1 Review of Quantum Mechanics (QM)

QM is constructed in terms of operators acting as transformations on the linear vector space of wavefunctions.
(i) Important operators are the linear momentum p, the position vector x and the Hamiltonian H, where

$$H = \frac{1}{2m}\mathbf{p}^2 + V(\mathbf{x}). \tag{1}$$

$V(\mathbf{x})$ is the potential energy function and H is the "energy" operator. In the Schrödinger representation we have:

- $\mathbf{x}$ represented by multiplication by $\mathbf{x}$;
- $\mathbf{p}$ represented by $-i\hbar\nabla$,

which imply the commutation relations:

$$[x_i, p_j] = i\hbar\delta_{ij}, \;\; [x_i, x_j] = [p_i, p_j] = 0. \tag{2}$$

Then from eqn 1, H is represented by

$$H == \frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{x}). \tag{3}$$

H and $\mathbf{p}$ are differential operators in the Schrödinger representation and so act on sufficiently differentiable functions of $\mathbf{x}$. These functions are called **wavefunctions** and embody all of the physics of the system under study. These wavefunctions are functions of postition, $\mathbf{x}$ and time t. If we know the wavefunction, $\psi(\mathbf{x}, t)$ for all $\mathbf{x}$ and t we can predict the outcome of all experimental measurements on the system.
(ii) The dynamics of the system which allow us to calculate $\psi(\mathbf{x}, t)$ are given by Schrödinger's equation for th time evolution of $\psi(\mathbf{x}, t)$. This is the "equation of motion" of QM. Schrödinger's equation is

$$i\hbar\frac{\partial}{\partial t}\psi(\mathbf{x}, t) = H\psi(\mathbf{x}, t). \tag{4}$$

(iii) **Energy eigenfunctions** $\psi(\mathbf{x}, t)$ satisfy

$$H\psi_n(\mathbf{x}, t) = E_n\psi_n(\mathbf{x}, t), \tag{5}$$

where n labels and distinguishs the different eigenfunctions. Together with eqn 4, this equation implies that

$$\psi_n(\mathbf{x},t) = \phi_n(\mathbf{x})e^{-iE_nt/\hbar}, \tag{6}$$

with

$$H\phi_n(\mathbf{x}) = E_n\phi_n(\mathbf{x}). \tag{7}$$

This last equation is Schrödinger's time-independent equation for the energy eigenvalues, E_n. The wavefunctions $\phi_n(\mathbf{x},t)$ are particularly important and are called stationary wavefunctions (or states). Eqn 7 is a differential equation which can be solved once the boundary conditions are given. Gernerally, the boundary conditions are such that only particular values of E_n are allowed. The sequence, $E_0, E_1, \ldots$ give the allowed **observable** values of the energy of the system.

The $\psi_n(\mathbf{x},t)$ form a **complete basis** of the linear space of wavefunctions. Hence, the most general solution to Schrödinger's time-dependent equation, eqn 4 can be written using this basis as

$$\psi(\mathbf{x},t) = \sum_n a_n\psi_n(\mathbf{x},t), \tag{8}$$

which, using eqn 6 becomes

$$\psi(\mathbf{x},t) = \sum_n a_n\phi_n(\mathbf{x})e^{-iE_nt/\hbar}. \tag{9}$$

This way of writing the general solution to eqn 4 is a standard maths methods technique of solving all such equations subject to given boundary equations and is not peculiar to QM.

(iv) The **inner product** of two wavefunctions ψ and χ is denoted by (χ,ϕ) and is given by

$$(\chi,\phi) = \int d^3x\chi^*(\mathbf{x},t)\psi(\mathbf{x},t). \tag{10}$$

In particular for two energy eignefunctions ψ_m and ψ_n

$$(\psi_m,\psi_n) = \delta_{mn} \quad \Rightarrow \quad (\phi_m,\phi_n) = \delta_{mn}. \tag{11}$$

ie. the energy eigenfunctions are **orthonormal**.

