Foundations of Quantum Mechanics

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TO CLAIRE
THANKS FOR YOUR PATIENCE

Contents

Introduction

These notes are based on the course "Foundations of Quantum Mechanics" given by Dr. H. Osborn in Cambridge in the Michælmas Term 1997. These typeset notes have been produced mainly for my own benefit but seem to be officially supported. Recommended books are discussed in the bibliography at the back.

A word or two about the philosophy of these notes seem in order. They are based in content on the lectures given, but I have felt free to expand and contract various details, as well as to clarify explanations and improve the narrative flow. Errors in content are (hopefully) mine and mine alone but I accept no responsibility for your use of these notes.

Other sets of notes are available for different courses. At the time of typing, these courses were:

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Richard Cameron	*Analysis*	Hugh Osborn	*Proofreading*
Claire Gough	*Proofreading*	Malcolm Perry	*Accomodation*
Kate Metcalfe	*Probability*	David Sanders	*Proofreading*

Although these notes are free of charge anyone who wishes to express their thanks could send a couple of bottles of interesting beer to Y1 Burrell's Field, Grange Road.

Paul Metcalfe
15th December 1997

Chapter 1

The Basics of Quantum Mechanics

Quantum mechanics is viewed as the most remarkable development in 20^{th} century physics. Its point of view is completely different from classical physics. Its predictions are often probabilistic.

We will develop the mathematical formalism and some applications. We will emphasize vector spaces (to which wavefunctions belong). These vector spaces are sometimes finite-dimensional, but more often infinite dimensional. The pure mathematical basis for these is in Hilbert Spaces but (fortunately!) no knowledge of this area is required for this course.

1.1 Review of earlier work

This is a *brief* review of the salient points of the 1B Quantum Mechanics course. If you anything here is unfamiliar it is as well to read up on the 1B Quantum Mechanics course. This section can be omitted by the brave.

A wavefunction $\psi(x)\colon \mathbb{R}^3 \mapsto \mathbb{C}$ is associated with a single particle in three dimensions. ψ represents the state of a physical system for a single particle. If ψ is *normalised*, that is

$$\|\psi\|^2 \equiv \int \mathrm{d}^3x \; |\psi|^2 = 1$$

then we say that $\mathrm{d}^3x \; |\psi|^2$ is the probability of finding the particle in the infinitesimal region d^3x (at x).

Superposition Principle

If ψ_1 and ψ_2 are two wavefunctions representing states of a particle, then so is the linear combination $a_1\psi_1 + a_2\psi_2$ ($a_1, a_2 \in \mathbb{C}$). This is obviously the statement that wavefunctions live in a vector space. If $\psi' = a\psi$ (with $a \neq 0$) then ψ and ψ' represent the same physical state. If ψ and ψ' are both normalised then $a = e^{\imath\alpha}$. We write $\psi \sim e^{\imath\alpha}\psi$ to show that they represent the same physical state.

For two wavefunctions ϕ and ψ we can define a scalar product

$$(\phi, \psi) \equiv \int \mathrm{d}^3x \, \phi^*\psi \in \mathbb{C}.$$

This has various properties which you can investigate at your leisure.

Interpretative Postulate

Given a particle in a state represented by a wavefunction ψ (henceforth "in a state ψ") then the probability of finding the particle in state ϕ is $\mathcal{P} = |(\phi, \psi)|^2$ and if the wavefunctions are normalised then $0 \leq \mathcal{P} \leq 1$. $\mathcal{P} = 1$ if $\psi \sim \phi$.

We wish to define (linear) operators on our vector space — do the obvious thing. In finite dimensions we can choose a basis and replace an operator with a matrix.

For a complex vector space we can define the Hermitian conjugate of the operator A to be the operator $A^\dagger$ satisfying $(\phi, A\psi) = (A^\dagger\phi, \psi)$. If $A = A^\dagger$ then A is Hermitian. Note that if A is linear then so is $A^\dagger$.

In quantum mechanics dynamical variables (such as energy, momentum or angular momentum) are represented by (linear) Hermitian operators, the values of the dynamical variables being given by the eigenvalues. For wavefunctions $\psi(x)$, A is usually a differential operator. For a single particle moving in a potential $V(x)$ we get the Hamiltonian $H = -\frac{\hbar^2}{2m}\nabla^2 + V(x)$. Operators may have either a continuous or discrete spectrum.

If A is Hermitian then the eigenfunctions corresponding to different eigenvalues are orthogonal. We assume completeness — that any wavefunction can be expanded as a linear combination of eigenfunctions.

The expectation value for A in a state with wavefunction ψ is $\langle A \rangle_\psi$, defined to be $\sum_i \lambda_i |a_i|^2 = (\psi, A\psi)$. We define the square deviation ΔA^2 to be $\langle (A - \langle A \rangle_\psi)^2 \rangle_\psi$ which is in general nonzero.

Time dependence

This is governed by the Schrödinger equation

$$\imath\hbar\frac{\partial\psi}{\partial t} = H\psi,$$

where H is the Hamiltonian. H must be Hermitian for the consistency of quantum mechanics:

$$\imath\hbar\frac{\partial}{\partial t}(\psi, \psi) = (\psi, H\psi) - (H\psi, \psi) = 0$$

if H is Hermitian. Thus we can impose the condition $(\psi, \psi) = 1$ for all time (if ψ is normalisable).

If we consider eigenfunctions ψ_i of H with eigenvalues E_i we can expand a general wavefunction as

$$\psi(x, t) = \sum_i a_i e^{-\frac{\imath E_i}{\hbar}t}\psi_i(x).$$

If ψ is normalised then the probability of finding the system with energy E_i is $|a_i|^2$.

1.2 The Dirac Formalism

This is where we take off into the wild blue yonder, or at least a more abstract form of quantum mechanics than that previously discussed. The essential structure of quantum

mechanics is based on operators acting on vectors in some vector space. A wavefunction ψ corresponds to some abstract vector $|\psi\rangle$, a *ket* vector. $|\psi\rangle$ represents the state of some physical system described by the vector space.

If $|\psi_1\rangle$ and $|\psi_2\rangle$ are ket vectors then $|\psi\rangle = a_1|\psi_1\rangle + a_2|\psi_2\rangle$ is a possible ket vector describing a state — this is the superposition principle again.

We define a dual space of *bra* vectors $\langle\phi|$ and a scalar product $\langle\phi|\psi\rangle$, a complex number.[1] For any $|\psi\rangle$ there corresponds a unique $\langle\psi|$ and we require $\langle\phi|\psi\rangle = \langle\psi|\phi\rangle^*$. We require the scalar product to be linear such that $|\psi\rangle = a_1|\psi_1\rangle + a_2|\psi_2\rangle$ implies $\langle\phi|\psi\rangle = a_1\langle\phi|\psi_1\rangle + a_2\langle\phi|\psi_2\rangle$. We see that $\langle\psi|\phi\rangle = a_1^*\langle\psi_1|\phi\rangle + a_2^*\langle\psi_2|\phi\rangle$ and so $\langle\psi| = a_1^*\langle\psi_1| + a_2^*\langle\psi_2|$.

We introduce linear operators $\hat{A}|\psi\rangle = |\psi'\rangle$ and we define operators acting on bra vectors to the left $\langle\phi|\hat{A} = \langle\phi'|$ by requiring $\langle\phi'|\psi\rangle = \langle\phi|\hat{A}|\psi\rangle$ for all ψ. In general, in $\langle\phi|\hat{A}|\psi\rangle$, $\hat{A}$ can act either to the right or the left. We define the *adjoint* $\hat{A}^\dagger$ of $\hat{A}$ such that if $\hat{A}|\psi\rangle = |\psi'\rangle$ then $\langle\psi|\hat{A}^\dagger = \langle\psi'|$. $\hat{A}$ is said to be Hermitian if $\hat{A} = \hat{A}^\dagger$.

If $\hat{A} = a_1\hat{A}_1 + a_2\hat{A}_2$ then $\hat{A}^\dagger = a_1^*\hat{A}_1^\dagger + a_2^*\hat{A}_2^\dagger$, which can be seen by appealing to the definitions. We also find the adjoint of $\hat{B}\hat{A}$ as follows:

Let $\hat{B}\hat{A}|\psi\rangle = \hat{B}|\psi'\rangle = |\psi''\rangle$. Then $\langle\psi''| = \langle\psi'|\hat{B}^\dagger = \langle\psi|\hat{A}^\dagger\hat{B}^\dagger$ and the result follows. Also, if $\langle\psi|\hat{A} = \langle\phi'|$ then $|\phi'\rangle = \hat{A}^\dagger|\phi\rangle$.

We have eigenvectors $\hat{A}|\psi\rangle = \lambda|\psi\rangle$ and it can be seen in the usual manner that the eigenvalues of a Hermitian operator are real and the eigenvectors corresponding to two different eigenvalues are orthogonal.

We assume completeness — that is any $|\phi\rangle$ can be expanded in terms of the basis ket vectors, $|\phi\rangle = \sum_i a_i|\psi_i\rangle$ where $\hat{A}|\psi_i\rangle = \lambda_i|\psi_i\rangle$ and $a_i = \langle\psi_i|\psi\rangle$. If $|\psi\rangle$ is normalised — $\langle\psi|\psi\rangle = 1$ — then the expected value of $\hat{A}$ is $\langle\hat{A}\rangle_\psi = \langle\psi|\hat{A}|\psi\rangle$, which is real if $\hat{A}$ is Hermitian.

The completeness relation for eigenvectors of $\hat{A}$ can be written as $\hat{1} = \sum_i |\psi_i\rangle\langle\psi_i|$, which gives (as before)

$$|\psi\rangle = \hat{1}|\psi\rangle = \sum_i |\psi_i\rangle\langle\psi_i|\psi\rangle.$$

We can also rewrite $\hat{A} = \sum_i |\psi_i\rangle\lambda_i\langle\psi_i|$ and if $\lambda_j \neq 0\ \forall j$ then we can define $\hat{A}^{-1} = \sum_i |\psi_i\rangle\lambda_i^{-1}\langle\psi_i|$.

We now choose an orthonormal basis $\{|n\rangle\}$ with $\langle n|m\rangle = \delta_{nm}$ and the completeness relation $\hat{1} = \sum_n |n\rangle\langle n|$. We can thus expand $|\psi\rangle = \sum_n a_n|n\rangle$ with $a_n = \langle n|\psi\rangle$. We now consider a linear operator $\hat{A}$, and then $\hat{A}|\psi\rangle = \sum_n a_n\hat{A}|n\rangle = \sum_m a'_m|m\rangle$, with $a'_m = \langle m|\hat{A}|\psi\rangle = \sum_n a_n\langle m|\hat{A}|n\rangle$. Further, putting $A_{mn} = \langle m|\hat{A}|n\rangle$ we get $a'_m = \sum_n A_{mn}a_n$ and therefore solving $\hat{A}|\psi\rangle = \lambda|\psi\rangle$ is equivalent to solving the matrix equation $A\mathbf{a} = \lambda\mathbf{a}$. A_{mn} is called the matrix representation of $\hat{A}$. We also have $\langle\psi| = \sum_n a_n^*\langle n|$, with $a'^*_n = \sum_m a_m^* A^\dagger_{mn}$, where $A^\dagger_{mn} = A^*_{nm}$ gives the Hermitian conjugate matrix. This is the matrix representation of $\hat{A}^\dagger$.

