ Smaller Energy $\to$ More Tightly Bound"

Stability:

As the number of protons increases, the coulomb repulsion force increases within the nucleus, meaning more neutrons are needed to balance this with the strong nuclear force...

Small Nuclei: $N \approx Z$ $\qquad$ Larger Nuclei: $N > Z$

Semi-Empirical Mass Formula

Binding Energy:

$$M(Z, N) = Zm_p + Nm_n - B(Z, N) \qquad A = Z + N$$

Liquid Drop Model:

The SEMF is built from the Liquid Drop model and observations, with its terms being...

Term	Description
Zm_p **Proton**	*Proton mass ignoring interactions*
$(A-Z)m_n$ **Neutron**	*Neutron mass ignoring interactions*
$-a_v A$ **Volume**	*Strong nuclear force stabilising the system and is proportional to the volume*
$a_s A^{2/3}$ **Surface**	*Accounts for overestimation of strong nuclear force on surface nucleons with fewer neighbours*
$a_c \dfrac{Z^2}{A^{1/3}}$ **Coulomb**	*Coulomb repulsion between the protons and is inversely proportional to the radius*
$a_a \dfrac{(Z-A/2)^2}{N}$ **Asymmetry**	*Accounts for the difference in stability of nuclei with $Z = N$ and $Z \neq N$*
$a_p \delta(Z,A) \dfrac{1}{A^{1/2}}$ **Pairing**	*Accounts for the increased stability of paired protons and neutrons*

$$\delta(Z, A) = \begin{cases} +1, & even\ A;\ odd\ Z \\ 0, & odd\ A \\ -1, & even\ A;\ even\ Z \end{cases}$$

Magic Numbers:

The SEMF is quite accurate, however, small nuclei ($A < 10$) where the volume/surface term breaks down or magic number nuclei are more stable and are lighter than predicted...
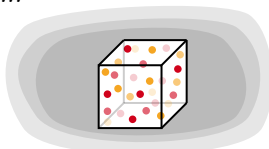
$$Z \text{ and/or } N = 2,\ 8,\ 20,\ 28,\ 50,\ 82,\ 126, \ldots$$

Why don't nucleons scatter and are magic numbers magic...

Nuclear Models

Fermi Gas Model:

We propose nucleons move freely in the nucleus within a net potential from all other nucleons. This is approximately a 3D finite square well...

"Low energy states occupied more meaning no scattering"

The Shell Model:

Solving the Fermi gas Model for a rounded square well, we get solutions characterised by nuclei quantum numbers n and ℓ, this time with no restrictions on ℓ for a given n...

Adding in a strong nuclear inverted (energy reduces for maximum $\mathbf{J}$) spin-orbit interaction helps explain magic numbers, which occur at large gaps when filling energy levels, like noble gases.

Nuclear Decay

Radioactive Decay:

Large nuclei are unstable due to Coulomb repulsion. To shed mass, they emit an alpha particle after tunnelling through a potential barrier. The resulting smaller nuclei often have an excess of neutrons, leading to beta decay, where neutrons turn into protons. These nuclei then release excess energy through gamma decay...
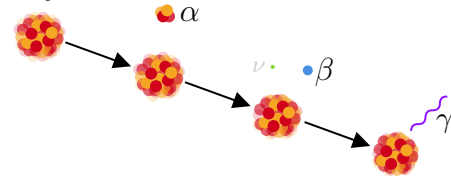
"Unstable nuclei often spontaneously decay multiple times"

The mass of an Isobar helps predict the beta decay mechanism...
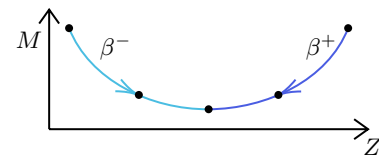
In large nuclei, a proton can capture an inner electron to become a neutron instead of β^+...

β^-	*Final mass must be lower than initial*
β^+	*Final mass must at least be $2m_e$ lower than initial*
e^-	*Final mass must be lower than the initial*

Nuclear Activity:

Activity is the number of decays in a given time...

$$A = \lambda N = -\frac{\mathrm{d}N}{\mathrm{d}t} \implies N(t) = N_0 e^{-\lambda t}$$

$$[A] = \mathrm{Bq} = Becquerel = \text{"one decay per second"}$$

Half life is the time taken for half the nuclei to decay...

$$t_{1/2} = \frac{\ln(2)}{\lambda}$$

Nuclear Fission:

In highly massive nuclei, splitting into smaller ones can release about 200 MeV. However, spontaneous fission is rare due to a large potential barrier of around 6 MeV. To induce fission more readily, kinetic neutrons are often employed...

Increase in Surface Area to Volume Ratio   *Coulomb $\gg$ Strong Nuclear*   *More Unstable*
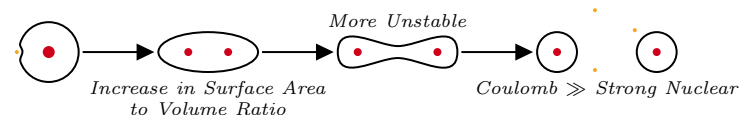
Nuclear Fusion:

Small nuclei can fuse to form larger ones, releasing energy. Despite a large Coulomb and Pauli electron exclusion barrier, natural fusion occurs at temperatures of 10^8 K where atoms are fully ionised. They overcome the remaining proton Coulomb barrier via kinetic energy and are attracted by the strong force.

*Solar fusion occurs via tunnelling as the temperature is too low. Elements fuse up to $^{56}_{26}\text{Fe}$, which has one of the highest binding energies per nucleon. Beyond this, heavier elements are formed through the **s-process**: a neutron is captured followed by beta decay. This allows formation up to $^{209}_{83}\text{Bi}$ due to the instability of $^{210}_{83}\text{Bi}$. Heavier elements are synthesised in supernovae via the **r-process**, where neutrons are repeatedly captured before decay occurs.*