

Phys 334 - Quantum Mechanics II

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1 Postulates of quantum mechanics

The game of quantum mechanics is played according to the following rules;

1. Every physically realizable state of a system is described by a *state vector* $|\psi\rangle$ which contains all accessible physical information about the system in that state.
2. If a system is in a quantum state represented by a wave function Ψ the $Pdu = |\Psi|^2 du$ is the probability that in a position measurement at time t , the particle will be detected in the infinitesimal volume element du .
3. Every observable is represented by an operator that is used to obtain information about the observable from state vectors. For an observable that is represented in classical physics by the function $Q(x, \rho)$, the corresponding operator is $\hat{Q}(\hat{x}, \hat{\rho})$.
4. The time development of the state function of an isolated quantum system is governed by the time-dependent Schrödinger equation $\hat{H}|\psi\rangle = i\hbar \frac{\partial}{\partial t} |\psi\rangle$ where $\hat{H} = \hat{T} + \hat{V}$ is the Hamiltonian of the system.

2 The wave function

This course will mainly be about the (time-independent) *Schrödinger Equation*

$$\boxed{\frac{-\hbar^2}{2m} \nabla^2 \psi(\vec{x}) + V(\vec{x})\psi(\vec{x}) = E\psi(\vec{x})} \quad (1)$$

and its solutions, or approximate solutions. $\psi(\vec{x})$ here is known as the *wave function* and is found by solving Equation (1) which is a *wave equation*.

Another wave equation is $ma = kx$ which is equivalent to $\ddot{x} = -\omega^2 x$ where $\omega^2 = k/m$. This is the *simple harmonic oscillator* and has solutions $x = A \cos(\omega t + \phi)$ with A, ϕ constants or $x = A_1 \cos(\omega t) + A_2 \sin(\omega t)$ with A_1, A_2 constant. We note that the constants give boundary conditions.

In the Schrödinger equation (1) with $U(\vec{x}) = 0$ in one-dimension one gets

$$-\frac{\hbar^2}{2m} \psi'' = E\psi \Leftrightarrow \psi'' = -k^2 \psi$$

with $k^2 = \frac{2mE}{\hbar^2}$. Recall that $\hbar$ here is *Plank's constant* ($\approx 10^{-34}$).

The equation $\ddot{x} = -k^2 x^3$ can be solved similarly using Fourier Analysis.

2.1 Born interpretation of the wave function

The *Born interpretation* is that $\int_a^b |\Psi(x, t)|^2 dx$ is the probability of finding a particle in the interval $[a, b]$.

All that quantum mechanics tells us is statistical information. $|\Psi|^2$ is the probability density and measuring the position of the particle collapses the wave function as we know where it is.

2.2 Probability

Let $p(x)$ be a probability density then $\int_{\mathbb{R}} p(x)dx = 1$ which is a “normalization condition” (a type of boundary condition). We calculate the average position $\langle x \rangle = \int_{\mathbb{R}} xp(x)dx$. Similarly $\langle x^2 \rangle = \int_{\mathbb{R}} x^2 p(x)dx$ and $\langle f(x) \rangle = \int_{\mathbb{R}} f(x)p(x)dx$.

One measures the width of a distribution by *standard deviation*

$$\sigma_x = \sqrt{\langle (x - \langle x \rangle)^2 \rangle}.$$

However, in quantum theory we usually work with the *variance* σ_x^2 instead.

2.3 Normalization

If $\psi(x)$ is a solution to Equation (1) then so is $A\psi(x)$ for any constant $A \in \mathbb{C}$ and as we said $\int_{\mathbb{R}} |\psi|^2 dx = 1$ is a boundary condition. This is how normalized distributions can always be achieved.

2.4 Momentum

In quantum mechanics momentum is different from classical mechanics. We can work out $\langle x \rangle = \int |\psi(x)|^2 dx$. Then since momentum $\rho = mv = m \frac{\partial x}{\partial t}$ so we can guess that

$$\begin{aligned} \langle \rho \rangle &= m \frac{\partial \langle x \rangle}{\partial t} = m \frac{\partial}{\partial t} \int_{-\infty}^{\infty} x |\psi(x, t)|^2 dx \\ &= m \int_{-\infty}^{\infty} x \frac{\partial}{\partial t} (\psi^* \psi) dx \\ &= m \int_{-\infty}^{\infty} x \left(\frac{\partial \psi^*}{\partial t} \psi + \psi^* \frac{\partial \psi}{\partial t} \right) dx \\ &= m \frac{i\hbar}{2m} \int_{-\infty}^{\infty} x \frac{\partial}{\partial x} \left(\psi^* \frac{\partial \psi}{\partial x} - \frac{\partial \psi^*}{\partial x} \psi \right) dx, \text{ Schrödinger Equation} \\ &= -\frac{i\hbar}{2} \int_{-\infty}^{\infty} \left(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x} \right) dx, \text{ by parts} \\ &= -i\hbar \int_{-\infty}^{\infty} \psi^* \frac{\partial \psi}{\partial x} dx \\ &= \int_{-\infty}^{\infty} \psi^* \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \psi dx = \left\langle \frac{\hbar}{i} \frac{\partial}{\partial x} \right\rangle \end{aligned}$$

Theorem 2.1 (Ehrenfest’s Theorem).

$$\frac{\partial \langle \rho \rangle}{\partial t} = - \left\langle \frac{\partial V}{\partial x} \right\rangle$$

where we note that $\vec{F} = \frac{\partial \vec{p}}{\partial t}$.

2.5 Uncertainty principle

A consistent sinusoidal wave has well defined wave length, but not so well-defined position. If the wave is given a sudden jolt then position becomes easy to recognize and wavelength is all of a sudden not so simple to determine.

Debroglies formula states that $\rho = h/\lambda = \hbar k$ where $k = 2\pi/\lambda$. This means that a well-defined wavelength corresponds to a well-defined momentum.

In fact, position and momentum are *conjugate variables* and *Heisenberg's Uncertainty principle* states that

$$\Delta x \Delta p \geq \hbar/2.$$

Also,

$$\Delta E \Delta t \geq \hbar/2.$$

3 Time independent Schrödinger equation

If the potential function is time independent then we may separate the spatial and temporal parts of the Schrödinger equation. Introduce that $\Psi(x, t) = \psi(x)\phi(t)$. Then, $\frac{\partial \Psi}{\partial t} = \psi \frac{\partial \phi}{\partial t}$ and $\frac{\partial^2 \Psi}{\partial x^2} = \frac{d^2 \psi}{dx^2} \phi$. Now, imposing Schrödinger's Equations yields

$$i\hbar \psi \frac{d\phi}{dt} = -\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} \phi + V \psi \phi$$

which is equivalent to

$$i\hbar \frac{1}{\phi} \frac{d\phi}{dt} = -\frac{\hbar^2}{2m} \cdot \frac{1}{\psi} \frac{d^2 \psi}{dx^2} + V$$

so now the left hand side depends on t and the right hand side depends on x which implies both sides are equal to a constant, call it E .

Examining the left hand side; then $i\hbar \frac{1}{\phi} \frac{d\phi}{dt} = E$ meaning $\phi(t) = e^{-iEt/\hbar}$ where we have left out the constant because it will go into the ψ -part.

Examining the right hand side; then

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + V \psi = E \psi \quad (2)$$

and this is the *Time-Independent Schrödinger Equation*.

Remark 1. Now, to make a note on normalization;

1. $|\phi|^2 = 1$ so we only need to worry about $\psi(x)$ in normalizing.
2. Expectation values of time independent operators will also be time independent.

$$\langle Q \rangle = \int_{\mathbb{R}} \Psi^\dagger Q \Psi dx = \int_{\mathbb{R}} \psi^\dagger Q \psi dx$$

Solutions to the time-independent Schrödinger equation are called *Stationary states* because they have no time dependence. However, the $\phi(t) = e^{-iEt/\hbar}$ will change the phase. *Euler's formula* may be useful ($e^{i\theta} = \cos \theta + i \sin \theta$ - proven by Taylor expansion) and the phase will change by $\omega = E/\hbar$.

The time independent Schrödinger equation is a differential equation which we write as $\hat{H}\psi = E\psi$ where

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V$$

is called the *Hamiltonian* differential operator.

Solutions to (2) are enumerated as $\hat{H}\psi_n E_n \psi_n$ and the general solution is

$$\Psi(x, t) = \sum_n c_n \psi_n(x) e^{-iEt/\hbar}$$

where $c_n \in \mathbb{C}$ are constants. We can write a representation of Ψ as $(c_1, c_2, c_3, \dots)$. Also

$$\langle \hat{H} \rangle = \int_{\mathbb{R}} \psi^\dagger \hat{H} \psi dx = \int_{\mathbb{R}} \psi^\dagger E \psi dx = E \int_{\mathbb{R}} \psi^\dagger \psi dx = E$$

and

$$\langle \hat{H}^2 \rangle = E^2$$

which together imply $\sigma_{\hat{H}}^2 = \langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2 = 0$.

3.1 The infinite square well

This is defined by having our potential $V(x) = 0$ on $(0, L)$ and $V(0) = V(L) = \infty$. This means that $\psi(0) = 0 = \psi(L)$ (our boundary conditions) and inside the well, we seek to solve $\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi = E\psi$ implying that $\psi'' = -k^2 \psi$ where $k = \frac{2mE}{\hbar^2}$. The solution to this is $\psi(x) = A \sin(kx) + B \cos(kx)$.

Boundary condition 1 implies that $B = 0$, normalization implies that $A = \sqrt{\frac{2}{L}}$, and boundary condition 2 implies $k = n\pi$ with $n \in \mathbb{N}$. So, $n^2 \pi^2 = k^2 = \frac{2mE}{\hbar^2}$ meaning that $E_n = \frac{n^2 \pi^2 \hbar^2}{2m}$ and $\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right)$ for each $n \in \mathbb{N}$.

Note:

1. If eigenfunction is bounded, we get discrete eigenvalues (that is, *quantized energy*). Otherwise they are continuous.
2. The n above is called the *quantum number*
3. The energies are quantized which means only certain values E_n are allowed by Equation (2) and boundary conditions.
4. The lowest energy state is called the *ground state* and the next lowest is called the *first excited state*, etc.
5. The solutions ψ_n are orthonormal. That is $\langle \psi_n | \psi_m \rangle = \delta_{n,m}$.
6. Furthermore, the set $\{\psi_n\}$ is complete in the sense that they span the function space.
7. $g(x) = \sum_n c_n \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right)$ is a *fourier series representation* of $g(x)$
8. If we operate with $\int dx \psi_m^\dagger$ on $g(x)$ from above, we find c_n as follows;

$$\int_0^L dx \psi_m^\dagger g(x) = \int_0^L dx \psi_m^\dagger \sum_n c_n \psi_n = \sum_n c_n \int_0^L \psi_m^\dagger \psi_n dx = c_m.$$

Notationally we write functions $|g\rangle = \sum_n c_n |\psi_n\rangle$ and operate with $\langle \psi_m|$ to get

$$\langle \psi_m | g \rangle = \sum_n c_n \langle \psi_m | \psi_n \rangle = \sum_n c_n \delta_{m,n} = c_m$$

and so $c_n = \langle \psi_n | g \rangle$.

Proposition 3.1. *Properties of bound state solutions;*

1. *Alternate between odd and even parity - only if $V(x)$ is even (i.e. not semi-infinite)*
2. *Increasing number of nodes at each increase in energy state*
3. *Solutions are orthogonal*
4. *Completeness*

We can write $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$ as well.

4 Algebraic preliminaries

4.1 Linear transformations

Write $|\alpha\rangle = \sum_i a_i |e_i\rangle$ where $\{|e_1\rangle, |e_2\rangle, \dots\}$ is a basis. A linear transformation $\hat{T}$ then acts as

$$\hat{T}|\alpha\rangle = \sum_i a_i \hat{T}|e_i\rangle = \sum_i a_i \left(\sum_j T_{ij} |e_j\rangle \right) = \sum_i a'_i |e_i\rangle$$

where $a'_i = \sum_j T_{ij} a_j$.

If the basis is orthonormal and $\hat{T}|e_j\rangle = \sum_i T_{ij} |e_i\rangle$ then

$$\langle e_k | \hat{T} | e_j \rangle = \sum_i T_{ij} \langle e_k | e_i \rangle = \sum_i T_{ij} \delta_{ki} = T_{kj}$$

so for an orthonormal basis $T_{kj} = \langle e_k | \hat{T} | e_j \rangle$. We will need to write ordered n -tuples as column vectors

$$|\alpha\rangle \leftrightarrow \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_n \end{pmatrix}$$

$$\text{and } |\alpha'\rangle = \hat{T}|\alpha\rangle = \sum_i \left(\sum_j T_{ij} a_j \right) |e_i\rangle \leftrightarrow \begin{pmatrix} a'_1 \\ a'_2 \\ \vdots \\ a'_n \end{pmatrix}.$$

4.2 Matrices

The *transpose* will be denoted $\tilde{T}_{ij} = T_{ji}$ and $\tilde{a} = (a_1, \dots, a_n)$. The *conjugate* $(T_{ij})^* = (T_{ij}^*)$. The *Hermitian-conjugate* $T^\dagger := \tilde{T}^*$.

