Principles of Quantum Mechanics

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Introduction

Recall the features of elementary QM:

We have the wave-particle duality: waves can behave like matter particles (quanta of light, i.e. photons) and vice versa.

Matter is described by a wavefunction $\psi(x)$, which gives a probability distribution $|\psi(x)|^2$ for the position of the particle.

In IB, once we had established this, we forgot about light and followed through on this approach to particles (with successful results):

Observables become operators on wavefunctions; their general lack of commutation leads to the uncertainty principle.

The Schrödinger equation specifies the dynamics, predicts energy levels and so on.

All this is enough to understand the Hydrogen atom, which we should not forget is a great triumph, totally beyond classical physics.

The aims of this course are:

To reformulate QM in a more abstract, but more powerful and useful form, the Dirac formalism.

To use this for a simpler solution of known problems such as the simple oscillator, but also new problems.

To consider atoms with many electrons - to do this we need to understand the implications of the uncertainty principle for indistinguishable particles (electrons); we then want to cover:

Spin of elementary particles

Symmetries, e.g. translations and rotations

Ultimately this approach allows a proper QM treatment of the EM field, which covers all non-gravitational physics outside the nucleus; we can then extend to the weak and strong nuclear forces too, thus covering all nongravitational physics.

1 Dirac Formalism

1.1 States and Operators

A quantum system is described at each instant by a state $|\psi\rangle$, which belongs to a complex vector space V; thus linear combinations of states are also valid states; we can see this as a superposition principle which will lead to wavelike behaviour (but these states are not wavefunctions). There are also dual states

$\langle\phi|$ belonging to the dual space $V^\dagger$; by definition we can combine states and duals to give a complex number, so we have a map $V^\dagger \times V \to \mathbb{C}$ $\langle\phi|, |\psi\rangle \mapsto \langle\phi|\psi\rangle$; this last symbol is a bracket, so Dirac referred to the first and second as a "bra" and "ket" respectively (a very lame joke), but these terms are now somewhat obsolete. This combination is linear in both arguments.

The spaces $V, V^\dagger$ also come with an inner product which is best described as a one-to-one correspondence $V \leftrightarrow V^\dagger$ $|\psi\rangle \mapsto \langle\psi|$ or $(|\psi\rangle)^\dagger$; then $\alpha|\psi\rangle + \beta|\phi\rangle \mapsto \alpha^\star\langle\psi| + \beta^\star\langle\phi|$; the inner product is then the $V \times V \to \mathbb{C}$ map $|\phi\rangle, |\psi\rangle \mapsto \langle\phi|\psi\rangle$. It is assumed to be Hermitian ($\langle\phi|\psi\rangle = \langle\psi|\phi\rangle^\star$; we define $\||\psi\rangle\|^2 = \langle\psi|\psi\rangle \geq 0$ and this is real by the above; we also assume $\||\psi\rangle\|^2 = 0 \Leftrightarrow |\psi\rangle = 0$ the zero state, i.e. the inner product is positive definite. From these assumptions we have that if $\langle\phi|\psi\rangle$ is specified for all $\langle\phi|$, this uniquely determines $|\psi\rangle$, and vice versa.

An operator Q is a linear map on states $V \to V$ $|\psi\rangle \mapsto Q|\psi\rangle$; in addition to acting "to the right on states" in this fashion we can also regard Q as acting "to the left on dual states", by defining $\langle\phi|Q$ by defining that $\langle\phi|Q|\psi\rangle$ is unambiguous; then we can consider $Q : V^\dagger \to V^\dagger$ $\langle\phi| \mapsto \langle\phi|Q$. For any Q the hermitian conjugate or adjoint $Q^\dagger$ is an operator defined by $\langle\phi|Q^\dagger = (Q|\phi\rangle)^\dagger$ (or equivalently $\langle\phi|Q^\dagger|\psi\rangle = \langle\psi|Q|\phi\rangle^\star$; the simple consequences of this are $(\alpha A + \beta B)^\dagger = \alpha^\star A^\dagger + \beta^\star B^\dagger, (AB)^\dagger = B^\dagger A^\dagger$.

As an excersise, the reader should verify that if we let the $|\phi\rangle$ be complex column vectors, the $\langle\psi|$ be complex row vectors, and the Q be complex matricies, "everything works".

Note that any state $|\psi\rangle$ is physically equivalent to $\alpha|\psi\rangle$ for any constant $\alpha \neq 0$; we usually require $\||\psi\rangle\|^2 = 1$ but we still have the freedom to shift $|\psi\rangle \to e^{i\theta}|\psi\rangle$.

Commutation relations of operators are particularly important (in some ways more important than multiplication of the operators); we consider the commutator $[A, B] = AB - BA = -[B, A]$. Note that $[A, B_1B_2] = [A, B_1]B_2 + B_1[A, B_2], [A_1A_2, B] = [A_1, B]A_2 + A_1[A_2, B]$.

For an operator Q we call $|\psi\rangle \neq 0$ an eigenstate with eigenvalue λ if $Q|\psi\rangle = \lambda|\psi\rangle$ (or equivalently $\langle\psi|Q^\dagger = \lambda^\star\langle\psi|$.

1.2 Observables and Measurements

An operator Q is called hermitian or self-adjoint if $Q^\dagger = Q$; such operators are also called observables since they correspond to physically measurable quantities such as position, momentum, energy and angular momentum. The key properties of a Hermitian Q are that all eigenvalues are real, eigenstates with distinct eigenvalues are orthogonal, and any state can be expanded (i.e. written as a linear combination) in terms of eigenstates: for the first of these, $Q|\psi\rangle = \lambda|\psi\rangle \therefore \langle\psi|Q = \lambda^\star\psi|$ since $Q^\dagger = Q$ but then $\langle\psi|Q|\psi\rangle = \lambda\langle\psi|\psi\rangle = \lambda^\star\langle\psi|\psi\rangle$ so $\lambda^\star = \lambda$ since $|\psi\rangle \neq 0$. For the second, let $|n\rangle$ denote the eigenstates of Q with respective eigenvalues q_n (note that in general we have infinitely many eigenvalues). Then $Q|n\rangle = q_n|n\rangle, Q|m\rangle = q_m|m\rangle \therefore \langle m|Q = q_m\langle m| \Rightarrow \langle m|Q|n\rangle = q_n\langle m|n\rangle = q_m\langle m|n\rangle \therefore q_n \neq q_m \Rightarrow \langle m|n\rangle = 0$. We shall leave a proof of the final property to the Functional Analysis course.

Combining these properties we have: for any observable Q, $\exists$ an orthonormal basis of eigenstates $\{|n\rangle\}$ for the space V with $Q|n\rangle = q_n|n\rangle, \langle m|n\rangle = \delta_{mn}$ i.e.

any state $|\psi\rangle$ can be written as $\sum_n \alpha_n |n\rangle$ with $\alpha_n = \langle n|\psi\rangle$. If $|\psi\rangle$ is normalized (i.e. $\||\psi\rangle\|^2 = 1$ then $(\sum_n \alpha_n^\star \langle n|)(\sum_m \alpha_m |m\rangle) = \sum_n |\alpha_n|^2 = 1$.

Note that there may be many states with the same eigenvalue λ; the number of such states is called the degeneracy of the eigenvalue λ; in the case where this is 1 we also say λ is non-degenerate.

1.2.1 Postulates for measurements

Measurements are assumed to be instantaneous. Consider measuring Q with the system in the state $|\psi\rangle$ immediately before. Then the result is some eigenvalue of Q; this is obtained with probability $p(\lambda) = \sum_{n:q_n=\lambda} |\alpha_n|^2$, and immediately afterwards the system is left in the state $c\sum_{n:q_n=\psi} \alpha_n |n\rangle$ (where c is just a normalization constant). Often we have the case where λ is non-degenerate, in which case $p(\lambda) = |\alpha_n|^2$ and the system is left in the state $|n\rangle$.

Note that in general (if $\||\psi\rangle\|^2 = 1$) the sum of all probabilities is $\sum_\lambda p(\lambda) = \sum_n |\alpha_n|^2 = 1$; we define the expectation value (mean) of X (in the state $|\psi\rangle$) is $\langle Q\rangle_\psi = \langle\psi|Q|\psi\rangle = \sum_\lambda \lambda p(\lambda) = \sum_n q_n |\alpha_n|^2$, and uncertainty (variance) $(\Delta Q)^2_\psi = \langle (Q - \langle Q\rangle_\psi)^2\rangle_\psi = \langle Q^2\rangle_\psi - \langle Q\rangle^2_\psi$. Note $|\psi\rangle$ is an eigenstate of Q with eigenvalue $\lambda \Leftrightarrow \langle Q\rangle_\psi = \lambda, (\Delta Q)^2_\psi = 0$.

1.3 Time evolution and Schrödinger Equation

This is in principle the last part of the actual content of this course; then we just need to learn more about its applications. States evolve in time, so are more properly written $|\psi(t)\rangle$. When the system is undisturbed (i.e. no measurements are made) this is governed by the Schrödinger equation $i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = H|\psi(t)\rangle$ where $H = H^\dagger$ is the Hamiltonian (equivalently we have $-i\hbar\frac{\partial}{\partial t}\langle\psi(t)| = \langle\psi(t)|H$; the - is simply from complex conjugation of the constant factor). Note that $\frac{\partial}{\partial t}(\langle\psi(t)|\psi(t)\rangle) = \langle\psi(t)\frac{1}{i\hbar}H|\psi(t)\rangle - \frac{1}{i\hbar}\langle\psi(t)|H|\psi(t)\rangle = 0$; this is crucial for the probability interpretation, since it means we can normalise ψ at one time and it will remain normalized at subsequent times.

H is an observable, the energy, and can introduce eigenstates $H|n\rangle = E_n|n\rangle$; if H is independent of time then so are these $|n\rangle$ and E_n, so we have solutions of the Schrödinger equation $|\psi(t)\rangle = e^{-\frac{iE_n t}{\hbar}}|n\rangle$ and these are the usual stationary states.

The SE is linear and first order in time, so if we can express $|\psi(0)\rangle = \sum_n \alpha_n |n\rangle$, then by the uniqueness of solutions to first order DEs we have a unique solution $|\psi(t) = \sum_n \alpha_n e^{-\frac{iE_n t}{\hbar}}|n\rangle$.

1.4 Bases and Representations

Consider a set of orthonormal states $\{|n\rangle\}$ (where n is a discrete label, for simplicity) so $\langle n|m\rangle = \delta_{nm}$. This set is a basis iff $\sum_n |n\rangle\langle n| = 1$ (as an operator); this condition is sometimes called the completeness condition or resolution of unity.

Generally, operators $|a\rangle\langle b|$ are defined in the obvious way; $(|a\rangle\langle b|)|\psi\rangle = |a\rangle(\langle b|\psi\rangle)$ where the last term is just a number.

Now consider an observable Q and let $|n\rangle$ be its eigenstates as usual, $Q|n\rangle = q_n|n\rangle$. The basis of eigenstates is usefil to define functions of Q; we can define

polynomials or functions with a power series like $\sin Q$ without reference to a basis, but for e.g. $\frac{1}{Q}$ or $\log Q$ we cannot do this. So for any f defined on all q_n we define $f(Q)$ by $f(Q)|n\rangle = f(q_n)|n\rangle$, so we can e.g. define $\frac{1}{Q}$ if Q has no zero eigenvalues.

The general definition can be written $f(Q) = \sum_n f(qn)|n\rangle\langle n|$ (we can check the correctness of this by applying it to an arbitrary basis state). Once we've chosen a basis $\{|n\rangle\}$ as above we can represent any state as a complex column (or row) vector $|\psi\rangle = \sum_n \alpha_n|n\rangle \to \{\alpha_n\}$; each $\alpha_n = \langle n|\psi\rangle$. Then if $\beta_n = \langle n|\phi\rangle$ we have $\langle\phi|\psi\rangle = \sum_n \beta_n^\star\alpha_n$ as we would expect for complex vectors. Operators are represented as matricies $A|n\rangle = \sum_m |m\rangle A_{mn}$, where A_{mn} are the matrix elements $\langle m|A|n\rangle$.

Now "everything works": if $|\phi\rangle = A|\psi\rangle$ then $\beta_m = \sum_n A_{mn}\alpha_n$ and $(AB)_{mn} = \sum_p A_{mp}B_{pn}$. This approach is most useful for dealing with a finite basis; we can use it for infinite ones too, but doing so requires more care.

Until now we have considered bases as being discretely labelled. To make the label continuous we must replace $\sum_n$ with $\int dn$; $\langle n|m\rangle = \delta_{mn}$ becomes $\langle n|m\rangle = \delta(n-m)$ and $|\psi\rangle = \sum_n \alpha_n|n\rangle$ becomes $|\psi\rangle \int dn\alpha_n|n\rangle$. We still have $\alpha_n = \langle n|\psi\rangle$, but this is now a function of n rather than a discrete set of numbers.

Measurements involve $|\alpha_n|^2$, which is now a probability density rather than a discrete probability. This is exactly the right setup for a particle in one dimension with position and momentum $\hat{x}, \hat{p}$, with eigenstates $\hat{x}|x\rangle = x|x\rangle, \hat{p}|p\rangle = p|p\rangle$ (i.e. we label the states by their corresponding eigenvalues). Then $|\psi\rangle = \int \psi(x)|x\rangle dx$ where $\psi(x) = \langle x|\psi\rangle$ is the familiar position space wavefunction. However, something new coming out of this theory is that we could also use momentum space wavefunctions.

1.5 Position and Momentum Representations

The essential features of these are all shown by considering a particle in 1D; it has position and momentum operators $\hat{x}, \hat{p}$ obeying $[\hat{x}, \hat{p}] = i\hbar$. Le $|x\rangle$ be a set of position eigenstates $\hat{x}|x\rangle = x|x\rangle$; x is the continuous eigenvalue labelling states, and $\langle x|x'\rangle = \delta(x-x')$, $\int dx|x\rangle\langle x| = 1$. Any state can be expanded as $|\psi\rangle = \int dx\psi(x)|x\rangle$ where $\psi(x) = \langle x|\psi\rangle$. The usual interpetation of $\psi(x)$ in terms of the probability density $|\psi(x)|^2$ now follows from the measurement postulates in section 1.2: $\langle\phi|\psi\rangle = (\int \phi(x)^\star\langle x|dx)(\int \psi(x')|x'\rangle dx') = \int dx \int dx'\phi(x)^\star\psi(x')\langle x|x'\rangle$, but this last term is just $\delta(x-x')$, so this becomes simply $\int dx\phi(x)^\star\psi(x)$ as we would expect; in particular $\||\psi\rangle\|^2 = \langle\psi|\psi\rangle = \int dx|\psi(x)|^2$.

But, alternatively, we could equally well work with momentum eigenstates $\hat{p}|p\rangle = p|p\rangle$ with $\langle p|p'\rangle = \delta(p-p'), \int dp|p\rangle\langle p| = 1$; now if we expand $|\psi\rangle = \int dp\tilde{\psi}(p)|p\rangle$ where $\tilde{\psi}(p) = \langle p|\psi\rangle$, then $|\tilde{\psi}(p)|^2$ is the probability density for finding the particle's momentum to be in some specified range. It is an important fact (which we shall justify later) that we can choose the $|x\rangle$ and $|p\rangle$ eigenstates to obey $\langle x|p\rangle = \frac{1}{\sqrt{2\pi\hbar}}e^{\frac{ixp}{\hbar}}$ or $\langle p|x\rangle = \frac{1}{\sqrt{2\pi\hbar}}e^{-\frac{ixp}{\hbar}}$ $(\star)$.

What are the position wavefurctions for $\hat{x}|\psi\rangle$ and $\hat{p}|\psi\rangle$? The $\hat{x}|\psi\rangle$ wavefunction is $\langle x|\hat{x}|\psi\rangle = x\langle x|\psi\rangle = x\psi(x)$; the $\hat{p}|\psi\rangle$ wavefunction is $\langle x|\hat{p}|\psi\rangle = \int dp\langle x|\hat{p}|p\rangle\langle p|\psi\rangle = \int dpp\langle x|p\rangle\langle p|\psi\rangle = \int dp - i\hbar\frac{\partial}{\partial x}(\langle x|p\rangle)\langle p|\psi\rangle$ using $(\star)$; this is $-i\hbar\frac{\partial}{\partial x}\int dp\langle x|p\rangle\langle p|\psi\rangle = -i\hbar\frac{\partial}{\partial x}\langle x|\psi\rangle = -i\hbar\frac{\partial}{\partial x}\psi(x)$.

By exactly similar calculations we have the momentum space wavefunctions for the same states: $\hat{x}|\psi\rangle$ has wavefunction $i\hbar\frac{\partial}{\partial p}\tilde{\psi}(p)$ and $\hat{p}|\psi\rangle$ has wavefunction

$p\tilde{\psi}(p)$, so we have two possible representations. In either representation we have $[\hat{x},\hat{p}] = i\hbar$.

To relate $\psi(x), \tilde{\psi}(p)$ directly we have $\tilde{\psi}(p) = \langle p|x\rangle = \int dx \langle p|x\rangle\langle x|\psi\rangle = \frac{1}{\sqrt{2\pi\hbar}}\int dx e^{-\frac{ixp}{\hbar}}\psi(x)$, a Fourier transform [note in this course we define the FT with some different constant factors to in the methods course; this is the definition of which $\tilde{\psi}$ corresponds to which ψ]; similarly $\psi(x) = \frac{1}{\sqrt{2\pi\hbar}}\int dp e^{\frac{ixp}{\hbar}}\tilde{\psi}(p)$.