1.2.1 Continuum basis

In the above we have assumed discrete eigenvalues λ_i and normalisable eigenvectors $|\psi_i\rangle$. However, in general, in quantum mechanics operators often have continuous

[1] *bra ket*. Who said that mathematicians have no sense of humour?

spectrum — for instance the position operator $\hat{\mathbf{x}}$ in 3 dimensions. $\hat{\mathbf{x}}$ must have eigenvalues $\mathbf{x}$ for any point $\mathbf{x} \in \mathbb{R}^3$. There exist eigenvectors $|\mathbf{x}\rangle$ such that $\hat{\mathbf{x}}|\mathbf{x}\rangle = \mathbf{x}|\mathbf{x}\rangle$ for any $\mathbf{x} \in \mathbb{R}^3$.

As $\hat{\mathbf{x}}$ must be Hermitian we have $\langle\mathbf{x}|\hat{\mathbf{x}} = \mathbf{x}\langle\mathbf{x}|$. We define the vector space required in the Dirac formalism as that spanned by $|\mathbf{x}\rangle$.

For any state $|\psi\rangle$ we can define a wavefunction $\psi(\mathbf{x}) = \langle\mathbf{x}|\psi\rangle$.

We also need to find some normalisation criterion, which uses the 3 dimensional Dirac delta function to get $\langle\mathbf{x}|\mathbf{x}'\rangle = \delta^3(\mathbf{x} - \mathbf{x}')$. Completeness gives

$$\int \mathrm{d}^3x |\mathbf{x}\rangle\langle\mathbf{x}| = 1.$$

We can also recover the ket vector from the wavefunction by

$$|\psi\rangle = \hat{1}|\psi\rangle = \int \mathrm{d}^3x |\mathbf{x}\rangle\psi(\mathbf{x}).$$

Also $\langle\mathbf{x}|\hat{\mathbf{x}}|\psi\rangle = \mathbf{x}\psi(\mathbf{x})$; the action of the operator $\hat{\mathbf{x}}$ on a wavefunction is multiplication by $\mathbf{x}$.

Something else reassuring is

$$\begin{aligned}\langle\psi|\psi\rangle = \langle\psi|\hat{1}|\psi\rangle &= \int \mathrm{d}^3x \langle\psi|\mathbf{x}\rangle\langle\mathbf{x}|\psi\rangle \\ &= \int \mathrm{d}^3x \left|\psi(\mathbf{x})\right|^2.\end{aligned}$$

The momentum operator $\hat{\mathbf{p}}$ is also expected to have continuum eigenvalues. We can similarly define states $|\mathbf{p}\rangle$ which satisfy $\hat{\mathbf{p}}|\mathbf{p}\rangle = \mathbf{p}|\mathbf{p}\rangle$. We can relate $\hat{\mathbf{x}}$ and $\hat{\mathbf{p}}$ using the commutator, which for two operators $\hat{A}$ and $\hat{B}$ is defined by

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

The relationship between $\hat{\mathbf{x}}$ and $\hat{\mathbf{p}}$ is $[\hat{x}_i, \hat{p}_j] = \imath\hbar\delta_{ij}$. In one dimension $[\hat{x}, \hat{p}] = \imath\hbar$.

We have a useful rule for calculating commutators, that is:

$$\left[\hat{A}, \hat{B}\hat{C}\right] = \left[\hat{A}, \hat{B}\right]\hat{C} + \hat{B}\left[\hat{A}, \hat{C}\right].$$

This can be easily proved simply by expanding the right hand side out. We can use this to calculate $\left[\hat{x}, \hat{p}^2\right]$.

$$\begin{aligned}\left[\hat{x}, \hat{p}^2\right] &= \left[\hat{x}, \hat{p}\right]\hat{p} + \hat{p}\left[\hat{x}, \hat{p}\right] \\ &= 2\imath\hbar\hat{p}.\end{aligned}$$

It is easy to show by induction that $[\hat{x}, \hat{p}^n] = n\imath\hbar\hat{p}^{n-1}$.

We can define an exponential by

$$e^{-\frac{\imath a\hat{p}}{\hbar}} = \sum_{n=0}^{\infty} \frac{1}{n!}\left(-\frac{\imath a\hat{p}}{\hbar}\right)^n.$$

We can evaluate $\left[\hat{x}, e^{-\frac{\imath a\hat{p}}{\hbar}}\right]$ by

$$\begin{aligned}\left[\hat{x}, e^{-\frac{\imath a\hat{p}}{\hbar}}\right] &= \left[\hat{x}, \sum_{n=0}^{\infty}\frac{1}{n!}\left(-\frac{\imath a\hat{p}}{\hbar}\right)^n\right] \\ &= \sum_{n=0}^{\infty}\frac{1}{n!}\left[\hat{x}, \left(-\frac{\imath a\hat{p}}{\hbar}\right)^n\right] \\ &= \sum_{n=0}^{\infty}\frac{1}{n!}\left(-\frac{\imath a}{\hbar}\right)^n [\hat{x}, \hat{p}^n] \\ &= \sum_{n=1}^{\infty}\frac{1}{(n-1)!}\left(-\frac{\imath a}{\hbar}\right)^n \imath\hbar\hat{p}^{n-1} \\ &= a\sum_{n=1}^{\infty}\left(-\frac{\imath a}{\hbar}\right)^{n-1}\hat{p}^{n-1} \\ &= ae^{-\frac{\imath a\hat{p}}{\hbar}}\end{aligned}$$

and by rearranging this we get that

$$\hat{x}e^{-\frac{\imath a\hat{p}}{\hbar}} = e^{-\frac{\imath a\hat{p}}{\hbar}}(\hat{x}+a)$$

and it follows that $e^{-\frac{\imath a\hat{p}}{\hbar}}|x\rangle$ is an eigenvalue of $\hat{x}$ with eigenvalue $x+a$. Thus we see $e^{-\frac{\imath a\hat{p}}{\hbar}}|x\rangle = |x+a\rangle$. We can do the same to the bra vectors with the Hermitian conjugate $e^{\frac{\imath a\hat{p}}{\hbar}}$ to get $\langle x+a| = \langle x|e^{\frac{\imath a\hat{p}}{\hbar}}$. Then we also have the normalisation $\langle x'+a|x+a\rangle = \langle x'|x\rangle$.

We now wish to consider $\langle x+a|p\rangle = \langle x|e^{\frac{\imath a\hat{p}}{\hbar}}|p\rangle = e^{\frac{\imath ap}{\hbar}}\langle x|p\rangle$. Setting $x=0$ gives $\langle a|p\rangle = e^{\frac{\imath ap}{\hbar}}N$, where $N = \langle 0|p\rangle$ is independent of x. We can determine N from the normalisation of $|p\rangle$.

$$\begin{aligned}\delta(p'-p) = \langle p'|p\rangle &= \int \mathrm{d}a\,\langle p'|a\rangle\langle a|p\rangle \\ &= |N|^2\int \mathrm{d}a\, e^{\frac{\imath a(p-p')}{\hbar}} \\ &= |N|^2\, 2\pi\hbar\,\delta(p'-p)\end{aligned}$$

So, because we are free to choose the phase of N, we can set $N = \left(\frac{1}{2\pi\hbar}\right)^{\frac{1}{2}}$ and thus $\langle x|p\rangle = \left(\frac{1}{2\pi\hbar}\right)^{\frac{1}{2}} e^{\frac{\imath xp}{\hbar}}$. We could *define* $|p\rangle$ by

$$|p\rangle = \int \mathrm{d}x\,|x\rangle\langle x|p\rangle = \left(\frac{1}{2\pi\hbar}\right)^{\frac{1}{2}}\int \mathrm{d}x\,|x\rangle e^{\frac{\imath xp}{\hbar}},$$

but we then have to check things like completeness.

1.2.2 Action of operators on wavefunctions

We recall the definition of the wavefunction ψ as $\psi(x) = \langle x|\psi\rangle$. We wish to see what operators (the position and momentum operators discussed) do to wavefunctions.

Now $\langle x|\hat{x}|\psi\rangle = x\langle x|\psi\rangle = x\psi(x)$, so the position operator acts on wavefunctions by multiplication. As for the momentum operator,

$$\begin{aligned}\langle x|\hat{p}|\psi\rangle &= \int \mathrm{d}p\, \langle x|\hat{p}|p\rangle\langle p|\psi\rangle \\ &= \int \mathrm{d}p\, p\langle x|p\rangle\langle p|\psi\rangle \\ &= \left(\frac{1}{2\pi\hbar}\right)^{\frac{1}{2}} \int \mathrm{d}p\, p e^{\frac{\imath x p}{\hbar}}\langle p|\psi\rangle \\ &= -\imath\hbar\frac{\mathrm{d}}{\mathrm{d}x}\int \mathrm{d}p\, \langle x|p\rangle\langle p|\psi\rangle \\ &= -\imath\hbar\frac{\mathrm{d}}{\mathrm{d}x}\langle x|\psi\rangle = -\imath\hbar\frac{\mathrm{d}}{\mathrm{d}x}\psi(x).\end{aligned}$$

The commutation relation $[\hat{x},\hat{p}] = \imath\hbar$ corresponds to $\left[x, -\imath\hbar\frac{\mathrm{d}}{\mathrm{d}x}\right] = \imath\hbar$ (acting on $\psi(x)$).

1.2.3 Momentum space

$|x\rangle \mapsto \psi(x) = \langle x|\psi\rangle$ defines a particular representation of the vector space. It is sometimes useful to use a momentum representation, $\tilde{\psi}(p) = \langle p|\psi\rangle$. We observe that

$$\begin{aligned}\tilde{\psi}(p) &= \int \mathrm{d}x\, \langle p|x\rangle\langle x|\psi\rangle \\ &= \left(\frac{1}{2\pi\hbar}\right)^{\frac{1}{2}} \int \mathrm{d}x\, e^{-\frac{\imath x p}{\hbar}}\psi(x).\end{aligned}$$

In momentum space, the operators act differently on wavefunctions. It is easy to see that $\langle p|\hat{p}|\psi\rangle = p\tilde{\psi}(p)$ and $\langle p|\hat{x}|\psi\rangle = \imath\hbar\frac{\mathrm{d}}{\mathrm{d}p}\tilde{\psi}(p)$.

We convert the Schrödinger equation into momentum space. We have the operator equation $\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x})$ and we just need to calculate how the potential operates on the wavefunction.

$$\begin{aligned}\langle p|V(\hat{x})|\psi\rangle &= \int \mathrm{d}x\, \langle p|V(\hat{x})|x\rangle\langle x|\psi\rangle \\ &= \left(\frac{1}{2\pi\hbar}\right)^{\frac{1}{2}} \int \mathrm{d}x\, e^{-\frac{\imath x p}{\hbar}} V(x)\langle x|\psi\rangle \\ &= \frac{1}{2\pi\hbar}\iint \mathrm{d}x\, \mathrm{d}p'\, V(x)\tilde{\psi}(p')e^{\frac{\imath x(p'-p)}{\hbar}} \\ &= \int \mathrm{d}p'\, \tilde{V}(p-p')\tilde{\psi}(p'),\end{aligned}$$

where $\tilde{V}(p) = \frac{1}{2\pi\hbar}\int \mathrm{d}p\, e^{-\frac{\imath x p}{\hbar}} V(x)$. Thus in momentum space,

$$H_p\tilde{\psi}(p) = \frac{p^2}{2m}\tilde{\psi}(p) + \int \mathrm{d}p'\, \tilde{V}(p-p')\tilde{\psi}(p').$$

1.2.4 Commuting operators

Suppose $\hat{A}$ and $\hat{B}$ are Hermitian and $\left[\hat{A}, \hat{B}\right] = 0$. Then $\hat{A}$ and $\hat{B}$ have simultaneous eigenvectors.

Proof. Suppose $\hat{A}|\psi\rangle = \lambda|\psi\rangle$ and the vector subspace V_λ is the span of the eigenvectors of $\hat{A}$ with eigenvalue λ. (If $\dim V_\lambda > 1$ then λ is said to be degenerate.)

