Quantum Mechanics - A Summary

1 Postulates & Basics

Every dynamical system can be represented by a wavefunction $\psi(x, y, z, t)$ from which all possible predictions about the system can be obtained. The wavefunction is normalised via:

$$\int \psi^* \psi \, d\tau = 1 \tag{1.1}$$

And orthonormal via:

$$\int \phi_m^* \phi_n \, d\tau = \delta_{mn} \tag{1.2}$$

Every dynamical variable can be represented by a Hermitian operator $\hat{Q}$. They have properties:

$$\hat{Q}\phi_n = q_n \phi_n \tag{1.3}$$

$$q_n^* = q_n \tag{1.4}$$

$$\int f \hat{Q} g \, d\tau = \int g \hat{Q}^* f \, d\tau \tag{1.5}$$

A wavefunction is composed of a complete set of orthogonal eigenfuctions, via. The probability that a result will be q_m is $|a_m|^2$, and the sum of all these probabilities is unity.

$$\psi = \sum_n a_n \phi_n \tag{1.6}$$

There are operators for dynamical variables:

$$\hat{r} = r \quad \hat{P} = -i\hbar\nabla \quad \hat{L} = -i\hbar(r \times \nabla) \tag{1.7}$$

Two eigenfunctions ϕ_m and ϕ_n are only orthogonal if they are not degenerate. That is, $q_m \neq q_n$. If ϕ_1 and ϕ_2 are degenerate, we can construct an eigenfunction ϕ_2' which is orthogonal to ϕ_1:

$$\phi_2' \equiv S_{12}\phi_1 - \phi_2 \qquad S_{12} \equiv \int \phi_1^* \phi_2 \, d\tau \tag{1.8}$$

2 Schrodinger Equation & Solutions

The time independant Schrodinger equation, in a potential V:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi \tag{2.1}$$

If $V = 0$, in 1D, there are solutions:

$$\psi(x) = A \sin kx + B \cos kx \qquad k^2 \equiv \frac{2mE}{\hbar^2} \tag{2.2}$$

If $V = V_0$, such as a finite potential well:

$$\psi(x) = Ae^{\mu x} + Be^{\mu x} \qquad \mu^2 \equiv \frac{2m}{\hbar^2}(V_0 - E) \tag{2.3}$$

Bound states exist for $E < V_0$. In potential wells, can find the coefficients by looking at the continuity boundary condtions as the interfaces.

3 Dirac Notation

We use a short hand for various things. $|\phi\rangle = \phi$, $\langle\phi| = \phi^*$; or sometimes just the quantum numbers inside the ket to specify the wavefunction: $|\ell, m_\ell\rangle = Y_{\ell,m_\ell}(\theta, \phi)$. The expectation value is written:

$$\langle\hat{Q}\rangle = \langle\phi|\hat{Q}|\phi\rangle = \int \phi^* \hat{Q}\phi \, d\tau \tag{3.1}$$

In matrix notation, we have the interpretation that $|v\rangle$ is a column matrix, and $\langle\phi|$ the complex conjugate-transpose. For example, if

$$|V\rangle = \begin{pmatrix} v_1 \\ v_2 \end{pmatrix}$$

Then:

$$\langle V| = (v_1^*, v_2^*)$$

Hence, we see orthogonality, via:

$$\langle V|V\rangle = (v_1^*, v_2^*) \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} = v_1^* v_1 + v_2^* v_2 = 1$$

We have:

$$\langle\phi_n|\phi_m\rangle = \delta_{nm} \tag{3.2}$$

4 Commutation Relations

Define the commutator:

$$\left[\hat{A}, \hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A} \tag{4.1}$$

If this is zero, then $\hat{A}$ and $\hat{B}$ are said to commute, and posses a common set of eigenfunctions.
For position and momentum:

$$\left[\hat{P_{x_j}}, \hat{x_k}\right] = -\delta_{jk} i\hbar \tag{4.2}$$

$$[\hat{x_i}, \hat{x_j}] = 0 \tag{4.3}$$

Notice that $\left[\hat{A}, \hat{B}\right] = -\left[\hat{B}, \hat{A}\right]$.

