I. FUNDAMENTAL CONCEPTS

A. Stern-Gerlach Experiment

Quantum mechanical particles have intrinsic magnetic moments due to their spin angular momentum:

$$\boldsymbol{\mu} \propto \boldsymbol{S}$$

Devices such as the *Stern-Gerlach apparatus* can measure the z-component of the magnetic moment and hence spin. Subsequent measurements with Stern-Gerlach apparatuses with non-commuting spins have results that are quite different from what we'd expect from our classical intuition.

B. Bras, Kets and Operators

Quantum mechanical states are described by vectors in an infinite complex vector space (Hilbert space). The vectors, kets, in this space are denoted by $|\alpha\rangle$ and their dual vectors, bras, are denoted by $\langle\alpha|$. These kets describe abstract vectors whose time evolution is governed by the Schrödinger equation

$$i\hbar\partial_t |\alpha\rangle = \hat{H} |\alpha\rangle$$

This can also be written for the bras:

$$-i\hbar\partial_t \langle\alpha| = \langle\alpha| \hat{H}$$

where I've used that $\hat{H}$ is a *Hermitian operator.*

The *inner product* of a bra and a ket gives you a scalar:

$$\langle\alpha|\beta\rangle = c \in \mathbb{C}$$

which tells you about the projection of β onto α.

The *outer product* gives you an operator:

$$|\alpha\rangle \langle\beta|$$

which is useful for changing basis.

1. *Hermitian Operators*

A Hermitian operator, $\hat{A}$, satisfies:

$$\hat{A}^\dagger = \hat{A}$$

The Hermiticity of an operator has two very useful implications:

- Real eigenvalues: hence observables are represented by Hermitian operators.
- Diagonalisability: There exists a basis in which $\hat{A}$ is diagonal.

2. *Projection Operators*

Define the projection operator:

$$\Lambda_a = |a\rangle \langle a|$$

If $\{|a\rangle\}$ forms an orthonormal set, we have

$$\mathbb{1} = \sum \Lambda_a$$

and if $\hat{A}|a\rangle = a|a\rangle$, for $a \in \mathbb{R}$, we can write the operator in terms of its spectral decomposition:

$$\hat{A} = \sum_n a_n \Lambda_{a_n}$$

Due to the fact that $\{|a\rangle\}$ is an orthonormal basis we have that $\Lambda_a\Lambda_b = \delta_{a,b}\Lambda_a$ and hence given an $f(x)$ that has a power expansion we can define $f(\hat{A}) = \sum_m c_m \hat{A}^m$ which in turn gives us

$$f(\hat{A}) = \sum_n f(a_n)\Lambda_{a_n} = \sum_n f(a_n) |a_n\rangle \langle a_n|$$

3. *Commuting Operators*

Given two operators $\hat{A}$ and $\hat{B}$, these operators commute given that

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A} = 0$$

in which case there exists a basis $\{|a\ b\rangle\}$ that is a simultaneous eigenbasis for both $\hat{A}$ and $\hat{B}$:

$$\hat{A}|a\ b\rangle = a|a\ b\rangle \qquad \hat{B}|a\ b\rangle = b|a\ b\rangle$$

if $[\hat{A}, \hat{B}] = 0$ then $[\hat{A}, f(\hat{B})] = 0$, which can be shown using the power expansion of $f(x)$.

4. *Non-commuting operators*

For non-commuting operators $[\hat{A}, \hat{B}] \neq 0$, which implies that there does not exist a simultaneous set of eigenkets. Additionally, in simple cases where the relevant commutators behave well, we can use identities of the form

$$[\hat{A}, f(\hat{B})] = [\hat{A}, \hat{B}] f'(\hat{B})$$

5. *Measurement*

Consider a general state

$$|\psi\rangle = \sum_n c_n |n\rangle$$

where $\hat{A}|n\rangle = a_n |n\rangle, \qquad a_n \in \mathbb{R}$. If we prepare a state $|\psi\rangle$ and then measure $\hat{A}$, we will obtain one of the eigenvalues of $\hat{A}$, a_n, with probability:

$$P(a_n) = |\langle a_n|\psi\rangle|^2$$

If we measure a_n we know for certain that $|\psi\rangle = |a_n\rangle$; we say the state *collapses* into $|a_n\rangle$. In the case that we have a degenerate eigenvalue we only know that a_n is measured, which implies that $|\psi\rangle$ collapses into the degenerate subspace. Hence after the measurement $|\psi\rangle$ can be written as a linear combination of the basis states that span the degenerate subspace.

6. *Change of Basis*

Given two orthonormal bases, $\{|a_n\rangle\}$ and $\{|b_n\rangle\}$ of the Hilbert space in question, there exists a unitary transformation, $\hat{U}$ such that

$$|b_n\rangle = \hat{U} |a_n\rangle$$

$\hat{U}$ can be written in terms of the outer products defined above:

$$\hat{U} = \sum_n |b_n\rangle \langle a_n|$$

7. *Matrix Representations of Operators*

Operators can be expressed as matrices given a basis:

$$A_{ij} = \langle i|\hat{A}|j\rangle$$

Clearly, A is a diagonal matrix if $\{|i\rangle\}$ form its eigenbasis. Using the change of basis from above we can write similarity transformations as

$$A' = U^\dagger A U$$

In this way we can diagonalise matrices, if we choose the new basis to be the eigenbasis of $\hat{A}$.

8. *Continuous Spectra*

Some operators have continuous eigenvalues and we have to treat these differently from discrete operators. In general we replace sums by integrals and Kronecker deltas by Dirac deltas:

$$\mathbb{1} = \int \mathrm{d}\alpha\, |\alpha\rangle\langle\alpha|$$
$$\langle\alpha|\beta\rangle = \delta(\alpha - \beta)$$

hence a general state can be written as

$$|\psi\rangle = \int \mathrm{d}\alpha\ \langle\alpha|\psi\rangle\, |\alpha\rangle$$

9. *Translation*

The (infinitesimal) translation operator $\mathcal{J}(\mathrm{d}\boldsymbol{x})$ takes an eigenket of the position operator and displaces it by $\mathrm{d}\boldsymbol{x}$:

$$\mathcal{J}(\mathrm{d}\boldsymbol{x})\, |\boldsymbol{x}\rangle = |\boldsymbol{x} + \mathrm{d}\boldsymbol{x}\rangle$$

In order for this to preserve probabilities it must be unitary, which has the implication that

$$\mathcal{J}^\dagger(\mathrm{d}\boldsymbol{x}) = \mathcal{J}(-\mathrm{d}\boldsymbol{x}), \qquad \mathcal{J}^{-1}(\mathrm{d}\boldsymbol{x}) = \mathcal{J}(-\mathrm{d}\boldsymbol{x})$$

for infinitesimal displacements we can write out the first order approximation for the displacement operator:

$$\mathcal{J}(\mathrm{d}\boldsymbol{x}) = \mathbb{1} - i\boldsymbol{K} \cdot \mathrm{d}\boldsymbol{x}$$

where $\boldsymbol{K}$ is Hermitian due to the unitarity of $\mathcal{J}$. This Hermitian operator is, in fact, the momentum operator: the momentum operator is the generator for displacement, as we would expect from classical mechanics:

$$\mathcal{J}(\mathrm{d}\boldsymbol{x}) = \mathbb{1} - \frac{i}{\hbar}\boldsymbol{p} \cdot \mathrm{d}\boldsymbol{x}$$

by repeatedly applying this for finite displacements:

$$\mathcal{J}(\boldsymbol{a}) = \lim_{N\to\infty}\left(\mathbb{1} - \frac{i\boldsymbol{p}\cdot\boldsymbol{a}}{N\hbar}\right)^N \equiv \exp\left(-\frac{i\boldsymbol{p}\cdot\boldsymbol{a}}{\hbar}\right)$$

Due to the fact that the displacement operator is only a function of $\boldsymbol{p}$ we see that $[\boldsymbol{p}, \mathcal{J}(\boldsymbol{a})] = 0$. Indeed:

$$\mathcal{J}(\boldsymbol{a})\left|\boldsymbol{p}\right\rangle = \exp\left(-\frac{i\hat{\boldsymbol{p}}\cdot\boldsymbol{a}}{\hbar}\right)\left|\boldsymbol{p}\right\rangle = \exp\left(-\frac{i\boldsymbol{p}\cdot\boldsymbol{a}}{\hbar}\right)\left|\boldsymbol{p}\right\rangle$$

C. Wave Functions

We can represent our abstract $|\alpha\rangle$ in the position and momentum bases:

$$\psi_\alpha(\boldsymbol{x}) \equiv \langle\boldsymbol{x}|\alpha\rangle\,, \qquad \phi_\alpha(\boldsymbol{p}) \equiv \langle\boldsymbol{p}|\alpha\rangle$$

with these wavefunctions we can calculate expectation values, as long as we know how the operators operate on the wavefunctions. For instance, we can establish what the momentum operator looks like in position basis up to linear order in the infinitesimal displacement $\mathrm{d}\boldsymbol{x}$:

$$\begin{aligned}\left(\mathbb{1} - \frac{i\boldsymbol{p}\cdot\mathrm{d}\boldsymbol{x}}{\hbar}\right)|\alpha\rangle &= \int \mathrm{d}\boldsymbol{x}'\ |\boldsymbol{x}'\rangle\langle\boldsymbol{x}'|\mathcal{J}(\mathrm{d}\boldsymbol{x})\,|\alpha\rangle \\ &= \int \mathrm{d}\boldsymbol{x}'\ |\boldsymbol{x}'\rangle\,\langle\boldsymbol{x}' - \mathrm{d}\boldsymbol{x}|\alpha\rangle \\ &= \int \mathrm{d}\boldsymbol{x}'\,|\boldsymbol{x}'\rangle\left(\langle\boldsymbol{x}'|\alpha\rangle - \mathrm{d}\boldsymbol{x}\cdot\frac{\partial}{\partial\boldsymbol{x}'}\langle\boldsymbol{x}'|\alpha\rangle\right)\end{aligned}$$

comparing the linear terms in $\mathrm{d}\boldsymbol{x}$ we get

$$\langle\boldsymbol{x}'|\boldsymbol{p}|\alpha\rangle = -i\hbar\nabla'\,\langle\boldsymbol{x}'|\alpha\rangle$$

where we've used $\langle\boldsymbol{x}|\boldsymbol{x}'\rangle = \delta(\boldsymbol{x}' - \boldsymbol{x})$.

1. *Fourier Transform*

The momentum- and position-space wavefunctions are related through the Fourier transform:

$$\phi_\alpha(\boldsymbol{p}) = \frac{1}{(2\pi\hbar)^{\frac{3}{2}}}\int \mathrm{d}^3\boldsymbol{x}\ \exp\left(-\frac{i\boldsymbol{p}\cdot\boldsymbol{x}}{\hbar}\right)\psi_\alpha(\boldsymbol{x})$$

II. QUANTUM DYNAMICS

Let us assume we know the ket of some state at $t = t_0$: $|\alpha, t_0\rangle$. Then there must exist a unitary operator that transforms $|\alpha, t_0\rangle \to |\alpha, t_0; t\rangle$, that is, the state ket at time t. This unitary operator is the time-evolution operator:

$$|\alpha, t_0; t\rangle = \mathcal{U}(t, t_0)\,|\alpha, t_0\rangle$$

For infinitesimal time differences $t \to t + \mathrm{d}t$:

$$|\alpha, t; t + \mathrm{d}t\rangle = \mathcal{U}(t + \mathrm{d}t, t)\,|\alpha, t\rangle$$

this gives us

$$\left(\mathbb{1} + \mathrm{d}t\frac{\partial}{\partial t}\right)|\alpha, t\rangle = \left(\mathbb{1} - i\hat{\Omega}\mathrm{d}t\right)|\alpha, t\rangle$$

hence

$$i\frac{\partial}{\partial t}\,|\alpha, t\rangle = \hat{\Omega}\,|\alpha, t\rangle$$

the operator $\hat{\Omega} = \frac{1}{\hbar}\hat{H}$ where $\hat{H}$ is the Hamiltonian operator, hence

$$i\hbar\frac{\partial}{\partial t}\,|\alpha, t\rangle = \hat{H}\,|\alpha, t\rangle$$

we can use the same trick as we did for the displacement operator to derive a closed form expression for the time-evolution operator:

$$\mathcal{U}(t, t_0) = \exp\left(-\frac{i\hat{H}(t - t_0)}{\hbar}\right)$$

however, *this assumes that $\hat{H}$ is not a function of time.* Generally if $\hat{H} = \hat{H}(t)$ and $[H(t), H(t')] \neq 0$ we can use the *Dyson series*:

$$\mathcal{U}(t, t_0) = 1 + \sum_{N=1}^{\infty}\left(\frac{-i}{\hbar}\right)^N \int_{t_0}^{t}\left(\prod_{n=1}^{N-1}\mathrm{d}t_n\int_{t_0}^{t_n}\right)\mathrm{d}t_N\prod_{n=1}^{N}H(t_n)$$

which simplifies if $[H(t), H(t')] = 0 \quad \forall t, t'$ to

$$\mathcal{U}(t, t_0) = \exp\left(-\frac{i}{\hbar}\int_{t_0}^{t}\mathrm{d}tH(t)\right)$$

