Quantum Mechanics Review Notes

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Contents

1 Introduction

These notes were compiled from the following classes (plus some self-study topics) during the following semesters to be used as a reference for future courses.

- Physics 731: Quantum Mechanics (Fall 2020) - Basic quantum dynamics, semiclassical approximations, theory of angular momentum, and brief introduction to symmetries.

- Physics 732: Quantum Mechanics (Spring 2021) - Perturbation theory, identical particles, scattering theory, brief discussion of relativistic effects.

The textbooks referenced/used in the courses are below

- Sakurai - Modern Quantum Mechanics

- Shankar - Principles of Quantum Mechanics

2 Fundamental Concepts

2.1 Mathematical Background

For any quantum mechanics problem there are two main components. The state of the system is given by a state vector which evolves according to the Schrodinger equation. The observables that we wish to measure are described by operators which act on the state vector. We start by describing state vectors.

Definition. *A field F is a set of scalars with two operations satisfying the field axioms.*

The most common encountered field is the field of real numbers $\mathbb{R}$, though we will often use the field of complex numbers instead $\mathbb{C}$.

Definition. *A vector space $V(F)$ is a set of vectors $\{\alpha, \beta, \ldots\}$ and a field F with two operations (vector addition and scalar multiplication) satisfying the vector space axioms.*

I omitted the vector space and field axioms because they should be familiar from any prerequisite abstract algebra or linear algebra class. The number of vectors in a vector space can be finite, countably infinite, or uncountably infinite. There are two main ways to indicate that a given quantity is a vector, that is it lies in the vector set. We may draw an arrow (common when handwritten) $\overrightarrow{x}$ or, in the case of more texts, we will simply use a boldface letter $\mathbf{x}$.

Example. The n-dimensional Cartesian vectors are a familiar vector space $V^n(\mathbb{R})$. The n-dimensional complex vectors $V^n(\mathbb{C})$ is often used to describe systems, for instance $V^2(\mathbb{C})$ describes a spin $1/2$ system.

Example. The space of nth order real polynomials where $x \in [A, B]$

$$p(x) = \sum_{i=1}^{n} a_i x^i$$

forms a $(n+1)$-dimensional vector space. As $n \to \infty$ this forms the function space and relate to Hilbert spaces, which are used to describe continuous systems in quantum mechanics.

Dirac notation is a convenient way to express vectors in a vector space, especially in the context on quantum mechanics. If we have some vector space $V^n(F)$, we can represent the vectors using a $n \times 1$ matrix

$$\alpha = (\alpha_1, \alpha_2, \ldots, \alpha_n)^T$$

These vectors can be represented as a ket $\alpha \mapsto |\alpha\rangle$ which obey the standard vector space laws

$$|\alpha\rangle + |\beta\rangle = |\alpha + \beta\rangle \qquad c\,|\alpha\rangle = |c\alpha\rangle$$

For the associated dual space we introduce the bra, which is a $1 \times n$ row vector. The map from vector space to dual space is

$$V^n(F) \to V^{dual}(F) \qquad \alpha \mapsto \alpha^\dagger = (\alpha_1^*, \alpha_2^*, \ldots, \alpha_n^*) = \langle \alpha |$$

While addition is the same, multiplication is different in the dual space

$$\langle \alpha | + \langle \beta | = \langle \alpha + \beta | \qquad c\,\langle \alpha | = \langle c^* \alpha |$$

Definition. *Consider some set of vectors $\{\alpha_1, \ldots, \alpha_n\}$. If there exists coefficients $c_i \neq 0$ such that*

$$c_1 \alpha_1 + \cdots + c_n \alpha_n = 0$$

then this set is said to be linearly dependent, otherwise the set if linearly independent.

Definition. *If the largest set of linearly independent vectors in $V(F)$ has n vectors, then $V(F)$ is n-dimensional and denoted $V^n(F)$.*

The notion of linear independence and dimensionality allows us to formulate the idea of a basis in which all other vectors can be expressed.

Theorem 2.1. Uf $\{\alpha_1, \ldots, \alpha_n\}$ are a linearly independent set of vectors in $V^n(F)$, then any vectors $\alpha \in V^n(F)$ can be uniquely expressed as the sum

$$\alpha = \sum_{i=1}^n c_i \alpha_i = c_1 \alpha_1 + \cdots + c_n \alpha_n$$

In this case the set is called a basis for $V^n(F)$ and the c_i are called the components for α.

In the Cartesian plane, vectors have an idea of length in that we can define the norm of a vector. For instance if $\mathbf{A}, \mathbf{B}$ are two vectors with angle θ between them

$$|\mathbf{A}| = \sqrt{\mathbf{A} \cdot \mathbf{A}} \qquad \mathbf{A} \cdot \mathbf{B} = |\mathbf{A}||\mathbf{B}| \cos \theta$$

To generalize this notion to some arbitrary n-dimensional vector space we want the following to hold for a basis $\{\alpha_i\}$

$$\alpha_i \cdot \alpha_j = \delta_{ij} \quad \text{(orthonormal)}$$

$$\beta = \sum \alpha(\alpha_i \cdot \beta) \quad \text{(completeness)}$$

Here δ_{ij} denotes the Kronecker delta. This defines the inner product

$$\alpha \cdot \beta = \sum \alpha_i \beta_i$$

In general we deal with vector spaces with an inner product.

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Definition. *An inner product space is a vector space with an addition operation* $\langle \alpha | \beta \rangle = c$ *where c is a scalar such that*

1. $\langle \alpha | \alpha \rangle = \begin{cases} c \in \mathbb{R} & \text{if } \alpha \neq 0 \\ 0 & \text{if } \alpha = 0 \end{cases}$

2. $\langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle^*$

3. $\langle \alpha | c_1 \beta + c_2 \gamma \rangle = c_1 \langle \alpha | \beta \rangle + c_2 \langle \alpha | \gamma \rangle$

4. $\langle c_1 \beta + c_2 \gamma | \alpha \rangle = c_1^* \langle \beta | \alpha \rangle + c_2 \langle \gamma | \alpha \rangle$

Using this we can generalize the notion of length.

Definition. *The norm of a vector α in an inner product space is*

$$|\alpha| = \sqrt{\langle \alpha | \alpha \rangle}$$

Example. Consider some n-dimensional space $V^n(F)$ with the inner product

$$\langle \beta | \alpha \rangle = \sum_{i,j=1}^{n} \beta_i M_{ij} \alpha_j = \beta M^T \alpha$$

This is valid only if M is a real symmetric matrix with positive eigenvalues.

Example. For the field of nth order polynomials we can define the inner product

$$\langle P | Q \rangle_F = \int_A^B P(x)^* F(x) Q(x) dx$$

where $F(X)$ is a real and positive weight function.

Definition. *Consider a set $\{\alpha_1, \dots, \alpha_n\}$ in $V^n(F)$ where $m \leq n$. This set is*

- *orthogonal if $\langle \alpha_i | \alpha_j \rangle = 0$ for $i \neq j$*

- *orthonormal if $\langle \alpha_i | \alpha_j \rangle = \delta_{ij}$*

Note that an orthonormal set is just an orthogonal set if the additional requirement that all vectors have unit length. An orthonormal basis will satisfy

1. $\langle i | j \rangle = \delta_{ij}$

2. $\sum_i \langle i | i \rangle = 1$

This allows us to decompose vectors as

$$|\beta\rangle = \left(\sum_i |\alpha_i\rangle \langle \alpha_i| \right) |\beta\rangle = \sum_i |\alpha_i\rangle \langle \alpha_i | \beta \rangle$$

We can also define the projection operator $\Lambda_i = |i\rangle \langle i|$ which projects a state onto its ith component. We can also decompose in the dual space as

$$\langle \beta| = \langle \beta| \left(\sum_i |\alpha_i\rangle \langle \alpha_i| \right) = \sum_i \langle \beta|\alpha_i\rangle \langle \alpha_i|$$

The relevant question to ask now is: Given a set of linearly independent vectors in $V^n(F)$, is it possible to construct an orthonormal basis. In fact we can, using a brute force method called the Gram-Schmidt process.

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How to Gram-Schmidt

Suppose we have a linearly independent set $\{|\beta_1\rangle, \ldots, |\beta_n\rangle\}$. We will first construct an orthogonal set $\{|\alpha_1'\rangle, \ldots, |\alpha_n'\rangle\}$. Start by taking $|\alpha_1'\rangle = |\beta_1\rangle$, orthogonality requires that $\langle \alpha_1'|\alpha_2'\rangle = 0$ so we can take

$$|\alpha_2'\rangle = |\beta_2\rangle - a_1 |\alpha_1'\rangle$$

the coefficient a_1 is given through the orthogonality condition

$$\langle \alpha_1'|\alpha_2'\rangle = \langle \alpha_1'|\beta_2\rangle - a_1 \langle \alpha_1'|\alpha_1'\rangle = 0 \rightarrow a_1 = \frac{\langle \alpha_1'|\beta_2\rangle}{\langle \alpha_1'|\alpha_1'\rangle}$$

Similarly the next term will be

$$|\alpha_3'\rangle = |\beta_3\rangle - \frac{\langle \alpha_2'|\beta_3\rangle}{\langle \alpha_2'|\alpha_2'\rangle} |\alpha_2'\rangle - \frac{\langle \alpha_1'|\beta_3\rangle}{\langle \alpha_1'|\alpha_1'\rangle} |\alpha_1'\rangle$$

Continuing on in this way we can construct

$$|\alpha_j'\rangle = |\beta_j\rangle - \sum_{i=1}^{j-1} |\alpha_i'\rangle \frac{\langle \alpha_i'|\beta_j'\rangle}{\langle \alpha_i'|\alpha_i'\rangle}$$

To make the set fully orthonormal, we can normalize by dividing out the norm

$$|\alpha_i\rangle = \frac{|\alpha_i'\rangle}{\sqrt{\langle \alpha_i'|\alpha_i'\rangle}}$$

The resulting set $\{|\alpha_1\rangle, \ldots, |\alpha_n\rangle\}$ is orthonormal.

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Now that we've adequately discussed vectors, we turn to the other component for any quantum mechanics problem.

Definition. *A linear operator is a map $A : V \rightarrow V$ such that*

$$A(a |\alpha\rangle + b |\beta\rangle) = a |\alpha'\rangle + b |\beta'\rangle$$

where $A |\alpha\rangle = |\alpha'\rangle$. Note that operators act to the right on kets.

Example. There are two trivial operators

$$\mathbb{1}\,|\alpha\rangle = |\alpha\rangle \qquad 0\,|\alpha\rangle = |0\rangle$$

Example. Consider two dimension space $V^2(\mathbb{R})$ and the rotation operator

$$R(\theta)\begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = \begin{pmatrix} a_1\cos\theta - a_2\sin\theta \\ a_1\sin\theta + a_2\cos\theta \end{pmatrix}$$

This is known as the active viewpoint for a rotation where we rotate the actual vector. In the passive viewpoint we rotate the coordinate axis instead.

Generally operators don't commute, that is $AB\,|\alpha\rangle \neq BA\,|\alpha\rangle$. We define the commutator as

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

if the commutator vanishes then the operators commute. Note that the commutator has the following properties

- $[A, B] = -[B, A]$

- $[A, B + C] = [A, B] + [A, C]$

- $[A, BC] = B[A, C] + [A, B]C$

- $[A, [B, C]] + [B, [C, A]] + [C, [A, B]] = 0$

We can also define the anticommutator as

$$\{A, B\} = AB + BA$$

Sometimes an inverse operator may exist, in other words there may exist A^{-1} such that $A^{-1}A = AA^{-1} = 1$. However in general these inverse operators do not exist.

Example. A simple example for where inverses exist is in the case of rotations. If an operator rotates one way the the inverse will simply rotate it back, that is $R^{-1}(\theta) = R(-\theta)$

Given an orthonormal basis it is also possible to express operators in terms of that basis. If A is an operator and $\{|1\rangle, \ldots, |n\rangle\}$ an orthonormal basis then

$$A\,|i\rangle = |i'\rangle = \sum_{j=1}^{n} A_{ji}\,|j\rangle \qquad A_{ji} = \langle j|\,A\,|i\rangle$$

Thus for an arbitrary ket $|\alpha\rangle$

$$A\,|\alpha\rangle = A\sum_{i} |i\rangle\,\langle i|\alpha\rangle = \sum_{i,j} |j\rangle\,A_{ji}\,\underbrace{\langle i|\alpha\rangle}_{a_i}$$

and so we get the relationship between coefficients

$$a'_j = \langle j|\,A\,|\alpha\rangle = \sum A_{ji}a_i$$

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Example. Recall that the rotation operator acts as

$$\begin{pmatrix} a_1' \\ a_2' \end{pmatrix} = \begin{pmatrix} a_1 \cos\theta - a_2 \sin\theta \\ a_1 \sin\theta + a_2 \cos\theta \end{pmatrix}$$

This implies that the matrix form of the rotation operator is

$$R(\theta) = \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix}$$

Indeed this is a familiar 2D rotation matrix.

We previously touched upon the outer product $|i\rangle \langle i|$ where $|i\rangle$ are orthonormal basis elements, this is a projection operator. We can generalize this notion to arbitrary state vectors.

Definition. *The outer product* $|\alpha\rangle \langle\beta|$ *is an operator that acts as*

$$(|\alpha\rangle \langle\beta|) |\gamma\rangle = |\alpha\rangle \langle\beta|\gamma\rangle$$

with matrix representation

$$|\alpha\rangle \langle\beta| = \begin{pmatrix} a_1 b_1^* & a_2 b_1^* & \cdots & a_n b_1^* \\ a_1 b_2^* & a_2 b_2^* & & \\ \vdots & & \ddots & \vdots \\ a_1 b_n^* & & \cdots & a_n b_n^* \end{pmatrix}$$

For an orthonormal basis $\{|i\rangle\}$

$$(|i\rangle \langle j|) |k\rangle = |i\rangle \langle j|k\rangle = |i\rangle \, \delta_{jk}$$

Example. We can use outer products to define the matrix representation of an operator A

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

and in the projection operator

$$\Lambda_i = |i\rangle \langle i| \qquad \Lambda_i |\alpha\rangle = \alpha_i |i\rangle$$

So far we've concerned ourselves with how operators act on kets, but we also should consider how it acts on bras. Since an operator acts to the right on kets, they will act to the left on bras.

Definition. *Given an operator* $A |\alpha\rangle = |A\alpha\rangle$, *the dual is*

$$\langle A\alpha| = \langle\alpha| A^\dagger$$

where $A^\dagger$ *is the Hermitian adjoint defined by*

$$\langle\beta| A^\dagger |\alpha\rangle = \langle\alpha| A |\beta\rangle^*$$

In the matrix representation $A^\dagger = (A^T)^*$ *and for the elements* $A_{ij}^\dagger = A_{ji}^*$.

Note that $(A^\dagger)^\dagger = A$ and $\langle\beta|\, A = \langle A^\dagger\beta|$.

Definition. *An operator is self-adjoint (Hermitian) if $A^\dagger = A$ and it is unitary if $A^\dagger = A^{-1}$*

Hermitian operators will be used to represent observables in quantum mechanics. Since unitary operators preserve inner products, they often represent symmetries in a system.

The matrix representation of the adjoint is

$$A = \sum_{i,j} A_{ij} |i\rangle \langle j| \quad \longleftrightarrow \quad A^\dagger = \sum_{i,j} A_{ji}^* |i\rangle \langle j|$$

Furthermore the adjoint has two useful properties

$$(AB)^\dagger = A^\dagger B^\dagger \qquad (cA)^\dagger = c^* A^\dagger$$

Definition. *Given an operator A, a vector $|\omega\rangle$ is an eigenvector if*

$$A |\omega\rangle = \omega |\omega\rangle$$

Then we say that $|\omega\rangle$ is an eigenvector of A with eigenvalue ω. There may be multiple eigenvectors per eigenvalue, this is called degeneracy.

Eigenvalues can be found as by solving the characteristic equation for ω

$$\det(A - \omega I) = 0$$

Eigenvalues and eigenvectors for Hermitian operators have special properties, namely

1. Eigenvectors corresponding to different eigenvalues are orthogonal

2. Eigenvalues are real

For a Hermitian operator A acting on $V^n(F)$ there are n linearly independent eigenvectors, however there may not be n distinct eigenvalues. These properties make it so that the set of eigenvectors for A form an orthogonal basis. We can diagonalize A using a unitary matrix U which contains the normalized eigenvectors as its columns, the ordering is arbitrary.

$$U^\dagger A U = A_{diag} \qquad U = \begin{pmatrix} | & | & & | \\ \omega_1 & \omega_2 & \cdots & \omega_n \\ | & | & & | \end{pmatrix}$$

The only issue with this process occurs in the case of degeneracy, we can work around this by constructing an orthonormal basis spanning the degenerate subspace. Generally we will normalize vectors so that the set of eigenvectors form an orthonormal basis, degenerate eigenvectors will be required to satisfy orthonormality.

Example. Consider an operator A with matrix representation

$$A = \begin{pmatrix} 5 & 0 & 2 \\ 0 & 1 & 0 \\ 2 & 0 & 2 \end{pmatrix}$$

which has the characteristic equation

$$\det(A - \omega I) = (1 - \omega)^2(6 - \omega) = 0$$

The eigenvalues are thus 1 with degeneracy 2 and 6. The corresponding (normalized) eigenvectors are

$$|\omega_1\rangle = \frac{1}{\sqrt{5}} \begin{pmatrix} 2 \\ 0 \\ 1 \end{pmatrix} \quad |\omega_2\rangle = \frac{1}{\sqrt{5}} \begin{pmatrix} 1 \\ 0 \\ -2 \end{pmatrix} \quad |\omega_3\rangle = 2 \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$$

Note that these are complete, that is $\sum |\omega_i\rangle \langle \omega_i| = 1$. The diagonalizing matrix is

$$U = \begin{pmatrix} \frac{2}{\sqrt{5}} & \frac{1}{\sqrt{5}} & 0 \\ 0 & 0 & 2 \\ \frac{1}{\sqrt{5}} & -\frac{2}{\sqrt{5}} & 0 \end{pmatrix}$$

We can also express a Hermitian operator A in terms of its eigenvectors, since they form an complete basis we can write

$$A = \left(\sum_i |\omega_i\rangle \langle \omega_i| \right) A \left(\sum_j |\omega_j\rangle \langle \omega_j| \right) = \sum_i \omega_i |\omega_i\rangle \langle \omega_i| = \sum_i \omega_i \Lambda_i$$

This is called the spectral representation of an operator which implies that an operator is the sum of it eigenvalues times the projection operator onto the associated eigenstate. This representation is useful because we can define functions of an operator, for instance the inverse is

$$A^{-1} = \sum_i \omega_i^{-1} \Lambda_i$$

and we see that inverse operators exist only if zero is not an eigenvalue. We can also define exponentials of an operator

$$e^A = 1 + A + \frac{A^2}{2} + \cdots = \sum_{m=0}^{\infty} \frac{A^m}{m!} = \sum_i e^{\omega_i} \Lambda_i$$

In fact for any function f, we can define the operator

$$f(A) = \sum_i f(\omega_i) \Lambda_i$$

This property is called the spectral representation theorem.

2.2 Postulates of Quantum Mechanics

In classical mechanics, a particular can be precisely described by it's position and momentum. Its trajectory over time is given by Hamilton's equations

$$\dot{x} = \frac{\partial H}{\partial p} \qquad \dot{p} = \frac{\partial H}{\partial x}$$

where $H = H(x, p)$ is the Hamiltonian of the system.

The first postulate of quantum mechanics is that every quantum state can be described by a state vector in a Hilbert space $|\alpha\rangle$. The sixth postulate of quantum mechanics states that in the Schrodinger picture, state vectors evolve in time according to the time-dependent Schrodinger equation.

$$|\alpha\rangle \to |\alpha(t)\rangle \qquad H |\alpha(t)\rangle = i\hbar \frac{\partial}{\partial t} |\alpha(t)\rangle$$

The second postulate states that every measurable observable corresponds to a Hermitian operator, Furthermore the third postulate states that the results of measuring an observable are the eigenvalues of its corresponding operator. In other words if we have some Hermitian operator A with eigenvectors $\{|a_i\rangle\}$ such that $A |a_i\rangle = a_i$, then for some arbitrary state $|\alpha\rangle$

- Measuring A yields one of the a_i's with probability $|\langle a_i | \alpha \rangle|^2$, this is the fourth postulate.

- If measuring A yields an eigenvalue a_i, then the system is changed by the measurement into the state $|a_i\rangle$. This is known as the Copenhagen interpretation or "wavefunction collapse" and is usually included as the fifth postulate.

- In the case of degeneracy the state is collapsed into the associated degenerate subspace rather than a single vector.

Let's expand on the issue of degeneracy some more. Suppose that A has a generate eigenvalue

$$A |a_{11}\rangle = a_1 |a_{11}\rangle \qquad A |a_{12}\rangle = a_1 |a_{12}\rangle$$

Then we can write any arbitrary state as

$$|\alpha\rangle = |a_{11}\rangle \langle a_{11} | \alpha \rangle + |a_{12}\rangle \langle a_{12} | \alpha \rangle + \cdots$$

The probability of measuring a_1 is $|\langle a_{11} | \alpha \rangle|^2 + |\langle a_{12} | \alpha \rangle|^2$ and in this case the state will collapse to

$$|\alpha\rangle = \frac{|a_{11}\rangle \langle a_{11} | \alpha \rangle + |a_{12}\rangle \langle a_{12} | \alpha \rangle}{\sqrt{|\langle a_{11} | \alpha \rangle|^2 + |\langle a_{12} | \alpha \rangle|^2}}$$

which we see is just the first two terms normalized.

Definition. *The expectation value of an operator A with respect to a state $|\alpha\rangle$ is*

$$\langle A \rangle_\alpha = \langle \alpha | A | \alpha \rangle = \sum_i a_i |\langle a_i | \alpha \rangle|^2$$

Note that this is the sum of all possible eigenvalues of A weighted by the probability of measuring them which is the same definition as a classical expectation value in statistics. Another reason we use Hermitian operators is because they will always have real expectation values.

Spin 1/2 Particles

This space is given by $V^2(\mathbb{C})$ and the states are called spinors.

$$|\alpha\rangle = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \qquad c_i \in \mathbb{C}$$

There are three spin operators, given by

$$S_i = \frac{\hbar}{2}\sigma_i$$

where the σ_i are the Pauli matrices. The indices are sometimes given by $i = \{1, 2, 3\}$ or given a physical meaning with $i = \{x, y, z\}$, we will use the latter. In this case we can refer to spin in the x, y, or z direction. The Pauli matrices are

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

The eigenvalues for all three operators are $\pm\hbar/2$ with eigenvectors

$$|\pm\rangle_x = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm 1 \end{pmatrix} \qquad |\pm\rangle_y = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm i \end{pmatrix} \quad |+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad |-\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

the subscripts are generally omitted for $|\pm\rangle_z$ which are taken to be the basis. Thus

$$|\pm\rangle_x = \frac{1}{\sqrt{2}}(|+\rangle \pm |-\rangle) \qquad |\pm\rangle_y = \frac{1}{\sqrt{2}}(|+\rangle \pm i|-\rangle)$$

The spectral representations for each operator are

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

To illustrate how probabilities can be unintuitive in quantum mechanics suppose we have an initial state $|\alpha\rangle = |+\rangle_x$. Suppose we measure this state's spin in the z direction, the possible results are $\pm\hbar/2$ with probability $1/2$. If we measure $+\hbar/2$ then the state is collapsed into $|+\rangle$. If we measure S_x again then we find that the possible outcomes

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are $\pm\hbar/2$ with probability $1/2$. Thus the state has somehow "forgotten" it's original configuration of $|+\rangle_x$.

It's generally useful in spin problems to define the raising and lowering (ladder) operators

$$S_+ = S_x + iS_y = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \qquad S_+ = S_x - iS_y = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

These operators act on the eigenstates according to

$$\begin{cases} S_+ |+\rangle = 0 \\ S_+ |-\rangle = |+\rangle \end{cases} \qquad \begin{cases} S_- |+\rangle = |-\rangle \\ S_- |-\rangle = 0 \end{cases}$$

these relations explain the name "ladder" operators. These will be generalized and applied to understand angular momentum in quantum mechanics. Returning to the standard spin operators, these satisfy the commutation relations

$$[S_x, S_y] = i\hbar S_z \qquad [S_i, S_j] = i\hbar \epsilon_{ijk} S_k$$

where ϵ is the Levi-Civita symbol. The anticommutator is

$$\{S_i, S_j\} = \frac{1}{2}\hbar^2 \delta_{ij} \mathbb{1}$$

The total spin operator is also useful and is defined as

$$S^2 = S \cdot S = \sum_i S_i^2 = \frac{3}{4}\hbar^2 \mathbb{1}$$

which commutes with all spin operators $[S^2, S_i] = 0$.

Definition. *Two operators are compatible if they commute, otherwise they are incompatible.*

Often when considering a system with multiple quantities of interest we will speak of compatible or incompatible observables/quantities. We've seen that measuring S_x will interfere with a measurement of S_z, this does not happen for compatible quantities. If A, B are compatible operators then it is possible to find a set of mutual eigenstates of both A and B.

This is particularly important in the case of degeneracy as diagonalizing a compatible operators allows us to label each state using a combination of eigenvalues from both operators, thus breaking degeneracy. Such a set is called a maximal or complete set of operators.

For an observable A with eigenstates $A |a_i\rangle = a_i |a_i\rangle$ acting on some state $|\alpha\rangle$, we can define the uncertainty as the operator

$$\Delta A = A - \langle A \rangle \mathbb{1}$$

Definition. *The dispersion (or variance) of A is*

$$\langle (\Delta A)^2 \rangle = \langle A^2 \rangle - \langle A \rangle^2 = \sum_i a_i^2 |\langle a_i | \alpha \rangle|^2 - \left(\sum_i a_i |\langle a_i | \alpha \rangle|^2 \right)^2$$

Note that the dispersion of an operator with respect to one of its eigenstates is zero. Using this definition the uncertainty relation for two operators is

$$\langle (\Delta A)^2 \rangle \langle (\Delta B)^2 \rangle \geq \frac{1}{4} |\langle [A, B] \rangle|^2$$

Thus for compatible operators it is possible to find states in which the dispersion for both operators is arbitrarily small, but there is a lower bound for incompatible operators.

We discussed earlier a matrix that changes between bases, in particular to the basis of eigenvectors. The operator analogue is

$$U = \sum_i |b_i\rangle \langle a_i|$$

where $\{|a_i\rangle\}$ is the source basis and $\{|b_i\rangle\}$ is the target basis. This works because $|b_i\rangle = U |a_i\rangle$ and $|a_i\rangle = U^\dagger |b_i\rangle$. For a general state $|\alpha\rangle$ such that

$$|\alpha\rangle = \sum c_i |a_i\rangle = \sum d_i |b_i\rangle$$

where $c_i = \langle a_i | \alpha \rangle$ and $d_i = \langle b_i | \alpha \rangle$, the coefficients are related by

$$d_j = \sum_i (U^\dagger)_{ji} c_i$$

We can do the same for a matrix representation of an operator X,

$$X'_{ij} = \langle b_i | X | b_j \rangle = (U^\dagger X U)_{ij}$$

2.3   Position and Momentum Space

We've already discussed the spin $1/2$ system which is an example of a finite system, specifically it consists of only two states. For continuous systems in quantum mechanics we turn to function spaces, which can be considered as infinite dimensional vector spaces for which vectors are normalizable (this imposes some convergence conditions on the functions). These spaces are traditionally called Hilbert spaces though we have been using this term for finite dimensional spaces as well.

Consider the set of complex functions of a real variable $x \in [a, b]$. The space of these functions which are square integrable with respect to a weight function $w(x)$ is denoted $L_w^2(a, b)$ and has an inner product

$$\langle f | g \rangle_w = \int_a^b f^*(x) g(x) w(x) dx$$

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If $|i\rangle = |f_i\rangle$ is an orthonormal basis, then

$$\langle i|j\rangle_w = \int_a^b f_i^*(x) f_j(x) w(x) dx \qquad \sum_{i=1}^\infty |i\rangle \langle i| = \mathbb{1}$$

For any function $f \in L_w^2(a, b)$ we can write it as

$$|f\rangle = \sum_{i=1}^\infty |i\rangle \langle i|f\rangle = \sum_{i=1}^\infty |i\rangle \alpha_i$$

where the coefficients are

$$\alpha_i = \int_a^b f_i^*(x) f(x) w(x) dx$$

The operators in this space map on vector to another

$$L |f\rangle = |Lf\rangle = |g\rangle$$

These are called linear differential operators and must satisfy boundary conditions. We've loosely defined $f(x) = \langle x|f\rangle$, this convention will be discussed later.

Definition. *An operator L is self-adjoint if $\langle f|Lg\rangle_w = \langle Lf|g\rangle_w$ for all functions f, g.*

We will generally only consider cases where $w(x) = 1$, which will be the default weight function unless otherwise specified.

Example. Consider the operator $L = -iD$ where D is defined as

$$\langle x| D |f\rangle = \langle x|Df\rangle = \frac{d}{dx} \langle x|f\rangle = \frac{d}{dx} f(x)$$

We see that

$$\langle f|Lg\rangle = \int_a^b -i f^*(x) \frac{dg}{dx} dx$$
$$= \int_a^b \left(-i \frac{df}{dx} \right)^* g(x) dx - i f^* g|_a^b$$
$$= \langle Lf|g\rangle - i f^* g|_a^b$$

Thus L is self-adjoint only if $i f^* g|_a^b = 0$ (i.e. functions vanish at endpoints or are periodic).

The eigenvalue problem in a continuous system can be stated as follows: Given a linear differential operator L and specified boundary conditions, we wish to find λ and f_λ such that

$$L |f_\lambda\rangle = \lambda |f_\lambda\rangle$$

Usually there will be a continuum of solutions which will become discrete once boundary conditions are imposed (for instance bound states are quantized). Just like in the finite case, the $|f_\lambda\rangle$ will form a complete orthonormal basis for the space $L_w^2(a, b)$.

Example. Some useful examples include:

- The inverval $[-1, 1]$, operator $L = -(1 - x^2)\frac{d^2}{dx^2} + 2x\frac{d}{dx}$ with the condition that $f(\pm 1)$ be finite. This gives the solutions

$$\lambda = n(n+1) \qquad |f_n\rangle = \sqrt{\frac{2n+1}{2}} P_n(x)$$

  where P_n are the Legendre polynomials.

- The inverval $[-\infty, \infty]$, operator $L = -\frac{d^2}{dx^2} + x^2$ with the condition that $f(\pm\infty)$ be finite. This gives the solutions

$$\lambda = 2n+1 \qquad |f_n\rangle = 2^{-n/2}\pi^{-1/4}(n!)^{-1/2}e^{-x^2/2}H_n(x)$$

  where H_n are the Hermite polynomials.

Definition. *A proper basis is one in which eigenvectors are in the Hilbert space. An improper basis will contain vectors which are not normalizable in the usual sense.*

The previous examples are examples of proper bases. We will see that the eigenstates of the position operator x and momentum operator p form an improper basis.