As $\hat{A}$ and $\hat{B}$ commute we know that $\lambda\hat{B}|\psi\rangle = \hat{A}\hat{B}|\psi\rangle$ and so $\hat{B}|\psi\rangle \in V_\lambda$. If λ is non-degenerate then $\hat{B}|\psi\rangle = \mu|\psi\rangle$ for some μ. Otherwise we have that $\hat{B}\colon V_\lambda \mapsto V_\lambda$ and we can therefore find eigenvectors of $\hat{B}$ which lie entirely inside V_λ. We can label these as $|\lambda, \mu\rangle$, and we know that

$$\hat{A}|\lambda, \mu\rangle = \lambda|\lambda, \mu\rangle$$
$$\hat{B}|\lambda, \mu\rangle = \mu|\lambda, \mu\rangle.$$

□

These may still be degenerate. However we can in principle remove this degeneracy by adding more commuting operators until each state is uniquely labeled by the eigenvalues of each common eigenvector. This set of operators is called a *complete commuting set*.

This isn't so odd: for a single particle in 3 dimensions we have the operators $\hat{x}_1$, $\hat{x}_2$ and $\hat{x}_3$. These all commute, so for a single particle with no other degrees of freedom we can label states uniquely by $|\mathbf{x}\rangle$. We also note from this example that a complete commuting set is not unique, we might just as easily have taken the momentum operators and labeled states by $|\mathbf{p}\rangle$. To ram the point in more, we could also have taken some weird combination like $\hat{x}_1$, $\hat{x}_2$ and $\hat{p}_3$.

For our single particle in 3 dimensions, a natural set of commuting operators involves the angular momentum operator, $\hat{\mathbf{L}} = \hat{\mathbf{x}} \wedge \hat{\mathbf{p}}$, or $\hat{L}_i = \epsilon_{ijk}\hat{x}_j\hat{p}_k$.

We can find commutation relations between $\hat{L}_i$ and the other operators we know. These are summarised here, proof is straightforward.

- $\left[\hat{L}_i, \hat{x}_l\right] = \imath\hbar\epsilon_{ilj}\hat{x}_j$
- $\left[\hat{L}_i, \hat{\mathbf{x}}^2\right] = 0$
- $\left[\hat{L}_i, \hat{p}_m\right] = \imath\hbar\epsilon_{imk}\hat{p}_k$
- $\left[\hat{L}_i, \hat{\mathbf{p}}^2\right] = 0$
- $\left[\hat{L}_i, \hat{L}_j\right] = \imath\hbar\epsilon_{ijk}\hat{L}_k$
- $\left[\hat{L}_i, \hat{\mathbf{L}}^2\right] = 0$

If we have a Hamiltonian $\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + V(|\hat{\mathbf{x}}|)$ then we can also see that $\left[\hat{\mathbf{L}}, \hat{H}\right] = 0$. We choose as a commuting set $\hat{H}$, $\hat{\mathbf{L}}^2$ and $\hat{L}_3$ and label states $|E, l, m\rangle$, where the eigenvalue of $\hat{\mathbf{L}}^2$ is $l(l+1)$ and the eigenvalue of $\hat{L}_3$ is m.

1.2.5 Unitary Operators

An operator $\hat{U}$ is said to be *unitary* if $\hat{U}^\dagger\hat{U} = \hat{1}$, or equivalently $\hat{U}^{-1} = \hat{U}^\dagger$.

Suppose $\hat{U}$ is unitary and $\hat{U}|\psi\rangle = |\psi'\rangle$, $\hat{U}|\phi\rangle = |\phi'\rangle$. Then $\langle\phi'| = \langle\phi|\hat{U}^\dagger$ and $\langle\phi'|\psi'\rangle = \langle\phi|\psi\rangle$. Thus the scalar product, which is the probability amplitude of finding the state $|\phi\rangle$ given the state $|\psi\rangle$, is invariant under unitary transformations of states.

For any operator $\hat{A}$ we can define $\hat{A}' = \hat{U}\hat{A}\hat{U}^\dagger$. Then $\langle\phi'|\hat{A}'|\psi'\rangle = \langle\phi|\hat{A}|\psi\rangle$ and matrix elements are unchanged under unitary transformations. We also note that if $\hat{C} = \hat{A}\hat{B}$ then $\hat{C}' = \hat{A}'\hat{B}'$.

The quantum mechanics for the $|\psi\rangle$, $|\phi\rangle$, $\hat{A}$, $\hat{B}$ etc. is the same as for $|\psi'\rangle$, $|\phi'\rangle$, $\hat{A}'$, $\hat{B}'$ and so on. A unitary transform in quantum mechanics is analogous to a canonical transformation in dynamics.

Note that if $\hat{O}$ is Hermitian then $\hat{U} = e^{\imath\hat{O}}$ is unitary, as $\hat{U}^\dagger = e^{-\imath\hat{O}^\dagger} = e^{-\imath\hat{O}}$.

1.2.6 Time dependence

This is governed by the Schrödinger equation,

$$\imath\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \hat{H}|\psi(t)\rangle.$$

$\hat{H}$ is the Hamiltonian and we require it to be Hermitian. We can get an explicit solution of this if $\hat{H}$ does not depend explicitly on t. We set $|\psi(t)\rangle = \hat{U}(t)|\psi(0)\rangle$, where $\hat{U}(t) = e^{-\frac{\imath\hat{H}t}{\hbar}}$. As $\hat{U}(t)$ is unitary, $\langle\phi(t)|\psi(t)\rangle = \langle\phi(0)|\psi(0)\rangle$.

If we measure the expectation of $\hat{A}$ at time t we get $\langle\psi(t)|\hat{A}|\psi(t)\rangle = a(t)$. This description is called the Schrödinger picture. Alternatively we can absorb the time dependence into the operator $\hat{A}$ to get the Heisenberg picture, $a(t) = \langle\psi|\hat{U}^\dagger(t)\hat{A}\hat{U}(t)|\psi\rangle$. We write $\hat{A}_H(t) = \hat{U}^\dagger(t)\hat{A}\hat{U}(t)$. In this description the operators are time dependent (as opposed to the states). $\hat{A}_H(t)$ is the Heisenberg picture time dependent operator. Its evolution is governed by

$$\imath\hbar\frac{\partial}{\partial t}\hat{A}_H(t) = \left[\hat{A}_H(t), \hat{H}\right],$$

which is easily proven.

For a Hamiltonian $\hat{H} = \frac{1}{2m}\hat{p}(t)^2 + V(\hat{x}(t))$ we can get the Heisenberg equations for the operators $\hat{x}_H$ and $\hat{p}_H$

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\hat{x}_H(t) &= \frac{1}{m}\hat{p}_H(t)\\ \frac{\mathrm{d}}{\mathrm{d}t}\hat{p}_H(t) &= -V'(\hat{x}_H(t)).\end{aligned}$$

These ought to remind you of something.

Chapter 2

The Harmonic Oscillator

In quantum mechanics there are two basic solvable systems, the harmonic oscillator and the hydrogen atom. We will examine the quantum harmonic oscillator using algebraic methods. In quantum mechanics the harmonic oscillator is governed by the Hamiltonian

$$\hat{H} = \frac{1}{2m}\hat{p}^2 + \tfrac{1}{2}m\omega^2\hat{x}^2,$$

with the condition that $[\hat{x}, \hat{p}] = \imath\hbar$. We wish to solve $\hat{H}|\psi\rangle = E|\psi\rangle$ to find the energy eigenvalues.

We define a new operator $\hat{a}$.

$$\hat{a} = \left(\frac{m\omega}{2\hbar}\right)^{\frac{1}{2}}\left(\hat{x} + \frac{\imath\hat{p}}{m\omega}\right)$$
$$\hat{a}^\dagger = \left(\frac{m\omega}{2\hbar}\right)^{\frac{1}{2}}\left(\hat{x} - \frac{\imath\hat{p}}{m\omega}\right).$$

$\hat{a}$ and $\hat{a}^\dagger$ are respectively called the annihilation and creation operators. We can easily obtain the commutation relation $\left[\hat{a}, \hat{a}^\dagger\right] = \hat{1}$. It is easy to show that, in terms of the annihilation and creation operators, the Hamiltonian $\hat{H} = \frac{1}{2}\hbar\omega\left(\hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a}\right)$, which reduces to $\hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right)$. Let $\hat{N} = \hat{a}^\dagger\hat{a}$. Then $\left[\hat{a}, \hat{N}\right] = \hat{a}$ and $\left[\hat{a}^\dagger, \hat{N}\right] = -\hat{a}^\dagger$. Therefore $\hat{N}\hat{a} = \hat{a}\left(\hat{N} - 1\right)$ and $\hat{N}\hat{a}^\dagger = \hat{a}^\dagger\left(\hat{N} + 1\right)$.

Suppose $|\psi\rangle$ is an eigenvector of $\hat{N}$ with eigenvalue λ. Then the commutation relations give that $\hat{N}\hat{a}|\psi\rangle = (\lambda - 1)\,\hat{a}|\psi\rangle$ and therefore unless $\hat{a}|\psi\rangle = 0$ it is an eigenvalue of $\hat{N}$ with eigenvalue $\lambda - 1$. Similarly $\hat{N}\hat{a}^\dagger|\psi\rangle = (\lambda + 1)\,\hat{a}^\dagger|\psi\rangle$.

But for any $|\psi\rangle$, $\langle\psi|\hat{N}|\psi\rangle \geq 0$ and equals 0 iff $\hat{a}|\psi\rangle = 0$. Now suppose we have an eigenvalue $\lambda \notin \{0, 1, 2, \dots\}$. Then $\exists n$ such that $\hat{a}^n|\psi\rangle$ is an eigenvector of $\hat{N}$ with eigenvalue $\lambda - n < 0$ and so we must have $\lambda \in \{0, 1, 2, \dots\}$. Returning to the Hamiltonian we get energy eigenvalues $E_n = \hbar\omega\left(n + \frac{1}{2}\right)$, the same result as using the Schrödinger equation for wavefunctions, but with much less effort.

We define $|n\rangle = C_n\hat{a}^{\dagger n}|0\rangle$, where C_n is such as to make $\langle n|n\rangle = 1$. We can take $C_n \in \mathbb{R}$, and evaluate $\langle 0|\hat{a}^n\hat{a}^{\dagger n}|0\rangle$ to find C_n.

$$\begin{aligned}
1 &= \langle n|n\rangle \\
&= C_n^2 \langle 0|\hat{a}^n \hat{a}^{\dagger n}|0\rangle \\
&= C_n^2 \langle 0|\hat{a}^{n-1}\hat{a}\hat{a}^\dagger \hat{a}^{\dagger n-1}|0\rangle \\
&= \frac{C_n^2}{C_{n-1}^2}\langle n-1|\hat{a}\hat{a}^\dagger|n-1\rangle \\
&= \frac{C_n^2}{C_{n-1}^2}\langle n-1|\hat{N}+1|n-1\rangle \\
&= \frac{C_n^2}{C_{n-1}^2}(n-1+1)\langle n-1|n-1\rangle \\
&= n\frac{C_n^2}{C_{n-1}^2}.
\end{aligned}$$

We thus require $C_n = C_{n-1}/\sqrt{n}$ and as $C_0 = 1$ we get $C_n = (n!)^{-\frac{1}{2}}$ and so we have the normalised eigenstate (of $\hat{N}$) $|n\rangle = \frac{1}{\sqrt{n!}}\hat{a}^\dagger|0\rangle$ (with eigenvalue n). $|n\rangle$ is also an eigenvector of $\hat{H}$ with eigenvalue $\hbar\omega\left(n+\frac{1}{2}\right)$. The space of states for the harmonic oscillator is spanned by $\{|n\rangle\}$.