T is *symmetric* if $\tilde{T} = T$, *antisymmetric* if $\tilde{T} = -T$, *real* if $T^* = T$, *imaginary* if $T^* = -T$, *Hermitian* if $T^\dagger = T$ and *skew-Hermitian* if $T^\dagger = -T$.

Inner products will be written as $\langle \alpha, \beta \rangle = \sum_i a_i^\dagger b_i$. In general, matrix multiplication is not commutative and we define *the commutator*

$$[A, B] = AB - BA.$$

Note that $\widetilde{ST} = \widetilde{T}\widetilde{S}$ and $(ST)^\dagger = T^\dagger S^\dagger$. The unit matrix (with 1's on the diagonal) is denoted by I so that inverses $TT^{-1} = I = T^{-1}T$ and exists if and only if $\det T \neq 0$. It is also easy to verify that $(ST)^{-1} = T^{-1}S^{-1}$.

A matrix is *unitary* if $UU^\dagger = I$ and this holds if and only if $U^\dagger = U^{-1}$. The rows and columns of unitary matrices form an orthonormal set.

If we have two orthonormal bases $\{|e_n\rangle\}$ and $\{|f_n\rangle\}$ we can represent one as a linear combination of the other as $|e_i\rangle = \sum_j S_{ij}|f_j\rangle$. This is a linear transformation and so we know the components of a vector transformation are

$$a_i^f = \sum_j S_{ij}a_j^e$$

meaning that $a^f = Sa^e$ and we can work out the matrix representing a linear transformation in a new basis. Let $a_i^{e'}$ be a vector that has been transformed by T in basis e . Then

$$a_i^{e'} = \sum_j T_{ij}a_j^e = \sum_j T_{ij} \left(\sum_k (S^{-1})_{kj}a_k^f \right) \Leftrightarrow a^{e'} = T^e S^{-1} a^f$$

and thus $T^f = ST^e S^{-1}$ (a similarity relation).

One can furthermore show that if both bases e and f are orthonormal, then S is unitary. Because of this, the determinant and trace of matrix representations for T are unchanged by unitary transform.

4.3 Eigenvalues and eigenvectors

$\vec{v}$ is an *eigenvector* of T if $T\vec{v} = \lambda\vec{v}$ and if so, then λ here is an *eigenvalue*. In real vector spaces there may or may not be eigenvalues, but in complex vector spaces every linear transformation will have eigenvectors and λ may be real or complex depending on T .

So, we are looking for solutions $\lambda, \vec{v}$ to the equation $(T - \lambda)\vec{v} = 0$. This will have non-trivial solutions if $\det(T - \lambda) = 0$ which gives a characteristic polynomial equation having n complex roots (where n is the dimension of the space) which are all eigenvalues.

Substituting the λ_i 's and solving for the kernels provides the eigenvectors and if these span the space, they form a basis. The matrix representing T with respect to the basis of its eigenvectors will be the diagonal $D = \text{diag}(\lambda_1, \lambda_2, \dots, \lambda_n)$ whose normalized eigenvectors take the form $v_1 = \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix}$, $v_2 = \begin{pmatrix} 0 \\ 1 \\ \vdots \\ 0 \end{pmatrix}$, etc.

A matrix T which can be brought to diagonal form is called *diagonalizable* and can be constructed using the normalized eigenvectors as column vector for P so that $D = P^{-1}TP$.

4.4 Hermitian transformations

Recall the *hermitian conjugate* $T^\dagger = \widetilde{T}^*$ is given as the conjugate-transpose of a matrix. However, for more abstract transformations (i.e. not matrices) this is defined as

$$\langle T^\dagger \alpha | \beta \rangle = \langle \alpha | T \beta \rangle \Leftrightarrow (T^\dagger \alpha)^\dagger \beta = \alpha^\dagger (T \beta).$$

Also note that for a scalar $c \in \mathbb{C}$, we have $\langle \alpha | c \beta \rangle = c \langle \alpha | \beta \rangle$ and $\langle c \alpha | \beta \rangle = c^* \langle \alpha | \beta \rangle$.

A *hermitian operator* is one for which $T^\dagger = T$ and these are very important in quantum mechanics because their eigenvalues and eigenvectors have nice properties.

Proposition 4.1 (Properties of Hermitian operators). *Let T be a Hermitian operator, then*

1. *Eigenvalues of T are real,*
2. *The eigenvectors for distinct eigenvalues are orthogonal, and*
3. *The eigenvectors span the space (i.e. T is diagonalizable).*

Proof. 1. $T|\alpha\rangle = \lambda|\alpha\rangle$ implies that

$$\lambda\langle\alpha|\alpha\rangle = \langle\alpha|T\alpha\rangle = \langle T^\dagger\alpha|\alpha\rangle = \langle T\alpha|\alpha\rangle = \lambda^*\langle\alpha|\alpha\rangle$$

so to say $\lambda = \lambda^*$ and hence $\lambda \in \mathbb{R}$.

2. Let $T|\alpha\rangle = \lambda|\alpha\rangle$ and $T|\beta\rangle = \gamma|\beta\rangle$ with $\lambda \neq \gamma$. Now, we have

$$\lambda\langle\alpha|\beta\rangle = \lambda^*\langle\alpha|\beta\rangle = \langle T\alpha|\beta\rangle = \langle T^\dagger\alpha|\beta\rangle = \langle\alpha|T\beta\rangle = \gamma\langle\alpha|\beta\rangle$$

hence $(\lambda - \gamma)\langle\alpha|\beta\rangle = 0$ and equivalently this means $\langle\alpha|\beta\rangle = 0$ since $\lambda \neq \gamma$.

3. If all eigenvalues are distinct then we have n mutually orthogonal eigenvectors and the dimension of their span is n . In the cases that there exist duplicate roots in the characteristic equation, we must show there are m linearly independent vectors corresponding to the m -fold degenerate eigenvalue (which can be shown by induction). □

This shows that any hermitian transformation is unitarily diagonalizable (i.e. can be diagonalized by a unitary similarity transformation).

4.5 Function spaces

A function space is an inner product space where vectors are functions and inner products are integrals. Note that this definition where $\langle f|g\rangle := \int f^*g dx$ satisfies all axioms of a vector space and inner product space.

All, except for one thing works here; For an inner product to be well-defined, the integral must exist (i.e. it is necessary that the functions be “square-integrable” = $\langle f|f\rangle < \infty$) and this turns out to be sufficient. Thus, we consider the space of square-integrable functions.

Example 4.2. The set of polynomials of degree $< n$ on the interval $(-1, 1)$. A basis is $|1\rangle = x^0, |2\rangle = x^1, \dots, |n\rangle = x^{n-1}$.

In a function space we have operators such as $\frac{d}{dx}, \frac{d^2}{dx^2}, x, x^2$ and these will behave as linear transformations. The eigenvectors of linear transformations in a function space are called *eigenfunctions* and hermitian operators satisfy the usual $\langle f|Tg\rangle = \langle T^\dagger f|g\rangle = \langle Tf|g\rangle$.

Example 4.3. Is $D := -\frac{d}{dx}$ hermitian?

$$\langle f|Dg\rangle = \int f^*(x) - \frac{dg(x)}{dx} dx = [f^*g] - \langle Df|g\rangle.$$

In quantum mechanics $[f^*g]$ is the boundary term which is usually zero. This would imply that D is skew-hermitian.

Now what about $\rho = \frac{\hbar}{i} \frac{d}{dx}$?

$$\langle f|\rho g\rangle = \int f^* \frac{\hbar}{i} \frac{dg}{dx} dx = \frac{\hbar}{i} [f^*g] - \frac{\hbar}{i} \int \frac{df^*}{dx} g dx = \frac{\hbar}{i} [f^*g] + \int \left(\frac{\hbar}{i} \frac{df}{dx} \right)^* g dx$$

so if the boundary term is zero then ρ is hermitian.

4.6 Hilbert spaces

A prime example of a Hilbert space is the set of all square-integrable functions on a relevant interval including all square-integrable convergent sequences of functions (e.g. Dirac delta functions).

The state of a quantum system is a vector in a Hilbert space. Its dimension is infinite, however this can invalidate property 3 of hermitian transformations (that eigenvectors of a hermitian operator span the space).

Example 4.4. What are the eigenvectors of the operator defined via multiplication by x ? That is, solve $xg_\lambda(x) = \lambda g_\lambda(x)$. So if $g_\lambda(x) = a_0 + a_1x + a_2x^2 + \dots$, then

$$x(a_0 + a_1x + a_2x^2 + \dots) = a_0 + a_1x + a_2x^2 + \dots$$

which has no solutions meaning there is no polynomial eigenvector.

Lets try the function $g_\lambda(x) = A\delta(x - \lambda)$; then $x A\delta(x - \lambda) = A\delta(x - \lambda)$.

How about ρ ? $\rho f_\lambda(x) = \lambda f_\lambda(x)$ means that $\frac{\hbar}{i} \frac{df_\lambda}{dx} = \lambda f_\lambda$ and has solutions $f_\lambda = A e^{\frac{i\lambda}{\hbar}x}$.

Note that for $\hat{x}, \hat{p}$, the eigenvalues are continuous and real. The set of all eigenvalues of an operator is called the *spectrum*. However, neither of these functions are square-integrable so they are not strictly part of a Hilbert space, but they are so useful that we normalize them as follows;

$$\begin{aligned} \langle g_\lambda | g_\mu \rangle &= \delta(\lambda - \mu) \text{ where } g_\lambda(x) = \delta(x - \lambda) \\ \langle f_\lambda | f_\mu \rangle &= \delta(\lambda - \mu) \text{ where } f_\lambda(x) = \frac{1}{\sqrt{2\pi}} e^{i\lambda x/\hbar} \end{aligned}$$

so

$$\langle f_\lambda | f_\mu \rangle = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i(\lambda-\mu)x/\hbar} dx$$

and we treat these as elements of the Hilbert space.

If we want to represent a state vector in the x -representation (i.e. the eigenvector in terms of the $\hat{x}$ -operator) $|\alpha\rangle = \sum_j a_j |e_j\rangle$ with $a_i = \langle e_i | \alpha \rangle = \sum_j a_j \underbrace{\langle e_i | e_j \rangle}_{=\delta_{ij}}$ for the finite dimensional space

with discrete spectra. In the continuous spectrum we have $|\alpha\rangle = \int a_\mu |f_\mu\rangle d\mu$ where $a_\lambda = \langle f_\lambda | \alpha \rangle = \int a_\mu \langle f_\lambda | f_\mu \rangle d\mu$.

So if we have a state vector represented by $g(x)$ then in the $\hat{x}$ -representation we have

$$a_\lambda = \langle g_\lambda | g(x) \rangle = \int dx \delta(x - \lambda) g(x) = g(\lambda)$$

so $g(x)$ is the x -representation!

In the $\hat{p}$ -representation we have $b_\lambda = \langle f_\lambda | g(x) \rangle = \frac{1}{\sqrt{2\pi}} \int dx e^{i\lambda x/\hbar} g(x) = G(\lambda/\hbar)$ where $G(\lambda/\hbar)$ is the Fourier transformation of $g(x)$. Note that $|\alpha\rangle$ is the state vector and $g(x), G(\lambda/\hbar)$ are representations of $|\alpha\rangle$.

5 The quantum oscillator

The hamiltonian for a classical oscillator is

$$H = T + V = \frac{\rho^2}{2m} + \frac{kx^2}{2} = \frac{\rho^2}{2m} + \frac{m\omega^2 x^2}{2}$$

So postulate 3 in quantum mechanics is that $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2 \hat{x}^2}{2}$ and the time-independent Schrödinger equation (with $\hat{p} \mapsto \frac{\hbar}{i} \frac{d}{dx}$) gives the second order linear differential equation

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) + \frac{1}{2} m\omega^2 x^2 \psi(x) = E\psi(x)$$

with solutions $\psi_n(x) = \left(\frac{1}{\pi a_0^2}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(x/a_0) e^{-x^2/2a_0}$ where $a_0 = \frac{\hbar}{m\omega}$, $H_n(\xi)$ are *Hermite* polynomials and n are integers.

The first few Hermite polynomials are

$$H_0(\xi) = 1, H_1(\xi) = 2\xi, H_2(\xi) = 4\xi^2 - 2, H_3(\xi) = 8\xi^3 - 12\xi$$

and the eigenvalues for these solutions are $E_n = \hbar\omega \left(n + \frac{1}{2}\right)$.

Now, we know the eigenvalues and eigenvectors of $\hat{H}$. We can write the T.I.S.E. as $\hat{H}|n\rangle = E_n|n\rangle$ which is the energy representation. So we will be able to compute quantities $\langle m|\hat{x}|n\rangle$ or $\langle m|\hat{p}|n\rangle$.