Consider the 1D position operator x_{op} (the subscript is only temporary, we will drop it later when it's clear we are referring to the operator). The eigenvalue equation takes the form

$$x_{op}|x'\rangle = x'|x'\rangle$$

We require that $\langle x|x'\rangle = x'(x) = 0$ for all $x \neq x'$ and $\int_{-\infty}^{\infty} |x'(x)|^2 dx = 1$. There are no conventional functions with these properties but this does define the dirac delta function $\delta(x - x')$, which are indeed the eigenstates of position. These states are definitely not normalizable but they are complete

$$\int_{-\infty}^{\infty} dx \, |x\rangle \langle x| = \mathbb{1}$$

Defining $\langle x|f\rangle = f(x)$ we now have the inner product

$$\langle f|g\rangle = \int dx \, \langle f|x\rangle \langle x|g\rangle = \int f^*(x)g(x)dx$$

The Delta Function

The defining relation of the delta function is how it behaves over an integral

$$\int_{-\infty}^{\infty} f(x')\delta(x - x')dx' = f(x)$$

The derivative of the delta functions satisfies

$$\delta'(x - x') = \frac{d}{dx}\delta(x - x') = \frac{d}{dx'}\delta(x - x') \qquad \int_{-\infty}^{\infty} f(x')\delta'(x - x')dx' = f'(x)$$

Some other useful properties of the delta function are

$$\int_{-\infty}^{\infty} f(x')\delta(cx')dx' = \frac{1}{|c|}f(0) \to \delta(cx) = \frac{\delta(x)}{|c|}$$

If f is a function such that $f(x_i) = 0$ then

$$\delta(f(x)) = \sum_i \frac{1}{|f'(x_i)|}\delta(x - x_i)$$

Although not technically a function, it is useful to have explicit characterizations of the delta function in order to recognize it in integrals. The canonical way to define a delta function is through limits

$$\delta(x) = \frac{1}{\pi}\lim_{\epsilon \to 0}\frac{\epsilon}{x^2 + \epsilon^2}$$

For our purposes we also sometimes use the integral definition

$$\delta(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{ipx}dp$$

Example. The matrix elements of $L = -iD$ discussed earlier is

$$\langle x| L |x'\rangle = -i\delta'(x - x') = \langle x'| L |x\rangle^*$$

Returning to the position operator, we can expand any state as

$$|\psi\rangle = \int_{-\infty}^{\infty} dx\, |x\rangle \langle x|\psi\rangle = \int_{-\infty}^{\infty} dx\, |x\rangle\, \psi(x)$$

This is simple to the discrete case except we now have an integral. The matrix elements of x are

$$\langle x| x |x'\rangle = x'\delta(x - x') \qquad \langle x| f(x) |x'\rangle = f(x')\delta(x - x')$$

If we measure $x \pm \Delta/2$ (i.e. we measured x with resolution Δ), the state collapses to

$$\int_{x-\Delta/2}^{x+\Delta/2} dx'\, |x'\rangle\, \psi(x')$$

The probability of measuring this is $|\langle x|\psi\rangle|^2\Delta$. This of course assumes that this quantity does not change within the range Δ. In practice we aren't so lucky and we must integrate. The probability of locating a particle in a range $[a, b]$ is given by

$$P = \int_a^b |\langle x|\psi\rangle|^2 dx = \int_a^b |\psi(x)|^2 dx$$

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and so $\psi(x)$ is just a probability density for the particle. Since the particle must exist somewhere, the normalization condition is

$$\int_{-\infty}^{\infty} dx' |\langle x'|\alpha \rangle|^2 = 1$$

The momentum operator is given by $p = -i\hbar\frac{d}{dx} = i - \hbar D$. Eigenstates will satisfy

$$p_{op}|p'\rangle = p'|p'\rangle$$

We also have the relation between position and momentum eigenstates

$$\langle x|p|p'\rangle = -i\hbar\frac{d}{dx}\langle x|p'\rangle = p'\langle x|p'\rangle$$

This gives the form of the wavefunction

$$\langle x|p\rangle = \phi_p(x) = Ne^{ikx} \qquad k = \frac{p}{\hbar}$$

where N is some normalization constant

$$\langle p|p'\rangle = \delta(p - p') = N^2 \int_{-\infty}^{\infty} \exp\left(\frac{e(p'-p)x}{\hbar}\right)dx = 2\pi\delta\left(\frac{p'-p}{\hbar}\right)$$

this implies that the normalization constant is

$$N = \frac{1}{\sqrt{2\pi\hbar}} \rightarrow \langle x|p\rangle = \phi_p(x) = \frac{1}{\sqrt{2\pi\hbar}}\exp\left(\frac{ipx}{\hbar}\right)$$

Note that these states form a complete orthonormal basis.

We can expand any state in terms of both position and momentum eigenstates

$$|\alpha\rangle = \int |x\rangle\,\psi_\alpha(x)dx = \int |p\rangle\,\phi_\alpha(p)dp$$

The two wavefunctions are related by a Fourier transform.

$$\psi_\alpha(x) = \frac{1}{\sqrt{2\pi\hbar}}\int \exp\left(\frac{ipx}{\hbar}\right)\phi_\alpha(p)dp$$

$$\phi_\alpha(p) = \frac{1}{\sqrt{2\pi\hbar}}\int \exp\left(-\frac{ipx}{\hbar}\right)\psi_\alpha(x)dx$$

So far we've been only working in 1 dimension, the generalization to three dimensions is fairly straightforward.

$$\langle \mathbf{x}|\mathbf{x'}\rangle = \delta^3(\mathbf{x} - \mathbf{x'})$$
$$\langle \mathbf{p}|\mathbf{p'}\rangle = \delta^3(\mathbf{p} - \mathbf{p'})$$
$$\langle \mathbf{x}|\mathbf{p}\rangle = \frac{1}{(2\pi\hbar)^{3/2}}\exp\left(\frac{i\mathbf{p}\cdot\mathbf{x}}{\hbar}\right)$$

These operators have the commutation relations, called the canonical commutation relations

$$[x_i, x_j] = 0 \qquad [p_i, p_j] = 0 \qquad [x_i, p_j] = i\hbar\delta_{ij}$$

A useful operator to consider which acts on position and momentum space is the translation operator. For some Cartesian vector $\mathbf{a}$ define

$$T(\mathbf{a}) = \exp\left(-\frac{i\mathbf{p}\cdot\mathbf{a}}{\hbar}\right) = \sum_{n=0}^{\infty} \frac{1}{n!}\left(-\frac{i\mathbf{p}\cdot\mathbf{a}}{\hbar}\right)^n$$

Note that this satisfies $T(-\mathbf{a}) = T(\mathbf{a})^{-1}$.

As an aside for operator exponentials it is generally not true that $e^A e^B = e^{A+B}$. This is only true if $[A, B] = 0$, otherwise

$$e^A e^B = e^A e^B e^{[A,B]/2}$$

Let's act on a momentum state with a translate, i.e. let's translate the particle by some vector $\mathbf{a}$.

$$T(\mathbf{a})\ket{\mathbf{p}} = \exp\left(-\frac{i\mathbf{p}\cdot\mathbf{a}}{\hbar}\right)\ket{\mathbf{p}}$$

Thus the momentum eignestates are also eigenstates of the translation operator. When acting on the position state however, we find

$$
\begin{aligned}
T(\mathbf{a})\ket{\mathbf{x}} &= \int d^3 T(\mathbf{a})\ket{\mathbf{p}}\braket{\mathbf{p}|\mathbf{x}} \\
&= \int d^3 p \exp\left(-\frac{i\mathbf{p}\cdot\mathbf{a}}{\hbar}\right)\ket{\mathbf{p}}\exp\left(-\frac{i\mathbf{p}\cdot\mathbf{x}}{\hbar}\right)\frac{1}{(2\pi\hbar)^{3/2}} \\
&= \int d^3 p \frac{1}{(2\pi\hbar)^{3/2}}\exp\left(-\frac{i\mathbf{p}\cdot(\mathbf{x}+\mathbf{a})}{\hbar}\right)\ket{\mathbf{p}} \\
&= \int d^3 p \ket{\mathbf{p}}\braket{\mathbf{p}|\mathbf{x}+\mathbf{a}} \\
&= \ket{\mathbf{x}+\mathbf{a}}
\end{aligned}
$$

All of this makes sense because a translation should translate the position state by some vector but this shouldn't affect momentum in any way. Suppose we take $\mathbf{a} \to \delta$ and consider an infinitesimal translation

$$T(\mathbf{a}) \to 1 - \frac{i\mathbf{p}\cdot\delta}{\hbar} + O(\delta^2)$$

Upon discarding higher order terms, we see that the momentum operator $\mathbf{p}$ generates translations. For finite translations, the operators commute

$$T(\mathbf{a})T(\mathbf{b}) = T(\mathbf{b})T(\mathbf{a}) = T(\mathbf{a}+\mathbf{b})$$

which mean the set of translations $\{T(\mathbf{a})\}$ form a Lie group. The associated commutation relations form the associated Lie algebra.

Gaussian Wavepackets
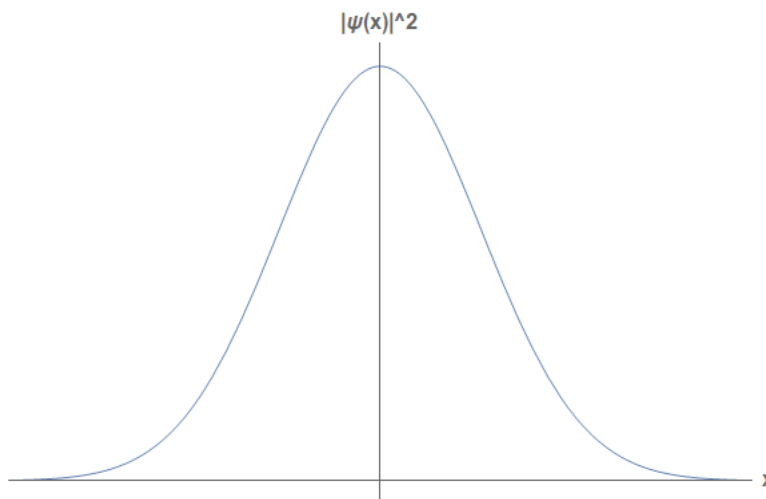
A 1D Gaussian wavepacket is given by the state

$$\psi_\alpha(x) = \langle x|\alpha\rangle = \frac{1}{\pi^{1/4}\sqrt{d}}\exp\left(ikx - \frac{x^2}{2d^2}\right)$$

We define $k = p/\hbar$ and d can be thought of as the length of the packet. Note that this state is already normalized, the probability density and expectation values are given by

$$|\psi_\alpha(x)|^2 = |\langle x|\alpha\rangle|^2 = \frac{1}{d\sqrt{\pi}}\exp\left(-\frac{x^2}{d^2}\right)$$

$$\langle x\rangle = \langle\alpha|\,x\,|\alpha\rangle = 0$$

$$\langle x^2\rangle = \langle\alpha|\,x^2\,|\alpha\rangle = \frac{d^2}{2}$$

These integrals are evaluated by recalling the Gaussian integral

$$\int_{-\infty}^{\infty} e^{-ax^2}dx = \sqrt{\frac{\pi}{a}}$$

through substitutions or derivatives we can evaluate most integrals of a Gaussian, for instance our integral is of the form

$$\int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} = -\frac{d}{da}\int_{\infty}^{\infty} e^{-\alpha x^2} = \frac{1}{2a}\sqrt{\frac{\pi}{a}}$$

This approach applies for all even powers of x, the odd powers will vanish by symmetry.

Returning back to the wavepacket, expected momenta are

$$\langle p \rangle = \int dx \psi_\alpha^*(x) - i\hbar \frac{d}{dx} \psi_\alpha(x) = \hbar k$$

$$\langle p^2 \rangle = \frac{\hbar^2}{2d^2} + \hbar^2 k^2$$

Thus the position and momentum uncertainties are

$$\langle (\Delta x)^2 \rangle = \frac{d^2}{2} \qquad \langle (\Delta p)^2 \rangle = \frac{\hbar^2}{2d^2}$$

The importance of using wavepackets become apparent when we calculate the uncertainty product

$$\langle (\Delta x)^2 \rangle \langle (\Delta p)^2 \rangle = \frac{\hbar^2}{4} = \frac{1}{4} |\langle [x, p] \rangle|^2$$

Our uncertainty product is independent of d so we will have equality in the uncertainty relation. The Gaussian wavepacket is often called a minimum uncertainty wavepacket because of this. For completeness we will also give the momentum state for a wavepacket

$$\phi_\alpha(p) = \langle p | \alpha \rangle = \sqrt{\frac{d}{\hbar \sqrt{\pi}}} \exp\left(-\frac{(p - \hbar k)^2 d^2}{2\hbar^2} \right)$$

Example. To better familiarize ourselves with how position/momentum states interact, let's calculate the expectation value $\langle x | [x, p] | \alpha \rangle$

$$\langle x | xp | \alpha \rangle = \int \langle x | x | x' \rangle \langle x' | p | p \rangle \langle p | x'' \rangle \langle x'' | \alpha \rangle \, dx' dx'' dp$$

$$= \int x' \delta(x - x') \left(-\frac{i\hbar}{2\pi\hbar} \frac{d}{dx'} e^{ipx'/\hbar} \right) e^{-ipx''/\hbar} \psi_\alpha(x'') dx' dx'' dp$$

$$= -\frac{ix}{2\pi} \frac{d}{dx} \int \exp\left(ip\frac{x - x''}{\hbar} \right) \psi_\alpha(x'') dx'' dp$$

$$= -i\hbar x \frac{d}{dx} \int \delta(x - x'') \psi_\alpha(x'') dx''$$

$$= -i\hbar x \frac{d}{dx} \psi_\alpha(x)$$

$$\langle x | px | \alpha \rangle = \int \langle x | p | p \rangle \langle p | x' \rangle \langle x' | x | x'' \rangle \langle x'' | \alpha \rangle \, dx' dx'' dp$$

$$= \frac{-i\hbar}{2\pi\hbar} \frac{d}{dx} \int \exp\left(ip\frac{x - x'}{\hbar} \right) x'' \delta(x' - x'') \psi_\alpha(x'') dx' dx'' dp$$

$$= -i\frac{d}{dx} \int \hbar \delta(x - x') x' \psi_\alpha(x') dx'$$

$$= -i\hbar \frac{d}{dx} (x \psi_\alpha(x))$$

$$\therefore \langle x | [x, p] | \alpha \rangle = \langle x | xp | \alpha \rangle - \langle x | px | \alpha \rangle = i\hbar \psi_\alpha(x)$$

2.4 Energy Eigenvalue Problems

The first step for any quantum mechanics problem is usually solving a given potential to get energy eigenstates. Suppose we have a Hamiltonian

$$H = \frac{p^2}{2m} + V(x) \qquad H \left| n \right\rangle = E_n \left| n \right\rangle$$

which will be done in position space for convenience. The corresponding wavefunctions will satisfy the Schrodinger equation

$$\left\langle x \right| H \left| n \right\rangle = E_n \left\langle x | n \right\rangle = E_n \psi_n(x)$$
$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right) \psi_n(x) = E_n \psi_n(x)$$

Depending on the form of the potential $V(x)$, solutions will fall into two categories

- Bound states where $E < V(\infty)$ are discrete and normalizable

- Scattering state where $E > V(\infty)$ are continuous and thus must be normalized with a delta function.

This chapter is dedicated to solving common problems found in quantum mechanics. We can expect to see some of these wavefunctions again later.

2.4.1 Free Particles

For a free particle, $V(x) = 0$, again we define $k = p/\hbar$

$$H = \frac{p^2}{2m} \qquad \psi_k(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ikx} \qquad E_k = \frac{\hbar^2 k^2}{2m}$$

Since these states are unbound, we cannot normalize them in the traditional way. Instead they can be delta function normalized

$$\int \psi_{k'}^*(x) \psi_k(x) dx = \delta(k - k')$$

It's possible to make free particle states "proper" using box normalization. This involves considering the particle on a box (of 1D or more) of length(s) L and then imposing period boundary conditions. This gives sufficient normalization and we can take $L \to \infty$ (though generally L drops out of the calculations so simply $L = 1$ is sometimes used).

2.4.2 The Infinite Square Well

The infinite square well is given by an infinite potential "wall" on either side, it's sometimes called a particle in a box for obvious reasons.

$$V(x) = \begin{cases} 0 & |x| < a \\ \infty & \text{otherwise} \end{cases}$$

Since the particle obviously can't tunnel out of an infinite box and furthermore the wavefunction must be continuous, we get boundary conditions

$$\psi(\pm a) = 0 \qquad \psi(|x| > a) = 0$$

For the wavefunction inside the box we have no limitations, thus we will go ahead and assume a free particle solution. We can't make any assumptions so we will include free particles in both plus and minus x. This can be written in two ways as follows

$$\psi_k(x) = Ae^{ikx} + Be^{-ikx}$$
$$= A\cos(kx) + B\sin(kx)$$

The boundary conditions permits two classes of solutions depending on whether we choose $A = 0$ or $B = 0$.

- If $A = 0$, then we have odd parity states (n even)

$$\psi_n(x) = \frac{1}{\sqrt{a}}\sin\left(\frac{n\pi x}{2a}\right)$$

- If $B = 0$, then we have even parity states (n odd)

$$\psi_n(x) = \frac{1}{\sqrt{a}}\cos\left(\frac{n\pi x}{2a}\right)$$

In both cases there are conditions on what values k can take

$$k = \frac{n\pi}{2a} \quad \longrightarrow \quad E_n = \frac{\hbar^2 k^2}{2m} = \frac{n^2\pi^2\hbar^2}{8ma^2}$$

2.4.3 The Finite Square Well

A much more involved example involves removing the condition that the walls be infinite. Having finite walls introduces the problem of quantum tunnelling, meaning that the wavefunction isn't required to be zero at the walls. The potential for the finite square wall (or finite box) is

$$V = \begin{cases} 0 & |x| < a \\ V_0 & \text{otherwise} \end{cases}$$

We are interested in obtaining the bound states $E < V_0$ for this potential, if $E > V_0$ then the particle will scatter off the potential. The boundary conditions for this problem are that the wavefunction and its first derivative be continuous across the boundary. We consider three different regions in this problem, region I before the well, region II in the well, and region III after. The wavefunction must satisfy Schrodinger's equation in each region

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V(x))\psi = 0$$

Similar to how we proceeded in the infinite well, $V = 0$ in region II and so we take the wavefunction to have the form

$$\psi_{II}(x) = A\cos(kx) + B\sin(kx)$$

On regions I and III, we take

$$\psi_I(x) = Ce^{-\kappa x} + De^{\kappa x}$$
$$\psi_{III}(x) = Fe^{-\kappa x} + Ge^{\kappa x}$$

where we've defined two constants

$$k = \sqrt{\frac{2mE}{\hbar}} \qquad \kappa = \sqrt{\frac{2m}{\hbar^2}(V_0 - E)}$$

In order for the wavefunction to be normalizable, we require that it be square integrable over all space. For our ansatz, this implies $C = G = 0$. Since our potential is even, we can assume without loss of generality that our wavefunction is either even or odd. Let's consider just the even case for now, though the odd parity solution proceeds similarly. First $\psi(x) = \psi(-x)$ implies

$$\psi(x) = \begin{cases} De^{\kappa x} & x < -a \\ A\cos(kx) & -a < x < a \\ De^{-\kappa x} & x < a \end{cases}$$

The advantage of considering parity solutions is that satisfying a boundary condition at $x = a$ automatically solves the condition at $x = -a$. We can build continuity into our solution by setting

$$\psi(x) = \begin{cases} Ae^{-\kappa|x|}\cos(ka) & |x| > a \\ Ae^{-\kappa a}\cos(kx) & -a < x < a \end{cases}$$

Thus the continuity of the first derivative gives the final condition

$$-Ae^{-\kappa a}k\sin(ka) = -\kappa Ae^{-\kappa a}\cos(ka)$$
$$\therefore (ka)\tan(ka) = \kappa a$$

Let's define two new variables

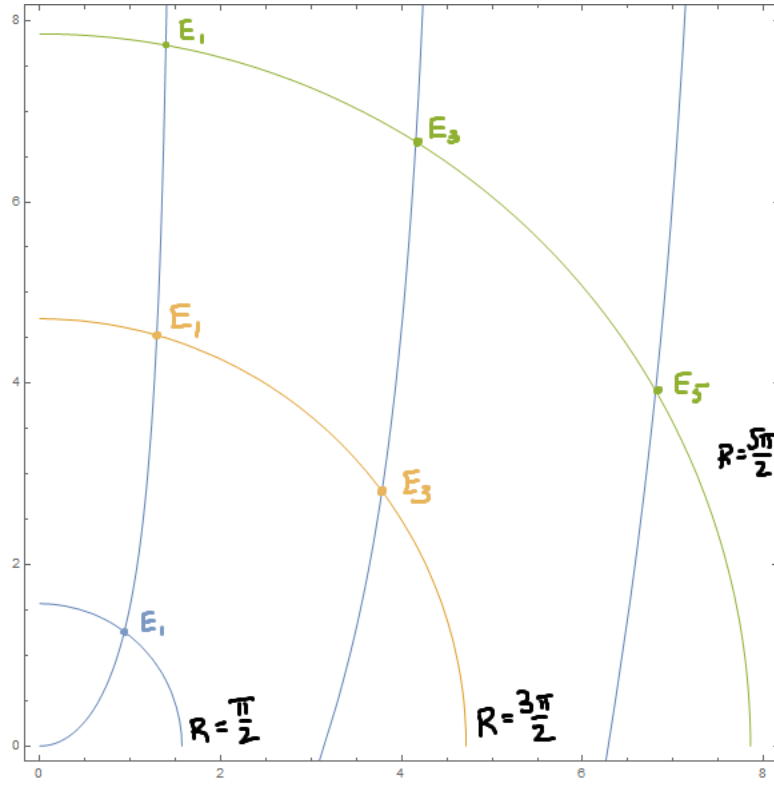$$\xi = ka = \sqrt{\frac{emEa^2}{\hbar^2}} \qquad \eta = \kappa a = \sqrt{\frac{2m}{\hbar^2}(V_0 - E)a^2}$$

so that our new boundary condition is

$$\xi\tan\xi = \eta$$

Note that

$$\xi^2 + \eta^2 = \frac{2mV_0a^2}{\hbar^2} = R^2$$

thus we can plot these two functions to get ξ and by extension E.

From the graph above we see that there will always be at least one bound state for any V_0

- $0 < R < \pi$ gives one bound state E_1

- $\pi < R < 2\pi$ gives two bound states E_1, E_3

- $2\pi < R < 3\pi$ gives three bound states E_1, E_3, E_5

The main difference between the finite and infinite wells is the addition of an exponential term. This gives an explicit reason for quantum tunneling, namely there is a penetration depth

$$d \sim \frac{1}{\kappa} = \frac{\hbar}{\sqrt{2m(V_0 - E)}}$$

2.4.4 Delta Function Potentials

A delta function potential is of the form

$$V(x) = \lambda \delta(x)$$

Depending on whether λ is positive or negative, this is referred to as either an attractive or repulsive delta function potential. We can think of these as an infinitely deep and thin potential well or infinitely high and thin potential wall respectively.

The main difference between the attractive and repulsive case is the sign of the resulting

energy so we'll just consider the attractive case. Bound states in this case have $E < 0$, the Schrodinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} - \lambda\delta(x)\psi = E\psi$$

The boundary conditions are that ψ is square integrable over all space and is continuous across $x = 0$. We will see that the first derivative is not continuous across the boundary however. Split the potential into two regions again and represent it as $-\lambda\delta(x)$ with $\lambda > 0$. Integrating from $-\epsilon$ to ϵ gives

$$-\frac{\hbar^2}{2m}\left(\frac{d\psi}{dx}\bigg|_{\epsilon} - \frac{d\psi}{dx}\bigg|_{-\epsilon}\right) - \lambda\psi(0) = 0$$

$$\therefore -\frac{\hbar^2}{2m}(\psi'_{II}(0) - \psi'_{I}(0)) - \lambda\psi(0) = 0$$

We will take as an ansatz

$$\psi(x) = Ae^{-k|x|} \qquad k = \sqrt{-\frac{2mE}{\hbar^2}}$$

This satisfies two of the three boundary conditions, the last one which we just derived is

$$-\frac{\hbar^2}{2m}(-k - k) = \lambda \qquad \longrightarrow \qquad k = \frac{m\lambda}{\hbar^2}$$

Thus the bound state energy is

$$E = -\frac{\hbar^2 k^2}{2m} = -\frac{m\lambda^2}{2\hbar^2}$$

Note that this is independent of λ, regardless of the parameter a delta function potential will always have only one bound state,

2.4.5 The Quantum Harmonic Oscillator

The final energy eigenvalue which we will study in depth is the quantum simple harmonic oscillator, one of the most important problems in quantum mechanics. Consider the potential

$$V(x) = \frac{1}{2}m\omega^2 x^2$$

where ω can be interpreted as an angular frequency. We will solve for eigenstates in two ways, first we will do so by solving the Schrodinger equation.

Suppose the eigenstates are $H\ket{n} = E_n\ket{n}$, we will first prove that the energies E_n are strictly positive. Let $\ket{\psi}$ be any state, the expected energy is

$$\langle H\rangle_\psi = \bra{\psi}H\ket{\psi}$$

$$= \bra{\psi}\frac{p^2}{2m}\ket{\psi} + \bra{\psi}\frac{1}{2}m\omega^2 x^2\ket{\psi}$$

$$= \frac{1}{2m}\braket{p\psi|p\psi} + \frac{1}{2}m\omega^2\braket{x\psi|x\psi} \geq 0$$

If we set $|\psi\rangle = |n\rangle$, then $\langle H \rangle = E_n \geq 0$. The only way we can get $E_n = 0$ is if $|n\rangle$ is trivially the null vector, such a solution isn't particularly interesting so we will ignore it. Thus without loss of generality, assume $E_n > 0$.

Start by considering position space

$$\langle x| H |n\rangle = E_n \langle x|n\rangle = E_n\psi_n(x)$$

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

Recast this equation in terms of some new variables

$$b = \sqrt{\frac{\hbar}{m\omega}} \qquad y = \frac{x}{b} \qquad \xi = \frac{E}{\hbar\omega}$$

$$\therefore \psi'' + (2\xi - y^2)\psi = 0$$

Consider the limiting behavior of ψ:

- ψ must be square integrable, so $\psi(\pm\infty) = 0$

- As $y \to 0$, the equation becomes $\psi'' + 2\xi\psi = 0$ which means for small y

$$\psi(y \to 0) \sim \cos\left(\sqrt{2\xi}y\right) + \sin\left(\sqrt{2\xi}y\right)$$

- As $y \to \pm\infty$, the ξ term gets dominated so $\psi'' - y^2\psi = 0$, thus for large y

$$\psi(y \to \pm\infty) \sim y^m e^{\pm y^2/2}(1 + O(1/y^2))$$

All this together suggests that a suitable ansatz is

$$\psi(y) = u(y)e^{-y^2/2}$$

where $u(y)$ is some polynomial with $u(y \to 0) = A + By$. Putting this back into the equation gives us the differential equation governing $u(y)$

$$u'' - 2yu' + (2\xi - 1)u = 0$$

This is known as the Hermite equation and defines the Hermite polynomials. We solve by assuming a series solution $u = \sum c_k y^k$ and inserting it into our equation, which gives the recurrence relation

$$c_{k+2} = \frac{2k + 1 - 2\xi}{(k+1)(k+2)}c_k$$

Note that due to the nature of the relation, every coefficient will be a multiple of c_0 or c_1, the first few terms of $u(y)$ can be written as

$$u(y) = c_0\left(1 + \frac{1 - 2\xi}{2}y^2 + O(y^2)\right) + c_1\left(y + \frac{3 - 2\xi}{6}y^3 + O(y^5)\right)$$

From this we see that $u(y)$ is not well behaved at $y \to \pm\infty$, the series will diverge except for when $\xi = (2n + 1)/2$. This leads to the energy quantization condition

$$\xi = n + \frac{1}{2} \quad \rightarrow \quad E_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

$u_n(y)$ are called the Hermite polynomials, denoted $H_n(y)$. The symmetry of the potential suggests that eigenstates are classified by parity. By examining the Hermite polynomials we see that this is indeed the case, even n polynomials have even parity and odd n have odd parity. The Hermite polynomials are given by

$$H_n(y) = \sum_{s=0}^{\lfloor n/2 \rfloor} (-1)^s (2y)^{n-2s} \frac{n!}{(n-2s)!s!} = e^{y^2/2}\left(y - \frac{d}{dy}\right)^n e^{-y^2/2}$$

where $\lfloor n/2 \rfloor$ is the floor function. This can also be written in terms of a generating function

$$g(y,t) = e^{-t^2+2ty} = \sum_{n=0}^{\infty} H_n(y)\frac{t^n}{n!}$$

so that we can find the nth Hermite polynomial using

$$H_n(y) = \left.\frac{\partial^n}{\partial t^n}g(y,t)\right|_{t=0}$$

The Hermite polynomials satisfy the recursion relations (which can be used to prove orthogonality)

$$H'_n(y) = 2nH_{n-1}(y)$$
$$H_{n+1}(y) = 2yH_n(y) - 2nH_{n-1}(y)$$
$$\int_\infty^\infty H_n(y)H_{n'}(y)e^{y-^2}dy = \delta_{n,n'}\sqrt{\pi}2^n n!$$

SHO Wavefunctions

Using the Hermite polynomials, the normalized eigenstates of the simple harmonic oscillator are

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar 2^n (n!)^2}\right)^{1/4} \exp\left(-\frac{m\omega x^2}{2\hbar}\right) H_n\left(\sqrt{\frac{m\omega}{2}}x\right)$$

The first few Hermite polynomials are

$$H_0(x) = 1$$
$$H_1(x) = 2x$$
$$H_2(x) = -2(1 - 2x^2)$$
$$H_3(x) = -12\left(x - \frac{2}{3}x^3\right)$$
$$H_4(x) = 12\left(1 - 4x^2 + \frac{4}{3}x^4\right)$$

Thus the first few normalized wavefunctions would be

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \exp\left(-\frac{m\omega x^2}{2\hbar}\right)$$

$$\psi_1(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} x \exp\left(-\frac{m\omega x^2}{2\hbar}\right)\sqrt{\frac{2m\omega}{\hbar}}$$

$$\psi_2(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2}}\left(\frac{2m\omega x^2}{\hbar} - 1\right)\exp\left(-\frac{m\omega x^2}{2\hbar}\right)$$

The momentum wavefunctions satisfy the equation

$$\left(\frac{p^2}{2m} - \frac{\hbar^2 m\omega^2}{2}\frac{d}{dp^2} - E_n\right)\phi_n(p) = 0$$

This is the same as the Schrodinger equation in position space with the mapping $x \mapsto p$, $1/m\omega \mapsto m\omega$. Thus the same replacements should give the momentum wavefunction (up to a phase factor). Note that since ψ, ϕ are Fourier transform pairs, we expect

$$\phi_n(p) = \int_{-\infty}^{\infty} \langle p|x\rangle \langle x|n\rangle \, dx$$

By computing this integral we find that we require a $(-i)^n$ phase factor which gives the normalized momentum wavefunctions as

$$\phi_n(p) = (-i)^n \left(\frac{1}{m\omega\pi\hbar 2^n (n!)^2}\right)^{1/4} \exp\left(-\frac{p^2}{2m\omega\hbar}\right) H_n\left(\frac{p}{\sqrt{m\omega\hbar}}\right)$$

The second way for computing eigenstates is to completely ignore wavefunctions and instead just consider some operators. Recall that the Hamiltonian is

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

Define two new operators

$$a = \sqrt{\frac{m\omega}{2\hbar}}x + \frac{ip}{\sqrt{2m\omega\hbar}} = \sqrt{\frac{m\omega}{2\hbar}}\left(x + \frac{ip}{m\omega}\right)$$

$$a^\dagger = \sqrt{\frac{m\omega}{2\hbar}}x - \frac{ip}{\sqrt{2m\omega\hbar}} = \sqrt{\frac{m\omega}{2\hbar}}\left(x - \frac{ip}{m\omega}\right)$$

a is called the lowering/annihilation operator and $a^\dagger$ is called the raising/creation operator. They obey the commutation relation

$$[a, a^\dagger] = \frac{m\omega}{2\hbar}\left[x + \frac{ip}{m\omega}, x - \frac{ip}{m\omega}\right]$$

$$= \frac{m\omega}{2\hbar}\left(\left[x, -\frac{ip}{m\omega}\right] + \left[\frac{ip}{m\omega}, x\right]\right)$$

$$= \frac{1}{2\hbar}(-i(i\hbar) + i(-i\hbar)) = 1$$

The number operator is defined to be $N = a^\dagger a$, note

$$N = \frac{m\omega}{2\hbar}\left(x^2 + \frac{p^2}{(m\omega)^2} + \frac{i[x,p]}{m\omega}\right)$$
$$= \frac{H}{\hbar\omega} - \frac{1}{2}$$
$$\therefore H = \left(N + \frac{1}{2}\right)\hbar\omega$$

This means that all we have to do is find the eigenvalues and eigenstates of N in order to find the eigenstates of H (and thus the energies). The process of rewriting the Hamiltonian in this way is called factorising the Hamiltonian.

$$N\ket{n} = n\ket{n}$$

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

Since N is Hermitian, the states $\ket{n}$ are complete and orthonormal

$$\braket{n|n'} = \delta_{n,n'} \qquad \sum_n \ket{n}\bra{n} = 1$$

The number operator commutes with the ladder operators as

$$[a, N] = a$$
$$[a^\dagger, N] = -a^\dagger$$

Let's act on the eigenvalue statement of N with a

$$a(N\ket{n} = n\ket{n})$$
$$aN\ket{n} = na\ket{n}$$
$$(Na + [a, N])\ket{n} = na\ket{n}$$
$$\therefore N(a\ket{n}) = (n-1)(a\ket{n})$$

If $\ket{n}$ is an eigenstates of N, then $a\ket{n}$ is either an eigenstate of N with eigenvalue $n-1$ or it is 0. To summarize

$$a\ket{n} = \begin{cases} c_n\ket{n-1} & \text{or} \\ 0 \end{cases}$$

This seems to imply that there is some sort of ground state n_0 such that $a\ket{n_0} = 0$. Note that

$$a\ket{n_0} = 0 \rightarrow a^\dagger a\ket{n_0} = 0 \rightarrow N\ket{n_0} = 0$$

which means $\ket{n_0} = \ket{0}$ which makes sense. To get the other states we use the raising operator

$$a^\dagger(N\ket{n} = n\ket{n})$$
$$(Na^\dagger + [a^\dagger, N])\ket{n} = na^\dagger\ket{n}$$
$$N(a^\dagger\ket{n}) = (n+1)(a^\dagger\ket{n})$$
$$\therefore a^\dagger\ket{n} = c'_n\ket{n+1}$$

To find the normalization constants we can form operator sandwiches

$$\langle n| a^\dagger a |n\rangle = |c_n|^2 \langle n-1|n-1\rangle$$
$$\therefore |c_n|^2 = n \rightarrow c_n = \sqrt{n}$$
$$\langle n| aa^\dagger |n\rangle = |c_n'|^2 \langle n+1|n+1\rangle$$
$$\therefore |c_n|'^2 = n+1 \rightarrow c_n' = \sqrt{n+1}$$