We also need to ask if there exists a non-zero state $|\psi\rangle$ such that $\hat{a}^\dagger|\psi\rangle = 0$. Then

$$0 = \langle\psi|\hat{a}\hat{a}^\dagger|\psi\rangle = \langle\psi|\psi\rangle + \langle\psi|\hat{a}^\dagger\hat{a}|\psi\rangle \geq \langle\psi|\psi\rangle > 0.$$

So there exist no non-zero states $|\psi\rangle$ such that $\hat{a}^\dagger|\psi\rangle = 0$.

2.1 Relation to wavefunctions

We evaluate

$$0 = \langle x|\hat{a}|0\rangle = \left(\frac{m\omega}{2\hbar}\right)^{\frac{1}{2}}\left(x + \frac{\hbar}{m\omega}\frac{\mathrm{d}}{\mathrm{d}x}\right)\langle x|0\rangle$$

and we see that $\psi_0(x) = \langle x|0\rangle$ satisfies the differential equation

$$\left(\frac{\mathrm{d}}{\mathrm{d}x} + \frac{m\omega}{\hbar}x\right)\psi_0(x) = 0.$$

This (obviously) has solution $\psi_0(x) = Ne^{-\frac{1}{2}\frac{m\omega}{\hbar}x^2}$ for some normalisation constant N. This is the ground state wavefunction which has energy $\frac{1}{2}\hbar\omega$.

For $\psi_1(x) = \langle x|1\rangle = \langle x|\hat{a}^\dagger|0\rangle$ we find

$$\begin{aligned}
\psi_1(x) &= \left(\frac{m\omega}{2\hbar}\right)^{\frac{1}{2}}\langle x|\left(\hat{x} - \frac{\imath}{m\omega}\hat{p}\right)|0\rangle \\
&= \left(\frac{m\omega}{2\hbar}\right)^{\frac{1}{2}}\left(x - \frac{\hbar}{m\omega}\frac{\mathrm{d}}{\mathrm{d}x}\right)\psi_0(x) \\
&= \left(\frac{2m\omega}{\hbar}\right)^{\frac{1}{2}} x\psi_0(x).
\end{aligned}$$

2.2 More comments

Many harmonic oscillator problems are simplified using the creation and annihilation operators.[1] For example

$$\begin{aligned}\langle m|\hat{x}|n\rangle &= \left(\frac{\hbar}{2m\omega}\right)^{\frac{1}{2}} \langle m|\hat{a}+\hat{a}^\dagger|n\rangle \\ &= \left(\frac{\hbar}{2m\omega}\right)^{\frac{1}{2}} \left(\sqrt{n}\,\langle m|n-1\rangle + \sqrt{n+1}\,\langle m|n+1\rangle\right) \\ &= \left(\frac{\hbar}{2m\omega}\right)^{\frac{1}{2}} \left(\sqrt{n}\,\delta_{m,n-1} + \sqrt{n+1}\,\delta_{m,n+1}\right).\end{aligned}$$

This is non-zero only if $m = n \pm 1$. We note that $\hat{x}^r$ contains terms $\hat{a}^s\hat{a}^{\dagger r-s}$, where $0 \le s \le r$ and so $\langle m|\hat{x}^r|n\rangle$ can be non-zero only if $n - r \le m \le n + r$.

It is easy to see that in the Heisenberg picture $\hat{a}_H(t) = e^{\imath\frac{\hat{H}t}{\hbar}}\hat{a}e^{-\imath\frac{\hat{H}t}{\hbar}} = e^{-\imath\omega t}\hat{a}$. Then using the equations for $\hat{x}_H(t)$ and $\hat{p}_H(t)$, we see that

$$\hat{x}_H(t) = \hat{x}\cos\omega t + \tfrac{1}{m\omega}\hat{p}\sin\omega t.$$

Also, $\hat{H}\hat{a}^\dagger_H(t) = \hat{a}^\dagger_H(t)(\hat{H} + \hbar\omega)$, so if $|\psi\rangle$ is an energy eigenstate with eigenvalue E then $\hat{a}^\dagger_H(t)|\psi\rangle$ is an energy eigenstate with eigenvalue $E + \hbar\omega$.

[1] And such problems *always* occur in Tripos papers. You have been warned.

Chapter 3

Multiparticle Systems

3.1 Combination of physical systems

In quantum mechanics each physical system has its own vector space of physical states and operators, which if Hermitian represent observed quantities.

If we consider two vector spaces V_1 and V_2 with bases $\{|r\rangle_1\}$ and $\{|s\rangle_2\}$ with $r = 1 \ldots \dim V_1$ and $s = 1 \ldots \dim V_2$. We define the tensor product $V_1 \otimes V_2$ as the vector space spanned by pairs of vectors

$$\{|r\rangle_1 |s\rangle_2 : r = 1 \ldots \dim V_1, s = 1 \ldots \dim V_2\}.$$

We see that $\dim(V_1 \otimes V_2) = \dim V_1 \dim V_2$. We also write the basis vectors of $V_1 \otimes V_2$ as $|r, s\rangle$. We can define a scalar product on $V_1 \otimes V_2$ in terms of the basis vectors: $\langle r', s'|r, s\rangle = \langle r'|r\rangle_1 \langle s'|s\rangle_2$. We can see that if $\{|r\rangle_1\}$ and $\{|s\rangle_2\}$ are orthonormal bases for their respective vector spaces then $\{|r, s\rangle\}$ is an orthonormal basis for $V_1 \otimes V_2$.

Suppose $\hat{A}_1$ is an operator on V_1 and $\hat{B}_2$ is an operator on V_2 we can define an operator $\hat{A}_1 \times \hat{B}_2$ on $V_1 \otimes V_2$ by its operation on the basis vectors:

$$\left(\hat{A}_1 \times \hat{B}_2\right) |r\rangle_1 |s\rangle_2 = \left(\hat{A}_1 |r\rangle_1\right) \left(\hat{B}_2 |s\rangle_2\right).$$

We write $\hat{A}_1 \times \hat{B}_2$ as $\hat{A}_1 \hat{B}_2$.

Two harmonic oscillators

We illustrate these comments by example. Suppose

$$\hat{H}_i = \frac{\hat{p}_i^2}{2m} + \tfrac{1}{2} m\omega \hat{x}_i^2 \qquad i = 1, 2.$$

We have two independent vector spaces V_i with bases $|n\rangle_i$ where $n = 0, 1, \ldots$ and $\hat{a}_i$ and $\hat{a}_i^\dagger$ are creation and annihilation operators on V_i, and

$$\hat{H}_i |n\rangle_i = \hbar\omega \left(n + \tfrac{1}{2}\right) |n\rangle_i.$$

For the combined system we form the tensor product $V_1 \otimes V_2$ with basis $|n_1, n_2\rangle$ and Hamiltonian $\hat{H} = \sum_i \hat{H}_i$, so $\hat{H}|n_1, n_2\rangle = \hbar\omega \left(n_1 + n_2 + 1\right) |n_1, n_2\rangle$. There are $N + 1$ ket vectors in the N^{th} excited state.

The three dimensional harmonic oscillator follows similarly. In general if $\hat{H}_1$ and $\hat{H}_2$ are two independent Hamiltonians which act on V_1 and V_2 respectively then the Hamiltonian for the combined system is $\hat{H} = \hat{H}_1 + \hat{H}_2$ acting on $V_1 \otimes V_2$. If $\{|\psi_r\rangle\}$ and $\{|\psi_s\rangle\}$ are eigenbases for V_1 and V_2 with energy eigenvalues $\{E_r^1\}$ and $\{E_s^2\}$ respectively then the basis vectors $\{|\Psi\rangle_{r,s}\}$ for $V_1 \otimes V_2$ have energies $E_{r,s} = E_r^1 + E_s^2$.

3.2 Multiparticle Systems

We have considered single particle systems with states $|\psi\rangle$ and wavefunctions $\psi(x) = \langle x|\psi\rangle$. The states belong to a space $\mathcal{H}$.

Consider an N particle system. We say the states belong to $\mathcal{H}^n = \mathcal{H}_1 \otimes \cdots \otimes \mathcal{H}_N$ and define a basis of states $|\psi_{r_1}\rangle_1 |\psi_{r_2}\rangle_2 \ldots |\psi_{r_N}\rangle_N$ where $\{|\psi_{r_i}\rangle_i\}$ is a basis for $\mathcal{H}_i$.

A general state $|\Psi\rangle$ is a linear combination of basis vectors and we can define the N particle wavefunction as $\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = \langle \mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N|\Psi\rangle$.

The normalisation condition is

$$\langle\Psi|\Psi\rangle = \int \mathrm{d}^3x_1 \ldots \mathrm{d}^3x_N \; |\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2 = 1 \qquad \text{if normalised.}$$

We can interpret $\mathrm{d}^3x_1 \ldots \mathrm{d}^3x_N \; |\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2$ as the probability density that particle i is in the volume element d^3x_i at $\mathbf{x}_i$. We can obtain the probability density for one particle by integrating out all the other $\mathbf{x}_j$'s.

For time evolution we get the equation $i\hbar\frac{\partial}{\partial t}|\Psi\rangle = \hat{H}|\Psi\rangle$, where $\hat{H}$ is an operator on $\mathcal{H}^N$.

If the particles do not interact then

$$\hat{H} = \sum_{i=1}^{N} \hat{H}_i$$

where $\hat{H}_i$ acts on $\mathcal{H}_i$ but leaves $\mathcal{H}_j$ alone for $j \neq i$. We have energy eigenstates in each $\mathcal{H}_i$ such that $\hat{H}_i|\psi_r\rangle_i = E_r|\psi_r\rangle_i$ and so $|\Psi\rangle = |\psi_{r_1}\rangle_1 |\psi_{r_2}\rangle_2 \ldots |\psi_{r_N}\rangle_N$ is an energy eigenstate with energy $E_{r_1} + \cdots + E_{r_N}$.

3.2.1 Identical particles

There are many such cases, for instance multielectron atoms. We will concentrate on two identical particles.

"Identical" means that physical quantities are be invariant under interchange of particles. For instance if we have $\hat{H} = H(\hat{\mathbf{x}}_1, \hat{\mathbf{p}}_1, \hat{\mathbf{x}}_2, \hat{\mathbf{p}}_2)$ then this must equal the permuted Hamiltonian $H(\hat{\mathbf{x}}_2, \hat{\mathbf{p}}_2, \hat{\mathbf{x}}_1, \hat{\mathbf{p}}_1)$ if we have identical particles. We introduce $\hat{U}$ such that

$$\hat{U}\hat{\mathbf{x}}_1\hat{U}^{-1} = \hat{\mathbf{x}}_2 \qquad \hat{U}\hat{\mathbf{x}}_2\hat{U}^{-1} = \hat{\mathbf{x}}_1$$
$$\hat{U}\hat{\mathbf{p}}_1\hat{U}^{-1} = \hat{\mathbf{p}}_2 \qquad \hat{U}\hat{\mathbf{p}}_2\hat{U}^{-1} = \hat{\mathbf{p}}_1.$$

We should also have $\hat{U}\hat{H}\hat{U}^{-1} = \hat{H}$ and more generally if $\hat{A}_1$ is an operator on particle 1 then $\hat{U}\hat{A}_1\hat{U}^{-1}$ is the corresponding operator on particle 2 (and vice versa).

Note that if $|\Psi\rangle$ is an energy eigenstate of $\hat{H}$ then so is $\hat{U}|\Psi\rangle$. Clearly $\hat{U}^2 = \hat{1}$ and we require $\hat{U}$ to be unitary, which implies that $\hat{U}$ is Hermitian.