The **matrix element** of an operator A is denoted by $(\chi, A\psi)$ and is given by

$$(\chi, A\psi) = \int d^3x\chi^*(\mathbf{x},t)(A\psi(\mathbf{x},t)). \tag{12}$$

The hermitian conjugate $A^\dagger$ of A is defined by

$$(A^\dagger\chi, \psi) = (\chi, A\psi). \tag{13}$$

(v) The solution to eqn 4 is then constructed as follows:

- (a) Solve Schrondinger's time-independent equation 7 using the physical boundary conditions to find the $\{E_n\}$ and the corresponding $\phi_n(\mathbf{x})$.
- (b) Construct the $\psi_n(\mathbf{x}, t)$ using eqn 6 and express the general solution, $\psi(\mathbf{x}, t)$ using the ψ_n as a basis as given in eqn 8.
- (c) Since Schrödinger's time-independent equation is first-order in time it is an initial value problem and we only need to know the solution at $t = 0$ to solve for all t. Suppose we are given $\psi(\mathbf{x}, 0) = f(\mathbf{x})$ then from eqn 6 we see that

  $$\psi(\mathbf{x}, 0) = f(\mathbf{x}) = \sum_n a_n\phi_n(\mathbf{x}). \tag{14}$$

  Hence, using orthonormality (eqn 11) we determine the coefficients $\{a_n\}$ by

  $$(\phi_n, f) = a_n. \tag{15}$$

  The general solution is given by substituting the $\{a_n\}$ which are usually complex, back into eqn 8.

(vi) Other operators have associated eigenvalues and eigenfunctions too. In general, we have

$$Ag_n(\mathbf{x}) = \lambda_n g_n(\mathbf{x}). \tag{16}$$

If $A^\dagger = A$ then A is said to be hermitian and the eigenvalues, λ_n are real. All observables have real eigenvalues and are this represented by hermitian operators. Like the ϕ_n the g_n are orthonormal and form a complete basis for the space of wavefunctions:

$$\psi(\mathbf{x}, t) = \sum_n c_n(t)g_n(\mathbf{x}), \tag{17}$$

with $c_n(t) = (g_n, \psi)$.

Note: in the special case $A = H$ we found

$$\psi(\mathbf{x}, t) = sum_n a_n e^{-iE_nt/\hbar}\phi_n(\mathbf{x}), \tag{18}$$

which identifies in this case

$$c_n(t) = a_n e^{-iE_nt/\hbar} \quad \text{and} \quad g_n(\mathbf{x}) = \phi_n(\mathbf{x}). \tag{19}$$

In general, however, the time-dependence of the $\{c_n(t)\}$ is not so simple: the energy operator is very special.
(vii) The interpretation of this expansion is explained by the question: "A system is described by the wavefunction $\psi(\mathbf{x}, t)$. What is the probability $P_n^A(t)$ of measuring the value of the observable represented by the hermitian operator A to have value λ_n?"

The answer is:

$$P_n^A(t) = |c_n(t)|^2 = |(g_n, \psi)|^2. \tag{20}$$

In the special case, $A = H$ we see from eqn 19 that

$$P_n^H(t) = |a_n e^{-iE_nt/\hbar} A|^2 = |a_n|^2 \tag{21}$$

which establishes that P_n^H is independent of time. Clearly we must have

$$\sum_n |c_n(t)|^2 = 1 \tag{22}$$

which is ensured by imposing

$$\int d^3x |\psi(\mathbf{x}, t)|^2 = 1. \tag{23}$$

1.1 Example of a two-state system

To illustrate the review above consider a two-state system. Such a system has only two energy eigenfunctions ψ_1 and ψ_2 with energies E_1 and E_2 respectively: $H\phi_n = E_n\phi_n, n = 1, 2$. The general solution for the wavefunction is thus

$$\begin{aligned} \psi(\mathbf{x}, t) &= a_1 e^{-iE_1t/\hbar}\phi_1(\mathbf{x}) + a_2 e^{-iE_2t/\hbar}\phi_2(\mathbf{x}), \\ |a_1|^2 &+ |a_2|^2 = 1. \end{aligned} \tag{24}$$