These operators are traditionally called the ladder operators for obvious reasons, we can now summarize how they act as follows

$$\begin{cases} a |n\rangle = \sqrt{n} |n-1\rangle \\ a^\dagger |n\rangle = \sqrt{n+1} |n+1\rangle \end{cases}$$
$$\langle n'| a |n\rangle = \sqrt{n} \, \delta_{n,n-1}$$
$$\langle n'| a^\dagger |n\rangle = \sqrt{n+1} \, \delta_{n,n+1}$$

It is sometimes also useful to consider the position/momentum of a particle in a simple harmonic oscillator. For that purpose, we can re-express those operators in terms of ladder operators

$$x = \sqrt{\frac{\hbar}{2m\omega}}(a + a^\dagger) \qquad p = i\sqrt{\frac{m\omega\hbar}{2}}(a^\dagger - a)$$

Using these relations, the uncertainty product for some state $|n\rangle$ is

$$\left\langle (\Delta x)^2 \right\rangle_n \left\langle (\Delta p)^2 \right\rangle_n = \frac{(n+1/2)^2}{\hbar^2}$$

The position wavefunction and probability density are plotted below.
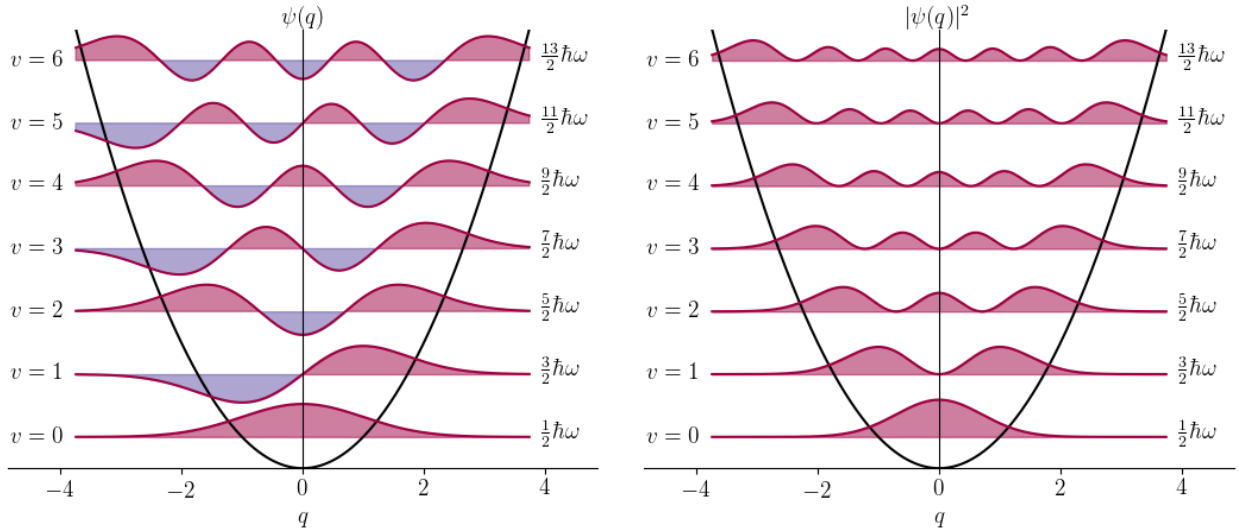
3 Quantum Dynamics

3.1 Basic Time Evolution

Having particles stationary in time is not interesting to anyone. In order to get some real science done we must allow states to evolve over time. It's important to note that time t is a parameter and not an operator. We can operate with x or p to ask a state what it's position or momentum is, but it makes no sense to observe a time. As before, we will treat time evolution using an unitary operator which takes two time parameters. If we have some initial state $|\alpha, t_0\rangle$, then it will evolve as

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

Note that it is unitary because the norm of a state must be preserved as it evolves, furthermore in order for time evolution to make sense we must have

$$U(t_2, t_0) = U(t_2, t_1)U(t_1, t_0)$$
$$U(t_0, t_0) = \mathbb{1}$$

By considering infinitesimal time translations it can be shown

$$i\hbar \frac{\partial}{\partial t} U(t, t_0) = HU(t, t_0)$$

$$\therefore i\hbar \frac{\partial}{\partial t} |\alpha, t_0; t\rangle = H |\alpha, t_0; t\rangle$$

The operator $U(t, t_0)$ is a special type of function called a Green's function, in particular it is called the propagator. Depending on the form of H, the propagator can have one of three possible forms

1. H is time independent:
$$U(t, t_0) = \exp\left(-\frac{i}{\hbar}H(t - t_0)\right)$$

2. H is time dependent but commutes with itself at later times:
$$U(t, t_0) = \exp\left(-\frac{i}{\hbar}\int_{t_0}^{t} H(t')dt'\right)$$

3. H is time dependent and does not commute with itself:
$$U(t, t_0) = \mathbb{1} + \sum_{n=1}^{\infty}\left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{n-1}} dt_n H(t_1)H(t_2)\cdots H(t_n)$$

   This solution is called a Dyson series

For now let's focus on the first case where H is time independent, the propagator is

$$U(t, 0) = \exp\left(-\frac{i}{\hbar}Ht\right) = \sum_{n}\exp\left(-\frac{iE_n t}{\hbar}\right) |n\rangle \langle n|$$

This assumes a discrete energy distribution (i.e. bound states), for a continuous distribution we have the same expression but with an integral instead of a sum.

Suppose we have the initial state

$$|\alpha(0)\rangle = \sum_n |n\rangle \langle n|\alpha(0)\rangle = \sum_n c_n(0) |n\rangle$$

Then this will evolve in time as

$$|\alpha(t)\rangle = \sum_n c_n(t) |n\rangle = \sum_n c_n(0) \exp\left(-\frac{iE_n t}{\hbar}\right) |n\rangle$$

By examining this form we see that if the initial state is an eigenstate of the Hamiltonian, then time evolution will only result in an (unobservable) global phase. Time evolution will only be nontrivial for superpositions of eigenstates.

For some operator A, if we try to measure it on some state we have two possibilities

- $[A, H] = 0$, in which case the eigenstates of A and H are the same

$$\langle\alpha(t)| A |\alpha(t)\rangle = \sum_n a_n |c_n|^2 = \sum_n a_n |c_n(0)|^2 = \langle\alpha(0)| A |\alpha(0)\rangle$$

- $[A, H] \neq 0$, in which case $\langle A \rangle$ will have some time dependence.

Example: Spin Precession

Consider a spin $1/2$ particle with magnetic moment $e\hbar/2m_e c$ in a static magnetic field B pointing in the z direction. We can write this as

$$H = -\left(\frac{e}{m_e c}\right) \mathbf{S} \cdot \mathbf{B} = -\left(\frac{eB}{m_e c}\right) S_z$$

Since the Hamiltonian is a multiple of S_z, they share eigenstates. The energies are

$$E_\pm = \mp\frac{e\hbar B}{2m_e c} = \mp\omega\hbar$$

where we define a new constant ω, this also rewrites the Hamiltonian as

$$H = \omega S_z \quad \longrightarrow \quad U(t,0) = \exp\left(-\frac{i\omega S_z t}{\hbar}\right)$$

For some arbitrary state $|\alpha\rangle = c_+ |+\rangle + c_- |-\rangle$, we have

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

Note that if $c_+ = 1, c_- = 0$, then the state will not evolve at all (only gaining a global phase). This agrees with out statement earlier that eigenstates will not evolve, we call

these states stationary. For a more interesting example, consider the S_x spin-up state

$$|\alpha(0)\rangle = |+\rangle_x = \frac{1}{\sqrt{2}}(|+\rangle + |-\rangle)$$

Using the evolved time derived earlier, the probabilities at a later time t are

$$P_{+x}(t) = \cos^2\left(\frac{\omega t}{2}\right)$$

$$P_{-x}(t) = \sin^2\left(\frac{\omega t}{2}\right)$$

$$\therefore \langle S_x \rangle = \frac{\hbar}{2}\cos(\omega t)$$

While the initial state is S_x spin-up, we see that the magnetic field in the z direction will cause the state to rotate. The rate of this rotation is seen in the expectation value, it's our parameter ω. By calculating the expectation values in the y, z directions, we see that this rotation is entirely in the xy plane.

Let's talk about the propagator a bit more, specifically in position space. Take a Hamiltonian of the form

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

$$\psi(\mathbf{x}, t) = \sum_n \exp\left(-\frac{E_n(t-t_0)}{\hbar}\right)\langle\mathbf{x}|n\rangle\langle n|\alpha, t_0\rangle$$

Inserting a complete set of state $|\mathbf{x}'\rangle$ gives

$$\psi(\mathbf{x}, t) = \sum_n \exp\left(-\frac{iE_n(t-t_0)}{\hbar}\right)\langle\mathbf{x}|n\rangle\int d^3x'\,\langle n|\mathbf{x}'\rangle\langle vecx'|\alpha, t_0\rangle$$

$$= \int d^3x' \sum_n \exp\left(-\frac{iE_n(t-t_0)}{\hbar}\right)\psi_n(\mathbf{x})\psi_n^*(\mathbf{x}')\psi(\mathbf{x}', t_0)$$

$$= \int d^3x'\,K(\mathbf{x}, t; \mathbf{x}', t_0)\psi(\mathbf{x}', t_0)$$

Where we've defined the propagator

$$K(\mathbf{x}, t; \mathbf{x}', t_0) = \langle\mathbf{x}|\,U(t, t_0)\,|\mathbf{x}'\rangle = \sum_n \exp\left(-\frac{iE_n(t-t_0)}{\hbar}\right)\psi_n(\mathbf{x})\psi_n^*(\mathbf{x}')$$

The propagator can be interpreted as the amplitude of a particle localized at $\mathbf{x}'$ during time t_0 to be found at another $\mathbf{x}$ during later time t. It is the Green's function for the 4 dimensional Schrodinger equation

$$\left(-\frac{\hbar^2}{2m}\nabla_\mathbf{x}^2 - i\hbar\frac{\partial}{\partial t} + V(\mathbf{x})\right)K(\mathbf{x}, t; \mathbf{x}', t_0)\theta(t-t_0) = -i\hbar\delta(\mathbf{x}-\mathbf{x}')\delta(t-t_0)$$

where θ is the unit step function.

Example. Consider a free particle $V(\mathbf{x}) = 0$. The eigenstates of the Hamiltonian are just the momentum states $|\mathbf{p}\rangle$ and thus

$$U(t, t_0) = \int d^3p \, |\mathbf{p}\rangle \langle \mathbf{p}| \exp\left(-\frac{ip^2t}{2m\hbar}\right)$$

The propagator can be directly evaluated

$$K(\mathbf{x}, t; \mathbf{x}', 0) = \langle \mathbf{x}| U(t, 0) |\mathbf{x}'\rangle = \int d^3p \, \langle \mathbf{x}|\mathbf{p}\rangle \langle \mathbf{p}|\mathbf{x}'\rangle \exp\left(-\frac{ip^2t}{2m\hbar}\right)$$

$$= \frac{1}{(2\pi\hbar)^3} \int d^3p \exp\left(\frac{i\mathbf{p}\cdot(\mathbf{x} - \mathbf{x}')}{\hbar}\right) \exp\left(-\frac{ip^2t}{2m\hbar}\right)$$

$$= \left(\frac{m}{2\pi i\hbar t}\right)^{3/2} \exp\left(\frac{im(\mathbf{x} - \mathbf{x}')^2}{2\hbar t}\right)$$

For instance in the unrealistic case of $\psi(\mathbf{x}', 0) = \delta^3(\mathbf{x}' - \mathbf{x}_0)$, it evolves to

$$\psi(\mathbf{x}, t) = \left(\frac{m}{2\pi i\hbar t}\right)^{3/2} \exp\left(\frac{im(\mathbf{x} - \mathbf{x}_0)^2}{2\hbar t}\right)$$

The propagator has two useful properties

$$\lim_{t \to t_0} K(\mathbf{x}, t; \mathbf{x}', t_0) = \delta^3(\mathbf{x} - \mathbf{x}')$$

$$\left(-\frac{\hbar^2}{2m}\nabla_\mathbf{x}^2 - i\hbar\frac{\partial}{\partial t} + V(\mathbf{x})\right) K(\mathbf{x}, t; \mathbf{x}', t_0) = 0$$

Recall that in classical electrodynamics we had a charge density ρ_E and current density $\mathbf{j}_E$. The continuity equation imposes conservation of charge

$$\frac{\partial \rho_E(\mathbf{x}, t)}{\partial t} = -\nabla \cdot \mathbf{j}_E(\mathbf{x}, t)$$

In quantum mechanics, the wavefunction defines a probability density. What we want to do is construct an analogous probability current density on which we can impose the conservation of probability on. Start by multiplying the Schrodinger equation by ψ^*

$$\psi^* \left(i\hbar\frac{\partial}{\partial t}\psi = -\frac{\hbar^2}{2m}\nabla^2\psi + V(x)\psi\right)$$

Subtracting the complex conjugate gives

$$\psi^* i\hbar\frac{\partial \psi}{\partial t} - \psi i\hbar\frac{\partial \psi^*}{\partial t} = -\frac{\hbar^2}{2m}\left(\psi^*\nabla\psi - \psi\nabla\psi^*\right) + \psi^*(V - V^*)\psi$$

We see that this is in the form

$$\frac{\partial}{\partial t}(|\psi|^2) = \frac{\partial}{\partial t}\rho = -\nabla \cdot \mathbf{j} + \frac{2}{\hbar}\psi^* Im(V)\psi$$

Thus we can define the probability current to be

$$\mathbf{j}(\mathbf{x}, t) = \frac{\hbar}{2mi}(\psi^* \nabla \psi - \psi \nabla \psi^*)$$

The remaining term vanishes because H is Hermitian, that is $Im(V) = 0$. For real wavefunctions (e.g. 1D bound states), the current is zero. For energy eigenstates the current is divergence-less since the probability density is constant in time.

Example. Consider a plane wave

$$\psi(\mathbf{x}, t) = \frac{1}{(2\pi\hbar)^{3/2}} \exp\left(\frac{i\mathbf{p} \cdot \mathbf{x}}{\hbar}\right) \exp\left(-\frac{ip^2 t}{2m\hbar}\right)$$

The probability density and current are

$$\rho(\mathbf{x}, t) = \frac{1}{(2\pi\hbar)^3}$$

$$\mathbf{j}(\mathbf{x}, t) = \frac{\hbar}{2mi} \frac{1}{(2\pi\hbar)^3} \frac{2i\mathbf{p}}{\hbar} = \frac{\mathbf{p}}{m}\rho(\mathbf{x}, t)$$

$$\therefore \mathbf{j}(\mathbf{x}, t) = \mathbf{v}\rho(\mathbf{x}, t)$$

3.2   One Dimensional Scattering

Recall that for energies $E > V(\infty)$ we have scattering states. These states form a continuous spectrum (as opposed to discrete) and must be delta function normalized. We can take linear combinations of scattering states to form a wavepacket and investigate how they scatter off a particular potential.

For a wavepacket sufficiently localize in momentum space, we can use a plane wave approach to solving the problem. If the incident wavepacket is sufficiently localized in both position and momentum then scattering at large t leads to two contributions

1. A reflected wave $\psi_R(\mathbf{x}, t)$

2. A transmitted wave $\psi_T(\mathbf{x}, t)$

We will investigate the 1D case for simplicity. If the incident wavepacket is assumed to be at $x = -a$ at time $t = 0$, then the condition for it to be considered "sufficiently localized" is

$$\Delta x = \sqrt{\langle (\Delta x)^2 \rangle} \ll a$$
$$\Delta p = \sqrt{\langle (\Delta p)^2 \rangle} \ll p_0$$

Under these conditions, we write the contributions as

$$\psi(x, t \gg 0) = \psi_R(x, t) + \psi_I(x, t)$$

The probability of reflection and transmission are defined as

$$R = \int |\psi_R|^2 dx \qquad T = \int |\psi_T|^2 dx$$

It's expected that $R+T=1$, that is there is negligable overlap between the two contributions.

Let's work this out with an initial Gaussian wavepacket of the form

$$\psi_I(x,0) = \frac{1}{\pi^{1/4}\sqrt{d}} e^{ik_0(x+a)} e^{-(x+a)^2/2d^2}$$

that is a wavepacket with parameters

$$\langle x \rangle = -a \qquad \langle p \rangle = p_0 = \hbar k_0 \qquad E_0 = \frac{\hbar^2 k_0^2}{2m}$$

We will work in the limit where the initial position $a \gg d$ and scatter this wavepacket off a step potential with $V_0 > 0$

$$V(x) = V_0 \theta(x) = \begin{cases} 0 & x < 0 \\ V_0 & x > 0 \end{cases}$$

Classically, if $E > V_0$ then there is 100% transmission otherwise if $E < V_0$ there is 100% reflection. In quantum mechanics this is only half true: if $\langle E \rangle < V_0$ then there will be only reflection, otherwise there will be a probability of both occurring.

Assume that there is enough energy for transmission, that is

$$\frac{p_0^2}{2m} = E_0 > V_0$$
$$p_0 - \sqrt{2mV_0} \gg \Delta p$$

To solve a scattering problem we have four general steps

1. Find normalized energy eigenstates of H, getting $\psi_E(x)$

2. Project the initial wavepacket $\psi_I(x,0)$ onto the eigenstates

3. Find $\psi(x,t)$ by evolving each component in time

4. Identify ψ_R and ψ_T in the large t limit

1) Eigenstates: Note that for this potential there are no bound states, only a continuum of positive energy solutions which satisfy

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi_E(x) + V(x)\psi_E(x) = E\psi_E(x)$$

There are two categories of solutions: $E > V_0$ and $E < V_0$. If $E < V_0$ then the eigenstates have negligible overlap with $\psi_I(x, 0)$ and thus can be safely ignored. For $E > V_0$ we can divide the potential into two regions, region I is $x < 0$ and region II is $x > 0$ as usual.

$$\psi_I(x) = Ae^{ik_1x} + Be^{-ik_1x}$$
$$\psi_{II}(x) = Ce^{ik_2x} + De^{-ik_2x}$$

where we've defined the constants

$$k_1 = \sqrt{\frac{2mE}{\hbar^2}} \qquad k_2 = \sqrt{\frac{2m(E - V_0)}{\hbar^2}} = \sqrt{k_1^2 - \frac{2mV_0}{\hbar^2}}$$

These are subject to the conditions that they, and their first derivatives, be continuous across the boundary. Again there are two subclasses of solutions

1. $D = 0$: incoming wave from the left

2. $A = 0$: incoming wave from the right

Once again there is only negligible overlap for an incoming wave from the right so we will take $D = 0$ to get the conditions

$$\frac{B}{A} = \frac{k_1 - k_2}{k_1 + k_2} \qquad \frac{C}{A} = \frac{2k_1}{k_1 + k_2}$$

Normalization gives an overall factor of $1/\sqrt{2\pi}$ so the energy eigenstates are

$$\psi_{k_1} = \frac{1}{\sqrt{2\pi}}\left[\left(e^{ik_1x} + \frac{B}{A}e^{-ik_1x}\right)\theta(-x) + \frac{C}{A}e^{ik_2x}\theta(x)\right]$$

where θ is the step function.

2) Projection: The wavepacket takes the form

$$|\psi_I\rangle = \int dk_1 |k_1\rangle \langle k_1|\psi_I\rangle = \int dk_1 a(k_1) |k_1\rangle$$

in which the coefficients are given by the integral

$$a(k_1) = \int_{-\infty}^{\infty} \psi_{k_1}^*(x)\psi_I(x)dx$$

Expanding this integral gives

$$a(k_1) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{0} \left(e^{-ik_1x} + \frac{B^*}{A^*}e^{ik_1x}\right)\psi_I(x, 0)dx + \frac{1}{\sqrt{2\pi}} \int_{0}^{\infty} \frac{C^*}{A^*}e^{-ik_2x}\psi_I(x, 0)dx$$

Since the incident wave is from the left, it has no support for $x > 0$, thus the second integral is exponentially suppressed and can be taken to be zero (with corrections of order e^{-a^2/d^2}). The first term can be written

$$\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{0} \frac{1}{\pi^{1/4}\sqrt{d}}e^{-ik_1x}e^{ik_0(x+a)}e^{-(x+a)^2/2d^2}$$

This looks like a Gaussian integral but to evaluate it as such requires extending the upper limit to infinity (which introduces corrections $\sim e^{-a^2/d^2}$). Under this approximation we get

$$\left(\frac{d^2}{\pi}\right)^{1/4} e^{-(k_1-k_0)^2 d^2/2} e^{ik_1 a}$$

The second term is identical with the replacement $k_1 \mapsto -k_1$, but this means the result will be of the order $e^{-(k_1+k_0)^2 d^2/2}$ which is highly suppressed since $k_1 + k_0$ is never negative. Thus we will drop this term to get

$$a(k_1) = \left(\frac{d^2}{\pi}\right)^{1/4} e^{-(k_1-k_0)^2 d^2/2} e^{ik_1 a}$$

3) Evolve: The time evolution of this state is

$$\psi(x,t) = \int dk_1 \psi_{k_1}(x) a(k_1) \exp\left(-\frac{i\hbar k_1^2 t}{2m}\right)$$

4) Large t limit [1]: Again we have three terms to consider, the first term is

$$\left(\frac{d^2}{4\pi^3}\right)^{1/4} \int dk_1 \exp\left(-\frac{i\hbar k_1^2 t}{2m}\right) \exp\left(-\frac{(k_1-k_0)^2 d^2}{2}\right) e^{ik_1(a+x)} \theta(-x)$$

which can be viewed as a Gaussian centered at $x = -a + p_0 t/m$ multiplied by $\theta(-x)$. But in the large t, limit this Gaussian would be centered at $x > 0$ and thus killed by the step function. We interpret this as the incident wave being killed after sufficient time has passed and is instead replaced by the reflected and transmitted waves.

Consider now the second term, which is

$$\left(\frac{d^2}{4\pi^3}\right)^{1/4} \int dk_1 \frac{B}{A} \exp\left(-\frac{i\hbar k_1^2 t}{2m}\right) \exp\left(-\frac{(k_1-k_0)^2 d^2}{2}\right) e^{-ik_1(a+x)} \theta(-x)$$

Since the integrand is sharply peaked at $k_1 = k_0$, we'll replace the B/A with it's value at $k_1 = k_0$ (which introduces power law corrections). If we convert this into a Gaussian wavepacket we can see that it travels to the left with momentum $-\hbar k_0$, it is the reflected wave. Thus the reflection coefficient is

$$R = \left|\frac{B}{A}\right|^2_{k_1=k_0} \qquad \longrightarrow \qquad T = 1 - R = \left(\frac{k_2}{k_1}\right)\left|\frac{C}{A}\right|^2_{k_1=k_0}$$

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[1] See treatment in Shankar Ch 5 or a better approximation in Norsen et al. 2008

Example: Scattering off a Delta Function

Assuming that conditions are such that plane wave approximation are valid, we scatter a particle of mass m and energy $E = \hbar^2 k^2/2m > 0$ off the delta function potential

$$V(x) = \lambda \delta(x)$$

Since we assume plane waves, we can write the wave function in this form

$$\psi(x) = \begin{cases} e^{ikx} + re^{-ikx} & x < 0 \\ te^{ikx} & x > 0 \end{cases}$$

where $k = \sqrt{2mE/\hbar^2}$. This form makes it easy to find the reflection/transmission coefficients. The boundary conditions give

$$1 + r = t$$

$$ikt - ik + ikr = \frac{2mV_0\lambda}{\hbar^2}$$

Putting this all together gives

$$r = \frac{m\lambda}{ik_0\hbar^2 - m\lambda} \rightarrow R = \frac{m^2\lambda^2}{m^2\lambda^2 + \hbar^4 k_0^2}$$

$$r = \frac{ik_0\hbar^2}{ik_0\hbar^2 - m\lambda} \rightarrow T = \frac{\hbar^4 k_0^2}{m^2\lambda^2 + \hbar^4 k_0^2}$$

3.3   The Heisenberg Picture

So far we've been solving problems by evolving state (kets) in time, this is called the Schrodinger picture. The alternative, the Heisenberg picture, is to let the operators evolve in time instead and let the state kets remain constant.

States and operators in the Heisenberg picture are given by

$$|a\rangle_H = e^{iHt/\hbar} |\alpha(t)\rangle_S = U^\dagger(t) |\alpha(t)\rangle_S$$

$$A_H = e^{iHt/\hbar} A_s e^{-iHt/\hbar} = U^\dagger(t) A_S U(t)$$

Note that the first equality will only hold in the case of a time independent H. From the definition of A_H we can show $\langle A_S \rangle_S = \langle A_H \rangle_H$, that is the physics is the same regardless of which picture we are in. We can write down the equations of motion for an operator

$$\frac{dA_H}{dt} = \frac{1}{i\hbar}[A, H] + \frac{\partial A_H}{\partial t}$$

where $\partial A_H / \partial t = U^\dagger(t)(\partial A_s / \partial t)U(t)$, which is nonzero only if the operator has explicit time dependence in the Schrodinger picture. If it doesn't then an operator would be a constant of motion if it commutes with the Hamiltonian.

Consider an operator A with

$$H = \frac{p^2}{2m} + V(\mathbf{x}) \qquad \frac{d}{dt}A_H = \frac{1}{i\hbar}[A_H, H]$$

that is A has no explicit time dependence. For $V = 0$

$$\frac{d}{dt}p_{i_H} = \frac{1}{i\hbar}[p_i, \frac{p^2}{2m}] = 0$$

$$\frac{d}{dt}x_{i_H} = \frac{1}{i\hbar}[x_i, \frac{p^2}{2m}] = \frac{p_i}{m}$$

$$\therefore x_{i_H} = \frac{p_{i_H}(0)}{m}t + x_{i_H}(0)$$

For the case that $V \neq 0$ then we have

$$\frac{d}{dt}p_{i_H} = \frac{1}{i\hbar}[p_i, V(\mathbf{x})] = -\frac{\partial}{\partial x_i}V(\mathbf{x})$$

$$\frac{d}{dt}x_{i_H} = \frac{d}{dt}\left(\frac{p_{i_H}}{m}\right) = -\frac{1}{m}\frac{\partial}{\partial x_i}V(\mathbf{x})$$

$$\therefore m\frac{d^2}{dt^2}\mathbf{x}_H = -\nabla V(\mathbf{x}_H)$$

This is an operator statement of Ehrenfest's theorem, which is traditionally stated as a theorem about expectation values

$$\boxed{m\frac{d^2}{dt^2}\langle \mathbf{x} \rangle = -\langle \nabla V(\mathbf{x}) \rangle}$$

Recall that the probability for some state $|\alpha\rangle$ to evolve to another state $|\beta\rangle$ in some time t is

$$\langle \beta | U(t, 0) | \alpha \rangle$$

In the Heisenberg picture the state kets are time independent but the "base" kets will still evolve. Since operators are evolving over time, we expect their eigenstates to change as well. If A_S satisfies

$$A_S |a_i\rangle_S = a_i |a_i\rangle_S$$

Then in the Heisenberg picture we'll have

$$U^\dagger(A_S U U^\dagger |a_i\rangle_S = a_i |a_i\rangle_S)$$

$$(U^\dagger A_S U)(U^\dagger |a_i\rangle_S) = a_i(U^\dagger |a_i\rangle_S)$$

$$\therefore A_H |a_i\rangle_H = a_i |a_i\rangle_H$$

where we've now defined the evolved basis state as $|a\rangle_H = U^\dagger |a\rangle_S$. Note that this still the same transition amplitude but in the Schrodinger picture we interpret $U(t) |\alpha\rangle = |\alpha(t)\rangle$ whereas in the Heisenberg picture $\langle \beta | U^\dagger = \langle \beta(t) |$.

Example. Consider the 1D harmonic oscillator $H = p^2/2m + m\omega^2 x^2/2$, using the definition of the ladder operators we can find equations of motion

$$\dot{p}_H = \frac{1}{i\hbar}[p_H, H] = -m\omega^2 x_H$$

$$\dot{x}_H = \frac{1}{i\hbar}[x_H, H] = \frac{p_H}{m}$$

$$\therefore \ddot{x}_H = \frac{1}{m}\dot{p}_H = -\omega^2 x_H$$

Alternatively we can choose to work with the ladder operators themselves

$$\dot{a}_H = \sqrt{\frac{m\omega}{2\hbar}}\left(\dot{x}_H + \frac{i}{m\omega}\dot{p}_H\right) = -i\omega a_H$$

$$\therefore a_H(t) = a_H(0)e^{-i\omega t} \qquad a_H^\dagger(t) = a_H^\dagger(0)e^{i\omega t}$$

which gives us the position and momentum operators

$$x_H(t) = x(0)\cos(\omega t) + \frac{p(0)}{m\omega}\sin(\omega t)$$

$$p_H(t) = -m\omega x(0)\sin(\omega t) + p(0)\cos(\omega t)$$

For a time-independent Hamiltonian, the following relation is useful in calculating time evolution

$$e^{i\lambda G}Ae^{-i\lambda G} = A + i\lambda[G, A] + \frac{(i\lambda)^2}{2!}[G, [G, A]] + \frac{(i\lambda)^3}{3!}[G, [G, [G, A]]] + \cdots$$

Example: Spin Precession but Heisenberg

We can solve the spin precession problem from earlier by writing down equations of motion for each operator. Recall that the Hamiltonian was written in the form $H = \omega S_z$

$$\dot{S}_x = \frac{1}{i\hbar}[S_x, H] = -\omega S_y$$

$$\dot{S}_y = \frac{1}{i\hbar}[S_y, H] = \omega S_x$$

$$\dot{S}_z = \frac{1}{i\hbar}[S_z, H] = 0$$

We can solve these coupled equations to get

$$S_x(t) = S_x(0)\cos(\omega t) - S_y(0)\sin(\omega t)$$

$$S_y(t) = S_y(0)\cos(\omega t) + S_x(0)\sin(\omega t)$$

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4 Semiclassical Approximations

4.1 The WKB Approximation

The correspondence principle states that we should be able to deduce classical physics from quantum mechanics in the appropriate limit. In our day to day lives we rarely see quantum effects in play, for instance a ball will not quantum tunnel through a fence. Thus at some large limit we expect quantum laws to converge to classical laws. We look for wavepackets with small spatial extent compared to the distance in which force changes.

The Ehrenfest theorem can be written using the Heisenberg equations of motion for an operator as

$$\frac{d}{dt}\langle A\rangle = \frac{1}{i\hbar}\langle[A,H]\rangle + \left\langle\frac{\partial A}{\partial t}\right\rangle$$

If we put in momentum and position operators we find the statements

$$\frac{d}{dt}\langle p_i\rangle = \frac{1}{i\hbar}\langle[p_i,H]\rangle = -\left\langle\frac{\partial H}{\partial x_i}\right\rangle$$

$$\frac{d}{dt}\langle x_i\rangle = \frac{1}{i\hbar}\langle[x_i,H]\rangle = -\left\langle\frac{\partial H}{\partial p_i}\right\rangle$$

note the similarity with the Hamilton equations

$$\dot{p}_i = -\frac{\partial H}{\partial x_i} \qquad \dot{x}_i = \frac{\partial H}{\partial p_i}$$

For the classical limit to be valid we must have

$$\frac{d}{dt}\langle p_i\rangle = -\frac{\partial H(\langle\mathbf{x}\rangle,\langle\mathbf{p}\rangle,t)}{\partial\langle x_i\rangle}$$

$$\frac{d}{dt}\langle x_i\rangle = -\frac{\partial H(\langle\mathbf{x}\rangle,\langle\mathbf{p}\rangle,t)}{\partial\langle p_i\rangle}$$

in which case we can treat $\langle\mathbf{x}\rangle$ as the trajectory of the particle. However in general these equalities will not hold, except for cases in which the potential V is slowly varying over space.