If we decompose $|\alpha\rangle$ into energy eigenstates the time evolution operator can easily be evaluated using the power-expansion method (we assume again that H is independent of time):

$$|\alpha, t_0\rangle = \sum_n c_n\,|a_n\rangle$$

then

$$|\alpha, t_0; t\rangle = \sum_n c_n\mathcal{U}(t, t_0)\,|a_n\rangle = \sum_n c_n\exp\left(-\frac{iE_n(t - t_0)}{\hbar}\right)|a_n\rangle$$

for $\hat{H}\,|a_n\rangle = E_n\,|a_n\rangle$

1. *Hamiltonian in position space*

The Hamiltonian operator in position space takes the form

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{x})$$

which can be derived from the classical Hamiltonian function by using that $\boldsymbol{p} \rightsquigarrow -i\hbar\nabla$

Note that the potential term only looks like this for local potentials, *i.e* ones for which

$$\langle \boldsymbol{x}''|V(\boldsymbol{x})|\boldsymbol{x}'\rangle = V(\boldsymbol{x}')\delta(\boldsymbol{x}' - \boldsymbol{x}'')$$

A. Heisenberg Picture

In the Schrödinger picture operators have no Hamiltonian evolution, whereas the states do. In the Heisenberg picture states are constant whereas the operators evolve due to the Hamiltonian operator. We can understand this by looking at a time-dependent expectation value:

$$\langle A\rangle(t) = \langle\alpha|\mathcal{U}^\dagger(t,t_0)\hat{A}\mathcal{U}(t,t_0)|\alpha\rangle$$

The Schrödinger picture lets the time-evolution operate on the states, but the Heisenberg picture instead defines

$$A^{(H)}(t) = \mathcal{U}^\dagger(t,t_0)\hat{A}^{(S)}\mathcal{U}(t,t_0)$$

and leaves $|\alpha\rangle$ unchanged (they do not evolve in time). In the Heisenberg picture the time-evolution of operators is governed by the *Heisenberg equation of motion*:

$$\frac{\mathrm{d}A^{(H)}}{\mathrm{d}t} = \frac{1}{i\hbar}\left[A^{(H)}, H\right]$$

which is almost identical to the time evolution of functions in classical physics, if we relate the commutators to Poisson brackets.

1. *Transition Amplitude*

The time-dependent transition amplitude from $|a\rangle$ to $|b\rangle$ is given by the inner product between the time-dependent $|a(t)\rangle = \mathcal{U}\,|a\rangle$ and $|b\rangle$:

$$\langle b|\mathcal{U}|a\rangle$$

B. Harmonic Oscillator

The Hamiltonian for the harmonic oscillator is given by

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

which can be rewritten as

$$\hat{H} = \frac{\hbar\omega}{2}\left(\hat{P}^2 + \hat{X}^2\right)$$

where $\hat{P} = \frac{\hat{p}}{\sqrt{m\hbar\omega}}$ and $\hat{X} = \sqrt{\frac{m\omega}{\hbar}}\hat{x}$. We have that

$$[\hat{X}, \hat{P}] = i$$

hence we can define

$$a = \frac{1}{\sqrt{2}}\left(\hat{X} + i\hat{P}\right), \qquad a^\dagger = \frac{1}{\sqrt{2}}\left(\hat{X} - i\hat{P}\right)$$

with which we can write

$$\hat{H} = \hbar\omega\left(a^\dagger a + \frac{1}{2}\right)$$

Defining the number operator, $\hat{N} = a^\dagger a$, we see that because $[\hat{H}, \hat{N}] = 0$ we can denote the eigenstates of $\hat{H}$ by the quantum number n, which tells us about the number of energy quanta stored in the oscillator. We can show that

$$a^\dagger\,|n\rangle = \sqrt{n+1}\,|n+1\rangle\,, \qquad a\,|n\rangle = \sqrt{n}\,|n-1\rangle$$

These operators are very powerful; they can, for instance, be used to find the wavefunctions. For example the wavefunction $\psi_0(x) = \langle x|0\rangle$ must satisfy

$$\left(x + x_0^2\frac{\mathrm{d}}{\mathrm{d}x}\right)\psi_0(x) = 0, \qquad x_0 \equiv \sqrt{\frac{\hbar}{m\omega}}$$

C. Interpretation of the Wavefunction

The standard interpretation of the Schrödinger wavefunction is that its modulus squared is a probability density:

$$\rho(\boldsymbol{x},t) = |\psi(\boldsymbol{x},t)|^2$$

which indeed leads to a continuity equation

$$\frac{\partial\rho}{\partial t} + \nabla\cdot\boldsymbol{j} = 0$$

where

$$\boldsymbol{j} = -\left(\frac{i\hbar}{2m}\right)\left[\psi^*\nabla\psi - \left(\nabla\psi^*\right)\psi\right]$$

Consider now the wavefunction as a real function times a phase:

$$\psi(\boldsymbol{x},t) = \sqrt{\rho(\boldsymbol{x},t)}\exp\left(\frac{iS(\boldsymbol{x},t)}{\hbar}\right)$$

this tells us that

$$\boldsymbol{j} = \frac{\rho\nabla S}{m}$$

So the probability flux is due to variations in the phase of ψ. Additionally, writing the Schrödinger equation out for this function we get, for $\sqrt{\rho} = f$

$$-\left(\frac{\hbar^2}{2m}\right)\left(\nabla^2 f + \frac{2i}{\hbar}\nabla f\cdot\nabla S - \frac{1}{\hbar^2}f|\nabla S|^2\right) \\ -\frac{i\hbar}{2m}f\nabla^2 S + fV = i\hbar\left(\frac{\partial f}{\partial t} + \left(\frac{i}{\hbar}\right)f\frac{\partial S}{\partial t}\right)$$

Let us assume the curvature of S is much smaller than the gradient:

$$\hbar|\nabla^2 S| \lll |\nabla S|^2$$

in this limit the Schrödinger equation simplifies to

$$H(\boldsymbol{x},\nabla S) + \frac{\partial S}{\partial t} = 0 \rightsquigarrow \frac{1}{2m}|\nabla S|^2 + V(\boldsymbol{x}) + \frac{\partial S}{\partial t} = 0$$

which is the Hamilton-Jacobi equation.

D. Propagators

Propagators are functions that relate the wavefunction at $(x^\mu)'$ to the wavefunction at x^μ. Let us consider a time-independent Hamiltonian, so the time-evolution operator has a simple form for eigenkets:

$$|\alpha,t';t\rangle = \exp\left(-\frac{iH(t-t_0)}{\hbar}\right)|\alpha,t'\rangle \\ = \sum_a |a\rangle\langle a|\alpha\rangle\exp\left(-\frac{iE_a(t-t')}{\hbar}\right)$$

Multiplying by an identity $\not\Vdash = \int \mathrm{d}\boldsymbol{x}'|\boldsymbol{x}'\rangle\langle\boldsymbol{x}'|$ we get

$$\psi(\boldsymbol{x},t) = \int \mathrm{d}^3\boldsymbol{x}' \sum_a \langle\boldsymbol{x}|a\rangle\langle a|\boldsymbol{x}'\rangle\,\psi(\boldsymbol{x}',t')e^{-\frac{iE_a(t-t')}{\hbar}}$$

This relates the wavefunction at $\psi(\boldsymbol{x}',t')$ to the wavefunction at $\psi(\boldsymbol{x},t)$. The quantity that propagates from $(\boldsymbol{x}',t')$ to $(\boldsymbol{x},t)$ is the *propagator*:

$$K(\boldsymbol{x},t;\boldsymbol{x}',t') \equiv \sum_a \langle\boldsymbol{x}|a\rangle\langle a|\boldsymbol{x}'\rangle\,e^{-\frac{iE_a(t-t')}{\hbar}}$$

more generally

$$K(\boldsymbol{x},t;\boldsymbol{x}',t') \equiv \sum_a \langle\boldsymbol{x}|a\rangle\langle a|\boldsymbol{x}'\rangle\,\langle a|\mathcal{U}(t,t')|a\rangle$$

but this only holds in this simple form if the Hamiltonians commute at different times, because otherwise the eigenbasis $\{|a\rangle\}$ can be time-dependent*.

Propagators can be written as the inner product between the state at $(\boldsymbol{x}',t')$ and $(\boldsymbol{x},t)$:

$$K(\boldsymbol{x},t;\boldsymbol{x}',t') = \langle\boldsymbol{x},t|\boldsymbol{x}',t'\rangle$$

We can compose propagators:

$$K(\boldsymbol{x},t;\boldsymbol{x}'',t'') = \int \mathrm{d}\boldsymbol{x}'\,\langle\boldsymbol{x},t|\boldsymbol{x}',t'\rangle\,\langle\boldsymbol{x}',t'|\boldsymbol{x}'',t''\rangle \\ t > t' > t''$$

The composition property can be taken to the extreme, such that

$$\langle x_N,t_N|x_1,t_1\rangle = \int \mathrm{d}x_{N-1}\int \mathrm{d}x_{N-2}\cdots\int \mathrm{d}x_2 \\ \times\langle x_N,t_N|x_{N-1},t_{N-1}\rangle\,\langle x_{N-1},t_{N-1}|x_{N-2},t_{N-2}\rangle\cdots \\ \times\langle x_2,t_2|x_1,t_1\rangle$$

where $t_m - t_{m-1}$ is infinitesimal. This form integrates over every possible path that connects (x_1,t_1) to (x_N,t_N).

1. *Feynman's Formulation*

The propagator defined above corresponds to:

$$\langle x_2,t_2|x_1,t_1\rangle \sim \exp\left(i\int_{t_1}^{t_2}\mathrm{d}t\;\frac{L_{\text{classical}}(x,\dot{x})}{\hbar}\right)$$

For compactness let

$$S_{n,n-1} \equiv \int_{t_{n-1}}^{t_n}\mathrm{d}t\;L_{\text{classical}}(x,\dot{x})$$

which means the total $\exp(iS_{N,1}/\hbar)$ can be written as

$$\exp\left(\frac{iS_{N,1}}{\hbar}\right) = \exp\left(\left(\frac{i}{\hbar}\right)\sum_{n=2}^{N}S_{n,n-1}\right)$$

* Does this still work in the adiabatic limit?