In quantum mechanics we require $|\Psi\rangle$ and $\hat{U}|\Psi\rangle$ to be the same states (for identical particles). This implies that $\hat{U}|\Psi\rangle = \lambda|\Psi\rangle$ and the requirement $\hat{U}^2 = \hat{1}$ gives that $\lambda = \pm 1$. In terms of wavefunctions this means that $\Psi(\hat{\mathbf{x}}_1, \hat{\mathbf{x}}_2) = \pm\Psi(\hat{\mathbf{x}}_2, \hat{\mathbf{x}}_1)$. If we have a plus sign then the particles are bosons (which have integral spin) and if a minus sign then the particles are fermions (which have spin $\frac{1}{2}, \frac{3}{2}, \ldots$).[1]

The generalisation to N identical particles is reasonably obvious. Let $\hat{U}_{ij}$ interchange particles i and j. Then $\hat{U}_{ij}\hat{H}\hat{U}_{ij}^{-1} = \hat{H}$ for all pairs (i, j).

The same physical requirement as before gives us that $\hat{U}_{ij}|\Psi\rangle = \pm|\Psi\rangle$ for all pairs (i, j).

If we have bosons (plus sign) then in terms of wavefunctions we must have

$$\Psi(\hat{\mathbf{x}}_1, \ldots, \hat{\mathbf{x}}_N) = \Psi(\hat{\mathbf{x}}_{p_1}, \ldots, \hat{\mathbf{x}}_{p_N}),$$

where $(p_1, \ldots, p_N)$ is a permutation of $(1, \ldots, N)$. If we have fermions then

$$\Psi(\hat{\mathbf{x}}_1, \ldots, \hat{\mathbf{x}}_N) = \lambda\Psi(\hat{\mathbf{x}}_{p_1}, \ldots, \hat{\mathbf{x}}_{p_N}),$$

where $\lambda = +1$ if we have an even permutation of $(1, \ldots, N)$ and -1 if we have an odd permutation.

Remark for pure mathematicians. 1 and $\{\pm 1\}$ are the two possible one dimensional representations of the permutation group.

3.2.2 Spinless bosons

(Which means that the only variables for a single particle are $\hat{\mathbf{x}}$ and $\hat{\mathbf{p}}$.) Suppose we have two identical non-interacting bosons. Then $\hat{H} = \hat{H}_i + \hat{H}_2$ and we have $\hat{H}_1|\psi_r\rangle_i = E_r|\psi_r\rangle_i$. The general space with two particles is $\mathcal{H}_1 \otimes \mathcal{H}_2$ which has a basis $\{|\psi_r\rangle_1|\psi_s\rangle_2\}$, but as the particles are identical the two particle state space is $(\mathcal{H}_1 \otimes \mathcal{H}_2)_S$ where we restrict to symmetric combinations of the basis vectors. That is, a basis for this in terms of the bases of $\mathcal{H}_1$ and $\mathcal{H}_2$ is

$$\left\{|\psi_r\rangle_1|\psi_r\rangle_2; \tfrac{1}{\sqrt{2}}\left(|\psi_r\rangle_1|\psi_s\rangle_2 + |\psi_s\rangle_1|\psi_r\rangle_2\right), r \neq s\right\}.$$

The corresponding wavefunctions are

$$\psi_r(\mathbf{x}_1)\psi_r(\mathbf{x}_2) \quad \text{and} \quad \tfrac{1}{\sqrt{2}}\left(\psi_r(\mathbf{x}_1)\psi_s(\mathbf{x}_2) + \psi_s(\mathbf{x}_1)\psi_r(\mathbf{x}_2)\right)$$

and the corresponding eigenvalues are $2E_r$ and $E_r + E_s$. The factor of $2^{-\frac{1}{2}}$ just ensures normalisation and

$$\tfrac{1}{\sqrt{2}}\left({}_1\langle\psi_{r'}|{}_2\langle\psi_{s'}| + {}_1\langle\psi_{s'}|{}_2\langle\psi_{r'}|\right)\tfrac{1}{\sqrt{2}}\left(|\psi_r\rangle_1|\psi_s\rangle_2 + |\psi_s\rangle_1|\psi_r\rangle_2\right)$$

evaluates to $\delta_{rr'}\delta_{ss'} + \delta_{rs'}\delta_{r's}$.

For N spinless bosons with $\hat{H} = \sum \hat{H}_i$ the appropriate completely symmetric states are

$$\tfrac{1}{\sqrt{N!}}\Big(|\psi_{r_1}\rangle_1 \ldots |\psi_{r_N}\rangle_N + \text{permutations thereof}\Big) \quad \text{if } r_i \neq r_j$$

[1] Spin will be studied later in the course.

3.2.3 Spin $\frac{1}{2}$ fermions

In this case (which covers electrons, for example) a single particle state (or wavefunction) depends on an additional discrete variable s. The wavefunctions are $\psi(\mathbf{x}, s)$ or $\psi_s(\mathbf{x})$. The space of states for a single electron $\mathcal{H} = L^2(\mathbb{R}^3) \otimes \mathbb{C}^2$ has a basis of the form $|\mathbf{x}\rangle|s\rangle \equiv |\mathbf{x}, s\rangle$ and the wavefunctions can be written $\psi_s(\mathbf{x}) = \langle \mathbf{x}, s|\psi\rangle$. A basis of wavefunctions is $\{\psi_{r\lambda}(\mathbf{x}, s) = \psi_r(\mathbf{x})\boldsymbol{\chi}_\lambda(s)\}$, where r and λ are labels for the basis. λ takes two values and it will later be seen to be natural to take $\lambda = \pm\frac{1}{2}$.

We can also think of the vector $\boldsymbol{\chi}_\lambda = \begin{pmatrix}\chi_\lambda(1)\\ \chi_\lambda(2)\end{pmatrix}$, in which case two possible basis vectors are $\begin{pmatrix}1\\0\end{pmatrix}$ and $\begin{pmatrix}0\\1\end{pmatrix}$. Note that $\boldsymbol{\chi}^\dagger_{\lambda'}\boldsymbol{\chi}_\lambda = \delta_{\lambda\lambda'}$.

The scalar product is defined in the obvious way: $\langle\phi_{r'\lambda'}|\phi_{r\lambda}\rangle = \langle\psi_{r'}|\psi_r\rangle\langle\chi_{\lambda'}|\chi_\lambda\rangle$, which equals $\delta_{rr'}\delta_{\lambda\lambda'}$ if the initial basis states are orthonormal.

The *two* electron wavefunction is $\Psi(\mathbf{x}_1, s_1; \mathbf{x}_2, s_2)$ and under the particle exchange operator $\hat{U}$ we must have $\Psi(\mathbf{x}_1, s_1; \mathbf{x}_2, s_2) \mapsto -\Psi(\mathbf{x}_2, s_2; \mathbf{x}_1, s_1)$. The two particle states belong to the antisymmetric combination $(\mathcal{H}_1 \otimes \mathcal{H}_2)_A$.

For N electrons the obvious thing can be done.

Basis for symmetric or antisymmetric 2 particle spin states

There is only one antisymmetric basis state

$$\chi_A(s_1, s_2) = \frac{1}{\sqrt{2}}\left(\chi_{\frac{1}{2}}(s_1)\chi_{-\frac{1}{2}}(s_2) - \chi_{-\frac{1}{2}}(s_1)\chi_{\frac{1}{2}}(s_2)\right),$$

and three symmetric possibilities:

$$\chi_S(s_1, s_2) = \begin{cases}\chi_{\frac{1}{2}}(s_1)\chi_{\frac{1}{2}}(s_2)\\ \frac{1}{\sqrt{2}}\left(\chi_{\frac{1}{2}}(s_1)\chi_{-\frac{1}{2}}(s_2) + \chi_{-\frac{1}{2}}(s_1)\chi_{\frac{1}{2}}(s_2)\right) \quad s_1 \neq s_2\\ \chi_{-\frac{1}{2}}(s_1)\chi_{-\frac{1}{2}}(s_2).\end{cases}$$

We can now examine two non-interacting electrons, with $\hat{H} = \hat{H}_1 + \hat{H}_2$ and take H_i independent of spin. The single particle states are $|\psi_i\rangle|\chi_s\rangle$.

The two electron states live in $(\mathcal{H}_1 \otimes \mathcal{H}_2)_A$, which has a basis

$$\begin{aligned}&|\psi_r\rangle_1|\psi_r\rangle_2|\chi_A\rangle;\\ &\frac{1}{\sqrt{2}}\left(|\psi_r\rangle_1|\psi_s\rangle_2 + |\psi_s\rangle_1|\psi_r\rangle_2\right)|\chi_A\rangle; \quad r \neq s\\ &\frac{1}{\sqrt{2}}\left(|\psi_r\rangle_1|\psi_s\rangle_2 - |\psi_s\rangle_1|\psi_r\rangle_2\right)|\chi_S\rangle; \quad r \neq s,\end{aligned}$$

with energy levels $2E_r$ (one spin state) and $E_r + E_s$ (one antisymmetric spin state and three symmetric spin states).

We thus obtain the Pauli exclusion principle: no two electrons can occupy the same state (taking account of spin).

As an example we can take the helium atom with Hamiltonian

$$\hat{H} = \frac{\hat{\mathbf{p}}_1^2}{2m} + \frac{\hat{\mathbf{p}}_2^2}{2m} - \frac{2e^2}{4\pi\epsilon_0\,|\hat{\mathbf{x}}_1|} - \frac{2e^2}{4\pi\epsilon_0\,|\hat{\mathbf{x}}_2|} + \frac{e^2}{4\pi\epsilon_0\,|\hat{\mathbf{x}}_1 - \hat{\mathbf{x}}_2|}.$$

If we neglect the interaction term we can analyse this as two hydrogen atoms and glue the results back together as above. The hydrogen atom (with a nuclear charge $2e$) has $E_n = -\frac{2e^2}{8\pi\epsilon_0 n^2}$, so we get a ground state for the helium atom with energy $2E_1$ with no degeneracy and a first excited state with energy $E_1 + E_2$ with a degeneracy of four. Hopefully these bear some relation to the results obtained by taking the interaction into account.

3.3 Two particle states and centre of mass

Suppose we have a Hamiltonian $\hat{H} = \frac{\hat{\mathbf{p}}_1^2}{2m} + \frac{\hat{\mathbf{p}}_2^2}{2m} + V(\hat{\mathbf{x}}_1 - \hat{\mathbf{x}}_2)$ defined on $\mathcal{H}^2$. We can separate out the centre of mass motion by letting

$$\hat{\mathbf{P}} = \hat{\mathbf{p}}_1 + \hat{\mathbf{p}}_2 \qquad \hat{\mathbf{p}} = \tfrac{1}{2}(\hat{\mathbf{p}}_1 - \hat{\mathbf{p}}_2)$$
$$\hat{\mathbf{X}} = \tfrac{1}{2}(\hat{\mathbf{x}}_1 + \hat{\mathbf{x}}_2) \qquad \hat{\mathbf{x}} = \hat{\mathbf{x}}_1 - \hat{\mathbf{x}}_2.$$

Then $\left[\hat{X}_i, \hat{P}_j\right] = \imath\hbar\delta_{ij}$, $[\hat{x}_i, \hat{p}_j] = \imath\hbar\delta_{ij}$ and $\hat{\mathbf{X}}$, $\hat{\mathbf{P}}$ and $\hat{\mathbf{x}}$, $\hat{\mathbf{p}}$ commute respectively. We can rewrite the Hamiltonian as $\hat{H} = \frac{\hat{\mathbf{P}}^2}{2M} + \hat{h}$, $\hat{h} = \frac{\hat{\mathbf{p}}^2}{m} + V(\hat{\mathbf{x}})$, where $M = 2m$ and we can decompose $\mathcal{H}^2$ into $\mathcal{H}_{\text{CM}} \otimes \mathcal{H}_{\text{int}}$. $\mathcal{H}_{\text{CM}}$ is acted on by $\hat{\mathbf{X}}$ and $\hat{\mathbf{P}}$ and has wavefunctions $\phi(\mathbf{X})$. $\mathcal{H}_{\text{int}}$ is acted on by $\hat{\mathbf{x}}$, $\hat{\mathbf{p}}$ and any spin operators. It has wavefunctions $\psi(\mathbf{x}, s_1, s_2)$. We take wavefunctions $\Psi(\mathbf{x_1}, s_1; \mathbf{x_2}, s_2) = \Phi(\mathbf{X})\psi(\mathbf{x}, s_1, s_2)$ in $\mathcal{H}^2$.