Under a slowly varying potential, we are allowed to assume the wavefunction is approximately a free particle. The WKB (Wentzel-Kramers-Brillouin) approximation is a semiclassical one in which we assume the ansatz

$$\psi(\mathbf{x},t) = Ae^{iW(\mathbf{x},t)/\hbar}$$

Substituting this into the Schrodinger equation gives

$$-\frac{\partial W}{\partial t} = -\frac{i\hbar}{2m}\nabla^2 W + \frac{1}{2m}(\nabla W)\cdot(\nabla W) + V$$

The idea behind WKB is to expand in powers of $\hbar$, which makes it valid in the domain $\hbar \to 0$. The leading order term is

$$-\frac{\partial W}{\partial t} = \frac{1}{2m}(\nabla W)^2 + V$$

This bears similarity to the normal Schrodinger equation with the identification $\mathbf{p} = \nabla W$ which motivates the expansion

$$W = W_0 + \left(\frac{\hbar}{i}\right) W_1 + \left(\frac{\hbar}{i}\right)^2 W_2 + \cdots$$

We can also rewrite the Schrodinger equation as

$$\frac{\partial W}{\partial t} + \frac{1}{2m}(\nabla W)^2 + V(\mathbf{x}) = \frac{i\hbar}{2m}\nabla^2 W$$

note that the left hand side is the classical Hamilton-Jacobi equation (for W_0). Equation powers of $\hbar$ gives a series of equations

$$\hbar^0 : -\frac{\partial W_0}{\partial t} = \frac{1}{2m}(\nabla W_0)^2 + V$$

$$\hbar^1 : -\frac{\partial W_1}{\partial t} = \frac{1}{2m}\left(2\nabla W_0 \cdot \nabla W_1 + \nabla^2 W_0\right)$$

$$\hbar^2 : -\frac{\partial W_2}{\partial t} = \frac{1}{2m}\left((\nabla W_1)^2 + 2\nabla W_0 \cdot \nabla W_2 + \nabla^2 W_1\right)$$

$$\vdots$$

So our solution is

$$\psi \sim \exp\left(W_1 + \frac{iW_0}{\hbar} + \cdots\right)$$

$$\rho(\mathbf{x}, t) = |\psi|^2 = e^{2W_1}$$

$$\mathbf{j}(\mathbf{x}, t) = \frac{\hbar}{2mi}(\psi^*\nabla\psi - \psi\nabla\psi^*) = \frac{1}{m}e^{2W_1}\nabla W_0$$

This process can be simplified by separating out the time dependence. For instance in the 1D case, let $W(x, t) = S(x) - Et$ which gives

$$\psi(x, t) = e^{iW/\hbar} = e^{iS(x)/\hbar}e^{-iEt/\hbar} = \psi(x)e^{-iEt/\hbar}$$

Then Schrodinger's equation gives

$$i\hbar S'' - (S')^2 + 2m(E - V(x)) = 0$$

As is tradition when solving problems like these, we'll define some constants

$$k^2(x) = \frac{2m(E - V(x))}{\hbar^2} \qquad \kappa^2(x) = \frac{2m(V(x) - E)}{\hbar^2}$$

$$E - V(x) = \begin{cases} \hbar^2 k^2(x) & E > V \\ \hbar^2 \kappa^2(x) & E < V \end{cases}$$

Just like before, we expand S in terms of powers of $\hbar$

$$S = S_0 + \hbar S_1 + \cdots$$

The first order condition is

$$-(S_0')^2 + 2m(E_V) = 0 \rightarrow S_0' = \pm\sqrt{2m(E_V(x))}$$

$$\therefore S_0 = \pm \int^x \sqrt{2m(E - V(x'))}dx'$$

We'll drop all higher order terms, so the WKB wavefunctions take the form

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1. $E > V(x)$, the classical region

$$\psi_{WKB} \sim \frac{1}{k(x)} \exp\left(\pm i \int^x k(x')dx'\right)$$

2. $E < V(x)$, the classically forbidden region

$$\psi_{WKB} \sim \frac{1}{\kappa(x)} \exp\left(\pm i \int^x \kappa(x')dx'\right)$$

For this approach to be valid we need the next order term to be negligible. Thus we must first calculate the $\hbar$ term

$$iS_0'' - 2S_0'S_1' = 0 \rightarrow S_1' = \frac{i}{2}\frac{S_0''}{S_0'}$$

which gives us

$$S_1' = \begin{cases} \frac{i}{2}\frac{k'(x)}{k(x)} \\ \frac{i}{2}\frac{\kappa'(x)}{\kappa(x)} \end{cases} \rightarrow S_1 = \begin{cases} \frac{i}{2}\ln k(x) & E > V \\ \frac{i}{2}\ln \kappa(x) & E < V \end{cases}$$

The validity condition is therefore

$$\left|\frac{\hbar S_1'}{S_0'}\right| \ll 1 \rightarrow \left|\frac{k'}{k^2}\right| \ll 1 \rightarrow \left|\frac{dV/dx}{k(x)(E - V(x))}\right| \ll 1$$
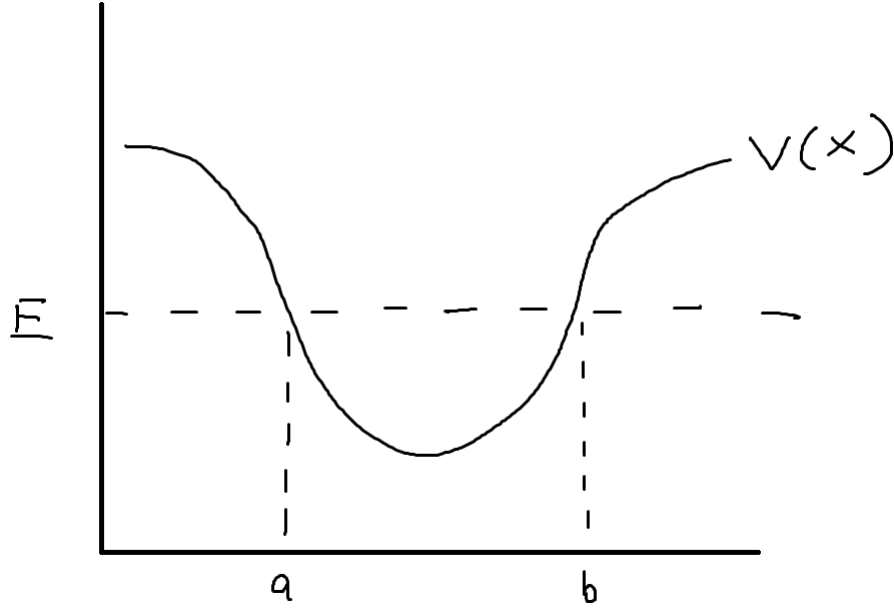
As a quick demonstration consider some potential well similar to the one shown above. Using the results we derived earlier, we again split the wavefunction into three pieces

$$\psi_I = \frac{A_I}{\sqrt{\kappa(x)}} \exp\left(\int_a^x \kappa(x')dx'\right)$$

$$\psi_{II} = \frac{1}{\sqrt{k(x)}} \left[A_{II}\cos\left(\int_a^x k(x')dx'\right) + B_{II}\sin\left(\int_a^x k(x')dx'\right)\right]$$

$$\psi_{III} = \frac{A_{III}}{\sqrt{\kappa(x)}} \exp\left(-\int_b^x \kappa(x')dx'\right)$$

These states must be matched across the classical turning points, the connection formulas are derived by solving the Airy equation. The connections rules can be summarized using the following formulas. To avoid instabilities in regions of large $|x|$ matching is best done from the left in the 2nd and 3rd formula and from the right in the 1st and 4th formula.

- For $V'(x) < 0$, a negative slope (e.g. at $x = a$)

$$\frac{1}{\sqrt{\kappa(x)}} \exp\left(\int_a^x \kappa(x')dx'\right) \longleftrightarrow \frac{2}{\sqrt{k(x)}} \cos\left(\int_a^x k(x')dx' - \frac{\pi}{4}\right)$$

$$-\frac{1}{\sqrt{\kappa(x)}} \exp\left(-\int_a^x \kappa(x')dx'\right) \longleftrightarrow \frac{1}{\sqrt{k(x)}} \sin\left(\int_a^b k(x')dx' - \frac{\pi}{4}\right)$$

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- For $V'(x) > 0$, a positive slope (e.g. at $x = b$)

$$\frac{2}{\sqrt{k(x)}} \cos\left(\int_x^b k(x')dx' - \frac{\pi}{4}\right) \longleftrightarrow \frac{1}{\sqrt{\kappa(x)}} \exp\left(-\int_b^x \kappa(x')dx'\right)$$

$$\frac{1}{\sqrt{k(x)}} \sin\left(\int_x^b k(x')dx' - \frac{\pi}{4}\right) \longleftrightarrow -\frac{1}{\sqrt{\kappa(x)}} \exp\left(\int_b^x \kappa(x')dx'\right)$$

The matching at $x = a$ occurs directly, but for $x = b$ we must do some extra work. Using some trig magic we can rewrite the wavefunction in region II as

$$\begin{aligned}
\psi_{II}(x) &= \frac{2}{\sqrt{k(x)}} \cos\left(\int_a^x k(x')dx' - \frac{\pi}{4}\right) \\
&= \frac{2}{\sqrt{k(x)}} \cos\left(\int_a^b k(x')dx' - \int_x^b k(x')dx' - \frac{\pi}{4}\right) \\
&= \frac{2}{\sqrt{k(x)}} \left[\cos\left(\int_a^b k(x')dx'\right) \cos\left(\int_x^b k(x')dx' + \frac{\pi}{4}\right) \right. \\
&\quad \left. + \sin\left(\int_a^b k(x')dx'\right) \sin\left(\int_x^b k(x')dx' + \frac{\pi}{4}\right)\right]
\end{aligned}$$

Furthermore, note that

$$\sin\left(x + \frac{\pi}{4}\right) = \cos\left(x - \frac{\pi}{4}\right)$$
$$\cos\left(x + \frac{\pi}{4}\right) = -\sin\left(x - \frac{\pi}{4}\right)$$

Thus matching gives another wavefunction with both an increasing and decaying exponential, but for this to properly match the increasing exponential must vanish (also for it to be a bound state). Since the increasing exponential is attached to the first term we get

$$\cos\left(\int_a^b k(x')dx'\right) = 0 \longrightarrow \int_a^b k(x')dx' = \left(n + \frac{1}{2}\right)\pi$$

This is known as the WKB single well quantization condition.

Example. We can modify the single well condition so solve familiar problems, for instance in the harmonic oscillator the turning points are $\pm x_0$ where

$$x_0 = \sqrt{\frac{2E}{m\omega^2}}$$

Thus the quantization condition is just

$$\int_{-x_0}^{x_0} \sqrt{\frac{2m}{\hbar^2}\left(E - \frac{m\omega^2 x^2}{2}\right)}dx = \left(n + \frac{1}{2}\right)\pi$$

We can solve this with a simple trig substitution to get

$$\frac{2E}{\omega}\int_0^\pi \sin^2\theta d\theta = \left(n + \frac{1}{2}\right)\pi\hbar \rightarrow E = \left(n + \frac{1}{2}\right)\hbar\omega$$

Example: Potential Barrier

This is essentially the opposite of the problem discussed earlier, we have a barrier with turning points $b > a$ (so upward sloping at $x = a$ and downward sloping at $x = b$). Using the WKB approximation, the wavefunction in each region can be written as

$$\psi_1 = \frac{1}{\sqrt{k(x)}} \left[A e^{i \int_a^x k(x')dx'} + B e^{-i \int_a^x k(x')dx'} \right]$$

$$\psi_2 = \frac{1}{\sqrt{\kappa(x)}} \left[C e^{\int_a^x \kappa(x')dx'} + D e^{-\int_a^x \kappa(x')dx'} \right]$$

$$\psi_3 = \frac{1}{\sqrt{k(x)}} \left[F e^{i \int_b^x k(x')dx'} + G e^{-i \int_b^x k(x')dx'} \right]$$

where we've defined

$$k(x) = \sqrt{\frac{2m}{\hbar^2}(E - V(x))} \quad \kappa(x) = \sqrt{\frac{2m}{\hbar^2}(V(x) - E)}$$

the coefficients can be related using a matrix

$$\begin{pmatrix} A \\ B \end{pmatrix} = \mathcal{M} \begin{pmatrix} F \\ G \end{pmatrix}$$

For convenience we will also introduce the parameter $\theta = \exp\left(\int_a^b \kappa(x')dx' \right)$. From region 3 we can manipulate the wavefunction

$$\psi_3 = \frac{F e^{i\pi/4}}{\sqrt{k(x)}} \exp\left(\int_b^x k(x')dx' - \frac{\pi}{4} \right) + \frac{G e^{-i\pi/4}}{\sqrt{k(x)}} \exp\left(-i(\int_b^x k(x')dx' - \frac{\pi}{4}) \right)$$

$$= \frac{e^{i\pi/4}(F - iG)}{\sqrt{k(x)}} \cos\left(\int_b^x k(x')dx' - \frac{\pi}{4} \right) - \frac{i e^{i\pi/4}(F + iG)}{\sqrt{k(x}} \sin\left(\int_b^x k(x')dx' - \frac{\pi}{4} \right)$$

$$\rightarrow \frac{e^{i\pi/4}(F - iG)}{2\sqrt{\kappa(x)}} \exp\left(-\int_x^b \kappa(x')dx' \right) + \frac{i e^{i\pi/4}(F + iG)}{\sqrt{\kappa(x)}} \exp\left(\int_x^b \kappa(x')dx' \right)$$

Note that it is possible to rewrite the integral

$$\int_x^b \kappa(x')dx' = \int_a^b \kappa(x')dx' - \int_a^x \kappa(x')dx' = \theta - \int_a^x \kappa(x')dx'$$

which means the wavefunction in region 2 can also be written

$$\psi_2 = \frac{e^{i\pi/4}(F - iG)}{2\theta\sqrt{\kappa(x)}} \exp\left(\int_a^x \kappa(x')dx' \right) + \frac{i\theta e^{i\pi/4}(F + iG)}{\sqrt{\kappa(x)}} \exp\left(-\int_a^x \kappa(x')dx' \right)$$

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Using the connection formulas again gives us the wavefunction in region 1

$$\psi_1 = -\frac{e^{i\pi/4}(F-iG)}{2\theta\sqrt{k(x}} \sin\left(\int_x^a k(x')dx' - \frac{\pi}{4}\right) + \frac{2\theta i e^{i\pi/4}(F+iG)}{\sqrt{k(x)}} \cos\left(\int_x^a k(x')dx' - \frac{\pi}{4}\right)$$

which can be simplified back into the form

$$\frac{1}{\sqrt{k(x)}}\left[Ae^{i\int_a^x k(x')dx'} + Be^{-i\int_a^x k(x')dx'}\right]$$

giving us the conversion matrix

$$\mathcal{M} = \frac{1}{4\theta}\begin{pmatrix} 4\theta^2+1 & i(4\theta^2+1) \\ -i(4\theta^2-1) & 4\theta^2+1 \end{pmatrix}$$

4.2 The Path Integral Formulation

Recall that for a 1D particle we have a Hamiltonian

$$H + \frac{p^2}{2m} + V(x)$$

which gives a propagator

$$K(x,t;x',0) = \langle x| U |x\rangle = \sum_n e^{-iE_n t/\hbar}\psi_n(x)\psi_n^*(x')$$

So far we've been using the Schrodinger formulation of quantum mechanics which is tied closely with Hamiltonian mechanics. Feynman, building off work by Dirac, introduced a different formulation which is tied to the Lagrangian. He proposed that the propagator be represented as a sum over all possible paths, a function integral

$$K(x,t;x',0) = \int_{x'}^x e^{iS[x(t)]/\hbar}\,\mathcal{D}[x(t)]$$

which is to be taken over all paths $x(t)$ from x' to x (hence the $\mathcal{D}$). The integrand uses an action $S = \int_0^t Ldt$ where $L = p\dot{x} - H(x,p)$ is the classical Lagrangian.

In a nutshell, Feynman's approach is:

1. Draw all paths from x',t' to x,t

2. Evaluate $S[x(t)]$ for that path (i.e. integrate the Lagrangian along the path)

3. Derive the propagator by summing over all paths (i.e. the integral earlier)

Example. For a free particle, the action is given by

$$S = \int_{t'}^{t} L \, dt = \int_{t'}^{t} \frac{1}{2} m v^2 dt$$

$$= \frac{1}{2} m v^2 (t - t')$$

$$= \frac{1}{2} m \frac{(x - x')^2}{t - t'}$$

We claim that the propagator will be of the form

$$K(x, t; x', t') = A(t) e^{iS/\hbar}$$

where $A(t)$ is some prefactor which is given by the condition

$$\lim_{t \to t'} K = \delta(x - x')$$

$$\therefore \lim_{d \to 0} \frac{1}{d\sqrt{\pi}} \exp\left(-\frac{(x - x')^2}{d}\right) = \delta(x - x')$$

$$\therefore d^2 = \frac{m}{2\pi i \hbar (t - t')}$$

$$\therefore A(t) = \left(\frac{m}{2\pi i \hbar (t - t')}\right)^{1/2}$$

This result is also true for a limited set of cases, in particular $V(x) = a + bx + cx^2$

Returning to the general case we must discretize the path using

$$t_n = t_0 + n\epsilon \qquad n = 0, 1, \ldots, N$$

$$\epsilon = \frac{t_0 - t_N}{N} \qquad x(t_j) = x_j$$

where we define $t_0 = t', t_N = t$. Consider the limit $N \to \infty, \epsilon \to 0$ such that $N\epsilon = t - t'$ is finite, this limit will give us the result. The action integral becomes

$$S = \int_{t_0}^{t_N} L \, dt = \int_{t_0}^{t_N} \frac{1}{2} m \dot{x}^2 dt$$

$$= \sum_{j=0}^{N-1} \frac{m}{2} \left(\frac{x_{j+1} - x_j}{\epsilon}\right) \epsilon$$

$$= \sum_{j=0}^{N-1} \frac{m(x_{j+1} - x_j)^2}{2\epsilon}$$

which allows us to write down the propagator

$$K = \lim A \int_{-\infty}^{\infty} dx_{N-1} \cdots \int_{-\infty}^{\infty} dx_1 \exp\left(\frac{im}{2\hbar} \sum_{j=0}^{N-1} \frac{(x_{j+1} - x_j)^2}{\epsilon}\right)$$

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where A is some scaling factor. To get this factor, we scale the entire integral so that it can be rewritten as a series of Gaussian integrals. Define

$$y_j = \sqrt{\frac{m}{2\hbar\epsilon}} x_j$$

and rewrite the integral as

$$K = \lim A' \int_{-\infty}^{\infty} dy_{N-1} \cdots \int_{-\infty}^{\infty} dy_1 \exp\left(i \sum_{j=0}^{N-1} (y_{j+1} - y_j)^2 \right)$$

Rescaling the integral also rescales the prefactor

$$A' = A \left(\frac{2\hbar\epsilon}{m}\right)\left(\frac{N-1}{2}\right)$$

Upon carrying out all the Gaussian integrals we get

$$K = \lim A' \left(\frac{(i\pi)^{N-1}}{N}\right)^{1/2} \exp\left(-\frac{(y_N - y_0)^2}{Ni}\right)$$

$$= \lim \left[A \left(\frac{2\pi i\hbar\epsilon}{m}\right)^{N/2} \right] \left(\frac{m}{2\pi i\hbar(t_N - t_0)}\right)^{1/2} \exp\left(\frac{im(x_N - x_0)^2}{2\hbar(t_N - t_0)}\right)$$

The second half is the same form as a free particle so the from factor can be defined to be 1

$$A = B^{-N} \qquad B = \left(\frac{2\pi i\hbar\epsilon}{m}\right)^{1/2}$$

so the path integral formula can be written

$$\int \mathcal{D}[x(t)] = \lim \left(\frac{m}{2\pi i\hbar\epsilon}\right)^{1/2} \prod_{n=1}^{N-1} \int_{-\infty}^{\infty} dx_n \left(\frac{m}{2\pi i\hbar\epsilon}\right)^{1/2}$$

Example. Since propagators are easy to calculate if the potential is of the form $V(x) = a + bx + cx^2$, consider a particle subject to a constant force F ($V = -Fx$) in one direction. We can calculate the classical action by first taking the classical equation of motion

$$x(t) = x_0 + v_0 t + \frac{1}{2} at^2 = x_0 + \frac{p_0 t}{m} + \frac{Ft^2}{2m}$$

Thue the action integral becomes

$$S_{cl} = \int_0^t \frac{m}{2} \left(\frac{p_o}{m} + \frac{Ft}{m}\right)^2 + Fx_0 \, dt$$

$$= \frac{p_0^2 t}{2m} + \frac{p_0 Ft^2}{m} + Fx_0 t + \frac{F^2 t^3}{3m}$$

$$= \frac{m(x - x_0)^2}{2t} + \frac{Ft(x + x_0)}{2} - \frac{F^2 t^3}{24m}$$

which gives the propagator

$$K(x, t; x_0, 0) = \left(\frac{m}{2\pi i\hbar t}\right)^{1/2} e^{iS_{cl}/\hbar}$$

5 Theory of Angular Momentum

5.1 Rotation Operators

In classical mechanics a rotation preserves length. A rotation about some action $\hat{n}$ of angle ϕ is denoted using the operator $R_{\hat{n}}(\phi)$. By introducing a rotation operator we are working in the active picture where vectors transform rather than the axis. We can derive the following properties

- $R^T R = R R^T = \mathbb{1}$ which implies $\det R = 1$

- $R(0) = \mathbb{1}$

- $R(-\phi) = R(\phi)^{-1}$

- $R_{\hat{n}}(\phi_1) R_{\hat{n}}(\phi_2) = R_{\hat{n}}(\phi_1 + \phi_2)$

The last statement essentially states that rotations about the same axis commute, but rotations about different axis generally will not commute. However the rotation operators still form a group, $SO(3)$, the group of 3x3 special ($\det = 1$) orthogonal matrices. For the main axes, we have

$$
R_{\hat{x}}(\phi) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\phi & -\sin\phi \\ 0 & \sin\phi & \cos\phi \end{pmatrix}
$$

$$
R_{\hat{y}}(\phi) = \begin{pmatrix} \cos\phi & 0 & \sin\phi \\ 0 & 1 & 0 \\ -\sin\phi & 0 & \cos\phi \end{pmatrix}
$$

$$
R_{\hat{z}}(\phi) = \begin{pmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix}
$$

Consider some infinitesimal rotation about $\hat{z}$ ($\phi \to \epsilon \ll 1$)

$$
R_{\hat{z}}(\epsilon) = \begin{pmatrix} 1 - \epsilon^2/2 & -\epsilon & 0 \\ \epsilon & 1 - \epsilon^2/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} + O(\epsilon^2)
$$

We can write down the rotation operators for the other axis and calculate commutation relations

$$
[R_{\hat{x}}(\epsilon), R_{\hat{y}}(\epsilon)] = R_{\hat{z}}(\epsilon^2) - \mathbb{1}
$$
$$
[R_{\hat{y}}(\epsilon), R_{\hat{z}}(\epsilon)] = R_{\hat{x}}(\epsilon^2) - \mathbb{1}
$$
$$
[R_{\hat{z}}(\epsilon), R_{\hat{x}}(\epsilon)] = R_{\hat{y}}(\epsilon^2) - \mathbb{1}
$$

In other words we have a general commutation relation

$$[R_{\hat{i}}(\epsilon), R_{\hat{j}}(\epsilon)] = \epsilon_{ijk} R_{\hat{k}}(\epsilon^2) - \mathbb{1}$$

this can be used to make our rotation group into a Lie group. Since we are doing quantum mechanics, we want an operator D such that

$$|\alpha\rangle_R = |R\alpha\rangle = D(R)|\alpha\rangle$$

Recall that translations were generated by the momentum operator $\mathbf{p}$

$$T(\mathbf{a}) = \exp\left(-\frac{i\mathbf{p}\cdot\mathbf{a}}{\hbar}\right)$$

Using a similar approach let's have $D(R)$ be generated by some operator $\mathbf{J}$

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

To be consistent with our classical rotation operators, we need

$$[D(R_{\hat{i}}(\epsilon)), D(R_{\hat{j}}(\epsilon))] = \epsilon_{ijk} D(R_{\hat{j}}(\epsilon^2)) - \mathbb{1}$$
$$\therefore [J_{\hat{i}}, J_{\hat{j}}] = i\hbar\epsilon_{ijk} J_{\hat{k}}$$

The operator $\mathbf{J}$, which generates rotations, is defined to be the rotational analogue of momentum: the angular momentum operator. Note that the J_i are all Hermitian operators. To help us find eigenstates, we will define

$$J^2 = \mathbf{J}\cdot\mathbf{J} = J_x^2 + J_y^2 + J_z^2$$

which notably commutes with each J_i. Thus we can just find simultaneous eigenstates of both the J^2 and one of the J_i (J_z by convention), these states will be labeled as $|a, b\rangle$

$$J^2|a,b\rangle = a|a,b\rangle$$
$$J_z|a,b\rangle = b|a,b\rangle$$

We can find these states using commutation relations and imposing conditions on the a, b. First we have

$$\langle a,b| J^2 - J_z |a,b\rangle = \langle a,b| J_x^2 + J_y^2 |a,b\rangle$$
$$= \langle a,b| J_x^2 |a,b\rangle + \langle a,b| J_y^2 |a,b\rangle$$
$$= a - b^2 \geq 0$$
$$\therefore a \geq b^2$$

It's useful to define ladder operators $J_{\pm} = J_x \pm iJ_y$ which commute as follows

$$[J_+, J_-] = 2\hbar J_z$$
$$[J_z, J_{\pm}] = \pm\hbar J_z$$
$$[J_{\pm}, J^2] = 0$$

Just like when solving for harmonic oscillator eigenstates, we form

$$J^2(J_\pm \ket{a,b}) = J_\pm J^2 \ket{a,b} = a(J_\pm \ket{a,b})$$
$$J_z(J_\pm \ket{a,b}) = (J_\pm J_z \pm \hbar J_\pm)\ket{a,b}$$
$$= (b \pm \hbar)(J_\pm \ket{a,b})$$

This seems to suggest that $J_\pm \ket{a,b}$ remains a simultaneous eigenket but with an increased (or decreased) b value. But $a \geq b^2$, so we cannot increment/decrements b infinitely, there must be some sopping point. For find these, consider

$$J_- J_+ \ket{a,b_{max}} = 0$$
$$(J^2 - J_z^2 - \hbar J_z)\ket{a,b_{max}} = 0$$
$$\therefore a = b_{max}(b_{max} + \hbar)$$
$$J_+ J_- \ket{a,b_{min}} = 0$$
$$(J^2 - J_z^2 + \hbar J_z)\ket{a,b_{min}} = 0$$
$$\therefore a = b_{min}(b_{min} - \hbar)$$
$$\therefore b_{min} = -b_{max}$$

Our calculations from before also show that b increments (or decrements) by $\hbar$ each time, so

$$b_{max} = b_{min} + n\hbar \to b_{max} = \frac{n\hbar}{2}$$

for some n. For simplicity, define

$$j = \frac{b_{max}}{\hbar} = 0, \frac{1}{2}, 1, \ldots \to a = \hbar^2 j(j+1)$$

Furthermore we'll define m (later rebranded m_j) so that

$$b = m\hbar \to m = -j, -j+1, \ldots, j-1, j$$

Thus our eigenstates can be represented as $\ket{j,m}$ with

$$\braket{j', m'|j.m} = \delta_{jj'}\delta_{mm'}$$
$$J^2 \ket{j,m} = \hbar^2 j(j+1)\ket{j,m}$$
$$J_z \ket{j,m} = \hbar m \ket{j,m}$$

For the ladder operators, we can calculate the coefficients using operator sandwiches

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

Now let's start constructing the $D(R)$ operators, starting with the case $j = 1/2$ (spin 1/2). This case is simple because we can just write

$$D(R_{\hat{n}}(\phi)) = \exp\left(-\frac{i\mathbf{S}\cdot\hat{n}\phi}{\hbar}\right) = \exp\left(-\frac{i\sigma\cdot n\phi}{2}\right)$$

where σ is a vector of the Pauli matrices and the states $D(R)$ acts on are just the familiar 2 component spinors.

$$|\alpha\rangle = a\,|+\rangle + b\,|-\rangle = \begin{pmatrix} a \\ b \end{pmatrix}$$

For a rotation about $\hat{z}$, we have

$$D(R_{\hat{z}}(\phi)) = D_{\hat{z}}(\phi) = \exp\left(-\frac{iS_z\phi}{\hbar}\right)$$

$$D_{\hat{z}}(\phi)\,|\alpha\rangle = \begin{pmatrix} ae^{-i\phi/2} \\ be^{i\phi/2} \end{pmatrix}$$

This implies that a 2π rotation simply flips the state

$$D_{\hat{z}}(2\pi)\,|\alpha\rangle = -\,|\alpha\rangle$$

in fact this is a general property, a 2π rotation about any axis will flip the state. Furthermore this is true for any half integer j, for integer j we have instead

$$D_{\hat{n}}\,|\alpha\rangle = |\alpha\rangle$$

This suggests that half integer j are not true representations of $SO(3)$, rather they are true one-to-one representations of $SU(2)$ which is locally isomorphic to $SO(3)$ but differs globally.

For a general axis and angle, the operator is

$$D(R_{\hat{n}}(\phi)) = \exp\left(-\frac{i\sigma\cdot\hat{n}\phi}{2}\right) = \sum_{k=0}^{\infty} \frac{(-i\sigma\cdot\hat{n}\phi/2)^k}{k!}$$

To simplify this expression we have the useful identity

$$(\sigma\cdot\mathbf{a})(\sigma\cdot\mathbf{b}) = (\mathbf{a}\cdot\mathbf{b})\mathbb{1} + i\sigma\cdot(\mathbf{a}\times\mathbf{b})$$

$$\therefore (\sigma\cdot n)^k = \begin{cases} 1 & k \text{ even} \\ \sigma\cdot\hat{n} & k \text{ odd} \end{cases}$$

This allows us to write down the explicit form

$$D(R_{\hat{n}}(\phi)) = \cos\left(\frac{\phi}{2}\right) - i\sigma\cdot\hat{n}\sin\left(\frac{\phi}{2}\right) = \begin{pmatrix} \cos(\phi/2) - in_z\sin(\phi/2) & (-in_x - n_y)\sin(\phi/2) \\ (-in_x + n_y)\sin(\phi/2) & \cos(\phi/2) + in_z\sin(\phi/2) \end{pmatrix}$$

where we take $\hat{n} = \langle n_x, n_y, n_z \rangle$

For a general j, it's better to parameterize rotations using the Euler angles α, β, γ instead of $\hat{n}, \phi$. Our operators with the Euler angles are

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

$$D(R(\alpha, \beta, \gamma)) = \exp\left(-\frac{iJ_z\alpha}{\hbar}\right) \exp\left(-\frac{iJ_y\beta}{\hbar}\right) \exp\left(-\frac{iJ_z\gamma}{\hbar}\right)$$

Since J^2 commutes with each of the J_i, the matrix elements of this operator will vanish unless $j' = j$, these functions are called the Wigner functions and denoted

$$D^{(j)}_{m'm}(\alpha, \beta, \gamma) = \langle jm' | D(\alpha, \beta, \gamma) | jm \rangle$$

With the Wigner functions, any rotation can be described

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

Note that since $J_z |jm\rangle = m\hbar |jm\rangle$, the expression for the Wigner functions can be simplified

$$\begin{aligned}
D^{(j)}_{m'm}(\alpha, \beta, \gamma) &= \langle jm' | e^{-iJ_z\alpha/\hbar} e^{-iJ_y\beta/\hbar} e^{-iJ_z\gamma/\hbar} | jm \rangle \\
&= e^{-i(m'\alpha + m\gamma)} \langle jm' | e^{-iJ_y\beta/\hbar} | jm \rangle \\
&= e^{-i(m'\alpha + m\gamma)} d^{(j)}_{m'm}(\beta)
\end{aligned}$$

So we can also compute rotations using $d^{(j)}_{m'm}$. Both of these can be computed through brute force, for instance in the $j = 1/2$ case

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

$$D^{(1/2)}(\alpha, \beta, \gamma) = \begin{pmatrix} e^{i(\alpha+\gamma)/2}\cos(\beta/2) & e^{i(\alpha-\gamma)/2}\sin(\beta/2) \\ e^{-i(\alpha-\gamma)/2}\sin(\beta/2) & e^{-i(\alpha+\gamma)/2}\cos(\beta/2) \end{pmatrix}$$

The $d^{(j)}$ functions have the following properties

$$d^{(j)}_{m'm}(\beta) = (-1)^{m-m'} d^{(j)}_{mm'}(\beta) = d^{(j)}_{-m,-m'}(\beta)$$

$$d^{(j)}_{m'm}(-\beta) = (-1)^{m-m'} d^{(j)}_{m'm}(\beta) = d^{(j)}_{mm'}(\beta)$$

$$d^{(j)}_{m'm}(0) = \delta_{mm'}$$

Example: $j = 1$ Wigner Functions

We will arrive at $d^{(1)}$ through a series of results. First we already have the result $\prod_a(A - a) = 0$ for which a are the eigenvalues of A. Let $\mathcal{J} = \mathbf{J}^{(1)} \cdot \hat{n}.\hbar$, then it's eigenvalues are $0, \pm 1$. Thus

$$(\mathcal{J} + 1)\mathcal{J}(\mathcal{J} - 1) = \mathcal{J}^3 - \mathcal{J} = 0 \to \mathcal{J}^3 = \mathcal{J}$$

This allows us to expand the Wigner function completely

$$D^{(1)}(R_{\hat{n}}(\phi)) = \sum_{n=0} \frac{(-i\phi)^n \mathcal{J}^n}{n!}$$

$$= 1 + \mathcal{J}\left((-i\phi) + \frac{(-i\phi)^3}{3!} + \cdots\right) + \mathcal{J}^2\left(\frac{(-i\phi)^2}{2!} + \frac{(-i\phi)^4}{4!} + \cdots\right)$$

$$= 1 - i\sin(\phi)\mathcal{J} + (\cos(\phi) - 1)\mathcal{J}^2$$

If we choose $\hat{n} = \hat{y}$, then

$$\mathcal{J} = \frac{J_y}{\hbar} = \frac{i}{\sqrt{2}}\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix} \qquad \mathcal{J}^2 = \frac{1}{2}\begin{pmatrix} 1 & 0 & -1 \\ 0 & 2 & 0 \\ -1 & 0 & 1 \end{pmatrix}$$

