Quantum Mechanics 2 Summary Notes

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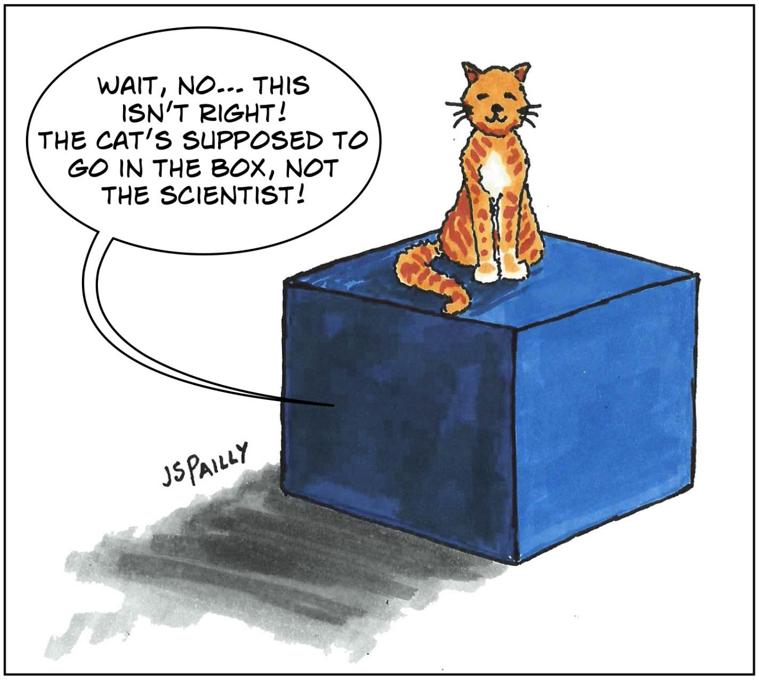

Contents

1 Wave Particle Duality and the Wavefunction

Double slit experiment implies wave-particle duality, electrons have de Broglie wavelength given by

$$\lambda = h/p. \tag{1}$$

Electrons behaving like a wave must have a wavefunction $\Psi(\mathbf{r}, t)$, we can localise a particle by adding multiple waves with different k, but this produces a spread in momentum $p = \hbar k$. This is the Heisenberg Uncertainty Principle,

$$\Delta x \Delta p \geq \hbar/2. \tag{2}$$

Wavefunction is complex, probability must be real,

$$\int P(x,t)\mathrm{d}x = \int \Psi^*(\mathbf{r},t)\Psi(\mathbf{r},t)\mathrm{d}x = 1, \tag{3}$$

by normalisation.

Note that we can determine the dimension of the normalisation constant by ensuring that (3) is dimensionless.

2 Operators and Expectation Values

The expectation value is the average value of an operator. All measurable quantities have an operator,

$$\hat{x} = x \tag{4}$$

$$\hat{p_x} = -i\hbar\frac{\partial}{\partial x} \tag{5}$$

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(x) \tag{6}$$

$$\hat{E} = i\hbar\frac{\partial}{\partial t} \tag{7}$$

For any such quantity, the associated expectation value is given by

$$\langle Q \rangle = \langle \Psi | \hat{Q} \Psi \rangle, \tag{8}$$

as $\langle Q \rangle$ is real, $\hat{Q}$ must be Hermitian.

Note that the expectation value is not the most probable value, which is instead found when the probability has its maximum value (at the turning point).

3 Uncertainty

Some operators that don't represent observable quantities are not Hermitian, such operators don't commute.

Ehrenfest's theorem states that Newton's laws are exactly satisfied by the expectation values of the corresponding operators in quantum mechanics.

4 The Schrödinger equation

4.1 Time Dependent Schrödinger Equation

$$\frac{-\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2}+V(x,t)\Psi(x,t)=i\hbar\frac{\partial}{\partial t}\Psi(x,t) \tag{9}$$

This simplifies to the time independent equation if the potential doesn't depend on time, as the wavefunction is separable

$$\Psi(x,t)=\psi(x)T(t). \tag{10}$$

We can show that

$$T(t)=e^{-iEt/\hbar}. \tag{11}$$

4.2 Time Independent Schrödinger Equation

$$\frac{-\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2}+V(x)\psi(x)=E\psi(x). \tag{12}$$

This is an eigenvalue equation,

$$\hat{H}(x)\psi_E(x)=E\psi_E(x), \tag{13}$$

the general solution to the time dependent Schrödinger equation is the weighted sum of each separate wavefunction multiplied by the corresponding $T(t)$.

Note, Hermitian operators yield real eigenvalues, and orthogonal eigenfunctions.

5 Eigenfunctions and Superposition

The general solution to the TISE is an arbitrary linear superposition of different stationary states,

$$|\Psi\rangle=\sum_n c_n|\psi_n\rangle, \tag{14}$$

if we measure the energy of the system, the superposition collapses to just one of these eigenstates.