Let an observable A operate on the eigenfunctions ϕ_1, ϕ_2 as

$$A\phi_1 = \phi_2, \;\; a\phi_2 = \phi_1. \tag{25}$$

What are the eigenfunctions of A? Let a generic eigenfunction be $g(\mathbf{x})$ with

$$Ag(\mathbf{x}) = \lambda g(\mathbf{x}). \tag{26}$$

Using that ϕ_1, phi_2 form a complete basis we must have

$$\begin{aligned} g &= b_1\phi_1 + b_2\phi_2 \\ |b_1|^2 &+ |b_2|^2 = 1, \end{aligned} \tag{27}$$

where b_1, b_2 are determined as follows.

Multiply both sides of eqn 27 with ϕ_1^* and integrate over all space. Repeat with ϕ_2^*. Using orthonormality of the ϕ_n we find

$$(\phi_1, g) = b_1, \ \ (\phi_2, g) = b_2. \tag{28}$$

This is just taking the inner product of eqn 27 with ϕ_1 and ϕ_2. Now operate with A on both sides of eqn 27 and use eqns 25 and 26 to give

$$\begin{aligned} Ag &= \lambda g \\ \Rightarrow b_1 A\phi_1 + b_2 A\phi_2 &= \lambda b_1\phi_2 + \lambda b_2\phi_1/ \end{aligned} \tag{29}$$

Taking the inner product of this equation with the ϕ_1 and ϕ_2 we find, using eqn 28,

$$\begin{aligned} \lambda b_1 &= b_2 \\ \lambda b_2 &= b_1 \end{aligned} \quad \Rightarrow \quad \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} b_1 \\ b_2 \end{pmatrix} = \lambda \begin{pmatrix} b_1 \\ b_2 \end{pmatrix} \tag{30}$$

Clearly the problem is now a 2 × 2 matrix eigenvalue problem. There are two eigenvectors corresponding to two eigenvalues. These are

$$\sqrt{\frac{1}{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} \qquad \sqrt{\frac{1}{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} \tag{31}$$

$$\lambda = \lambda_1 = 1 \qquad \lambda = \lambda_2 = -1 \tag{32}$$

Then we have

$$g_1 = \sqrt{\frac{1}{2}}\phi_1 + \sqrt{\frac{1}{2}}\phi_2 \tag{33}$$

$$g_2 = \sqrt{\frac{1}{2}}\phi_1 - \sqrt{\frac{1}{2}}\phi_2, \tag{34}$$

with corresponding eigenvalues $\lambda_1 = 1$ and $\lambda_2 = -1$.

Now suppose that the system has been prepared at $t = 0$ to be in the eigenstate with eignefunction $g_1(\mathbf{x})$ of A. This is the initial condition for the evolution of the system. This means we set $\phi(\mathbf{x}, 0) = g_1(\mathbf{x})$. This initial condition can be ensured, for instance, by taking an ensemble of many similar systems and measuring the observable A for each at $t = 0$. Then consider **only** those systems in the ensemble for which the measurement yielded the value λ_1. Thus

$$\psi(\mathbf{x}, 0) = g_1(\mathbf{x}) = a_1\phi_1(\mathbf{x}) + a_2\phi_2(\mathbf{x}), \tag{35}$$

and from eqn 34 we can identify

$$a_1 = \sqrt{\frac{1}{2}} \quad \text{and} \quad a_2 = \sqrt{\frac{1}{2}}. \tag{36}$$

The wavefunction $\psi(\mathbf{x}, t)$ is given by (eqn 6)

$$\psi(\mathbf{x}, t) = \sqrt{\frac{1}{2}}\left(e^{-iE_1t/\hbar}\phi_1(\mathbf{x}) + e^{-iE_2t/\hbar}\phi_2(\mathbf{x})\right). \tag{37}$$