Consider corresponding representations of a Hamiltonian of the form $H(\hat{x},\hat{p}) = \frac{\hat{p}^2}{2m} + V(\hat{x})$; on $\psi(x)$ this becomes $-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$, on $\tilde{\psi}(p)$ it becomes $\frac{p^2}{2m} + V(i\hbar\frac{\partial}{\partial p}$; we can easily interpret the last term for e.g. $V(\hat{x}) = \lambda\hat{x}^n$, but in general we need to take the following approach: $\langle p|V(\hat{x})|\psi\rangle = \int dx \langle p|V(\hat{x})|x\rangle\langle x|\psi\rangle = \int dx V(x)\langle p|x\rangle \int dp'\langle x|p'\rangle\langle p'|\psi\rangle = \int dp'(\int dx V(x)\frac{1}{2\pi\hbar}e^{\frac{ix(p'-p)}{\hbar}})\tilde{\psi}(p')$, but the bracket in the middle is just $\frac{1}{\sqrt{2\pi\hbar}}\tilde{V}(p-p')$ so the SE $H|\psi\rangle = E|\psi\rangle$ (which is $(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x))\psi(x) = E\psi(x)$ in position space) becomes $\frac{p^2}{2m}\tilde{\psi}(p) + \frac{1}{\sqrt{2\pi\hbar}}\int dp\tilde{V}(p-p')\tilde{\psi}(p') = E\tilde{\psi}(p)$ in momentum space. Of course with Fourier theory we see this is just a special case of the convolution theorem, but we have derived it rather than appealing to results from a previous course.

For the generalisation to 3D, a particle has position operators $\hat{x}_i$ and momentum operators $\hat{p}_i$ obeying $[\hat{x}_i,\hat{p}_j] = i\hbar\delta_{ij}$, and these can introduce joint eigenstates $|\vec{x}\rangle$ with $\hat{x}_i|\vec{x}\rangle = x_i|\vec{x}\rangle$, and similarly for momentum; the only place this differs from the 1D case is if we wanted to use wavefunctions in some peverse space where some directions represented position and others momentum. The position space wavefunction is $\psi(\vec{x}) = \langle\vec{x}|\psi\rangle$, the momentum space wavefunction is $\tilde{\psi}(\vec{p}) = \langle\vec{p}|\psi\rangle$, and in place of $(\star)$ we have $\langle\vec{x}|\vec{p}\rangle = \frac{1}{(2\pi\hbar)^{\frac{3}{2}}}e^{\frac{i\vec{x}\cdot\vec{p}}{\hbar}}$; the only other change when moving from 1D to 3D is to replace $\sqrt{2\pi\hbar}$ with $(2\pi\hbar)^{\frac{3}{2}}$ in all our FT formulae.

Example: A one dimensional particle in $V(x) = \frac{-\hbar^2\lambda}{m}\delta(x)$ (the constants other than λ are there to make the solution simple); in momentum space the SE becomes $\frac{p^2}{2m}\tilde{\psi}(p) + \frac{1}{\sqrt{2\pi\hbar}}\int dp'\tilde{V}(p-p')\tilde{\psi}(p') = E\tilde{\psi}(p)$, and here $\frac{1}{\sqrt{2\pi\hbar}}\tilde{V}(p-p') = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dx e^{-\frac{ixp}{\hbar}}\delta(x)\frac{\hbar^2\lambda}{m}$; rearranging $(\frac{p^2}{2m} - E)\tilde{\psi}(p) = \frac{\hbar\lambda}{2\pi m}\int_{-\infty}^{\infty} dp'\tilde{\psi}(p')$; this is easy to solve since this last integral is going to be a constant; the solution is of the form $\tilde{\psi}(p) = \frac{N}{p^2+\alpha^2}$ where $E = -\frac{\alpha^2}{2m}$; as always the solution to the SE is only determined up to multiplication by a constant factor since the equation is linear.

As a verification, we have that $(\frac{p^2}{2m} + \frac{\alpha^2}{2m})\frac{N}{p^2+\alpha^2} = \frac{\hbar\lambda}{2\pi m}N\int_{-\infty}^{\infty} dp'\frac{1}{p^2+\alpha^2} = \frac{\hbar\lambda}{2\pi m}N\frac{\pi}{a}$, so $\alpha = \hbar\lambda, E = -\frac{\hbar^2\lambda^2}{2m}$; this is the unique bound state solution.

We compare this with the position space solution, which has wavefunction $\psi(x) = \sqrt{\lambda}e^{-\lambda|x|}$, and we can verify that the FT of this is $\tilde{\psi}$ as given above (note that we have $N = \sqrt{\frac{2\lambda^3\hbar^3}{\pi}}$ from the condition that $\int_{-\infty}^{\infty} dp|\tilde{\psi}(p)|^2 = 1$).

Now we will justify $(\star)$, above, the claim that we can choose our position and momentum eigenstates to obey $\langle x|p\rangle = \frac{1}{\sqrt{2\pi\hbar}}e^{\frac{ixp}{\hbar}}$: let $|x_0\rangle$ be a fixed position eigenstate, and define all other position eigenstates in terms of it by $u(a)|x_0\rangle$ where $u(a) = \exp(-\frac{ia}{\hbar}\hat{p})$, i.e. $\sum_{n=0}^{\infty}\frac{1}{n!}(\frac{-ia}{\hbar})^n\hat{p}^n$. We first verify that this is an eigenstate of $\hat{x}$ using that $[\hat{x},\hat{p}] = i\hbar$: we have that $[\hat{x},\hat{p}^2] = [\hat{x},\hat{p}]\hat{p} + \hat{p}[\hat{x},\hat{p}] = 2i\hbar\hat{p}$, and inductively $[\hat{x},\hat{p}^n] = ni\hbar\hat{p}^{n-1}$. Therefore $[\hat{x},u(a)] = \sum_{n=0}^{\infty}(\frac{-ia}{\hbar})^n\frac{1}{n!}ni\hbar\hat{p}^{n-1} = au(a)$; then $\hat{x}|u(a)|x_0\rangle = (u(a)\hat{x} + [\hat{x},u(a)])|x_0\rangle =$

$(u(a)x_0 + au(a))|x_0\rangle = (x_0 + a)u(a)|x_0\rangle$; this is a general technique for calculating $AB|x\rangle$ when we know $A|x\rangle$ but not $B|x\rangle$.

So this is an eigenstate of $\hat{x}$ with eigenvalue $x_0 + a$; thus we can define all the position eigenstates by $|x_0 + a\rangle = u(a)|x_0\rangle$, and it is easy to verify that $\langle x'|x\rangle = \langle x' + a|x + a\rangle = \delta(x - x')$; we similarly define the momentum eigenstates by $|p_0 + b\rangle = e^{\frac{ip\hat{x}}{\hbar}}|p_0\rangle$ relative to some "reference" state p_0. Now we have $\langle x_0 + a|p_0 + b\rangle = \langle x_0|e^{\frac{ia\hat{p}}{\hbar}}|p_0 + b\rangle = e^{\frac{ia(p_0+b)}{\hbar}}\langle x_0|p_0 + b\rangle = e^{\frac{ia(p_0+b)}{\hbar}}\langle x_0|e^{\frac{ib\hat{x}}{\hbar}}|p_0\rangle = e^{\frac{i(ap_0+ab+bx_0)}{\hbar}}\langle x_0|p_0\rangle$; now we set $\langle x_0|p_0\rangle = \frac{1}{\sqrt{2\pi\hbar}}$ and take reference values $x_0 = p_0 = 0$ (the explanation was clearer with these values included). Note that the modulus of $\langle x_0|p_0\rangle$ ensures the momentum states are correctly normalized: $\langle p|p'\rangle = \int dx \langle p|x\rangle\langle x|p' = \int dx \frac{1}{2\pi\hbar} e^{-\frac{ix(p-p')}{\hbar}} = \delta(p - p')$.

1.6 Simultaneous Measurements and Commutators

Observables which don't commute cannot be simultaneously measured; we have the generalised uncertainty principle $(\Delta A)_\psi(\Delta B)_\psi \geq \frac{1}{2}|\langle[A, B]\rangle_\psi|$ (the proof is exactly the same as last year, by using the fact that $\|(A + i\lambda B)|\psi\rangle\|^2 \geq 0 \forall \lambda$ and considering this as a quadratic in λ.

If $Q, Q', Q'', \ldots$ do all commute they can be simultaneously measured, and there is a basis of joint eigenstates $|\lambda, \lambda', \ldots\rangle$ labelled by eigenvalues. We call $\{Q, Q', \ldots\}$ a complete commuting set (CCS) if these eigenvalues label the base states uniquely; an equivalent criterion is that any observable A which commutes with each of $Q, Q', \ldots$ must be some function of them. Note that in 1D we can take $\{\hat{x}\}$ or $\{\hat{p}\}$ as a CCS if the particle truly is structureless (or we are approximating it as such); in 3D there are various possibilities like $\{\hat{x}_1, \hat{x}_2, \hat{x}_3\}, \{\hat{p}_1, \hat{p}_2, \hat{x}_3\}$ etc.

2 The Harmonic Oscillator

This is not just a "toy" example; it is useful for a huge amount of physics.

2.1 Analysis Using Creation/Annihilation and Number Operators

The oscillator is a particle in 1D with $H = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2$, with $[\hat{x}, \hat{p}] = i\hbar$. We define $a = \sqrt{\frac{m\omega}{2\hbar}}(\hat{x} + \frac{i\hat{p}}{m\omega})$; $a^\dagger = \sqrt{\frac{m\omega}{2\hbar}}(\hat{x} - \frac{i\hat{p}}{m\omega})$ and note that these are both dimensionless. Then $\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}(a + a^\dagger), \hat{p} = \sqrt{\frac{\hbar m\omega}{2}}i(a^\dagger - a)$. These operators are motivated by trying to write H in terms of $a, a^\dagger$, analagously to writing x, y in terms of $z, \overline{z}$.

Notice that $aa^\dagger = \frac{m\omega}{2\hbar}\hat{x}^2 + \frac{1}{2m\omega\hbar}\hat{p}^2 - \frac{i}{2\hbar}[\hat{x}, \hat{p}] = \frac{1}{\hbar\omega}H + \frac{1}{2}$ - this "almost works" [in terms of giving us H], but just fails because $\hat{x}, \hat{p}$ do not commute. However, we similarly have $a^\dagger a = \frac{1}{\hbar\omega}H - \frac{1}{2}$, so $[a, a^\dagger] = 1$ and $H = \hbar\omega(N + \frac{1}{2})$ where N is the number operator defined by $N = a^\dagger a$.

Consider any eigenstate $|\lambda\rangle$ of N (or equivalently of H); $N|\lambda\rangle = \lambda|\lambda\rangle \Leftrightarrow H|\lambda\rangle = E|\lambda\rangle$ with $E = \hbar\omega(\lambda + \frac{1}{2})$, by the above. There is at least one such eigenstate since N is Hermitian. For any eigenstate, normalized by $\||\lambda\rangle\|^2 = 1$ as usual, we have $\lambda = \langle\lambda|N|\lambda\rangle = \langle\lambda|a^\dagger a|\lambda\rangle = \|a|\lambda\rangle\|^2$, hence $\lambda \geq 0$ with equality

iff $a|\lambda\rangle = 0$; this is unsurprising since H "looks like" a sum of squares (but of course that alone does not proove this result).

We claim that $a, a^\dagger$ act on eigenstates of N by lowering and raising the eigenvalue by 1 - they represent annihilation and creation of energy - provided the new states are nonzero; to show this, consider $[N, a^\dagger] = [a^\dagger a, a^\dagger] = a^\dagger[a, a^\dagger] = a^\dagger$; similarly $[N, a] = -a$. Then $N(a^\dagger|\lambda\rangle) = (a^\dagger N + [N, a^\dagger])|\lambda\rangle = (a^\dagger\lambda + a^\dagger)|\lambda\rangle = (\lambda+1)a^\dagger|\lambda\rangle$; similarly $N(a|\lambda\rangle) = (\lambda-1)a|\lambda\rangle$. So $a^\dagger|\lambda\rangle, a|\lambda\rangle$ are new eigenstates provided they are nonzero; to verify when they are 0 we calculate norms; as per above, $\|a|\lambda\rangle\|^2 = \lambda$, so $a|\lambda\rangle = 0 \Leftrightarrow \lambda = 0$; $\|a^\dagger|\lambda\rangle\|^2 = \langle\lambda|aa^\dagger|\lambda\rangle = \langle\lambda|(a^\dagger a + 1)|\lambda\rangle = \lambda + 1$; which is never 0 since we have $\lambda \geq 0$ always.

Therefore the eigenvalues of N are precisely the nonnegative integers $0, 1, \ldots$; if $|\lambda\rangle$ is an eigenstate then $a|\lambda\rangle, a^2|\lambda\rangle, \ldots$ are, as above, and if λ is not an integer then all of these are nonzero states, with respective eigenvalues $\lambda-1, \lambda-2, \ldots$, and eventually one of these is an eigenvalue < 0, a contradiction; since at least one eigenvalue exists, it must be an integer n, and then we have eigenstates $a|n\rangle, a^2|n\rangle, \ldots, a^n|n\rangle$ with eigenvalues $n-1, n-2, \ldots, 0$ but then $a^m|n\rangle = 0 \forall m > n$, so we have no states with negative eigenvalues; we also have eigenstates $a^\dagger|n\rangle, a^{\dagger 2}|n\rangle, \ldots$ with eigenvalues $n+1, n+2, \ldots$, so the eigenvalues of N are precisely the nonnegative integers; thus the energy levels of the oscillator are $E_n = \hbar\omega(n + \frac{1}{2})$ for $n = 0, 1, \ldots$.

From our calculations of norms, we can introduce normalised eigenstates related by $a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle, a|n\rangle = \sqrt{n}|n-1\rangle \forall n$; in particular we can start from a ground state $|0\rangle$ characterised by $a|0\rangle = 0$, and then define $|n\rangle = \frac{(a^\dagger)^n}{\sqrt{n!}}|0\rangle$.

We usually call $a^\dagger, a$ the creation, annihilation operators; sometimes the two together are called the ladder operators, since they move us "up" and "down" "rungs" on a "ladder" of energy levels.

Note that the energy levels are non-degenerate if we define the system by saying that all observables are constructed from $\hat{x}$ and $\hat{p}$ (or equivalently, and more easily for proof, a and $a^\dagger$), since there is no function of them which commutes with N other than functions of N itself; $\{N\}$ is a CCS and its eigenvalues label basis states uniquely; alternatively we can view $\{\hat{x}\}$ as a CCS and show that we have a unique solution for the wavefunction for any chosen state, e.g. the ground state: Consider wavefunctions in e.g. position space; $|0\rangle \to \psi_0(x) = \langle x|0\rangle$, $a = \sqrt{\frac{m\omega}{2\hbar}}(\hat{x} + \frac{i\hat{p}}{m\omega}) \to \sqrt{\frac{m\omega}{2\hbar}}(x + \frac{\hbar}{m\omega}\frac{\partial}{\partial x})$. So $a|0\rangle = 0 \Leftrightarrow (x + \frac{\hbar}{m\omega}\frac{\partial}{\partial x})\psi_0(x) = 0 \Leftrightarrow \psi_0(x) = Ne^{-\frac{1}{2}\frac{m\omega}{\hbar}x^2}$, where N is a normalization factor which we can calculate to be $\sqrt[4]{\frac{m\omega}{\pi\hbar}}$; similarly $|1\rangle = a^\dagger|0\rangle \Leftrightarrow \psi_1(x) = \sqrt{\frac{m\omega}{2\hbar}}(x - \frac{\hbar}{m\omega}\frac{\partial}{\partial x})\psi_0(x) = \sqrt{\frac{2m\omega}{\hbar}}x\psi_0(x)$, etc.

2.2 Importance of the Oscillator

Together with the Hydrogen atom, the oscillator is one of relatively few QM systems we can solve exactly, and it can be applied in many different contexts: for any potential $V(x)$ with an equilibrium point at $x = x_0$ (i.e. $V'(x_0) = 0$) we can expand $V(x) = V(x_0) + \frac{1}{2}V''(x_0)(x - x_0)^2 + O((x - x_0)^3)$ and the system behaves like an oscillator provided the higher order terms can be neglected; for example, a diatomic molecule has a vibrational mode, and this appears when we study the internal energy or heat capacity of a gas of such as a function of temperature (see part II statistical physics).

More complicated systems can be analysed in terms of normal modes, coherent behaviour in which all oscillations are at the same frequency. Consider the general classical solution of the oscillator $x(t) = Ae^{-i\omega t} + A^\star e^{i\omega t}$ for some $A \in \mathbb{C}$; then a crystal of 10^{23} atoms has (approximate) normal mode solutions $x_I(t) = Au_I e^{-i\omega t} + A^\star u_I^\star e^{i\omega t}$, where I runs over all the atoms and all three directions in which they can oscillate; this gives us information about the thermodynamics of the crystal.

Similarly, the electromagnetic field can be treated using normal modes $\vec{E}(\vec{x},t) = A\vec{u}(\vec{x})e^{-i\omega t} + A^\star\vec{u}(\vec{x})^\star e^{i\omega t}$. Now the oscillations are in EM field space rather than position, but the energy levels can still be inferred and this gives us the thermodynamics of radiation (which is the original source of planck's constant).