We can write

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2 \hat{x}^2}{2} = \hbar\omega \left(\frac{m\omega \hat{x} - i\hat{p}}{2m\hbar\omega} \right),$$

introduce the operators

$$\hat{A} = \frac{m\omega \hat{x} + i\hat{p}}{\sqrt{2m\hbar\omega}} \text{ and } \hat{A}^\dagger = \frac{m\omega \hat{x} - i\hat{p}}{\sqrt{2m\hbar\omega}}$$

and calculate

$$\begin{aligned} \hat{A}^\dagger \hat{A} &= \frac{(m\omega \hat{x} - i\hat{p})(m\omega \hat{x} + i\hat{p})}{2m\hbar\omega} \\ &= \frac{m^2\omega^2 \hat{x}^2 + \hat{p}^2 - m\omega i(\hat{p}\hat{x} - \hat{x}\hat{p})}{2m\hbar\omega} \\ &= \frac{1}{\hbar\omega} \hat{H} + \frac{i}{2\hbar} [\hat{x}, \hat{p}]. \end{aligned}$$

We need to compute the commutator $[\hat{x}, \hat{p}]f = \hat{x}\hat{p}f - \hat{p}\hat{x}f$. Using the $\hat{x}$ -representation;

$$[\hat{x}, \hat{p}]f(x) = x \frac{\hbar}{i} \frac{d}{dx} f(x) - \frac{\hbar}{i} \frac{d}{dx} (xf(x)) = \frac{\hbar}{i} (xf' - f - xf') = -\frac{\hbar}{i} f.$$

So, $\hbar\omega \hat{A}^\dagger \hat{A} = \hat{H} + \frac{i\omega}{2} \left(-\frac{\hbar}{i}\right) = \hat{H} - \frac{1}{2}\hbar\omega$ implying that

$$\boxed{\hat{H} = \hbar\omega(\hat{A}^\dagger \hat{A} + 1/2)}$$

and this is how $\hat{H}$ is represented in terms of the $\hat{A}^\dagger, \hat{A}$ operators. These operators, $\hat{A}, \hat{A}^\dagger$, are not hermitian, but together $(\hat{A}^\dagger \hat{A})^\dagger = \hat{A}^\dagger (\hat{A}^\dagger)^\dagger = \hat{A}^\dagger \hat{A}$ it is! Furthermore, $\hat{H}|n\rangle = \hbar\omega(n + 1/2)|n\rangle$ so that $\hbar\omega(\hat{A}^\dagger \hat{A} + 1/2)|n\rangle = \hbar\omega(n + 1/2)|n\rangle$ if and only if

$$\hat{A}^\dagger \hat{A}|n\rangle = n|n\rangle. \quad (3)$$

Often we write $\hat{N} = \hat{A}^\dagger \hat{A}$ and call it the *number operator* and the eigenvectors of $\hat{N}$ are the same as those of $\hat{H}$.

Proposition 5.1. *Properties of our operators;*

1. $[\hat{A}, \hat{A}^\dagger] = 1$
2. $[\hat{H}, \hat{A}^\dagger] = \hbar\omega\hat{A}^\dagger$
3. $[\hat{A}^\dagger\hat{A}, \hat{A}] = -\hat{A}$
4. $[\hat{A}^\dagger\hat{A}, \hat{A}^\dagger] = \hat{A}^\dagger$

Using this, then

$$\begin{aligned}
(\hat{A}^\dagger\hat{A})(\hat{A}^\dagger|n\rangle) &= ([\hat{A}^\dagger\hat{A}, \hat{A}^\dagger] + \hat{A}^\dagger\hat{A}^\dagger\hat{A})|n\rangle \\
&= (\hat{A}^\dagger + \hat{A}^\dagger\hat{A}^\dagger\hat{A})|n\rangle \\
&= \hat{A}^\dagger(1 + \hat{A}^\dagger\hat{A})|n\rangle \\
&= \hat{A}^\dagger(1 + n)|n\rangle
\end{aligned}$$

so $\hat{N}(\hat{A}^\dagger|n\rangle) = (n+1)(\hat{A}^\dagger|n\rangle)$ which, together with equation (3), implies

$$\hat{A}^\dagger|n\rangle = c_n|n+1\rangle.$$

Similarly, we may show that

$$\hat{A}|n\rangle = d_n|n-1\rangle$$

which means $\hat{A}^\dagger|n\rangle$ and $\hat{A}|n\rangle$ are also eigenvectors of $\hat{N}$ (also $\hat{H}$) with n increased or decreased by one. Hence, $\hat{A}$ and $\hat{A}^\dagger$ are called *Ladder operators*. More particularly, these are called *creation* and *annihilation* operators respectively.

With this information, we compute the c_n 's as follows; $\langle \hat{A}n | \hat{A}n \rangle = c_n^* c_n \langle n-1 | n-1 \rangle$ and equivalently, that is

$$|d_n|^2 = \langle n | \hat{A}^\dagger \hat{A} n \rangle = n \langle n | n \rangle = n \Rightarrow d_n = \sqrt{n}.$$

Hence, $\hat{A}|n\rangle = \sqrt{n}|n-1\rangle$ and similarly $\hat{A}^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle$. Now,

$$\hat{A}^2|n\rangle = \sqrt{n}\sqrt{n-1}|n-2\rangle$$

and thats fine but what is $|n\rangle$?

$$n = \langle n | \hat{A}^\dagger \hat{A} n \rangle = \langle \hat{A}n | \hat{A}n \rangle \geq 0$$

so the eigenvalues are real, positive and there can only be a lower limit for $\hat{A}|n\rangle$ if n is an integer so that $\hat{A}|0\rangle = \sqrt{0}| -1\rangle = \vec{0}$. Otherwise, the sequence $|n\rangle, \hat{A}|n\rangle = \sqrt{n}|n-1\rangle, \hat{A}|n-1\rangle = \sqrt{n-1}|n-2\rangle, \dots$ would not terminate and would violate $\langle \hat{A}n | \hat{A}n \rangle \geq 0$. Note $\hat{A}|1/2\rangle = \frac{1}{\sqrt{2}}| -1/2\rangle$.

We have $\hat{H}|n\rangle = \hbar\omega(n+1/2)|n\rangle = E_n|n\rangle$. So the ground state is $E_0 = \frac{1}{2}\hbar\omega$ and $E_n = \hbar\omega(n+1/2)$ with $|1\rangle = \hat{A}^\dagger|0\rangle, |2\rangle = \frac{1}{\sqrt{2}}\hat{A}^\dagger|1\rangle$ and more generally, by induction,

$$|n\rangle = \frac{1}{\sqrt{n!}}(\hat{A}^\dagger)^n|0\rangle.$$

Since $\hat{A}|n\rangle = \sqrt{n}|n-1\rangle$ and $\hat{A}^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle$, then $\langle m | \hat{A}n \rangle = \sqrt{n}\langle m | n-1 \rangle = \sqrt{n}\delta_{m,n-1}$, $\langle m | \hat{A}^\dagger n \rangle = \sqrt{n+1}\langle m | n+1 \rangle = \sqrt{n+1}\delta_{m,n+1}$ and

$$\hat{A}^\dagger + \hat{A} = \frac{m\omega\hat{x} - i\hat{p}}{\sqrt{2m\hbar\omega}} + \frac{m\omega\hat{x} + i\hat{p}}{\sqrt{2m\hbar\omega}} = \frac{2m\omega\hat{x}}{\sqrt{2m\hbar\omega}}$$

implying

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}(\hat{A}^\dagger + \hat{A}) = \frac{a_0}{\sqrt{2}}(\hat{A}^\dagger + \hat{A}).$$

Similarly,

$$\hat{p} = i\sqrt{\frac{m\hbar\omega}{2}}(\hat{A}^\dagger - \hat{A}) = \frac{i\hbar}{\sqrt{2}}\sqrt{\frac{m\omega}{\hbar}}(\hat{A}^\dagger - \hat{A}) = \frac{i\hbar}{\sqrt{2}a_0}(\hat{A}^\dagger - \hat{A}).$$

Now we can easily work out

$$\begin{aligned}\langle m|\hat{A}n\rangle &= \frac{a_0}{\sqrt{2}}\langle m|\hat{A}^\dagger + \hat{A}|n\rangle \\ &= \frac{a_0}{\sqrt{2}}(\langle m|\hat{A}^\dagger n\rangle + \langle m|\hat{A}n\rangle) \\ &= \frac{a_0}{\sqrt{2}}(\sqrt{n+1}\delta_{m,n+1} + \sqrt{n}\delta_{m,n-1})\end{aligned}$$

Finally, we can find the ground state wave vector in the x -representation $\hat{A}|0\rangle = \vec{0}$ so if $|0\rangle \rightarrow \psi_0(x)$ this is $(m\omega\hat{x} + i\hat{p})|0\rangle = \hat{0}$ which means (because $\hat{p} \rightarrow \frac{\hbar}{i}\frac{d}{dx}$ and $\hat{x} \rightarrow x$) that

$$\left(m\omega x + \hbar\frac{d}{dx}\right)\psi_0(x) = 0 \Rightarrow \frac{d\psi_0}{dx} = -\frac{m\omega x}{\hbar}\psi_0 = -\frac{x}{a_0^2}\psi_0$$

and finally, implying that the ground state vector in the x -representation is

$$\psi_0(x) = \frac{1}{\sqrt{a_0\sqrt{\pi}}}e^{-x^2/2a_0^2}. \quad (4)$$

5.1 Comparable observables

In quantum mechanics when an observation is made of a quantity, then the operator corresponding to that quantity must be hermitian (so that its expectation value will be real) and the measurement will result in one of the eigenvalues. If there is a second observable whose operator commutes with the first then, mathematically, we have $\hat{C}|\psi_n\rangle = c_n|\psi_n\rangle$ and there is $\hat{B}$ such that $[\hat{C}, \hat{B}] = 0$.

So $\hat{C}(\hat{B}|\psi_n\rangle) = \hat{B}\hat{C}|\psi_n\rangle = c_n\hat{B}|\psi_n\rangle$ and $\hat{B}|\psi_n\rangle$ is also an eigenvector of $\hat{C}$ with eigenvalue c_n . If c_n is a non-degenerate eigenvalue then $\hat{B}|\psi_n\rangle = b_n|\psi_n\rangle$ and the $|\psi_n\rangle$ are the eigenvalues of $\hat{B}$.

If c_n are degenerate of order α with linear independent eigenvectors $|\psi_{n,r}\rangle$ for $r = 1, \dots, \alpha$, then (inside the degenerate subspace) since $[\hat{C}, \hat{B}] = 0$ we have $\hat{B}|\psi_{n,r}\rangle$ as an eigenvector of $\hat{C}$ with eigen value c_n and so can expand this in terms of the set $\{|\psi_{n,r}\rangle\}$. That is,

$$\hat{B}|\psi_{n,r}\rangle = \sum_{s=1}^{\alpha} g_{n,s}|\psi_{n,s}\rangle$$

and some combination of the $|\psi_{n,r}\rangle$'s will be eigenvectors of $\hat{B}$ with eigenvalues b_n . Using this, then we have

$$b_n \sum_{r=1}^{\alpha} d_r |\psi_{n,r}\rangle = \hat{B} \sum_{r=1}^{\alpha} d_r |\psi_{n,r}\rangle = \sum_{r=1}^{\alpha} d_r \sum_{s=1}^{\alpha} g_{r,s} |\psi_{n,s}\rangle$$

which is

$$\sum_{s=1}^{\alpha} (b_n d_s - \sum_{r=1}^{\alpha} d_r g_{r,s}) |\psi_{n,s}\rangle = 0$$

and yields a characteristic equation (polynomial of degree α) with roots $b_n^{(1)}, b_n^{(2)}, \dots, b_n^{(\alpha)}$. These are the eigenvalues of $\hat{B}$ within the degeneracy.

Note that $\{b_n^{(k)}\}$ may also be degenerate in which case one must find another comparable observable and do it again. This process can be continued until we have removed all the degeneracy and have a complete set of comparable observables.

Anyway, for each $b_n^{(k)}$ there will be an eigenvector d_r determining the combination of degenerate eigenvectors of $\hat{C}$ which are simultaneous eigenvectors of $\hat{B}$. Write $|\phi_n^{(k)}\rangle = \sum_{r=1}^{\alpha} d_r |\psi_{n,r}\rangle$ and notice $\hat{C}|\phi_n^{(k)}\rangle = \sum_{r=1}^{\alpha} d_r \hat{C}|\psi_{n,r}\rangle = c_n \sum_{r=1}^{\alpha} d_r |\psi_{n,r}\rangle = c_n |\phi_n^{(k)}\rangle$ so the eigenvalue c_n of $\hat{C}$ along with the eigenvalue $b_n^{(k)}$ of $\hat{B}$ specify a particular simultaneous eigen vector of both $\hat{B}$ and $\hat{C}$. Often such a state is written as $|n, k\rangle$ and if another observable was necessary to remove the degeneracy, we would write something like $|n, k, l\rangle$.