The other two angular momentum operators are also sometimes useful

$$J_x = \frac{\hbar}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \qquad J_z = \hbar\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

We can now write down $d^{(1)}$ explicity

$$d^{(1)}(\beta) = 1 - i\sin(\phi)\mathcal{J} + (\cos(\phi) - 1)\mathcal{J}^2$$

$$= 2\begin{pmatrix} 1 + \cos\beta & -\sqrt{2}\sin\beta & 1 - \cos\beta \\ \sqrt{2}\sin\beta & 2\cos\beta & -\sqrt{2}\sin\beta \\ 1 - \cos\beta & \sqrt{2}\sin\beta & 1 + \cos\beta \end{pmatrix}$$

5.2   Orbital Angular Momentum

Now suppose we want to project the angular momentum state $|jm\rangle$ into position space. This can only be done consistently in the case $j = \ell$, where ℓ is an integer. In position space, the angular momentum operator $\mathbf{J}$ is replaced by $\mathbf{L}$, where

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

$$\begin{cases} L_x = yp_z - zp_y \\ L_y = zp_x - xp_z \qquad [L_i, L_j] = i\hbar\epsilon_{ijk}L_k \\ L_z = xp_y - yp_x \end{cases}$$

For an infinitesimal rotation about the z-axis

$$D_{\hat{z}}(\epsilon) = \exp\left(-\frac{iL_z\epsilon}{\hbar}\right) = 1 - -\frac{iL_z\epsilon}{\hbar} + \cdots = \mathbb{1} - \frac{i\epsilon}{\hbar}(xp_y - yp_x) + \cdots$$

If we take some arbitrary state $|\mathbf{x}\rangle = |xyz\rangle$, then this will act as

$$D_{\hat{z}}(\epsilon)|\mathbf{x}\rangle = |x - \epsilon y, y + \epsilon x, z\rangle \equiv |x'y'z'\rangle |\mathbf{x}'\rangle$$

This indicates $\mathbf{x}$ and $\mathbf{x}'$ are related by the rotation $R_{\hat{z}}(\epsilon)$, namely

$$\mathbf{x}' = R_{\hat{z}}(\epsilon)\mathbf{x} = \begin{pmatrix} 1 & -\epsilon & 0 \\ \epsilon & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x - \epsilon y \\ y + \epsilon x \\ z \end{pmatrix}$$

More generally we have (as expected)

$$D(R)\ket{\mathbf{x}} = \ket{\mathbf{x}'} = \ket{R\mathbf{x}}$$

so that for an arbitrary state $\ket{\alpha}$, we have the rotation wavefunction

$$\begin{aligned}
\psi_{R_\alpha}(\mathbf{x}) = \braket{\mathbf{x}|\alpha}_R &= \bra{\mathbf{x}} D(R) \ket{\alpha} \\
&= \braket{D^\dagger(R)\mathbf{x}|\alpha} = \braket{D(R)^{-1}\mathbf{x}|\alpha} \\
&= \braket{R^{-1}\mathbf{x}|\alpha} \\
&= \psi_\alpha(R^{-1}\mathbf{x})
\end{aligned}$$

For most purposes it's better to work in spherical coordinates $\ket{\mathbf{x}} = \ket{r\theta\phi}$ so that a rotation about z takes the form

$$\bra{r\theta\phi} D(R_{\hat{z}}(\epsilon)) \ket{\alpha} = \braket{r, \theta, \phi - \epsilon|\alpha} = \braket{r\theta\phi|\alpha} - \epsilon\frac{\partial}{\partial\phi}\braket{r\theta\phi|\alpha}$$

which can be further Taylor expanded to get the relation

$$\bra{r\theta\phi} \mathbb{1} - \frac{i\epsilon}{\hbar}L_z \ket{\alpha} = \braket{r\theta\phi|\alpha} - \epsilon\frac{\partial}{\partial\phi}\braket{r\theta\phi|\alpha}$$

Thus we can identify

$$\boxed{L_z = -i\hbar\frac{\partial}{\partial\phi}}$$

Similar considerations (e.g. infinitesimal rotations in other axis) give

$$\boxed{\begin{aligned}
L_x &= i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right) \\
L_y &= -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right) \\
\therefore L_\pm &= L_x \pm iL_y = -i\hbar e^{\pm i\phi}\left(\pm i\frac{\partial}{\partial\theta} - \cot\theta\frac{\partial}{\partial\phi}\right) \\
L^2 &= -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]
\end{aligned}}$$

Note that the magnitude operator is just the angular part of the kinetic energy term $\nabla^2\braket{\mathbf{x}|\alpha}$. It also has the useful property

$$L^2 = x^2p^2 - (\mathbf{x}\cdot\mathbf{p})^2 + i\hbar\mathbf{x}\cdot\mathbf{p}$$

Suppose the potential is independent of θ, ϕ so that angular part of the eigenstates will be $|\ell m\rangle$ projected into position space.

$$L^2 \, |\ell m\rangle = \hbar^2 \ell(\ell+1) \, |\ell m\rangle \qquad L_z \, |\ell m\rangle = \hbar m \, |\ell m\rangle$$

Since we can separate the Schrodinger equation into radial and spherical parts, let $|\hat{n}\rangle = |\theta\phi\rangle$ be the position eigenstates restricted onto a sphere (to get the spherical part). The spherical harmonics are defined to be

$$\langle \hat{n}|\ell m\rangle = Y_{\ell m}(\hat{n}) \quad \text{or} \quad \langle \theta\phi|\ell m\rangle = Y_{\ell m}(\theta, \phi)$$

There are two ways to solve for the spherical harmonics (just like the oscillator), the first is to solve using the operators directly.

$$\langle \hat{n}| \, L_z \, |\ell m\rangle = \hbar m \, \langle \hat{n}|\ell m\rangle \rightarrow -i\hbar \frac{\partial}{\partial \phi} Y_{\ell m} = \hbar m Y_{\ell m}$$

This seems to suggest that we take the form

$$Y_{\ell m} = f(\theta) e^{im\phi}$$

From the L^2 operator, we get the condition

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

$$\therefore -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right] Y_{\ell m} = \hbar^2 \ell(\ell+1) Y_{\ell m}$$

$$\therefore \left[\frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) - \frac{m^2}{\sin^2\theta} + \ell(\ell+1) \right] Y_{\ell m} = 0$$

The last expression, which gives the θ dependence of the spherical harmonics, defines the associated Legendre polynomials $P_{\ell m}(\cos\theta)$. These are defined in terms of the normal Legendre polynomials

$$P_{\ell m}(x) = (1-x^2)^{m/2} \frac{d^m}{dx^m} P_\ell(x) = \frac{1}{2^\ell \ell!} (1-x^2)^{m/2} \frac{d^{\ell+m}}{dx^{\ell+m}} (x^2-1)^\ell$$

Thus the normalized spherical harmonics are

- For $m > 0$

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

- For $m < 0$ we use the relation

$$Y_{\ell,-m} = (-1)^m Y_{\ell m}^*$$

Alternatively we can solve for the spherical harmonics using ladder operators. For instance, we know that L_+ annihilates the state $|\ell\ell\rangle$ which gives the equation

$$\left(\frac{\partial}{\partial\theta} - \ell\cot\theta\right)Y_{\ell\ell} = 0$$

We can integrate this to get

$$Y_{\ell\ell} = c_{\ell\ell}\sin^\ell\theta e^{i\ell\phi}$$

Repeated applications of the lowering operator gives the other spherical harmonics, which we can then normalize. Note that for $m = 0$, we have the useful property

$$Y_{\ell 0}(\theta, \phi) = \delta_{m0}P_\ell(\cos\theta)\sqrt{\frac{2\ell+1}{4\pi}}$$

The $|\ell m\rangle$ states are orthogonal and complete

$$\langle\ell'm'|\ell m\rangle = \delta_{\ell\ell'}\delta_{mm'} \qquad \sum_{\ell,m}|\ell m\rangle\langle\ell m| = \mathbb{1}$$

Translating this to the language of spherical harmonics tells us

$$\int Y_{\ell'm'}^* Y_{\ell m}d\Omega = \delta_{\ell\ell'}\delta_{mm'}$$

$$\sum_{\ell,m}Y_{\ell m}^*(\theta', \phi')Y_{\ell m}(\theta, \phi) = \delta(\cos\theta - \cos\theta')\delta(\phi - \phi') = \frac{\delta(\theta-\theta')\delta(\phi-\phi')}{\sin\theta}$$

Just like any $|jm\rangle$ state, the $|\ell m\rangle$ states can also be rotated, with the implication that spherical harmonics can be acted on by the rotation operators as well.

$$Y_{\ell,m}(\theta', \phi') = \sum_{m'}Y_{\ell m}(\theta, .\phi)D_{m'm}^{(\ell)}(R)$$

In fact the spherical harmonics can be directly related to the Wigner functions with

$$Y_{\ell m}^*(\theta, \phi) = \sqrt{\frac{\ell+1}{4\pi}}D_{m0}^{(\ell)}(\phi, \theta, \gamma = \text{arbitrary})$$

If α, β give the transform $(\theta, \phi) \to (\theta', \phi')$ then we also have

$$P_\ell(\cos\theta') = \frac{4\pi}{2\ell+1}\sum_m Y_{\ell m}(\theta, \phi)Y_{\ell m}^*(\beta, \alpha)$$

First Few Spherical Harmonics

Here we list some spherical harmonics for convenience:

$$Y_{00}(\theta, \phi) = \frac{1}{2\sqrt{\pi}}$$

$$Y_{11}(\theta, \phi) = -\sqrt{\frac{3}{8\pi}} \sin \theta e^{i\phi}$$

$$Y_{10}(\theta, \phi) = \sqrt{\frac{3}{4\pi}} \cos \theta$$

$$Y_{22}(\theta, \phi) = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{2i\phi}$$

$$Y_{21}(\theta, \phi) = -\sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{i\phi}$$

$$Y_{20}(\theta, \phi) = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$$

$m < 0$ states will be omitted since they can be obtained from the $m > 0$ states.

Example. As a demonstration of how to use the spherical harmonics, suppose we have a wavefunction

$$\psi(\mathbf{x}) = (x + y + 3z)f(r)$$

and we know that it is in a spherically symmetric potential. Using spherical harmonics (and converting them to Cartesian coordinates), we can rewrite the state as

$$\psi(\mathbf{x}) = \sqrt{\frac{4\pi}{3}} r f(r)(-e^{-i\pi/4}Y_{11} + e^{i\pi/4}Y_{1,-1} + 3Y_{10})$$

which would indicate that this is an eigenstates of L^2 with eigenvalue $\ell = 1$. In fact we can write it more generally as

$$|\psi\rangle = |R\rangle \otimes \frac{1}{\sqrt{11}}(-e^{-i\pi/4}|11\rangle + e^{i\pi/4}|1,-1\rangle + 3|10\rangle)$$

which means we have have $m = \pm 1$ with probability $1/11$ and $m = 0$ with probability $3/11$.

5.3 Rotational Invariance

We say a Hamiltonian is rotationally invariant if it is of the form

$$H = \frac{p^2}{2m} + V(r)$$

in which case $[H, L_i] = 0$ and also $[H, L_\pm] = 0$. This means we can label the states using ℓ, m as well as the energies.

$$H\,|E\ell m\rangle = E\,|E\ell m\rangle$$
$$L^2\,|E\ell m\rangle = \hbar^2\ell(\ell+1)\,|E\ell m\rangle$$
$$L_z\,|E\ell m\rangle = \hbar m\,|E\ell m\rangle$$
$$L_\pm H\,|E\ell m\rangle = H(L_\pm\,|E\ell m\rangle) = E(L_\pm\,|E\ell m\rangle)$$

This implies $L_\pm\,|E\ell m\rangle$ are also energy eigenstates and suggests that E does not depend on m. Thus we can denote the energies with $E_{n\ell}$. Eigenstates can be separated into two components, we've already solved the angular component to get spherical harmonics, what remains is the radial component which will depend on the potential.

$$\psi(r, \theta, \phi) = R_{E\ell}(r)Y_{\ell m}(\theta, \phi)$$
$$\left[-\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{L^2}{\hbar^2 r^2}\right) + V(r)\right]\psi_{E\ell m} = E\psi_{E\ell m}$$

We will introduce $u(r) = rR(r)$ (and drop subscripts) to rewrite the equation as

$$\left[\frac{d^2}{dr^2} + \frac{2m}{\hbar^2}\left(E - V(r) - \frac{\ell(\ell+1)\hbar^2}{2mr^2}\right)\right]u(r) = 0$$

This is very similar to a 1D problem except with domain $0 \le r < \infty$ and with an effective potential

$$V_{eff} = V(r) + \frac{\ell(\ell+1)\hbar^2}{2mr^2}$$

The additional contribution to the potential is known as the centrifugal barrier term. Now let's discuss some boundary conditions. There are three boundary conditions that we can consider, from weakest to strongest.

1. $u(r)$ must be well behaved, i.e. it is square integrable

$$\int_0^\infty |R(r)|^2 r^2 dr = \int_0^\infty |u(r)|^2 dr$$

This restricts the behavior of $u(r)$ as $r \to \infty$, in particular we have

$$u(r) \to \begin{cases} 0 & \text{bound state} \\ e^{ikr} & \text{scattering state} \end{cases}$$

For normalization purposes, as $r \to 0$ we need $u(r)$ to be less singular than $1/\sqrt{r}$

$$\text{if } u(r) \to r^s, \text{ then } s > -1/2$$
$$\text{if } R(r) \to r^q, \text{ then } q > -3/2$$

2. H is self-adjoint, which carries the condition

$$\int_0^\infty u_1^* D_\ell u_2 dr = u_1^*\frac{du_2}{dr} - u_2\frac{du_1^*}{dr}\bigg|_0^\infty = 0$$

3. H is Hermitian (strongest condition), so $u(r) \to c$ as $r \to 0$. But unless $V(r)$ contains a delta function, then $c = 0$.

$$\nabla^2 \psi \to \nabla^2 \frac{1}{r} = -4\pi\delta^3(\mathbf{x})$$

Let's examine the $r \to 0$ limit more closely. If $r^2 V(r) \to 0$, then the potential can be neglected in favor of the centrifugal term. In this case

$$\frac{d^2 u}{dr^2} \sim \frac{\ell(\ell+1)}{r^2} u(r) \to u \sim r^{\ell+1}$$

which implies $R_\ell(r) \to r^\ell$ as $r \to 0$.

In the other direction, for $r \to \infty$, the potential term will always dominate and so the behavior of the solution will depend on the form of the given potential. In particular there are three main cases to consider:

1. $rV(r) \to 0$ as $r \to \infty$, which indicates the potential is also negligible

$$\frac{d^2 u}{dr^2} = -\frac{2mE}{\hbar^2} u(r)$$

   Thus for $E > 0$ we have the scattering states

$$u(r) = Ae^{ikr} + Be^{-ikr} \qquad k = \sqrt{\frac{2mE}{\hbar^2}}$$

   and for $E < 0$ we have the bound states

$$u(r) = Ce^{-\kappa r} \qquad \kappa = \sqrt{-\frac{2mE}{\hbar^2}}$$

   Note that we discard the growing exponential to maintain square integrability.

2. $rV(r) \to \infty$ as $r \to \infty$, then the solution will depend on what $V(r)$ is

3. $rV(r) \to$ constant (e.g. in the Coulomb potential). For $E > 0$ we can take

$$u(r) \to f(r)e^{\pm ikr} \qquad f'' \pm 2ikf' - \frac{2mV(r)}{\hbar^2}f = 0$$

   If we assume f follows a power law, then f'' is negligible, giving

$$\pm 2ikf' = \frac{2mV(r)}{\hbar^2}f \to f(r) = f(r_0)\exp\left(\pm\frac{im}{\hbar^2 k}\int_{r_0}^r V(r)dr\right)$$

   For the Coulomb potential $V(r) = -e^2/r$, we find

$$f(r) = f(r_0)\left(\frac{r}{r_0}\right)^{\pm ime^2/\hbar^2 k}$$

   which means the actual radial component is

$$u(r) \to r^{\pm ime^2/\hbar^2 k}e^{\pm ikr}$$

   A similar story occurs for $E < 0$ and essentially we see that the effects of the potential will never be negligible in this case.

5.3.1 Particles and Wells: The Return

First we discuss the free particle in spherical coordinates. Generally there are two approaches to solving rotationally invariant problems: we can either compute $R(r)$ directly, or work with $u(r)$ instead.

1) If we work with $R(r)$ directly, we get the equation

$$\left[-\frac{\hbar^2}{2mr^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \frac{\hbar^2\ell(\ell+1)}{2mr^2}\right]R(r) = ER(r)$$

It's useful to define $\rho = kr$ where $k = \sqrt{2mE/\hbar^2}$ so that

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \left(1 - \frac{\ell(\ell+1)}{\rho}\right)R = 0$$

The solutions take the form

$$R_{E\ell}(r) = Aj_\ell(kr) + Bn_\ell(kr)$$

where we have the spherical Bessel functions

$$j_\ell(x) = \sqrt{\frac{\pi}{2x}}J_{\ell+1/2}(x) = (-x)^\ell\left(\frac{1}{x}\frac{d}{dx}\right)^\ell\left(\frac{\sin x}{x}\right)$$

and the spherical Neumann functions

$$n_\ell(x) = \sqrt{\frac{\pi}{2x}}N_{\ell+1/2}(x) = (-x)^\ell\left(\frac{1}{x}\frac{d}{dx}\right)^\ell\left(\frac{\cos x}{x}\right)$$

As $x \to 0$ we have the asymptotic behavior

$$j_\ell(x) \to \frac{x^\ell}{(2\ell+1)!!} \qquad n_\ell(x) \to -\frac{(2\ell-1)!!}{x^{\ell+1}}$$

However only j_ℓ converges regularly, so if the region contains $r = 0$, then $B = 0$ since we must discard the n_ℓ term. In such a case the wavefunction is

$$\psi_{E\ell m} = Aj_\ell(kr)Y_{\ell m}(\theta, \phi)$$

with normalization condition

$$\int d^3x\, Y_{E\ell m}^* Y_{E'\ell'm'} = \frac{|A|^2\pi}{2k^2}\delta(k-k')\delta_{\ell\ell'}\delta_{mm'}$$

2) If we choose to work with $u(r)$ instead, we have the equation

$$\left(\frac{d^2}{dr^2} + k^2 - \frac{\ell(\ell+1)}{r^2}\right)u_\ell = 0$$

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Again we will define $\rho = kr$ to simplify the equation

$$\left(-\frac{d^2}{d\rho^2} + \frac{\ell(\ell+1)}{\rho^2}\right) u_\ell = u_\ell$$

$$\left(\frac{d}{d\rho} + \frac{\ell+1}{\rho}\right)\left(-\frac{d}{d\rho} + \frac{\ell+1}{\rho}\right) u_\ell = u_\ell$$

$$\left(-\frac{d}{d\rho} + \frac{\ell+1}{\rho}\right)\left(\frac{d}{d\rho} + \frac{\ell+1}{\rho}\right)\left(-\frac{d}{d\rho} + \frac{\ell+1}{\rho}\right) u_\ell = \left(-\frac{d}{d\rho} + \frac{\ell+1}{\rho}\right) u_\ell$$

Let $\ell' = \ell + 1$, which transforms the equation into

$$\left(-\frac{d^2}{d\rho^2} + \frac{\ell'(\ell+1)}{\rho^2}\right)\left(-\frac{d}{d\rho} + \frac{\ell+1}{\rho}\right) u_\ell = \left(-\frac{d}{d\rho} + \frac{\ell+1}{\rho}\right) u_\ell$$

$$\therefore \left(-\frac{d}{d\rho} + \frac{\ell+1}{\rho}\right) u_\ell = c_\ell u_{\ell+1}$$

In other words, we've arrived at a sort of raising operator for u_ℓ. This is particularly useful because we can now consider $\ell = 0$ as a starting point for all other states.

$$-\frac{d^2}{d\rho^2} u_0 = u_0 \rightarrow u_0 = A\sin\rho + B\cos\rho$$

For instance the next state up would be

$$u_1 = \left(-\frac{d}{d\rho} + \frac{1}{\rho}\right) = \left(\frac{B}{\rho} - A\right)\cos\rho + \left(\frac{A}{\rho} + B\right)\sin\rho$$

Thus we can express the radial functions as

$$R_0 = \frac{u_0(\rho)}{\rho} \qquad R_\ell(\rho) = (-\rho)^\ell \left(\frac{1}{\rho}\frac{d}{d\rho}\right)^\rho R_0(\rho)$$

Note that energies still don't depend on ℓ since k has no ℓ dependence. We can compare this to a free particle in Caresian coordinates to get the useful relation (setting $\mathbf{k} = k\hat{z}$)

$$e^{ikz} = \sum_\ell i^\ell (2\ell+1) j_\ell(kr) P_\ell(\cos\theta)$$

Let's also discuss the infinite well, the potential is very similar but in spherical coordinates

$$V(r) = \begin{cases} 0 & r < r_0 \\ \infty & r > r_0 \end{cases}$$

The radial equation can be solved to give the states

$$\psi_{k\ell m} = A j_\ell(kr) Y_{\ell m}(\theta, \phi)$$

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However we have the boundary condition

$$\psi_{k\ell m}(r_0, \theta, \phi) = A j_\ell(kr_0) Y_{\ell m}(\theta, \phi) = 0$$

Since this must hold for all θ, ϕ, the spherical Bessel function must vanish

$$j_\ell(kr_0) = 0 \rightarrow k = \frac{\alpha_{\ell n}}{r_0}$$

where $\alpha_{\ell n}$ denotes the nth zero of $j_\ell(kr_0)$. This gives the energies

$$E = \frac{\hbar^2 \alpha_{\ell n}^2}{2mr_0^2}$$

5.3.2 The Isotropic 3D Oscillator

The last minor example to discuss the the Isotropic 3D oscillator, given by

$$V(r) = \frac{1}{2}m\omega^2 r^2$$

Again we will let $u(r) = rR(r)$ which has to satisfy

$$\left[\frac{d^2}{dr^2} + \frac{2m}{\hbar^2} \left(E - \frac{1}{2}m\omega^2 r^2 - \frac{\ell(\ell+1)}{2mr^2}\hbar^2 \right) \right] u(r) = 0$$

This can be simplified by defining two quantities

$$\rho = \sqrt{\frac{m\omega}{\hbar}}r \qquad \lambda = \frac{E}{\hbar\omega}$$

to give

$$\left[\frac{d^2}{d\rho^2} + 2\lambda - \rho^2 - \frac{\ell(\ell+1)}{\rho^2} \right] u(\rho) = 0$$

We'll take the ansatz

$$u = e^{-\rho^2/2}v \qquad v = \rho^{\ell+1}\sum c_k \rho^k$$

$$v'' - 2\rho v' + \left(2\lambda - 1 - \frac{\ell(\ell+1)}{\rho} \right)v = 0$$

By analyzing asymptotic behavior, we see that only even terms can remain. We can truncate the series to arrive at

$$E_n = \left(n + \frac{3}{2} \right)\hbar\omega \qquad n = 2k' + \ell$$

where $k' = 0, 1, 2$ (so that $k = 2k'$ to remove odd terms). This agrees with the normal 3D oscillator however each state will have degeneracy

$$\sum_{\ell=0}^{n/2} 2\ell + 1 = \frac{(n+1)(n+2)}{2}$$

There is no ℓ dependence due to an addition $U(3)$ symmetry which can be seen by rewriting the Hamiltonian using ladder operators.

5.4 The Hydrogen Atom

The potential in a hydrogen atom is the Coulomb potential $V = -e^2/r$, thus the Schrodinger equation for the electron-proton system is

$$\left[-\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_p}\nabla_p^2 - \frac{e^2}{|\mathbf{x}_e - \mathbf{x}_p|} \right]\psi(\mathbf{x}_e, \mathbf{x}_p) = E\psi(\mathbf{x}_e, \mathbf{x}_p)$$

Let $M = m_e + m_p$ be the total mass and separate the equation into center of mass motion and relative motion

$$\mathbf{x}_{cm} = \frac{m_e\mathbf{x}_e + m_p\mathbf{x}_p}{m_e + m_p} \qquad \mathbf{x} = \mathbf{x}_e - \mathbf{x}_p$$

$$\mathbf{p}_{cm} = \mathbf{p}_e + \mathbf{p}_p = \frac{m_p\mathbf{p}_e - m_e\mathbf{p}_p}{m_e + m_p}$$

We will also define the reduced mass

$$\mu = \frac{m_e m_p}{M} \approx m_e$$

In terms of these new quantities the Hamiltonian is

$$H = \frac{p_{cm}^2}{2M} + \frac{p^2}{2\mu} - \frac{e^2}{r}$$

We see that the center of mass motion is just like that of a free particle (which makes sense because the hydrogen atom is free), thus the overall wavefunction is separated as

$$\psi(\mathbf{x}_e, \mathbf{x}_p) = \frac{e^{i\mathbf{p}_{cm}\cdot\mathbf{x}_{cm}}}{(2\pi\hbar)^{3/2}}\psi_{E\ell m}(r, \theta, \phi)$$

From now on, we will only consider the bound state problem ($E < 0$) for relative motion in the hydrogen atom. Due to the symmetry of the Coulomb potential we know that the wavefunction can be separated into the product of a spherical harmonic and some radial component. This radial component can again be solved in two ways: by working with $u(r) = rR(r)$ or with $R(r)$ directly.

1) If we start with $u(r)$ we get the equation

$$\left[\frac{d^2}{dr^2} - \kappa^2 + \frac{2\mu}{\hbar^2}\frac{e^2}{r} - \frac{\ell(\ell+1)}{r^2} \right] u(r) = 0$$

in which we've defined

$$\kappa = -\frac{2\mu E}{\hbar^2}$$

and where we keep in mind $u(r) \to 0$ as $r \to 0, \infty$ as boundary conditions.

Once again we will change variables to $\rho = \kappa r$, but first we define the quantity

$$\lambda = \frac{2\mu}{\hbar^2\kappa} = \sqrt{-\frac{2\mu}{\hbar^2 E}}$$

so that our equation becomes

$$\frac{d^2u}{d\rho^2} + \left[-1 + \frac{e^2\lambda}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right]u(\rho) = 0$$

From previous discussions we expect something like $u_{E\ell}(\rho) = e^{-\rho}v_{E\ell}(\rho)$ where v is of power law form. Putting this in gives

$$v'' - 2v' + \left(\frac{e^2\lambda}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right)v = 0$$

Suppose v takes the form

$$v = \rho^{\ell+1}\sum_{k=0}c_k\rho^k$$

Substituting this into the equation gives the recurrence relations

$$\frac{c_{k+1}}{c_k} = \frac{2(\ell+k+1) - e^2\lambda}{(k+\ell+2)(k+\ell+1) - \ell(\ell+1)}$$

This solution must not diverge, so at some point we have $e^2\lambda = 2(\ell+k+1)$. By defining the principle quantum number $n = \ell+k+1 = 0, 1, \ldots$, we get the energies

$$E = -\frac{\mu e^4}{2\hbar^2(\ell+k+1)^2} = -\frac{\mu e^4}{2\hbar^2 n}$$

This also means that for some n, the angular momentum quantum number ℓ runs from 0 to $n-1$, introducing an n^2 degeneracy for each level.

To actually get the states, let $v = \rho^{\ell+1}\tilde{v}$ and $\tilde{\rho} = 2\rho$ to get

$$\tilde{\rho}\tilde{v}'' + [2(\ell+1) - \tilde{\rho}]\tilde{v}' + k\tilde{v} = 0$$

This takes the form of the Laguerre equation

$$xy'' + (\alpha+1-x)y' + ny = 0$$

$$\therefore v = y = L_n^\alpha(x) = L_{n-\ell-1}^{2\ell+1}(2\rho)$$

There is another way this can be written, which we will use, which is

$$\tilde{\rho}v'' + (p+1-\rho)v' + (p-q)v = 0$$

$$\therefore v = L_{n+\ell}^{2\ell+1}(2\rho)$$

Thus our solutions written using this notation is

$$u_{n\ell}(\rho) = Ae^{-\rho}\rho^{\ell+1}L_{n+\ell}^{2\ell+1}(2\rho)$$

2) If we use $R(r)$ directly, we get the equation

$$\left[-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \frac{\hbar^2}{2\mu}\frac{\ell(\ell+1)}{r^2} - \frac{e^2}{r}\right]R(r) = ER(r)$$

To simplify this, we change variables to $\rho = \alpha r$ with the new quantities

$$\alpha = \sqrt{-\frac{8\mu E}{\hbar^2}} \qquad \lambda = \frac{2e^2\mu}{\hbar^2\alpha} = \frac{e^2}{\hbar}\sqrt{-\frac{\mu}{2E}}$$

which gives the new equation

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{dR}{d\rho}\right) + \left(\frac{\lambda}{\rho} - \frac{1}{4} - \frac{\ell(\ell+1)}{\rho^2}\right)R = 0$$

Since we have asymptotic behavior of $R \to e^{-\rho/2}$ as $\rho \to \infty$ and from general discussion the requirement $R \sim r^\ell$ as $r \to 0$, we take the ansatz

$$R(r)\sum \rho^\ell e^{-\rho/2}L(\rho) \qquad L(\rho) = \sum_{k=0} a_k\rho^k$$

which gives the recurrence relation

$$\frac{a_{k+1}}{a_k} = \frac{k+\ell+1-\lambda}{(k+\ell+2)(k+\ell+1)-\ell(\ell+1)}$$

Again the series must truncate for it not to diverge, so we choose $\lambda = n = k+\ell+1$ which is the same definition of principle quantum number as before. Thus we re-arrive at the energy

$$E = -\frac{\mu e^4}{2\hbar^2 n^2}$$

This can be approximated with $\mu = m_e$ (since $m_p \sim 1000 m_e$) to get

$$\boxed{E_n = -\frac{R_y}{n^2} = -\frac{e^2}{2a_0}\frac{1}{n^2}}$$

where R_y is the Rydberg constant

$$R_y = \frac{m_e e^4}{2\hbar^2} \approx 13.6 \text{ eV}$$

and a_0 is the Bohr radius (which can be interpreted as the radius of hydrogen)

$$a_0 = \frac{\hbar^2}{me^2} \approx 0.053 \text{ nm}$$

For a "hydrogen-like" atom which has potential $V(r) = -Ze^2/r$ (where Z is the atomic number), the energies shift to

$$E_n = -\frac{Z^2 R_y}{n^2} = -\frac{Z^2 e^2}{2a_0}\frac{1}{n^2}$$

Thus the radial wavefunctions are

$$R_{n\ell}(\rho) = A\rho^\ell e^{-\rho/2} L_{n+1}^{2\ell+1}(\rho)$$

where now $\rho = \alpha r = 2Zr/na_0$. The atomic number is accounted for by taking $e^2 \mapsto Ze^2$ and thus $a_0 \mapsto a_0/Z$ (originally $\rho = 2r/na_0$). The normalization condition is

$$\int_0^\infty e^{-\rho} L_{n+1}^{2\ell+1}(\rho)^2 \rho^2 d\rho = \frac{2n((n+1)!)^3}{(n-\ell-1)!}$$

which gives the prefactor

$$A^2 = \left(\frac{2Z}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n((n+1)!)^3}$$

Hydrogenic Wavefunctions

Here we will list the wavefunctions (as well as the radial components) of the first few hydrogen atom bound states

$$R_{10}(r) = \left(\frac{1}{a_0}\right)^{3/2} 2e^{-r/a_0} \qquad \psi_{100} = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}$$

$$R_{20}(r) = \left(\frac{1}{2a_0}\right)^{3/2} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0} \qquad \psi_{200} = \left(\frac{1}{32\pi a_0^3}\right)^{1/2} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$$

$$R_{21}(r) = \left(\frac{1}{2a_0}\right)^{3/2} \frac{r}{\sqrt{3}a_0} e^{-r/2a_0} \qquad \psi_{210} = \left(\frac{1}{32\pi a_0^3}\right)^{1/2} \frac{r\cos\theta}{a_0} e^{-r/2a_0}$$

$$\psi_{21\pm1} = \mp \left(\frac{1}{64\pi a_0^3}\right)^{1/2} \frac{r\sin\theta}{a_0} e^{\pm i\phi} e^{-r/2a_0}$$

For the case of a hydrogen-like atom of atomic number Z, the substitutions $e^2 \mapsto Ze^2$ and $a_0 \mapsto a_0/Z$ will give the desired wavefunctions.

Note that there is no ℓ dependence in the energies. The rotational invariance stipulates that E have no m dependence, however the lack of ℓ dependence is due to an additional (hidden or dynamical) symmetry. Additional symmetries are usually the consequence of hidden constants of motion which allow us to split H into multiple coordinate systems.