The above remarks refer to applications where we only consider the energy levels; consider the meaning of $a, a^\dagger$ for these examples. For a crystal or EM field we have a pair of ladder operators for each normal mode; acting on a ground state $|0\rangle$ we find $a^\dagger|0\rangle$ has a definite energy (of course) and momentum; it behaves just like a particle, so $a^\dagger, a$ create and destroy particles. The relevant particles are called phonons in crystals and photons in the EM field; see part II Applications of Quantum Mechanics.

Finally, the modern view is that all particles (e.g. electrons, quarks, pions) arise from quantizing some field; see part III Quantum Field Theory and Advanced Quantum Field Theory.

3 Pictures and Quantisation

3.1 Unitary operators

The physical predictions of QM are given by probability amplitudes, eigenvalues, expectation values etc, all of which are given by expressions like $\langle\phi|\psi\rangle, \langle\phi|A|\psi\rangle$. An operator u is unitary if $u^\dagger = u^{-1}$, i.e. $uu^\dagger = u^\dagger u = 1$. Given such a u we can map states $|\psi\rangle \mapsto |\psi'\rangle = u|\psi\rangle, \langle\psi| \mapsto \langle\psi'| = \langle\psi|u^\dagger$ and operators $A \mapsto A' = uAu^\dagger$, and all physical predictions remain unaltered: $\langle\phi|\psi\rangle \mapsto \langle\phi'|\psi'\rangle = \langle\phi|u^\dagger u|\psi\rangle = \langle\phi|\psi\rangle$ and $\langle\phi|A|\psi\rangle \mapsto \langle\phi'|A'|\psi'\rangle = \langle\phi|u^\dagger uAu^\dagger u|\psi\rangle = \langle\phi|A|\psi\rangle$; furthermore $C = [A,B] \mapsto C' = [A',B']$ and Q' is hermitian iff Q is; $Q|\psi\rangle = \lambda|\psi\rangle \mapsto Q'|\psi'\rangle = \lambda|\psi'\rangle$ so eigenvalues are unchanged. This process is calleda change of picture.

3.2 Schrödinger and Heisenberg Pictures

The Schrödinger equation $i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = H|\psi(t)\rangle$ has solution $|\psi(t)\rangle = u(t)|\psi(0)\rangle$ where $u(t) = e^{-\frac{iHt}{\hbar}}$, assuming H is independent of t (of course this is no help in actually calculating the solution). Formally this $u(t) = \sum_{n=0}^\infty \left(-\frac{it}{\hbar}\right)^n \frac{H^n}{n!}$, and we observe that indeed $i\hbar\frac{\partial}{\partial t}u(t) = Hu(t)$. Note that $u(t)^\dagger = u(t)^{-1} = u(-t)$ and $u(t_1)u(t_2) = u(t_1+t_2)$; the time-evolution operator $u(t)$ is unitary.

We can use this to transform from the Schrödinger picture, herafter referred to with subscripts S, which we have used exclusively until now, to the Heisenberg picture (subscripts H): states $|\psi(t)\rangle_S \to |\psi\rangle_H = e^{\frac{iHt}{\hbar}}|\psi(t)\rangle_S = |\psi(0)\rangle_S$, operators $A_S \to A_H(t) = e^{\frac{iHt}{\hbar}}A_S e^{-\frac{iHt}{\hbar}}$; ${}_S\langle\phi(t)|A_S|\psi(t)\rangle_S = {}_H\langle\phi|A_H(t)|\psi\rangle_H$. This picture "looks a lot more like classical mechanics"; instead of position, momentum etc. becoming fixed operators and the "strange objects" of states

evolving in time, we have a fixed state and the operators for position, momentum etc. change in time.

Note that $H_H = H_S = H$ (All of what we are doing here depends entirely on H being independent of time in the S-picture); also note we have free choice of the "reference time" at which the pictures coincide; we have taken $t = 0$ here, $t = -\infty$ is another common choice useful in some problems.

Dynamics in the H-picture involves the operators: $i\hbar\frac{d}{dt}(A_H(t)) = i\hbar\frac{d}{dt}(e^{\frac{iHt}{\hbar}}A_S E^{-\frac{iHt}{\hbar}}) = i\hbar(\frac{i}{\hbar}e^{\frac{iHt}{\hbar}}HA_s e^{-\frac{iHt}{\hbar}} - \frac{i}{\hbar}e^{\frac{iHt}{\hbar}}A_S H e^{-\frac{iHt}{\hbar}}) = -[H, A_H(t)]$. So instead of the SE we have the Heisenberg equation of motion $i\hbar\frac{d}{dt}A_H(t) = [A_H(t), H]$. For example, consider a particle in 1D with $H = \frac{\hat{p}^2}{2m} + V(\hat{x})$; we will work in the H-picture and drop the subscripts, so we have $\hat{x}(t), \hat{p}(t)$. $\frac{d}{dt}\hat{x}(t) = \frac{1}{i\hbar}[\hat{x}(t), H] = \frac{1}{m}\hat{p}(t)$, $\frac{d}{dt} = \frac{1}{i\hbar}[\hat{p}(t), H] = -V'(\hat{x}(t))$ (assuming V has a power series). Thus, unlike in the Schrödinger picture where it was a significant amount of work to obtain, Ehrenfest's theorem that $\frac{d}{dt}\langle\hat{x}\rangle = \frac{1}{m}\langle\hat{p}\rangle, \frac{d}{dt}\langle\hat{p}\rangle = -\langle V'(\hat{x})\rangle$ is now immediate; recall that these are the results that show the reduction to classical mechanics.

As a subexample, for the harmonic oscillator $V(\hat{x}) = \frac{1}{2}m\omega^2\hat{x}^2$, the Heisenberg equations can be easily solved and the solution can be expressed as $\hat{x}(t) = \sqrt{\frac{\hbar}{2m\omega}}(ae^{-i\omega t} + a^\dagger e^{i\omega t}), \hat{p}(t) = \sqrt{\frac{\hbar m\omega}{2}}\frac{1}{i}(ae^{-i\omega t} - a^\dagger e^{i\omega t})$, where $a, a^\dagger$ are the annihilation and creation operators defined in terms of $\hat{x}(0), \hat{p}(0)$.

3.3 Quantization

This section is non-examinable: normally we form a QM system by translating a classical system into QM, rather than creating something entirely new. Often the most important question in this process is how the operators relate to each other; specifically, what are the commutators? This is the final step in Dirac's systematic formulation of QM.

The Hamiltonian formulation of any classical system involves a set of generalised coordinates and momenta $x_i(t), p_i(t)$ for $1 \leq i \leq N$ and a Hamiltonian $H(x_i, p_i)$. The Poisson bracket of two functions $f(x_i, p_i), g(x_i, p_i)$ is defined as $\{f, g\} = \sum_i \frac{\partial f}{\partial x_i}\frac{\partial g}{\partial p_i} - \frac{\partial f}{\partial p_i}\frac{\partial g}{\partial x_i}$; then the equation of motion for any $f(x_i, p_i) = \frac{df}{dt} = \{f, H\}$. Furthermore we have $\{x_i, p_j\} = \delta_{ij}$.

In canonical quantization (this is not the only quantization scheme; cf Feynmann) we define the quantum mechanics of this system by mapping classical functions f, g to quantum operators $\hat{f}, \hat{g}$ with $[\hat{f}, \hat{g}] = i\hbar\widehat{\{f, g\}}$; in particular this implies $[\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij}$. Then Hamiltonian's equation becomes the Heisenberg equation.

4 Composite Systems and Identical Particles

4.1 Tersor Products

This is a general approach to constructing quantum systems from simpler subsystems: suppose $|\psi\rangle \in V_1, |\phi\rangle \in V_2$ are states in spaces for two systems. Then the tensor product space $V = V_1 \otimes V_2$ consists of all linear combinations of tensor product states $|\psi\rangle \otimes |\phi\rangle$ (with duals $\langle\psi| \otimes \langle\phi|$) subject to $(|\psi\rangle + |\psi'\rangle) \otimes |\phi\rangle = |\psi\rangle \otimes |\phi\rangle + |\psi'\rangle \otimes |\phi\rangle, |\psi\rangle \otimes (|\phi\rangle + |\phi'\rangle) = |\psi\rangle \otimes |\phi\rangle + |\psi\rangle \otimes |\phi'\rangle, (\alpha|\psi\rangle) \otimes |\phi\rangle = |\psi\rangle \otimes (\alpha|\phi\rangle) = \alpha(|\psi\rangle \otimes |\phi\rangle)$ and similarly for duals. The inner product is

$(\langle\psi'| \otimes \langle\phi'|)(|\psi\rangle \otimes |\phi\rangle) = \langle\psi'|\psi\rangle\langle\phi'|\phi\rangle$, extended by linearity. If $\{|n\rangle\}, \{|m\rangle\}$ are bases for V_1, V_2 then $\{|n\rangle \otimes |\psi\rangle\}$ is a basis for $V_1 \otimes V_2$.

For operators A, B on V_1, V_2 respectively we define $A \otimes B$ on $V_1 \otimes V_2$ by $(A \otimes B)(|\psi\rangle \otimes |\phi\rangle) = (A|\psi\rangle) \otimes (B|\phi\rangle)$; in particular A corresponds to $A \otimes 1$ acting just on "the V_1 part of" a composite state; and similarly B corresponds to $1 \otimes B$; operators of these forms automatically commute [that is, A on V_1 and B on V_2 commute; A_1 and A_2 both on V_1 do not in general].

Common abuses of notation are to write $|\psi\rangle|\phi\rangle$ for $|\psi\rangle \otimes |\phi\rangle$, and to leave out the $\otimes 1$ or $1\otimes$ for operators acting on just one subsystem.

Example: consider a particle in 2D with position operators $\hat{x}_1, \hat{x}_2$. We construct simustaneous eigenstates $|x_1, x_2\rangle = |x_1\rangle \otimes |x_2\rangle$, then $\hat{x}_1 \mapsto \hat{x}_1 \otimes 1, \hat{x}_2 \mapsto 1 \otimes \hat{x}_2$, and the wavefunction for $|\psi\rangle \otimes |\phi\rangle$ is $(\langle x_1| \otimes \langle x_2|)(|\psi\rangle \otimes |\phi\rangle) = \langle x_1|\psi\rangle\langle x_2|\phi\rangle = \psi(x_1)\phi(x_2)$. Note that, just as when we solve an equation with separation of variables, the general wavefunction is not a product of wavefunctions but a linear combination of such products.

Example: the 2D oscillator, $H = \frac{1}{2m}(\hat{p}_1^2 + \hat{p}_2^2) + \frac{1}{2}m\omega^2(\hat{x}_1^2 + \hat{x}_2^2) =: H_1 + H_2$ where $H_i = \hbar\omega(N_i + \frac{1}{2})$, wher $N_i = a_i^\dagger a_i, [a_i, a_j^\dagger] = \delta_i j$. Take simultaneous eigenstates of as many commuting observables as possible - in this case, we take simultaneous eigenstates of N_1, N_2, constructed as $|n_1, n_2\rangle = |n_1\rangle \otimes |n_2\rangle$. $H|n_1, n_2\rangle = (H_1|n_1\rangle) \otimes |n_2\rangle + |n_1\rangle \otimes (H_2|N_2\rangle) = E_{n_1 n_2}|n_1, n_2\rangle$ with $E_{n_1 n_2} = \hbar\omega(n_1 + n_2 + 1)$.

4.2 Spin

Experiment shows that particles generally carry an internal degree of freedom, called spin or intrinsic angular momentum; thus even if a particle appears "elementary" or pointlike, its space of states will be of the form $V_{\text{space}} \otimes V_{\text{spin}}$ with basis states $|\vec{x}, r\rangle = |\vec{x}\rangle \otimes |r\rangle$ where r takes finitely many values. So the particle is not "structureless" and the position operators $\hat{x}_i$ are not a CCS by themselves; there are observables Q acting on V_{spin} with $[\hat{x}_i, Q] = 0$. We shall return to actually study these observables in section 6; for now we concentrate on states.

Each kind of particle has a definite total spin $s \in 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$, which is a characteristic of the particle like its mass or electric charge. For a particle of spin s we have $2s + 1$ basis states in V_{spin}, labelled $|s\rangle, |s-1\rangle, \ldots, |-s\rangle$. For example, an $s = 0$ particle has basis states $|0\rangle$ and we can almost entirely ignore spin; however, no known elementary particles have $s = 0$. For $s = \frac{1}{2}$ there are two basis states $|\frac{1}{2}\rangle, |-\frac{1}{2}\rangle$ also labelled as $|\uparrow\rangle, \downarrow\rangle$ (spin "up" and "down"); most particles currently believed to be elementary have $s = \frac{1}{2}$. For $s = 1$ there are three base states $|1\rangle, |0\rangle, |-1\rangle$, and so on.

The existence of spin states is revealed by (among many experiments) the Stern-Gerlach experiment: we pass a beam of particles between magnets shaped to give an inhomogenous field, which affects particles in different spin states differently; thus the beam splits into one beam for each spin state, e.g. two beams if the particles have spin $\frac{1}{2}$.

A state $|\psi\rangle$ in V has a $(2s+1)$-component wavefunction $\psi(\vec{x}, r) = \langle\vec{x}, r|\psi\rangle$; we'll also use mixed notation with state $\sum_r \psi(\vec{x}, r)|r\rangle$.

4.3 Multiparticle States: Bosons and Fermions

Consider N particles, labelled by $1 \leq \alpha \leq N$, with V_α the space of states for each, with basis $\{|\vec{x}_\alpha, r_\alpha\rangle\}$. In general, multiparticle states belong to $V_1 \otimes V_2 \otimes \cdots \otimes V_N$ with basis states $|\vec{x}_1, r_1, \vec{x}_2, r_2, \ldots, \vec{x}_N, r_N\rangle = |\vec{x}_1, r_1\rangle \otimes \cdots \otimes |\vec{x}_N, r_N\rangle$.

If the particles are identical, $V_\alpha \cong$ some fixed V, we can say more; first consider the simple case $N = 2$. Introduce the operator u which exchanges particles, $u|\vec{x}_1, r_1, \vec{x}_2, r_2\rangle = |\vec{x}_2, r_2, \vec{x}_1, r_1\rangle$. Clearly we have $u^2 = 1$. For a general state $|\Psi\rangle$ we must have $u|\Psi\rangle = \eta|\Psi\rangle$ for some constant η as $|\Psi\rangle, u|\Psi\rangle$ are physically indistinguishable. But $u^2|\Psi\rangle = |\Psi\rangle \Rightarrow \eta^2 = 1 \Rightarrow \eta = \pm 1$. So for two identical particles the two-particle states do not belong merely to $V \otimes V$ but rather to either $(V \otimes V)_S$ (where the S denotes "symmetrised") spanned by $\{|\psi\rangle \otimes |\phi\rangle + |\phi\rangle \otimes |\psi\rangle\}$, for which $\eta = 1$, or $(V \otimes V)_A$ (the A standing for "antisymmetrised") spanned by $\{|\psi\rangle \otimes |\phi\rangle - |\phi\rangle \otimes |\psi\rangle\}$, for which $\eta = -1$.

More generally, for multiparticle states $N \geq 2$ we can define $u_{(a,b)}$, an operator exchanging particles a and b, and on a general multiparticle state, $u_{(a,b)}|\Psi\rangle = \eta_{(a,b)}|\Psi\rangle$, with $\eta_{(a,b)} = \pm 1$. Now for any permutation π of $\{1, \ldots, N\}$ we can define $u_\pi|\vec{x}_1, r_1, \ldots, \vec{x}_N, r_N\rangle = |\vec{x}_{\pi(1)}, r_{\pi(1)}, \ldots, \vec{x}_{\pi(N)}, r_{\pi(N)}\rangle$, and on a general state, $u_\pi|\Psi\rangle = \eta_\pi|\Psi\rangle$. But the algebra of transpositions implies $\eta_{(a,b)}$ has the same value $\forall a, b$, and so since any π can be obtained by a sequence of transpositions, if this is 1 then $\eta_\pi = 1 \forall \pi$, and if this is -1 then $\eta_\pi = \mathrm{sgn}(\pi)$ $(:= (-1)^{\#(\text{ transpositions in } \pi)}$.

Hence, we have two fundamentally different kind s of particles: Bosons, obeying Bose-Einstein statistics, for which the interchange of identical particles leaves the state unchanged, and Fermions, obeying Fermi-Dirac statistics, for which the interchange of identicle particles changes the state by a sign. In addition, there is the following important fact:

Spin-statistics relation: All integral spin particles ($s = 0, 1, 2, \ldots$) are bosons, all $\frac{1}{2}$-integral spin particles ($s = \frac{1}{2}, \frac{3}{2}, \ldots$) are fermions; this is confirmed by experiment, but somewhat mysterious at this stage; we can only derive it using relativistic QM as is done in the part III QFT course, wheer it becomes the spin-statistics theorem. This makes it an unusual example of a relativistic effect which is enormously important in "everyday", low speed situations.

Most common elementary particles are fermions, e.g. protons, neutrons, electrons and neutrinos are all spin $\frac{1}{2}$; Pions, kaons and the theoretical Higgs are spin 0, while photons, gluons, and the weak-nuclear-force-carrying particles $w^\pm, z$ are spin 1.