This simplifies the Schrödinger equation, we can just have $\phi(\mathbf{X}) = e^{\imath\frac{\mathbf{P}\cdot\mathbf{X}}{\hbar}}$ and then $E = \frac{\mathbf{P}^2}{2M} + E_{\text{int}}$. We thus need only to solve the one particle equation $\hat{h}\psi = E_{\text{int}}\psi$.

Under the particle exchange operator $\hat{U}$ we have

$$\psi(\mathbf{x}, s_1, s_2) \mapsto \psi(-\mathbf{x}, s_2, s_1) = \pm\psi(\mathbf{x}, s_1, s_2),$$

with a plus sign for bosons and a minus sign for fermions. In the spinless case then $\psi(\mathbf{x}) = \psi(-\mathbf{x})$.

If we have a potential $V(|\hat{\mathbf{x}}|)$ then we may separate variables to get

$$\psi(\mathbf{x}, s_1, s_2) = Y_l\left(\frac{\mathbf{x}}{|\mathbf{x}|}\right) R(|\mathbf{x}|)\chi(s_1, s_2)$$

with $Y_l\left(-\frac{\mathbf{x}}{|\mathbf{x}|}\right) = (-1)^l Y_l\left(\frac{\mathbf{x}}{|\mathbf{x}|}\right)$. For spinless bosons we therefore require l to be even.

3.4 Observation

Consider the tensor product of two systems $\mathcal{H}_1$ and $\mathcal{H}_2$. A general state $|\Psi\rangle$ in $\mathcal{H}_1 \otimes \mathcal{H}_2$ can be written as

$$|\Psi\rangle = \sum_{i,j} a_{ij}|\psi_i\rangle_1|\phi_j\rangle_2$$

with $|\psi_i\rangle_1 \in \mathcal{H}_1$ and $|\phi_j\rangle_2 \in \mathcal{H}_2$ assumed orthonormal bases for their respective vector spaces.

Suppose we make a measurement on the first system leaving the second system unchanged, and find the first system in a state $|\psi_i\rangle_1$. Then ${}_1\langle\psi_i|\Psi\rangle = \sum_j a_{ij}|\phi_j\rangle_2$, which we write as $A_i|\phi\rangle_2$, where $|\phi\rangle_2$ is a normalised state of the second system. We

interpret $|A_i|^2$ as the probability of finding system 1 in state $|\psi_i\rangle_1$. After measurement system 2 is in a state $|\phi\rangle_2$.

If $a_{ij} = \lambda_i \delta_{ij}$ (no summation) then $A_i = \lambda_i$ and measurement of system 1 as $|\psi_i\rangle_1$ determines system 2 to be in state $|\phi_i\rangle_2$.

Chapter 4

Perturbation Expansions

4.1 Introduction

Most problems in quantum mechanics are not exactly solvable and it it necessary to find approximate answers to them. The simplest method is a perturbation expansion. We write $\hat{H} = \hat{H}_0 + \hat{H}'$ where $\hat{H}_0$ describes a solvable system with known eigenvalues and eigenvectors, and $\hat{H}'$ is in some sense small.

We write $\hat{H}(\lambda) = \hat{H}_0 + \lambda\hat{H}'$ and expand the eigenvalues and eigenvectors in powers of λ. Finally we set $\lambda = 1$ to get the result. Note that we do not necessarily have to introduce λ; the problem may have some small parameter which we can use. This theory can be applied to the time dependent problem but here we will only discuss the time independent Schrödinger equation.

4.2 Non-degenerate perturbation theory

Suppose that $\hat{H}_0|n\rangle = \epsilon_n|n\rangle$ for $n = 0, 1, \ldots$. We thus assume discrete energy levels and we assume further that the energy levels are non-degenerate. We also require $\hat{H}'$ to be sufficiently non-singular to make a power series expansion possible.

We have the equation $\hat{H}(\lambda)|\psi_n(\lambda)\rangle = E_n(\lambda)|\psi_n(\lambda)\rangle$. We suppose that $E_n(\lambda)$ tends to ϵ_n as $\lambda \to 0$ and $|\psi_n(\lambda)\rangle \to |n\rangle$ as $\lambda \to 0$. We pose the power series expansions

$$E_n(\lambda) = \epsilon_n + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots$$
$$|\psi_n(\lambda)\rangle = N|n\rangle + \lambda|\psi_n^{(1)}\rangle + \ldots,$$

substitute into the Schrödinger equation and require it to be satisfied at each power of λ. The normalisation constant N is easily seen to be $1 + \mathcal{O}(\lambda^2)$. The $\mathcal{O}(1)$ equation is automatically satisfied and the $\mathcal{O}(\lambda)$ equation is

$$\hat{H}_0|\psi_n^{(1)}\rangle + \hat{H}'|n\rangle = E_n^{(1)}|n\rangle + \epsilon_n|\psi_n^{(1)}\rangle.$$

Note that we can always replace $|\psi_n^{(1)}\rangle$ with $|\psi_n^{(1)}\rangle + \alpha|n\rangle$ and leave this equation unchanged. We can therefore impose the condition $\langle n|\psi_n^{(1)}\rangle = 0$. If we apply $\langle n|$ to

this equation we get $E_n^{(1)} = \langle n|\hat{H}'|n\rangle$ — the first order perturbation in energy. If we apply $\langle r|$ where $r \neq n$ we see that

$$\langle r|\psi_n^{(1)}\rangle = -\frac{\langle r|\hat{H}'|n\rangle}{\epsilon_r - \epsilon_n}$$

and therefore

$$|\psi_n^{(1)}\rangle = -\sum_{r\neq n} \frac{|r\rangle\langle r|\hat{H}'|n\rangle}{\epsilon_r - \epsilon_n}.$$

Note that we are justified in these divisions as we have assumed that the eigenvalues are non-degenerate. On doing the same thing to the $\mathcal{O}(\lambda^2)$ equation we see that

$$\begin{aligned} E_n^{(2)} &= \langle n|\hat{H}'|\psi_n^{(1)}\rangle \\ &= -\sum_{r\neq n} \frac{\left|\langle r|\hat{H}'|n\rangle\right|^2}{\epsilon_r - \epsilon_n}. \end{aligned}$$

This procedure is valid if $\epsilon_r - \epsilon_n$ is not very small when $\langle r|\hat{H}'|n\rangle \neq 0$.
Using these results we can see that $\frac{\mathrm{d}}{\mathrm{d}\lambda}E_n(\lambda) = \langle\psi_n(\lambda)|\hat{H}'|\psi_n(\lambda)\rangle$ and

$$\frac{\partial}{\partial\lambda}|\psi_n(\lambda)\rangle = -\sum_{r\neq n} \frac{1}{E_r(\lambda) - E_n(\lambda)}|\psi_r(\lambda)\rangle\langle\psi_r(\lambda)|\hat{H}'|\psi_n(\lambda)\rangle.$$

Also $\frac{\partial\hat{H}}{\partial\lambda} = \hat{H}'$ and so

$$\frac{\partial^2}{\partial\lambda^2}E_n(\lambda) = 2\langle\psi_n(\lambda)|\hat{H}'\frac{\partial}{\partial\lambda}|\psi_n(\lambda)\rangle.$$

Example: harmonic oscillator

Consider $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 + \lambda m\omega^2\hat{x}^2$, which can be viewed as $\hat{H}_0 + \hat{H}'$, where $\hat{H}_0$ is the plain vanilla quantum harmonic oscillator Hamiltonian.

Calculating the matrix elements $\langle r|\hat{x}^2|n\rangle$ required is an extended exercise in manipulations of the annihilation and creation operators and is omitted. The results are

$$\begin{aligned} E_n^{(1)} &= \hbar\omega\left(n + \tfrac{1}{2}\right) \\ E_n^{(2)} &= -\tfrac{1}{2}\hbar\omega\left(n + \tfrac{1}{2}\right). \end{aligned}$$

We thus get the perturbation expansion for E_n'

$$E_n' = \hbar\omega\left(n + \tfrac{1}{2}\right)\left(1 + \lambda - \tfrac{1}{2}\lambda^2 + \mathcal{O}(\lambda^3)\right).$$

This system can also be solved exactly to give $E_n' = \hbar\omega\left(n + \frac{1}{2}\right)\sqrt{1 + 2\lambda}$ which agrees with the perturbation expansion.

4.3 Degeneracy

The method given here breaks down if $\epsilon_r = \epsilon_n$ for $r \neq n$. Perturbation theory can be extended to the degenerate case, but we will consider only the first order shift in ϵ_r. We suppose that the states $|n, s\rangle$, $s = 1 \ldots N_n$ have the same energy ϵ_n. N_s is the degeneracy of this energy level.

As before we pose a Hamiltonian $\hat{H} = \hat{H}_0 + \lambda \hat{H}'$ such that $\hat{H}_0|n, s\rangle = \epsilon_n|n, s\rangle$ and look for states $|\psi(\lambda)\rangle$ with energy $E(\lambda) \to \epsilon_n$ as $\lambda \to 0$.

The difference with the previous method is that we expand $|\psi(\lambda)\rangle$ as a power series in λ *in the basis of eigenvectors of* $\hat{H}_0$. That is

$$|\psi(\lambda)\rangle = \sum_s |n, s\rangle a_s + \lambda |\psi^{(1)}\rangle.$$

As the a_s are arbitrary we can impose the conditions $\langle n, s|\psi^{(1)}\rangle = 0$ for each s and n. We thus have to solve $\hat{H}|\psi(\lambda)\rangle = E(\lambda)|\psi(\lambda)\rangle$ with $E(\lambda) = \epsilon_n + \lambda E^{(1)}$. If we take the $\mathcal{O}(\lambda)$ equation and apply $\langle n, r|$ to it we get

$$\sum_s a_s \langle n, r|\hat{H}'|n, s\rangle = a_r E_r^{(1)}$$

which is a matrix eigenvalue problem. Thus the first order perturbations in ϵ_n are the eigenvalues of the matrix $\langle n, r|\hat{H}'|n, s\rangle$. If all the eigenvalues are distinct then the perturbation "lifts the degeneracy". It is convenient for the purpose of calculation to choose a basis for the space spanned by the degenerate eigenvectors in which this matrix is "as diagonal as possible".[1]

[1] Don't ask...

Chapter 5

General theory of angular momentum

For a particle with position and momentum operators $\hat{\mathbf{x}}$ and $\hat{\mathbf{p}}$ with the commutation relations $[\hat{x_i}, \hat{p_j}] = \imath\hbar\delta_{ij}$ we define $\hat{\mathbf{L}} = \hat{\mathbf{x}} \wedge \hat{\mathbf{p}}$. It can be seen that $\hat{\mathbf{L}}$ is Hermitian and it is easy to show $\left[\hat{L}_i, \hat{L}_j\right] = \imath\hbar\epsilon_{ijk}\hat{L}_k$.

5.1 Introduction

More generally we define Hermitian angular momentum operators $\mathbf{J}$ with the commutation relation $[J_i, J_j] = \imath\hbar\epsilon_{ijk}J_k$.[1] We ask on what space of states can this algebra of operators be realised, or alternatively, what are the representations?