5.2 2 dimensional quantum oscillator

The Hamiltonian here is

$$\hat{H} = \frac{\hat{p}_x^2}{2m} + \frac{\hat{p}_y^2}{2m} + \frac{1}{2}k(\hat{x}^2 + \hat{y}^2)$$

where $[\hat{x}, \hat{p}_x] = [\hat{y}, \hat{p}_y] = i\hbar$ and all other commutators are zero. This Hamiltonian is separable; so set $\psi(x, y) = X(x) \cdot Y(y)$ and solve $H\psi = E\psi$. That is

$$\frac{1}{X(x)} \left(\frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega^2 \hat{x}^2 \right) X(x) = E - \frac{1}{Y(y)} \left(\frac{\hat{p}_y^2}{2m} + \frac{1}{2}m\omega^2 \hat{y}^2 \right) Y(y)$$

so that $\left(\frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega^2 \hat{x}^2 \right) X(x) = E_{n_x} X(x)$ which has solutions $X(x) = |n_x\rangle$ with $E_{n_x} = \hbar\omega(n_x + 1/2)$ and similarly $Y(y) = |n_y\rangle$ with $E_{n_y} = \hbar\omega(n_y + 1/2)$. So solutions to the 2 dimensional quantum oscillator are $\psi(x, y) = |n_x\rangle \cdot |n_y\rangle$ with $E_{n_x, n_y} = \hbar\omega(n_x + n_y + 1)$ and this system acts as two independent 1 dimensional oscillators. An interesting difference here is that the system is now $(n+1)$ -fold degenerate where $n = n_x + n_y$.

Looking at the ladder operators $\hat{A}_x = \frac{m\omega\hat{x} + i\hat{p}_x}{\sqrt{2m\hbar\omega}}$ and $\hat{A}_y = \frac{m\omega\hat{y} + i\hat{p}_y}{\sqrt{2m\hbar\omega}}$ along with they hermitian conjugates (adjoints), we can write

$$\hat{H} = \hbar\omega(\hat{A}_x^\dagger \hat{A}_x + \hat{A}_y^\dagger \hat{A}_y + 1)$$

with eigenvector $|n_x, n_y\rangle = \frac{1}{\sqrt{n_x! n_y!}} (\hat{A}_x^\dagger)^{n_x} (\hat{A}_y^\dagger)^{n_y} |00\rangle$ where $|00\rangle$ is the ground state in number or energy representation (since $\hat{H}$ or $\hat{N}_x, \hat{N}_y$ have the same eigenvectors). We have $\hat{A}_x^\dagger \hat{A}_x |n_x, n_y\rangle = n_x |n_x, n_y\rangle$ and $\hat{H} |n_x, n_y\rangle = \hbar\omega(n_x + n_y + 1) |n_x, n_y\rangle$ with commutators $[\hat{A}_x, \hat{A}_x^\dagger] = 1$.

To pass between bases set $n = n_x + n_y$ and $\ell = n_x - n_y$ (so that $n_x = \frac{1}{2}(n + \ell)$ and $n_y = \frac{1}{2}(n - \ell)$). For the $(n+1)$ -fold degeneracy, we require a comparable observable which leads us to examining the angular momentum $\vec{L} = \vec{r} \times \vec{p}$. For the 2 dimensional system this has only one non-zero component

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x$$

which after simplification becomes $i\hbar(\hat{A}_x^\dagger \hat{A}_y - \hat{A}_y^\dagger \hat{A}_x)$. Is $\hat{L}_z$ compatible with $\hat{H}$? For compatibility, we require commutativity so check

$$[\hat{L}_z, \hat{H}] = i\hbar^2\omega[\hat{A}_x^\dagger \hat{A}_x + \hat{A}_y^\dagger \hat{A}_y + 1, \hat{A}_x^\dagger \hat{A}_y - \hat{A}_y^\dagger \hat{A}_x] = 0.$$

We now have two sets of comparable observables $\{\hat{N}_x, \hat{N}_y\}$ and $\{\hat{H}, \hat{L}_z\}$ and we may use either to completely specify the state of the system with eigenvectors $|n_x, n_y\rangle, |00\rangle$ and/or $|n, l\rangle, |00\rangle$ (depending on choice of representation). Either representation is fine to work with, but the $|n, l\rangle$ is more likely to be measurable.

Quickly recapping, for the 1 dimensional oscillator we had $|n\rangle$ which were simultaneous eigenvectors of $\hat{H}$ and $\hat{N}$ and there was no degeneracy. For the 2 dimensional oscillator the eigenvalues of $\hat{H}$ are $(n+1)$ -fold degenerate. We have found a second observable $\hat{L}_z$ which is compatible with $\hat{H}$ so it remains to find a set of simultaneous eigenvectors of both for the purpose of removing the degeneracy.

Introduce, $\hat{A}_L = \frac{1}{\sqrt{2}}(\hat{A}_x + i\hat{A}_y)$ and $\hat{A}_R = \frac{1}{\sqrt{2}}(\hat{A}_x - i\hat{A}_y)$ so that

$$\hat{A}_L^\dagger \hat{A}_L = \frac{1}{2}(\hat{A}_x^\dagger \hat{A}_x + \hat{A}_y^\dagger \hat{A}_y + i(\hat{A}_x^\dagger \hat{A}_y - \hat{A}_y^\dagger \hat{A}_x))$$

and

$$\hat{A}_R^\dagger \hat{A}_R = \frac{1}{2}(\hat{A}_x^\dagger \hat{A}_x + \hat{A}_y^\dagger \hat{A}_y - i(\hat{A}_x^\dagger \hat{A}_y - \hat{A}_y^\dagger \hat{A}_x)).$$

Now $\hat{H}$ can be represented in terms of these new operators as

$$\hat{H} = \hbar\omega(\hat{A}_L^\dagger \hat{A}_L + \hat{A}_R^\dagger \hat{A}_R + 1) = \hbar\omega(\hat{N}_L + \hat{N}_R + 1)$$

and similarly

$$\hat{L}_z = i\hbar(\hat{A}_L^\dagger \hat{A}_L - \hat{A}_R^\dagger \hat{A}_R) = i\hbar(\hat{N}_L - \hat{N}_R).$$

The operators $\hat{N}_L, \hat{N}_R$ can be used, as before, to create eigenvectors

$$|n_L, n_R\rangle = \frac{1}{\sqrt{n_L! n_R!}} (\hat{A}_L^\dagger)^{n_L} (\hat{A}_R^\dagger)^{n_R} |00\rangle.$$

These states are simultaneous eigenvectors of $\{\hat{N}_R, \hat{N}_L, \hat{H}, \hat{L}_z\}$ where

$$\begin{aligned}\hat{N}_L |n_L, n_R\rangle &= n_L |n_L, n_R\rangle \\ \hat{N}_R |n_L, n_R\rangle &= n_R |n_L, n_R\rangle \\ \hat{H} |n_L, n_R\rangle &= \hbar\omega(n_L + n_R + 1) |n_L, n_R\rangle \\ \hat{L}_z |n_L, n_R\rangle &= \hbar(n_L - n_R) |n_L, n_R\rangle\end{aligned}$$

however, it is more common to use the eigenvalues of $\hat{H}$ and $\hat{L}_z$ as quantum numbers so that

$$\begin{aligned}\hat{H} |n, m\rangle &= \hbar\omega(n+1) |n, m\rangle \\ \hat{L}_z |n, m\rangle &= \hbar m |n, m\rangle\end{aligned}$$

where $n = n_L + n_R \in \mathbb{N}$ is the *energy* and $m = n_L - n_R$ with $-n \leq m \leq n$ is the *angular momentum*.

6 Time-independent perturbation theory

We would like to solve the TISE equation (2) for a potential $V(x)$ that is similar to one for which we already know the exact solution, say $V_0(x)$. Mathematically we have $V(x) = V_0(x) + \lambda V'(x)$. This means our Hamiltonian is now

$$\hat{H} = \frac{\rho^2}{2m} + V(x) = \left(\frac{\rho^2}{2m} + V_0(x) \right) + \lambda V'(x) = H_0 + \lambda H'.$$

If the solutions to the known problem are $H_0|\psi_n^{(0)}\rangle = E_n^{(0)}|\psi_n^{(0)}\rangle$ with $\langle\psi_m^{(0)}|\psi_n^{(0)}\rangle = \delta_{m,n}$, then for the perturbed problem we have

$$H|\psi_n\rangle = (H_0 + \lambda H')|\psi_n\rangle = E_n|\psi_n\rangle$$

where

$$\begin{aligned} |\psi_n\rangle &= |\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \dots, \\ E_n &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \end{aligned}$$

and λ is use the count the order of approximation. That is $E_n^{(1)}$ will be used to count the first order correction to the n^{th} energy level and $|\psi_n^{(1)}\rangle$ will be the first order correction to the n^{th} eigenvector of $\hat{H}$.

Substituting these power series into the above formulation gives

$$(H_0 + \lambda H')(|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \dots) = (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots)(|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \dots)$$

expands (in powers of λ) as

$$\lambda^0(H_0\psi_n^0) + \lambda(H_0\psi_n^1 + H_1\psi_n^0) + \lambda^2(H_0\psi_n^2 + H'\psi_n^1) + \dots = \lambda^0(E_n^0\psi_n^0) + \lambda(E_n^0\psi_n^1 + E_n^1\psi_n^0) + \dots$$

and implies (comparing coefficients) that

$$\begin{aligned} H_0\psi_n^0 &= E_n^0\psi_n^0 \\ H_0\psi_n^1 + H'\psi_n^0 &= E_n^0\psi_n^1 + E_n^1\psi_n^0 \end{aligned}$$

and so on for higher orders.

6.0.1 First order correction

Now, taking the inner product of $|\psi_n^0\rangle$ and the λ coefficients yields

$$\langle\psi_n^0|H_0\psi_n^1\rangle + \langle\psi_n^0|H'\psi_n^0\rangle = \langle\psi_n^0|E_n^0\psi_n^1\rangle + \langle\psi_n^0|E_n^1\psi_n^0\rangle$$

which reduces to

$$E_n^0\langle\psi_n^0|\psi_n^1\rangle + \langle\psi_n^0|H'\psi_n^0\rangle = E_n^0\langle\psi_n^0|\psi_n^1\rangle + E_n^1\langle\psi_n^0|\psi_n^0\rangle$$

and hence merely that

$$\boxed{E_n^{(1)} = \langle\psi_n^0|H'\psi_n^0\rangle} \quad (5)$$

since $\langle\psi_m^{(0)}|\psi_n^{(0)}\rangle = \delta_{m,n}$.

Going back, and rearranging the λ -coefficient as $(H_0 - E_n^0)\psi_n^1 = -(H' - E_n^1)\psi_n^0$ then expanding ψ_n^1 in terms of our basis $\{\psi_m^0\}$ as

$$|\psi_n^1\rangle = \sum_{m \neq n} c_m |\psi_m^0\rangle$$

where we have excluded ψ_n^0 since it already appears in the expansion $\psi_n = \psi_n^0 + \lambda\psi_n^1 + \dots$. These together imply that

$$\sum_{m \neq n} (H_0 - E_n^0)c_m |\psi_m^0\rangle = -(H' - E_n^1)|\psi_n^0\rangle.$$

Taking the inner product of this with $\langle \psi_l^0 \rangle$ (with $l \neq n$ so not to get equation (5) again) reads

$$\sum_{m \neq n} c_m (E_m^0 - E_n^0) \delta_{l,m} = -\langle \psi_l^0 | H' | \psi_n^0 \rangle + E_n^1 \underbrace{\delta_{l,n}}_{=0}$$

and implies that the coefficients are

$$c_m = \frac{\langle m | H' | n \rangle}{E_n^0 - E_m^0}. \quad (6)$$

Note that this holds only in a non degenerate system because of the denominator.

6.0.2 Second order correction

Taking the inner product of $\langle \psi_n^0 |$ with the λ^2 coefficient of our above power series simplifies to yield

$$E_n^{(2)} = \langle \psi_n^{(0)} | H' \psi_n^{(1)} \rangle - E_n^{(1)} \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle.$$

We had that $\psi_n^1 = \sum_{m \neq n} c_m \psi_m^0$ which implies $\langle \psi_n^0 | \psi_n^1 \rangle = \sum_{m \neq n} \langle \psi_n^0 | \psi_m^0 \rangle = 0$ and

$$\langle \psi_n^{(0)} | H' \psi_n^{(1)} \rangle = \sum_{m \neq n} c_m \langle \psi_n^0 | H' \psi_m^0 \rangle = \sum_{m \neq n} \frac{\langle m | H' | n \rangle \langle n | H' | m \rangle}{E_n^0 - E_m^0}$$

So,

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle m | H' | n \rangle|^2}{E_n^0 - E_m^0} \quad (7)$$

6.1 Degenerate perturbation theory

Suppose we now have 2-fold degeneracy and the two degenerate states are $|na\rangle$ and $|nb\rangle$ with energies E_n . That is, two eigenfunctions $|na\rangle, |nb\rangle$ have the same energies so that $\hat{H}_0 |na\rangle = E_n |na\rangle$ and $\hat{H}_0 |nb\rangle = E_n |nb\rangle$ where $\langle na | nb \rangle = 0$.

The first thing to notice is that any (normalized) combination of these states will also be an eigenvector for $\hat{H}_0$. That is $\alpha |na\rangle + \beta |nb\rangle$ is an eigenvector and having $|\alpha|^2 + |\beta|^2 = 1$ keeps things normalized.

With $\hat{H} = H_0 + H^1$, the states $|na\rangle, |nb\rangle$ will no longer be eigenvectors of $\hat{H}$, but to first order, a linear combination will be. Furthermore, they will not longer be degenerate.