In the case of the hydrogen atom, we can split H into spherical and parabolic coordinates to the conservation of the Runge-Lenze vector, defined as

$$\mathbf{M} = \frac{1}{\mu}\mathbf{p} \times \mathbf{L} - e^2\hat{r}$$

The vector (classically) satisfies the relations

$$M^2 = \frac{2H}{\mu}L^2 + e^4 \qquad \mathbf{L} \cdot \mathbf{M} = 0$$

In quantum mechanics, we promote this vector to an operator

$$\mathbf{M} = \frac{1}{2\mu}(\mathbf{p} \times \mathbf{L} - \mathbf{L} \times \mathbf{p}) - e^2 r$$

and note that it still satisfies same expressions as the classical vector (with some tweaks).

$$M^2 = \frac{2H}{\mu}(L^2 + \hbar^2) \qquad \mathbf{L} \cdot \mathbf{M} = 0$$

It can be shown that $[H, \mathbf{M}] = 0$, giving us the additional symmetry we were looking for.

5.5 Addition of Angular Momenta

Suppose we have two distinct angular momenta, $\mathbf{J}_1$ and $\mathbf{J}_2$, which act on different spaces so that $[\mathbf{J}_1, \mathbf{J}_2] = 0$ (for instance spin $\mathbf{S}$ and orbital $\mathbf{L}$). We can define the total angular momentum to be $\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$. Since the two angular momenta commute, we have one set of eigenstates we can use

$$|j_1 m_1 j_2 m_2\rangle = |j_1 m_1\rangle \otimes |j_2 m_2\rangle$$

But at the same time we can consider eigenstates of the total momentum

$$|jm j_1 j_2\rangle$$

There is no standard basis to use, in fact some problems are better suited for one basis than another. Thus we need a way to convert between the two, but first let's formalize the problem.

If we have two Hilbert spaces V_1, V_2 with bases $\{x_i\}, \{y_i\}$, then their direct product space is spanned by the products $x_i \otimes y_j$. If we have an operator A_1 which acts on V_1 and an operator A_2 which acts on V_2, then the product $A_1 \otimes A_2$ will act on the product space $V_1 \otimes V_2$.

Example. In 3D space we've already had two examples of product spaces

$$|\mathbf{x}\rangle = |x\rangle |y\rangle |z\rangle = |x\rangle \otimes |y\rangle \otimes |z\rangle$$

$$|n\ell m\rangle = |n\ell\rangle \otimes |\ell m\rangle$$

Example. Our first notable example is the product of spin $1/2$ and orbital momentum. We can represent states with two terms

$$|\psi\rangle = |\psi\rangle_+ \otimes |+\rangle + |\psi\rangle_- \otimes |-\rangle$$

where $\psi_\pm$ are the orbital (spatial) states with wavefunctions

$$\langle \mathbf{x}|\psi_\pm\rangle = \psi_\pm(\mathbf{x})$$

We can also just define $|\mathbf{x}, \pm\rangle = |\mathbf{x}\rangle \otimes |\pm\rangle$ and write the state as a spinor

$$\begin{pmatrix} \psi_+(x) \\ \psi_-(x) \end{pmatrix}$$

A general operator will be written as $O = O_{space} \otimes O_{spin}$ with spin operators acting as

$$S_i = \mathbb{1}_{space} \otimes S_i$$

and space operators acting as

$$O(\mathbf{x}, \mathbf{p}) = O(\mathbf{x}, \mathbf{p}) \otimes \mathbb{1}_{spin}$$

For instance one useful operator is the total angular momentum operator $\mathbf{J} = \mathbf{L} + \mathbf{S}$

$$\mathbf{J} \,|\psi\rangle = \mathbf{L} \,|\psi_+\rangle \otimes |+\rangle + |\psi_+\rangle \otimes \mathbf{S} \,|+\rangle + \mathbf{L} \,|\psi_-\rangle \otimes |-\rangle + |\psi_-\rangle \otimes \mathbf{S} \,|-\rangle$$

Another useful operator is $\mathbf{L} \cdot \mathbf{S}$ which acts as

$$\mathbf{L} \cdot \mathbf{S} \,|\psi\rangle = \mathbf{L} \otimes \mathbf{S} \,|\psi\rangle = \left(\sum_i L_i \otimes S_i \right) |\psi\rangle = \sum_i (L_i \,|\psi_+\rangle \otimes S_i \,|+\rangle + L_i \,|\psi_-\rangle \otimes S_i \,|-\rangle)$$

Similarly as rotation operator can be split

$$D(R) = \exp\left(-\frac{i\mathbf{J} \cdot \hat{n}\phi}{\hbar} \right) = \exp\left(-\frac{i\mathbf{L} \cdot \hat{n}\phi}{\hbar} \right) \exp\left(-\frac{i\mathbf{S} \cdot \hat{n}\phi}{\hbar} \right) = D_L(R) \otimes D_S(R)$$

As a second example, suppose we have two distinguishable spin $1/2$ particles (the indistinguishable case will be explored in the identical particles section). We can represent states as a product of two eigenstates of $\mathbf{J} = \mathbf{S}$

$$|j_1 m_1 j_2 m_2\rangle = |1/2 \, m_1\rangle \otimes |1/2 \, m_2\rangle = |m_1 m_2\rangle$$

where we drop the j_1, j_2 (or s_1, s_2) for convenience. Since we are in spin $1/2$, these states can just be represent with $\pm$, for instance all the possible states are

$$|1/2, 1/2\rangle = |++\rangle \quad |+-\rangle \quad |-+\rangle \quad |--\rangle = |-1/2, -1/2\rangle$$

and so on. The total spin operator is defined as $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$ and as it's own eigenstates, labeled as $|sm\rangle$ with possible states

$$|1, 0\rangle \quad |1, \pm 1\rangle \quad |0, 0\rangle$$

in which the $s = 1$ states are referred to as a spin triplet (since there are 3) and $s = 0$ as a spin singlet (since there's one). We can also define total spins in each of the three directs as $S_z = S_{1_z} + S_{2_z}$ with the commutation relations

$$\begin{aligned}
[S_1^2, S] &= 0 & [S_{1_z}, S] &\neq 0 \\
[S_2^2, S] &= 0 & [S_{2_z}, S] &\neq 0 \\
[S_{1_z}, S_z] &= 0 & [S_{2_z}, S_z] &= 0
\end{aligned}$$

and the operators act as

$$S^2 \ket{sm_s} = \hbar^2 s(s+1)\ket{sm_s}$$
$$S_z \ket{sm_s} = \hbar m_s \ket{sm_s}$$
$$S_i^2 \ket{m_1 m_2} = \hbar^2 s_i(s_i+1)\ket{s_1 m_1 s_2 m_2} \quad \text{(the } s_i \text{ labels are usually suppressed)}$$
$$S_{i_z} \ket{m_1 m_2} = \hbar m_i \ket{m_1 m_2}$$
$$S_z \ket{m_1 m_2} = \hbar(m_1 + m_2)\ket{m_1 m_2}$$

To get the conversion between the two bases we have to diagonalize S_z and S^2 in the $\ket{m_1 m_2}$ basis. S_z is clearly already diagonal, so we just need to work with S^2, the following formula is useful:

$$\mathbf{S}^2 = (\mathbf{S}_1 + \mathbf{S}_2)^2 = \mathbf{S}_1^2 + \mathbf{S}_2^2 + 2\mathbf{S}_1 \cdot \mathbf{S}_2 = \mathbf{S}_1^2 + \mathbf{S}_2^2 + 2S_{1_z}S_{2_z} + S_{1+}S_{2+} + S_{1-}S_{2-}$$

We find

$$\bra{m_1' m_2'} S^2 \ket{m_1 m_2} = \frac{3}{2}\delta_{m_1' m_1}\delta_{m_2' m_2} + \bra{m_1' m_2'} 2\mathbf{S}_1 \cdot \mathbf{S}_2 \ket{m_1 m_2}$$

Which allows us to compute the matrix

$$\frac{S^2}{\hbar} = \begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 2 \end{pmatrix}$$

and diagonalizing this gives the following conversions

$$\ket{11} = \ket{++}$$
$$\ket{10} = \frac{1}{\sqrt{2}}(\ket{+-} + \ket{-+})$$
$$\ket{00} = \frac{1}{\sqrt{2}}(\ket{+-} - \ket{--+})$$
$$\ket{1-1} = \ket{--}$$

Our results can be summarized (in general) as

$$\ket{sm} = \sum_{m_1, m_2} \ket{s_1 m_1 s_2 m_2}\braket{s_1 m_1 s_2 m_2 | sm s_1 s_2}$$

in which the $\braket{s_1 m_1 s_2 m_2 | sm s_1 s_2}$ are called Clebsch-Gordon coefficients and are given by widely available reference tables. [2]

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[2] For instance here

Another (arguably easier) way to calculate the Clebsch-Gordon coefficients is to use ladder operators. The highest and lowest states are known, for instance $|11\rangle = |++\rangle$ and we can calculate

$$\frac{S_-}{\hbar}|11\rangle = \sqrt{2}|10\rangle = \left(\frac{S_{1-}}{\hbar} + \frac{S_{2-}}{\hbar}\right)|++\rangle$$

$$= \frac{S_{1-}}{\hbar}|+\rangle \otimes |+\rangle + |+\rangle \otimes \frac{S_{2-}}{\hbar}|+\rangle$$

$$= |-+\rangle + |+-\rangle$$

$$\therefore |10\rangle = \frac{1}{\sqrt{2}}(|+-\rangle + |-+\rangle)$$

and it's simple to show that $(S_-/\hbar)|10\rangle = |1-1\rangle$. The remaining ket is given by orthogonality

$$\langle 00|10\rangle = 0 \rightarrow |00\rangle = \frac{1}{\sqrt{2}}(|+-\rangle - |-+\rangle))$$

This particular choice of phase is known as the Condon-Shortley convention.

Now that we've proven that the two bases are equivalent, the question remains of which one is better and in which situation. Suppose our Hamiltonian can be separated $H = H_0 + H_S$, the better basis will depend on H_S

1. $H_S = -\gamma_1 \mathbf{S}_1 \cdot \mathbf{B}_1 - \gamma_2 \mathbf{S}_2 \cdot \mathbf{B}_2$ (e.g. spin in a B field)

$$[H_S, S_{1_z}] = 0 \qquad [H_S, S_{2_z}] = 0$$
$$[H_S, S_z] = 0 \qquad [H_S, S^2] \neq 0$$

   The $|m_1 m_2\rangle$ are already eigenstates.

2. $H_S = \alpha \mathbf{S}_1 \cdot \mathbf{S}_2$ (e.g. a magnetic interaction)

$$[H_S, S_{1_z}] \neq 0 \qquad [H_S, S_{2_z}] \neq 0$$
$$[H_S, S] = 0 \qquad [H_S, S_z] = 0 \qquad [H_S, S^2] = 0$$

   The $|sm\rangle$ are already eigenstates.

3. $H_S = -\gamma_1 B S_{1_z} - \gamma_2 B S_{1_z} + \alpha \mathbf{S}_1 \cdot \mathbf{S}_2$

$$[H_S, S_z] = 0$$

   $|11\rangle = |++\rangle$ and $|1, -1\rangle = |--\rangle$ are already eigenstates. This is now a 2x2 diagonalization problem like the one we just did.

4. $H_S = -\gamma_1 \mathbf{S}_1 \cdot \mathbf{B}_1 - \gamma_2 \mathbf{S}_2 \cdot \mathbf{B}_2 + \alpha \mathbf{S}_1 \cdot \mathbf{S}_2$ Nothing commutes and we must diagonalize the whole 4x4 matrix.

The ladder operator approach is useful because it generalizes easily to arbitrary angular momenta. For instance suppose we have $[\mathbf{J}_1, \mathbf{J}_2] = 0$, then we have eigenstates

$$|j_1 m_1\rangle \otimes |j_2 m_2\rangle = |j_1 m_1 j_2 m_2\rangle$$

These are eigenstates of J_i^2, J_{i_z} and also J_z but not J^2. Instead we have the states $|jmj_1j_2\rangle$ as eigenstates of J^2, J_i^2, J_z. The uppermost state has $j = j_{max} = j_1 + j_2$ and $m_{max} = j_{max}$, this conversion is well known and is just

$$|j_{max}, m_{max}\rangle = |j_1, j_2\rangle$$

Proceeding downward, the next lowest states can be found using the ladder operator, it is

$$|j_{max}, m_{max} - 1, j_1 j_2\rangle = \sqrt{\frac{j_1}{j_1 + j_2}} |j_1 - 1, j_2\rangle + \sqrt{\frac{j_2}{j_1 + j_2}} |j_1, j_2 - 1\rangle$$

The other state with this given m is found using orthogonality

$$|j_{max} - 1, m_{max} - 1\rangle = -\sqrt{\frac{j_1}{j_1 + j_2}} |j_1 - 1, j_2\rangle + \sqrt{\frac{j_2}{j_1 + j_2}} |j_1, j_2 - 1\rangle$$

where again we've used the Condon-Shortley phase convention (explained below). As usual a general state is given by

$$|jm\rangle = \sum_{m_1, m_2} = |m_1 m_2\rangle \langle m_1 m_2 | jm\rangle$$

$$|m_1 m_2\rangle = \sum_{jm} |jm\rangle \langle m_1 m_2 | jm\rangle$$

The Clebsch-Gordon coefficients all have the properties

1. $\langle j_1 m_2 00 | jm\rangle = \delta_{j_1 j}\delta_{m_1 m}$

2. $\langle j_1 m_1 j_2 m_2 | jm\rangle = 0$ unless $m = m_1 + m_2$ and $j = j_1 + j_2, j_1 + j_2 - 1, \ldots, |j_1 - j_2|$

3. The Clebsch-Gordon coefficients are all real $\langle j_1 m_1 j_2 m_2 | jm\rangle = \langle jm | j_1 m_1 j_2 m_2\rangle$

4. The coefficients satisfy the Condon-Shortley convention

$$\langle j_1, j_1, j_2, j - j_1 | jm\rangle \geq 0$$

5. $\langle j_1 m_1 j_2 m_2 | jm\rangle = (-1)^{j_1 + j_2 - j} \langle j_1, -m_1, j_2, -m_2 | j, -m\rangle$

6. $\langle j_1 m_1 j_2 m_2 | jm\rangle = (-1)^{j_1 + j_2 - j} \langle j_2 m_2 j_1 m_1 | jm\rangle$

Our discussion of angular momenta also has an application to rotations. We've proven that

$$j_1 \otimes j_2 = (j_1 + j_2) \oplus (j_1 + j_2 - 1) \oplus \cdots \oplus |j_1 - j_2|$$

In terms of rotation operators, this becomes

$$D^{(j_1)} \otimes D^{(j_2)} = D^{(j_1+j_2)} \oplus D^{(j_1+j_2-1)} \oplus \cdots \oplus D^{(|j_1-j_2|)}$$

Thus we can express two rotations by summing over lower dimensional operators in a Clebsch-Gordon series

$$D^{(j_1)}_{m'_1 m_1} D^{(j_2)}_{m'_2 m_2} = \sum_j \sum_m \sum_{m'} \langle m'_1 m'_2 | j m' \rangle \, D^{(j)}_{m'm}(R) \, \langle m_1 m_2 | j m \rangle$$

$$D^{(j)}_{m'm} = \sum_{m_1,m_2} \sum_{m'_1,m'_2} \langle j m' | m'_1 m'_2 \rangle \, D^{(j_1)}_{m'_1 m_1} D^{(j_2)}_{m'_2 m_2} \, \langle m_1 m_2 | j m \rangle$$

Thus if we know $D^{(j)}_{m'm}$ for small j, we can easily compute them for larger j. Recalling our previous discussing of Wigner functions and the spherical harmonics we can derive the famous triple product formula

$$\int d\Omega \, Y^*_{\ell m} Y_{\ell_1 m_1} Y_{\ell_2 m_2} = \sqrt{\frac{(2\ell_1 + 1)(2\ell_2 + 1)}{4\pi(2\ell + 1)}} \, \langle 00 | \ell 0 \rangle \, \langle \ell m | \ell_1 \ell_2 \rangle$$

These results can also be used to derive a closed form expression for the $d^{(j)}_{m'm}$ functions. One way of doing so is to start with the fundamental spin $1/2$ spinors and adding multiples of them together to get any arbitrary $|jm\rangle$ state. We then require that the spinor products transform accordingly and compare values to get a closed form expression. An elegant way to do this involves using ladder operators of two independent harmonic oscillators [3]

$$d^{(j)}_{m'm}(\beta) = \sum_k (-1)^{k-m+m'} \mathcal{N}_{jmm'k} \left(\cos \frac{\beta}{2} \right)^{2j} \left(\tan \frac{\beta}{2} \right)^{2k-m+m'}$$

where

$$\mathcal{N}_{jmm'k} = \frac{\sqrt{(j+m)!(j+m')!(j-m)!(j-m')!}}{(j+m-k)!k!(j-m'-k)!(m'-m+k)!}$$

and the sum over k is taken so that none of the arguments in the denominator factorials are negative (i.e. so that the sum makes sense).

[3] A full demonstration of the method is in Sakurai section 3.9

5.6 Tensor Operators

Suppose we want to evaluate the matrix elements of an operator O in the angular momentum basis

$$\langle \alpha'; j'm' | O | \alpha; jm \rangle$$

This process is simplified by investigating how O transforms under rotations

$$O_R = D(R)OD(R)^\dagger$$

which allows us to

1. derive selection rules for the operator

2. relate nonzero matrix elements using Clebsch-Gordon coefficients

First we start with some rotation on an arbitrary state

$$D(R) | jm \rangle = \sum_{m'} | jm' \rangle D^{(j)}_{m'm}(R) \qquad D(R) | \psi \rangle = | \psi \rangle_R$$

allowing us to form the operator sandwich

$$\langle \psi | O | \psi \rangle = \langle \psi | D(R)^\dagger D(R) O D(R)^\dagger D(R) | \psi \rangle = {}_R\langle \psi | O_R | \psi \rangle_R$$

For arbitrarily complication operators O, we can break them into smaller pieces which transform differently under rotations. In other words each piece carriers a different label $j = 0, 1, \ldots$ and $m = -j, -j+1, \ldots, j$. Each piece then transforms as

$$D(R)O_{jm}D(R)^\dagger = \sum_{m'} O_{jm'} D^{(j)}_{m'm}(R)$$

In other words the O_{jm} transform just like the state $| jm \rangle$, these are referred to as irreducible (or spherical) tensor operators.

Example. As an simple example, consider some scalar operator $O = S$ (not the spin operator!) which will transform as

$$S_R = D(R)SD(R)^\dagger = S$$

where the rotation operator is the familiar

$$D(R) = \exp\left(\frac{i\mathbf{J} \cdot \hat{n}\phi}{\hbar}\right)$$

Thus the condition that S is invariant under rotations is the same as saying $[S, J_i] = 0$, there will be only one nonzero matrix element given by

$$\langle \alpha'; j'm' | S | \alpha; jm \rangle = \langle \alpha'; j| |S| |\alpha; j \rangle \, \delta_{j'j}\delta_{m'm}$$

The two Kronecker deltas reflect rotational properties and the double bar matrix element is known as the reduced matrix element, given by

$$\langle \alpha'; j' | |S| |\alpha; j \rangle = \langle \alpha'; jj | S | \alpha; jj \rangle \sqrt{2j_1 + 1}$$

The reduced matrix element being m independent implies that the matrix element $\langle \alpha_2 jm | S | \alpha_1 jm \rangle$ is the same for all m, a special case of the Wigner-Eckart theorem, discussed later

For a better example, a vector operator V_i for which $i = 1, 2, 3$ (or $i = x, y, z$) will transform according to

$$D(R)V_iD(R)^\dagger = \sum_{j=1}^{3} R_{ji}V_j$$

which is equivalent to $[J_i, V_j] = i\hbar\epsilon_{ijk}V_k$. A vector is an instance of a rank 1 tensor, for a rank 2 tensor (e.g. a matrix) we'll have T_{ij} for which $i, j = 1, 2, 3$. A matrix (rank 2 tensor) operator will transform according to

$$D(R)T_{ij}D(R)^\dagger = \sum_{k\ell} R_{ki}R_{\ell j}T_{k\ell}$$

which is equivalent to $[T_{ij}, J_k] = i\hbar(\epsilon_{ik\ell}T_{\ell j} + \epsilon_{jkm}T_{im})$. This is incredibly inconvenient, but luckily for us rank 2 and above tensors are reducible. For instance we can write $T_{ij} = V_iW_j$ and derive the relation

$$T_{ij} = \mathbf{V} \cdot \mathbf{W}\frac{\delta_{ij}}{3} + \frac{1}{2}(V_iW_j - V_jW_i) + \left[\frac{1}{2}(V_iW_j + V_jW_i) - \mathbf{V} \cdot \mathbf{W}\frac{\delta_{ij}}{3}\right]$$

The first part transforms like a scalar (1 component), the second part like a vector (3 components), and the third part like a traceless symmetric tensor (5 components: choose three upper half and two on the diagonal). In other words

$$3 \otimes 3 = 1 \oplus 3 \oplus 5$$

Since each term transforms amongst themselves, it's useful to define irreducible tensors $T_q^{(k)}$ which transform amongst themselves in an analogous way

$$D(R)T_q^{(k)}D(R)^\dagger = \sum_{q'} T{q'}^{(k)} D_{q'q}^{(k)}(R)$$

It's important to emphasize that the operators transform exactly like the angular moment states with $j = k, m = q$

$$D(R)|kq\rangle = \sum_{q'} |kq'\rangle D_{q'q}^{(k)}(R)$$

In other words we can think of $T_q^{(k)}|00\rangle \sim |kq\rangle$ which is the same as saying

$$[J_\pm, T_q^{(k)}] = \hbar\sqrt{k(k+1) - q(q\pm 1)}T_{q\pm 1}^{(k)} \qquad [J_z, T_q^{(k)}] = \hbar q T_q^{(k)}$$

Note that $T_0^{(0}$ is a scalar operator, $T_q^{(1)}$ is a vector operator, and so on. Furthermore the spherical harmonics are also irreducible tensor operators with

$$Y_{1\pm 1} \sim \mp\frac{V_x \pm iV_y}{\sqrt{2}} = T_{\pm 1}^{(1)}$$

$$Y_{10} \sim V_z = T_0^{(1)}$$

$$Y_{\ell m} \sim T_m^{(\ell)}$$

that is with $k = \ell$ and $q = m$.

The irreducible tensors also satisfy the product theorem. If we have two tensors $X_{q_1}^{(k_1)}$, $Z_{q_2}^{(k_2)}$ of rank k_1, k_2 then

$$X_{q_1}^{(k_1)} Z_{q_2}^{(k_2)} = \sum_{k,q} \langle kq|k_1 q_1 k_2 q_2\rangle \, T_q^{(k)}$$

and we can also go the other way

$$T_q^{(k)} = \sum_{q_1, q_2} \langle k_1 q_1 k_2 q_2 | kq\rangle \, X_{q_1}^{(k_1)} Z_{q_2}^{(k_2)}$$

The matrix elements of the irreducible tensors are given by the Wigner-Eckart Theorem

$$\langle \alpha'; j'm'|\, T_q^{(k)}\, |\alpha; jm\rangle = \frac{\langle \alpha'; j'||T^{(k)}||\alpha; j\rangle}{\sqrt{2j+1}} \, \langle j'm'|jmkq\rangle$$

in which the $\langle \alpha_2 j_2||T^{(k)}||\alpha_1 j_1\rangle$ is called the reduced or double bar matrix element. Note that it's just a number and does not depend on m_1, m_2, q. Essentially the theorem shows that M is the product of some dynamical piece (the reduced matrix element) and a symmetry piece (the Clebsch-Gordon coefficient). It also gives two selection rules:

The matrix element $\langle \alpha'; j'm'|\, T_q^{(k)}\, |\alpha; jm\rangle = 0$ unless:

1. $m' = q + m$

2. $j' = k + j, k + j - 1, \ldots, |k - j|$

Example. As an example of how to use the Wigner-Eckart Theorem, suppose we have a spinless particle bound to a fixed center by a central force potential. The states in this case can be denoted $|n\ell m\rangle$ (e.g. a hydrogen atom). We have two matrix elements of interest

$$\langle n'\ell'm'|\mp \frac{1}{\sqrt{2}}(x \pm iy)\,|n\ell m\rangle \qquad \langle n'\ell'm'|\, z\,|n\ell m\rangle$$

Recall that $T^{(1)}$ are the vector operators and since $\mathbf{x}$ is a vector operator, we have

$$T_{\pm 1}^{(1)} \sim \mp \frac{x \pm iy}{\sqrt{2}} \qquad T_0^{(1)} \sim z$$

Thus, using the Wigner-Eckart Theorem, we can write down the matrix elements as

$$\langle n'\ell'm'|\mp \frac{1}{\sqrt{2}}(x \pm iy)\,|n\ell m\rangle = \frac{\langle n'\ell'||T^{(1)}||n\ell\rangle}{\sqrt{2\ell+1}} \, \langle \ell'm'|\ell m, 1, \pm 1\rangle$$

$$\langle n'\ell'm'|\, z\,|n\ell m\rangle = \frac{\langle n'\ell'||T^{(1)}||n\ell\rangle}{\sqrt{2\ell+1}} \, \langle \ell'm'|\ell m, 0, 1\rangle$$

The first expression is nonzero only if $m' = m \pm 1$ and the second only if $m' = m$. In both cases we also require $\ell' = \ell + 1, \ldots, |\ell - 1|$. Putting this all together gives the relationship

$$\langle n'\ell'm'|\mp \frac{1}{\sqrt{2}}(x \pm iy)\,|n\ell m\rangle = \frac{\langle \ell', m \pm 1|\ell m, 1, \pm 1\rangle}{\langle \ell'm|\ell m, 0, 1\rangle} \, \langle n'\ell'm'|\, z\,|n\ell m\rangle$$

Example. We want to calculate the reduced matrix element $\langle \alpha'j' | |\mathbf{J}| | \alpha j \rangle$. Since $\mathbf{J}$ is again a vector operator, we want to consider the irreducible tensors $T_q^{(1)}$. Furthermore the reduced matrix element will not depend on q so we may as well use $T_0^{(1)} \sim J_z$ for simplicity. This gives the selection rules $m = m'$ and so

$$\langle \alpha'j'm | T_0^{(1)} | \alpha j m \rangle = \frac{\langle \alpha'j' | |\mathbf{J}| | \alpha j \rangle}{\sqrt{2j+1}} \langle j'm | jm, 1, 0 \rangle$$

We can choose $m = j$ and evaluate the left hand side directly

$$\langle J_z | \alpha'j'j \rangle \, \alpha j j = \hbar j \delta_{j'j} \delta_{\alpha'\alpha}$$

thus we can also choose $j' = j$ and use the identity

$$\langle jj | jj, 1, 0 \rangle = \sqrt{\frac{j}{j+1}}$$

and so we arrive at

$$\langle \alpha'j' | |\mathbf{J}| | \alpha j \rangle = \frac{\sqrt{2j+1}}{\langle jj | jj, 1, 0 \rangle} \langle J_z | \alpha'jj \rangle \, \alpha j j = \hbar \sqrt{j(j+1)(2j+1)} \delta_{\alpha',\alpha}$$

6 Symmetry and More

6.1 Classical vs Quantum Symmetry

We've already discussed the consequences of translational and rotational invariance in the previous sections. From a general standpoint, symmetries have two consequences:

1. They give rise to conservation laws (by Noether's theorem)

$$\text{translational} \rightarrow \text{momentum}$$
$$\text{time} \rightarrow \text{energy}$$
$$\text{rotational} \rightarrow \text{angular momentum}$$

2. They relate solutions of equations of motions (e.g. degeneracy)

In classical mechanics, we have the generalized coordinates p_i and momenta p_i which satisfy the Poisson bracket

$$\{q_i, p_j\} = \sum_k \left(\frac{\partial q_i}{\partial q_k} \frac{\partial p_j}{\partial p_k} - \frac{\partial q_i}{\partial p_k} \frac{\partial p_i}{\partial q_k} \right) = \delta_{ij}$$

Furthermore these variables are conjugate

$$\{q_i, q_j\} = 0 \qquad \{p_i, p_j\} = 0$$

For a Hamiltonian $H(q_i, p_i)$, the equations of motion are

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \qquad \dot{p}_i = -\frac{\partial H}{\partial q_i}$$

If $\omega(q_i, p_i)$ is a time independent observable, then it will evolve according to

$$\dot{\omega} = \sum_i \left(\frac{\partial \omega}{\partial q_i} \frac{dq_i}{dt} - \frac{p\omega}{\partial p_i} \frac{dp_i}{dt} \right) = \sum_i \left(\frac{\partial \omega}{\partial q_i} \partial H \partial p_i - \frac{\partial \omega}{\partial p_i} \frac{\partial H}{\partial q_i} \right) = \{\omega, H\}$$

The quantum mechanical analog to this is the equation

$$\frac{d \langle A \rangle}{dt} = \frac{1}{i\hbar} \langle [A, H] \rangle$$

in which the generalized coordinates satisfy

$$[q_i, p_j] = i\hbar \delta ij \qquad [q_i, q_j] = 0 \qquad [p_i, p_j] = 0$$

A canonical transformation is one that maintains the Poisson brackets, that is

$$q_i \mapsto \overline{q}_i \qquad p_i \mapsto \overline{p}_i \qquad \{\overline{q}_i, \overline{p}_i\} = \delta_{ij}$$

Consider an infinitesimal canonical transform, one of the form

$$q_i \mapsto \bar{q}_i = q_i + \delta q_i = q_i + \epsilon \frac{\partial g}{\partial q_i}$$

$$p_i \mapsto \bar{p}_i = p_i + \delta p_i = p_i + \epsilon \frac{\partial g}{\partial p_i}$$

where $g(p_i, q_i)$ is known as the generating function of the transformation. Certain choices of g keep the equations of motion the same, if $H(q_i, p_i) = H(\bar{q}_i, \bar{p}_i)$, then we say g generates a symmetry.

Example. Consider a general Hamiltonian

$$H = \frac{p^2}{2m} + V(r)$$

and let the generating function of a transformation be

$$g = x p_y - y p_x = L_z$$

Then we can evaluate

$$\delta x = \epsilon \frac{\partial L_z}{\partial p_x} = -\epsilon y \qquad \delta y = \epsilon x \qquad \delta z = 0$$

$$\delta p_x = -\epsilon \frac{\partial L_z}{\partial x} = -\epsilon p_y \qquad \delta p_y = \epsilon p_x \qquad \delta p_z = 0$$

and we see that H will be invariant. Furthermore r^2, p^2 are left invariant up to $O(\epsilon)$, in other words g is the generating function for rotations.

If the generated transform is a symmetry then

$$\delta = H(\bar{q}_i, \bar{p}_i) - H(q_i, p_i) = 0$$

Expanding this, we find

$$\delta H = H(q_i + \delta q_i, p_i + \delta p_i) - H(q_i, p_i)$$
$$= \sum_i \left(\frac{\partial H}{\partial q_i} \delta q_i + \frac{\partial H}{\partial p_i} \delta p_i \right)$$
$$= \epsilon \sum_i \left(\frac{\partial H}{\partial q_i} \frac{\partial g}{\partial p_i} - \frac{\partial H}{\partial p_i} \frac{\partial g}{\partial q_i} \right)$$
$$= \epsilon \{H, g\} = 0$$
$$\therefore \frac{dg}{dt} = -\{H, g\} = 0$$

which implies g is a conserved quantity of the system. Note that if $q_i(t), p_i(t)$ are solutions to the original equations of motion, then so is $\bar{q}_i(t), \bar{p}_i(t)$ (the solutions are related).

In quantum mechanics we define the unitary operator

$$U(\epsilon) = \exp\left(-\frac{i\epsilon G}{\hbar}\right)$$

where $G = G^\dagger$ is the generator. For this to be a symmetry, we must have

$$UHU^\dagger = H \quad \longrightarrow \quad [G, H] = 0$$

We've seen this operator before, in fact we've had

- The translation operator

$$T(\mathbf{a}) = \exp\left(-\frac{i\mathbf{p} \cdot \mathbf{a}}{\hbar}\right)$$

- The time evolution operator

$$U(t) = \exp\left(-\frac{iHt}{\hbar}\right)$$

- The rotation operator

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

For all these cases, which are continuous symmetries, we find that

$$\frac{\partial \langle G \rangle}{\partial t} = \frac{\langle [G, H] \rangle}{i\hbar} = 0$$

In other words $\langle G \rangle$ can be thought of as a conserved "charge" independent of picture. Thus we can construct a basis of simultaneous eigenstates of H and G, particularly useful for bound state (but not always for scattering state) problems.