4.4 Two-particle examples

The states of two identical particles belong to $(V \otimes V)_S$ for bosons or $(V \otimes V)_A$ for fermions, where $V = V_{\text{space}} \otimes V_{\text{spin}}$; it is useful to construct the states we require by taking $(V_{\text{space}} \otimes V_{\text{space}})_{S \text{ or } A}$ and $(V_{\text{spin}} \otimes V_{\text{spin}})_{S \text{ or } A}$ and then recombining.

Let $H(\vec{x}, \vec{p})$ be a Hamiltonian (spin-independent) for a single particle, with non-degenerate energies $E_0 < E_1 < \ldots$ with respective wavefunctions $\psi_0(\vec{x}), \psi_1(\vec{x}), \ldots$ for states in V_{space} (e.g. a particle in a box). The Hamiltonian for the two-particle system (assuming the particles don't interact) is then $H(\vec{x}_1, \vec{p}_1) + H(\vec{x}_2, \vec{p}_2)$, so a basis for $V_{\text{space}} \otimes V_{\text{space}}$ is given by the energy eigenfunctions $\psi_0(\vec{x}_1)\psi_0(\vec{x}_2) =: \Psi_0$ with eigenvalue $2E_0$, $\psi_0(\vec{x}_1)\psi_1(\vec{x}_2), \psi_1(\vec{x}_1)\psi_0(\vec{x}_2)$ with energy $E_0 + E_1$, and so on. Form combinations with definite symmetry: $\Psi_1^S(\vec{x}_1, \vec{x}_2) =$

$\frac{1}{\sqrt{2}}(\psi_0(\vec{x}_1)\psi_1(\vec{x}_2)+\psi_1(\vec{x}_1)\psi_0(\vec{x}_2))$, $\Psi_1^A(\vec{x}_1,\vec{x}_2)=\frac{1}{\sqrt{2}}(\psi_0(\vec{x}_1)\psi_1(\vec{x}_2)-\psi_1(\vec{x}_1)\psi_0(\vec{x}_2))$ and so on to higher energies.

For $(V_{\text{spin}}\otimes V_{\text{spin}})_{S \text{ or } A}$ consider first $s=0$, then there is only one state in V_{spin}, and $V_{\text{spin}}\otimes V_{\text{spin}}$ is the single state $|0\rangle\otimes|0\rangle$. So for identical spin 0 particles the allowed states are $\Psi_0(\vec{x}_1,\vec{x}_2)$, $\Psi_1^S(\vec{x}_1,\vec{x}_2),\ldots$ as these are symmetric, and not $\psi_1^A(\vec{x}_1,\vec{x}_2)$.

Now we consider spin $\frac{1}{2}$; V_{spin} is $\{|\uparrow\rangle,|\downarrow\rangle\}$ so $V_{\text{spin}}\otimes V_{\text{spin}}$ has basis $\{|\uparrow\rangle|\uparrow\rangle,|\uparrow\rangle|\downarrow\rangle,|\downarrow\rangle|\uparrow\rangle,|\downarrow\rangle|\downarrow\rangle\}$ (dropping the $\otimes$ between states). Combinations with definite symmetry (appropriately normalized) are $|\uparrow\rangle|\uparrow\rangle$, $\frac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle+|\downarrow\rangle|\uparrow\rangle)$, $|\downarrow\rangle|\downarrow\rangle$ symmetric and $\frac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle-|\downarrow\rangle|\uparrow\rangle)$ antisymmetric, giving bases for $(V_{\text{spin}}\otimes V_{\text{spin}})_S$, $(V_{\text{spin}}\otimes V_{\text{spin}})_A$ respectively.

Identical spin $\frac{1}{2}$ particles obey Fermi statistics; the lowest possible energy state is $\Psi_0(\vec{x}_1,\vec{x}_2)\frac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle-|\downarrow\rangle|\uparrow\rangle)$ with energy E_0, and this is the unique state with this energy. At the next level we have one state $\Psi_1^S(\vec{x}_1,\vec{x}_2)$ ($\times$ the antisymmetric spin state) and three states given by $\Psi_1^A(\vec{x}_1,\vec{x}_2)\times$ the symmetric spin states, giving 4 states in total with energy E_0+E_1.

4.5 Pauli Exclusion Principle and Atomic Structure

A state of N identical fermions must be totally antisymmetric, so it can be specified completele by giving N distinct 1-particle states - then we take the tensor product and antisymmetrise to obtain the states. For the result of the antisymmetrisation to be nonzero the N particles must occupy different one-particle states.

The original application of this was to atomic structure: consider N electrons bound to a nucleus with Z protons. Ignoring the electrons' interactions with each other the Hamiltonian is $H(\vec{x}_1,\vec{p}_1)+\cdots+H(\vec{x}_N,\vec{p}_N)$ with $H(\vec{x},\vec{p})=\frac{1}{2m}\vec{p}^2-\frac{Ze^2}{4\pi\epsilon_0}\frac{1}{|\vec{x}|}$. The one particle energy eigenstates are $|n,l,m\rangle$, labelled according to their eigenvalues with respect to the commuting set $H,\vec{L}^2,L_3$ which are respectively $E_n,\hbar^2 l(l+1),\hbar m$ where $e_n=-\frac{M}{2}(\frac{Ze^2}{4\pi\epsilon_0\hbar})^2\frac{1}{n^2}$.

n is called the principal quantum number; for fixed n (and hence E_n) the possible values for the others are $l=0,1,\ldots,n-1, m=0,\pm1,\ldots,\pm l$, giving $2l+1$ total states for each l, so the total degeneracy ignoring electron spin is $1+3+\cdots+(2n-1)=n^2$; with the two possible states for electron spin the degeneracy is $2n^2$.

For electrically neutral atoms $N=Z$; as this number increases, more levels are filled up by the Pauli principle, and we have the broad features of the periodic table, e.g. especially unreactive elements for filled levels $N=2$ (Helium) or $N=10$) (Neon), and even valences of elements, from thinking about partially filled levels.

5 Perturbation Theory

Few QM systems can be solved exactly; in perturbation theory we start with a known, soluble system $H|n\rangle=E_n|n\rangle$ where the $\{|n\rangle\}$ form an ON basis of eigenstates, and then calculate energies and eigenstates for a perturbed Hamiltonian $(H+\lambda v)|\psi\rangle=E|\psi\rangle(\star)$ order-by-order in the parameter λ (Note that V may

be some general Hermitian operator, not just a potential). Our key assumption here is that everything depends smoothly on λ.

5.1 Non-Degenerate Case

Suppose that as $\lambda \to 0$, $|\psi\rangle \to |r\rangle, E \to E_r$ where $|r\rangle$ is the unique eigenstate with this energy, i.e. E_r is a non-degenerate energy level. The states $\{|n\rangle\}$ are still a basis for $\lambda \neq 0$, so we write $|\psi\rangle = \alpha|r\rangle + \sum_{j\neq r} \beta_j|j\rangle$ (the standard approach is to first expand in terms of λ and then use our basis like this, but the lecturer for this course considers this approach superior) $= \alpha(|r\rangle + \sum_{j\neq r} \gamma_j|j\rangle)$ where $\alpha, \beta_j, \gamma_j = \frac{\beta_j}{\alpha}$ are power series in λ such that $\lambda \to 1, \beta_j, \gamma_j \to 0$ as $\lambda \to 0$. We are aiming to calculate some early coefficients in expansions: $E = E_r + E_r'\lambda + E_r''\lambda^2 + \ldots, \alpha = 1 + a\lambda + \ldots, \gamma_j = c_j\lambda + \ldots$.

First we just substitute for $|\psi\rangle$ in $(\star)$: $(E_r + \lambda v)|r\rangle + \sum_{j\neq r} \gamma_j(E_j + \lambda v)|j\rangle = E(|r\rangle + \sum_{j\neq r} \gamma_j|j\rangle)$ or $(E - E_r)|r\rangle = \sum_{j\neq r} \gamma_j(E - E_j)|j\rangle = \lambda v|r\rangle + \lambda \sum_{j\neq r} \gamma_j v|j\rangle (\star\star)$; from $\langle r|(\star\star)$ we have $E - E_r = \lambda\langle r|v|r\rangle + \lambda \sum_{j\neq r} \gamma_j\langle r|v|j\rangle$. So far this is exact in λ; now comparing the LHS$=E_r'\lambda + E_r''\lambda^2 + \ldots$ with the RHS we see by comparing the terms of order λ that the first order energy shift $E_r' = \langle r : v : r\rangle$. Comparing terms of order λ^2 we have $E_r''\lambda^2 = \lambda \sum_{j\neq r} c_j\lambda\langle r : v : j\rangle$.

To find the c_j we return to $(\star\star)$: $\langle i|(\star\star)$ gives us $\gamma_i(E - E_i) = \lambda\langle i|v|r\rangle + \lambda \sum_{j\neq r} \gamma_j\langle i|v|j\rangle$; again this equation is exact, but taking just the leading terms (i.e. dropping all terms of order λ^2 or higher) we ahve $\lambda c_i(E_r - E_i) = \lambda\langle i|v|r\rangle$ so $c_i = \frac{\langle i|v|r\rangle}{E_r - E_i}$ (and this is why we needed E_r to be non-degenerate, so that we can divide by $E_r - E_i$ and know it is nonzero) and $E_r'' = \sum_{j\neq r} \frac{|\langle j|v|r\rangle|^2}{E_r - E_j}$; in summary $E = E_r + \lambda\langle r|v|r\rangle + \lambda^2 \sum_{j\neq r} \frac{|\langle j|v|r\rangle|^2}{E_r - E_j} + O(\lambda^3)$; this is second order non-degenerate perturbation theory.

Example: $H = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 = \hbar\omega(a^\dagger a + \frac{1}{2}$; we have states $|n\rangle$ with energies $E_n = \hbar\omega(n + \frac{1}{2})$ for $n = 0, 1, \ldots$. Consider a perturbation $v = m\omega^2\hat{x}^2$ which can be found to $= \frac{1}{2}\hbar\omega(a^2 + a^{\dagger 2} + 2a^\dagger a + 1)$ (the 1 being a result of the noncommutation of $a, a^\dagger$); note $\langle n|v|n\rangle = \frac{1}{2}\hbar\omega(2n+1), \langle n+2|v|n\rangle = \frac{1}{2}\hbar\omega\sqrt{n+1}\sqrt{n+2}, \langle n-2|v|n\rangle = \frac{1}{2}\hbar\omega\sqrt{n}\sqrt{n-1}$ and all other $\langle m|v|n\rangle$ are 0; the perturbed energy of the nth level (to order λ^2) is then $E_n + \lambda\langle n|v|n\rangle + \lambda^2 \sum_{m\neq n} \frac{|\langle m|v|n\rangle|^2}{E_n - E_m} = \hbar\omega(n + \frac{1}{2}) + \lambda\hbar\omega(n + \frac{1}{2}) + \lambda^2(\frac{\hbar\omega}{2})^2(\frac{(n+1)(n+2}{-2\hbar\omega} + \frac{n(n-1)}{2\hbar\omega}) = \hbar\omega(n + \frac{1}{2})(1 + \lambda - \frac{\lambda^2}{2})$. But the effect of adding λv to H is clearly just $\omega \mapsto \omega' = \omega\sqrt{1 + 2\lambda}$, so the new energies (exactly) are $\hbar\omega'(n + \frac{1}{2})$, whuch $= \hbar\omega(n + \frac{1}{2})(1 + \lambda - \frac{1}{2}\lambda^2 + O(\lambda^3))$, so everything works.

Now we consider validity/usefulness of perturbation theory: of course it is meaningless to say a dimensional quantity is small (except in comparison to another quantity of the same dimension), but since λ is dimensionless we might expect $\lambda \ll 1$ to suffice for good (or even rapid) convergence of the power series (but a moment's thought will show this to be nonsense, since we can multiply v by e.g. 10000 and reduce λ by the same factor); however, our expansion is really in $\frac{|\lambda\langle i|v|j\rangle|}{|E_j - E_j|}$ and similar quantities. So the condition for accuracy is therefore a very natural condition from the physical problem, which is that the size of the energy shifts from v, the numerator, must be $\ll$ the original energy differences, the denominator in that expression.

Example: the ground state energy for Helium. The unperturbed problem has $H = H(\hat{\vec{x}}_1, \hat{\vec{p}}_1) + H(\hat{\vec{x}}_2, \hat{\vec{p}}_2)$ where $H(\vec{x}, \vec{p}) = \frac{\vec{p}^2}{2m} - \frac{2e^2}{4\pi\epsilon_0|\vec{x}|}$ (the nucleus has charge $+2e$). As we saw in section 4.5, we introduce single-electron states $|n, l, m\rangle$ with wavefunctions $\psi_{nlm}(\vec{x})$ and $E_n = -\frac{M}{2}(\frac{2e^2}{4\pi\epsilon_0\hbar})^2\frac{1}{n^2}$; the lowest energy eigenstate for two electrons is $|\Psi\rangle = |1, 0, 0, \rangle \otimes |1, 0, 0\rangle \otimes |\chi\rangle$, where $|\chi\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle)$, obeying Fermi statistics; the two-electron wavefunction is $\Psi(\vec{x}_1, \vec{x}_2) = \psi_{100}(\vec{x}_1)\psi_{100}(\vec{x}_2)$ where $\psi_{100}(\vec{x}) = \frac{1}{\sqrt{\pi}}(\frac{2}{a_2})^{\frac{3}{2}}e^{-\frac{|\vec{x}|}{a_2}}$ where $a_2 = \frac{1}{2}\frac{4\pi\epsilon_0}{e^2}\frac{\hbar^2}{M}$; the energy of this is $2E_1 \approx -108.8eV$.

Experimentally, we find the ground state energy is $-79.0eV$. Restoring the electron-electron interaction and treating it as a perturbation we can have $\lambda = \frac{e^2}{4\pi\epsilon_0}, V(\vec{x}_1, \vec{x}_2) = \frac{1}{|\vec{x}_1 - \vec{x}_2|}$; the first-order correction to the ground state energy is then $\lambda\langle\Psi|v|\Psi\rangle = \lambda\int d^3\vec{x}_1 \int d^3\vec{x}_2 \Psi(\vec{x}_1, \vec{x}_2)^\star V(\vec{x}_1, \vec{x}_2)\Psi(\vec{x}_1, \vec{x}_2) = \lambda\int d^3\vec{x}_1 \int d^3\vec{x}_2 |\psi_{100}(\vec{x}_1)|^2|\psi_{100}(\vec{x}_2)|^2|\vec{x}_1 - \vec{x}_2|^{-1}$, which we can integrate by writing $\vec{x}_2$ in spherical polars with the axis in the direction of $\vec{x}_1$ (but the mechanics of this calculation is really irrelevant to the theory) and find to be $\approx 34.0eV$, so the corrected ground state energy is $-108.8eV + 34.0eV \approx 74.8eV$, which is much better, though can still be improved upon; we could take more terms in the expansion to increase the accuracy of this, but shall see later there is a superior technique for solving this problem. The physics of this situation is that if we have one electron around the nucleus and introduce a second one, the potential of the nucleus is "screened" somewhat to the second electron by the presence of the first electron, so the second electron "sees" a smaller potential and as such has a smaller (and hence, since it is negative, higher) binding energy than that of a single electron around a Helium nucleus.

5.2 Degenerate Case

Consider $(\star)$ again, but suppose that as $\lambda \to 0$, $E \to E_r = E_s = \ldots$, a degenerate energy level with states $|r\rangle, |s\rangle, \ldots$; we shall use r, s to label states in this degenerate set and j to label other basis states. Then as $\lambda \to 0$, $|\psi\rangle \to \sum_r a_r|r\rangle$.

Expand $|\psi\rangle = \sum_r \alpha_r|r\rangle + \sum_j \beta_j|j\rangle$ with $\alpha_r(\lambda = a_r + O(\lambda), \beta_j(\lambda) = O(\lambda$; substitute this into $(\star)$: $\sum_r \alpha_r(E_r + \lambda v)|r\rangle + \sum_j \beta_j(E_j + \lambda v)|j\rangle = E(\sum_r \alpha_r|r\rangle + \sum_j \beta_j|j\rangle)$, or, rearranging, $\sum_r \alpha_r(E - E_r)|r\rangle + \sum_j \beta_j(E - E_j)|j\rangle = \lambda\sum_r \alpha_r v|r\rangle + \lambda\sum_j \beta_j v|j\rangle (\star\star)$. We seek $E = E_r + \lambda E' + \ldots$; note the correction is no longer associated with some particular basis state $|r\rangle$ (since in general it will be associated with some linear combination of $|r\rangle, |s\rangle, \ldots$). $\langle s|(\star\star)$ gives $(E - E_s)\alpha_s = \lambda\sum_r \alpha_r\langle s|v|r\rangle + \lambda\sum_j \beta_j\langle s|v|j\rangle$; comparing coefficients of order λ, $\sum_r\langle s|v|r\rangle a_r = E'a_s$; thus E' is an eigenvalue of the matrix $\langle s|v|r\rangle$ and a_r are the components of a corresponding eigenvector; if there were originally N degenerate states there will be N possible eigenvalues (counted with multiplicity); thus the typical effect of the perturbation is to split up the originally degenerate levels by $O(\lambda)$.