Starting with the TISE equation (2) $\hat{H} |n\ell\rangle = E_{n,\ell} |n\ell\rangle$ where $|n\ell\rangle = \alpha |na\rangle + \beta |nb\rangle$, make the following substitutions; $\hat{H} = H_0 + H^1$, $E_{n,\ell} = \sum_{i \geq 0} \lambda^i E_n^{(i)}$ and $|n\ell\rangle = \sum_{i \geq 0} \lambda^i |n\ell^{(i)}\rangle$. Extracting the λ^1 coefficient reads

$$H_0 |n\ell^{(1)}\rangle + H^1 |n\ell^{(0)}\rangle = E_n^{(0)} |n\ell^{(1)}\rangle + E_n^{(1)} |n\ell^{(0)}\rangle$$

and for two new equations, take the inner product of this with $|na^{(0)}\rangle$ and $|nb^{(0)}\rangle$. The first inner product simplifies to say

$$\langle na^{(0)} | H^1 | n\ell^{(0)} \rangle = E_n^{(1)} \langle na^{(0)} | n\ell^{(0)} \rangle$$

which, along with the fact that $|n\ell^{(0)}\rangle = \alpha |na^{(0)}\rangle + \beta |nb^{(0)}\rangle$, gives

$$\alpha W_{aa} + \beta W_{ab} = \alpha E_n^{(1)}$$

where $W_{ij} := \langle ni^{(0)} | H^1 | nj^{(0)} \rangle = \langle \psi_i^{(0)} | H^1 | \psi_j^{(0)} \rangle$. Similarly, from the second inner product, we get

$$\alpha W_{ba} + \beta W_{bb} = \beta E_n^{(1)}.$$

This provides us with the matrix equation $\begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E_n^{(1)} \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$ and the new characteristic polynomial is

$$(W_{aa} - E_n^{(1)})(W_{bb} - E_n^{(1)}) - |W_{ab}|^2 = 0$$

which implies

$$E_{n,\pm}^{(1)} = \frac{W_{aa} + W_{bb}}{2} \pm \sqrt{\frac{(W_{aa} - W_{bb})^2}{4} + |W_{ab}|^2} \quad (8)$$

where we have declared that

$$W_{ij} = \langle \psi_i^{(0)} | H^1 | \psi_j^{(0)} \rangle. \quad (9)$$

The eigenvectors of W determine the linear combinations of degenerate unperturbed system that are the non-degenerate eigenvectors of the perturbed system. If $W_{ab} = W_{ba} = 0$ then $|na\rangle, |nb\rangle$ are already the answers we seek and $E_{n,\pm}^{(1)} = W_{aa}$ and W_{bb} respectively so would be the first order corrections to the energy.

Theorem 6.1. *If $|na^{(0)}\rangle$ and $|nb^{(0)}\rangle$ are degenerate eigenvectors of $\hat{H}_0$ and $\hat{B}$ is a hermitian operator commuting with $\hat{H}^1$ having distinct eigenvalues $\gamma \neq \mu$ then $W_{ab} = W_{ba} = 0$ and $|na^{(0)}\rangle, |nb^{(0)}\rangle$ will be the eigenvectors of $\hat{H}_0 + \hat{H}^1$.*

Proof. Having $[\hat{B}, \hat{H}^1] = 0$ and $\mu \neq \gamma$ compute

$$\begin{aligned} 0 &= \langle na^{(0)} | [\hat{B}, \hat{H}^1] | nb^{(0)} \rangle = \langle na^{(0)} | \hat{B} \hat{H}^1 | nb^{(0)} \rangle - \langle na^{(0)} | \hat{H}^1 \hat{B} | nb^{(0)} \rangle \\ &= \langle na^{(0)} | \hat{H}^1 \hat{B} | nb^{(0)} \rangle - \mu \langle na^{(0)} | \hat{H}^1 | nb^{(0)} \rangle \\ &= \gamma \langle na^{(0)} | \hat{H}^1 | nb^{(0)} \rangle - \mu \langle na^{(0)} | \hat{H}^1 | nb^{(0)} \rangle \\ &= (\gamma - \mu) \langle na^{(0)} | \hat{H}^1 | nb^{(0)} \rangle \\ &\Leftrightarrow W_{ab} = 0 \end{aligned}$$

□

6.2 Variational principle

The variational principle states that calculating $E = \langle \psi_n | \hat{H} | \psi_n \rangle$ with any wave vector, then the result will be greater than, or equal to the ground state energy. That is The ground state energy is a lower bound for the entire function space and this can be useful information if we do not know the ground state.

Proof of this is straight forward if we denote the unknown eigenvectors of $\hat{H}$ as $\{\psi_n\}$ and since they form a complete set, we can write any $\psi = \sum_n c_n \psi_n$ where ψ is an arbitrary normalized test function.

Now,

$$\langle \psi | \hat{H} | \psi \rangle = \sum_{m,n} c_m^* c_n \langle \psi_m | \hat{H} | \psi_n \rangle = \sum_{m,n} |c_n|^2 E_n$$

The ground state is the infimum of $\{E_n\}$ so that $E_g \leq E_n, \forall n$. Hence,

$$E_g = E_g \sum_n |c_n|^2 \leq \sum_n |c_n|^2 E_n = \langle \psi | \hat{H} | \psi \rangle.$$

If we didn't know the ground state wave vector for the 1 dimensional simple harmonic oscillator (which is gaussian) we might guess that $\psi(x) = \begin{cases} A(a^2 - x^2), & |x| < a \\ 0, & \text{else} \end{cases}$ and follow the proceeding four steps;

1. Normalize;

$$1 = A^2 \int_{-a}^a (a^2 - x^2) dx = A^2 \frac{16a^5}{15} \Rightarrow A = \sqrt{\frac{15}{16a^5}}$$

2. Compute $\langle \psi | \hat{H} | \psi \rangle$;

$$\begin{aligned} E_a = \langle \psi | \hat{H} | \psi \rangle &= A^2 \int_{-a}^a dx (a^2 - x^2) \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m \omega^2 x^2 \right) (a^2 - x^2) \\ &= \frac{5\hbar^2}{4ma^2} + \frac{m\omega^2 a^2}{14} \\ &= \frac{5\hbar\omega}{4} \left[\frac{\hbar}{m\omega} \cdot \frac{1}{a^2} \right] + \frac{1}{14} \hbar\omega \left[\frac{m\omega}{\hbar} \cdot a^2 \right] \end{aligned}$$

Note that it is very important to analyze the dimension (units) of this result - and it should be in energy units.

3. Minimize E_a with respect to a ;

$$\frac{dE_a}{da} = -2 \frac{5\hbar^2}{4ma^3} + \frac{2m\omega^2 a}{14}$$

vanishes when $a^4 = \frac{35\hbar^2}{2m^2\omega^2} = \frac{35}{2} \cdot \left(\frac{\hbar}{m\omega} \right)^2$

4. Substitue a_{min} in to E_a to get

$$E_{a_{min}} = \hbar\omega \left(\frac{5}{4} \sqrt{\frac{2}{35}} + \frac{1}{14} \sqrt{\frac{35}{2}} \right) \approx 0.6\hbar\omega > \frac{1}{2}\hbar\omega.$$

We could have initially guessed that $\psi(x) = Ae^{-x^2/a^2}$ (a Gaussian distribution) and gotten $a_{min}^2 = \frac{2\hbar}{m\omega}$ so that $E_a = \frac{1}{2}\hbar\omega$ which is the exact ground state energy because Ae^{-x^2/a^2} is the ground state vector as found in (4).

We could also guess that $\psi = \sum_{i=1}^N a_i \psi_i$ where a_i are adjustable parameters and the ψ_i are some subset of orthonormal vectors. In this case, we would then compute $E_{a_i} = \langle \psi_i | \hat{H} | \psi_i \rangle$ and $\frac{dE_i}{da_i} = 0$ for each $i = 1, \dots, N$ gives N equations in N unknowns.

Often one may choose a set of functions $\{\psi_i\}$ which are already familiar and orthonormal (this is a key fact) so to calculate $\langle \psi_i | \hat{\rho} | \psi_j \rangle$ and $\langle \psi_i | V | \psi_j \rangle$.

For example, if $V(x) = \frac{m\omega^2}{\hbar} x^4$ then the $\{\psi_i\}$ from the simple harmonic oscillator would be a good guess to begin with (since easy to compute $\langle \psi_i | \hat{\rho} | \psi_j \rangle$ and $\langle \psi_i | x^4 | \psi_j \rangle$).

6.3 Angular momentum

Classically, the angular momentum is

$$\vec{L} = \vec{r} \times \vec{p} = (yp_z - zp_y)\mathbf{i} + (zp_x - xp_z)\mathbf{j} + (xp_y - yp_x)\mathbf{k}$$

and in quantum mechanics we set $\rho_x = \frac{\hbar}{i} \frac{d}{dx}$. The commutation relations for angular momentum operators are important so

$$[\hat{L}_x, \hat{L}_y] = \left(\frac{\hbar}{i}\right)^2 \left[\left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y}\right) \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z}\right) - \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z}\right) \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y}\right) \right] = i\hbar \hat{L}_z$$

and similarly $[\hat{L}_y, \hat{L}_z] = i\hbar \hat{L}_x$, $[\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y$.

Also, the *total angular momentum* is $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$ and we can show that $[\hat{L}^2, \hat{L}_x] = 0$ and $[\hat{L}^2, \hat{L}] = 0$. This means, for one, that $\hat{L}^2$ commutes with its components but its components don't commute.

Consider the commutator of two operators acting upon an eigenvector of the first. That is $\hat{A}f_a = af_a$ and we seek to compute

$$[\hat{A}, \hat{B}]f_a = \hat{A}\hat{B}f_a - \hat{B}\hat{A}f_a = (\hat{A} - a)\hat{B}f_a.$$

If these operators commute (i.e. $[\hat{A}, \hat{B}] = 0$), then $\hat{B}f_a$ is also an eigenvector of $\hat{A}$ with eigenvalue a and $\hat{A}, \hat{B}$ are called *comparable operators*. In this case, we can find simultaneous eigenvectors of both operators.

Since $[\hat{L}^2, \hat{L}_z] = 0$ let f be a simultaneous eigenvector of $\hat{L}^2$ and $\hat{L}_z$ with eigenvalues λ, μ respectively. Using a ladder technique similar to the quantum harmonic oscillator we introduce $\hat{L}_{\pm} = \hat{L}_x \pm i\hat{L}_y$. It can be shown that

- (i) $[\hat{L}_z, \hat{L}_{\pm}] = \pm\hbar \hat{L}_{\pm}$,
- (ii) both $\hat{L}_{\pm}$ are hermitian and
- (iii) they commute with $\hat{L}^2$.

So, if f is an eigenvector of $\hat{L}^2$ then it is also an eigenvector of both $\hat{L}_{\pm}$. Also,

$$\hat{L}^2(\hat{L}_{\pm}f) = \hat{L}_{\pm}(\hat{L}^2f) = \hat{L}_{\pm}(\lambda f) = \lambda(\hat{L}_{\pm}f)$$

and

$$\begin{aligned} \hat{L}_z(\hat{L}_{\pm}f) &= [\hat{L}_z, \hat{L}_{\pm}]f - \hat{L}_{\pm}\hat{L}_zf \\ &= \pm\hbar \hat{L}_{\pm}f + \mu \hat{L}_{\pm}f \\ &= (\mu \pm \hbar)\hat{L}_{\pm}f \end{aligned}$$

which is an eigenvalue equation with eigenvector $\hat{L}_{\pm}f$ and eigenvalue $\mu \pm \hbar$. We thus call $\hat{L}_{\pm}$ the *raising* and *lowering* operators respectively since the increase/decrease the eigenvalues.

For a given eigenvalue λ of $\hat{L}^2$, the operators $\hat{L}_{\pm}$ increase/decrease the eigenvalues of $\hat{L}_z$, however there is an upper and lower bound for the eigenvalues of $\hat{L}_z$ (coming from the fact that the z -component of angular momentum cannot be larger in magnitude than the total). This means there must be top and bottom rungs. Denote the top eigenvector by f_T so we must have $\hat{L}_+f_T = 0$. Let $\hbar\ell$ denote the maximum eigenvalues of $\hat{L}_z$ so that $\hat{L}_zf_T = \hbar\ell f_T$ and, of course, $\hat{L}^2f_T = \lambda f_T$.

Through operator composition we obtain the following relation

$$\begin{aligned} \hat{L}_{\pm}\hat{L}_{\mp} &= (\hat{L}_x \pm i\hat{L}_y)(\hat{L}_x \mp i\hat{L}_y) \\ &= \hat{L}_x^2 + \hat{L}_y^2 \mp i(\hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x) \\ &= \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 - \hat{L}^2 \mp i\hbar \hat{L}_z \\ &= \hat{L}^2 - \hat{L}_z^2 \pm \hbar \hat{L}_z \end{aligned}$$

which says that $\hat{L}^2 = \hat{L}_\pm \hat{L}_\mp + \hat{L}_z^2 \mp \hbar \hat{L}_z$. Using this relation, then

$$\hat{L}^2 f_T = (\hat{L}_- \hat{L}_+ + \hat{L}_z^2 + \hbar \hat{L}_z) f_T = (0 + \hbar^2 \ell^2 + \hbar^2 \ell^2) f_T = \hbar^2 \ell(\ell + 1) f_T$$

implying that

$$\lambda = \hbar^2 \ell(\ell + 1).$$

Applying the same technique to the bottom rung f_B with $\hat{L}_z f_B = \ell' f_B$, we find that $\lambda f_B = \hat{L}^2 f_B = \hbar^2 \ell'(\ell' - 1) f_B$ so that

$$\lambda = \hbar^2 \ell'(\ell' - 1).$$

Equating these two values for λ implies $\ell(\ell + 1) = \ell'(\ell' - 1)$ means that $\ell' = \ell + 1$ or $\ell' = -\ell$. The first possibility is not valid because then the bottom rung would be higher than the top, so $\ell' = -\ell$.