There is a statement of the uncertainty principle:

$$\Delta q \Delta r \geq \frac{1}{2}\left|\langle\left[\hat{Q}, \hat{R}\right]\rangle\right| \tag{4.4}$$

5 Orbital Angular Momentum

We can show:

$$\left[\hat{L_x}, \hat{L_y}\right] = i\hbar\hat{L}_z \tag{5.1}$$
$$\left[\hat{L^2}, \hat{L_z}\right] = 0 \tag{5.2}$$

We have that the common set of eigenfunctions between $\hat{L}^2$ and $\hat{L}_z$ are the spherical harmonics:

$$\hat{L}^2 Y_{\ell,m_\ell}(\theta,\phi) = \ell(\ell+1)\hbar^2 Y_{\ell,m_\ell}(\theta,\phi) \tag{5.3}$$
$$\hat{L}_z Y_{\ell,m_\ell}(\theta,\phi) = m_\ell \hbar Y_{\ell,m_\ell}(\theta,\phi) \tag{5.4}$$

Where we have that $\ell = 0, 1, 2, \ldots, n-1$ and $|m_\ell| \leq \ell$. In Dirac notation this is:

$$\hat{L}^2|\ell, m_\ell\rangle = \ell(\ell+1)\hbar^2|\ell, m_\ell\rangle \quad \hat{L}_z|\ell, m_\ell\rangle = m_\ell\hbar|\ell, m_\ell\rangle$$

We define ladder operators:

$$\hat{L}_\pm \equiv \hat{L}_x \pm i\hat{L}_y \tag{5.5}$$

These have the following effect, where the final wavefunction is now normalised:

$$\hat{L}_\pm|\ell, m_\ell\rangle = \hbar\sqrt{\ell(\ell+1) - m_\ell(m_\ell \pm 1)}|\ell, m_\ell \pm 1\rangle \tag{5.6}$$

We can also use the ladder operators (also refered to as raising/lowering operators) to write:

$$\hat{L}_x = \frac{1}{2}(\hat{L}_+ + \hat{L}_-) \tag{5.7}$$
$$\hat{L}_y = \frac{1}{2i}(\hat{L}_+ - \hat{L}_-) \tag{5.8}$$

We use these objects to find things like $\langle\hat{L}_x\rangle = 0$.

6 Spin Angular Momentum

This is analogous to orbital angular momentum, so we define objects:

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 \tag{6.1}$$
$$\left[\hat{S_x}, \hat{S_y}\right] = i\hbar\hat{S}_z \tag{6.2}$$
$$\left[\hat{S^2}, \hat{S_z}\right] = 0 \tag{6.3}$$
$$\hat{S}_\pm = \hat{S}_x \pm i\hat{S}_y \tag{6.4}$$
$$\hat{S}_\pm|s, m_s\rangle = \hbar\sqrt{s(s+1) - m_s(m_s \pm 1)}|s, m_s \pm 1\rangle \tag{6.5}$$

However, we do not have differential forms of the spin operator. We have to use matrix methods, and base it around the eigenvectors of the $\hat{S}_z$ operator. Which we define:

$$\hat{S}_z\alpha = \frac{1}{2}\hbar\alpha \tag{6.6}$$

$$\hat{S}_z\beta = -\frac{1}{2}\hbar\beta \tag{6.7}$$

Hence, applying the ladder operators to these:

$$\hat{S}_+\alpha = 0 \quad \hat{S}_-\alpha = \hbar\beta$$
$$\hat{S}_+\beta = \hbar\alpha \quad \hat{S}_-\beta = 0$$

7 Matrix Representation

If we start with a standard eigenvalue equation, we will be able to expand it in terms of its set of eigenfunction, and will allow us to eventualy write:

$$\sum_n Q_{mn}a_n = qa_m \tag{7.1}$$

Where:

$$Q_{mn} \equiv \langle\phi_m|\hat{Q}|\phi_n\rangle = \int \phi_m^*\hat{Q}\phi_n\, d\tau \tag{7.2}$$

Thus, we have written matrix elements Q_{mn} in terms of eigenfunctions, which may or may not be of the operator $\hat{Q}$.
We can use this formalism to write down some operators for spin. We do this by expressing some operator in terms of some known basis functions of another.
So, for $\hat{S}_z$:

$$[S_z] = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} = \begin{pmatrix} \langle\alpha|\hat{S}_z|\alpha\rangle & \langle\alpha|\hat{S}_z|\beta\rangle \\ \langle\beta|\hat{S}_z|\alpha\rangle & \langle\beta|\hat{S}_z|\beta\rangle \end{pmatrix} \tag{7.3}$$

We use the previously defined $\hat{S}_z\alpha = \frac{1}{2}\hbar\alpha$ and $\hat{S}_z = -\frac{1}{2}\hbar\beta$ to then evaluate the elements:

$$[S_z] = \frac{1}{2}\hbar\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \frac{1}{2}\hbar\sigma_z \tag{7.4}$$