Example: a particle in a box in two dimensions $0 \le x, y \le a$: for the unperturbed problem we have states $|p, q\rangle$ with wavefunctions $\psi_{pq}(x, y) = \frac{2}{a}\sin\frac{p\pi x}{a}\sin\frac{q\pi y}{a}$ and energy $E_{pq} = \frac{\hbar^2\pi^2}{2ma^2}(p^2 + q^2)$ for $p, q \in 1, 2, \ldots$; the lowest energy level is $E_{11} = \frac{\hbar^2\pi^2}{ma^2}$ which is non-degenerate, but the next level is $E_{12} = E_{21} = \frac{5\hbar^2\pi^2}{2ma^2}$ with degeneracy 2. Consider a perturbation $V(x, y) = \frac{xy}{a^2}$ (with the constant factor chosen so that λ has the dimensions of energy); the shift in the lowest energy

level $\lambda\langle 11|v|11\rangle = \lambda\int_0^a dx\int_0^a dy\frac{xy}{a^2}|\psi_{11}(x,y)|^2 = \lambda(\frac{2}{a})^2\frac{1}{a^2}(\int_0^a dxx\sin^2\frac{\pi x}{a})(\int_0^a dyy\sin^2\frac{\pi y}{a}) = \cdots = \frac{\lambda}{4}$ (which has the correct dimensions); the shifts in the next value are given by the eigenvalues of $\begin{pmatrix}\langle 12|v|12\rangle & \langle 12|v|21\rangle\\ \langle 21|v|12\rangle & \langle 21|v|21\rangle\end{pmatrix}$; this matrix is of the form $\begin{pmatrix}\alpha & \beta\\ \beta & \alpha\end{pmatrix}$ and we can find $\alpha = \frac{1}{4}, \beta = (\frac{16}{9\pi^2})^2$ (the reader may of course verify the calculations, but they are really irrelevant to an understanding of the QM); the eigenvalues of the matrix are $\alpha \pm \beta$, so the energy shifts are $\frac{\lambda}{4} + \lambda(\frac{4}{3\pi})^4$ to first order in λ.

6 Angular Momentum

6.1 Recap of Orbital Angular Momentum

For a particle with position and momentum $\hat{\vec{x}}, \hat{\vec{p}}$ the orbital angular momentum (about the origin) is $\vec{L} = \hat{\vec{x}} \times \hat{\vec{p}}$ or $L_i = \epsilon_{ijk}\hat{x}_j\hat{p}_k$, and $\vec{L}^2 = L_iL_i$. Since $[\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij}$, $[L_i, L_j] = i\hbar\epsilon_{ijk}L_k, [\vec{L}^2, L_i] = 0$; additionally $[L_i, \hat{x}_j] = i\hbar\epsilon_{ijk}\hat{x}_k, [L_i, \hat{p}_j] = i\hbar\epsilon_{ijk}\hat{p}_k$.

Joint eigenstates of $\vec{L}^2, L_3$ (say) can be yound in terms of wavefunctions: $\vec{L}^2Y_{lm} = \hbar^2 l(l+1)Y_{lm}, L_3Y_{lm} = \hbar mY_{lm}$ where $Y_{lm}(\theta,\phi)$ are the so-called spherical harmonics (for θ, ϕ angles in spherical polars); these solutions exist for the entire physical range of θ, ϕ only if $l \in 0, 1, 2, \ldots, m \in 0, \pm 1, \ldots, \pm l$. If the SE for a particular problem has a spherically symmetric potential $V(r)$ then we have separable solutions $\psi_{lm}(\vec{x}) = R_l(r)Y_{lm}(\theta,\phi)$ where $R_l(r)$ is a solution of the radial SE. Note (we can take this as a known property of the Y_{lm} that under $\vec{x} \mapsto -\vec{x}$ we have $r \mapsto r, \phi \mapsto \phi + \pi, \theta \mapsto \pi - \theta, \psi_{lm}(-\vec{x}) = (-1)^l\psi_{lm}(\vec{x})$. For example, consider a two-particle system with $H = \frac{\hat{\vec{p}}_1^2}{2m_1} + \frac{\hat{\vec{p}}_2^2}{2m_3} + V(|\hat{\vec{x}}_1 - \hat{\vec{x}}_2|)$; this is $\frac{\hat{\vec{P}}^2}{2M} + \frac{\hat{\vec{p}}^2}{2m} + V(|\hat{\vec{x}}|)$ where the unused $\hat{\vec{X}} = \frac{m_1\hat{\vec{x}}_1 + m_2\hat{\vec{x}}_2}{M}, \hat{\vec{P}} = \hat{\vec{p}}_1 + \hat{\vec{p}}_2, \hat{\vec{x}} = \hat{\vec{x}}_1 - \hat{\vec{x}}_2, \hat{\vec{p}} = \frac{m_2\hat{\vec{p}}_1 - m_1\hat{\vec{p}}_2}{M}$ (this last can be found by the fact that it is the unique $\hat{p}$ satisfying the canonical commutation relation between $\hat{\vec{x}}, \hat{\vec{p}}$ with $[\hat{\vec{X}}, \hat{\vec{p}}] = 0$. The CM dynamics are esentially trivial; if we take a state with definite CM momentum $\hat{\vec{p}} = \hbar\vec{k}$ the wavefunction for the system is $\Psi(\vec{X}, \vec{x}) = e^{i\vec{k}\cdot\vec{X}}\psi_{lm}(\vec{x})$; notice that for this system $\vec{x} \mapsto -\vec{x}$ is exchange of particles.

6.2 General Analysis of Angular Momentum Eigenstates

Consider $\vec{J} = (J_1, J_2, J_3)$ with $J_i^\dagger = J_i$, obeying $[J_i, J_j] = i\hbar\epsilon_{ijk}J_k$. Define $\vec{J}^2 = J_iJ_i$; then $[J_i, \vec{J}^2] = 0$, and so we look for joint eigenstates of $J_3, \vec{J}^2$. If $\vec{J}^2|\psi\rangle = \lambda|\psi\rangle$ for some normalized $|\psi\rangle$, $\lambda = \langle\psi|\vec{J}^2|\psi\rangle = \|J_1|\lambda\rangle\|^2 + \|J_2|\lambda\rangle\|^2 + \|J_3|\lambda\rangle\|^2 \geq 0$; it is convenient to let $\lambda = \hbar^2 j(j+1)$, and we may wlog take $j \geq 0$. Label the joint eigenstates by $\vec{J}^2|j,m\rangle = \hbar^2 j(j+1)|j,m\rangle, J_3|j,m\rangle = \hbar m|j,m\rangle$; we have j, m real and $j \geq 0$. Introduce $J_\pm = J_1 \pm iJ_2$; we have $J_\pm^\dagger = J_\mp$, and it is easy to verify $[J_3, J_\pm] = \pm\hbar J_\pm, [J_+, J_-] = 2\hbar J_3, [\vec{J}^2, J_\pm] = 0$; we also have $J_+J_- = \vec{J}^2 - J_3^2 + \hbar J_3, J_-J_+ = \vec{J}^2 - J_3^2 - \hbar J_3$. Now given any state $|j,m\rangle$, $J_\pm|j,m\rangle$ are eigenstates of J_3 with eigenvalues $\hbar(m \pm 1)$, provided the new states are nonzero: $J_3(J_\pm|j,m\rangle) = (J_\pm J_3 + [J_3, J_\pm])|j,m\rangle = (J_\pm\hbar m + (\pm\hbar J_\pm))|j,m\rangle = \hbar(m \pm 1)J_\pm|j,m\rangle$; to find out whether the new states vanish

we compute $\|J_+|j,m\rangle\|^2 = \langle j,m|J_-J_+|j,m\rangle = \langle j,m|\vec{J}^2 - J_3^2 - \hbar J_3|j,m\rangle = \hbar^2(j(j+1)-m(m+1)) = \hbar^2(j-m)(j+m+1)$, and this must be ≥ 0; similarly $\|J_-|j,m\rangle\|^2 = \hbar^2(j+m)(j-m+1) \geq 0$, and the states can only vanish when these inequalities become equalities. So $j \geq m \geq -j$ and $J_+|j,m\rangle = 0 \Leftrightarrow m = j, J_-|j,m\rangle = 0 \Leftrightarrow m = -j$.

Starting from any given $|j,m\rangle$, if $J_+^n|j,m\rangle$ is non-vanishing we have an eigenvalue $\hbar(m+n)$ of J_3. But we also have $j \geq m+n$, so there must be some integer k with $j = m+k$; similarly we have J_3 eigenvalues $\hbar(m-n)$ so $-j = m-k'$ for some integer k'; combining these, $2j = k+k'$, an integer.

Thus angular momentum states $\{|j,m\rangle\}$ have either j an integer and $m \in 0, \pm 1, \ldots, \pm j$, or j a half-integer and $m \in \pm\frac{1}{2}, \pm\frac{3}{2}, \ldots, \pm j$; in either case there are $2j+1$ states.

The first case (j an integer) is realised in orbital angular momentum $\vec{J} = \vec{L} = \hat{\vec{x}} \times \hat{\vec{p}}$; the states $|j,m\rangle$ are elements of V_{space} since they were constructed from $\hat{\vec{x}}, \hat{\vec{p}}$, and correspond to wavefuctions $\psi_{jm}(\vec{x}) = R(r)Y_{jm}(\theta,\phi)$. The second case cannot arise in this way; there are no well-behaved solutions of the diferential equations with j not an integer.

However, we have a new realisation of the second possibility as intrinsic angular momentum or spin, $\vec{J} = \vec{S}$, with states $|s,m\rangle$ in V_{spin}, where $j = s$ is fixed for a given particle and can be either an integer or half-integer. This matches our earlier description of spin, in section 4.2; we are now identifying the operators acting on it as S_i.

So a particle of spin s has both orbital and intrinsic angular momentum, with $[S_i, \hat{x}_j] = [S_i, \hat{P}_j] = [S_i, L_j] = 0$ (recall that the total space is $V_{\text{space}} \otimes V_{\text{spin}}$): we have various CCSs of observables, e.g. $\{\hat{x}_i, \vec{S}^2, S_3\}$ or $\{\vec{L}^2, L_3, \vec{S}^2, S_3, \ldots\}$.

In general, the joint eigenstates $\{|j,m\rangle\}$ for $\vec{J}^2, J_3$ are called an angular momentum multiplet or representation. From our calculations of $\|J_\pm|j,m\rangle\|^2$ above we can define an orthonormal basis of states with $J_\pm|j,m\rangle = \hbar\sqrt{(j \mp m)(j \pm m + 1)}|j, m \pm 1\rangle$; the whole multiplet will then be generated by this relation from a single state. Usually we work from the top state $m = j$, characterised by $J_+|j,j\rangle = 0$.

Note that we could use joint eigenstates of $\vec{J}^2, \vec{n}\cdot\vec{J}$ for any unit vector $\vec{n}$, e.g. J_1, J_2; we would have the same eigenvalues (though of course the m-eigenstate of J_3 is not the same as the m-eigenstate of J_2, and similarly; the relationship between the eigenstates of different $\vec{n}\cdot\vec{J}$ is quite involved).

6.3 Matrix Representations - Pauli Matricies

Recall from section 1.4 that given a basis $\{|n\rangle\}$ we can represent each operator A by a matrix $A_{mn} = \langle m|A|n\rangle$. Consider $j = 1$, giving a 3-dimensional state space with states $|1,1\rangle \to \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, |1,0\rangle \to \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, |1,-1\rangle \to \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$. Then we can calculate $J_3 \to \hbar\begin{pmatrix} 1 & & \\ & 0 & \\ & & -1 \end{pmatrix}, J_+ \to \hbar\sqrt{2}\begin{pmatrix} 0 & 1 & \\ & 0 & 1 \\ & & 0 \end{pmatrix}, J_- \to \hbar\sqrt{2}\begin{pmatrix} 0 & & \\ 1 & 0 & \\ & 1 & 0 \end{pmatrix}$ (where the matrix elements not written are 0).

This technique is actually most widely used for spin $j = \frac{1}{2}$; recall $|\frac{1}{2}, \frac{1}{2}\rangle = |\uparrow\rangle$ and similarly, then we have $|\uparrow\rangle \to \begin{pmatrix} 1 \\ 0 \end{pmatrix}, |\downarrow\rangle \to \begin{pmatrix} 0 \\ 1 \end{pmatrix}$, then $S_3 \to \frac{1}{2}\hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, S_+ \to \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, S_- \to \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$; expressing S_1, S_2 as linear combinations of $S_\pm$ we have $S_i \to \frac{1}{2}\hbar\sigma_i$ where $\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$ are the Pauli matricies; note that these are Hermitian traceless 2×2 matricies. They obey $\sigma_1^2 = \sigma_2^2 = \sigma_3^2 = 1, \sigma_1\sigma_2 = -\sigma_2\sigma_1 = i\sigma_3$, and cyclic permutations therof; we can express this by $\sigma_i\sigma_j = \delta_{ij}1 + i\epsilon_{ijk}\sigma_k$ (the antisymmetric part of this is equivalent to the statement that $[S_i, S_j] = i\hbar\epsilon_{ijk}S_k$, as then $[\sigma_i, \sigma_j] = 2i\epsilon_{ijk}\sigma_k$). The Pauli matricies can be seen as components of a vector $\vec{\sigma} = (\sigma_1, \sigma_2, \sigma_3)$; If $\vec{a}, \vec{b}$ are vectors (defining $\vec{a} \cdot \vec{\sigma} = a_i\sigma_i$ as usual) then contracting this identity with a_ib_j we can express it as $(\vec{a} \cdot \vec{\sigma})(\vec{b} \cdot \vec{\sigma}) = (\vec{a} \cdot \vec{b})1 + i(\vec{a} \times \vec{b}) \cdot \vec{\sigma}$.

Note in particular $(\vec{n} \cdot \vec{\sigma})^2 = 1$ for any unit vector $\vec{n}$, $\Leftrightarrow \vec{n} \cdot \vec{\sigma}$ has eigenvalues $\pm 1 \Leftrightarrow \vec{n} \cdot \vec{S}$ has eigenvalues $\pm\frac{\hbar}{2}$, as we would expect. Also we have $\vec{\sigma}^2 = \sigma_1^2 + \sigma_2^2 + \sigma_3^2 = 3 \Leftrightarrow \vec{S}^2 = \hbar^2\frac{1}{2}(\frac{1}{2} + 1) = \frac{3}{4}\hbar^2$.

6.4 Physical predictions involving Angular Momentum and Spin

From basic EM theory, we compre the standard electric and magnetic interactions, respectively $q\phi(\vec{x})$ where q is electric charge and ϕ electrostatic potential, and $-\vec{\mu} \cdot \vec{B}(\vec{x})$ where $\vec{\mu}$ is the magnetic dipole moment and $\vec{B}$ is the magnetic field. These are interaction enegies, i.e. the terms in the Hamiltonian. In the magnetic case this interaction means $\vec{\mu}$ tends to point along $\vec{B}$, so as to minimise the energy. From EM we have that for a particle of charge q moving with orbital angular momentum $\vec{L}$ there is a dipole moment μ proportional to q and $\vec{L}$, so the interaction energy is $-\gamma_L\vec{L} \cdot \vec{B}$; this remains the case in QM, but now we also have spin, which gives a similar interaction $-\gamma_S\vec{S} \cdot \vec{B}$.

Some examples of effects based on these interactions:

The Zeeman Effect: consider a Hydrogen-like atom with states $|n, l, m\rangle$ for the unperturbed system. Apply a magnetic field of size B along the 3-direction; the states $|n, l, m\rangle$ are still eigenstates when the interaction terms are added, but the energy E_n changes by $-\gamma_L\hbar mB$ or $\mp\gamma_S\frac{\hbar}{2}B$ ($-l \leq m \leq l$ as always); this effect is observed, and the latter term gives direct evidence that the electron is spin-$\frac{1}{2}$ (This effect is the reason m is called the magnetic quantum number).

Stern-Gerlach, as described in section 4.2: a field $\vec{B}(\vec{x})$ can split a beam of particles into beams of different spin states.

Returning to the nature of the intetracions, just as $\phi(\vec{x})$ can be proodduccee by a second charge, $\vec{B}$ may arise from a second dipole; then the dipole-dipole interaction is of the form $\vec{J}^{(1)} \cdot \vec{J}^{(2)}$ for independent angular momenta $J^{(i)}$. Then another example is:

Spin-orbit coupling: For a Hydrogen atom (and no external field), we have an interaction term proportional to $\vec{L} \cdot \vec{S}$ (where $\vec{L}, \vec{S}$ are the orbital and spin angular momenta; we shall leave out the position dependence). This produces

effects of the same order as the first relativistic correction, $\frac{3}{8}\frac{p^4}{m^3c^2}$; together these produce the fine structure in Hydrogen energy levels.

There is a very weak interaction of proton-electron spins $\vec{I}\cdot\vec{S}$; there are two levels, since the only two possibilities are that $\vec{I},\vec{S}$ are aligned or anti-aligned (since both are the spins of spin-$\frac{1}{2}$ particles). There is a very small energy gap detween them, giving the hyperfine structure of Hydrogen. This gives a 21cm wavelength emission for transitions between them, which is observed from interstellar hydrogen, and important in astrophysics.

The orders of the effects discussed are that the Bohr energies are of order $(mc^2)\alpha^2$, the fine structure is of order $(mc^2)\alpha^4$, and the hyperfine structure is of order $(mc^2)\alpha^4\frac{m}{m_p}$ where m is the electron mass, m_p is the proton mass and $\alpha=\frac{e^2}{4\pi\epsilon_0\hbar c}\approx\frac{1}{137}$.