Thus, the eigenvalues of $\hat{L}_z$ are $\{-\hbar\ell, -\hbar(\ell + 1), \dots, \hbar(\ell - 1), \hbar\ell\}$ (integer multiples of $\hbar$ running from $-\ell$ to ℓ in $N = 2\ell$ -steps. This implies that $\ell = N/2$ so is either an integer or a half integer. Finally, the eigenfunctions are characterized by $\ell = 0, 1/2, 1, 3/2, \dots$ and $m = -\ell, -\ell + 1, \dots, \ell$.

7 Quantum mechanics in 3 dimensions

Here we write our Hamiltonian as

$$\hat{H} = \frac{\hat{\rho}_x^2 + \hat{\rho}_y^2 + \hat{\rho}_z^2}{2m} + \hat{V}(r) = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \quad (10)$$

where we recall that $\hat{\rho}_x = \frac{\hbar}{i} \frac{\partial}{\partial x}$.

Normalization here looks like the 3-dimensional integral

$$1 = \int d\vec{r} |\Psi|^2 = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz |\psi(x, y, z)|^2$$

however, when the potential is a function of $\vec{r}$ we would probably rather use spherical coordinates and the normalization integral looks more like

$$1 = \int_0^{\infty} dr \int_0^{2\pi} d\phi \int_0^{\pi} d\theta r^2 \sin \theta |\psi(r, \phi, \theta)|^2$$

Some potential examples¹ include

1. $V(\vec{r}) = \frac{1}{2}kr^2 = \frac{1}{2}k(x^2 + y^2 + z^2)$
2. $V(\vec{r}) = \begin{cases} 0, r < R \\ \infty, r \geq R \end{cases}$ (the 3 dimensional infinite square well)
3. $V(\vec{r}) = e^2/r$ - the potential for a hydrogen-like atom. For other atoms with different number of protons/neutrons in the nucleus, use $V = Ze^2/r$.

¹pun intended... or is it a double entendre?

The gradient operator in spherical coordinates looks like

$$\nabla = \hat{r} \frac{\partial}{\partial r} + \hat{\theta} \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{\phi} \frac{1}{\sin \theta} \frac{\partial}{\partial \phi}$$

and $\vec{r} = r \cdot \hat{r}$ so the angular momentum becomes

$$\vec{L} = \vec{r} \times \vec{p} = \frac{\hbar}{i} \left[r(\hat{r} \times \hat{r}) \frac{\partial}{\partial r} + r(\hat{r} \times \hat{\theta}) \frac{1}{r} \frac{\partial}{\partial \theta} + r(\hat{r} \times \hat{\phi}) \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} \right] = \frac{\hbar}{i} \left(\frac{\partial}{\partial \theta} \hat{\phi} - \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \hat{\theta} \right)$$

Now, with the spherical Laplacian given² as

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

so the time independent S.E. becomes

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right) \psi = E\psi$$

which is separable when $\psi(r, \theta, \phi) = R(r) \cdot Y(\theta, \phi)$. Indeed, in this case simplification reveals

$$\frac{1}{R(r)} \left(\frac{\partial}{\partial r} r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} (V(r) - E) = -\frac{1}{Y(\theta, \phi)} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right)$$

so we set both sides to be equal the constant $\ell(\ell + 1)$.

7.0.1 Solving for angular component

Upon further separation of variables with $Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$ we find the right hand side from above to be

$$\frac{1}{\Theta(\theta)} \left(\sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \ell(\ell + 1) \sin^2 \theta \right) = -\frac{1}{\Phi(\phi)} \frac{d^2 \Phi}{d\phi^2}$$

and again, we set both sides equal to the constant m^2 .

One equation is then $\Phi''(\phi) = -m^2 \Phi(\phi)$ and solved by $\Phi(\phi) = e^{-im\phi}$. We require $\phi(\vec{r})$ to be single-valued³ so m must be an integer. This constant integer m is called the *azimuthal quantum number* or *magnetic quantum number*.

Now, the $\Theta(\theta)$ part of this has *associate Legendre functions* as solutions. That is,

$$\Theta(\theta) = AP_\ell^m(\cos \theta)$$

where $P_\ell^m(x) = (1 - x^2)^{\frac{|m|}{2}} \left(\frac{d}{dx} \right)^{|m|} P_\ell(x)$ and $P_\ell(x)$ are the *Legendre polynomials*⁴ which are orthogonal and not normalized on $[-1, 1]$.

Note; there are $2\ell + 1$ possible values for m then $m = -\ell, \dots, \ell - 1, \ell$

Putting all of this together yields the *angular equation*,

$$Y_\ell^m(\theta, \phi) = \epsilon \sqrt{\frac{2\ell + 1}{4\pi} \cdot \frac{(\ell - |m|)!}{(\ell + |m|)!}} \cdot e^{-im\phi} P_\ell^m(\cos \theta) \quad (11)$$

²This is a long tedious exercise in vector calculus - that deserves its own set of notes

³apparently single-valued implies $\Phi(\phi + 2\pi) = \Phi(\phi)$ which forces m to be an integer

⁴E.g. $P_0(x) = 1, P_1(x) = x, P_2(x) = \frac{1}{2}(3x^2 - 1), P_3(x) = \frac{1}{2}(5x^3 - 3x), \dots$

where $\epsilon = \begin{cases} (-1)^m, m \geq 0 \\ 1, m \leq 0 \end{cases}$ and these satisfy the orthonormality constraint that

$$\langle \ell, m | \ell', m' \rangle = \int \sin \theta d\theta d\phi Y_\ell^m Y_{\ell'}^{m'} = \delta_{\ell, \ell'} \delta_{m, m'}.$$

7.0.2 Solving for the radial component

We have $\left(\frac{\partial}{\partial r} r^2 \frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2} (V(r) - E)R = \ell(\ell+1)R$ which is simplified by substituting $U(r) = rR(r)$ so that $\frac{dR}{dr} = \frac{1}{r^2} (r \frac{dU}{dr} - U)$ and $\frac{d}{dr} (r^2 \frac{dR}{dr}) = r \frac{d^2 U}{dr^2}$ which gives us

$$\boxed{-\frac{\hbar^2}{2m} \frac{d^2 U}{dr^2} + V(r)U + \frac{\hbar^2}{2m} \cdot \frac{\ell(\ell+1)}{r^2} U = EU}$$

and, except for the term $\frac{\hbar^2}{2m} \cdot \frac{\ell(\ell+1)}{r^2}$ is the 1 dimensional TISE. This is called the *radial equation* and the extra term (involving $\ell(\ell+1)$) is called the *centrifugal term* because it pushes the particle from the origin.

Note; that $0 \leq r < \infty$ here.

7.1 3 dimensional infinite potential well

Let us illustrate what we have just shown with an example,

Example 7.1. Suppose $V(\vec{r}) = \begin{cases} 0, r < a \\ \infty, r \geq a \end{cases}$. Then inside radius a our radial equation becomes

$$U'' = \left(\frac{\ell(\ell+1)}{r^2} - k^2 \right) U$$

where $k^2 = \frac{2mE}{\hbar^2}$.

First, when $\ell = 0$ this has solution $U(r) = A \sin(kr) + B \cos(kr)$, but $R = U/r$ implies the second term would be $\frac{\cos(kr)}{r}$ which tends to ∞ as $r \rightarrow 0$. Since we must be able to normalize these solutions, this means the constant $B = 0$ and so $R(r) = \sqrt{\frac{2}{a}} \frac{\sin(kr)}{r}$. Furthermore, the boundary condition requires $0 = R(a) = \sqrt{\frac{2}{a}} \frac{\sin(ka)}{a}$ so we must have $ka = n\pi$ meaning $E_{n,0} = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$. So, with $\psi_{n,\ell,m} = R_{n,\ell} Y_\ell^m$ and $Y_0^0 = \frac{1}{\sqrt{4\pi}}$ then we have found

$$\psi_{n,0,0} = \frac{1}{\sqrt{2ma}} \cdot 1r \sin\left(\frac{n\pi r}{a}\right).$$

The general solution to the infinite potential well is $U(r) = A r j_\ell(kr) + B r n_\ell(kr)$ where

$$j_\ell(x) = (-x)^\ell \left(\frac{1}{x} \frac{d}{dx} \right)^\ell \frac{\sin x}{x} \quad - \text{ Spherical Bessel function}$$

$$n_\ell(x) = -(-x)^\ell \left(\frac{1}{x} \frac{d}{dx} \right)^\ell \frac{\cos x}{x} \quad - \text{ Neuman function}$$

However, we still require $R(r)$ to be normalizable implying, again, that $B = 0$ and energies $E_{n,\ell}$ are given by the zeros⁵ of the $j_\ell(ka)$. Finally, then the wave functions are

$$|n, \ell, m\rangle = A_{n,\ell} \cdot j_\ell(k_\ell r) \cdot Y_\ell^m(\theta, \phi)$$

with $n \in \mathbb{N}, \ell \in \{0, 1, \dots, n-1\}, m \in [-\ell, \ell] \cap \mathbb{Z}$.

7.2 Hydrogen atom

We seek to solve the radial equation for the potential $V(\vec{r}) = -\frac{Ze^2}{r}$ (or $\frac{e^2}{4\pi\epsilon_0 r}$). That is

$$-\frac{\hbar^2}{2m} \frac{d^2 U}{dr^2} + \left(-\frac{Ze^2}{r} + \frac{\hbar^2}{2m} \cdot \frac{\ell(\ell+1)}{r^2} \right) U = EU$$

Upon solving this, the eigenvalues are found to be $E_n = \frac{-me^4}{2\hbar^2 n^2}$ for $n \in \mathbb{N}$.

We introduce the constant $a_0 = \frac{\hbar^2}{me^2} \approx 0.529 \times 10^{-10} m$ the *Bohr radius* so then $E_n = -mc^2 \frac{(Z\alpha)^2}{2n^2}$ where $\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}$ is the *fine structure constant*.

Coming back to the potential for the radial equation, we get

$$|n, \ell, m\rangle = \sqrt{\left(\frac{2}{na}\right)^2 \cdot \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}} \cdot e^{-r/na} \left(\frac{2r}{na}\right)^\ell L_{n-\ell-1}^{2\ell+1} Y_\ell^m(\theta, \phi)$$

where $L_{q-p}^p(x) = (-1)^p \left(\frac{d}{dx}\right)^p L_q(x)$ and $L_q(x) = e^x \left(\frac{d}{dx}\right)^q (e^{-x} x^q)$ is the q^{th} *Leguerre polynomial*. Furthermore, as usual, we have $\langle n, \ell, m | n', \ell', m' \rangle = \delta_{n,n'} \delta_{\ell,\ell'} \delta_{m,m'}$ and $E_n = E_{1/n^2} = \frac{-13.6\text{eV}}{n^2}$.

In summary, then we have⁶

$$\begin{aligned} \hat{H}|n, \ell, m\rangle &= -mc^2 \left(\frac{Z\alpha}{n}\right)^2 |n, \ell, m\rangle \\ \hat{L}^2|n, \ell, m\rangle &= \hbar^2 \ell(\ell+1) |n, \ell, m\rangle \\ \hat{L}_z|n, \ell, m\rangle &= \hbar m |n, \ell, m\rangle \end{aligned}$$

and $\{\hat{H}, \hat{L}^2, \hat{L}_z\}$ form a complete set of commuting observables. Sometimes, when examining only the angular momentum we use $|\ell, m\rangle$ instead of $|n, \ell, m\rangle$.

7.3 Spin

Elementary particles such as electrons, protons, neutrons, photons, gravitons, gluons, etc... have properties such as mass and charge which are characteristic intrinsic properties. Another such property is *spin* which is defined as an intrinsic angular momentum.

For the hydrogen atom, the electron will have both *orbital angular momentum*

$$\langle \hat{L}^2 \rangle = \hbar^2 \ell(\ell+1), \langle \hat{L}_z \rangle = \hbar m$$

and *spin angular momentum*

$$\langle \hat{S}^2 \rangle = \hbar^2 s(s+1), \langle \hat{S}_z \rangle = \hbar m_s.$$

The theory of spin is very similar to that of angular momentum. We have the following analogous operators and relations;

⁵which are not regular periodic spaces like our trig function $\sin(ka) = 0$

⁶with c - the speed of light, Z - the charge of the nucleus and mc^2 - rest energy of an electron

- $[\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z$
- $\hat{S}_z|s, m_s\rangle = \hbar m_s|s, m_s\rangle$
- $\hat{S}^2|s, m_s\rangle = \hbar^2 s(s+1)|s, m_s\rangle$
- $\hat{S}_\pm = \hat{S}_x \pm i\hat{S}_y$

so

$$\hat{S}_\pm|s, m_s\rangle = \hbar\sqrt{s(s+1) - m(m \pm 1)}|s, m_s \pm 1\rangle.$$

Now, unlike the orbital angular momentum operator which can only yield integers because the wave function must be single valued, the spin quantum number can also take on half integers $s \in \frac{1}{2}\mathbb{N}$.