Using eqn 34 we can rewrite this equation as

$$\psi(\mathbf{x}, t) = c_1(t)g_1(\mathbf{x}) + c_2(t)g_2(\mathbf{x}), \tag{38}$$

where

$$c_1(t) = \frac{1}{2}\left(e^{-iE_1t/\hbar} + e^{-iE_2t/\hbar}\right) \;\; ; \;\; c_2(t) = \frac{1}{2}\left(e^{-iE_1t/\hbar} - e^{-iE_2t/\hbar}\right). \tag{39}$$

Now, to answer the question: "Given that at $t = 0$ the system is in the eigenstate with eigenfunction g_1 of operator A, what is the probability, $P_1^A(t)$ that the observable corresponding to A will be measured to be λ_1 at time t?". From the discussion so far we know that

$$P_1^A(t) = |c_1(t)|^2 = cos^2\left(\frac{(E_1 - E_2)t}{2\hbar}\right). \tag{40}$$

This means that from our ensemble of prepared systems a proportion $P_1^A(t)$ will yield the value λ_1 on measurement of the observable corresponding to the operator A.

2 Many-particle wavefunctions

Consider a system of two particles which is described by the wavefunction $\phi(\mathbf{x}_1, \alpha_1, \mathbf{x}_2, \alpha_2, t)$ where α_i stands for the other degrees of freedom eg. for an electron it is the spin which takes values in $[-\frac{1}{2}, \frac{1}{2}]$. The state is normalised:

$$\sum_{\alpha_1\alpha_2}\int |\psi(\mathbf{x}_1, \alpha_1, \mathbf{x}_2, \alpha_2, t)|^2 d^3x_1 d^3x_2 = 1, \tag{41}$$

and the function

$$P(\mathbf{x}_1, \alpha_1, \mathbf{x}_2, \alpha_2, t) = |\psi(\mathbf{x}_1, \alpha_1, \mathbf{x}_2, \alpha_2, t)|^2 \tag{42}$$

gives the probability density at time t for finding particle 1 at $\mathbf{x}_1$ with spin α_1 and particle 2 at $\mathbf{x}_2$ with spin α_2. The single particle probability density for particle 1 is given by

$$P(\mathbf{x}_1, \alpha_1, t) = \sum_{\alpha_2} \int |\psi(\mathbf{x}_1, \alpha_1, \mathbf{x}_2, \alpha_2, t)|^2 d^3x_2, \tag{43}$$

and likewise for particle 2.

The Hamiltonian will in general take the form

$$H = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(\mathbf{x}_1, \mathbf{x}_2), \tag{44}$$

where the subscripts “1” and “2” label the two particles. (Note that in principle H can depend on the α_i eg. for electrons it would depend on spin if magnetic fields acted on the system. However, this is an unnecessary complication for this discussion.)

In the special case that $V(\mathbf{x}_1, \mathbf{x}_2) = V_1(\mathbf{x}_1) + V_2(\mathbf{x}_2)$ the Hamiltonian is **separable** which means that

$$H = H_1 + H_2 \tag{45}$$

We can write

$$H_1\phi_n^{(1)}(\mathbf{x}_1, \alpha_1) = E_n^{(1)}\phi_n^{(1)}(\mathbf{x}_1, \alpha_1) \quad \text{and} \quad H_2\phi_n^{(2)}(\mathbf{x}_2, \alpha_2) = E_n^{(2)}\phi_n^{(2)}(\mathbf{x}_2, \alpha_2), \tag{46}$$

and therefore

$$H\phi_n^{(1)}(\mathbf{x}_1, \alpha_1) = (E_n^{(1)} + E_n^{(2)})\phi_n^{(1)}(\mathbf{x}_1, \alpha_1)\phi_n^{(2)}(\mathbf{x}_2, \alpha_2). \tag{47}$$