For the case of discrete symmetries there will be no conserved "charge," but there will still be relationships between the eigenstates which we can discover. The standard example is the parity transform. If we have some classical trajectory for a particle

$$\mathbf{x}(t) \qquad \mathbf{p}(t) \qquad \mathbf{L}(t) = \mathbf{x}(t) \times \mathbf{p}(t)$$

Then the space-reflected transformation is

$$\mathbf{x}(t) \to \overline{\mathbf{x}}(t) = -\mathbf{x}(t)$$
$$\mathbf{p}(t) \to \overline{\mathbf{p}}(t) = -\mathbf{p}(t)$$
$$\mathbf{L}(t) \to \overline{\mathbf{L}}(t) = \mathbf{L}(t)$$

From this we see that there are two types of vectors which we can classify based on how they transform under spatial reflection. Recall that the difference between vectors and scalars is how they act under rotations (amongst over trivial details)

$$V_i \to V_i' = R_{ij}V_j \qquad S \to S' = S$$

These are further categorized based on what happens under a reflection

- A (polar) vector gets inverted: e.g. $\mathbf{x}, \mathbf{p}$

- A psuedovector (axial vector) stays the same: e.g. $\mathbf{L}$

- A scalar stays the same: e.g. $\mathbf{x} \cdot \mathbf{x}, \mathbf{p} \cdot \mathbf{p}$

- A psuedoscalar will get inverted: e.g. $\mathbf{x} \cdot \mathbf{L}$

Note that the dot product of two vectors or two psuedovectors is a scalar, while the dot product of a vector and an psuedovector is a pseudoscalar. Let's investigate $\mathbf{x}$ more, define the parity operator

$$\overline{x}_i = \Pi_{ij} x_j \qquad \det \Pi = -1$$

Π is a 3x3 orthogonal matrix, so we have properties

$$\Pi^\dagger \Pi = \Pi^T \Pi = \Pi^2 = \Pi^{-1} \Pi = \mathbb{1}$$

In the language of quantum mechanics we have

$$\Pi \ket{\mathbf{x}} = \eta_a \ket{-\mathbf{x}}$$

$$\Pi^1 \ket{\mathbf{x}} = \eta_a^2 \ket{\mathbf{x}} = \ket{\mathbf{x}}$$

which implies $\eta_a = \pm 1$, we take $\eta_a = 1$ by convention.

$$\Pi \ket{\mathbf{x}} = \ket{-\mathbf{x}} \qquad \Pi \ket{\mathbf{p}} = \ket{-\mathbf{p}}$$

For some arbitrary wavefunction we also see that

$$\psi_\pi(x) = \bra{\mathbf{x}} \Pi \ket{\psi} = \braket{-\mathbf{x}|\psi} = \psi(-\mathbf{x})$$

as expected. Using various properties, we can derive

$$\Pi \mathbf{x} \Pi^\dagger = -\mathbf{x} \qquad \Pi \mathbf{p} \Pi^\dagger = -\mathbf{p}$$
$$\Pi \mathbf{L} \Pi^\dagger = \mathbf{L} \qquad \Pi \mathbf{J} \Pi^\dagger = \mathbf{J} \qquad \Pi \mathbf{S} \Pi^\dagger = \mathbf{S}$$
$$\Pi H(\mathbf{x}, \mathbf{p}, \mathbf{S}, \ldots) \pi^\dagger = H(-\mathbf{x}, -\mathbf{p}, \mathbf{S}, \ldots)$$

If $\Pi H \Pi^\dagger = H$, then $[\Pi, H] = 0$ and H is reflection invariant. In this case we can construct simultaneous eigenstates of Π and H. The action on these states is

$$\Pi \ket{\psi} = \lambda \ket{\psi} \qquad \Pi^2 \ket{\psi} = \ket{\psi}$$

which means $\lambda = \pm 1$ (as expected) and also gives two sets of states: even states $\ket{\psi_+}$ and odd state $\ket{\psi_-}$. This classification system should be familiar, we've used it before for square wells.

For rotationally invariant systems

$$\psi_{E\ell m}(\mathbf{x}) = R_{E\ell}(r)Y_{\ell m}(\theta, \phi)$$

we have the transformation rules

$$\mathbf{x} \mapsto -\mathbf{x} \qquad r \mapsto r \qquad \theta \mapsto \pi - \theta \qquad \phi \mapsto \pi + \phi$$

The spherical harmonics have parity $(-1)^\ell$, so the states reflect as

$$\psi_{E\ell m}(-\mathbf{x}) = R_{E\ell}(r)Y_{\ell m}(\pi\theta, \pi + \phi) = (-1)^\ell R_{E\ell}(r)Y_{\ell m}(\theta, \phi)$$

Now we discuss selection rules which result from parity. Suppose we have some operator with parity given by

$$\Pi O \Pi^\dagger = \epsilon_O O$$

where $\epsilon_O = \pm 1$, suppose the operator has eigenstates with parity

$$\Pi \ket{\alpha} = \epsilon_\alpha \ket{\alpha} \qquad \Pi \ket{\beta} = \epsilon_\beta \ket{\beta}$$

Then the matrix element can be written

$$\bra{\beta} O \ket{\alpha} = \bra{\beta} \Pi^\dagger \Pi O \Pi^\dagger \Pi \ket{\alpha} = \epsilon_O \epsilon_\alpha \epsilon_\beta \bra{\beta} O \ket{\alpha}$$

and we see that if $\epsilon_O \epsilon_\alpha \epsilon_\beta = -1$, then the matrix element must be zero.

Example. As a simple example, consider the matrix element

$$\bra{n'\ell'm'} \mathbf{x} \ket{n\ell m}$$

From the Wigner-Eckart Theorem, we already know that we must have $\ell' = \ell, \ell \pm 1$. Now since $\mathbf{x}$ is a normal vector, reflection invariant requires $(-1)(-1)^\ell(-1)^{\ell'} = 1$ and thus only the $\ell' = \ell \pm 1$ elements are allowed. If we were to consider an pseudovector (like $\mathbf{J}$), then only the $\ell' = \ell$ states will survive.

Example. As another (also simple) example, suppose we have the following potential (possibly due to weak neutral-current interactions)

$$V = \lambda \left[\delta^3(\mathbf{x})\mathbf{S} \cdot \mathbf{p} + \mathbf{S} \cdot \mathbf{p}\delta^3(\mathbf{x}) \right]$$

We'll label these states (since they're atoms) with $\ket{n\ell jm}$. Since V is a pseudoscalar (check this), the matrix elements will only be nonzero if $j' = j, m' = m$ and $\ell' = \ell \pm 1$.

6.2 Time Reversal Symmetry

Suppose we have two observers O and O' that share an origin (e.g. one is rotated). Intuitively we expect there to be some relations between the kets in O and the corresponding kets in O'. For instance if we consider the angular momentum states

$$\text{In } O: \ket{jm} \qquad J^2 = \hbar j(j+1) \qquad J_z = \hbar m$$
$$\text{In } O': \ket{jm : R} \qquad J^2 = \hbar j(j+1) \qquad J_z = \hbar m$$

where R is the relation between the two axis. If observer O proposes some state $|u\rangle$ and the other observer O' proposed the corresponding ket $|u : R\rangle$, then the respective probabilities are $|\langle jm|u\rangle|^2$ and $|\langle jm : R|u : R\rangle|^2$. But physics dictates the probabilities be equal

$$|\langle jm|u\rangle|^2 = |\langle jm : R|u : R\rangle|^2$$

This implies that the physical state corresponds to the "ray" rather than the ket itself. The two observers O, O' are called equivalent descriptions, we would like the know exactly the relationship between the two. If kets actually described the physical states, then R must be unitary, however we see that this is not the case.

More generally suppose we have kets $|\alpha\rangle, |\beta\rangle$ with corresponding equivalent descriptions $|\alpha'\rangle, |\beta'\rangle$. We have the relationship

$$|\langle\alpha|\beta\rangle| = |\langle\alpha'|\beta'\rangle|$$

which gives two possibilities for the transformation

- Unitary and linear

$$\langle\alpha|\beta\rangle = \langle\alpha'|\beta'\rangle \qquad (c_1|\alpha_1\rangle + c_2|\alpha_2\rangle)' = c_1|\alpha'\rangle + c_2|\alpha_2\rangle$$

- Anti-unitary and anti-linear

$$\langle\alpha|\beta\rangle = \langle\alpha'|\beta'\rangle^* = \langle\beta'|\alpha'\rangle \qquad (c_1|\alpha_1\rangle + c_2|\alpha_2\rangle)' = c_1^*|\alpha'\rangle + c_2^*|\alpha_2\rangle$$

If phases had any physical significance in quantum mechanics then we are forced to choose the unitary case, but since they don't we are allowed to consider the anti-unitary case as well. Note that for a particular transformation $O \to O'$, all vectors are transformed unitarily or anti-unitarily and not a mixture of both. If Λ is the operator connecting the bases

$$\Lambda|\alpha_n\rangle = |\alpha_n'\rangle \qquad \Lambda^{-1}|\alpha_n'\rangle = |\alpha_n\rangle$$

we can represent a general ket as

- Unitary case:

$$|\alpha'\rangle = \Lambda|\alpha\rangle = \sum(\Lambda|\alpha_n\rangle)\langle\alpha_n|\alpha\rangle = \sum|\alpha_n'\rangle\langle\alpha_n|\alpha\rangle$$

- Anti-unitary case:

$$|\alpha'\rangle = \Lambda|\alpha\rangle = \sum(\Lambda|\alpha_n\rangle)\langle\alpha_n|\alpha\rangle^* = \sum|\alpha_n'\rangle\langle\alpha|\alpha_n\rangle$$

The question of whether to use a unitary or anti-unitary transformation is a physics questions. In the case of continuous transformations which are connected to the identity (such as translations or rotations), we must use unitary transformations. This is because any transformation can be split into the product of two equal transformations and the square of an

anti-unitary transform is unitary, a direct contradiction to any assumption of an anti-unitary continuous transformation.

For discrete symmetries this argument does not apply and we require additional physics input. For instance consider the parity operation

$$\Pi\mathbf{x}\Pi^{-1} = -\mathbf{x} \qquad \Pi\mathbf{p}\Pi^{-1} = -\mathbf{p} \qquad \Pi\mathbf{J}\Pi^{-1} = \mathbf{J}$$

Given a vector $\mathbf{x}$, translation by $\mathbf{a}$ and reflecting it should be equivalent to first reflecting it and then translating by $-\mathbf{a}$. In operator terms this is

$$\Pi T(\mathbf{a}) = T(-\mathbf{a})\Pi$$

$$\Pi \exp\left(-\frac{i\mathbf{p}\cdot\mathbf{a}}{\hbar}\right) = \exp\left(\frac{i\mathbf{p}\cdot\mathbf{a}}{\hbar}\right)\Pi$$

$$\therefore \Pi \exp\left(-\frac{i\mathbf{p}\cdot\mathbf{a}}{\hbar}\right)\Pi^{-1} = \exp\left(\frac{i\mathbf{p}\cdot\mathbf{a}}{\hbar}\right)$$

Given that $\Pi\mathbf{p}\Pi^{-1} = -\mathbf{p}$, this shows Π is unitary.

The classic example of an anti-unitary transformation is a time reversal transformation. For a classical trajectory, this takes the form

$$\mathbf{x}(t) \to \overline{\mathbf{x}(t)} = \mathbf{x}(-t) \qquad \mathbf{p}(t) \to \overline{\mathbf{p}(t)} = -\mathbf{p}(-t) \qquad \mathbf{L}(t) \to \overline{\mathbf{L}(t)} = -\mathbf{L}(-t)$$

In quantum mechanics we introduce the operator θ

$$\theta\left|\psi\right\rangle = \left|\psi_\theta\right\rangle = \left|\theta\psi\right\rangle$$

with the properties

$$\theta\mathbf{x}\theta^{-1} = \mathbf{x} \qquad \theta\mathbf{p}\theta^{-1} = -\mathbf{p}$$

$$\theta\mathbf{L}\theta^{-1} = -\mathbf{L} \qquad \theta\mathbf{S}\theta^{-1} = -\mathbf{S} \qquad \theta\mathbf{J}\theta^{-1} = -\mathbf{J}$$

We claim that generally

$$\theta\left|\mathbf{x}\right\rangle = \left|\mathbf{x}\right\rangle \qquad \theta\left|\mathbf{p}\right\rangle = \left|-\mathbf{p}\right\rangle$$

The second identity can be shown with

$$\theta(\mathbf{p}_{op}\left|\mathbf{p}\right\rangle = \mathbf{p}\left|\mathbf{p}\right\rangle)$$
$$\theta\mathbf{p}_{op}\theta^{-1}\theta\left|\mathbf{p}\right\rangle = \mathbf{p}\theta\left|\mathbf{p}\right\rangle$$
$$-\mathbf{p}_{op}(\theta\mathbf{p}) = \mathbf{p}(\theta\mathbf{p})$$
$$\therefore \theta\left|\mathbf{p}\right\rangle = \left|-\mathbf{p}\right\rangle$$

and the first one can be shown the same way. The question now is whether this is unitary or anti-unitary. One way to find out is to consider a Hamiltonian H which is invariant under time reversal.

In such a system the following transforms should be equivalent:

1. Evolving over some time t, time reversal, evolving for another t

2. Time reversal only

In operator terms, this is

$$\exp\left(-\frac{iHt}{\hbar}\right)\theta\exp\left(-\frac{iHt}{\hbar}\right) = \theta \rightarrow \exp\left(-\frac{iHt}{\hbar}\right)\theta = \theta\exp\left(\frac{iHt}{\hbar}\right)$$

If θ is unitary, then we would have $\{\theta, H\} = 0$, which means we can write

$$H\,|E\rangle = E\,|E\rangle$$
$$\theta(H\,|E\rangle = E\,|E\rangle)$$
$$-H\theta\,|E\rangle = E\theta\,|E\rangle$$
$$H(\theta\,|E\rangle) = -E(\theta\,|E\rangle)$$

Thus for any eigenstates $|E\rangle$, the time reversed state $\theta\,|E\rangle$ is also an eigenstate but with energy $-E$. This implies a cascade down to $-\infty$, a contradiction, so θ must be unitary which implies $[\theta, H] = 0$.

Another way we can prove this is to use commutation relations

$$[x_i, p_j] = i\hbar\delta_{ij}$$
$$\theta[x_i, p_j]\theta^{-1} = \theta i\hbar\delta_{ij}\theta^{-1}$$
$$-[x_i, p_j] = -i\hbar\delta_{ij}$$

Since $\mathbf{x}$ keeps it's sign while $\mathbf{p}$ flips, θ must be anti-unitary to maintain signs.

Suppose we have two states $|\psi\rangle$ and $|\chi\rangle$ which are acted on by θ

$$\theta\,|\psi\rangle = |\psi_\theta\rangle = |\theta\psi\rangle \qquad \theta\,|\chi\rangle = |\chi_\theta\rangle = |\theta\chi\rangle$$

Since θ is anti-unitary and anti-linear

$$\langle\chi_\theta|\psi_\theta\rangle = \langle\psi|\chi\rangle = \langle\chi|\psi\rangle^* \qquad \theta(c\,|\psi\rangle) = c^*(\theta\,|\psi\rangle)$$

$$\therefore \theta(c_1\,|\psi\rangle + c_2\,|\chi\rangle) = c_1^*\theta\,|\psi\rangle + c_2^*k\theta\,|\chi\rangle$$

If we were to expand the state $|\psi\rangle$

$$|\psi\rangle = \sum|a_n\rangle\langle a_n|\psi\rangle \qquad |\psi'\rangle = \theta\,|\psi\rangle = \sum\theta\,|a_n\rangle\langle a_n|\psi\rangle^*$$

and act with some operator A

$$\theta(A\,|\psi\rangle) = \theta A\theta^{-1}\theta\,|\psi\rangle = \theta A\theta^{-1}\,|\psi'\rangle$$
$$= \sum\theta\,|a_n\rangle\langle a_n|\,A\theta^{-1}\,|\psi'\rangle^*$$
$$= \sum|a_n'\rangle\langle a_n|\,A\,|\psi\rangle^*$$
$$= \sum|a_n'\rangle\langle\psi|\,A^\dagger\,|a_n\rangle$$

We can also investigate how operator sandwiches behave under time reversal

$$\langle \chi' | \, \theta A \theta^{-1} \, | \psi' \rangle = \sum \langle \psi | \, A^\dagger \, | a_n \rangle \, \langle \phi' | a_n \rangle$$
$$= \sum \langle \psi | \, A^\dagger \, | a_n \rangle \, \langle a_n | \phi \rangle$$
$$= \langle \psi | \, A^\dagger \, | \phi \rangle$$

We must be careful with anti-linear operators since

$$\langle \chi | \, (\theta \, | \psi \rangle) \neq (\langle \chi | \, \theta) \, | \psi \rangle$$

For spinless particles which satisfy $\theta^2 = 1$, we actually have

$$\langle \chi | \, (\theta \, | \psi \rangle) = [(\langle \chi | \, \theta) \, | \psi \rangle]^*$$

Returning to the issue of phases, suppose

$$\theta \, | \mathbf{x} \rangle = e^{i\delta} \, | \mathbf{x} \rangle \qquad \theta \, | \mathbf{p} \rangle = e^{i\phi} \, | \mathbf{p} \rangle$$

We can redefine the transformed states as

$$| \mathbf{x}' \rangle = e^{i\delta/2} \, | \mathbf{x} \rangle \qquad | \mathbf{p} \rangle = e^{i\phi/2} \, | \mathbf{p} \rangle$$

$$\theta \, | \mathbf{x}' \rangle = e^{-i\delta/2} \theta \, | \mathbf{x} \rangle = e^{-i\delta/2} e^{i\delta} \, | \mathbf{x} \rangle = e^{i\delta/2} \, | \mathbf{x} \rangle = | \mathbf{x}' \rangle$$

This means that without loss of generality we can ignore phases since the kets can be redefined to absorb them anyway.

Wavefunctions transform under time reversal as

$$\psi_\theta(\mathbf{x}) = \langle \mathbf{x} | \psi_\theta \rangle = \langle \mathbf{x} | \theta \psi \rangle$$
$$= \langle \theta \mathbf{x} | \theta \psi \rangle = \langle \psi | \mathbf{x} \rangle$$
$$= \psi^*(\mathbf{x})$$
$$\phi_\theta(\mathbf{p}) = \phi^*(-\mathbf{p})$$

Now we consider what happens if we have time dependence. The first matter of concern is whether or not H is time reversal invariant, that is if $[\theta, H] = 0$ or equivalently

$$\theta H \theta^{-1} = H$$

If this is the case then the time reversed solutions will also satisfy the Schrodinger equation

$$\theta H \, | \psi(t) \rangle = \theta i \hbar \frac{d}{dt} \, | \psi(t) \rangle = H \theta \, | \psi(t) \rangle = -i \hbar \frac{d}{dt} (\theta \, | \psi(t) \rangle)$$

By taking $t \to -t$, we get

$$\psi_\theta(\mathbf{x}, t) = \langle \mathbf{x} | \, \theta \, | \psi(-t) \rangle = \psi^*(\mathbf{x}, -t)$$

Example. As an example, consider a 1D plane wave moving to the right

$$\psi(x,t) = \frac{1}{\sqrt{2\pi\hbar}} e^{ikx - iEt/\hbar}$$

The time reversed state is now a plane wave moving to the left

$$\psi_\theta(x,t) = \psi^*(x,-t) = \frac{1}{\sqrt{2\pi\hbar}} e^{-ikx - iEt/\hbar}$$

In fact for arbitrary energy eigenstates, we have

$$\psi(x,t) = \psi_n(\mathbf{x})e^{-iE_n t/\hbar} \longleftrightarrow \psi_\theta(\mathbf{x},t) = \psi_n^*(x)e^{-iE_n t/\hbar}$$

Thus is $[\theta, H] = 0$, then for an eigenstate $\psi_n(\mathbf{x})$ of energy E_n, $\psi_n^*(\mathbf{x})$ is also an eigenstate of energy E_n. Hence either the states are degenerate (e.g. in the plane wave case) or they are actually the same state (up to a global phase).

Let's examine the operator θ^2. Classically it's the case that $\theta^2 = 1$ but in quantum mechanics we can also have $\theta^2 = -1$

$$\langle \theta\psi_1 | \psi_2 \rangle = \langle \theta\psi_2 | \theta^2 \psi_1 \rangle = c \langle \theta\psi_2 | \psi_1 \rangle = c \langle \theta\psi_1 | \theta^2 \psi_2 \rangle = c^2 \langle \theta\psi_1 | \psi_2 \rangle$$

So $c^2 = \pm 1$ implies $\theta^2 = \pm 1$. This actually gives us a general theorem

- For a system with integer spin or even number of fermions, $c = 1$

- For a system with half-integer spin or odd number of fermions $c = -1$

  - This also implies $\langle \theta\psi | \psi \rangle = 0$ for all ψ

To summarize the theorem, if $c = -1$ then $|\psi\rangle$ and $|\theta\psi\rangle$ are different (orthogonal) states. Thus if $[H, \theta] = 0$ then there is a guaranteed double degeneracy in each energy level, known as Kramer's degeneracy.

Finally we investigate the effects of time reversing angular momentum states. Recall that

$$\theta \mathbf{J} \theta^{-1} = -\mathbf{J} \quad \longrightarrow \quad \theta \, |jm\rangle = (\ldots) \, |j, -m\rangle$$

So a time reversed state will flip m, but it may not lie in the same multiplet (for instance if there are degenerate multiplets). For $m = 0$, $|j0\rangle$ and $\theta \, |j0\rangle$ may be the same state but for other values of m they will be orthogonal.

Take the state $|\alpha jm\rangle$

$$J_z \, |\alpha jm\rangle = \hbar m \, |\alpha jm\rangle$$
$$\theta(J_z \, |\alpha jm\rangle = \hbar m \, |\alpha jm\rangle)$$
$$-J_z(\theta \, |\alpha jm\rangle) = \hbar m(\theta \, |\alpha jk\rangle)$$
$$\therefore J_z(\theta \, |\alpha jm\rangle) = -\hbar m(\theta \, |\alpha jm\rangle)$$
$$J^2(\theta \, |\alpha jm\rangle) = \hbar^2 j(j+1)(\theta \, |\alpha jm\rangle)$$

These all follow from properties of the angular momentum operators under time reversal and show that $[J^2, H] = 0$, thus the time reversed state remains an eigenstate of J^2, J_z. The question still remains of whether this state has the same labels and to answer that we have a theorem.

Theorem 6.1. If $[\theta, H] = 0$ and $|\alpha j m\rangle$ are eigenstates of H, then it is always possible to choose a basis such that

$$\theta |\alpha j m\rangle = e^{i\delta(\alpha, j, m)} |\alpha j, -m\rangle$$

so that the time reversed state lies in the same multiplet.

The phase can actually be split into two parts, one that depends on m and the other on α, j (that is, on the multiplet). Recall the ladder operators

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

which will act under time reversal as

$$\theta J_\pm \theta^{-1} = J_\mp$$

$$\therefore -J_\mp(\theta |\alpha j m\rangle) = \hbar\sqrt{j(j+1) - m(m \pm 1)}(\theta |\alpha j m\rangle)$$

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

Thus if we use the definition given in the theorem we get two expressions

$$-J_\mp e^{i\delta(m)} = \hbar\sqrt{j(j+1) - m(m \pm 1)} e^{i\delta(m \pm 1)} |\alpha j, -m \mp 1\rangle$$

$$= -\hbar\sqrt{j(j+1) - m(m \pm 1)} e^{i\delta(m)} |\alpha j, -m \mp 1\rangle$$

$$\therefore -e^{-i\delta(m \pm 1)} = e^{i\delta(m)}$$

which implies that the phase is alternating, giving the general result

$$\theta |\alpha j m\rangle = e^{i\delta(\alpha, j)}(-1)^m |\alpha j, -m\rangle$$

The $\delta(\alpha, j)$ is a phase common to the whole multiplet while

$$(-1)^m = \begin{cases} \pm 1 & \text{for integer } m \\ \pm i & \text{for half integer } m \end{cases}$$

In the case of θ^2, we can now derive

$$\theta^2 |\alpha j m\rangle = \theta e^{i\delta} i^{2m} |\alpha j, -m\rangle$$

$$= e^{-i\delta(\alpha, j)}(-i)^{2m} |\alpha j m\rangle$$

$$= (-1)^{2m} |\alpha j m\rangle$$

$$= (-1)^{2j} |\alpha j m\rangle$$

Which gives us the general result

$$\theta^2 |\alpha j m\rangle = \begin{cases} |\alpha j m\rangle & \text{for integer } j \\ -|\alpha j m\rangle & \text{for half integer } j \end{cases}$$

Finally, we discuss the irreducible tensor operators. Recall that

$$D(R)T_q^{(k)}D(R)^{-1} = \sum_{q'} T_{q'}^{(k)} D_{q'q}^{(k)}(R)$$

These can be classified according to how they act under time reversal

$$\theta T_q(k)\theta^{-1} = \begin{cases} (-1)^q T_{-q}^{(k)} & \text{even} \\ -(-1)^q T_{-1}^{(k)} & \text{odd} \end{cases}$$

Example. For the angular momentum operator $\mathbf{J}$, we have

$$\theta J_{\pm 1}^{(1)} \theta^{-1} = \theta \left(\mp \frac{J_{\pm}}{\sqrt{2}} \right) \theta^{-1} = \mp \frac{-1}{\sqrt{2}} J_{\mp} = -(-1)^{\pm 1} J_{\mp 1}^{(1)}$$

$$\theta J_0^{(1)} \theta^{-1} = \theta J_z \theta^{-1} = -J_z = (-1)^0 J_0^{(1)}$$

and thus it is odd. In general there is no guarantee that an operator be either even or odd under time reversal.

For tensor operators which can be classified as either even or odd, these properties can be used to provide more selection rules for its matrix elements, as given by the next theorem.

Theorem 6.2. If $\theta |\alpha j m\rangle = e^{i\delta}(-1)^m |\alpha j, -m\rangle$, $[\theta, H] = 0$, and $\theta T_q^{(k)}\theta^{-1} = \pm(-1)^q T_{-q}^{(k)}$, then

$$\langle \alpha j | |T^{(k)}| |\alpha j\rangle = \pm(-1)^k \langle \alpha j| |T^{(k)}| |\alpha j\rangle^*$$

Furthermore if $T_0^{(k)}$ is Hermitian, then the reduced matrix element is real. Thus even operators require even k for nonzero matrix elements and odd operators require odd k.

Example. As an example, consider the electric dipole moment $Q^{(1)}$, which is even under time reversal. Since $k = 1$, then reduced matrix element will be zero for all state of definite j.

6.3   Electromagnetic Interactions

In classical electrodynamics, the electric and magnetic fields can be expressed using two potentials: one scalar, one vector.

$$\mathbf{E} = -\nabla\Phi - \frac{1}{c}\frac{d\mathbf{A}}{dt} \qquad \mathbf{B} = \nabla \times \mathbf{A}$$

The electromagnetic fields are gauge invariant, that is for some gauge transformation $\Lambda(\mathbf{x}, t)$

$$\mathbf{A}(\mathbf{x}, t) \to \mathbf{A}'(\mathbf{x}, t) = \mathbf{A} + \nabla\Lambda$$

$$\Phi(\mathbf{x}, t) \to \Phi'(\mathbf{x}, t) = \Phi - \frac{1}{c}\frac{d\Lambda}{dt}$$

and $\mathbf{A}', \Phi$ will give the same electric and magnetic fields. Charged particles in an electromagnetic field will experience a Lorentz force given by

$$\mathbf{F} = q\mathbf{E} + q\frac{\mathbf{v}}{c} \times \mathbf{B}$$

which allows us to construct the classical Hamiltonian

$$H = \frac{(\mathbf{p} - q\mathbf{A}/c)^2}{2m} + q\Phi$$

Note that $\mathbf{p}$ is the canonically conjugate momentum and is not equal to $m\dot{\mathbf{x}}$. We can derive it's definition from the Lagrangian

$$\mathcal{L} = \frac{1}{2}m\dot{\mathbf{x}}^2 - q\Phi + \frac{q}{c}\dot{\mathbf{x}} \cdot \mathbf{A}$$

$$\therefore p_i = \frac{\partial \mathcal{L}}{\partial q_i} = mx_i + \frac{q}{c}A_i$$

Now for electromagnetic interactions in quantum mechanics, we take the classical Hamiltonian as an ansatz. The canonical coordinates/momenta become operators $[x_i, p_j] = i\hbar\delta_{ij}$, this is known as the minimal E&M substitution. Gauge transformations now mean the states transform as

$$|\psi\rangle \to |\psi'\rangle = \exp\left(\frac{iq\Lambda(\mathbf{x}, t)}{\hbar c}\right)|\psi\rangle \equiv G|\psi\rangle$$

$$\psi(\mathbf{x}, t) \to \psi'(\mathbf{x}, t) = \exp\left(\frac{iq\Lambda(\mathbf{x}, t)}{\hbar c}\right)\psi(\mathbf{x}, t)$$

where G is defined to be the gauge transformation operator. Thus gauge invariance in quantum mechanics means that: if $\mathbf{A}, \Phi, |\psi\rangle$ satisfy the Schrodinger equation, then so does $\mathbf{A}', \Phi', |\psi'\rangle$. The Schrodinger equation, using our ansatz, is given by

$$\boxed{\frac{(\mathbf{p} - q\mathbf{A}/c)^2}{2m}|\psi\rangle = \left(i\hbar\frac{\partial}{\partial t} - q\Phi\right)|\psi\rangle}$$

Note that

$$G\mathbf{p}G^\dagger = \mathbf{p} - \frac{q}{c}\nabla\Lambda$$

$$G(\mathbf{p} - q\mathbf{A}/c)G^\dagger = \mathbf{p} - q\mathbf{A}'/c$$

$$G\left(i\hbar\frac{\partial}{\partial t} - q\Phi\right) = i\hbar\frac{\partial}{\partial t} - q\Phi'$$

$$\therefore G\frac{(\mathbf{p} - q\mathbf{A}/c)^2}{2m}G^\dagger G|\psi\rangle = G\left(i\hbar\frac{\partial}{\partial t} - q\Phi\right)G^\dagger G|\psi\rangle$$

$$\therefore \frac{(\mathbf{p} - q\mathbf{A}'/c)^2}{2m}|\psi'\rangle = \left(i\hbar\frac{\partial}{\partial t} - q\Phi'\right)|\psi'\rangle$$

which means that gauge invariance is satisfied with this choice of Hamiltonian.

Take $\Phi = 0$ and $\mathbf{A} \neq 0$ and let's investigate orbital motion in a magnetic field. Note that this implies $\partial \mathbf{A}/\partial t = 0$ as well.

$$H = \frac{1}{2m}\left[\mathbf{p}^2 - \frac{q}{c}(\mathbf{p}\cdot\mathbf{A} + \mathbf{A}\cdot\mathbf{p}) + \frac{q^2}{c^2}\mathbf{A}^2\right]$$

$$= \frac{\mathbf{p}^2}{2m} - \frac{q}{mc}\mathbf{A}\cdot\mathbf{p} + \frac{q}{2mc}i\hbar\nabla\cdot\mathbf{A} + \frac{q}{2mc^2}\mathbf{A}^2$$

where we use the fact

$$p_i A_i - A_i p_i = (-i\hbar\nabla\cdot A)_i = i\hbar\partial_i A_i$$

Suppose we are in a uniform magnetic field $\mathbf{B} = B\hat{z}$, then

$$\mathbf{A} = -\frac{1}{2}(\mathbf{x}\times\mathbf{B}) = \frac{B}{2}(-y\hat{x} + x\hat{y}) \qquad \nabla\cdot\mathbf{A} = 0$$

which means the Hamiltonian simplifies to

$$H = \frac{\mathbf{p}^2}{2m} - \frac{q}{mc}(\mathbf{A}\cdot\mathbf{p}) + \frac{q^2}{2mc^2}\frac{B^2}{4}(x^2 + y^2)$$

The last term, which is $O(B^2)$, is the quadratic Zeeman term. The $\mathbf{A}\cdot\mathbf{p}$ term gives rise to a magnetic dipole interaction, allowing us to rewrite

$$2\mathbf{A}\cdot\mathbf{p} = -(\mathbf{x}\times\mathbf{B})\cdot\mathbf{p} = \mathbf{B}\cdot(\mathbf{x}\times\mathbf{p}) = \mathbf{B}\cdot\mathbf{L}$$

$$\therefore H = \frac{\mathbf{p}^2}{2m} - \frac{q}{2mc}\mathbf{B}\cdot\mathbf{L} + O(B^2)$$

$$H = \frac{p^2}{2m} - \mu\cdot\mathbf{B} + O(B^2)$$

where $\mu = q\mathbf{L}/2mc$ is the magnetic dipole moment.