However to calculate $\exp\left(\frac{iS_{N,1}}{\hbar}\right)$ we need to have a parametrisation for the path taken, therefore we now also need to sum over all possible paths:

$$\langle x_N, t_N | x_1, t_1 \rangle \sim \sum_{\text{all paths}} \exp\left(\frac{iS_{N,1}}{\hbar}\right)$$

The full form of this is **Feynman's path integral**:

$$\langle x_N, t_N | x_1, t_1 \rangle = \int_{x_1}^{x_N} \mathcal{D}\left[x(t)\right] \, \exp\left[\frac{i}{\hbar}\int_{t_1}^{t_N} \mathrm{d}t \, L_{\text{classical}}\right]$$

where

$$\mathcal{D}\left[x(t)\right] = \lim_{N\to\infty}\left(\frac{m}{2\pi i\hbar\Delta t}\right)^{\left(\frac{N-1}{2}\right)} \prod_{n=N}^{2} \int \mathrm{d}x_n$$

E. Gauge Transformations in Electromagnetism

Using the scalar and vector potentials from electromagnetism we can formulate the Hamiltonian of charged particles in electromagnetic fields:

$$H = \frac{1}{2m}\left(\boldsymbol{p} - \frac{e}{c}\boldsymbol{A}\right)^2 + e\phi$$

however, we need to be careful when we multiply the product out, because in general the momentum and vector potential operators do not commute:

$$\left(\boldsymbol{p} - \frac{e}{c}\boldsymbol{A}\right)^2 = |\boldsymbol{p}|^2 + \left(\frac{e}{c}\right)^2 |\boldsymbol{A}|^2 - \frac{e}{c}\left(\boldsymbol{p}\cdot\boldsymbol{A} + \boldsymbol{A}\cdot\boldsymbol{p}\right)$$

The canonical momentum, $\boldsymbol{p}$, is no longer the conjugate variable to $\boldsymbol{x}$, however, we can define the kinematic momentum:

$$\boldsymbol{\Pi} \equiv \boldsymbol{p} - \frac{e\boldsymbol{A}}{c}$$

Note that it is the kinematic momentum and not the canonical momentum that is a conserved quantity. The continuity equation still looks the same, if we redefine the probability flux:

$$\boldsymbol{j} = -\left(\frac{i\hbar}{2m}\right)\left[\psi^*\nabla\psi - \left(\nabla\psi^*\right)\psi\right] - \left(\frac{e}{mc}\right)\boldsymbol{A}\rho$$

Maxwell's equations are invariant under gauge transformations:

$$\phi \rightsquigarrow \phi - \frac{1}{c}\frac{\partial\Lambda}{\partial t}, \qquad \boldsymbol{A} \rightsquigarrow \boldsymbol{A} + \nabla\Lambda$$

The equations of motion in quantum mechanics are invariant under gauge transformations too; however, these transformations do leave a phase in the state:

$$|\alpha\rangle \rightsquigarrow \exp\left(\frac{ie\Lambda}{\hbar c}\right)|\alpha\rangle$$

F. Aharonov-Bohm Effect

The fact that the Schrödinger equation depends on the scalar and vector potentials and not only on the electromagnetic fields implies that there are instances where a wavefunction can be influenced by the electromagnetic potential even though both $\boldsymbol{E} = 0$ and $\boldsymbol{B} = 0$ along its path. Consider for example a region where $B \neq 0$, but where this region is shielded such that the wavefunction cannot enter it. The vector potential is nonzero outside of the region. Two paths that fly past the impenetrable region will obtain a different phase depending on whether they pass the region in the same way (with the region on their right or left). This phase difference results in a peculiar interference pattern, which can be and has been measured.

III. THEORY OF ANGULAR MOMENTUM

We have considered the displacement-transformation previously, which we described with a unitary operator and in looking at infinitesimal displacements we found the generator for displacements, the momentum operator. We will now do the same for rotations. Consider an infinitesimal rotation, $\mathrm{d}\phi$, about the unit vector $\hat{\boldsymbol{n}}$. The rotation operator can be expanded to first order in the generator, which we will call $\boldsymbol{J}$:

$$\mathcal{D}(\hat{\boldsymbol{n}}, \mathrm{d}\phi) \approx \mathbb{1} - i\left(\frac{\boldsymbol{J}\cdot\hat{\boldsymbol{n}}}{\hbar}\right)\mathrm{d}\phi$$

we can once again do N infinitesimal subsequent rotations and let $N \rightsquigarrow \infty$ to get a finite rotation:

$$\mathcal{D}(\hat{\boldsymbol{n}}, \phi) = \exp\left(-i\left(\frac{\boldsymbol{J}\cdot\hat{\boldsymbol{n}}}{\hbar}\right)\phi\right)$$

Due to the fact that we know how physical rotations commute, we can require that $\mathcal{D}$ satisfies the same commutation relations, which tells us how the $\boldsymbol{J}$ operators commute. For instance for rotations by an infinitesimal angle, ε, we have that

$$R_x(\varepsilon)R_y(\varepsilon) - R_y(\varepsilon)R_x(\varepsilon) = R_z(\varepsilon^2) - 1 + \mathcal{O}(\varepsilon^4)$$

Hence we can require that

$$\mathcal{D}(\hat{\boldsymbol{x}}, \varepsilon)\mathcal{D}(\hat{\boldsymbol{y}}, \varepsilon) - \mathcal{D}(\hat{\boldsymbol{y}}, \varepsilon)\mathcal{D}(\hat{\boldsymbol{x}}, \varepsilon) = \mathcal{D}(\hat{\boldsymbol{z}}, \varepsilon^2) - 1$$

up to $\mathcal{O}(\varepsilon^4)$. This results in

$$-\frac{(J_xJ_y - J_yJ_x)\varepsilon^2}{\hbar^2} = \left(1 - \frac{iJ_z\varepsilon^2}{\hbar}\right) - 1$$

which simplifies to

$$[J_x, J_y] = i\hbar J_z$$

By rotating and mirroring our coordinate system we can show

$$[J_i, J_j] = i\hbar\varepsilon_{ijk}J_k$$

A. Rotations of Spin-$\frac{1}{2}$ systems

For spin-$\frac{1}{2}$ systems the generators of rotations are

$$S_x = \left(\frac{\hbar}{2}\right)(|+\rangle\langle-| + |-\rangle\langle+|)$$
$$S_y = \left(\frac{i\hbar}{2}\right)(-|+\rangle\langle-| + |-\rangle\langle+|)$$
$$S_z = \left(\frac{\hbar}{2}\right)(|+\rangle\langle+| - |-\rangle\langle-|)$$

Consider, for instance, rotations about the z-axis:

$$|\alpha'\rangle = \exp\left(-\left(\frac{iS_z}{\hbar}\right)\phi\right)|\alpha\rangle$$

Expanding $|\alpha\rangle = \langle+|\alpha\rangle\,|+\rangle + \langle-|\alpha\rangle\,|-\rangle$:

$$|\alpha'\rangle = \exp\left(-\frac{i\phi}{2}\right)|+\rangle\langle+|\alpha\rangle + \exp\left(\frac{i\phi}{2}\right)|-\rangle\langle-|\alpha\rangle$$

which implies that for rotations by $\phi = 2\pi$ we do not return to the original state, but rather

$$|\alpha\rangle \overset{\mathcal{D}(\hat{\boldsymbol{z}},2\pi)}{\longrightarrow} -|\alpha\rangle$$

hence we require a 4π rotation to return back to the original state.

For instance the rotation of the expectation value of S_x:

$$\begin{aligned}\langle S_x'\rangle =& \exp(-i\phi)\,\langle\alpha|-\rangle\ \langle-|S_x|+\rangle\,\langle+|\alpha\rangle \\ &+ \exp(i\phi)\,\langle\alpha|+\rangle\ \langle+|S_x|-\rangle\,\langle-|\alpha\rangle \\ =& \frac{\hbar}{2}\left(\exp(-i\phi)\,\langle\alpha|-\rangle\,\langle+|\alpha\rangle + \exp(i\phi)\,\langle\alpha|+\rangle\,\langle-|\alpha\rangle\right) \\ =& \cos(\phi)\langle S_x\rangle - \sin(\phi)\langle S_y\rangle\end{aligned}$$

1. *Spin Precession*

The Hamiltonian that describes a spin-$\frac{1}{2}$ particle in the presence of a magnetic field is

$$H = -\left(\frac{e}{mc}\right)\boldsymbol{S}\cdot\boldsymbol{B} = \omega S_z$$

hence the time evolution operator is

$$\mathcal{U}(t,0) = \exp\left(-\frac{iS_z\omega t}{\hbar}\right)$$

which, as per our calculation above, tells us that

$$|\alpha(t)\rangle = \exp\left(-\frac{i\omega t}{2}\right)|+\rangle\langle+|\alpha_0\rangle + \exp\left(\frac{i\omega t}{2}\right)|-\rangle\langle-|\alpha_0\rangle$$

and that

$$\langle S_x\rangle_t = \langle S_x\rangle_{t=0}\cos(\omega t) - \langle S_y\rangle_{t=0}\sin(\omega t)$$

2. *Pauli Formalism*

The Pauli formalism expresses the state kets as spinors:

$$|+\rangle \sim \begin{pmatrix}1\\0\end{pmatrix} \equiv \chi_+, \qquad |-\rangle \sim \begin{pmatrix}0\\1\end{pmatrix} \equiv \chi_-$$

hence a general spinor can be written as

$$\chi = \langle+|\alpha\rangle\,\chi_+ + \langle-|\alpha\rangle\,\chi_- = \begin{pmatrix}\langle+|\alpha\rangle\\ \langle-|\alpha\rangle\end{pmatrix}$$

In this basis the spin operators are given by the Pauli matrices:

$$S_x = \frac{\hbar}{2}\sigma_x, \qquad S_y = \frac{\hbar}{2}\sigma_y, \qquad S_z = \frac{\hbar}{2}\sigma_z$$

where

$$\sigma_x = \begin{pmatrix}0&1\\1&0\end{pmatrix}, \qquad \sigma_y = \begin{pmatrix}0&-i\\i&0\end{pmatrix}, \qquad \sigma_z = \begin{pmatrix}1&0\\0&-1\end{pmatrix}$$

3. *Rotations in the Pauli Formalism*

Using the Pauli matrices we can express the rotation operator in a simpler fashion:

$$\exp\left(-\frac{i\boldsymbol{\sigma}\cdot\hat{\boldsymbol{n}}\phi}{2}\right) = \mathbb{1}\cos\left(\frac{\phi}{2}\right) - i\boldsymbol{\sigma}\cdot\hat{\boldsymbol{n}}\sin\left(\frac{\phi}{2}\right)$$

which also works generally for spin-$\frac{1}{2}$:

$$\exp\left(-\frac{i\boldsymbol{S}\cdot\hat{\boldsymbol{n}}\phi}{\hbar}\right) = \mathbb{1}\cos\left(\frac{\phi}{2}\right) - 2i\left(\frac{\boldsymbol{S}\cdot\hat{\boldsymbol{n}}}{\hbar}\right)\sin\left(\frac{\phi}{2}\right)$$

Using these rotations we can construct the eigenspinors of spin operators about an arbitrary axis $\hat{\boldsymbol{n}}$ (instead of the z-axis). This is achieved by rotating the system twice, once about the y-axis (for instance), and once about the z-axis, with angles α and β respectively. Rotating χ_+ gives us

$$\begin{aligned}\chi'_+ &= \mathcal{D}(\hat{\boldsymbol{z}},\beta)\mathcal{D}(\hat{\boldsymbol{y}},\alpha)\chi_+ \\ &= \left(\mathbb{1}\cos\left(\frac{\beta}{2}\right) - i\sigma_z \sin\left(\frac{\beta}{2}\right)\right)\left(\mathbb{1}\cos\left(\frac{\alpha}{2}\right) - i\sigma_y \sin\left(\frac{\alpha}{2}\right)\right)\begin{pmatrix}1\\0\end{pmatrix}\end{aligned}$$

resulting in

$$\chi'_+ = \begin{pmatrix}\cos\left(\frac{\alpha}{2}\right)\exp\left(-\frac{i\beta}{2}\right)\\ \sin\left(\frac{\alpha}{2}\right)\exp\left(\frac{i\beta}{2}\right)\end{pmatrix}$$

4. Euler Rotations

An arbitrary rotation can be accomplished by rotating three times:

$$R(\alpha,\beta,\gamma) = R_{z'}(\gamma)R_{y'}(\beta)R_z(\alpha)$$

where y' and z' refer to the rotated y and z axes. It can be shown that this arbitrary rotation can equivalently be accomplished by rotating about the original axes:

$$R(\alpha,\beta,\gamma) = R_z(\alpha)R_y(\beta)R_z(\gamma)$$

where the rotations now take place with respect to the fixed axis. Note that the angles have switched around! We can generalise this to our quantum mechanical rotation operators too:

$$\mathcal{D}(\alpha,\beta,\gamma) = \mathcal{D}_z(\alpha)\mathcal{D}_y(\beta)\mathcal{D}_z(\gamma)$$

which we can express as a matrix in the Pauli formalism:

$$\begin{aligned}&\exp\left(-\frac{i\sigma_z\alpha}{2}\right)\exp\left(-\frac{i\sigma_y\beta}{2}\right)\exp\left(-\frac{i\sigma_z\gamma}{2}\right) \\ &= \begin{pmatrix} e^{-\frac{i(\alpha+\gamma)}{2}}\cos\left(\frac{\beta}{2}\right) & e^{-\frac{i(\alpha-\gamma)}{2}}\sin\left(\frac{\beta}{2}\right) \\ e^{\frac{i(\alpha-\gamma)}{2}}\sin\left(\frac{\beta}{2}\right) & e^{\frac{i(\alpha+\gamma)}{2}}\cos\left(\frac{\beta}{2}\right)\end{pmatrix}\end{aligned}$$