Thus in the separable case the two-particle eigenfunctions take the form

$$\psi_{n_1 n_2}(\mathbf{x}_1, \alpha_1, \mathbf{x}_2, \alpha_2, t) = \psi_{n_1}^{(1)}(\mathbf{x}_1, \alpha_1, t)\psi_{n_2}^{(2)}(\mathbf{x}_2, \alpha_2, t), \tag{48}$$

with energy $E_{n_1}^{(1)} + E_{n_2}^{(2)}$. These eigenfunctions form a complete basis for the space of all two-particle wavefunctions and thus

$$\psi(\mathbf{x}_1, \alpha_1, \mathbf{x}_2, \alpha_2, t) = \sum_{n_1 n_2} c_{n_1 n_2}\psi_{n_1 n_2}(\mathbf{x}_1, \alpha_1, \mathbf{x}_2, \alpha_2, t). \tag{49}$$

This analysis can be easily be extended to systems of N particles.

2.1 Identical particles

Suppose the system consists of N identicle particles. Then labelling them $1, 2, \ldots$ wrongly distinguishes them. For example, there is no way of distinguishing $\psi(\mathbf{x}_1, \alpha_1, \mathbf{x}_2, \alpha_2, t)$ and $\psi(\mathbf{x}_2, \alpha_2, \mathbf{x}_1, \alpha_1, t)$, experimentally. They must be the **same**state with the **same** energy. They may differ by a phase since this does not affect probabilities or energies. Somehow, we must construct the states to take into account the indistinguishability of the particles. This is done in one of the two following ways which have far reaching consequences for most physical systems:

(i) **Fermi-Dirac statistics** states that the wavefunction must be **antisymmetric** under interchange of any two particles. In the example above this means that $1 \leftrightarrow 2$ with a phase factor of -1. Particles which obey Fermi-Dirac statistics are called **fermions** and include all spin-1/2 particles and in particular the electron.

(ii) **Bose-Einstein statistics** states that the wavefunction for identical particles is **symmetric** under interchange of any pair of particles. Particles which obey Bose-Einstein statistics are called **bosons** and include the photon.

Thus we have:

Fermi-Dirac: $\psi(\mathbf{x}_1, \alpha_1, \mathbf{x}_2, \alpha_2, t) = -\psi(\mathbf{x}_2, \alpha_2, \mathbf{x}_1, \alpha_1, t)$
Bose-Einstein: $\psi(\mathbf{x}_1, \alpha_1, \mathbf{x}_2, \alpha_2, t) = +\psi(\mathbf{x}_2, \alpha_2, \mathbf{x}_1, \alpha_1, t)$

In the separable case for two particles

$$H = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 + V(\mathbf{x}_1) + V(\mathbf{x}_2), \tag{50}$$

the wavefunction becomes

$$\Psi = \sqrt{\frac{1}{2}}(\psi_1(\mathbf{x}_1, \alpha_1, t)\psi_2(\mathbf{x}_2, \alpha_2, t) \pm \psi_1(\mathbf{x}_2, \alpha_2, t)\psi_2(\mathbf{x}_1, \alpha_1, t)) \tag{51}$$

with + for Bose-Einstein and − for Fermi-Dirac.

2.2 The exclusion principle

Consider two electrons and neglect the interaction between them. The Hamiltonian is then separable. Put one in single particle state $\psi_1(\mathbf{x}_1, s, t)$ and the other in $\psi_2(\mathbf{x}_2, s, t)$. The total energy is $E = E_1 + E_2$ and the correct wavefunction is

$$\Psi(\mathbf{x}_1, s_1, \mathbf{x}_2, s_2, t) = \sqrt{\frac{1}{2}}(\psi_1(\mathbf{x}_1, s_1, t)\psi_2(\mathbf{x}_2, s_2, t) - \psi_1(\mathbf{x}_2, s_2, t)\psi_2(\mathbf{x}_1, s_1, t)). \tag{52}$$

