QUANTUM MECHANICS MEGA TUTORIAL

Not handwritten this time, because my handwriting sucks. This sheet is a bit of a quick tour through things that came up from the marking.

The Big Picture

The whole aim of QM in chemistry is to understand the solutions to the time-independent Schrödinger equation:

$$\hat{H}\Psi = E\Psi \tag{0.1}$$

Where Ψ is the **wavefunction** describing a molecule (or part of a molecule), the energies E will tell us about the corresponding energy of the molecule.

Unfortunately, Equation 0.1 is impossible to solve *analytically* for any useful system. But we can still get accurate *numerical* solutions, and make approximations (Born-Oppenheimer, Orbital Approximation) that allow us to get essential insight.

Normalisation

The **Born Interpretation** of Ψ is that it is a **probability amplitude**. That means that the probability of funding the particle described by Ψ at position x is:

$$P(x) \propto |\Psi(x)^2|$$

Obviously, our particle (electron, nucleus, etc) has to be *somewhere*,so:

$$\int_\infty P(x)\ \mathrm{d}\tau = 1 \tag{0.2}$$

Where $\mathrm{d}\tau$ means we integrate over all coordinates, and $\int_\infty$ means over all space.

To ensure that we satisfy Equation 0.2, we can just scale Ψ by a constant, the **normalisation constant**, N:

$$\Psi \rightarrow N\Psi$$

Which leads to the definition of N:

$$N = \sqrt{\frac{1}{\int_\infty |\Psi(x)^2| dxx}}$$

Radial Distribution Functions

For an atom, we might want to know things like what distance the valence electron is from the nucleus (so we can think about how it interacts with other atoms, for example). The total atomic wavefunction depends on three coordinates, which we can separate into *radial* and *angular* parts:

$$\Psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

The probability of finding the electron at a location (r, θ, phi) is given by Ψ^2, as before. If we just care about r (the distance from the nucleus), we can integrate out the angular dependence and obtain the **radial distribution function**, $F(r)$:

$$F(r) = R(r)^2 \int_0^{2\pi} \int_0^{\pi} Y(\theta, \phi)^2 r^2 \sin\theta\ \mathrm{d}\theta\ \mathrm{d}\phi$$

Where $r^2 \sin\theta$ is called the **volume element** of integration. For an $s - orbital$, where there is no angular dependence (imagine $Y = 1$):

$$F(r) = 4\pi r^2 R(r)^2$$

Thus we can see that as $r \rightarrow 0$, $F(r) \rightarrow 0$, as there is no chance of finding the electron right by the nucleus.

Nodes

A node is defined as a point **where the wavefunction changes sign**, or where the **wavefunction passes through zero**. This is a stricter requirement than just:

$$\Psi(x) = 0$$

Because the above equation could also be true as $x \rightarrow \infty$ for some orbitals.

When our wavefunction depends on more than one coordinate (as above for the atomic case), then different parts of it can pass through zero at different times:

$$R(r) = 0 \rightarrow \text{radial node}$$
$$Y(\theta, \phi) = 0 \rightarrow \text{angular node}$$

A consequence of $\Psi(x) = 0$ is that $P(x) = 0$, and there is no chance of finding the particle at the node.

Quantum Harmonic Oscillator

What a cool system – basically a quantum mechanical pendulum, or quantum mechanical spring. This is the way that we model molecular vibrations using quantum mechanics. We saw in the tutorial that:

$$\psi_v(x) = N_v H_v(\alpha x) \exp\left(-\frac{\alpha^2 x^2}{2}\right)$$

Which, if you think about it, is like:

$$\psi_v(x) = \text{Normalisation constant} \times \text{Polynomial term} \times \text{Gaussian function}$$

The polynomial term produces nodes (as you saw in the tutorial). $H_v(\alpha x)$ are the **Hermite Polynomials**, because if you write down the full Schrödinger equation for the system it has the same form as a famous differential equation called the **Hermite Equation**, which the Hermite polynomials are used to solve.

Recall from CH2200 that the energies of the quantum harmonic oscillator are:

$$E_v = \left(v + \frac{1}{2}\right) \hbar\omega = \left(v + \frac{1}{2}\right) \hbar\sqrt{\frac{k}{\mu}}$$

Where $v = 0, 1, 2....$ The constant α relates to ω, μ, and k:

$$\alpha = \sqrt{\frac{\mu\omega}{\hbar}}$$

It is interesting (or, I think it is), to compare the quantum harmonic oscillator to the classical one (imagine a pendulum, for example):

- **Energy**:
  - Classical: can be zero, can take any value (ω can be whatever).
  - Quantum: **cannot** be zero (zero point energy), is quantised.
- **Position**:
  - Classical: can be anywhere, more likely to be at edges (turning points).
  - Quantum: There are **nodes**. More likely to be in the center at low v.
- **Weird Stuff**:
  - Classical: totally boring. Particle can't pass a barrier without enough energy to jump over.
  - Quantum: **tunnelling** can happen, where even if it hasn't got enough energy, the particle can pass over a barrier (we will discuss).