B. Eigenvalues and Eigenstates of Angular Momentum

1. Ladder operators

The operators $\boldsymbol{J}^2$ and J_z commute; therefore, there exists a simultaneous eigenbasis, which we will denote $|j\ m\rangle$, for which

$$J^2\,|j\ m\rangle = \hbar^2 j(j+1)\,|j\ m\rangle\,,\quad J_z\,|j\ m\rangle = \hbar m\,|j\ m\rangle$$

Just like for the harmonic oscillator we can introduce ladder operators that take us from one state to one of the adjacent states:

$$J_\pm = J_x \pm iJ_y$$

for which

$$J_\pm\,|j\ m\rangle = \hbar\sqrt{(j\mp m)(j\pm m+1)}\,|j, m\pm 1\rangle$$

Notice that this implies that any matrix representation of the rotation operator is block diagonal, where different values of j are not mixed with each other, which means it suffices to express the rotation of $|j\ m\rangle$ in terms of the different m values with total angular momentum unchanged.

$$\mathcal{D}(R)\,|j\ m\rangle = \sum_{m'}|j\ m'\rangle\,\mathcal{D}^{(j)}_{m'\,m}(R)$$

Generally

$$\mathcal{D}^{(j)}_{m'\,m}(\alpha,\beta,\gamma) = e^{-i(m'\alpha+m\gamma)}d^{(j)}_{m'\,m}$$

where

$$d^{(j)}_{m'\,m} = \langle j\ m'|\exp\left(-\frac{iJ_y\beta}{\hbar}\right)|j\ m\rangle$$

for $j=\frac{1}{2}$ this becomes

$$d^{\frac{1}{2}} = \begin{pmatrix}\cos\left(\frac{\beta}{2}\right) & -\sin\left(\frac{\beta}{2}\right)\\ \sin\left(\frac{\beta}{2}\right) & \cos\left(\frac{\beta}{2}\right)\end{pmatrix}$$

as we saw previously. Using this method it is quite easy to find the matrix representations of rotations for larger values of j.

2. Orbital Angular Momentum

When $j\in\mathbb{Z}$ the angular momentum operator, $\boldsymbol{L}$, can be written as

$$\boldsymbol{L} = \boldsymbol{x}\times\boldsymbol{p}$$

Consider now the position representation of a state in spherical coordinates, $\langle\boldsymbol{x}|\alpha\rangle = \langle r,\theta,\phi|\alpha\rangle$. In this basis we can more easily handle rotations. Let us establish the effect of the angular momentum operators on these wavefunctions. For instance an infinitesimal rotation about the z-axis:

$$\begin{aligned}\langle r,\theta,\phi|\mathbb{1}-i\left(\frac{\delta\phi}{\hbar}\right)L_z|\alpha\rangle &= \langle r,\theta,\phi-\delta\phi|\alpha\rangle \\ &= \langle r,\theta,\phi|\alpha\rangle-\delta\phi\frac{\partial}{\partial\phi}\langle r,\theta,\phi|\alpha\rangle\end{aligned}$$

which tells us that

$$L_z\langle r,\theta,\phi|\alpha\rangle=-i\hbar\frac{\partial}{\partial\phi}\langle r,\theta,\phi|\alpha\rangle$$

we can do similar calculations for L_x and L_y. Using these expressions we can derive differential equations that describe $\langle r,\theta,\phi|\ell\,\ell\rangle$ (because using L_+ on this gives you zero). From there we can use the lowering operators on this wavefunction to get the remaining functions, as we did for the harmonic oscillator. The angular wavefunctions are given by the spherical harmonics:

$$\langle r,\theta,\phi|n\,\ell\,m\rangle=R_{n\ell}(r)Y_\ell^m(\theta,\phi)$$

though the radial part is not part of this discussion, so we should rather say

$$\langle\theta,\phi|\ell\,m\rangle=Y_\ell^m(\theta,\phi)$$

3. *Schrödinger Equation for Central Potentials*

Spherically symmetric potentials are symmetric under rotations. Thus a spherically symmetric potential will lead to a Hamiltonian whose angular eigenfunctions are given by the spherical harmonics. For spherical potentials we can thus find a basis in which H, $\boldsymbol{L}^2$ and L_z are simultaneously diagonal:

$$\begin{aligned}H\,|n\,\ell\,m\rangle &= E\,|n\,\ell\,m\rangle \\ \boldsymbol{L}^2\,|n\,\ell\,m\rangle &= \hbar^2\ell(\ell+1)\,|n\,\ell\,m\rangle \\ L_z\,|n\,\ell\,m\rangle &= \hbar m\,|n\,\ell\,m\rangle\end{aligned}$$

We already know that the angular part of the wavefunctions is given by the spherical harmonics. We are now looking for the radial part, which is described by the radial equation:

$$\left(-\frac{\hbar^2}{2mr^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}}{\mathrm{d}r}\right)+\frac{\hbar^2\ell(\ell+1)}{2mr^2}+V(r)\right)R_{n\ell}(r)=ER_{n\ell}$$

Using this we can solve the Schrödinger equation for the hydrogen atom, and hydrogenic atoms alike. It also serves as an unperturbed Hamiltonian in the helium atom, for instance.

4. *Addition of Angular Momentum*

Now we will concern ourselves with coupled angular momenta. The total angular momentum can be written as

$$\boldsymbol{J}=\boldsymbol{J_1}\otimes\mathbb{1}+\mathbb{1}\otimes\boldsymbol{J_2}$$

due to some form of coupling the uncoupled states $|j_1\,m_1\,j_2\,m_2\rangle$ are no longer sufficient and we wish to find an eigenbasis of $\{J^2,J_z,J_1^2,J_2^2\}$. This is done using Clebsch-Gordan decomposition. Consider, for instance, the maximal state $|j_1\,j_1\,j_2\,j_2\rangle$; this *must* be equal to the maximal angular momentum state in the new basis too: $|j_1\,j_2\,j\,j\rangle$. From here we can use the lowering operator to find other states with the same value of j, and thereafter use orthonormality to find the other Hilbert subspaces.

IV. SYMMETRY IN QUANTUM MECHANICS

Let us define a general symmetry operator, $\mathcal{S}$, which is unitary because we need probability conservation. If the symmetry parameter is infinitesimal the first order expansion of the symmetry operator suffices:

$$\mathcal{S}=\mathbb{1}-\frac{i\varepsilon}{\hbar}G$$

where G is the Hermitian generator of the symmetry. In cases where $[G,H]=0$ we also have $[\mathcal{S},H]=0$ in which case G is a constant of motion. This allows us to find a basis of states that are eigenstates of both H and G.

A. Symmetry

Consider, for example, a rotationally invariant Hamiltonian. We know that

$$[\boldsymbol{J},H]=\boldsymbol{0},\qquad [J^2,H]=0$$

hence there exists a basis that is diagonal in $\{H,J^2,J_z\}$, which we once again denote $|n\,j\,m\rangle$. Due to the rotational invariance we know that

$$H\mathcal{D}(R)\,|n\,j\,m\rangle=\mathcal{D}(R)H\,|n\,j\,m\rangle$$

hence we know that the unrotated and the rotated kets have the same energy. As we saw previously rotations mix different values of m together (all with the same value of j), therefore we can conclude that $\{|n,j,-j\rangle\,,|n,j,(1-j)\rangle\,,\cdots,|n,j,(j-1)\rangle\,,|n,j,j\rangle\}$

forms a degenerate space. Alternatively we see this through the fact that $[J_\pm, H] = 0$.

This tells us that the degeneracy can only be broken by a perturbation that is *not* rotationally invariant, which we saw for the Hydrogen atom when we apply a magnetic field.

B. Discrete Symmetries

Until now we have only concerned ourselves with continuous symmetry operations; ones for which we could make an infinitesimal expansion. However, there exist symmetry operations that are discrete, the first of which is the *parity* operation.

1. *Parity*

The parity operation, also called space-inversion, is represented by a unitary operator, π, which inverts all of our spatial coordinates:

$$\langle\alpha|\pi^\dagger \boldsymbol{x}\pi|\alpha\rangle = -\langle\alpha|\boldsymbol{x}|\alpha\rangle$$

which tells us that the parity operator also inverts our spatial eigenkets:

$$\pi\,|\boldsymbol{x}\rangle = e^{i\delta}\,|-\boldsymbol{x}\rangle$$

up to some phase factor. Let us look at infinitesimal translations:

$$\pi\mathcal{T}(\mathrm{d}\boldsymbol{x}) = \mathcal{T}(-\mathrm{d}\boldsymbol{x})\pi$$

so

$$\pi\left(\mathbb{1} - \frac{i\boldsymbol{p}\cdot\mathrm{d}\boldsymbol{x}}{\hbar}\right)\pi^\dagger = \left(\mathbb{1} + \frac{i\boldsymbol{p}\cdot\mathrm{d}\boldsymbol{x}}{\hbar}\right)$$

and so

$$\pi^\dagger\boldsymbol{p}\pi = -\boldsymbol{p}$$

this makes intuitive sense: if we invert our coordinate systems, things moving in direction $\hat{\boldsymbol{n}}$ will move in direction $-\hat{\boldsymbol{n}}$ in our new coordinate system.

However, rotations commute with the parity operator, hence

$$\pi^\dagger\boldsymbol{J}\pi = \boldsymbol{J}$$

This implies

$$\pi^\dagger\boldsymbol{S}\cdot\boldsymbol{x}\pi = -\boldsymbol{S}\cdot\boldsymbol{x}$$

and

$$\pi^\dagger\boldsymbol{L}\cdot\boldsymbol{S}\pi = \boldsymbol{L}\cdot\boldsymbol{S}$$

2. *Parity of wavefunctions*

Suppose $[H, \pi] = 0$, then we can find mutual eigenstates, therefore, it must be the case that the eigenstates are either even or odd under parity operations.

For instance the harmonic oscillator has a Hamiltonian that is invariant under parity, which is why we know that its eigenfunctions are either symmetric or antisymmetric under spatial inversion.

3. *Parity selection rule*

Consider eigenkets of a Hamiltonian that commutes with π. These eigenkets must be parity eigenkets,

$$\pi\,|i\rangle = \varepsilon_i\,|i\rangle\,, \qquad \varepsilon_i^2 = 1$$

This tells us the matrix elements of (for instance) x are zero unless the initial and final states have opposite parity.

$$\langle f|\boldsymbol{x}|i\rangle = \langle f|\pi^\dagger\pi\boldsymbol{x}\pi^\dagger\pi|i\rangle = -\varepsilon_i\varepsilon_f\,\langle f|\boldsymbol{x}|i\rangle$$

4. *Lattice Translations*

Consider a periodic potential, with lattice constant a:

$$\mathcal{T}^\dagger(a)V(x)\mathcal{T}(a) = V(x+a) = V(x)$$

therefore we should expect that the energy eigenfunctions also are invariant under (discrete) translations. We can construct the ground state by looking at the ground state of the n^{th} unit cell. This is obviously not an energy eigenstate, as we have $\mathcal{T}(a)\,|n\rangle = e^{i\delta}\,|n+1\rangle$. Thus the translation operator relates every local ground state to its neighbour's ground state: the total ground state must be a linear combination of all these:

$$|\theta\rangle = \sum_n e^{in\theta}\,|n\rangle$$

for this we have

$$\mathcal{T}(a)\,|\theta\rangle = e^{i\delta}\sum_n e^{in\theta}\,|n+1\rangle = e^{i(\delta-\theta)}\,|\theta\rangle$$

we choose $\delta = 0$ by convention.

To evaluate the energy of this state let us assume that

$$\langle n'|H|n\rangle = E_0\delta_{n,n'} - \Delta\delta_{n,n'+1} - \Delta\delta_{n,n'-1}$$

this is the tight-binding approximation. Then

$$E_\theta = E_0 - 2\Delta\cos\theta$$

so the ground state is $|\theta = 0\rangle$. Bloch's theorem states that a periodic potential with lattice constant a has eigenstates of the form

$$\psi_k(x) = u_k(x)e^{ikx}$$

where $u_k(x) = u_k(x+a)$, which tells us that the phase kx is related to the wavenumber, k: the solution to this problem is hence a slight (periodic) modification to plane waves.