We choose one component of $\mathbf{J}$ whose eigenvalues label the states; in accordance with convention we choose J_3. Then we have $J_3|m\rangle = m\hbar|m\rangle$ for $m \in \mathbb{R}$ (discrete) and we also have $\langle m'|m\rangle = \delta_{m'm}$.

By applying the commutation relation we get (easily) that $\left[J_3, \mathbf{J}^2\right] = 0$, so as $\mathbf{J}^2$ is Hermitian we can choose a simultaneous eigenbasis. That is, $\mathbf{J}^2|m\rangle = \lambda\hbar^2|m\rangle$. We know that $\lambda \geq 0$ since $\mathbf{J}^2$ is the sum of the squares of Hermitian operators.

At this stage we choose an alternate basis; that is we split $\mathbf{J}$ into J_+, J_- and J_3, with $J_\pm = J_1 \pm \imath J_2$. Note that $J_\pm^\dagger = J_\mp$. The commutation relations for J_i give that $[J_3, J_\pm] = \pm\imath\hbar J_\pm$ and $[J_+, J_-] = 2\hbar J_3$. It will be useful later to note that

$$\mathbf{J}^2 = \tfrac{1}{2}\left(J_+J_- + J_-J_+\right) + J_3^2 = \begin{cases} J_-J_+ + J_3^2 + \hbar J_3 \\ J_+J_- + J_3^2 - \hbar J_3 \end{cases} .$$

Proof of this is immediate. We can now rewrite the $[J_3, J_\pm]$ commutation relation as $J_3J_\pm = J_\pm\left(J_3 \pm \hbar\right)$ and so we see that $J_\pm|m\rangle$ is an eigenvector of J_3 with eigenvalue $(m+1)\hbar$ and so $J_\pm|m\rangle = \hbar N_m^\pm|m \pm 1\rangle$, with some normalisation constant $N_m^\pm$. By evaluating the norm of $J_\pm|m\rangle$, and noting that $\langle m|m\rangle = 1$ we see that $\left(N_m^\pm\right)^2 = \lambda - m^2 \mp m$.

We can now define states $|m \pm n\rangle$ for $n = 0, 1, 2, \ldots$. We can pin them down more by noting that $\left(N_m^\pm\right)^2 \geq 0$ for positive norms. However the formulae we have are,

[1] Because we are now grown up we will omit the hats if they do not add to clarity.

given λ, negative for sufficiently large $|m|$ and so to avoid this we must have $m_{\max} = j$ such that $J_+|j\rangle = 0$ and so $\left(N_j^+\right)^2 = \lambda - j^2 - j = 0$ and so $\lambda = j(j+1)$.

We can perform a similar trick with J_-; there must exist $m_{\min} = -j'$ such that $J_-|-j'\rangle = 0$; thus $\lambda = j'(j'+1)$. So $j' = j$ and as $-j' = -j = j - n$ for some $n \in \{0, 1, 2, \dots\}$ we have $j = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots$.

In summary the states can be labelled by $|j\ m\rangle$ such that

$$\begin{aligned}
\mathbf{J}^2|j\ m\rangle &= \hbar^2 j(j+1)|j\ m\rangle \\
J_3|j\ m\rangle &= \hbar m|j\ m\rangle \\
J_\pm|j\ m\rangle &= \hbar\left((j \mp m)\,(j \pm m + 1)\right)^{\frac{1}{2}}|j\ m+1\rangle
\end{aligned}$$

with $m \in \{-j, -j+1, \dots, j-1, j\}$ and $j \in \{0, \frac{1}{2}, 1, \frac{3}{2}, \dots\}$. There are $2j+1$ states with different m for the same j. $|j\ m\rangle$ is the standard basis of the angular momentum states.

We have obtained a representation of the algebra labelled by j. If $\mathbf{J} = \mathbf{L} = \hat{\mathbf{x}} \wedge \hat{\mathbf{p}}$ we must have j an integer.

Recall that if we have $\hat{A}$ we can define a matrix $A_{\lambda'\lambda}$ by $\hat{A}|\lambda\rangle = \sum_{\lambda'} |\lambda'\rangle A_{\lambda'\lambda}$. Note that $(BA)_{\lambda'\lambda} = \sum_\mu B_{\lambda'\mu}A_{\mu\lambda}$. Given j, we have $(J_3)_{m'm} = \hbar m\,\delta_{m'm}$ and $(J_\pm)_{m'm} = \hbar\sqrt{(j \mp m)\,(j \pm m + 1)}\,\delta_{m',m\pm1}$, giving us $(2j+1)\times(2j+1)$ matrices satisfying the three commutation relations $[J_3, J_\pm] = \pm\hbar J_\pm$ and $[J_+, J_-] = 2\hbar J_3$.

If $\mathbf{J}$ are angular momentum operators which act on a vector space V and we have $|\psi\rangle \in V$ such that $J_3|\psi\rangle = \hbar k|\psi\rangle$ and $J_+|\psi\rangle = 0$ then ψ is a state with angular momentum $j = k$. The other states are given by $J_-^n|\psi\rangle$, $1 \le n \le 2k$. The conditions also give $\mathbf{J}^2|\psi\rangle = \hbar^2 k\,(k+1)\,|\psi\rangle$

5.1.1 Spin $\frac{1}{2}$ particles

This is the simplest non-trivial case. We have $j = \frac{1}{2}$ and a two dimensional state space with a basis $|\frac{1}{2}\ \frac{1}{2}\rangle$ and $|\frac{1}{2}\ -\frac{1}{2}\rangle$. We have the relations $J_3|\frac{1}{2}\ \pm\frac{1}{2}\rangle = \pm\frac{1}{2}\hbar|\frac{1}{2}\ \pm\frac{1}{2}\rangle$ and

$$\begin{aligned}
J_+|\tfrac{1}{2}\ \tfrac{1}{2}\rangle &= 0 & \qquad J_-|\tfrac{1}{2}\ \tfrac{1}{2}\rangle &= \hbar|\tfrac{1}{2}\ -\tfrac{1}{2}\rangle \\
J_-|\tfrac{1}{2}\ -\tfrac{1}{2}\rangle &= 0 & \qquad J_+|\tfrac{1}{2}\ -\tfrac{1}{2}\rangle &= \hbar|\tfrac{1}{2}\ \tfrac{1}{2}\rangle.
\end{aligned}$$

It is convenient to introduce explicit matrices $\boldsymbol{\sigma}$ such that

$$\mathbf{J}|\tfrac{1}{2}\ m\rangle = \sum_{m'} |\tfrac{1}{2}\ m'\rangle \tfrac{1}{2}\hbar\,(\boldsymbol{\sigma})_{m'm}\,.$$

The matrices $\boldsymbol{\sigma}$ are 2×2 matrices (called the Pauli spin matrices). Explicitly, they are

$$\begin{aligned}
\sigma_+ &= \begin{pmatrix} 0 & 2 \\ 0 & 0 \end{pmatrix} \qquad \sigma_- = \begin{pmatrix} 0 & 0 \\ 2 & 0 \end{pmatrix} \qquad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \\
\sigma_1 &= \frac{1}{2}\,(\sigma_+ + \sigma_-) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_2 = -\frac{\imath}{2}\,(\sigma_+ - \sigma_-) = \begin{pmatrix} 0 & -\imath \\ \imath & 0 \end{pmatrix}.
\end{aligned}$$

Note that $\sigma_1^2 = \sigma_2^2 = \sigma_3^2 = \mathbf{1}$ and $\boldsymbol{\sigma}^\dagger = \boldsymbol{\sigma}$. These satisfy the commutation relations $[\sigma_i, \sigma_j] = 2\imath\epsilon_{ijk}\sigma_k$ (a slightly modified angular momentum commutation relation) and we also have $\sigma_2\sigma_3 = \imath\sigma_1$ (and the relations obtained by cyclic permutation), so

$\sigma_i\sigma_j + \sigma_j\sigma_i = 2\delta_{ij}\mathbf{1}$. Thus if $\hat{\mathbf{n}}$ is a unit vector we have $(\boldsymbol{\sigma}.\hat{\mathbf{n}})^2 = 1$ and we see that $\boldsymbol{\sigma}.\hat{\mathbf{n}}$ has eigenvalues ± 1.

We define the angular momentum matrices $\mathbf{s} = \frac{1}{2}\hbar\boldsymbol{\sigma}$ and so $\mathbf{s}^2 = \frac{3}{4}\hbar^2\mathbf{1}$.

The basis states are $\boldsymbol{\chi}_{\frac{1}{2}} = \begin{pmatrix}1\\0\end{pmatrix}$ and $\boldsymbol{\chi}_{-\frac{1}{2}} = \begin{pmatrix}0\\1\end{pmatrix}$.

5.1.2 Spin 1 particles

We apply the theory as above to get

$$S_3 = \begin{pmatrix}1 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & -1\end{pmatrix} \qquad S_+ = \begin{pmatrix}0 & \sqrt{2} & 0\\ 0 & 0 & \sqrt{2}\\ 0 & 0 & 0\end{pmatrix}$$

and $S_- = {S_+}^\dagger$.

5.1.3 Electrons

Electrons are particles with intrinsic spin $\frac{1}{2}$. The angular momentum $\mathbf{J} = \hat{\mathbf{x}} \wedge \hat{\mathbf{p}} + \mathbf{s}$, where $\mathbf{s}$ are the spin operators for spin $\frac{1}{2}$.

The basic operators for an electron are $\hat{\mathbf{x}}$, $\hat{\mathbf{p}}$ and $\mathbf{s}$. We can represent these operators by their action on two component wavefunctions:

$$\boldsymbol{\psi}(\mathbf{x}) = \sum_{\lambda=\pm\frac{1}{2}} \psi_\lambda(\mathbf{x})\boldsymbol{\chi}_\lambda.$$

In this basis $\hat{\mathbf{x}} \mapsto \mathbf{x}$, $\hat{\mathbf{p}} \mapsto -\imath\hbar\nabla$ and $\mathbf{s} \mapsto \frac{1}{2}\hbar\boldsymbol{\sigma}$. All other operators are constructed in terms of these, for instance we may have a Hamiltonian

$$H = \frac{\hat{\mathbf{p}}^2}{2m} + V(\mathbf{x}) + U(\mathbf{x})\boldsymbol{\sigma}.\mathbf{L}$$

where $\mathbf{L} = \hat{\mathbf{x}} \wedge \hat{\mathbf{p}}$.

If V and U depend only on $|\mathbf{x}|$ then $[\mathbf{J}, H] = 0$.

5.2 Addition of angular momentum

Consider two independent angular momentum operators $\mathbf{J}^{(1)}$ and $\mathbf{J}^{(2)}$ with $\mathbf{J}^{(r)}$ acting on some space $V^{(r)}$ and $V^{(r)}$ having spin j_r for $r = 1, 2$.

We now define an angular momentum $\mathbf{J}$ acting on $V^{(1)} \otimes V^{(2)}$ by $\mathbf{J} = \mathbf{J}^{(1)} + \mathbf{J}^{(2)}$. Using the commutation relations for $\mathbf{J}^{(r)}$ we can get $[J_i, J_j] = \imath\hbar\epsilon_{ijk}J_k$.