Note, $[S_z]$ is written in a basis spanned by its own eigenfunctions. Hence, it is a diagonal matrix whose entries are its eigenvalues.
To do this for $[S_x]$, we use the fact that $\hat{S}_x = \frac{1}{2}(\hat{S}_+ + \hat{S}_-)$, and the previously written results for what happens to α, β if operated on by the ladder operators:

$$[S_x] = \begin{pmatrix} \langle\alpha|\hat{S}_x|\alpha\rangle & \langle\alpha|\hat{S}_x|\beta\rangle \\ \langle\beta|\hat{S}_x|\alpha\rangle & \langle\beta|\hat{S}_x|\beta\rangle \end{pmatrix} = \frac{1}{2}\hbar\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \frac{1}{2}\hbar\sigma_x \tag{7.5}$$

Similarly, for $[S_y]$, we use $\hat{S}_y = \frac{1}{2i}(\hat{S}_+ - \hat{S}_y)$ to get:

$$[S_y] = \frac{1}{2}\hbar \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = \frac{1}{2}\hbar\sigma_y \tag{7.6}$$

To summarise:

Hence, we have expressions for the spin operators, in terms of the Pauli-spin matrices. We can use them to compute things like:

$$\left[\hat{S_x}, \hat{S_y}\right] = \frac{1}{4}\hbar^2(\sigma_x\sigma_y - \sigma_y\sigma_x) = i\hbar\hat{S}_z \tag{7.7}$$

$$\hat{S}^2 = \frac{1}{4}\hbar^2(\sigma_x^2 + \sigma_y^2 + \sigma_z^2) = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{7.8}$$

Each spin-matrix has eigenvalues $\pm\frac{1}{2}\hbar$, which can be verified. For each eigenvalue, each matrix then has its own eigenvectors, in terms of the basis in m_s, the projection of spin along the z-axis. Suppose that the normalised eigenvector of $[S_x]$ is $\begin{pmatrix} a \\ b \end{pmatrix}$, corresponding to the eigenvalue $m_x = +\frac{1}{2}\hbar$, then this is equivalent to writing:

$$|m_x = +\frac{1}{2}\hbar\rangle = a|m_s = +\frac{1}{2}\hbar\rangle + b|m_s = -\frac{1}{2}\hbar\rangle$$

We are expanding spin in any direction, in terms of its components along the z-axis.

We can do exactly the same thing for orbital-angular momentum. We use the basis of eigenvalues of $\hat{L}_z$ for a spin-1 system. That is, for $m_\ell = 1, 0, -1$. So, the matrix representation of $\hat{L}_x$ in this basis:

$$[L_x] = \begin{pmatrix} \langle 1|\hat{L}_x|1\rangle & \langle 1|\hat{L}_x|0\rangle & \langle 1|\hat{L}_x|-1\rangle \\ \langle 0|\hat{L}_x|1\rangle & \langle 0|\hat{L}_x|0\rangle & \langle 0|\hat{L}_x|-1\rangle \\ \langle -1|\hat{L}_x|1\rangle & \langle -1|\hat{L}_x|0\rangle & \langle -1|\hat{L}_x|-1\rangle \end{pmatrix}$$

Where we use the following to evaluate the elements:

$$\hat{L}_x = \frac{1}{2}(\hat{L}_+ + \hat{L}_-) \quad \hat{L}_\pm|\ell, m_\ell\rangle = \hbar\sqrt{\ell(\ell+1) - m_\ell(m_{\ell\pm1})}|\ell, m_\ell \pm 1\rangle$$

And we end up with:

$$[L_x] = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

Note, if we write $[L_z]$, in the basis spanned by its own eigenvectors, we expect to get a diagonal matrix, whose elements are its eigenvalues. This is what we find:

$$[L_z] = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

8 Moments & Precession

Magnetic moment due to orb.ang.mom is given by:

$$\boldsymbol{\mu}_\ell = g_\ell \boldsymbol{\ell} \mu_B \tag{8.1}$$
$$\mu_z = g_\ell \ell_z \mu_B = g_\ell m_\ell \mu_B \tag{8.2}$$

Where the Bohr Magneton is:

$$\mu_B = \frac{e\hbar}{2m_e} \tag{8.3}$$

Similarly, moment due to spin angular momentum is $\boldsymbol{\mu}_s = g_s \boldsymbol{s} \mu_B$, and QFT gives $g_s \approx -2$.