6.5 Addition of angular momenta

We set $\hbar=1$ in this section. The standard relations for joint eigenstates are $\vec{J}^2|j,m\rangle=j(j+1)|j,m\rangle, J_3|j,m\rangle=m|j,m\rangle$; $J_\pm|j,m\rangle=\sqrt{(j\mp m)(j\pm m+1)}|j,m\pm 1\rangle$. Consider two independent systems, angular momentum operators $\vec{J}^{(1)},\vec{J}^{(2)}$ acting on a space of states $V^{(1)}\otimes V^{(2)}$, with bases $\{|j_i,m_i\rangle\}$ for spaces $V^{(i)}$. Fix j_1,j_2; a basis of $V^{(1)}\otimes V^{(2)}$ is then defined by $|m_1;m_2\rangle=|j_1,m_1\rangle\otimes|j_2,m_2\rangle$; we will sometimes write this as $|m_1\rangle|m_2\rangle$.

The sum of angular momenta is $\vec{J}=\vec{J}^{(1)}\otimes 1+1\otimes\vec{J}^{(2)}$, written $\vec{J}^{(1)}+\vec{J}^{(2)}$; our aim is to find eigenstates $|J,M\rangle$ of $\vec{J}^2$ and J_3. Since $J_3=J_3^{(1)}+J_3^{(2)}$, we have $J_3|m_1;m_2\rangle=(J_3^{(1)}|m_1\rangle)|m_2\rangle+|m_1\rangle(J_3^{(2)}|m_2\rangle=M|m_1\rangle|m_2\rangle$ where $M=m_1+m_2$. Note we have $|m_1|\le j_1,|m_2|\le j_2$ so $-(j_1+j_2)\le M\le j_1+j_2$. We want to write $|J,M\rangle=\sum_{m_1+m_2=M}C^J_{m_1m_2}|m_1;m_2\rangle$ for some Clebsch-Gordon coefficients $C^J_{m_1m_2}$. We have $C^J_{m_1m_2}=\langle m_1;m_2|J,M\rangle$.

The key idea for finding these is to identify the top-states $M=J$, which are found by the fact that $J_+|J,M\rangle=0\Leftrightarrow M=J$. Consider the simplest nontrivial example, $j_1=j_2=\frac{1}{2}$. $|m_1;m_2\rangle=|m_1\rangle|m_2\rangle$ with $m_i=\pm\frac{1}{2}$, so there are 4 states in total. The state with the largest value of M is $|\frac{1}{2}\rangle|\frac{1}{2}\rangle$; we claim this is $|1,1\rangle$ as there is no state with a higher value of M, so this must be a top state. Now apply $J_-=J_-^{(1)}+J_-^{(2)}$ to both sides (recall $J_-|j,m\rangle=\sqrt{(j+m)(j-m+1)}|j,m-1\rangle$), to get $\sqrt{2}|1,0\rangle=|-\frac{1}{2}\rangle|\frac{1}{2}\rangle+|\frac{1}{2}\rangle|-\frac{1}{2}\rangle$, i.e. $|1,0\rangle=\frac{1}{\sqrt{2}}(|-\frac{1}{2}\rangle|\frac{1}{2}\rangle+|\frac{1}{2}\rangle|-\frac{1}{2}\rangle)$; note that this state is correctly normalized. Applying J_- again, $\sqrt{2}|1,-1\rangle=\frac{1}{\sqrt{2}}(|-\frac{1}{2}\rangle|-\frac{1}{2}\rangle+|-\frac{1}{2}\rangle|-\frac{1}{2}\rangle)$, i.e. $|1,-1\rangle=|-\frac{1}{2}\rangle|-\frac{1}{2}\rangle$; this completes the $J=1$ multiplet. But we have an additional state with $M=0$: $|0,0\rangle=\frac{1}{\sqrt{2}}(|\frac{1}{2}\rangle|-\frac{1}{2}\rangle-|-\frac{1}{2}\rangle|\frac{1}{2}\rangle)$; this cannot be raised to any other state as there are no other possible state, so it must be a top state and we have $J=0$ (or we can check this directly by applying J_+. So we have a triplet with $J=1$ and a singlet with $J=0$; adding $j_1=\frac{1}{2},j_2=-\frac{1}{2}$ gives $J=1,0$.

Now we return to the general case; we begin with $(2j_1+1)(2j_2+1)$ product states $|m_1\rangle|m_2\rangle$. There is a unique state with $J=M=j_1+j_2$: $|j_1+j_2,j_1+j_2\rangle=|j_1\rangle|j_2\rangle$. Applying J_-, we obtain that $\sqrt{2(j_1+j_2)}|j_1+j_2,j_1+j_1\rangle=\sqrt{2j_1}|j_1-1\rangle|j_2\rangle+\sqrt{2j_2}|j_1\rangle|j_2-1\rangle$; hence $|j_1+j_2,j_1+j_2-1\rangle=\sqrt{\frac{j_1}{j_1+j_2}}|j_1-1\rangle|j_2\rangle+\sqrt{\frac{j_2}{j_1+j_2}}|j_1\rangle|j_2-1\rangle$ (correctly normalized); applying J_- repeatedly we obtain a

multiplet $|j_1+j_2, M\rangle$ with $j_1+j_2 \geq M \geq -(j_1+j_2)$, but at the level $M = j_1+j_2-1$ we also have an orthogonal state $\sqrt{\frac{j_1}{j_1+j_2}}|j_1-1\rangle|j_2\rangle - \sqrt{\frac{j_2}{j_1+j_2}}|j_1\rangle|j_2-1\rangle$, which must then be $|j_1+j_2-1, j_1+j_2-1\rangle$; this is a top state for a multiplet with $J = j_1+j_2-1$. We can continue in this fashion, forming complete multiplets and then taking a state orthogonal to all the states with successively smaller values of M to get new top states; by counting states, this process stops with $J = |j_1-j_2|$: $\sum_{J=|j_1-j_2|}^{j_1+j_2}(2J+1) = \sum_{J=|j_1-j_2|}^{j_1+j_2}((J+1)^2 - J^2) = (j_1+j_2+1)^2 - (j_1-j_2)^2 = (2j_1+1)(2j_2+1)$, which is the correct number of states.

The top states $|\psi\rangle$ so found can be confirmed as such by applying J_+ directly, but they are guaranteed to be top states anyway, as $|\psi\rangle \perp J_-|\phi\rangle \forall |\phi\rangle$ with the correct M eigenvalue, so $\langle\phi|J_+|\psi\rangle = 0\forall$ such $|\phi\rangle$ and $J_+|\psi\rangle = 0$.

In summary, addition of j_1 and j_2 gives $J = j_1+j_2, j_1+j_2-1, \ldots, |j_1-j_2|$; this makes intuitive sense if we visualise the j_i as the lengths of vectors $\vec{J}^{(i)}$.

7 Transformations and Symmetries

Given a unitary operator u, we define a transformation of a quantum system to be either a map of states alone by $|\phi\rangle \mapsto u|\phi\rangle, \langle\phi| \mapsto \langle\phi|u^\dagger$, or a map of operators only, $A \mapsto u^\dagger A u$ (these are equivalent); this results in a change of matrix elements, and thus of physical quantities, by $\langle\phi|A|\psi\rangle \mapsto \langle\phi|u^\dagger A u|\psi\rangle$.

A symmetry of a QM system is a transformation which obeys $u^\dagger H u = H$, or equivalently $[u, H] = 0$; this implies that in the S-picture, $|\psi(t)\rangle$ is a solution of the SE $\Rightarrow u|\psi(t)\rangle$ is also a solution, or in the H-picture, if $A(t)$ is a solution of the Heisenberg equations then $u^\dagger A(t) u$ is too.

7.1 Transformation groups and an example

Consider a (possibly infinite) group G and associated transformations of a QM system, $u(g)$ for each $g \in G$, with $u(g_1)u(g_2) = u(g_1 g_2), u(1_G) = 1$ and (therefore) $u(g^{-1}) = u(g)^{-1} = u(g)^\dagger$. We will aim to find $u(g)$ when G is a gorup of translations, rotations or reflections; in these cases we know how G acts geometrically on position, $\vec{x} \mapsto g(\vec{x})$ (or similarly we know how G acts on momentum $\vec{p}$); we can then infer how $u(g)$ acts on position eigenstates: $u(g)|\vec{x}\rangle = |g(\vec{x})\rangle$ (or considering $u(g)$ as acting on operators instead, $u(g)^\dagger \hat{\vec{x}} u(g) = g(\hat{\vec{x}})$). On a general state, $|\psi\rangle \mapsto u(g)|\psi\rangle$, and the position space wavefunction of the new state is then $\langle\vec{x} : u(g)|\psi\rangle = (u(g)^\dagger|\vec{x}\rangle)^\dagger|\psi\rangle = (u(g^{-1})|\vec{x}\rangle)^\dagger|\psi\rangle = (|g^{-1}(\vec{x})\rangle)^\dagger|\psi\rangle = \langle g^{-1}(x)|\psi\rangle = \psi(g^{-1}(x)$. So for e.g. a translation in one dimension $x \mapsto g_a(x) = x + a$, writing $u(a)$ for $u(g_a)$ we have $u(a)|x\rangle = |x+a\rangle$ and $u(a)^\dagger \hat{x} u(a) = \hat{x} + a$, but we showed in section 1 that $u(a) = \exp(-\frac{ia}{\hbar}\hat{p})$ has exactly these properties.

Now notice taht the effect of a translation on a wavefunction $\psi(x)$ is to send it to $\psi(x-a)$; note that the graph of this is precisely the graph of $\psi(x)$ translated to the right by a, as we would expect; thus the appearance of $\psi(g^{-1}(x))$ rather than $\psi(g(x))$ above really was correct.

Also, acting on wavefunctions, $\hat{p} \to i\hbar\frac{\partial}{\partial x}$ and hence $u(a) \to \exp(-a\frac{\partial}{\partial x})$, so acting on a wavefunction, $u(a)\psi(x) = \exp(-a\frac{\partial}{\partial x})\psi(x) = \psi(x) - a\psi'(x) + \frac{1}{2!}a^2\psi''(x) + \ldots$, which $= \psi(x-a)$ by Taylor's theorem.

7.2 Generators and Conservation Laws

Consider a general continuous group and let g_α for α real be a one-parameter family of elements with $g_\alpha g_\beta = g_\beta g_\alpha = g_{\alpha+\beta}, g_0 = 1_G$, and assume we know $g_\alpha(A) = A + \alpha f(A) + O(\alpha^2)$ for our quantities of interest A, e.g. position and momentum. The corresponding unitary operators $u(\alpha) = u(g_\alpha)$ then obey $u(\alpha)u(\beta) = u(\beta)u(\alpha) = u(\alpha+\beta), u(0) = 1$; $u(\alpha)^\dagger A u(\alpha) = g_\alpha(A)$. Define $Q = i\hbar \frac{\partial u(\alpha)}{\partial \alpha} \mid_{\alpha=0}$, so that $u(\delta\alpha) = 1 - \frac{i}{\hbar}\delta\alpha Q + O(\delta\alpha^2), u(-\delta\alpha) = 1 + \frac{i}{\hbar}\delta\alpha Q + O(\delta\alpha^2)$; then $u(-\delta\alpha) = u(\delta\alpha)^{-1} = u(\delta\alpha)^\dagger$, so $Q^\dagger = Q$ and Q is an observable. But we also have $u(\alpha+\delta\alpha) = u(\alpha)u(\delta\alpha) = u(\delta\alpha)u(\alpha)$, so $[Q, u(\alpha)] = 0$ and, taking the limit as $\delta\alpha \to 0$, $\frac{\partial u(\alpha)}{\partial \alpha} = -\frac{i}{\hbar} Q u(\alpha)$, for any value of α. Integrating, $u(\alpha) = \exp(-\frac{i\alpha}{\hbar} Q)$ (the constant factor being determined since we know $u(0) = 1$). Q is called the generator of this family of transformations within G.

To find Q, we equate $g_\alpha(A) = A + \alpha f(A) + O(\alpha^2)$ with $u(\alpha)^\dagger A u(\alpha) = (1 + \frac{i}{\hbar}\alpha Q + \dots) A (1 - \frac{i}{\hbar}\alpha Q + \dots) = A + \frac{i}{\hbar}\alpha [Q, A] + O(\alpha^2)$; we obtain $[Q, \alpha] = -i\hbar f(A)$, so a transformation of any quantity is fixed by its commutation relations with a generator Q.

Now suppose g_α is actually a symmetry, $[u(\alpha), H] = 0 \Leftrightarrow [Q, H] = 0$, i.e. the observable Q is a conserved quantity; in the S picture, $Q|\psi(0)\rangle = q|\psi(0)\rangle \Rightarrow Q|\psi(t)\rangle = q|\psi(t)\rangle$, or in the H picture $\frac{\partial Q(t)}{\partial t} = 0$.

Noether's Theorem

For each continuous family of transformations of a quantum system, there is a hermitian generator, Q, and if the transformation is a symmetry then Q is conserved; Q is often called the Noether charge.

Example: consider a system of particles $r, s, \dots$ with positions $\hat{\vec{x}}^{(r)}$ and momenta $\hat{\vec{p}}^{(r)}$ obeying $[\hat{x}_i^{(r)}, \hat{p}_j^{(s)}] = i\hbar\delta_{ij}\delta_{rs}$. Our transformation is a translation along the k direction ($k \in 1, 2, 3$): $g_a(\hat{x}_i^{(r)}) = \hat{x}_i^{(r)} + a\delta_{ij} \therefore f(\hat{x}_i^{(r)}) = \delta_{ik}$. $g_a(\hat{p}_i^{(r)}) = \hat{p}_i^{(r)}, f(\hat{p}_i^{(r)} = 0, \forall r$. So the generator Q must obey $[Q, \hat{x}_i^{(r)}] = -i\hbar\delta_{ik}, [Q, \hat{p}_i^{(r)}] = [$ (and this will define Q uniquely); hence $Q = \hat{P}_k = \sum \hat{p}_k^{(r)}$, total momentum in the k direction. in general, translation through $\vec{a}$ is generated by total momentum $\hat{\vec{\mathcal{P}}}$ and $u(\vec{a}) = \exp(-\frac{i}{\hbar}\vec{a}\cdot\hat{\vec{\mathcal{P}}})$. Noether's theorem thus gives that for particles interacting only through a potential depending only on relative positions $\hat{\vec{x}}^{(r)} - \hat{\vec{x}}^{(s)}$, H is translation invariant and $\hat{\vec{\mathcal{P}}}$ is conserved.

7.3 Angular Momentum and Rotations

Rotations form a non-abelian group, but for a fixed axis $\vec{n}$ we have an abelian subgroup of rotations g_θ through angle θ about $\vec{n}$. For A a scalaro, $g_\theta(A) = A$ unchanged, so $f(A) = 0$; if $\vec{V} = (V_1, V_2, V_3)$ is a vector then $g_\theta(\vec{V}) = \vec{V} + \theta\vec{n} \times \vec{V} + O(\theta^2)$ so $f(\vec{V}) = \vec{n} \times \vec{V}$. The corresponding unitary operator is $u(\theta\vec{n}) = 1 - \frac{i}{\hbar}\theta Q + O(\theta^2)$.

For a single particle, both $\hat{\vec{x}}$ and $\hat{\vec{p}}$ are vectors, so $[Q, \hat{\vec{x}}] = -i\hbar\vec{n}\times\hat{\vec{x}}, [Q, \hat{\vec{p}}] = -i\hbar\vec{n}\times\hat{\vec{p}}$. Recall $[L_i, \hat{x}_j] = i\hbar\epsilon_{ijk}\hat{x}_j, [L_i, \hat{p}_j] = i\hbar\epsilon_{ijk}\hat{p}_k$ for $\vec{L} = \hat{\vec{x}} \times \hat{\vec{p}}$, so [dotting with $\vec{n}$ it follows that $Q = \vec{n}\cdot\vec{L}$ is our generator.

For a spinless particle this is all we need. For $\vec{L}$ itself, we have $[Q, \vec{L}] = i\hbar\vec{n} \times \vec{L}$, i.e. $\vec{L}$ transforms as a vector, from the commutation relations for $\vec{L}$.

Now for a particle with spin, $\vec{S}$ must also transform as a vector; we must have $[Q, \vec{S}] = -i\hbar\vec{n} \times \vec{S}$. This is achieved by taking $Q = \vec{n} \cdot \vec{J}$ where $\vec{J}$ is total angular momentum $\vec{L}+\vec{S}$ (recall $[S_i, \hat{x}_j] = [S_i, \hat{p}_j] = [S_i, L_j] = 0$, so the previous equations still hold).

This analysis can be generalised to many-particle systems, and the unitary operator for rotation through $\vec{\theta} = \theta\vec{n}$ is $u(\vec{\theta}) = \exp(-\frac{i}{\hbar}\theta\vec{n} \cdot \vec{J})$ where $\vec{J}$ is the total angular momentum. The Noether's theorem gives that for a rotationally-invariant quantum system, total angular momentum is conserved (e.g. a single particle with $H = \frac{1}{2m}\hat{\vec{p}}^2 + V(|\hat{\vec{x}}|) + U(|\hat{\vec{x}}|)\vec{L} \cdot \vec{S}$ (e.g. the Hydrogen atom) clearly has a rotationally invariant hamiltonian, so $[J_i, H] = 0$ and $\vec{J}$ is conserved - but note that $\vec{L}, \vec{S}$ are not separately conserved unless $u(|\hat{\vec{x}}|) = 0$).

