1 Summary of things you should already know

"I think I can safely say that nobody understands quantum mechanics" Richard Feynman

1.0 Prerequisite

All material covered in Junior Honours Quantum Mechanics is part of the syllabus of this course.

1.1 Understanding Nature

Quantum Theory encompasses our best understanding of how nature works: what will be the result of any experiment. We arbitrarily split the universe into "system" (wavefunction), an environment or measurement (Hamiltonian, or operator) and a measureable quantity (eigenvalue). There is no unique associated mathematics, but since all measurements on systems yield real numbers, we need mathematics which gives real eigenvalues. So it is a premise of quantum theory that any measurable quantity is associated with a Hermitian operator.

1.2 Matrix and operator mechanics

There are two equivalent mathematical ways of calculating physical properties, Schroedinger's wave mechanics and Heisenberg's matrix mechanics. In each systems are represented in terms of eigenstates and measurables as eigenvalues. In matrix mechanics the operator is represented by a Hermitian matrix of elements $\langle m|\hat{Q}|n\rangle$ which depends on the choice of basis set $|m\rangle$. Any state can represented by a normalised *vector*, which also depends on the basis set. The eigenvalues and eigenvectors of the matrix, however, do not depend on the choice of basis - the eigenvectors are, in fact, the eigenbasis of the operator.

For a set of basis 'vectors' of size N, there are $N \times N$ possible matrix elements.

1.3 Operators and Observables

In addition to position, a full description of a system must contain some implicit information. The abstract bra-ket notation includes this.

Consider the electric charge. Obviously this is measurable, so it should be associated with an operator $\hat{Q}$, such that e.g.

$$\hat{Q}|\Phi\rangle = -e|\Phi\rangle$$

where Φ is the wavefunction of an electron. $-e$ meets all the criteria for a quantum number, and the above equation is obviously a true representation of reality. Thus the meaning of the ket $|\Phi\rangle$ is broader than a simple spatial function, and operators can also be non-algebraic. This is especially important in particle physics where all manner of quantum numbers appear (isospin, strangeness, baryon number etc. etc.)

1.4 Changes in time

Schroedinger's equation $\hat{H}\phi = i\hbar\partial\phi/\partial t$ shows us that the Hamiltonian (energy operator) is related to the change in wavefunction in time. A system prepared in an eigenstate of the Hamiltonian has time-invariant probability density. A system prepared in an eigenstate of a non-commuting operator has a probability density which varies in time. It is this time independence (conservation law) which makes eigenstates of the energy operator so useful.

When we measure some property of a system, the act of making the measurement collapses the system into an eigenstate of the appropriate operator. All memory of the previous state of the system is lost in this collapse, except in the special case when the state is degenerate, as we'll see later. The system then evolves according to its Hamiltonian.

1.5 Formal definition of a complete, orthonormal basis set

Consider a basis set $|i_n\rangle$. It is *orthonormal* if $\langle i_n|i_m\rangle = \delta_{mn}$. It is *complete* if any wavefunction can be written as $|\phi\rangle = \sum_n c_n|i_n\rangle$ and the c_n are uniquely defined. If the wavefunction cannot be so written, the basis set is *incomplete*, if there exists more than one possible set of c_n, the basis set is *overcomplete*. Choosing a basis set in a Hilbert space (see 1.7) is analogous to choosing a set of coordinates in a vector space. Note that completeness and orthonormality are well defined concepts for both vector spaces and function spaces.

1.6 Example of matrix representation method and choice of basis

In practical quantum problems, we almost always describe the state of the system in terms of some basis set. Consider a simple spin 1/2 system, choosing as basis states $S_z = \pm\frac{1}{2}$. Consider this system in a magnetic field pointing in the x direction, the operator corresponding to this is $\mu B\hat{S}_x$. We wish to find the eigenstates and eigenenergies.