Now we may classify particles into those with integral spin (called *bosons*) and those with half integer spin (called *fermions*).

The solutions for spin 1/2 are as follows; $s = 1/2$ implying that $m_s = \pm 1/2$, $\hat{S}^2|1/2, m_s\rangle = \frac{3}{4}\hbar^2|1/2, m_s\rangle$ and $\hat{S}_z|1/2, m_s\rangle = \hbar m_s|1/2, m_s\rangle$. If we suppose that $m_s = 1/2$ then $\hat{S}_+|1/2, 1/2\rangle = \hbar\sqrt{\frac{1}{2}(1/2+1) - \frac{1}{2}(1/2+1)}|1/2, 1/2+1\rangle = 0$ and $\hat{S}_-|1/2, 1/2\rangle = \hbar|1/2, -1/2\rangle$.

Note that the possible states are represented in the following ways;

- $|1/2, 1/2\rangle, |\uparrow\rangle, up, \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \chi_+$
- $|1/2, -1/2\rangle, |\downarrow\rangle, down, \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \chi_-$

Furthermore, we can deduce some facts about the matrix representations of our operators

$$\left. \begin{array}{l} \hat{S}^2 \uparrow = \frac{3}{4}\hbar^2 \uparrow \\ \hat{S}^2 \downarrow = \frac{3}{4}\hbar^2 \downarrow \end{array} \right\} \Rightarrow \hat{S}^2 \longleftrightarrow \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\left. \begin{array}{l} \hat{S}_z \uparrow = \frac{1}{2}\hbar \uparrow \\ \hat{S}_z \downarrow = -\frac{1}{2}\hbar \downarrow \end{array} \right\} \Rightarrow \hat{S}_z \leftrightarrow \frac{1}{2}\hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\left. \begin{array}{l} \hat{S}_+ \uparrow = 0 \\ \hat{S}_+ \downarrow = \hbar \uparrow \end{array} \right\} \Rightarrow \hat{S}_+ \leftrightarrow \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

$$\left. \begin{array}{l} \hat{S}_- \uparrow = \hbar \downarrow \\ \hat{S}_- \downarrow = 0 \end{array} \right\} \Rightarrow \hat{S}_- \leftrightarrow \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

The general spin state is $|\chi\rangle = \sum_{\forall \text{ states}} a_n|\chi_n\rangle = a\uparrow + b\downarrow$. That is $\chi = \begin{pmatrix} a \\ b \end{pmatrix}$ with $|a|^2 + |b|^2 = 1$.

To measure $\hat{S}_x$ and $\hat{S}_y$ we need to get their matrix representations. Recall that $\hat{S}_x = \frac{1}{2}(\hat{S}_+ + \hat{S}_-) = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$ and $\hat{S}_y = \frac{1}{2i}(\hat{S}_+ - \hat{S}_-) = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$. So then $\hat{S}_x\chi = \frac{\hbar}{2} \begin{pmatrix} b \\ a \end{pmatrix}$. Thus, the eigenvalues of $\hat{S}_x$ are clearly $\pm \frac{\hbar}{2}$ with eigenvectors $\chi_+ = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$ and $\chi_- = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$ and hence, in this basis, a general $\chi = \begin{pmatrix} a \\ b \end{pmatrix} = \frac{a+b}{2}\chi_+ + \frac{a-b}{2}\chi_-$.

It will be convenient to introduce the *Pauli spin matrices*

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

and $\vec{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$. We first notice that $\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = I_2$ and commutators look like $[\sigma_x, \sigma_y] = 2i\sigma_z$.

7.4 The electron in a magnetic field $\hat{H} = -\vec{B} \cdot \vec{M}$

The electron is both charged and has angular momentum, so it will have a magnetic moment. Classically, we have $\vec{M} = \frac{q}{2m}\vec{S}$ where $\vec{S} = \vec{r} \times \vec{p}$. However, with a relativistic equation (Dirac) we get $\vec{M} = \frac{2q}{2m}\vec{S}$ and in quantum electrodynamics $\vec{M} = g\frac{q}{2m}\vec{S}$ where $g = 2\left(1 + \frac{\alpha}{2\pi} + \dots\right)$ with $\alpha = \frac{e^2}{\hbar c}$ as the fine structure constant.

introduce the Bohr magneton $\mu_B = \frac{e\hbar}{2m} \approx 9.27 \times 10^{-24} J/T$ so that $\vec{M} = \frac{1}{2}g\mu_B\vec{\sigma}$ with $\vec{\sigma}$ as the Pauli spin vector. If there exists an external magnetic field then the Hamiltonian gains the term $\hat{H}' = -\vec{B} \cdot \vec{M}$.

There are two state vectors for an electron and these are $\chi_{\pm}$ so we can compute the possible energies;

$$\langle \chi_+ | \hat{H} | \chi_+ \rangle = -\langle \chi_+ | \vec{B} \cdot \vec{M} | \chi_+ \rangle$$

choose $\vec{B}$ parallel to $\vec{k}$ so that $\vec{B} = B \cdot \vec{k}$ and $\hat{H} = -\frac{1}{2}g\mu_B B \sigma_z$. Now,

$$\langle \chi_+ | \hat{H} | \chi_+ \rangle = -\frac{1}{2}g\mu_B B \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = -\frac{1}{2}g\mu_B B = E_{\uparrow}.$$

Similarly,

$$E_{\downarrow} = \langle \chi_- | \hat{H} | \chi_- \rangle = \frac{1}{2}g\mu_B B$$

and from this we can see that $E_{\uparrow} = -E_{\downarrow}$.

The time-dependent Schrödinger equation for the general spin state $\chi = a\chi_+ + b\chi_-$ is then

$$i\hbar \frac{\partial \chi}{\partial t} = \hat{H} \chi$$

which, according to our eigen decomposition of $\hat{H}$, has solutions

$$\chi(t) = a\chi_+ e^{-iE_{\uparrow}t/\hbar} + b\chi_- e^{iE_{\downarrow}t/\hbar}$$

and it is convenient to write $a = \cos(\alpha/2)$, $b = \sin(\alpha/2)$ so that, in vector form,

$$\chi(t) = \begin{pmatrix} \cos(\alpha/2)e^{-iE_{\uparrow}t/\hbar} \\ \sin(\alpha/2)e^{iE_{\downarrow}t/\hbar} \end{pmatrix}.$$

Now we may compute $\langle \hat{S} \rangle$ as a function of time

$$\begin{aligned} \langle \hat{S}_x \rangle &= \langle \chi(t) | \hat{S}_x | \chi(t) \rangle \\ &= \begin{pmatrix} \cos(\alpha/2)e^{iE_{\uparrow}t/\hbar} & \sin(\alpha/2)e^{-iE_{\downarrow}t/\hbar} \end{pmatrix} \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \cos(\alpha/2)e^{-iE_{\uparrow}t/\hbar} \\ \sin(\alpha/2)e^{iE_{\downarrow}t/\hbar} \end{pmatrix} \\ &= \frac{\hbar}{2} \cos(\alpha/2) \sin(\alpha/2) \left(e^{i(E_{\uparrow}-E_{\downarrow})t/\hbar} + e^{i(E_{\downarrow}-E_{\uparrow})t/\hbar} \right) \\ &= \frac{\hbar}{4} \sin \alpha \left[2 \cos \left(\frac{E_{\uparrow}-E_{\downarrow}}{\hbar} t \right) \right] \\ &= \frac{\hbar}{2} \sin \alpha \cos \left(\frac{2\mu_B B}{\hbar} t \right) = \frac{\hbar}{2} \sin \alpha \cos(\omega_L t) \end{aligned}$$

where $\omega_L := \frac{2\mu_B B}{\hbar}$ is called the *Larmour frequency*.

Similarly, $\langle \hat{S}_y \rangle = -\frac{\hbar}{2} \sin \alpha \sin(\omega_L t)$ and $\langle \hat{S}_z \rangle = \frac{\hbar}{2} \cos \alpha$ and we note that $\langle \hat{S}_z \rangle$ has no time dependence.

7.5 Addition of angular momentum

If we have two different spin 1/2 particles (i.e. an electron and a proton) then there are 4 possible states $|\uparrow, \uparrow\rangle, |\uparrow, \downarrow\rangle, |\downarrow, \uparrow\rangle, |\downarrow, \downarrow\rangle$ and the total angular momentum will be $\hat{S} = \hat{S}^{(1)} + \hat{S}^{(2)}$.

Compute,

$$\begin{aligned}\hat{S}_z|\chi_1\chi_2\rangle &= (\hat{S}_z^{(1)} + \hat{S}_z^{(2)})|\chi_1\chi_2\rangle \\ &= (\hat{S}_z^{(1)}|\chi_1\rangle)|\chi_2\rangle + |\chi_1\rangle(\hat{S}_z^{(2)}|\chi_2\rangle) \\ &= \hbar m_{s_1}|\chi_1\chi_2\rangle + \hbar m_{s_2}|\chi_1\chi_2\rangle \\ &= \hbar(m_{s_1} + m_{s_2})|\chi_1\chi_2\rangle\end{aligned}$$

and the possible results are

$$\begin{aligned}|\uparrow\uparrow\rangle &\rightarrow m_s = 1 \\ |\uparrow\downarrow\rangle &\rightarrow m_s = 0 \\ |\downarrow\uparrow\rangle &\rightarrow m_s = 0 \\ |\downarrow\downarrow\rangle &\rightarrow m_s = -1\end{aligned}$$

but wait! Aren't we supposed to have $m = -s, \dots, +s$ in integer steps? Let us try operating with the lower operator $\hat{S}_- = \hat{S}_-^{(1)} + \hat{S}_-^{(2)}$ on $|\uparrow\uparrow\rangle$. We find that

$$\hat{S}_-|\uparrow\uparrow\rangle = \frac{\hbar}{2}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$$

and again

$$\hat{S}_-(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) = \frac{\hbar}{2}|\downarrow\downarrow\rangle.$$

Thus, these states $|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle$ are eigenstates of $(\hat{S}^{(1)})^2, (\hat{S}^{(2)})^2, \hat{S}_z^{(1)}$ and $\hat{S}_z^{(2)}$, but we want those of $\hat{S}_z = \hat{S}_z^{(1)} + \hat{S}_z^{(2)}$ and $\hat{S}^2 = (\hat{S}^{(1)} + \hat{S}^{(2)})^2$.

7.5.1 Tensor products

The state $|\phi\rangle \otimes |\psi\rangle = |\phi\psi\rangle$ is defined as an element of a new Hilbert space with inner product specified as

$$(\langle\phi_1| \otimes \langle\psi_1|) \cdot (|\phi_2\rangle \otimes |\psi_2\rangle) = \langle\phi_1|\phi_2\rangle \cdot \langle\psi_1|\psi_2\rangle$$

so that normalizing gives vectors $|1, 1\rangle = |\uparrow\uparrow\rangle, |1, 0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle), |1, -1\rangle = |\downarrow\downarrow\rangle$ which evidently have total angular momentum $s = 1$ (called *triplet states*) and $|0, 0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$ with $s = 0$ called *singlet state*.

Thus, we claim that two spin 1/2 particles carry a total spin of 1 or 0 depending on whether they occupy the singlet or triplet state. To prove this, we must show that triplet states are eigenvectors of $\hat{S}^2$ with eigenvalue $\hbar^2$ and that the single state is an eigenvector with eigenvalue 0. Indeed, $\hat{S}^2|\uparrow\uparrow\rangle = \hbar^2 2|\uparrow\uparrow\rangle = \hbar^2 \cdot 1 \cdot (1+1)|\uparrow\uparrow\rangle$ and this is verified as follows;

First notice that $\hat{S}^2 = (S_1 + S_2)^2 = \hat{S}_1^2 + \hat{S}_2^2 + 2\hat{S}_1 \cdot \hat{S}_2$ and that

$$\begin{aligned}\hat{S}_1 \cdot \hat{S}_2 &= S_{1,x}S_{2,x} + S_{1,y}S_{2,y} + S_{1,z}S_{2,z} \\ &= \frac{1}{2}(S_{1,+}S_{2,-} + S_{1,-}S_{2,+}) + S_{1,z}S_{2,z}.\end{aligned}$$

Now,

$$\begin{aligned}
\hat{S}^2|\uparrow\uparrow\rangle &= \left[\hat{S}_1^2 + \hat{S}_2^2 + \frac{1}{2} (S_{1,+}S_{2,-} + S_{1,-}S_{2,+}) + S_{1,z}S_{2,z} \right] |\uparrow\uparrow\rangle \\
&= (\hat{S}_1^2\uparrow) \otimes \uparrow + \uparrow \otimes (\hat{S}_2^2\uparrow) + 2(\hat{S}_z\uparrow) \otimes (\hat{S}_z\uparrow) + (\hat{S}_+\uparrow)^0 \otimes (\hat{S}_-\uparrow) + (\hat{S}_-\uparrow) \otimes (\hat{S}_+\uparrow)^0 \\
&= \frac{3}{4}\hbar^2|\uparrow\uparrow\rangle + \frac{3}{4}\hbar^2|\uparrow\uparrow\rangle + 2 \cdot \frac{1}{4}\hbar^2|\uparrow\uparrow\rangle \\
&= 2\hbar^2|\uparrow\uparrow\rangle
\end{aligned}$$

as required. The same calculation can be performed for the other claimed triple and singlet states.