5. *Time-Reversal Symmetry*

The next discrete symmetry operation is time reversal, which is often also thought of as motion inversion. Kepler's problem is invariant under time-reversal: if a trajectory $\boldsymbol{r}(t)$ is a solution to Kepler's equations, then so is $\boldsymbol{r}(-t)$. The operator, Θ, that represents time-reversal in quantum mechanics is *antiunitary*†:

$$\Theta = U_\Theta K$$

where U_Θ is unitary and K is the complex conjugation operator. The antiunitarity is a necessity, otherwise we would get that time-reversed energy eigenstates have negative energies‡. This is a new kind of operator, which has some unusual properties. For instance, let

$$|\tilde{\alpha}\rangle = \Theta|\alpha\rangle, \qquad |\tilde{\beta}\rangle = \Theta|\beta\rangle$$

Then

$$\langle\tilde{\alpha}|\tilde{\beta}\rangle = \langle\beta|\alpha\rangle$$

NB: The time-reversal operator only preserves the magnitude of inner products.

For a linear operator, X:

$$\langle\alpha|X|\beta\rangle = \langle\tilde{\alpha}|\Theta X^\dagger\Theta^{-1}|\tilde{\beta}\rangle$$

We say that an observable is odd or even under time reversal according to whether we have the upper or lower sign in

$$\Theta A\Theta^{-1} = \pm A$$

† Antiunitary operators still preserve the norm, but they do not preserve inner products, due to the complex conjugation

‡ Isn't that exactly what we said for QFT?

Momentum is odd under time-reversal, as we require, and position is even

$$\Theta\boldsymbol{p}\Theta^{-1} = -\boldsymbol{p}, \qquad \Theta\boldsymbol{x}\Theta^{-1} = \boldsymbol{x}$$

Angular momentum is odd

$$\Theta\boldsymbol{J}\Theta^{-1} = -\boldsymbol{J}$$

6. *Wavefunctions*

Consider a state in its position representation

$$|\alpha\rangle = \int \mathrm{d}^3x\ |\boldsymbol{x}\rangle\langle\boldsymbol{x}|\alpha\rangle$$

Applying time-reversal

$$\Theta|\alpha\rangle = \int \mathrm{d}^3x\ |\boldsymbol{x}\rangle\langle\alpha|\boldsymbol{x}\rangle$$

which tells us that

$$\psi(\boldsymbol{x}) \xrightarrow{\Theta} \psi^*(\boldsymbol{x})$$

This can also be seen by looking at the Schrödinger equation

$$i\hbar\partial_t\psi(\boldsymbol{x}) = \hat{H}\psi(x)$$

(for H invariant under time-reversal). Applying Θ

$$-i\hbar\partial_t\left(\Theta\psi(\boldsymbol{x})\right) = \hat{H}\left(\Theta\psi(\boldsymbol{x})\right)$$

But by simply taking the complex conjugate of the Schrödinger equation we obtain the same differential equation

$$-i\hbar\partial_t\psi^*(\boldsymbol{x}) = \hat{H}\psi^*(\boldsymbol{x})$$

thus

$$\psi(-t,\boldsymbol{x}) = \psi^*(t,\boldsymbol{x})$$

7. *Time-reversal of spin-$\frac{1}{2}$ systems*

Consider the eigenket of $\boldsymbol{S}\cdot\hat{\boldsymbol{n}}$ with eigenvalue $\frac{\hbar}{2}$

$$|\hat{\boldsymbol{n}},+\rangle = \exp\left(-\frac{iS_z\alpha}{\hbar}\right)\exp\left(-\frac{iS_y\beta}{\hbar}\right)|+\rangle$$

and we know that

$$\Theta|\hat{\boldsymbol{n}},+\rangle = \eta|\hat{\boldsymbol{n}},-\rangle$$

for some phase factor η. We can also construct this state through

$$|\hat{\boldsymbol{n}}, -\rangle = \exp\left(-\frac{iS_z\alpha}{\hbar}\right)\exp\left(-\frac{iS_y(\beta+\pi)}{\hbar}\right)|+\rangle$$

hence

$$\Theta = \eta\exp\left(-\frac{i\pi S_y}{\hbar}\right)K$$

and in fact this holds generally

$$\Theta = \eta\exp\left(-\frac{i\pi J_y}{\hbar}\right)K$$

which we can use to show that

$$\Theta^2 = (-1)^{2j}$$

8. *Kramer's Degeneracy*

For half-integer-spin systems where $[H, \Theta] = 0$ we have that

$$\Theta^2|n\rangle = -|n\rangle$$

assume now that E_n is non-degenerate, then

$$\Theta|n\rangle = e^{i\delta}|n\rangle, \qquad \Theta^2|n\rangle = |n\rangle$$

however, this contradicts our assumption. Therefore we *know* that Hamiltonians that are invariant under time reversal have at least two-fold degeneracies at each energy level, assuming they describe a half-integer spin system.

V. APPROXIMATION METHODS

We will now consider Hamiltonians that cannot be solved analytically and must be approximated.

A. Perturbation Theory: Non-Degenerate

The first approximation method we will look at is perturbation theory, where we split the Hamiltonian up into an unperturbed Hamiltonian, H_0, which we can solve analytically, and a perturbation V. However, it is standard procedure to introduce a perturbation parameter λ which is used to keep track of the order of the perturbation:

$$H = H_0 + \lambda V$$

As mentioned, we know the eigenkets and eigenenergies of H_0:

$$H_0\left|n^{(0)}\right\rangle = E_n^{(0)}\left|n^{(0)}\right\rangle$$

The effect of the perturbation is now written as a power series:

$$\begin{aligned}|n\rangle &= \left|n^{(0)}\right\rangle + \lambda\left|n^{(1)}\right\rangle + \lambda^2\left|n^{(2)}\right\rangle + \cdots \\ E_n &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots\end{aligned}$$

where we refer to the n^{th} term in the sum as the n^{th} order correction. Up to second order we have

$$E_n = E_n^{(0)} + \lambda\left\langle n^{(0)}\middle|V\middle|n^{(0)}\right\rangle + \lambda^2\sum_{k\neq n}\frac{|\langle n^{(0)}|V|k^{(0)}\rangle|^2}{E_n^{(0)} - E_k^{(0)}}$$

and

$$\begin{aligned}|n\rangle &= \left|n^{(0)}\right\rangle + \lambda\sum_{k\neq n}\frac{\langle n^{(0)}|V|k^{(0)}\rangle}{E_n^{(0)} - E_k^{(0)}}\left|k^{(0)}\right\rangle \\ &+ \lambda^2\left(\sum_{k,\ell\neq n}\frac{\left|k^{(0)}\right\rangle V_{k\ell}V_{\ell n}}{(E_n^{(0)} - E_k^{(0)})(E_n^{(0)} - E_\ell^{(0)})} - \sum_{k\neq n}\frac{\left|k^{(0)}\right\rangle V_{nn}V_{k\ell}}{\left(E_n^{(0)} - E_k^{(0)}\right)^2}\right)\end{aligned}$$

where

$$V_{ij} = \left\langle i^{(0)}\middle|V\middle|j^{(0)}\right\rangle$$

Note that $\langle n^{(0)}|n^{(0)}\rangle = 1$, therefore these wavefunctions are not normalized. However, using the formulae above it is quite easy to show that the normalisation constant $\sqrt{Z_n}$ can be found through

$$Z_n^{-1} = \langle n|n\rangle = 1 + \lambda^2\sum_{k\neq n}\frac{|V_{kn}|^2}{\left(E_n^{(0)} - E_k^{(0)}\right)^2} + \mathcal{O}(\lambda^3)$$

1. *Harmonic Oscillator*

Let us look at the harmonic oscillator

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

And we will add a perturbation $\varepsilon V = \frac{1}{2}\varepsilon m\omega^2x^2$. We can quite easily find the matrix elements of the perturbation using the raising and lowering operators:

$$\begin{aligned}V_{00} &= \varepsilon\frac{\hbar\omega}{4} \\ V_{20} &= \varepsilon\frac{\hbar\omega}{2\sqrt{2}}\end{aligned}$$

These are the only two terms that contribute to the first order correction of the ground state

$$|0\rangle = \left|0^{(0)}\right\rangle - \frac{\varepsilon}{4\sqrt{2}}\left|2^{(0)}\right\rangle + \mathcal{O}(\varepsilon^2)$$

and

$$E_0 = \frac{\hbar\omega}{2}\left(1 + \frac{\varepsilon}{2} - \frac{\varepsilon^2}{8} + \mathcal{O}(\varepsilon^3)\right)$$

which coincides with the first three terms in the full solution, which we can calculate exactly: $E_0 = \left(\frac{\hbar\omega}{2}\right)\sqrt{1+\varepsilon}$. Naturally this approach also holds in position space; therefore the terms in Equation V A 1 tell us about the corrections to the wavefunction. Notice that the potential is still even under parity, therefore the perturbed wavefunctions will still either be odd or even under parity, which is why $\left|0^{(0)}\right\rangle$ is mixed with $\left|2^{(0)}\right\rangle$ and *not* $\left|1^{(0)}\right\rangle$.

B. Perturbation Theory: Degenerate

In the case that we have degenerate eigenvalues we cannot use the previous expressions, because even though there are two kets $|n\rangle$ and $|k\rangle$, we cannot know that they do not have the same energy. However, the perturbation often removes the degeneracy, which means that every ket in the degenerate space has its own energy. Thus, there exists a basis within the degenerate space such that the perturbation is diagonal. Therefore in degenerate perturbation theory, we look exclusively inside the degenerate space and perform the perturbation theory in the appropriate basis, which is found by finding the eigenkets of V.

Interestingly, the second order correction from within the degenerate space is zero, so the second order correction is

$$E_\ell^{(2)} = \sum_{k\notin D}\frac{|V_{k\ell}|^2}{E_D^{(0)} - E_k^{(0)}}$$

where D is the *degenerate subspace*; the sum only goes over kets that are not degenerate with $\left|\ell^{(0)}\right\rangle$, hence we need not worry about the fraction exploding.

C. Perturbation Theory: Time-Dependent

Consider now a time-dependent perturbation

$$H = H_0 + V(t)\Theta(t - t_0)$$

where we once again know the solution to H_0. We wish to find $c_n(t)$ for $t > t_0$ such that

$$|\alpha, t_0; t\rangle = \sum_n c_n(t)e^{-i\frac{E_n t}{\hbar}}|n\rangle$$

1. *Interaction Picture*

The interaction picture is useful to time-dependent perturbation theory, as we will see. The interaction picture state ket is defined by

$$|\alpha, t_0; t\rangle_I = e^{iH_0 t/\hbar}|\alpha, t_0; t\rangle_S$$

Operators are

$$A_I \equiv e^{iH_0 t/\hbar}A_S e^{-iH_0 t/\hbar}$$

Using these definitions we can show that the Schrödinger equation becomes

$$i\hbar\partial_t|\alpha, t_0; t\rangle_I = V_I|\alpha, t_0; t\rangle_I$$

The time-evolution is only due to the (time-dependent) perturbation. On the other hand, the time-evolution of operators is due to the unperturbed Hamiltonian only:

$$\frac{\mathrm{d}A_I}{\mathrm{d}t} = \frac{1}{i\hbar}[A_I, H_0]$$

We can rewrite the Schrödinger equation for kets such that it includes the terms $c_n(t)$ mentioned above. In order to do so we expand using the eigenkets of the unperturbed Hamiltonian:

$$i\hbar\partial_t\langle n|\alpha, t_0; t\rangle_I = \sum_m \langle n|V_I|m\rangle\langle m|\alpha, t_0; t\rangle_I$$

but

$$\langle n|V_I|m\rangle = \langle n|e^{iE_n t/\hbar}V_S e^{-iE_m t/\hbar}|m\rangle = e^{-i(E_m - E_n)t/\hbar}V_{nm}(t)$$

and naturally $\langle n|\alpha, t_0; t\rangle = c_n(t)$. Thus we can write this as a matrix differential equation with time-dependent coefficients

$$i\hbar\partial_t\begin{pmatrix}c_1\\c_2\\c_3\\\vdots\end{pmatrix} = \begin{pmatrix}V_{11} & V_{12}e^{i\omega_{12}t} & & \cdots\\ V_{21}e^{i\omega_{21}t} & V_{22} & & \cdots\\ & & V_{33} & \cdots\\ \vdots & \cdots & & \ddots\end{pmatrix}\begin{pmatrix}c_1\\c_2\\c_3\\\vdots\end{pmatrix}$$

For instance, consider a two-level system with Hamiltonian

$$H = \begin{pmatrix}E_1 & \gamma e^{i\omega t}\\ \gamma e^{-i\omega t} & E_2\end{pmatrix}$$

clearly

$$i\hbar\begin{pmatrix}\dot c_1\\ \dot c_2\end{pmatrix}=\begin{pmatrix}0 & \gamma e^{i(\omega-\omega_0)t/\hbar}\\ \gamma e^{-i(\omega-\omega_0)t/\hbar} & 0\end{pmatrix}\begin{pmatrix}c_1\\ c_2\end{pmatrix}$$