Now that we have identified angular momentum as the generator of rotations we can view the relations $[J_i, A] = 0, [J_i, V_j] = i\hbar\epsilon_{ijk}V_k$ as the definition of what it means to be a scalar or vector operator; we can then see that $\hat{\vec{x}}, \hat{\vec{p}}, \vec{L}, \vec{S}, \vec{J}$ are all vector operators as they obey the second of these commutation relations.

7.4 Rotations on States

On angular momentum eigenstates $|j, m\rangle$ for fixed j, the operators J_i are realised as $(2j + 1) \times (2j + 1)$ matricies. Then $u(\vec{\theta}) = \exp(-\frac{i}{\hbar}\vec{\theta} \cdot \vec{J})$ can be computed in some cases. For $j = 1$ we have a single state $|0, 0\rangle$ on which $\vec{J} = \vec{0}$, then by this formula $u(\vec{\theta}) = 1$ and $|0, 0\rangle \mapsto |0, 0\rangle$ under rotations, as we would expect. We will study the $j = \frac{1}{2}$ case below. For $j = 1$, we have states $|1, m\rangle$ with $m \in 0, \pm 1$. Generators are 3×3 matricies; consider $J_3 = \hbar \begin{pmatrix} 1 & & \\ & 0 & \\ & & -1 \end{pmatrix}$; a rotation about the 3 (i.e. z) axis is given by $u(\theta\hat{z}) = \exp(-\frac{i}{\hbar}\theta J_3) = \exp(-i\theta \begin{pmatrix} 1 & & \\ & 0 & \\ & & -1 \end{pmatrix}) = \begin{pmatrix} e^{-i\theta} & & \\ & 1 & \\ & & e^{i\theta} \end{pmatrix}$, so the states transform by $|1, \pm 1\rangle \mapsto e^{\mp i\theta}|1, \pm 1\rangle, |1, 0\rangle \mapsto |1, 0\rangle$, which is the transformation of a vector; cf the behaviour of $x \pm iy$ in $\mathbb{R}^3$.

For $j = 2$ there are 5 states, which transform like a symmetric, traceless [rank 2] tensor (we can split a general rank 2 tensor into the antisymmetrised part, which acts like a vector, the trace, which acts like a scalar, and the symmetric traceless part). For $j = \frac{1}{2}$ we have states $|\frac{1}{2}, \pm\frac{1}{2}\rangle$ or $|\uparrow\rangle, |\downarrow\rangle$, on which $\vec{J} = \frac{\hbar}{2}\vec{\sigma}$. The property $(\vec{n} \cdot \vec{\sigma})^2 = 1$ means we can compute $u(\vec{\theta}) = \exp(-\frac{i}{\hbar}\theta\vec{n} \cdot \vec{J}) = \exp(-\frac{i}{2}\theta\vec{n} \cdot \vec{\sigma}) = \sum_{p=0}^{\infty} \frac{1}{p!}(-\frac{i\theta}{2})^p(\vec{n} \cdot \vec{\sigma})^p = \cos\frac{\theta}{2} - i\vec{n} \cdot \vec{\sigma}\sin\frac{\sigma}{2}$ (because $(\vec{n} \cdot \vec{\sigma})^{2n} = 1$ etc.). The effect of this rotation on any state is $|\chi\rangle \mapsto u(\vec{\theta})|\chi\rangle = (\cos\frac{\theta}{2} - i\vec{n} \cdot \vec{\sigma}\sin\frac{\theta}{2})|\chi\rangle$; note that the $\frac{\theta}{2}$ here implies that under any rotation by 2π, $|\chi\rangle \mapsto u(2\pi\vec{n})|\chi\rangle = -|\chi\rangle$; the state is changed by a sign. This does not worry us overmuch, since $-|\chi\rangle, |\chi\rangle$ have the same physical content; nevertheless, this change is detectable, because changes in relative sign between states lead to measurable effects. Under a rotation by 4π we do get exactly the same state back. This same effect is observed in any particle with half-integral spin. The origin of the - sign here is that a "loop" of rotations starting at $\theta = 0$ and ending at $\theta = 2\pi$ cannot be smoothy deformed to a point, but a loop beginning at $\theta = 0$ and ending at $\theta = 4\pi$ can. QM keeps track of this, and this kind of

transformation is called a spinnor

7.5 Reflections and Parity

Spatial reflection or parity is defined by $P : \vec{x} \mapsto -\vec{x}, \vec{p} \mapsto -\vec{p}$; reflections in planes may be obtained by composing this with rotations. The corresponding unitary operator acts on position eigenstates by $u|\vec{x}\rangle = |-\vec{x}\rangle$; hence $u^2 = 1$. Since u is unitary we have $u^\dagger = u^{-1} = u$. There is no one-parameter family here so no generator, but u itself is observable. If $u|\psi\rangle = \eta_\psi|\psi\rangle$ then from $u^2 = 1$, $\eta_\psi^2 = 1$ so the eigenvalues are $\eta_\psi = \pm 1$, called the parity oyf the state $|\psi\rangle$. Action on operators has $u\hat{\vec{x}}u = -\hat{\vec{x}}, u\hat{\vec{p}}u = -\hat{\vec{p}}$, which imply $u\vec{L}u = \vec{L}$ as $\vec{L} = \hat{\vec{x}} \times \hat{\vec{p}}$. We have $u\vec{S}u = \vec{S}, u\vec{J}u = \vec{J}$. This transformation is a symmetry of a QM system if $uHu = H$, and in this case there are joint eigenstates of H and U.

This is familiar in 1D; if $H = \frac{\hat{p}^2}{2m} + V(\hat{x})$ where $V(-\hat{x}) = V(\hat{x})$ then we can choose our eigenfunctions $\psi(x)$ of H to be even or odd. In 3D with $H = \frac{\hat{p}^2}{2m} + V(|\hat{\vec{x}}|)$ we have definite orbital angular momentum states $\psi_{lm}(\vec{x})$ with $\psi_{lm}(-\vec{x}) = (s-1)^l \psi_{lm}(\vec{x})$, so these are already parity eigenstates with parity $\eta = (-1)^l$.

There is also a notion of intrinsic parity, whereby a single particle state $|a\rangle$ changes by $u|a\rangle = \eta_a|a\rangle$ with $\eta_a = \pm 1$. In general, for a system of particles, the total parity is the product of the spatial parity with the product of all intrinsic parities, e.g. suppose we have particles a, b with $\overrightarrow{ab} = \vec{x}$, in an angular momentum state $\psi_{lm}(\vec{x})$. Then the total parity is $(-1)^l \eta_a \eta_b$.

If parity is conserved (as is the case in EM and strong nuclear, but not weak nuclear (e.g. β-decay $n \to pe\bar{\nu}$), interactions), we have a multiplicative conservation law; physically, we cannot distinguish systems observed directly from those viewed in a mirror.

7.6 Example of use of conservation laws

Consider the process $\pi d \to nn$, where π is a pion, d a "deuteron" (a pn bound state) and n a neutron. Total momentum is conserved, so we work in the center of mass frame. This is a strong interaction, so total angular momentum and parity are conserved. For the πd system, assume we know $s_\pi = 0, s_d = 1$, and the experimenters have found or arranged the situation such that we initially have the orbital angular momentum $l = 0$, so total spin is 1 and total angular momentum $j = 1$. Then for the nn system, we know $s_n = \frac{1}{2}$; the orbital angular momentum is unknown at first. We know the spatial wavefunction must have symmetry $(-1)^l$. The total spin s must be 0 or 1; if it is 0, we have an antisymmetric spin state, so Fermi statistics will be obeyed implying l is even, so $j = l$ is even contradicting conservation of j. So we must have $s = 1$, a symmetric combination of spin states, so l is odd. Then $j \in l-1, l, l+1$, so we must have $j = l = s = 1$.

Now consider parity; it was initially $(-1)^0 \eta_\pi \eta_d$, and now is $(-1)^1 \eta_n^2$, but whatever η_n is we must have $\eta_n^2 = 1$, so if we know $\eta_d = 1$ we can deduce that $\eta_\pi = -1$.

Other discrete symmetries are time reversal T and "charge conjugation" C, which exchanges particles with their corresponding antiparticles (it is a pre-

diction of relativistic QM that every particle has an "antiparticle" (which is occasionally the same particle) with the same mass and spin but opposite electric charge). Combining these with parity P we have the CPT theorem, which is that the product transformation CPT is always a symmetry in relativistic QM.

8 Time-dependent perturbation theory

Consider a system with Hamiltonian $H_0 + V(t)$ where H_0 is time-independent with known eigenstates and eigenvalues, and $V(t)$ is small in comparison. We aim to calculate a probability for transition between eigenstates of H_0 (order-by-order in V), e.g. consider H_0 an atomic Hamiltonian and $V(t)$ representing the EM field, then we would like to calculate the probability of an atomic transition (accompanied by the emission or absorption of a photon).

8.1 The interaction picture

Start in the Schrödinger picture, with states obeying $i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = H|\psi(t)\rangle = (H_0+V(t))|\psi(t)\rangle$. The interaction picture is defined by "moving the known part of the time evolution into operators": $\overline{|\psi(t)\rangle} = e^{\frac{iH_0t}{\hbar}}|\psi(t)\rangle, \overline{A(t)} = e^{\frac{iH_0t}{\hbar}}Ae^{-\frac{iH_0t}{\hbar}}$ (where $\overline{x}$ denotes things in the interaction picture). Then the remaining time-dependence of states is given by $i\hbar\frac{\partial}{\partial t}\overline{|\psi(t)\rangle} = e^{\frac{iH_0t}{\hbar}}(-H_0 + H_0 + V(t))|\psi(t)\rangle = e^{\frac{iH_0t}{\hbar}}V(t)|\psi(t)\rangle = \overline{V(t)|\psi(t)\rangle}$; this can be re-cast as $\overline{|\psi(t)\rangle} = \overline{|\psi(0)\rangle} - \frac{i}{\hbar}\int_0^t dt'\overline{V(t')|\psi(t')\rangle}$, which is well suited to approximation order-by-order in $V((t)$: consider iterating the equation. $\overline{|\psi(t)\rangle} = \overline{|\psi(0)\rangle} - \frac{i}{\hbar}\int_0^t dt'\overline{V(t)|\psi(0)\rangle} + (-\frac{i}{\hbar})^2\int_0^t dt'\int_0^{t'} dt''\overline{V(t')V(t'')|\psi(t'')\rangle}$. The unknown $\overline{|\psi(t)\rangle}$ still appears on the RHS, but if we work to first order in $V(t)$ we have $\overline{|\psi(t)\rangle} = \overline{|\psi(0)\rangle} - \frac{i}{\hbar}\int_0^t dt'\overline{V(t')|\psi(0)\rangle} + O(V^2)$.

Now let $|a\rangle, |b\rangle$ be eigenstates of H_0 with [respective] energies E_a, E_b and let $\langle b|a\rangle = 0$. A transition from a state [initially] $|\psi(0)\rangle = \overline{|\psi(0)\rangle} = |a\rangle$ at $t = 0$ (when the Schrödinger and interaction pictures coincide) to state $|b\rangle$ occurs at time t with probability $|\langle b|\psi(t)\rangle|^2 = |\langle b|\overline{|\psi(t)\rangle}|^2$ (since $\langle b|\psi(t)\rangle = \langle b|e^{-\frac{iH_0t}{\hbar}}\overline{|\psi(t)\rangle} = e^{-\frac{iE_bt}{\hbar}}\langle b|\overline{|\psi(t)\rangle}$. Hence, working to order V, we have amplitude $\langle b|\overline{|\psi(t)\rangle} = \langle b|a\rangle - \frac{i}{\hbar}\int_0^t dt'\langle b|\overline{V(t')}|a\rangle = -\frac{i}{\hbar}\int_0^t dt'\langle b|e^{\frac{iH_0t'}{\hbar}}V(t)e^{-\frac{iH_0t'}{\hbar}}|a\rangle = -\frac{i}{\hbar}\int_0^t dt' e^{\frac{i(E_b-E_a)t'}{\hbar}}\langle b|V(t')|a\rangle$; thus the probability is (to order V^2) $\frac{1}{\hbar^2}|\int_0^t e^{i\omega t'}\langle b|V(t')|a\rangle|^2$ where $\omega = \frac{E_b-E_a}{\hbar}$.

An important special case is when $V(t')$ is constant (at least for t' from 0 to t); the amplitude then becomes $-\frac{i}{\hbar}\int_0^t e^{i\omega t'}dt'\langle b|V|a\rangle = \frac{1}{\hbar\omega}(1-e^{i\omega t})\langle b:V:a\rangle$, and the probability becomes $P(t) = \frac{1}{\hbar^2}(\frac{\sin\frac{\omega t}{2}}{\frac{\omega}{2}})^2|\langle b:V:a\rangle|^2$ (to order V^2); for fixed ω we have a periodic function of time.

8.2 Transition rates and Fermi's Golden Rule

The probability for a transition $a \to b$, above, is $P(t) = \frac{t}{\hbar^2}f_t(\omega):\langle b|V|a\rangle|^2$ with $f_t(\omega) = \frac{1}{t}(\frac{\sin\frac{\omega t}{2}}{\frac{\omega}{2}})^2$; if we graph $f_t(\omega)$ against ω, observe that $\lim_{\omega\to 0} f_t(\omega) = t$; above 0, the graph oscillates with period $\frac{2\pi}{t}$, with oscillations bounded by 0 and the curve $\frac{4}{t\omega^2}$. Observe that $\int_{-\infty}^{\infty} f_t(\omega)d\omega = 2\int_{-\infty}^{\infty}\frac{\sin^2 x}{x^2}dx = 2\pi$, independent

of t. As t increases, $f_t(\omega)$ is concentrated more and more around $\omega = 0$ [in fact the function tends towards $2\pi\delta(\omega)$; the lecturer promised us more detail on this later, but appears to have failed to deliver on this] and the probability for a transition becomes neglegible unless $\omega \approx 0$ or $E_b \approx E_a$.

The total probability for a transition to one of a number of possible final states is $P(t) = \sum_b \frac{t}{\hbar} f_t(\frac{E_b - E_a}{\hbar})|\langle b|V|a\rangle|^2$. In many applications we encounter a closely packed [i.e. approximatable by a continuum] set of final states, e.g. for atom $\rightarrow$ atom + photon there is a continuous range of possible photon states. Suppose the possible final states have certain parameters fixed, but the energy E_b is a variable. Define the density of states $\rho(E_b)$ by $\rho(E_b)\delta E = \#$ states (with suitable parameters) with energy between E_b and $E_b + \Delta$. The probability of a transition to a state in some band B of final states is obtained from the above equation by replacing $\sum_b$ with $\int_B dE_b \rho(E_b)$.

For t sufficiently large, $f_t(\omega) \approx 2\pi\delta(\omega) = 2\pi\hbar\delta(E_b - E_a)$ [lol what?], and then $P(t) = \frac{t}{\hbar^2}\int_B dE_\rho(E_b) 2\pi\hbar\delta(E_b - E_a)|\langle b|V|a\rangle|^2 = 0$ if $E_a \notin B$, $\frac{2\pi t}{\hbar}\rho(E_a)|\langle b|V|a\rangle|^2 \,|_{E_b = E_a}$ if $E_a \in B$.

For this to be a good approximation, we must have t not so large that first order perturbation theory breaks down, but large enough that the δ-function approximation is valid. So the changes in $\rho(E_b)|\langle b|V|a\rangle|^2$ must be shall for changes in E_b of order $\frac{\hbar}{t}$. Under these conditions we have a constant transition rate $\frac{dP(t)}{dt} = \frac{2\pi}{\hbar}\rho(E_a)|\langle b|V|a\rangle|^2$ - Fermi's Golden Rule.

8.3 Interaction of radiation/EM field with atoms

Take the Hydrogen hamiltonian H_0 and a perturbation $V(t) = e\hat{\vec{x}}\cdot\vec{\epsilon}\cos\omega_0 t$; this represents interaction with a classical EM wave of frequency $\omega > 0$; take the wavelength $\frac{2\pi c}{\omega_0}$ to be $>>$ the Bohr radius. This is a very good approximation for visible light.

The first order transition amplitude $a \rightarrow b$ is $-\frac{i}{\hbar}\int_0^t dt' e^{\frac{i(E_b - E_a)t'}{\hbar}}\langle b|V(t')|a\rangle = -\frac{ie}{\hbar}\int_0^t dt' e^{\frac{i(E_b - E_a)t'}{\hbar}}\cos\omega_0 t'\langle b|\vec{\epsilon}\cdot\hat{\vec{x}}|a\rangle$. We shall analyse this formula in two steps: first we shall consider the time dependence, then the time independent matrix element.

i) Time dependence: split the cos into exponentials, giving two terms $\int_0^t dt' e^{\frac{i(E_b - E_a)t'}{\hbar}} e^{\mp i\omega_0 t'}$. Evaluating these and taking the modulus squared to get the probability gives us terms $\frac{\sin^2\frac{(\omega\mp\omega_0)t}{2}}{\frac{(\omega\mp\omega_0)^2}{4}}$ (where $\omega = \frac{E_b - E_a}{\hbar}$ as usual), and a cross term which we shall see is irrelevant: for t large, these functions are peaked around $\omega = \pm\omega_0$, respectively, and the cross term is then small in comparison [and the cross term, and in fact all terms, are small away from these]. Proceeding just as in our derivation of the Golden Rule, we could derive the precise transition rates in the two cases $E_b - E_a = \pm\hbar\omega_0$; note that the rate is the same in each case.

ii) The matrix element $\vec{\epsilon}\cdot\langle b|\hat{\vec{x}}|a\rangle$; we need this to be nonzero for a transition to be possible. When it is nonzero, the probability will be proportional to $|\vec{\epsilon}|^2$, and therefore proportional to the intensity of EM radiation.