Evaluating the required matrix elements such as $\langle S_z = \frac{1}{2}|\mu B\hat{S}_x|S_z = \frac{1}{2}\rangle$ (see QP3) gives a matrix:

$$\begin{pmatrix} 0 & \mu B/2 \\ \mu B/2 & 0 \end{pmatrix}$$

The normalised eigenvectors of this matrix are $\left(\sqrt{\frac{1}{2}}, \sqrt{\frac{1}{2}}\right)$ and $\left(\sqrt{\frac{1}{2}}, -\sqrt{\frac{1}{2}}\right)$ with eigenvalues $(\mu B/2)$ and $(-\mu B/2)$. Of course these represent the eigenstates $|S_x = \pm\frac{1}{2}\rangle$ in the basis of $|S_z = \pm\frac{1}{2}\rangle$:

$$|S_x = \pm\frac{1}{2}\rangle = \left[|S_z = \frac{1}{2}\rangle \pm |S_z = -\frac{1}{2}\rangle\right]/\sqrt{2}$$

Had we chosen $|S_y = \pm\frac{1}{2}\rangle$ as our basis set, then the matrix would have been:

$$\begin{pmatrix} 0 & -i\mu B/2 \\ i\mu B/2 & 0 \end{pmatrix}$$

Once again, the eigenvalues of this matrix are $(\mu B/2)$ and $(-\mu B/2)$, as they must be since these are the measurable quantities. Coincidently, the eigenvectors in this basis set are also $\left(\sqrt{\frac{1}{2}}, \sqrt{\frac{1}{2}}\right)$ and $\left(\sqrt{\frac{1}{2}}, -\sqrt{\frac{1}{2}}\right)$.

Had we chosen $|S_x = \pm\frac{1}{2}\rangle$ as our basis set in the first place, the problem would have been much simplified. The matrix would then be:

$$\begin{pmatrix} \mu B/2 & 0 \\ 0 & -\mu B/2 \end{pmatrix}$$

Once again, the eigenvalues of this matrix are $(\mu B/2)$ and $(-\mu B/2)$, and now the eigenvectors are (1,0) and (0,1): i.e. the eigenstates are simply the basis states.

1.7 Dirac Notation - Analogies with vectors and matrices

You probably remember Dirac notation as a shorthand for integrals, for example the overlap between two wavefunctions can be written as:

$$\langle\chi|\phi\rangle \quad \text{instead of} \quad \int\int\int \chi^*(\mathbf{r})\phi(\mathbf{r})d^3\mathbf{r}.$$

(Where $d^3\mathbf{r}$ is the scalar volume element, sometimes called $r^2\sin\theta d\theta d\phi dr$, dxdydz, dV or d$\tau$)

But also if we have a complete set of orthonormal basis states i, the overlap is also the sum of the overlaps between each i and χ and ϕ

$$\langle\chi|\phi\rangle = \sum_i \langle\chi|i\rangle\langle i|\phi\rangle$$

Warning: A summation convention is also sometimes used, such that when a state symbol appears twice, first as a ket, then as a bra, it is assumed to be summed over a complete set of orthonormal basis states. The expression above is then further abbreviated to $\langle\chi|i\rangle\langle i|\phi\rangle$. This convention can be confusing and will not be used in these notes.

Compare this with the vector dot product formula

$$\mathbf{b}.\mathbf{a} = b_x a_x + b_y a_y + b_z a_z = \sum_i (\mathbf{b}.\mathbf{e_i})(\mathbf{e_i}.\mathbf{a})$$

where $\mathbf{e_i}$ are the unit vectors in x, y and z directions. Just as any vector can be expressed as a linear combination of $\mathbf{e_i}$, so any quantum state can be expressed as a linear combination of basis states i. There are certain conditions on the basis states, e.g. they must be 'orthonormal' $\langle j|i\rangle = \delta_{ij}$ just as $\mathbf{e_i}.\mathbf{e_j} = \delta_{ij}$. Just as the three Cartesian vectors span a three dimensional space, so the many basis states span a many-dimensional space. In some cases (e.g. Fourier expansions, hydrogen wavefunctions) there are an infinite number of basis states which are therefore related to spanning an infinite-dimensional space. Mathematicians call these 'Hilbert spaces'. Any state ϕ can thus be viewed as a vector in a multi-dimensional space, where each dimension corresponds to one of the basis functions. It is thus common to use the words eigenstate and eigenvector interchangeably to refer to $|\phi\rangle$ Even before the discovery of quantum mechanics, mathematicians had solved many of the problems in this area.

In Dirac notation we have two quantities, the bra and the ket, whereas in vector algebra we have only one, this is because there is not an exact analogy to commutation for Dirac brackets: $\langle\chi|\phi\rangle = \langle\phi|\chi\rangle^*$ includes taking a complex conjugate. Consider manipulating the bras and kets. We can write a vector in terms of its components thus

$$\mathbf{A} = \sum_i \mathbf{e_i}(\mathbf{e_i}.\mathbf{A})$$

where $(e_i.A)$ is the amount of $\mathbf{A}$ along the $\mathbf{e_i}$ axis; the components. The quantities on either side of the equation are not numbers but *vectors*. We can generate a whole algebra based on vectors.