We can decouple these to a second order differential equation with constant coefficients

$$\ddot c_1 = i\delta\dot c_1-\left(\frac{\gamma}{\hbar}\right)^2 c_1,\qquad \delta=\omega-\omega_0$$

which can be solved using a Laplace transform. The result is given by *Rabi's formula*

$$|c_2(t)|^2=\frac{\gamma^2/\hbar^2}{\gamma^2/\hbar^2+\delta^2/4}\sin^2\left[\left(\frac{\gamma^2}{\hbar^2}+\frac{\delta^2}{4}\right)^{\frac{1}{2}}t\right]$$
$$|c_1(t)|^2=1-|c_2(t)|^2$$

(the initial condition used to solve this is $c_1(0)=1$)

2. Dyson Series

Seeing as the Schrödinger equation only depends on the perturbation, we can write the time-evolution operator only as a function of $V_I(t)$ too:

$$U_I(t,t_0)=\mathbb{1}-\frac{i}{\hbar}\int_{t_0}^{t}\mathrm{d}t'V_I(t') +\left(\frac{-i}{\hbar}\right)^2\int_{t_0}^{t}\mathrm{d}t'\int_{t_0}^{t'}\mathrm{d}t''V_I(t')V_I(t'')+\cdots$$

3. Transition Probability

Using the Dyson series one can derive a perturbative expression for the transition probability:

$$c_f(t)=\langle f|U_I(t,t_0)|i\rangle$$

so the first and second order terms would be

$$c_f^{(1)}=-\frac{i}{\hbar}\int_{t_0}^{t}\mathrm{d}t'\ \langle f|V_I(t')|i\rangle=-\frac{i}{\hbar}\int_{t_0}^{t}\mathrm{d}t'\ e^{i\omega_{fi}t}V_{fi}(t)$$

$$c_f^{(2)}=\left(\frac{-i}{\hbar}\right)^2\sum_m\int_{t_0}^{t}\mathrm{d}t'\int_{t_0}^{t'}\mathrm{d}t''e^{i(\omega_{fm}t'+\omega_{mi}t'')}V_{fm}(t')V_{mi}(t'')$$

Let us, for instance, consider a constant perturbation

$$H=H_0+V\Theta(t-t_0)$$

here, for $t_0=0$

$$c_f^{(1)}=-\frac{i}{\hbar}V_{fi}\int_0^t\mathrm{d}t'\ e^{i\omega_{fi}t'} =\frac{V_{fi}}{E_f-E_i}\left(1-e^{i\omega_{fi}t}\right)$$

which means

$$\left|c_f^{(1)}\right|^2=\frac{|V_{fi}|^2}{|E_f-E_i|^2}\sin^2\left[\frac{(E_n-E_i)t}{2\hbar}\right]$$

D. Fermi's Golden Rule

In cases where we have a continuous energy spectrum and are looking at transitions where $E_f\approx E_i$ we can replace a sum such as $\sum_{f,E_f\approx E_i}\left|c_n^{(1)}\right|^2$ with

$$\sum_{f,E_f\approx E_i}\left|c_f^{(1)}\right|^2\quad\rightsquigarrow\quad\int\mathrm{d}E_f\rho(E_f)\left|c_f^{(1)}\right|^2$$

where the density of states $\rho(E)\mathrm{d}E$ is defined as the number of states within the energy interval $(E,E+\mathrm{d}E)$. Using this we can define the transition rate

$$w_{i\to[f]}=\frac{2\pi}{\hbar}\overline{|V_{fi}|^2}\rho(E_f)_{E_f\approx E_i}$$

where $[f]$ is the set of final states in the neighbourhood of $|i\rangle$. We sometimes also write this expression as

$$w_{i\to f}=\frac{2\pi}{\hbar}|V_{fi}|^2\,\delta(E_n-E_i)$$

where it must be understood that this expression is integrated with the measure $\int\mathrm{d}E_f\rho(E_f)$.

E. Harmonic Perturbation

Consider now a harmonic perturbation of the form

$$V(t)=\left(\mathcal{V}e^{i\omega t}+\mathcal{V}^\dagger e^{-i\omega t}\right)\Theta(t-0)$$

for $\mathcal{V}$ some operator that may further depend on position, momentum, spin, etc. Using our time-dependent perturbation theory we can write

$$c_n^{(1)}=-\frac{i}{\hbar}\int_0^t\mathrm{d}t'\ \left(\mathcal{V}_{ni}e^{i\omega t'}+\mathcal{V}_{ni}^\dagger e^{-i\omega t'}\right)e^{i\omega_{ni}t'} =\frac{1}{\hbar}\left[\frac{1-e^{i(\omega+\omega_{ni})t}}{\omega+\omega_{ni}}-\frac{1-e^{i(\omega-\omega_{ni})t}}{\omega-\omega_{ni}}\right]$$

This looks a lot like the term we saw for the constant perturbation, if we just let $\omega_{ni} \rightsquigarrow \omega_{ni} \pm \omega$. The transition probability is only appreciable if $\omega_{ni} \pm \omega \approx 0$. These two situations correspond to stimulated emission and absorption respectively. Note that we have assumed that the perturbation is classical, so we have not limited the amount of energy it can give away or absorb; we can freely take as much energy as needed from a bath, but also give as much energy as needed to the bath. Here the transition rates become

$$w_{i\to n} = \frac{2\pi}{\hbar}\begin{cases} |V_{ni}|^2\,\delta(E_n - E_i + \hbar\omega) \\ \left|V_{ni}^\dagger\right|^2\,\delta(E_n - E_i - \hbar\omega) \end{cases}$$

however, naturally $|V_{ni}| = \left|V_{ni}^\dagger\right|$ which tells us that the if the density of states is constant we have as much emission as we do absorption. However, if the density of states is different we get

$$\frac{w_{E_i\to E_i-\hbar\omega}}{\rho(E_i - \hbar\omega)} = \frac{w_{E_i\to E_i+\hbar\omega}}{\rho(E_i + \hbar\omega)} = \frac{2\pi}{\hbar}$$

F. Energy Shift and Decay Width

Consider a constant perturbation, V, which is turned on very slowly $e^{\eta t}V$. At $t = -\infty$ the perturbation is switched off and it gradually gets turned on. In the limit $\eta \to 0$ we retrieve our original constant perturbation.

We are now interested in the coefficient $c_i(t)$, that is, we want to know how the population of $|i\rangle$ disappears as its energy is dispersed throughout the system.

$$c_i^{(1)} = -\frac{i}{\hbar}V_{ii}\int_{-\infty}^{t}\mathrm{d}t'\;e^{\eta t'} = -\frac{i}{\hbar\eta}V_{ii}e^{\eta t}$$

$$c_i^{(2)} = \left(\frac{-i}{\hbar}\right)^2 |V_{ii}|^2\,\frac{e^{2\eta t}}{2\eta^2} + \left(\frac{-i}{\hbar}\right)\sum_{m\neq i}\frac{|V_{mi}|^2\,e^{2\eta t}}{2\eta(E_i - E_m + i\hbar\eta)}$$

Let us choose the ansatz $c_i(t) = e^{-i\Delta_i t/\hbar}$; we expect the population of the initial state to decay exponentially and to have an oscillatory part. Using our first two corrections to c_i and some fancy maths, we get that

$$\Delta_i^{(2)} = \left(\mathrm{Pr}\sum_{m\neq i}\frac{|V_{mi}|^2}{E_i - E_m}\right) - i\left(\pi\sum_{m\neq i}|V_{mi}|^2\,\delta\left(E_i - E_m\right)\right)$$

The population indeed dies exponentially:

$$|c_i(t)|^2 = e^{-\Gamma_i t/\hbar}, \qquad \Gamma_i = -2\mathrm{Im}(\Delta_i^{(2)})$$

We can interpret this Γ_i as a decay *width*.

VI. SCATTERING THEORY

Consider a Hamiltonian of the form

$$H = \underbrace{\frac{\boldsymbol{p}^2}{2m}}_{H_0} + V(\boldsymbol{x})$$

the unperturbed energy-levels are

$$E_{\boldsymbol{k}} = \frac{\hbar|\boldsymbol{k}|^2}{2m}$$

The eigenvectors are plane waves, which we denote by $|\boldsymbol{k}\rangle$. Once again the transition amplitude is $\langle n|U_I(t,t_0)|i\rangle$ which is

$$\langle n|U_I(t,t_0)|i\rangle = \mathbb{1}\delta_{ni} - \frac{i}{\hbar}\sum_m V_{nm}\int_{t_0}^{t}\mathrm{d}t'\;e^{i\omega_{nm}t'}\,\langle m|U_I(t',t_0)|i\rangle$$

Let us define a matrix T, such that

$$\langle n|U_I(t,t_0)|i\rangle = \mathbb{1}\delta_{ni} - \frac{i}{\hbar}T_{ni}\int_{t_0}^{t}\mathrm{d}t'\;e^{(i\omega_{ni}+\varepsilon)t'}$$

with $0 < \varepsilon \ll t^{-1}$. Now also define the scattering matrix, S, such that

$$\begin{aligned} S_{ni} &\equiv \lim_{t\to\infty}\left(\lim_{\varepsilon\to 0}\,\langle n|U_I(t,-\infty)|i\rangle\right) \\ &= \delta_{ni} - 2\pi i\delta(E_n - E_i)T_{ni} \end{aligned}$$

Note that it is important that we take the ε limit first!

Because the perturbation is time-independent we can evaluate the integral

$$c_n(t) = \langle n|U_I(t,-\infty)|i\rangle = -\frac{i}{\hbar}T_{ni}\left(\frac{e^{(i\omega_{ni}+\varepsilon)t}}{i\omega_{ni}+\varepsilon}\right)$$

and hence the transition rate

$$w_{i\to n} = \frac{\mathrm{d}}{\mathrm{d}t}\,|c_n(t)|^2 = \frac{1}{\hbar^2}\,|T_{ni}|^2\,\frac{2\varepsilon e^{2\varepsilon t}}{\omega_{ni}^2 + \varepsilon^2}$$

Taking the limit as $\varepsilon \to 0$ gives us $\sim \delta(\omega_{ni})$, because the fraction involving ε goes to zero in this limit unless ω_{ni} is zero, which again enforces energy conservation:

$$\lim_{\varepsilon\to 0}\frac{2\varepsilon e^{2\varepsilon t}}{\omega_{ni}^2 + \varepsilon^2} = 2\pi\hbar\delta(E_n - E_i)$$

giving us Fermi's golden rule once again:

$$w_{i\to n} = \frac{2\pi}{\hbar}\,|T_{ni}|^2\,\delta(E_n - E_i)$$

Consider now free particles confined inside a box of volume L^3. We can always let $L \to \infty$ again to return to the fully free particles. Now due to our boundary conditions we get that

$$E_{\boldsymbol{n}} = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)(\boldsymbol{n})^2$$

and hence

$$\rho(E_n) = \frac{\Delta n}{\Delta E_n} = \frac{mk}{\hbar}\left(\frac{L}{2\pi}\right)^2 \mathrm{d}\Omega$$

where Ω is the solid angle in $\boldsymbol{n}$-space. The flux is $\boldsymbol{j} = \frac{\hbar \boldsymbol{k}}{mL^3}$ and the transition rate is

$$w_{i\to n} = \frac{mkL^3}{(2\pi)^2\hbar^3}\left|T_{ni}\right|^2 \mathrm{d}\Omega$$

The cross section times transition rate must be equal to the flux, hence we can isolate for the cross section (per steradian)

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \left(\frac{mL^3}{2\pi\hbar^2}\right)^2 \left|T_{ni}\right|^2$$

A. Finding the T-Matrix

It is by no means straightforward to find T, because in the only equation we have to describe it we cannot directly isolate it:

$$T_{ni} = V_{ni} + \sum_m V_{nm}\frac{T_{mi}}{E_i - E_m + i\hbar\varepsilon}$$

However we can expand this equation and write it in such a way that it is clear which terms are of order $\mathcal{O}(V^n)$:

$$T = V\left(1 + \sum_n \left(\frac{1}{E_i - H_0 + i\hbar\varepsilon}V\right)^n\right)$$

note that the *operator* H_0 appears in the denominator. Therefore we need to be careful when we multiply the terms out; for instance, the third order term is

$$V\frac{1}{E_i - H_0 + i\hbar\varepsilon}V\frac{1}{E_i - H_0 + i\hbar\varepsilon}V \neq V^3\left(\frac{1}{E_i - H_0 + i\hbar\varepsilon}\right)^2$$

this is because in general $[H_0, V] \neq 0$. Equation VI A was derived through the *Lippmann-Schwinger Equation*, which defines a state, $|\psi^+\rangle$:

$$\left|\psi^\pm\right\rangle = |i\rangle + \frac{1}{E_i - H_0 \pm i\hbar\varepsilon}V\left|\psi^\pm\right\rangle$$

which we will use in the following.