Example 7.2. For two particles with spin 1 and 1/2 we get 6 possible states; These are beginning with $|3/2, 3/2\rangle = |1, 1\rangle \otimes |1/2, 1/2\rangle$ and each of $|3/2, 1/2\rangle, |3/2, -1/2\rangle, |3/2, -3/2\rangle$ are achieved by successively applying the lowering operator to the first. Finally, we can also achieve a total spin of 1/2 in this system when the particles are aligned anti-parallel to each other. This gives states $|1/2, 1/2\rangle$ and $|1/2, -1/2\rangle$.

These ideas lead to the Clebsch-Gordon coefficient tables which will not be defined in great detail except to say that they can be use to solve the following exercise;

As an exercise, suppose we are given two particles with $(s_1, s_2) = (1, 1/2)$ so that total angular momentum is either $s = 3/2$ or $1/2$ since $s \in \{s_1 + s_2, s_1 + s_2 - 1, \dots, |s_1 - s_2|\}$ so that $m \in \{-3/2, -1/2, 1/2, 3/2\}$. Show that

$$|3/2, 1/2\rangle = \frac{1}{\sqrt{3}}|1, 1\rangle \otimes |1/2, -1/2\rangle + \sqrt{\frac{2}{3}}|1, 0\rangle \otimes |1/2, 1/2\rangle.$$

These Clebsch-Gordon coefficient tables can be used the other way to show that

$$|1, -1\rangle \otimes |1/2, 1/2\rangle = \frac{1}{\sqrt{3}}|3/2, -1/2\rangle - \sqrt{\frac{2}{3}}|1/2, -1/2\rangle.$$

8 Identical particles and the exchange operator

If we had two identical particles at positions $\vec{r}_1$ and $\vec{r}_2$ the the TISE will be $\hat{H}\psi(r_1, r_2) = E\psi(r_1, r_2)$. Since the particle are identical, then the energy will be degenerate with the state $\psi(r_2, r_1)$. That is to say $\hat{H}\psi(r_2, r_1) = E\psi(r_2, r_1)$. We can guess that the good states will be the even and odd linear combinations of these and the operator with distinct eigenvalues will be the exchange operator $\hat{P}_{12}$ which essentially permutes $1 \leftrightarrow 2$. Clearly $P^2 = 1$ has eigenvalues ± 1 and if two particles are identical then $\hat{H}$ must treat $\psi(r_1, r_2)$ the same as $\psi(r_2, r_1)$ so to say $[\hat{H}, \hat{P}] = 0$. Hence, we can find a complete set of functions which are simultaneous eigenstates of both.

The +1 eigenstates $\psi(r_1, r_2) + \psi(r_2, r_1)$ are called symmetric and the other is the anti-symmetric wave function. A general function can be expressed as a combination of the symmetric and anti-symmetric parts.

The Pauli exclusion principle and the vague allusion to quantum statistics suggests that bosons have symmetric wave functions and fermions are anti-symmetric. This is due to the claim that two identical fermions cannot occupy the same space, whereas bosons can... I do not understand this and encourage the reader to investigate this in much greater detail.

Thus we examine three cases of identical particles

1. Distinguishable particles $\psi(r_1, r_2) = \psi_a(r_1)\psi_b(r_2)$
2. identical bosons (symmetric) $\psi(r_1, r_2) = \frac{1}{\sqrt{2}}[\psi_a(r_1)\psi_b(r_2) + \psi_a(r_2)\psi_b(r_1)]$
3. identical fermions (anti-symmetric) $\psi(r_1, r_2) = \frac{1}{\sqrt{2}}[\psi_a(r_1)\psi_b(r_2) - \psi_a(r_2)\psi_b(r_1)]$

We compute probability densities as follows;

$$|\psi(r_1, r_2)|^2 = |\psi_a(r_1)|^2 |\psi_b(r_2)|^2$$

for distinguishable particles and

$$\begin{aligned} |\psi(r_1, r_2)|^2 &= \frac{1}{2} \left(|\psi_a(r_1)|^2 |\psi_b(r_2)|^2 + |\psi_a(r_2)|^2 |\psi_b(r_1)|^2 \pm \psi_a(r_1)\psi_b(r_2)\psi_a^\dagger(r_2)\psi_b^\dagger(r_1) \pm \psi_a^\dagger(r_1)\psi_b^\dagger(r_2)\psi_a(r_2)\psi_b(r_1) \right) \end{aligned}$$

in 2 and 3. We will see the consequences of this are non-intuitive and there is no classical analogue to identical particles.

We compute $\langle (r_1 - r_2)^2 \rangle = \langle \psi | (r_1 - r_2)^2 | \psi \rangle = \langle r_1^2 \rangle + \langle r_2^2 \rangle - 2\langle r_1 r_2 \rangle$;

Distinguishable;

$$\begin{aligned} \langle r_1^2 \rangle &= \int dr_1 \int dr_2 r_1^2 |\psi_a(r_1)|^2 |\psi_b(r_2)|^2 \\ &= \int \psi_a(r_1)^\dagger r_1^2 \psi_a(r_1) dr_1 \cdot \underbrace{\int |\psi_b(r_2)|^2 dr_2}_{=1} \\ &= \langle r_1^2 \rangle_{aa} \end{aligned}$$

and similarly, $\langle r_2^2 \rangle = \langle r_2^2 \rangle_{bb}$ and $\langle r_1 r_2 \rangle = \langle r_1 \rangle_{aa} \langle r_2 \rangle_{bb}$ so

$$\langle (r_1 - r_2)^2 \rangle = \langle r_1^2 \rangle_{aa} + \langle r_2^2 \rangle_{bb} - 2\langle r_1 \rangle_{aa} \langle r_2 \rangle_{bb}.$$

Indistinguishable;

$$\begin{aligned} \langle r_1^2 \rangle &= \frac{1}{2} \left[\int dr_1 r_1^2 |\psi_1(r_1)|^2 \cdot \int dr_2 |\psi_b(r_2)|^2 + \int dr_1 r_1^2 |\psi_b(r_1)|^2 \cdot \int dr_2 |\psi_a(r_2)|^2 \right. \\ &\quad \left. \pm \int dr_1 r_1^2 \psi_a^\dagger(r_1) \psi_b(r_1) \cdot \underbrace{\int dr_2 \psi_b^\dagger(r_2) \psi_a(r_2)}_{=0} \pm \int dr_1 r_1^2 \psi_b^\dagger(r_1) \psi_a(r_1) \cdot \underbrace{\int dr_2 \psi_a^\dagger(r_2) \psi_b(r_2)}_{=0} \right] \\ &= \frac{1}{2} [\langle r_1^2 \rangle_{aa} + \langle r_1^2 \rangle_{bb}] \end{aligned}$$

Similarly, we find $\langle r_2^2 \rangle = \frac{1}{2} (\langle r_2^2 \rangle_{aa} + \langle r_2^2 \rangle_{bb})$ and

$$\begin{aligned} \langle r_1 r_2 \rangle &= \frac{1}{2} (\langle r_1 \rangle_{aa} \langle r_2 \rangle_{bb} + \langle r_2 \rangle_{aa} \langle r_1 \rangle_{bb} \pm \langle r_1 \rangle_{ab} \langle r_2 \rangle_{ba} \pm \langle r_2 \rangle_{ab} \langle r_1 \rangle_{ba}) \\ &= \langle r \rangle_{aa} \langle r \rangle_{bb} \pm |\langle r \rangle_{ab}|^2 \end{aligned}$$

meaning that

$$\langle (r_1 - r_2)^2 \rangle = \langle r^2 \rangle_{aa} + \langle r^2 \rangle_{bb} - 2\langle r \rangle_{aa} \langle r \rangle_{bb} \mp 2|\langle r \rangle_{ab}|^2.$$

This result is nearly identical to the distinguishable particle case except for the term $\mp 2|\langle r \rangle_{ab}|^2$ so let us examine this carefully;

$$\langle r \rangle_{ab} = \int dr \psi_a^\dagger(r) r \psi_b(r)$$

and this is called the overlap or *exchange integral*. This is only important if particles are close enough to each other that their wave function overlaps. The effect of this term is to make $\langle (r_1 - r_2)^2 \rangle$ smaller for bosons and bigger for fermions which is sometimes attributed to a non-existent *exchange force* because it is solely a consequence of the statistics.

There is, of course, one more twist.. spin. That is, the overall state vector, rather than just the spatial part, must be either symmetric or anti-symmetric.

8.1 Solids

For the 1 dimensional infinite square well we have

$$|n\rangle = \sqrt{\frac{2}{\ell}} \sin \frac{n\pi}{\ell} x$$

with energies $E_n = \frac{\hbar^2 k^2}{2m}$ where $k = \frac{n\pi}{\ell}$.

For the 3 dimensional infinite square well we get

$$|n_x, n_y, n_z\rangle = \left(\frac{2}{\ell}\right)^{3/2} \sin\left(\frac{n_x\pi x}{\ell}\right) \sin\left(\frac{n_y\pi y}{\ell}\right) \sin\left(\frac{n_z\pi z}{\ell}\right)$$

by ignoring the coulomb potential and this is called the *free electron model* (a.k.a the *Sommerfeld model*). Here, we have

$$E = E_x + E_y + E_z = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2}{2m} \vec{k}^2$$

where $\vec{k} = \frac{\pi}{\ell}(n_x, n_y, n_z)$.

Examining the grid formed in k -space, the volume of each allowed point⁷ is $\left(\frac{\pi}{\ell}\right)^3 = \frac{\pi}{V}$. Suppose now that our sample contains N atoms where each atom has q electrons (so that N will be the order of Avagadro's number if we have a very small sample) If the electrons were bosons they would all settle down to the ground state ψ_{111} , but in reality electrons are fermions subject to the Pauli exclusion principle meaning that only 2 of them can occupy any given state. They will fill up one octant of the sphere in k -space whose radius is K_f which is determined by the fact that every pair of electrons requires π^3/V amount of volume. Hence,

$$\frac{1}{8} \left(\frac{4}{3} \pi K_f^3 \right) = \frac{Nq}{2} \cdot \frac{\pi^3}{V} \Rightarrow K_f = \left(\frac{3\pi^3 Nq}{V} \right)^{1/3} = (3\pi^2 \rho)^{1/3}$$

where $\rho = \frac{Nq}{V}$ is the *charge density*.

The boundary separating occupied and unoccupied states in k -space is called the *fermi-surface* and the corresponding energy is the *fermi-energy*

$$E_F = \frac{\hbar^2 K_f^2}{2m} = \frac{\hbar^2}{2m} (3\pi^2 \rho)^{2/3}$$

⁷wut?

which evaluates to $\approx 10^4 k$ for a typical metal.

Now, the total energy of the electron gas can be computed as follows;

A shell of thickness dK contained a volume $\frac{1}{8}(4\pi K^2)dK$ so that

$$E_{tot} = \sum_{n_x, n_y, n_z}^{\text{fermi-level}}$$

and this summation more concretely expressed as the sum over all integers $|n_x|, |n_y|, |n_z| \leq K_f$ such that $\frac{\pi}{\ell} \sqrt{n_x^2 + n_y^2 + n_z^2} \leq K_f$ and this summation is approximately expressed as the integral

$$\int_0^{K_f} dK E(\vec{k}) = \frac{\hbar^2 K_f^5 V}{10\pi^2 m} = \frac{\hbar^2 (3\pi^2 Nq)^{5/3}}{10\pi^2 m V^{2/3}}.$$

8.2 Degeneracy pressure

We would like to compute the total energy of a fermi-gas by noting that a shell (in k -space) of thickness dk has a volume $\frac{1}{8}4\pi k^2 dk = \frac{\pi k^2}{2} dk$. This implies that it contains $2 \times \frac{\pi k^2}{2} \frac{dk}{\frac{\pi^3}{V}}$ fermions with energy $E = \frac{\hbar^2 k^2}{2m}$ so the energy of these is $dE = \frac{\hbar^2 k^2}{2m} \cdot \frac{V}{\pi^2} k^2 dk$ and the total energy becomes

$$\frac{\hbar^2 V}{2m} \int_0^{K_f} k^2 dk k^2 = \frac{\hbar^2 V}{10\pi^2 m} \left(\frac{3\pi^2 Nq}{V} \right)^{5/3}$$

and this is interesting if we look at $\frac{dE_{tot}}{dv} = -\frac{2}{3} \frac{E_{tot}}{v} = -\mathbb{P}$ (the pressure). This implies that

$$\mathbb{P} = \frac{(3\pi^2)^{2/3} \hbar^2}{5m} \rho^{5/3}$$

and this is called *degeneracy pressure*.