If $\psi_1 = \psi_2$ then $\Psi = 0$. This is the **exclusion principle** which states that *no two electrons may occupy identical single particle states.* For a system of N electrons with separable Hamiltonian the energy eigenfunctions take the form

$$\Psi(\mathbf{x}_1, s_1, \ldots, \mathbf{x}_N, s_N, t) = \Phi(\mathbf{x}_1, s_1, \ldots, \mathbf{x}_N, s_N, t)e^{-iEt/\hbar}, \tag{53}$$

where Φ can be written

$$\Phi = \sqrt{\frac{1}{N!}} \begin{vmatrix} \phi_1(\mathbf{x}_1, s_1) & \phi_1(\mathbf{x}_2, s_2) & \ldots & \phi_1(\mathbf{x}_N, s_N) \\ \phi_2(\mathbf{x}_1, s_1) & \phi_2(\mathbf{x}_2, s_2) & \ldots & \phi_2(\mathbf{x}_N, s_N) \\ \vdots & & & \vdots \\ \phi_N(\mathbf{x}_1, s_1) & \phi_N(\mathbf{x}_2, s_2) & \ldots & \phi_N(\mathbf{x}_N, s_N) \end{vmatrix} \tag{54}$$

with $E = \sum_{i=1}^{N} E_i$. Fermi-Dirac statistics are automatically satisfied. This is the **Slater determinant** and eigenfunctions of this kind form the complete basis set of functions for all atomic physics calculations.

In the case that the Hamiltonian doe not depend on the spin of the electron the energy eigenstate which differ by just spin orientation have the **same** energy and **same** spatial wavefunction. In this circumstance we can ignore the presence of spin in many calculations except to remember that any **given** state may be occupied by at most two electrons: one spin “up” (+1/2) and one spin “down” (-1/2). Eg. in the lithium atom which has 3 electrons, the (non-degenerate) ground state is occupied by 2 electrons with opposing spins and the Exclusion principle then requires the third electron occupy the first excited state.

The Exclusion Principle is the key to atomic structure and the periodic table - if it were not true all atomic electrons would be in the lowest (ground) state and the chemical richness of elements would not occur.

3 Quantum Statistical Physics

To deal with large systems of many particles statistical methods are essential. We can write down the classical equations of motion or the Schrödinger equation for the system but with, typically, 10^{23} particles in a system we have no hope of solving for the full microscopic motion or wavefunction of the system. In the following discussion we assume a system in **equilibrium** so that its properties can be described by a few **macroscopic** variable eg. pressure, temperature, volume etc.

(1) The whole system can occupy any one of a sequence of macrosscopic energy eigenstates each of which is uniquely specified by a complete (and very large) set of quantum numbers. For a **given** energy eigenvalue there will be a large number of states with that energy. That is, the **degeneracy** of the energy level is large.

(2) The important principle underlying statistical physics is that

The system will occupy all macroscopic eigenstates of a given energy with equal probability.

And important example with wide applicability is a system with N non-interacting particles.

(i) A gien particle can occupy any one of a sequence of single-particle energy eigenstates of energy $E_i, i = 1, 2, \ldots, \infty$. In general, there is more than one state with a given energy and the number, g_i of states with energ E_i is the degeneracy of the energy level.

(ii) A given macroscopic energy eigenstate of the whole system will be described by a wavefunction which is the product of the individual single-particle wavefunctions in a form which generalises eqns 48 and 51. The whole system will have very many such eigenstates with the same macroscopic energy and so a given energy level has a large degeneracy.

(iii) Consider all macroscopic eigenstates of a given energy, E and total particle number N. Let the number of particles with energy E_i be N_i: the N_i are the **occupation numbers** of the single particle levels. All macroscopic observables will be functions only of the N_i and so we shall average over all other quantum numbers which distinguish the states.

(iv) There will be many macroscopic energy eigenstates associated with the same set of occupation numbers, $\{N_i\}$ and equilibrium is characterised by the set $\{\bar{N}_i\}$ which is the **most probable**. Using (2) above this will be that set of occupation numbers which is associated with the largest number of macroscopic states of the system.

(v) Because N is large the most probably set is **overwhelmingly dominant** and there are unique values for the macroscopic quantities which then characterise the equilibrium.