$|c_n|^2$ gives the probability of measuring the system in the state $|\psi_n\rangle$.

The probability of measuring a particular state oscillates over time thanks to the $T(t)$ term above. Superposed states are not stationary states.

6 Transitions

Wavefunctions which are a superposition of energy eigenstates give expectation values which depend on time, pure energy eigenstates do not.

7 Eigenfunctions of Various Potentials

For the infinite square well, the probability of finding the particle outside the well is 0.

For other potentials, $P(x)$ will penetrate into the classically forbidden region. Considering the Schrödinger equation separately in each region, we find different solutions. The finite square well looks like the infinite square well inside, but the wavefunction decays exponentially outside.

If $V(x)$ is continuous, then $\psi(x)$ and its derivatives must all be continuous, we can use this to sketch wavefunctions.

7.1 Ladder Operators

Ladder operators allow us to move up and down the 'ladder' in energies, if

$$H\psi_n = E_n\psi_n, \tag{15}$$

then

$$Ha_+\psi_n = (E_n\hbar\omega)a_+\psi_n. \tag{16}$$

7.2 Commutators and Uncertainty

If two operators $\hat{A}$ and $\hat{B}$ commute, they have a common set of eigenfunctions. This means A and B can be known simultaneously, if we measure A and subsequently B, we get values corresponding to the same eigenfunction.

If two operators don't commute, then they don't share a common set of eigenfunctions and we can express the eigenfunctions of one operator and a superposition of the eigenfunctions of the other. Therefore, knowing A does not determine the value of B, only probabilities.

The fundamental commutator is

$$[x, \hat{p}] = i\hbar. \tag{17}$$

Some useful identities are

$$[\hat{A}, \hat{B}\hat{C}] = \hat{B}[\hat{A}, \hat{C}] + [\hat{A}, \hat{B}]\hat{C}, \tag{18}$$

$$[\hat{A}\hat{B}, \hat{C}] = \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B}. \tag{19}$$

8 The 3-D Schrödinger Equation

We can solve the 3-D Schrödinger equation by seeking solutions that are separable. If

$$V(x, y, z) = V_x(x) = V_y(y) + V_z(z), \tag{20}$$

then Schrödinger's equation is separable in Cartesian coordinates,

$$\psi(x, y, z) = \psi_x(x)\psi_y(y)\psi_z(z). \tag{21}$$

If, instead, the potential is spherically symmetric, then Schrödinger's equation is separable in spherical polar coordinates, and

$$\psi = R(r)Y(\theta, \phi). \tag{22}$$

9 Angular Momentum

The angular momentum operator in Cartesian coordinates is given by

$$\hat{\mathbf{L}} = -i\hbar(\mathbf{r} \times \nabla). \tag{23}$$

Its components don't commute,

$$[L_x, L_y] = i\hbar L_z, \tag{24}$$

and similarly for other combinations of x, y, z. $\hat{L}^2$ does commute with each component.

10 Angular Momentum and Spherical Harmonics

The total angular momentum operator is $\hat{L}^2$, and its eigenfunctions are the spherical harmonics $Y_{lm}(\theta, \phi)$, which satisfy

$$\hat{L}^2 Y_{lm} = l(l+1)\hbar^2 Y_{lm} \quad \text{and} \quad \hat{L}_z Y_{lm} = m\hbar Y_{lm}, \tag{25}$$

with $-l \leq m \leq l$.

The radial probability density is given by

$$P(r)dr = \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} R_{nl}^2 Y_{lm}^* Y_{lm} r^2 \sin\theta d\theta d\phi dr = R_{nl}^2 r^2 dr, \tag{26}$$

where we have used the volume element in spherical polars, and the normalisation of $Y_{lm}(\theta, \phi)$.

11 Finding the Hydrogen Wavefunction

Rearranging the Schrödinger equation, and substituting eigenvalues, we find the radial equation, which is identical to the 1-D Schrödinger equation, but with a new effective potential $V_{\text{eff}}(r)$ term.

In the Hydrogen atom, we replace the mass m with the reduced mass $\mu = m_p m_e/(m_p + m_e)$ to account for the two particles. Solving this gives an equation for the quantised energies.

11.1 Degeneracy

For a given n, there are n values of l, and $2l + 1$ values of m, which have the same energy, so the level is degenerate.

12 Generalising Angular Momentum

Particles have intrinsic angular momentum, spin, as well as extrinsic orbital angular momentum.

Any vector $\mathbf{J}$ is defined to be an angular momentum if its components satisfy

$$[J_x, J_y] = i\hbar J_z \quad , \quad [J_y, J_z] = i\hbar J_x \quad \text{and} \quad [J_z, J_x] = i\hbar J_y, \tag{27}$$

and commute with J^2. $\mathbf{J}$ then has all the same properties as $\mathbf{L}$ above.