B. Scattering Amplitude

Consider the position-space representation of $|\psi^\pm\rangle$:

$$\left\langle \boldsymbol{x}\middle|\psi^\pm\right\rangle = \langle \boldsymbol{x}|i\rangle + \int \mathrm{d}\boldsymbol{x}' \underbrace{\langle \boldsymbol{x}|\frac{1}{E_i - H_0 \pm i\hbar\varepsilon}|\boldsymbol{x}'\rangle}_{\frac{2m}{\hbar^2}G_\pm(\boldsymbol{x},\boldsymbol{x}')} \left\langle \boldsymbol{x}'\middle|V\middle|\psi^\pm\right\rangle$$

$[H_0, \boldsymbol{x}] \neq 0$ but $[H_0, \boldsymbol{k}] = 0$, so it is easiest to evaluate the Green's function, $G_\pm$, in the momentum basis:

$$G_\pm(\boldsymbol{x},\boldsymbol{x}') = \frac{1}{(2\pi)^3}\int \mathrm{d}\boldsymbol{k}' \frac{e^{i\boldsymbol{k}'\cdot(\boldsymbol{x}-\boldsymbol{x}')}}{k^2 - k'^2 \pm i\varepsilon}$$

we can evaluate this with the Residue theorem:

$$G_\pm(\boldsymbol{x},\boldsymbol{x}') = -\frac{1}{4\pi}\frac{e^{\pm ik|\boldsymbol{x}-\boldsymbol{x}'|}}{|\boldsymbol{x}-\boldsymbol{x}'|}$$

So

$$\left\langle \boldsymbol{x}\middle|\psi^\pm\right\rangle = \langle \boldsymbol{x}|i\rangle - \frac{2m}{\hbar^2}\int \mathrm{d}\boldsymbol{x}' \frac{e^{\pm ik|\boldsymbol{x}-\boldsymbol{x}'|}}{4\pi|\boldsymbol{x}-\boldsymbol{x}'|}V(\boldsymbol{x}')\left\langle \boldsymbol{x}'\middle|\psi^\pm\right\rangle$$

The value $k|\boldsymbol{x}-\boldsymbol{x}'|$ is rather odd, so let us approximate it, in the limit where $r \gg r'$ where $r = |\boldsymbol{x}|$ and $r' = |\boldsymbol{x}'|$.

$$|\boldsymbol{x}-\boldsymbol{x}'| = \sqrt{r^2 - 2rr'\cos\alpha + r'^2} \approx r - \hat{\boldsymbol{r}}\cdot\boldsymbol{x}'$$

We get

$$\left\langle \boldsymbol{x}\middle|\psi^+\right\rangle \overset{\text{large } r}{\to} \frac{1}{L^{\frac{3}{2}}}\left[e^{i\boldsymbol{k}\cdot\boldsymbol{x}} + \frac{e^{ikr}}{r}f(\boldsymbol{k},\boldsymbol{k}')\right]$$

thus, at large r (large distance from the localised potential) we can approximate the outgoing wave as the ingoing wave plus a *spherical* wave with amplitude $f(\boldsymbol{k},\boldsymbol{k}')$. We have assumed that $|i\rangle = |\boldsymbol{k}\rangle$, i.e. that we sent plane waves into the sample.

$$f(\boldsymbol{k},\boldsymbol{k}') = -\frac{mL^3}{2\pi\hbar^2}\left\langle \boldsymbol{k}'\middle|V\middle|\psi^+\right\rangle$$

We refer to $f(\boldsymbol{k},\boldsymbol{k}')$ as the *scattering amplitude*. The differential cross section becomes

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = |f(\boldsymbol{k},\boldsymbol{k}')|^2$$

C. Born Approximation

Let us consider again Equation VI A:

$$T = V\left(1 + \sum_n \left(\frac{1}{E_i - H_0 + i\hbar\varepsilon}V\right)^n\right)$$

Taking this up to first order, where $T = V$ is the (first order) *Born Approximation*:

$$f^{(1)}(\boldsymbol{k}, \boldsymbol{k}') = -\frac{m}{2\pi\hbar^2} \int \mathrm{d}\boldsymbol{x}\, e^{i(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{x}} V(\boldsymbol{x})$$

for the finite spherical well of radius a and height V_0 we get

$$f^{(1)}(\theta) = -\frac{2m}{\hbar^2} \frac{V_0 a}{(qa)^3} \left[\frac{\sin qa}{qa} - \cos qa\right]$$

where θ is defined indirectly through $q = |\boldsymbol{k} - \boldsymbol{k}'| = 2k \sin \frac{\theta}{2}$. Thus by scattering particles off a spherical well, such as a model proton, we can establish the radius of the scatterer.

In general, if $f(\boldsymbol{k}, \boldsymbol{k}')$ can be approximated by the first order Born amplitude $f^{(1)}$ we know that

1. $\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}$ of $f(\theta)$ is a function of q only; that is $f(\theta)$ depends on the energy $\hbar^2 k^2/(2m)$ and the angle θ only through the combination $k^2(1 - \cos\theta)$.
2. $f(\theta)$ is always real
3. $\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}$ is independent of the sign of V.

VII. IDENTICAL PARTICLES

Fundamental particles are indistinguishable; that is, you cannot label one electron as A and another as B and then follow each of their time-evolutions separately. There exists a permutation symmetry, which leads to some interesting physics. Consider the state $|k'\rangle\,|k''\rangle$ ($k' \neq k''$), that is, two quantum mechanical particles, one with wavenumber k' and the other with k''. Due to the permutation symmetry, we cannot distinguish between this state and the state $|k''\rangle\,|k'\rangle$. These two states are indistinguishable, and hence also degenerate: this is referred to as *exchange degeneracy.* In fact, all states of the form

$$\alpha\,|k'\rangle\,|k''\rangle + \beta\,|k''\rangle\,|k'\rangle\,, \qquad |\alpha|^2 + |\beta|^2 = 1$$

are degenerate. Define the permutation operator P_{12} which switches the two particles

$$P_{12}\,|k'\rangle\,|k''\rangle = P_{21}\,|k'\rangle\,|k''\rangle = |k''\rangle\,|k'\rangle$$

Suppose we have an operator A_1 which only operates on the first ket, then we can show that

$$P_{12} A_1 P_{12}^{-1} = A_2$$

where A_2 is the same operator but operating on the second particle. Using the permutation operator we can define a symmetriser, S_{12}, and an antisymmetriser, A_{12}:

$$S_{12} = \frac{1}{2}\left(1 + P_{12}\right), \quad A_{12} = \frac{1}{2}\left(1 - P_{12}\right)$$

They take any state $|\psi'\rangle\,|\psi''\rangle$ and put them in a symmetric or antisymmetric configuration.

A. Symmetrisation Postulate

A system of N particles is either completely symmetric under a permutation of two particles (bosons) or completely antisymmetric under a permutation of two particles (fermions):

$$P_{ij}\,|\text{N identical bosons}\rangle = +\,|\text{N identical bosons}\rangle$$
$$P_{ij}\,|\text{N identical fermions}\rangle = -\,|\text{N identical fermions}\rangle$$

It can be shown that the particle type is determined by its spin: fermions have half-integer spin and bosons have integer spin.

An immediate implication of Equation VII A is that two fermions can never occupy the same quantum state; if they *did* then the wavefunction would have to be equal to zero, implying that the probability of this occurring is zero.

For two spin-$\frac{1}{2}$ particles, fermions with a symmetric spatial state occupy the singlet spin state (antisymmetric under permutation), while bosons may occupy the three triplet spin states (symmetric under permutation). However, it should be noted that it is the *total* state that is to be totally symmetric or antisymmetric:

$$|\alpha\rangle = |\psi(x)\rangle \otimes |\chi\rangle$$

that is, for a fermionic system, the (tensor) product of the spatial wavefunction and the spin wavefunction have to be antisymmetric under permutation, thus if the spin configuration is in a triplet state, we know that the spatial wavefunction must be antisymmetric under permutation.

1. *Helium Atom*

Consider the helium atom, which has a nucleus of charge $2e$ and two electrons. These electrons, like all electrons, are identical, therefore our rules about their permutation symmetry hold; their total wavefunction must be totally antisymmetric. Consider an excited state where one of the electrons is in its ground state and the other in an excited state

$$\phi(\boldsymbol{x}_1, \boldsymbol{x}_2) = \frac{1}{\sqrt{2}} \left[\psi_{100}(\boldsymbol{x}_1)\psi_{n\ell m}(\boldsymbol{x}_2) \pm \psi_{n\ell m}(\boldsymbol{x}_1)\psi_{100}(\boldsymbol{x}_2)\right]$$

The energy of this state must be

$$E = E_{100} + E_{n\ell m} + \Delta E$$

where ΔE is due to the interaction between the electrons. First order *degenerate* perturbation theory tells us that ΔE is given by

$$\Delta E = \langle \frac{e^2}{r_{12}} \rangle = I \pm J$$

where the direct integral and exchange integral are

$$I \equiv \int\int \mathrm{d}\boldsymbol{x}_1 \mathrm{d}\boldsymbol{x}_2 \ |\psi_{100}(\boldsymbol{x}_1)|^2 \, |\psi_{n\ell m}(\boldsymbol{x}_2)|^2 \, \frac{e^2}{r_{12}}$$

$$J \equiv \int\int \mathrm{d}\boldsymbol{x}_1 \mathrm{d}\boldsymbol{x}_2 \ \psi_{100}(\boldsymbol{x}_1)\psi_{n\ell m}(\boldsymbol{x}_2) \frac{e^2}{r_{12}} \psi^*_{100}(\boldsymbol{x}_2)\psi^*_{n\ell m}(\boldsymbol{x}_1)$$

where $r_{12} \equiv |\boldsymbol{x}_1 - \boldsymbol{x}_2|$

2. *Multiparticle Systems*

For higher numbers of particles things become quite complicated, however it is quite easy to write the totally antisymmetric state, which quite often is the lowest energy level. Using the *Slater determinant*, for three particles we have

$$|k'k''k'''\rangle_{\text{antisymmetric}} = \begin{vmatrix} |k'\rangle & |k''\rangle & |k'''\rangle \\ |k'\rangle & |k''\rangle & |k'''\rangle \\ |k'\rangle & |k''\rangle & |k'''\rangle \end{vmatrix}$$

Note that this is not zero; because we cannot let the kets commute with each other, $|k'\rangle |k''\rangle \neq |k''\rangle |k'\rangle$. Hence it is important that when we calculate the determinant we iterate over the first row, not the first column.

B. Quantum Fields

One of the major attractions of Quantum Field Theory is that it can deal with (special) relativistic quantum mechanics. However, the techniques, such as second quantisation, are useful even in the non-relativistic limit.