Consider Hydrogen atom states $|a\rangle = |n, l, m\rangle, |b\rangle = |n', l', m'\rangle$, labelled in the usual way by principal quantum number, $\vec{L}^2$ eigenvalue and L_3 eigenvalue. Information on whether $\langle b|\hat{x}_i|a\rangle$ vanishes can be obtained from parity and angular momentum arguments. The parity operator u obeys $u^2 = 1, u|n, l, m\rangle = (-1)^l|n, l, m\rangle, u\hat{x}_i u = -\hat{x}_i$. So $\langle n', l', m'|\hat{x}_i|n, l, m\rangle = \langle n', l', m'|uu\hat{x}_i uu|n, l, m\rangle =$

$(-1)^{l+l'+1}\langle n',l',m'|\hat{x}_i|n,l,m\rangle$, which must therefore $=0$ if $l+l'$ is even. So our first selection rule is that $l+l'$ is odd.

Now consider the consequences of angular momentum (i.e. rotational symmetry): we claim that the states $\hat{x}_i|n,l,m\rangle$ behave exactly as [addition of angular momentum] states with $j_1=1, j_2=l$, since the $\hat{x}_i$ are components of vectors so transform like states with angular momentum 1: recall $[L_i,\hat{x}_j]=i\hbar\epsilon_{ijk}\hat{x}_k$, i.e. $\hat{x}_i$ is a vector operator. Define $X_1=-\frac{1}{\sqrt{2}}(\hat{x}_1+i\hat{x}_2), X_0=\hat{x}_3, X_{-1}=\frac{1}{\sqrt{2}}(\hat{x}_1-i\hat{x}_2)$; it is easy to verify that $[L_3,X_q]=\hbar q X_q, [L_\pm,X_j]=\hbar\sqrt{(1\mp q)(1\pm q+1)}X_{q\pm1}$; compare this with our standard formulas for $L_3, L_\pm$ (in section 6) on states with $j=1$.

This implies $X_q|n,l,m\rangle$ behave just like product states $|1,q\rangle|l,m\rangle$, since $\vec{L}(X_q|n,l,m\rangle)=[\vec{L},X_q]|n,l,m\rangle+X_q(\vec{L}|n,l,m\rangle)$ corresponds precisely to $\vec{L}(|1,q\rangle|l,m\rangle)=(\vec{L}|1,q\rangle)|l,m\rangle+|1,q\rangle(\vec{L}|l,m\rangle)$.

Now by standard results on addition of angular momenta, $X_q|n,l,m\rangle$ has angular momentum quantum numbers $\in l+1,l,l-1$ for $\vec{L}^2$ and $=m+q$ for L_3. Hence for $\langle n',l',m'|X_q|n,l,m\rangle$ to be nonzero, we need $l'\in l+1,l,l-1$ and $m'=m+q$ (recall $q\in 0,\pm1$). Recall we have $l\neq l'$ by parity.

So in summary, i) the time-dependence: contributions from $e^{-i\omega_0 t}, e^{i\omega_0 t}$ in $\cos\omega_0 t$ dominate as t becomes sufficiently large, with $E_{n'}-E_n=\pm\hbar\omega_0$. This is the classical version of photon absorption/emission (still classical since we assumed a classical EM field - see later), ii) the matrix element $\vec{\epsilon}\cdot\langle n',l',m'|\hat{\vec{x}}|n,l,m\rangle$ - we have selection rules, this is non-zero only if $l'=l\pm1$ and $m'=m+q$, so $m'=m$ [is possible] if $\epsilon_3\neq0$, and m' [can] $=m\pm1$ if ϵ_1 or ϵ_2 is $\neq0$. The probability or transition rate is proportional to $|\vec{\epsilon}|^2$, i.e. proportional to the intensity of radiation.

8.4 Emission and absorption of photons (non-examinable outline)

Quantisation of the EM field is done by expanding in normal modes, reducing it to a set of oscillators (see section 2.2). Here we'll consider just one mode, of frequency ω_0. The EM field is then a single oscillator, and the electric field in the Heisenberg picture is $\propto ae^{-i\omega_0 t}+a|daggere^{i\omega_0 t}$. The initial and final states are now $|a\rangle=|n,l,m\rangle|N\rangle, |b\rangle=|n',l',m'\rangle|N'\rangle$, where N,N' are oscillator levels (or equivalently numbers of photons, or the quantum version of the intensity of the EM field). Terms involving $e^{\mp i\omega_0 t}$ now have factors in their amplitudes of $\langle N'|a|N\rangle$ (which $=\sqrt{N}$ if $N'=N-1$, 0 otherwise) or $\langle N'|a^\dagger|N\rangle$ (which $=\sqrt{N+1}$ if $N'=N+1$, 0 otherwise) respectively. Hence the probabilities and transition rates for absorption and emission of photons are equal except for the factors $N, N+1$; N is the intensity in "photon units", and the 1 is the new effect due to quantizing the EM field. So we can now have spontaneous emission - emission when $N=0$.

In general, for atomic energy levels with EM radiation of frequency $\frac{|E_i-E_j|}{\hbar}$, we have transitions from E_i down to E_j at a photon emission rate $A_{i\to j}+B_{i\to j}\times$ intensity, and transitions from E_j up to E_i at absorption rate $B_{j\to i}\times$ intensity. A and B are called the Einstein A and B coefficients; it is a general result that $B_{i\to j}=B_{j\to i}$, and if intensity is measured as the number of photons then these $=A_{i\to j}$ as well.

9 Quantum Basics

QM is inherently probabilistic, wheras classical mechanics is not. We ask, could the probabilities in QM actually just be the manifestation of our ignorance of some "hidden" degrees of freedom [in the same way that e.g. the probabilistic Boltzmann distribution of a classical gas arises from entirely deterministic mechanics]? We will address this question via Bell's inequality (there are many other interesting, and even open, questions in QM, e.g. a more satisfactory treatment of the role of the observer, but we won't discuss these).

9.1 Classical and Quantum Data

Consider the simplest possible system, a single measurable quantity S with outcomes 0 or 1. Classically, specifying S gives one bit of information. In QM S is an operator with eigenstates $|0\rangle, |1\rangle$; a general state is $|\psi\rangle = \alpha|0\rangle + \beta|1\rangle$ for some $|\alpha|^2 + |\beta|^2 = 1$, so there is an (uncountably) infinite set of possible states. This is called a quantum bit or qbit; it seems to contain vastly more information than a classical bit. However, if we measure S we destroy the state $|\psi\rangle$, forcing it into the state $|0\rangle$ or $|1\rangle$. To find $|\alpha|^2, |\beta|^2$ by making many measurements, we would need a large number of copies of $|\psi\rangle$. Could we find a mechanism for copying $|\psi\rangle$ as many times as we need? No, this is forbidden by the no-cloning theorem. As a simple version of this, suppose we have a device which copies any unknown state $|\psi\rangle$ onto a previously "blank" state $|b\rangle$ by a linear, unitary change $|\psi\rangle \otimes |b\rangle \overset{u}{\mapsto} |\psi\rangle \otimes |\psi\rangle$; similarly for another state $|\phi\rangle$, $|\phi\rangle \otimes |b\rangle \overset{u}{\mapsto} |\phi\rangle \otimes |\phi\rangle$ (all states here being taken to be normalized). Since u is unitary, we then have $\langle\phi|\psi\rangle\langle b|b\rangle = \langle\phi|\psi\rangle\langle\phi|\psi\rangle$, implying $\langle\phi|\psi\rangle$ must be 0 or 1. So we cannot copy a general linear combination of two independent states.

9.2 Hidden sectors and density operators

Consider a space of states $V = U \otimes W$ where the states of U are "observed" and those of W are "hidden". A general state is $|\Psi\rangle = \sum_{ia} \alpha_{ia}|\psi_i\rangle \otimes |\phi_a\rangle$ where $\{|\psi_i\rangle\}, \{|\phi_a\rangle\}$ are orthonormal bases for U, W, and $\||\Psi\rangle\|^2 = \sum_{ia} |\alpha_{ia}|^2 = 1$.

If an observable Q acts only on U, then $\langle Q\rangle = \langle\Psi|Q|\Psi\rangle = \sum_{ia}\sum_{jb} \alpha^\star_{jb}\alpha_{ia}\langle\psi_j|Q|\psi_i\rangle\langle\phi_b|\phi_a\rangle$. This last bracket is δ_{ab} and the result becomes $\sum_{ij} \beta_{ij}\langle\psi_j|Q|\psi_i\rangle$, where the matrix $\beta_{ij} = \sum_a \alpha_{ia}\alpha^\star_{ja}$, which is clearly Hermitian, positive definite, and of trace 1. There is a unitary matrix U_{ij} with $U\beta U^\dagger = \mathrm{diag}(p_i)$ (i.e. the diagonal matrix $A_{ii} = p_i, A_{ij} = 0$ otherwise), and $\sum_i p_i = 1$ (each $p_i \geq 0$), and if we define new orthonormal states $|\chi_i\rangle = \sum_j u_{ij}|\psi_j\rangle$, then $\langle Q\rangle = \sum_i p_i\langle Q\rangle_{\chi_i}$ where $\langle Q\rangle_{\chi_i} = \langle\chi_i|Q|\chi_i\rangle$. The effect of the hidden sector is to produce a probability distribution p_i for states $|\chi_i\rangle$ in U.

It is often convenient to write this using density operators $\rho = |\Psi\rangle\langle\Psi|$, a "pure state" in V. Defining the trace of any operator by $\mathrm{tr}A = \sum_n \langle n|A|n\rangle$ for any orthonormal basis $\{|n\rangle\}$, we have $\langle Q\rangle = \mathrm{tr}_V(Q\rho)$. The reduced density operator is $\bar\rho = \sum_{ij} \alpha_{ia}\alpha^\star_{ja}|\psi_i\rangle\langle\psi_j|$, a "mixed state", $= \sum_i p_i|\chi_i\rangle\langle\chi_i|$, so $\langle Q\rangle = \mathrm{tr}_V(Q\bar\rho)$.

9.3 EPR Experiments and Bell's Inequality

The Einstein-Podolsky-Rosen thought experiment: in modern language, consider two spin-$\frac{1}{2}$ particles being created in the state $|\psi\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle)$. Let the spin operators on the first and second particles be $\vec{\sigma}^{(A)}, \vec{\sigma}^{(B)}$ respectively. Imagine the particles are carried far apart in space by [respective] experimenters Alice (A) and Bob (B), without altering $|\psi\rangle$.

Suppose Alice measures $\sigma_z^{(A)}$; she gets the result $+1$ or -1, each with probability $|\frac{1}{\sqrt{2}}|^2 = \frac{1}{2}$. Say Alice measures 1 - then aftarwards, the state has become $|\uparrow\rangle|\downarrow\rangle$. Now if Bob measures $\sigma_z^{(B)}$ he gets the result -1 with probability 1; Alice knows this in advance, but Bob doesn't. Einstein termed this "spooky action at a distance". But note that there is no actual inconsistency, nor violation of causality.

The unexpected correlation arises because there was entanglement of two systems in the state $|\psi\rangle$; $|\psi\rangle$ was not a simple product $|\psi^{(A)}\rangle \otimes |\psi^{(B)}\rangle$.

Could the correlation be explained in a deterministic fashion, by some hidden variables which take definite values (according to some probability distribution) when the particle pair is created?

First consider a single particle, and think of measuring a single component of spin along the direction $\vec{n}$. $\sigma_\theta = \vec{n}\cdot\vec{\sigma} = \begin{pmatrix} \cos\theta & \sin\theta \\ \sin\theta & -\cos\theta \end{pmatrix}$ where $\vec{n} = (\sin\theta, 0, \cos\theta)$. This has eigenstates $|\uparrow\theta\rangle = \cos\frac{\theta}{2}|\uparrow\rangle + \sin\frac{\theta}{2}|\downarrow\rangle = \begin{pmatrix} \cos\frac{\theta}{2} \\ \sin\frac{\theta}{2} \end{pmatrix}$ with eigenvalue 1, $|\downarrow\theta\rangle = -\sin\frac{\theta}{2}|\uparrow\rangle + \cos\frac{\theta}{2}|\downarrow\rangle = \begin{pmatrix} -\sin\frac{\theta}{2} \\ \cos\frac{\theta}{2} \end{pmatrix}$ with eigenvalue -1. Note the inner products $|\langle\uparrow\theta|\uparrow\rangle|^2 = |\langle\downarrow\theta|\downarrow\rangle|^2 = \cos^2\frac{\theta}{2}, |\langle\uparrow\theta|\downarrow\rangle|^2 = |\langle\downarrow\theta|\uparrow\rangle|^2 = \sin^2\frac{\theta}{2}$. But these results could only depend on the angle between the directions of $\hat{z}, \vec{n}$, as the choice of axes is arbitrary. So $|\langle\uparrow\theta|\uparrow\phi\rangle|^2 = |\langle\downarrow\theta|\downarrow\phi\rangle|^2 = \cos^2\frac{\theta-\phi}{2}, |\langle\uparrow\theta|\downarrow\phi\rangle|^2 = \sin^2\frac{\theta-\phi}{2}$.

Now we return to a two-particle system, in state $|\psi\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle) = \frac{1}{\sqrt{2}}(|\uparrow\theta\rangle|\downarrow\theta\rangle - |\downarrow\theta\rangle|\uparrow\theta\rangle)$. Suppose Alice measures one of $\sigma_z^{(A)}, \sigma_\theta^{(A)}, \sigma_\phi^{(A)}$ and then Bob measures one of $\sigma_z^{(B)}, \sigma_\theta^{(B)}, \sigma_\phi^{(B)}$, e.g. $\sigma_z^{(A)} = +1$ (which occurs with probability $\frac{1}{2}$), so $|\psi\rangle$ becomes $|\uparrow\rangle|\downarrow\rangle$. Then $\sigma_\theta^{(B)} = -1$ with probability $|\langle\downarrow\theta|\downarrow\rangle|^2 = \cos^2\frac{\theta}{2}$. So we write $P(\sigma_z^{(A)} = +1, \sigma_\theta^{(B)} = -1) = \frac{1}{2}\cos^2\frac{\theta}{2}$; similarly $P(\sigma_z^{(A)} = -1, \sigma_\phi^{(B)} = +1) = \frac{1}{2}\cos^2\frac{\phi}{2}$ and $P(\sigma_\theta^{(A)} = 1, \sigma_\phi^{(B)} = 1) = \frac{1}{2}\sin^2\frac{\theta-\phi}{2}$.

Suppose these results were produced by some classical variables $S_z^{(A)}, S_\theta^{(A)}, S_\phi^{(A)}, S_z^{(B)}, S_\theta^{(B)}, S_\phi^{(B)}$, with each $S_i = \pm 1$ according to some probability distribution [and this value being fixed when $|\psi\rangle$ is created]. Since we know $s_z^{(A)} = \pm 1 \Leftrightarrow S_z^{(B)} = \mp 1$ and similarly, we can write the distribution as a function of Alice's variables alone, as $p(S_z^{(A)}, s_\theta^{(A)}, s_\phi^{(A)})$. Suppose this is possible; then $P(S_\theta^{(A)}, S_\phi^{(B)} = 1) = P(S_\theta^{(A)} = 1, S_\phi^{(A)} = -1) = p(1,1,-1) + p(-1,1,-1) \leq p(1,1,-1) + p(1,1,1) + p(-1,-1,-1) + p(-1,1,-1)$ (since probabilities are always ≥ 0), but this $= P(S_z^{(A)} = 1, S_\theta^{(A)} = 1) + P(S_z^{(A)} = -1, S_\phi^{(A)} = -1) = P(S_z^{(A)} = 1, S_\theta^{(B)} = -1) + P(S_z^{(A)} = -1, S_\phi^{(B)} = 1)$.

So we have (a version of) Bell's inequality: $P(S_\theta^{(A)}, S_\phi^{(B)} = 1) \leq P(S_z^{(A)} =$

$1, S_\theta^{(B)} = -1) + P(S_z^{(A)} = -1, S_\phi^{(B)} = 1)$. This implies $\sin^2 \frac{\theta-\phi}{2} \leq \cos^2 \frac{\theta}{2} + \cos^2 \frac{\phi}{2}$ by comparison with the results above. But this must hold $\forall \theta, \phi$, and it does not, e.g. for $\theta = \frac{3\pi}{4}, \phi = \frac{3\pi}{2}$ it would mean $-\cos^2 \frac{3\pi}{8} - \sin^2 \frac{3\pi}{8} \leq \cos^2 \frac{3\pi}{4}$, i.e. $-\cos \frac{3\pi}{4} \leq \cos^3 \frac{3\pi}{4}$, implying $\frac{1}{\sqrt{2}} \leq \frac{1}{2}$, a contradiction.

[This is the end of the course]