A general angular momentum can have integer or half integer values of j, with m_j running up to $\pm j$.

13 Spin

We define $\hat{\mathbf{S}}$ as an angular momentum spin operator. S^2 has eigenvalues $s(s+1)\hbar^2$, and S_z has eigenvalues $m_s\hbar$. They do not have spherical harmonics as eigenfunctions, and their eigenstates are not functions of spatial coordinates.

Fermions have half integer spin, for electrons $s = 1/2$, so exists in one of two eigenstates: spin-up, $m_s = 1/2$, or spin-down, $m_s = -1/2$.

Stern-Gerlach experiment gave evidence for the existence of spin, they took silver atoms which have a single outer electron in the $n = 5, l = 0, m = 0$ level. $l = 0$ means the electron has no orbital angular momentum and therefore produces no current loop, it should not interact with an external magnetic field. Instead, the beam was separated into two distinct parts, each due to the electron being either spin-up or spin-down.

14 Non-Degenerate Perturbation Theory

If we perturb a system whose unperturbed Hamiltonian, eigenfunctions and energy levels satisfy

$$H_0\psi_n^0 = E_n^0\psi_n^0, \tag{28}$$

such that the perturbed Hamiltonian is $H = H_0 + H'$, then the corresponding perturbations to the energy levels are

$$E_n^1 = \langle\psi_n^0|H'|\psi_n^0\rangle. \tag{29}$$

15 Degenerate Perturbation Theory

If we have two degenerate states that satisfy

$$H_0\psi_a^0 = E^0\psi_a^0 \quad \text{and} \quad H_0\psi_b^0 = E^0\psi_b^0, \tag{30}$$

then the eigenfunctions of the perturbed Hamiltonian are

$$\psi = \alpha\psi_a + \beta\psi_b, \tag{31}$$

where the coefficients and the first order approximation to the energy, E^1, are given by

$$\begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^1 \begin{pmatrix} \alpha \\ \beta \end{pmatrix}, \tag{32}$$

where $W_{ij} = \langle\psi_i|H'|\psi_j\rangle$. If the off-diagonals are equal to 0, then this reduces to the non-degenerate perturbation theory result.

If the perturbation and the unperturbed Hamiltonian don't share symmetry, then the degeneracy is broken. When the perturbation is lifted, the wavefunctions settle down to two 'good' eigenfunctions.

Good eigenfunctions are eigenfunctions of both the perturbed and unperturbed Hamiltonian, they share symmetry with the perturbation and diagonalise W.

16 Hydrogen Quantum Numbers and Fine Structure

The solutions to the basic Schrödinger equation for Hydrogen are highly degenerate. To fully specify the wavefunction ψ_{nlmm_s}, we must define

- n: principle quantum number, $n = 1, 2, 3...$
- l: total orbital angular momentum quantum number, $L^2\psi = l(l+1)\hbar^2\psi$, $l = 0, 1, ..., n-1$
- m: magnetic quantum number, component of orbital angular momentum along the z-axis, $L_z\psi = m\hbar\psi$, $m = -l, ..., l$

- m_s: component of spin angular momentum along the z-axis, $S_z\psi = m_s\hbar\psi$, $m_s = \pm 1/2$.

The energy levels only depend on n, and so are $2n^2$-fold degenerate.

We can alternatively label the wavefunction ψ_{nljm_j}, where

- n: principle quantum number, $n = 1, 2, 3...$
- l: total orbital angular momentum quantum number, $L^2\psi = l(l+1)\hbar^2\psi$, $l = 0, 1, ..., n-1$
- j: total angular momentum quantum number, $J^2\psi = j(j+1)\hbar^2\psi$, $j = |l - 1/2|$ or $|l + 1/2|$as j must be positive
- m_j: component of total angular momentum along the z-axis, $J_z\psi = m_j\hbar\psi$, $m = -j, ..., j$

There is a perturbation to the Hamiltonian due to the interaction of the spin and orbit of the particle proportional to $\mathbf{S}\cdot\mathbf{L}$. Our Hamiltonian therefore has an extra term due to this, the perturbation H' does not commute with all of the operators associated with $\mathbf{S}$ and $\mathbf{L}$, but does with the operators of the total angular momentum $\mathbf{J} = \mathbf{S} + \mathbf{L}$. $\mathbf{J}$ and J_z are conserved under the perturbation, so use H^0, L^2, S^2, J^2 and J_z.

Note, two other corrections are needed, the Darwin term resulting from smearing of the electrostatic interaction over a volume defined by the Compton wavelength, and relativistic corrections to kinetic energy. These give rise to the fine structure of Hydrogen.