Likewise we can write a state thus: $|\phi\rangle = \sum_i |i\rangle\langle i|\phi\rangle$

where $\langle i|\phi\rangle$ is the amount of ϕ along the i basis state; the components or *expansion coefficients*. The quantities on each side of this equation are not numbers but *functions*. ϕ is a normalised wavefunction iff $\sum_i |\langle\mathbf{i}|\phi\rangle|^2 = 1$. We can then generate a whole algebra based on bras and kets.

For any different complete sets of basis states i and j, we can write: $|\phi\rangle = \sum_j |j\rangle\langle j|\phi\rangle$, and $|\phi\rangle = \sum_i |i\rangle\langle i|\phi\rangle$. Expansions in i and j are called different *representations* of ϕ. This is very

similar to using different coordinate systems: the bases i and j are analogous to two sets of axes rotated with respect to one another. We might choose complete set of wavefunctions as a representation which includes ϕ, just as we sometimes choose axes such that some special vector points along the z-axis.

Going even further, the expansion in a basis can be done for any $|\phi\rangle$, so we can dispense with $|\phi\rangle$ and write:

$$| = \sum_i |i\rangle\langle i|, \text{ the unit operator}$$

All this means is that in any equation you can always proceed by breaking the states down into a complete, orthonormal set of basis functions. This may be useful when dealing with a Hamiltonian for which the eigenstates i with eigenenergies E_i are already known. A general mixed state $|\phi\rangle$ has energy:

$$\langle\phi|H_0|\phi\rangle = \sum_i \sum_j \langle\phi|i\rangle\langle i|H_0|j\rangle\langle j|\phi\rangle = \sum_i |\langle\phi|i\rangle|^2 E_i \quad \text{since for } i \neq j \quad \langle j|E_i|i\rangle, \langle j|i\rangle = 0$$

So we could use the solution to an easier problem (the eigenvalue problem, which we need solve only once per Hamiltonian) so that we never need to apply the complicated Hamiltonian to the complicated mixed state! This is a very useful trick - reformulating a problem so that we can make use of some work that has already been done. In this case the single, hard, problem of finding the energy of a mixed state is changed to the many, easier, problems of finding the energy of the eigenstates and the amount of each eigenstate in the mixed state.

1.8 Using Bras to pick Kets

One of the most useful algebraic tricks in quantum mechanics is to multiply a sum of terms by a complex conjugate wavefunction, and integrate the product over all space. Orthogonality often means that this procedure can be used to 'pick' a single term from the sum. In Dirac notation this procedure simply becomes applying $\langle i_m|$.

For example, if we have an expansion of a mixed state Φ in eigenstates i_n: $\hat{H}|\Phi\rangle = \sum_n \hat{H}|i_n\rangle\langle i_n|\Phi\rangle$, we can remove the sum by $\langle i_m|$:

$$\langle i_m|\hat{H}|\Phi\rangle = \langle i_m| \sum_n \hat{H}|i_n\rangle\langle i_n|\Phi\rangle = E_m\langle i_m|\Phi\rangle$$

This works because $\langle i_m|\hat{H}|i_n\rangle = E_m\delta_{nm}$; it is analogous to taking components of a vector.

1.9 Good quantum numbers

It is normal to think of the eigenvalues as labelling states. In that case they are just called quantum numbers. A set of eigenvalues from a complete commuting set of operators are called good quantum numbers. The eigenvalues from a non-commuting operator are a bad quantum numbers, because their values cannot be known simultaneously.

This is not quite as simple as it seems. In real systems the Hamiltonian may contain many small terms (perturbations) which may not commute with the operators which commute with the unperturbed Hamiltonian. Although in principle the quantum numbers are no longer good, in practice they are often used.

An example of this is in spin-orbit coupling of angular momenta in many-electron atoms. Here $L_z = \sum_i l_{iz}$ is a good quantum number in the absence of spin-orbit coupling, but $\hat{l}_{iz}$ does not commute with the spin orbit coupling operator $\sum_i \hat{l}_i.\hat{s}_i$. Thus for light atoms, where spin-orbit coupling is weak, L_z is often used although it is not strictly a good quantum number.