We want to construct states $|J\ M\rangle$ forming a standard angular momentum basis, that is such that:

$$J_3|J\ M\rangle = \hbar M|J\ M\rangle$$
$$J_\pm|J\ M\rangle = \hbar N^\pm_{J,M}|J\ M\pm 1\rangle$$

with $N^\pm_{J,M} = \sqrt{(J \mp M)(J \pm M + 1)}$. We look first for states in V which satisfy $J_+|J\ J\rangle = 0$ and $J_3|J\ J\rangle = \hbar J|J\ J\rangle$. The maximum value of J we can get is $j_1 + j_2$; and $|j_1{+}j_2\ j_1{+}j_2\rangle = |j_1\ j_1\rangle_1|j_2\ j_2\rangle_2$. Then $J_+|j_1{+}j_2\ j_1{+}j_2\rangle = 0$. Similarly this is

an eigenvector of J_3 with eigenvalue $\hbar\,(j_1 + j_2)$. We can now apply J_- repeatedly to form all the $|J\ M\rangle$ states. Applying J_- we get

$$|J\ M{-}1\rangle = \alpha|j_1\ j_1{-}1\rangle_1|j_2\ j_2\rangle_2 + \beta|j_1\ j_1\rangle_1|j_2\ j_2{-}1\rangle_2.$$

The coefficents α and β can be determined from the coefficents $N^-_{a,b}$, and we must have $\alpha^2 + \beta^2 = 1$. If we choose $|\psi\rangle$ a state orthogonal to this

$$|\psi\rangle = -\beta|j_1\ j_1{-}1\rangle_1|j_2\ j_2\rangle_2 + \alpha|j_2\ j_2\rangle_1|j_2\ j_2{-}1\rangle_2.$$

$J_3|\psi\rangle$ can be computed and it shows that $|\psi\rangle$ is an eigenvector of J_3 with eigenvalue $\hbar\,(j_1 + j_2 - 1)$. Now

$$0 = \langle\psi|j_1{+}j_2\ j_1{+}j_2{-}1\rangle \propto \langle\psi|J_-|j_1{+}j_2\ j_1{+}j_2\rangle$$

and so $\langle\psi|J_-|\phi\rangle = 0$ for all states $|\phi\rangle$ in V. Thus $J_+|\psi\rangle = 0$ and hence we have $|\psi\rangle = |j_1{+}j_2{-}1\ j_1{+}j_2{-}1\rangle$. We can then construct the states $|j_1{+}j_2{-}1\ M\rangle$ by repeatedly applying J_-.

For each J such that $|j_1 - j_2| \le J \le j_1 + j_2$ we can construct a state $|J\ J\rangle$. We define the Clebsch-Gordan coefficients $\langle j_1\ m_1\ j_2\ m_2|J\ M\rangle$, and so

$$|J\ M\rangle = \sum_{m_1,m_2} \langle j_1\ m_1\ j_2\ m_2|J\ M\rangle|j_1\ m_1\rangle|j_2\ m_2\rangle.$$

The Clebsch-Gordan coefficients are nonzero only when $M = m_1 + m_2$.

We can check the number of states;

$$\sum_{J=|j_1-j_2|}^{j_1+j_2} (2J+1) = \sum_{J=|j_1-j_2|}^{j_1+j_2} \left\{(J+1)^2 - J^2\right\} = (2j_1+1)\,(2j_2+1)\,.$$

Electrons

Electrons have spin $\frac{1}{2}$ and we can represent their spin states with $\boldsymbol{\chi}_{\pm\frac{1}{2}}(s)$. Using this notation we see that two electrons can form a symmetric spin 1 triplet

$$\boldsymbol{\chi}_m(s_1,s_2) = \begin{cases} \boldsymbol{\chi}_{\frac{1}{2}}(s_1)\boldsymbol{\chi}_{\frac{1}{2}}(s_2) \\ \frac{1}{\sqrt{2}}\left(\boldsymbol{\chi}_{\frac{1}{2}}(s_1)\boldsymbol{\chi}_{-\frac{1}{2}}(s_2) + \boldsymbol{\chi}_{-\frac{1}{2}}(s_1)\boldsymbol{\chi}_{\frac{1}{2}}(s_2)\right) \\ \boldsymbol{\chi}_{-\frac{1}{2}}(s_1)\boldsymbol{\chi}_{-\frac{1}{2}}(s_2) \end{cases}$$

and an antisymmetric spin 0 singlet;

$$\boldsymbol{\chi}_0(s_1,s_2) = \frac{1}{\sqrt{2}}\left(\boldsymbol{\chi}_{\frac{1}{2}}(s_1)\boldsymbol{\chi}_{-\frac{1}{2}}(s_2) - \boldsymbol{\chi}_{-\frac{1}{2}}(s_1)\boldsymbol{\chi}_{\frac{1}{2}}(s_2)\right).$$

5.3 The meaning of quantum mechanics

Quantum mechanics deals in probabilities, whereas classical mechanics is deterministic *if we have complete information*. If we have incomplete information classical mechanics is also probabilistic.

Inspired by this we ask if there can be "hidden variables" in quantum mechanics such that the theory is deterministic. Assuming that local effects have local causes, this is not possible.

We will take a spin example to show this. Consider a spin $\frac{1}{2}$ particle, with two spin states $|\uparrow\rangle$ and $|\downarrow\rangle$ which are eigenvectors of $S_3 = \frac{1}{2}\hbar\sigma_3$. If we choose to use two component vectors we have

$$\boldsymbol{\chi}_\uparrow = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \boldsymbol{\chi}_\downarrow = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

Suppose $\mathbf{n} = (\sin\theta, 0, \cos\theta)$ (a unit vector) and let us find the eigenvectors of

$$\boldsymbol{\sigma}.\mathbf{n} = \begin{pmatrix} \cos\theta & \sin\theta \\ \sin\theta & -\cos\theta \end{pmatrix}.$$

As $(\boldsymbol{\sigma}.\mathbf{n})^2 = 1$ we must have eigenvalues ± 1 and an inspired guess gives $\boldsymbol{\chi}_{\uparrow,\mathbf{n}}$ and $\boldsymbol{\chi}_{\downarrow,\mathbf{n}}$ as

$$\boldsymbol{\chi}_{\uparrow,\mathbf{n}} = \cos\tfrac{\theta}{2}\boldsymbol{\chi}_\uparrow + \sin\tfrac{\theta}{2}\boldsymbol{\chi}_\downarrow \qquad \text{and} \qquad \boldsymbol{\chi}_{\downarrow,\mathbf{n}} = -\sin\tfrac{\theta}{2}\boldsymbol{\chi}_\uparrow + \cos\tfrac{\theta}{2}\boldsymbol{\chi}_\downarrow.$$

Thus (reverting to ket vector notation) if an electron is in a state $|\uparrow\rangle$ then the probability of finding it in a state $|\uparrow, \mathbf{n}\rangle$ is $\cos^2\frac{\theta}{2}$ and the probability of finding it in a state $|\downarrow, \mathbf{n}\rangle$ is $\sin^2\frac{\theta}{2}$.

Now, suppose we have two electrons in a spin 0 singlet state;

$$|\Phi\rangle = \frac{1}{\sqrt{2}}\left\{|\uparrow\rangle_1|\downarrow\rangle_2 - |\downarrow\rangle_1|\uparrow\rangle_2\right\}.$$

Then the probability of finding electron 1 with spin up is $\frac{1}{2}$, and after making this measurement electron 2 must be spin down. Similarly, if we find electron 1 with spin down (probability $\frac{1}{2}$ again) then electron 2 must have spin up. More generally, suppose we measure electron 1's spin along direction $\mathbf{n}$. Then we see that the probability for electron 1 to have spin up in direction $\mathbf{n}$ (aligned) is $\frac{1}{2}$ and then electron 2 must be in the state $|\downarrow, \mathbf{n}\rangle_2$.

If we have two electrons (say electron 1 and electron 2) in a spin 0 state we may physically separate them and consider independent experiments on them.

We will consider three directions as sketched. For electron 1 there are three variables which we may measure (in separate experiments); $S^{(1)}_{\mathbf{z}} = \pm 1$, $S^{(1)}_{\mathbf{n}} = \pm 1$ and $S^{(1)}_{\mathbf{m}} = \pm 1$. We can also do this for electron 2.

We see that if we find electron 1 has $S^{(1)}_{\mathbf{z}} = 1$ then electron 2 has $S^{(2)}_{\mathbf{z}} = -1$ (etc.).

If there exists an underlying deterministic theory then we could expect some probability distribution p for this set of experiments;

$$0 \le p\Big(S^{(1)}_{\mathbf{z}}, S^{(1)}_{\mathbf{n}}, S^{(1)}_{\mathbf{m}}, S^{(2)}_{\mathbf{z}}, S^{(2)}_{\mathbf{n}}, S^{(2)}_{\mathbf{m}}\Big) \le 1$$

which is nonzero only if $S^{(1)}_{\text{dirn}} = -S^{(2)}_{\text{dirn}}$ and

$$\sum_{\{s\}} p(\{s\}) = 1.$$

Bell inequality

Suppose we have a probability distribution $p(a, b, c)$ with $a, b, c = \pm 1$. We define partial probabilities $p_{bc}(b, c) = \sum_a p(a, b, c)$ and similarly for $p_{ac}(a, c)$ and $p_{ab}(a, b)$. Then

$$\begin{aligned} p_{bc}(1,-1) &= p(1,1,-1) + p(-1,1,-1) \\ &\leq p(1,1,-1) + p(1,1,1) + p(-1,1,-1) + p(-1,-1,-1) \\ &\leq p_{ab}(1,1) + p_{ac}(-1,-1). \end{aligned}$$

Applying this to the two electron system we get

$$\mathcal{P}\Big(S^{(1)}_{\mathbf{n}} = 1, S^{(2)}_{\mathbf{m}} = 1\Big) \leq \mathcal{P}\Big(S^{(1)}_{\mathbf{z}} = 1, S^{(2)}_{\mathbf{n}} = -1\Big) + \mathcal{P}\Big(S^{(1)}_{\mathbf{z}} = -1, S^{(2)}_{\mathbf{m}} = 1\Big).$$

We can calculate these probabilities from quantum mechanics

$$\begin{aligned} \mathcal{P}\Big(S^{(1)}_{\mathbf{z}} = 1, S^{(2)}_{\mathbf{n}} = -1\Big) &= \mathcal{P}\Big(S^{(1)}_{\mathbf{z}} = 1, S^{(1)}_{\mathbf{n}} = 1\Big) = \cos^2\tfrac{\theta}{2} \\ \mathcal{P}\Big(S^{(1)}_{\mathbf{z}} = -1, S^{(2)}_{\mathbf{m}} = 1\Big) &= \cos^2\tfrac{\theta+\phi}{2} \qquad \text{and} \\ \mathcal{P}\Big(S^{(1)}_{\mathbf{n}} = 1, S^{(2)}_{\mathbf{m}} = 1\Big) &= \sin^2\tfrac{\theta}{2}. \end{aligned}$$

The Bell inequality gives $\sin^2\frac{\phi}{2} \leq \cos^2\frac{\theta}{2} + \cos^2\frac{\theta+\phi}{2}$ which is not in general true.

References

- P.A.M. Dirac, *The Principles of Quantum Mechanics*, Fourth ed., OUP, 1958.

  I enjoyed this book as a good read but it is also an eminently suitable textbook.

- Feynman, Leighton, Sands, *The Feynman Lectures on Physics Vol. 3*, Addison-Wesley, 1964.

  Excellent reading but not a very appropriate textbook for this course. I read it as a companion to the course and enjoyed every chapter.

- E. Merzbacher, *Quantum Mechanics*, Wiley, 1970.

  This is a recommended textbook for this course (according to the Schedules). I wasn't particularly impressed but you may like it.

There must be a good, modern textbook for this course. If you know of one please send me a *brief* review and I will include it if I think it is suitable. In any case, with these marvellous notes you don't need a textbook, do you?

Related courses

There are courses on *Statistical Physics* and *Applications of Quantum Mechanics* in Part 2B and courses on *Quantum Physics* and *Symmetries and Groups in Quantum Physics* in Part 2A.