1. *Second Quantisation*

The space used to describe second quantisation is *Fock space*, where we denote states by the number of particles in each state. So the ket $|n_1, n_2, \ldots, n_i, \ldots\rangle$ has n_1 electrons in the state $|k_1\rangle$, n_2 in the state $|k_2\rangle$ etc. There are two special states: the vacuum state

$$|\mathbf{0}\rangle \equiv |0, 0, \ldots, 0, \ldots\rangle$$

which is void of any particles, and the single particle state

$$|k_i\rangle \equiv |0, 0, \ldots, 0, n_i = 1, 0, \ldots\rangle$$

Next we define the annihilation operator, a_i, and its Hermitian conjugate, the creation operator $a_i^\dagger$. These annihilate and create a particle in state $|k_i\rangle$, respectively, hence

$$a_i^\dagger \, |n_1, n_2, \ldots, n_i, \ldots\rangle \propto |n_1, n_2, \ldots, n_i + 1, \ldots\rangle$$

similarly

$$a_i \, |n_1, n_2, \ldots, n_i, \ldots\rangle \propto |n_1, n_2, \ldots, n_i - 1, \ldots\rangle$$

Consider now the state $a_i^\dagger a_j^\dagger \, |\mathbf{0}\rangle$ and $a_j^\dagger a_i^\dagger \, |\mathbf{0}\rangle$. Effectively these are the same states, except that we've swapped k_i and k_j. Therefore we expect that

$$a_i^\dagger a_j^\dagger \, |\mathbf{0}\rangle = \pm a_j^\dagger a_i^\dagger \, |\mathbf{0}\rangle$$

depending on which type of particle we are describing. This tells us that depending on whether we are dealing with bosons or fermions we either have a commutation relation or an anti-commutation relation for the creation and annihilation operators:

$$\left\{a_i^\dagger, a_j^\dagger\right\} = 0 \qquad \text{Fermions}$$

$$\left[a_i^\dagger, a_j^\dagger\right] = 0 \qquad \text{Bosons}$$

we can also take the Hermitian adjoint to get the same (anti-)commutation relation for the annihilation operators. Additionally we have that

$$\left\{a_i, a_j^\dagger\right\} = \delta_{ij} \qquad \text{Fermions}$$

$$\left[a_i, a_j^\dagger\right] = \delta_{ij} \qquad \text{Bosons}$$

Finally, for both bosons and fermions we define the number operator:

$$N = \sum_i a_i^\dagger a_i$$

which counts the total number of particles. Any operator that acts on each of the particles individually can be decomposed into a linear combination of projections:

$$\mathcal{K} = \sum_{n,m} a_m^\dagger a_n \langle k_m|K|k_n\rangle$$

The momentum and kinetic energy operators are two examples of many operators that can be written in this way. This, however, does not include inter-particle interactions, consider a real matrix, V, whose ij^{th} component specifies the interaction energy between $|k_i\rangle$ and $|k_j\rangle$, then the second quantisation version of this operator is

$$\mathcal{V} = \frac{1}{2}\sum_{i\neq j} V_{ij}N_iN_j + \frac{1}{2}\sum_i V_{ii}N_i(N_i-1)$$

for $V_{ij} \in \mathbb{R}$, which ensures $\mathcal{V}$'s hermiticity. The second term accounts for "self-interaction". However, by writing the N operators out and using the (anti-)commutation relations it can be shown that this second-quantisation operator takes on a simpler form

$$\mathcal{V} = \frac{1}{2}\sum_{ij} V_{ij} a_i^\dagger a_j^\dagger a_j a_i$$

the ordering of the creation and annihilation operators is referred to as "normal ordering"; we annihilate the i^{th} particle first and then the j^{th}, and then create them in the opposite order. For fermions there are no diagonal contributions because we cannot annihilate more than one of each particle.

2. Degenerate Electron Gas

The electrons in a degenerate electron gas interact with one another (H_{el}) but also with the background energy level ($H_{\text{b-el}}$), which in itself has energy (H_{b}). We can show that the background interaction and the background energy sum up to a simple term, and we continue to write the electron-interaction part as is:

$$H = -\frac{1}{2}\frac{e^2N^2}{V}\frac{4\pi}{\mu^2} + \sum_i \left(\frac{|\boldsymbol{p}_i|^2}{2m} + \frac{e^2}{2}\sum_{j\neq i}\frac{e^{-\mu|\boldsymbol{x}_i-\boldsymbol{x}_j|}}{|\boldsymbol{x}_i-\boldsymbol{x}_j|}\right)$$

where μ is the *screening* parameter which we will let $\mu\to 0$ once we have our solution. We can begin by converting the kinetic energy into a second quantisation operator: the kinetic energy is $\frac{\hbar^2|\boldsymbol{k}|^2}{2m}$ times the number of electrons with that momentum $\boldsymbol{k}$, summed over all possible values of $\boldsymbol{k}$:

$$\sum_i \frac{|\boldsymbol{p_i}|^2}{2m} \to \mathcal{K} = \sum_{\boldsymbol{k}\sigma}\frac{\hbar^2|\boldsymbol{k}|^2}{2m} a_{\boldsymbol{k}\sigma}^\dagger a_{\boldsymbol{k}\sigma}$$

where $\sigma \in \{+,-\}$ denotes the spin of the electron. The potential term (Coulomb interaction between the electrons) can be written as

$$\frac{e^2}{2V}\sum_{\boldsymbol{k},\boldsymbol{p},(\boldsymbol{q}\neq\boldsymbol{0})}\sum_{\sigma_1\sigma_2}\frac{4\pi}{q^2} a_{\boldsymbol{k}+\boldsymbol{q},\sigma_2}^\dagger a_{\boldsymbol{p}-\boldsymbol{q},\sigma_2}^\dagger a_{\boldsymbol{p},\sigma_2} a_{\boldsymbol{k},\sigma_1}$$

This can be approximated using perturbation theory giving a ground state energy of

$$\frac{E}{N} = \frac{e^2}{2a_0}\left(\frac{9\pi}{4}\right)^{\frac{2}{3}}\left(\frac{3}{5}\left(\frac{1}{r_s}\right)^2 - \frac{3}{2\pi}\frac{1}{r_s}\right)$$

where r_s is the Wigner-Seitz radius, which is a dimensionless distance scale defined as the ratio between the lattice constant and the Bohr radius.

C. Quantisation of the Electromagnetic Field

We can express the classical energy in an electromagnetic field in terms of two *numbers* $A_{\boldsymbol{k},\sigma}$ and $A_{\boldsymbol{k},\sigma}^*$:

$$\mathcal{E} = \frac{1}{4\pi}V\sum_{\boldsymbol{k},\sigma}\frac{\omega_k^2}{c^2}\left[A_{\boldsymbol{k},\sigma}^* A_{\boldsymbol{k},\sigma} + A_{\boldsymbol{k},\sigma}A_{\boldsymbol{k},\sigma}^*\right]$$

in the quantum mechanical version thereof they become creation and annihilation operators, and we write this as

$$\mathcal{H} = \sum_{\boldsymbol{k},\sigma}\hbar\omega_k a_\sigma^\dagger(\boldsymbol{k})a_\sigma(\boldsymbol{k}) + E_0$$

photons are spin-1 particles, therefore they are bosons. The zero point energy $E_0 = \sum_{\boldsymbol{k}}\hbar\omega_k$ is also referred to as the *vacuum energy* and is responsible for the Casimir effect, where two parallel plates that are put very close to each other feel an attractive force, even though they are both electrically neutral.

VIII. RELATIVISTIC QUANTUM MECHANICS

In the following we will use natural units; $c = \hbar = 1$.

In special relativity we define the total energy of a particle as

$$E = \sqrt{p^2 + m^2}$$

which in the low velocity limit became the rest energy plus the kinetic energy. However, for large values of p we need to include higher terms, or resort to a different method of calculating the energy.

A. Klein-Gordon Equation

The Klein-Gordon equation tackles relativistic quantum mechanics by expressing the differential equation that describes time-evolution as a *second*-order differential equation:

$$\left[\partial_\mu \partial^\mu - m^2\right] \Psi(\boldsymbol{x}, t) = 0$$

where $\partial^\mu = \eta_{\mu\nu}\partial_\nu$ and $\eta_{\mu\nu}$ is the Minkowski metric[§]. This differential equation is solved by

$$\Psi(\boldsymbol{x}, t) = N e^{-ip_\mu x^\mu}$$

provided

$$E^2 = \boldsymbol{p}^2 + m^2$$

so p^μ is the relativistic four-momentum

$$p^\mu = (E, p^1, p^2, p^3)$$

This leads to a probability four-current, j^μ:

$$j^\mu = \frac{i}{2m}\left[\Psi^* \partial^\mu \Psi - (\partial^\mu \Psi^*)\Psi\right]$$

so, for instance

$$\rho(\boldsymbol{x}, t) = \frac{i}{2m}\left[\Psi^* \partial_t \Psi - (\partial_t \Psi^*)\Psi\right]$$

though this is a conserved quantity, it is not positive definite. This is due to the issue that the Klein-Gordon equation predicts *negative*-energy states. This issue was quite serious, because it suggested that we cannot think of ρ as a *probability* density because probabilities are positive definite.

B. Dirac Equation

Let us instead factorise the Klein-Gordon equation, so that the differential equation only depends on first order temporal and spatial derivatives:

$$E = \boldsymbol{\alpha} \cdot \boldsymbol{p} + \beta m, \quad \text{s.t} \quad E^2 = \boldsymbol{p}^2 + m^2$$

[§] I use the $(-,+,+,+)$ signature

writing this out

$$E^2 = \boldsymbol{\alpha}^2 \boldsymbol{p}^2 + \beta^2 m^2 + m\left(\boldsymbol{\alpha}\beta \cdot \boldsymbol{p} + \beta \boldsymbol{\alpha} \cdot \boldsymbol{p}\right)$$

clearly

$$\alpha_i^2 = \mathbb{1}, \quad \beta^2 = \mathbb{1}, \quad \{\alpha_i, \beta\} = 0$$

However, this is usually written slightly differently. Define $\gamma^0\gamma^i = \alpha_i$ and $\beta = \gamma^0$, then this becomes

$$\{\gamma^\mu, \gamma^\nu\} = -2\eta^{\mu\nu}$$

the minus is because I use the $(-,+,+,+)$ signature. This is the Clifford algebra. The lowest number of dimensions required for this is 4, in which we have

$$\boldsymbol{\alpha} = \sigma_x \otimes \boldsymbol{\sigma}, \quad \beta = \sigma_z \otimes \mathbb{1}$$

1. *Free Particle*

Consider now a free particle of mass m and momentum $\boldsymbol{p} = p\hat{\boldsymbol{z}}$. In this case

$$\begin{pmatrix} m & 0 & p & 0 \\ 0 & m & 0 & -p \\ p & 0 & -m & 0 \\ 0 & -p & 0 & -m \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \end{pmatrix} = E \begin{pmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \end{pmatrix}$$

The components u_1 and u_2 are the spinor components and u_3 and u_4 are the time-reversed (anti-particle) versions thereof. We see this because the upper two entries have positive energy levels, whereas the lower two have negative energy levels. We can find the eigenvectors quite easily:

$$u_R^+ = \begin{pmatrix} 1 \\ 0 \\ \frac{p}{E+m} \\ 0 \end{pmatrix}, \quad u_L^+ = \begin{pmatrix} 0 \\ 1 \\ 0 \\ -\frac{p}{E+m} \end{pmatrix} \quad \text{for} \quad E > 0$$

the subscript stands for the handedness (helicity) of the state and the superscript tells us that these are the positive energy states. The negative energy states are quite similar:

$$u_R^- = \begin{pmatrix} \frac{-p}{E+m} \\ 0 \\ 1 \\ 0 \end{pmatrix}, \quad u_L^- = \begin{pmatrix} 0 \\ \frac{p}{E+m} \\ 0 \\ 1 \end{pmatrix} \quad \text{for} \quad E < 0$$

2. *Electromagnetic Interactions in the Non-Relativistic Limit*

Due to the presence of an electromagnetic field we need to use the kinetic momentum:

$$\boldsymbol{p} \rightsquigarrow \boldsymbol{p} - e\boldsymbol{A}$$

The Dirac equation then becomes

$$\begin{pmatrix} m & \boldsymbol{\sigma}\cdot\boldsymbol{p} \\ \boldsymbol{\sigma}\cdot\boldsymbol{p} & -m \end{pmatrix}\begin{pmatrix} u \\ v \end{pmatrix} = E\begin{pmatrix} u \\ v \end{pmatrix}$$

In the non-relativistic limit we can approximate the lower equation as

$$\boldsymbol{\sigma}\cdot\boldsymbol{p}u \approx 2mv$$

which means that the upper equation becomes

$$\frac{(\boldsymbol{\sigma}\cdot\boldsymbol{p})(\boldsymbol{\sigma}\cdot\boldsymbol{p})}{2m}u = \left(\frac{\boldsymbol{p}^2}{2m} + \frac{i\boldsymbol{\sigma}}{2m}\cdot(\boldsymbol{p}\times\boldsymbol{p})\right)u$$

note that the cross product is nonzero because the kinetic momentum components do not commute in a magnetic field. Writing it all out we get that

$$\left[\frac{\boldsymbol{p}^2}{2m} - \boldsymbol{\mu}\cdot\boldsymbol{B}\right]u = Ku$$

where

$$\boldsymbol{\mu} = \frac{ge}{2m}\underbrace{\frac{\hbar}{2}\boldsymbol{\sigma}}_{\boldsymbol{S}}$$

thus the existence of spin *falls out* of the Dirac equation; it is not something we need to justify empirically.

CONTENTS