A state will evolve thus, in time:

$$|\psi(t)\rangle = \sum_n a_n e^{-i\omega_n t} |\phi_n\rangle$$

This will give rise to quantum beating for linear superpositions of eigenstate.

The Hamiltonian due to an applied magnetic field is:

$$\hat{H}_{mag} = -\boldsymbol{\mu} \cdot \boldsymbol{B} = -g_\ell \mu_B B \frac{\hat{L}_z}{\hbar}$$

Thus, this being applied to an eigenstate $|\ell, m_\ell\rangle$ sees a factor $\hat{L}_z|\ell, m_\ell\rangle = m_\ell|\ell, m_\ell\rangle$; thus:

$$\hat{H}_{mag}|\ell, m_\ell\rangle = -g_\ell m_\ell \mu_B B |\ell, m_\ell\rangle$$

We can hence say that $E = \hbar\omega m_\ell$, where the precession frequency is:

$$\omega = \frac{g_\ell \mu_B B}{\hbar}$$

We generally use $g_\ell = -1, g_s = -2$. Using this formalism, we are able to compute $\langle\psi|\hat{L}_x|\psi\rangle$, for a (single-electron) atom in a magentic field; and we find that the expectation value changes in time: precession.

9 Addition of Angular Momenta

We say:

$$\hat{J} = \hat{L} + \hat{S} \tag{9.1}$$

From this, we are able to derive a form for the operator $\hat{L} \cdot \hat{S}$; by squaring the above expression. $\hat{J}$ has identical commutation and ladder operators as before. We use Clebsch-Gordan coefficients to express $|j, m_j, \ell, s\rangle$ in terms of $|\ell, m_\ell, s, m_s\rangle$.

9.1 S-O Splitting

We find that the operator for spin-orbit coupling comes from considering the magnetic field generated by a spinning electron, and that due to an electron orbiting a central nucleus. To comes out to be:

$$\hat{H}_{SO} = A\hat{L}\cdot\hat{S} \tag{9.2}$$

$$A \equiv \frac{\mu_0 Z e^2}{8\pi m_e^2 r^3} \tag{9.3}$$

In the computation, we used $E = \frac{1}{2}\boldsymbol{\mu}\cdot\boldsymbol{B}$; where the $\frac{1}{2}$ comes from a relativistic effect. Its not very hard to then show:

$$\hat{H}_{SO}|j, m_j, \ell, s\rangle = \frac{A\hbar^2}{2}\left(j(j+1) - \ell(\ell+1) - s(s+1)\right)|j, m_j, \ell, s\rangle$$

This SO coupling splits $\ell \pm s$ states, which would otherwise be untouched. For example, if $\ell = 1, s = \frac{1}{2}$; then, if SO coupling is not considered, then $j = \frac{3}{2}$. When SO splitting is considered, $j = \frac{3}{2}, \frac{1}{2}$. We find that the two energy levels are splitted asymmetrically. We are able to easily show (by substituting things in) that the magnitude of SO splitting is $\frac{3}{2}R_\infty\alpha^2$.

9.2 Zeeman Effect

We modify a Hamiltonian thus:

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} + \hat{V} \tag{9.4}$$

$$\hat{H}_{SO} = A\hat{L}\cdot\hat{S} \tag{9.5}$$

$$\hat{H}_{mag} = -\frac{\mu_B}{\hbar}B(g_\ell\hat{L}_z + g_s\hat{L}_s) \tag{9.6}$$

So that the total Hamiltonian of a system is a sum of the above terms.
For weak applied fields, $\hat{H}_{mag}$ is very small, so can be neglected; so, we use $|j, m_j, \ell, s\rangle$ as eigenstates. For a strong applied field, $\hat{h}_{mag}$ is large, We find that L and S precess independantly, so we use $|\ell, m_\ell, s, m_s\rangle$ eigenstates.

10 Time Independent Perturbation Theory

We are able to derive, using lots of orthonormality integrals, that the change in energy of a perturbed system is:

$$E_n' = \int u_n^* \hat{H}' u_n \, d\tau \tag{10.1}$$

Notice, we use eigenfunctions of the unperturbed system.
Basically, if we have $\hat{H} = \hat{H}_0 + \hat{H}'$, with eigenvalue $E = E_0 + \Delta E$; supposing that the unperturbed system looks like $\hat{H}_0 u = Eu$, then:

$$\Delta E = \langle u_n|\hat{H}'|u_n\rangle$$