Example. Suppose a particle is in a central potential with a weak magnetic field $\mathbf{B} = B\hat{z}$

$$H = H_0 + H_B = \left(\frac{\mathbf{p}^2}{2m} + V(r)\right) + \left(-\frac{q\hbar}{2mc}\frac{\mathbf{L}\cdot\mathbf{B}}{\hbar}\right)$$

In general $[H, L_i] \neq 0$, but for $\mathbf{B} = B\hat{z}$ we do have

$$[H, L_z] = 0 \qquad [H, L^2] = 0$$

Thus we have eigenstates

$$H\left|n\ell m_\ell\right\rangle = E_{n\ell m_\ell}\left|n\ell m_\ell\right\rangle \qquad E_{n\ell m_\ell} = E_{n\ell}^0 + \mu m_\ell B$$

Now supposed we have a spinless charge particle in a magnetic field $\mathbf{B} = B\hat{z}$ and where we take the Landau gauge

$$A_x = -By \qquad A_y = A_z = 0 \qquad \nabla\cdot\mathbf{A} = 0$$

The Hamiltonian then is

$$H = \frac{1}{2m}\left[\left(p_x + \frac{q}{c}By\left(62 + p_y^2 + p_z^2\right)\right]$$

and we can immediately note $[H, p_x] = 0$ and $[H, p_z] = 0$. Thus we can take the ansatz

$$\psi(\mathbf{x}) = e^{i(p_x x + p_z z)/\hbar}\chi(y)$$

This can be put into the Schrodinger equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + \frac{2qBy}{2mc}\left(--i\hbar\frac{\partial}{\partial x}\right) + \frac{q^2}{2mc^2}B^2y^2\right]\psi = E\psi$$

$$\chi'' + \frac{2m}{\hbar^2}\left[E - \frac{p_z^2}{2m} - \frac{1}{2}m\omega_B^2(y - y_0)^2\right]\chi = 0$$

where we've defined two constants

$$y_0 = -\frac{cp_x}{qB} \qquad \omega_B = \frac{|q|B}{mc}$$

Note that (x_0, y_0) are the center of motion. Motion along the field is not quantized, but motion perpendicular to the field has energies given by a simple harmonic oscillator

$$E_n = \frac{p_z^2}{2m} + \left(n + \frac{1}{2}\right)\hbar\omega_B$$

The second term gives discrete energy levels known as the Landau levels.

6.4 Density Operators

Density operators provide a useful formalism for working with complicated systems which can only be described with probabilities. So far we've been working with pure states, which can be described with a single normalized ket $|\alpha\rangle$. The density operator for this system is

$$\rho = |\alpha\rangle\langle\alpha|$$

If we have some orthonormal basis $\{|i\rangle\}$, the operator becomes a density matrix

$$\rho_{ij} = \langle i|\rho|j\rangle = \langle i|\alpha\rangle\langle\alpha|j\rangle = a_i a_j^*$$

We can also do this in a continuum space

$$\langle\mathbf{x}|\rho|\mathbf{x}'\rangle = \rho(\mathbf{x}, \mathbf{x}') = \psi_\alpha(\mathbf{x})\psi_\alpha^*(\mathbf{x}')$$

but in a pure state ρ is just the projection operator. Note that

1. $\rho = \rho^\dagger$, it is Hermitian

2. $\rho^2 = \rho$, it's a projection operator

3. $\text{Tr}\, \rho = 1$

The last property follows from

$$\text{Tr}\, \rho = \sum_i \langle i | \rho | i \rangle = \sum |a_i|^2 = 1$$

The advantage of using this formalism is that it allows us to easily calculate expectation values

$$\langle A \rangle = \langle \alpha | A | \alpha \rangle = \text{Tr}(\rho A)$$

which can be seen using

$$\langle \alpha | A | \alpha \rangle = \sum \langle \alpha | A | i \rangle \langle i | \alpha \rangle = \sum \langle i | \alpha \rangle \langle \alpha | A | i \rangle = \sum \langle i | \rho A | i \rangle$$

ρ evolves in time as

$$i\hbar \frac{d\rho}{dt} = H | \alpha \rangle \langle \alpha | - | \alpha \rangle \langle \alpha | H = -[\rho, H]$$

As mentioned before, the usefulness of the density operator formalism comes when we work with complicated states. The idea of a mixed state is a collection of states $\left| \alpha^{(i)} \right\rangle$ with some weight w_i (note the w_i must sum to 1). Naturally for a pure state we have one $w_i = 1$ and all other equal to zero. For a mixed state

$$\rho = \sum w_i \left| \alpha^{(i)} \right\rangle \left\langle \alpha^{(i)} \right|$$

and instead of an expectation value, we consider ensemble averages

$$[A] = \text{Tr}(\rho A)$$

Note that in this case we still have $\rho = \rho^\dagger$ and $\text{Tr}\, \rho = 1$, but we no longer have $\rho^2 = \rho$ so this is no longer a projection due to the mixed state. In general $0 \leq \text{Tr}\, \rho^2 \leq 1$, for a pure state this will be equal to 1 while mixed states will have square traces which tend to 0.

Example. Consider a uniform ensemble with weights $w_i = 1/N$

$$\rho = \frac{1}{N} \sum | i \rangle \langle i | = \frac{1}{N}$$

Then the traces are

$$\text{Tr}\, \rho = 1 \qquad \text{Tr}\, \rho^2 = \frac{N}{N^2} = \frac{1}{N} \to 0$$

The density operator can be used to define entropy

$$S = -k_B \text{Tr}(\rho \ln \rho)$$

where k_B is the Boltzmann constant. If ρ is diagonal, then this simplifies to

$$S = -k_B \sum w_i \ln w_i$$

Example. For an ensemble of spin 1/2 particles, the density matrix is

$$\rho = \frac{1}{2}(1 + \sigma \cdot \mathbf{P})$$

where $\mathbf{P} = [\sigma] = \frac{2}{\hbar}[\mathbf{S}]$ is the polarization. If we happen to know that expectation values $\langle S_x \rangle, \langle S_y \rangle, \langle S_z \rangle$, then the density matrix can be reconstructed

$$\rho = \frac{1}{2\hbar} \begin{pmatrix} \hbar + 2[S_z] & 2([S_x] - i[S_y]) \\ 2([S_x] + i[S_y]) & \hbar - 2[S_z] \end{pmatrix}$$

Density operators are commonly used in the field of quantum computing, where it's easier to describe multi-qubit open systems in terms of density matrices.

7 Perturbation Theory

7.1 The Variational Method

Also called the Rayleigh-Ritz method, the variational method uses a trial state to determine the ground state energy of a given system. We use the fact that for a Hamiltonian H with exact ground energy E_0 and ground state $|\psi_0\rangle$

$$E[\psi] = \frac{\langle\psi|\,H\,|\psi\rangle}{\langle\psi|\psi\rangle}$$

Thus the ground state is the minimum of the functional. To see that E_0 is the minimum in the space of $E[\psi]$, we can expand in terms of energy eigenstates $|a_n\rangle$

$$\begin{aligned}
E[\psi] &= \frac{\langle\psi|\,H\,|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\sum \langle\psi|a_n\rangle \langle a_n|\,H\,|a_n'\rangle \langle a_n'|\psi\rangle}{\sum \langle\psi|a_n\rangle \langle a_n|a_n'\rangle \langle a_n'|\psi\rangle} \\
&= \frac{\sum E_n|\langle a_n|\psi\rangle|^2}{\sum |\langle a_n|\psi\rangle|^2} \\
&= E_0 + \frac{\sum (E_n - E_0)|\langle a_n|\psi\rangle|^2}{\sum |\langle a_n|\psi\rangle|^2} \geq E_0
\end{aligned}$$

since $E_n > E_0$, meaning that the second term is strictly positive. If there are no degeneracies, then the inequality is strict. If degeneracies do exist, then it is sufficient that the variational method find a state which lies in the degenerate manifold of ψ_0.

How to Variational Method

The actual procedure for the variational method is

1. Guess a trial state ψ_T based on some general features (such as symmetry) which depends on some parameters

$$\psi_T = \psi_T(x, \lambda_1, \ldots, \lambda_k)$$

2. Compute the functional

$$E_T(\lambda_1, \ldots, \lambda_k) = E[\psi_T] = \frac{\langle\psi_T|\,H\,|\psi_T\rangle}{\langle\psi_T|\psi_T\rangle}$$

3. Solve for the parameters with

$$\frac{\partial}{\partial\lambda_i} E_T(\lambda_1, \ldots, \lambda_k) = 0$$

to get an upper bound on the energy

Example. Consider the Coulomb potential with a Gaussian trial function

$$H = \frac{p^2}{2m} - \frac{e^2}{r} \qquad \psi_T(\mathbf{x}, \lambda) = e^{-\lambda r^2}$$

The functional is evaluated in parts

$$\int |\psi_T|^2 d^3x = 4\pi \int_0^\infty r^2 e^{-2\lambda r^2} dr$$

$$= \frac{\pi}{2\lambda} \sqrt{\frac{\pi}{2\lambda}}$$

$$\int \psi_T^* H \psi_T d^3x = \frac{3\pi\hbar^2}{4m} \sqrt{\frac{\pi}{2\lambda}} - \frac{e^2\pi}{\lambda}$$

$$\therefore E_T(\lambda) = -\frac{3\hbar^2 e^2 \lambda}{m} \sqrt{\frac{2\lambda}{\pi}}$$

which we can solve to get the parameter λ_0

$$\frac{dE}{d\lambda} = \frac{3\hbar^2}{2m} - e^2 \sqrt{\frac{2}{\pi\lambda}} = 0 \longrightarrow \lambda_0 = \frac{8}{9\pi} \left(\frac{me^2}{\hbar^2}\right)^2 = \frac{8}{9\pi a_0^2}$$

which gives an energy of

$$E_T(\lambda_0) = -\frac{4}{3\pi} \left(\frac{me^4}{\hbar^2}\right) = -\frac{8}{3\pi} R_y \approx -0.85 R_y$$

Since the exact value is $E_0 = -R_y$, this does indeed give an upper bound, this bound can be improved with a better trial function

$$\psi_T(\lambda_1, \lambda_2) = e^{-\lambda_1 r - \lambda_2 r^2}$$

which gives an exact answer with $\lambda_1 = 1/a_0, \lambda_2 = 0$

7.2 Time Independent Perturbation Theory

Here we introduce the idea of perturbation theory, a powerful tool which allows us to solve complicated problems by approximating the Hamiltonian. Suppose we have a system $H = H_0 + H'$ in which we know the solutions to H_0 and H' is "small" (a perturbation). Suppose $H_0 |\phi_n\rangle = E_n |\phi_n\rangle$ and furthermore assume there is no degeneracy (we will visit this later). We introduce the bookkeeping parameter

$$H = H_0 + \lambda H'$$

and expand in terms of lambda

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \cdots$$

$$|\psi\rangle = |\psi_0\rangle + \lambda |\psi_1\rangle + \lambda^2 |\psi_2\rangle + \cdots$$

Putting this into the energy eigenvalue statement gives

$$(H_0 + \lambda H')(|\psi_0\rangle + \lambda |\psi_1\rangle + \cdots) = (E^{(0)} + \lambda E^{(1)} + \cdots)(|\psi_0\rangle + \lambda |\psi_1\rangle + \cdots)$$

allowing us to match powers of λ

$$\lambda^0 : (H_0 - E^{(0)}) |\psi_0\rangle = 0$$
$$\lambda^1 : (H_0 - E^{(0)}) |\psi_1\rangle = (E^{(1)} - H') |\psi_0\rangle$$
$$\lambda^2 : (H_0 - E^{(0)}) |\psi_2\rangle = (E^{(1)} - H') |\psi_1\rangle + E^{(2)} |\psi_0\rangle$$
$$\vdots$$

Let's start with the zeroth order case

$$(H_0 - E^{(0)}) |\psi_0\rangle \longrightarrow H_0 |\psi_0\rangle = E^{(0)} |\psi_0\rangle$$

which means we can simply select some state $|\psi_m\rangle$ as a starting point. Such a choice is a physics problem and will depend on the specific problem being considered.

$$\boxed{|\psi_0\rangle = |\phi_m\rangle \qquad E^{(0)} = E_m}$$

For 1st order perturbation theory, we have the condition

$$(H_0 - E_m) |\psi_1\rangle = (E^{(1)} - H') |\phi_m\rangle$$

The 1st order state $|\psi_1\rangle$ can be expanded in terms of known eigenkets

$$|\psi_1\rangle = \sum_k c_k^{(1)} |\phi_k\rangle$$

Putting this into the condition and taking the inner product with $\langle \phi_m|$, we get the perturbed energy (to 1st order)

$$E^{(1)} = \langle \phi_m| H' |\phi_m\rangle$$

To actually the the coefficients, we must take the inner product with $\langle \phi_k|$ where $n \neq m$

$$c_k^{(1)} = \frac{\langle \phi_k| H' |\phi_m\rangle}{E_m - E_k} \qquad k \neq m$$

Now we may ask the question: what about $c_m^{(1)}$? The answer is that we can just set it to zero without loss of generality. From the normalization condition (up to $O(\lambda)$)

$$\langle \psi|\psi\rangle = 1 + \lambda(\langle \phi_m|\psi_1\rangle + \langle \psi_1|\phi_m\rangle) + O(\lambda^2) = 1$$
$$\therefore \lambda(c_m^{(1)} + c_m^{(1)*}) + O(\lambda^2) = 0$$
$$\therefore \operatorname{Re} c_m^{(1)} = 0$$

The fact that Im $c_m^{(1)}$ is unknown is irrelevant because either it's zero (and so it actually doesn't matter) or it's just the start of a phase factor (and so it basically doesn't matter). Thus the 1st order corrections are

$$|\psi_1\rangle = \sum_{k \neq m} \frac{\langle\phi_k| H' |\phi_m\rangle}{E_m - E_k} |\phi_k\rangle \qquad E^{(1)} = \langle H'|\phi_m\rangle \phi_m$$

The 2nd order condition is given by

$$(H_0 - E_m) |\psi_2\rangle = (E^{(1)} - H') |\psi_1\rangle + E^{(2)} |\phi_m\rangle$$

As with before, we expand the state in terms of known eigenkets

$$|\psi_2\rangle = \sum_k c_k^{(2)} |\phi_k\rangle$$

to get

$$\sum_k (E_k - E_m) c_k^{(2)} |\phi_k\rangle = (E^{(1)} - H') |\psi_1\rangle + E^{(2)} |\psi_0\rangle$$

By taking the inner product with $\langle\phi_m|$, we can derive 2nd order energy corrections

$$0 = E^{(1)} \langle\phi_m|\psi_1\rangle - \langle H'|\phi_m\rangle \psi_1 + E^{(2)}$$

and noting that $\langle\phi_m|\psi_1\rangle$ (since we defined $c_m^{(1)} = 0$)

$$E^{(2)} = \langle\phi_m| H' |\psi_1\rangle = \sum_{k \neq m} \frac{\langle\phi_m| H' |\phi_k\rangle \langle\phi_k| H' |\phi_m\rangle}{E_m - E_k}$$

Similarly, by taking the inner product with $\langle\phi_n|$, we derive

$$(E_n - E_m) c_m^{(2)} = E^{(1)} \langle\phi_n|\psi_1\rangle - \langle\phi_n| H' |\psi_1\rangle$$

which gives the coefficients

$$c_n^{(2)} = \sum_{k \neq m} \frac{\langle\phi_n| H' |\phi_k\rangle \langle\phi_k| H' |\phi_m\rangle}{(E_m - E_k)(E_m - E_n)} - \frac{\langle\phi_m| H' |\phi_m\rangle \langle\phi_n| H' |\phi_m\rangle}{(E_m - E_n)^2} \qquad n \neq m$$

Again, $c_m^{(2)}$ can be set to zero by imposing the condition $\langle\psi_0|\psi_2\rangle = 0$.

The validity of this expansion requires that the perturbing Hamiltonian be "small"

$$\left| \frac{\langle\phi_k| H' |\phi_m\rangle}{E_m - E_k} \right| \ll 1$$

Example. Suppose we have a perturbed harmonic oscillator

$$H = H_0 + H' = \left(\frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2\right) + \left(\frac{\epsilon}{2}m\omega^2 x^2\right)$$

The known solutions are

$$|psi_0\rangle = |n_0\rangle \qquad E_n^{(0)} = \left(n + \frac{1}{2}\right)\hbar\omega$$

and the first and second order energy corrections are

$$E_n^{(1)} = \langle n_0| H' |n_0\rangle = \frac{\epsilon m\omega^2}{2}\langle x^2|n_0\rangle n_0$$

$$E_n^{(2)} = \sum_{k\neq n}\frac{|\langle k_0| H' |n_0\rangle|^2}{E_n^{(0)} - E_k^{(0)}}$$

We evaluate the matrix element to get

$$\langle k_0| x^2 |n_0\rangle = \frac{\hbar}{2m\omega}\begin{cases}\sqrt{(n+1)(n+2)}\delta_{k,n+2} + \sqrt{n(n-1)}\delta_{k,n-2} & k \neq n \\ 2n+1 & k = n\end{cases}$$

which gives use the corrections

$$E_n^{(1)} = \frac{\epsilon\hbar\omega}{2}\left(n + \frac{1}{2}\right)$$

$$E_n^{(2)} = -\frac{\epsilon^2\hbar\omega}{8}\left(n + \frac{1}{2}\right)$$

7.2.1 The Quadratic Stark Effect

The Stark effect is the splitting of energy levels due to the presence of an external magnetic field. The Hamiltonian can be represented as the standard Coulomb potential Hamiltonian and an extra perturbing electric field term.

$$H = H_0 + H' = \left(\frac{p^2}{2m} - \frac{e^2}{r}\right) + (-e\mathbf{E} \cdot \mathbf{x})$$

In particular, we take an electric field in the $\hat{z}$ direction

$$\mathbf{E} = E\hat{z} \qquad H' = -eEz$$

and the known states are just the hydrogen bound states, we'll take the ground state for simplicity. The energy corrections are given by the epxressions

$$E^{(0)} = E_0 = -R_y$$

$$E^{(1)} = \langle 100| H' |100\rangle$$

$$E^{(2)} = \sum_{k\neq 0}\frac{|\langle 100| H' |k\ell m_\ell\rangle|}{E_0 - E_k}$$

Note the symmetry properties of z

$$z \sim T_0^{(1)} \qquad \Pi z \Pi^{-1} = -z$$

which means we must have $\ell = 1$ and $m_\ell = 0$ for nonvanishing matrix elements. In particular, the first order correction is zero and the second order correction can be written

$$E^{(2)} = e^2 E^2 \sum_{k=1}^{\infty} \frac{|\langle 100| z |k10\rangle|^2}{E_0 - E_k}$$

This infinite sum can be approximated in various ways, one way is to pretend the denominator is roughly constant and instead take the sum over all k

$$\sum_{k \neq 0} |\langle 100| z |k10\rangle|^2 = \sum_{k=0} |\langle 100| z |k10\rangle|^2$$
$$= \sum_{k=0} \langle 100| z |k\rangle \langle k| z |100\rangle$$
$$= \langle 100| z^2 |100\rangle = a_0^2$$

so the energy correction is approximately

$$E^{(2)} \approx \frac{e^2 E^2 a_0^2}{-3/4(e^2/2a0^2)} = -\frac{8}{3} a_0^3 E^2$$

7.2.2 Degenerate Perturbation Theory

So far we've assumed that $|\psi_0\rangle = |\phi_m\rangle$ is nondegenerate. Obviously our expansion breaks down if degeneracy exists due to the energy denominator being zero for some state. Suppose that we have two degenerate states $|\phi_m\rangle, |\phi_k\rangle$. In this case, the starting energy E_m does not actually specify an initial state. If we assume that H' will lift degeneracy at some order, then there will be two different combinations of $|\phi_m\rangle, |\phi_k\rangle$ with different energies. We wish to find these two combinations.

For the degenerate case we start with a linear combination

$$|\psi_0\rangle = c_m^{(0)} |\phi_m\rangle + c_k^{(0)} |\phi_k\rangle$$

The first order condition becomes

$$(H_0 - E^{(0)}) |\psi_1\rangle = (E^{(1)} - H') |\psi_0\rangle = (E^{(1)} - H')(c_m^{(0)} |\phi_m\rangle + c_k^{(0)} |\phi_k\rangle$$

Taking inner products with $\langle \phi_m|$ and $\langle \phi_k|$ gives two conditions

$$E^{(1)} c_m^{(0)} = \langle \phi_m| H' |\phi_m\rangle c_m^{(0)} + \langle \phi_m| H' |\phi_k\rangle c_k^{(0)}$$

$$E^{(1)} c_k^{(0)} = \langle \phi_k| H' |\phi_m\rangle c_m^{(0)} + \langle \phi_k| H' |\phi_k\rangle c_k^{(0)}$$

Thus to determine the first order energy correction, we must diagonalize the matrix

$$
\begin{pmatrix}
\langle \phi_m | H' | \phi_m \rangle & \langle \phi_m | H' | \phi_k \rangle \\
\langle \phi_k | H' | \phi_m \rangle & \langle \phi_k | H' | \phi_k \rangle
\end{pmatrix}
$$

This gives two distinct energy shifts $E_{\pm}^{(1)}$ and the associated eigenvectors give the linear combinations which we should take to be the zeroth order states. The first order corrections to the states can be taken to be zero so that diagonalizing the matrix gives the correct energies and associated eigenstates up to first order.

However, this process does not always work. We won't get distinct eigenvalues (and thus energies) if

$$
\begin{cases}
\langle \phi_m | H' | \phi_m \rangle = \langle \phi_k | H' | \phi_k \rangle \\
\langle \phi_m | H' | \phi_k \rangle = 0
\end{cases}
$$

Thus degeneracy is lifted at first order if and only if $\langle \phi_m | H' | \phi_k \rangle \neq 0$. In the event that it isn't, we must move to second order with the condition

$$
(H_0 - E^{(0)}) |\psi_1\rangle = (E^{(1)} - H') |\psi_1\rangle + E^{(2)}(c_m^{(0)} |\phi_m\rangle + c_k^{(0)} |\phi_k\rangle = 0
$$

Noting that $\langle \phi_{m,k} | \psi_1 \rangle = 0$ and taking inner products with $\langle \phi_m |$ and $\langle \phi_k |$, we get two conditions again

$$
- \langle \phi_m | H' | \psi_1 \rangle + E^{(2)} c_m^{(0)} = 0 \qquad - \langle \phi_k | H' | \psi_1 \rangle + E^{(2)} c_k^{(0)}
$$

We also have from taking the inner product of the first order condition with $\langle \phi_\ell |$

$$
(E_\ell - E_m) c_\ell^{(1)} = - \langle \phi_\ell | H' | \phi_m \rangle c_m^{(0)} - \langle \phi_\ell | H' | \phi_k \rangle c_k^{(0)} \qquad \ell \neq k, m
$$

Combining all this together gives us a system of two equations

$$
\left[\sum_{\ell \neq m,k} \frac{|\langle \phi_m | H' | \phi_\ell \rangle|^2}{E_m - E_\ell} - E^{(2)} \right] c_m^{(0)} + \left[\sum_{\ell \neq m,k} \frac{\langle \phi_m | H' | \phi_\ell \rangle \langle \phi_\ell | H' | \phi_k \rangle}{E_m - E_\ell} \right] c_k^{(0)} = 0
$$

$$
\left[\sum_{\ell \neq m,k} \frac{\langle \phi_k | H' | \phi_\ell \rangle \langle \phi_\ell | H' | \phi_m \rangle}{E_k - E_\ell} \right] c_m^{(0)} + \left[\sum_{\ell \neq m,k} \frac{|\langle \phi_k | H' | \phi_\ell \rangle|^2}{E_k - E_\ell} - E^{(2)} \right] c_k^{(0)} = 0
$$

which gives us another diagonlization problem to find $E^{(2)}$. Again, all other order corrections can be chosen to be zero so that diagonalization gives states (and energies) correct up to second order. Degeneracy is lifted at second order if there exists some state $|\phi_\ell\rangle$ (not in the degenerate subspace) such that

$$
\langle \phi_m | H' | \phi_\ell \rangle \langle \phi_\ell | H' | \phi_k \rangle \neq 0
$$

Although we've worked with two-fold degeneracy in our discussion of degenerate perturbation theory, the same approaches work for higher level degeneracy (we'd just have 3x3, 4x4, ... matrices to diagonalize).

7.3 Application: Fine Structure of Hydrogen

As an application of the formalism we've just developed, we will investigate various corrections to the hydrogen atom.

$$H = \frac{p^2}{2m} - \frac{e^2}{r} \qquad E_n^{(0)} = -\frac{R_y}{n^2}$$

where $m = m_e$ is the electron mass and the constants are

$$R_y = \frac{me^4}{2\hbar^2} = \frac{e^2}{2a_0} = 13.6 \text{ eV} \qquad a_0 = \frac{\hbar^2}{me^2} = 0.53 \times 10^{-8} \text{ cm}$$

It's useful to define the fine structure constant

$$\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}$$

and rewrite the previous constants as

$$R_y = \frac{mc^2}{2}\alpha^2 \qquad a_0 = \frac{\hbar}{mc\alpha}$$

A simple correction we can make right away is to replace m with the reduced mass

$$\mu = \frac{mm_p}{m + m_p}$$

which results in a shift

$$E_n^{(0)} \to \frac{\mu}{m} E_n^{(0)} \approx 0.9995 E_n^{(0)}$$

a small but measurable change for hydrogren.

The fine structure corrections are $O(\alpha^2 E_n^{(0)})$ effects due to two sources:

1. Relativistic corrections due to kinetic energy

2. Spin-orbit coupling between electron spin and the magnetic field generated by the proton's electric field (since it's moving in the non-inertial reference frame of the electron)

Beginning with the kinetic energy correction, we must replace

$$\frac{p^2}{2m} \mapsto \sqrt{p^2c^2 + m^2c^4} - mc^2$$

which, in the limit $v/c \ll 1$, gives us a perturbation

$$H'_{KE} = -\frac{p^4}{8m^3c^2} + O(p^6)$$

Using naive nondegenerate perturbation theory, we can write

$$E_{n,KE}^{(1)} = \langle n\ell m_\ell | H'_{KE} | n\ell m_\ell \rangle = -\frac{1}{8m_e^3c^2} \langle n\ell m_\ell | p^4 | n\ell m_\ell \rangle$$

The trick to evaluating this matrix element is two write

$$p^4 = 4m^2 \left(\frac{p^2}{2m} \right)^2 = 4m^2 \left(H_0 + \frac{e^2}{r} \right)^2$$

showing that to compute $\langle p^4 \rangle$ we just need $\langle 1/r \rangle, \langle 1/r^2 \rangle$

$$\langle n\ell m_\ell | \frac{e^2}{r} | n\ell m_\ell \rangle = \frac{e}{a_0 n^2} \qquad \langle n\ell m_\ell | \frac{e^4}{r^2} | n\ell m_\ell \rangle = \frac{e^4}{a_0 n^3 (\ell + 1/2)}$$

$$\therefore E_{n,KE}^{(1)} = -\frac{1}{2} mc^2 \alpha^4 \left[-\frac{3}{4n^2} + \frac{1}{n^2(\ell + 1/2)} \right] \sim 10^{-9} E_n^{(0)}$$

The spin-orbit interaction is due to a proton moving (relative to the electron) at a velocity $-\mathbf{v}$, generating a magnetic field

$$\mathbf{B} = -\frac{\mathbf{v}}{c} \times \mathbf{E} = -\frac{|e|}{c} \frac{\mathbf{v} \times \mathbf{r}}{r^3} = \frac{|e|}{m_e c r^3} \mathbf{L}$$

which gives a spin-orbit perturbation

$$H_{SO}' = -\mu_e \cdot \mathbf{B} = -\frac{|e|}{m_e c} \frac{\mu_e \cdot \mathbf{L}}{r^3} = \frac{e^2}{2m_e^2 c^2 r^3} \mathbf{L} \cdot \mathbf{S}$$

where the magnetic moment of the electron is $\mu_e = |e|\mathbf{S}/mc$. This expression is actually not accurate due to the effect of Thomas precession, which occurs because the electron rest frame is not inertial. This results in an additional $1/2$ factor

$$H_{SO}' = \frac{1}{2m_e^2 c^2 r^3} \mathbf{L} \cdot \mathbf{S}$$

or more generally for a hydrogen-like (aka alkali) atom

$$H_{SO}' = \frac{1}{2m_e^2 c^2} \frac{1}{r} \frac{\partial V}{\partial r} \mathbf{L} \cdot \mathbf{S}$$

While the kinetic energy perturbation was a scalar under rotation, allowing us to use any basis, the spin-orbit perturbation is already diagonal in the $|njm; \ell s\rangle$ basis, in which

$$E_{n,SO}^{(1)} = \frac{e^2}{2m_e^2 c^2} \langle njm; \ell 1/2| \frac{\mathbf{L} \cdot \mathbf{S}}{r^3} |njm; \ell 1/2 \rangle = \frac{e^2}{\hbar^2} 4m_e^2 c^2 \left\langle \frac{1}{r^3} \right\rangle \left[j(j+1) - \ell(\ell+1) - \frac{3}{4} \right]$$

where $j = \ell \pm 1/2$. The remaining expectation value can be calculated using various tricks [4]

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{a_0^3} \frac{1}{n^3 (\ell + 1/2)(\ell + 1)\ell}$$

to give a first order correction

$$E_{n,SO}^{(1)} = \frac{1}{a_0^3} \frac{1}{n^3 \ell(\ell + 1/2)(\ell + 1)} \cdot \begin{cases} \ell & j = \ell + 1/2 \\ -(\ell + 1) & j = \ell - 1/2 \end{cases}$$

---

[4] See Shankar's discussion

Putting all this together, we get a fine structure correction

$$E_{n,FS}^{(1)} = -\frac{1}{2}m_e^2 c^2 \alpha^4 \left(-\frac{3}{4n^4} + \frac{1}{n^3(j+1/2)} \right) = -\frac{E_n^{(0)}\alpha^2}{n}\left(\frac{1}{j+1/2} - \frac{3}{4n} \right)$$

This splits the degeneracy of j levels for a given value of ℓ. The remaining states splits due to the Lamb shift, which is a relativist quantum effect, famously explained using quantum electrodynamics.

We can also discuss the hyperfine structure of hydrogen, which results from magnetic dipole interactions between the spins of the proton and electron. They are of the order

$$E_{HF} \sim \left\langle \mu_e \cdot \mu_p r^{-3} \right\rangle \sim \frac{e}{m_e c}\frac{e}{m_p c}g_p \left\langle \mathbf{S}_e \cdot \mathbf{S}_p r^{-3} \right\rangle \sim \frac{m_e}{m_p}E_{FS} \sim \frac{1}{2000}E_{FS}$$

and note the suppression due to the proton mass.

It's also possible to craft a model in which the nucleus is treated as a spherical ball of charge of radius R to account for it's finite size. This results in an energy correction

$$E_e^{(1)} \sim \frac{e^2}{R^2}a_0^3 \sim R_y \left(\frac{R}{a_0} \right)^2$$

For the hydrogen atom $R \sim 10^{-5}a_0$ is results in a negligible energy shift, but for other systems (like sodium) there could be a significant shift.

7.4 Time Dependent Hamiltonians

Recall that for a time independent Hamiltonian, time evolution is given by

$$-\hbar\frac{\partial}{\partial t}U(t,t_0) = HU(t,t_0) \longrightarrow U(t,t_0) = \exp\left(--\frac{iH(t-t_0)}{\hbar} \right)$$

which gives the formula

$$U(t,t_0) = \sum \exp\left(-\frac{iE_n(t-t_0)}{\hbar} \right)|n\rangle\langle n| \qquad H|n\rangle = E_n|n\rangle$$

with the consequence that $\langle E \rangle$ is conserved over time.

However, if H has time dependence then these methods will no longer work because there are no longer any stationary states. Thus $\langle E \rangle$ cannot be conserved. If we are fortunate enough to have $[H(t_0), H(t)] = 0$, then

$$U(t,t_0) = \exp\left(-\frac{i}{\hbar}\int_{t_0}^{t}H(t')dt' \right)$$

but this is generally not true. Instead the time evolution operator is generally given by the Dyson series

$$U(t, t_0) = \mathbb{1} + \sum_{n=1}^{\infty} \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{n-1}} dt_n H(t_1) H(t_2) \cdots H(t_n)$$

Clearly this sum is highly nontrivial, which means we must approximate. In general there are three methods to doing so

1. Time Dependent Perturbation Theory: Assume $H(t) = H_0 + H'(t)$ and treat the time evolution as a perturbation

2. Sudden Approximation: Assume that H changes rapidly between two states, that is we can write
$$H = \theta(t - t_0) H_1 + \theta(t_0 - t) H_2$$

3. Adiabatic Approximation: Assume that H changes slowly over time

7.4.1 Time Dependent Perturbation Theory

Suppose $H(t) = H_0 + H'(t)$ and that H_0 has known eigenstates $|\phi_n\rangle$. Taking $t_0 = 0$ for simplicity, we can expand the state at later time t as

$$|\psi(t)\rangle = \sum c_n(t) e^{-iE_n t/\hbar} |\phi_n\rangle$$

This separates out the trivial (already known) time evolution of H_0 such that the $c_n(t)$ is governed only by $H'(t)$ (this is also called the interaction picture).

The Schrodinger equation gives

$$\left(-i\hbar \frac{d}{dt} - H_0 - H'(t)\right) |\psi(t)\rangle = 0$$

$$\sum_n i\hbar \dot{c}_n - H'(t) c_n) e^{-iE_n t/\hbar} |\phi_n\rangle = 0$$

An inner product with $\langle \phi_k |$ yields

$$i\hbar \dot{c}_k = \sum_n \langle \phi_k | H' | \phi_n \rangle e^{i\omega_{kn} t} c_n(t) \qquad \omega_{kn} = \frac{E_k - E_n}{\hbar}$$

The coefficients can be series expanded

$$c_k(t) = c_k^{(0)}(t) + c_k^{(1)}(t) + c_k^{(2)}(t) + \cdots$$

and equation powers gives

$$i\hbar \dot{c}_k^{(p)} = \sum \langle \phi_k | H' | \phi_n \rangle e^{i\omega_{kn} t} c_k^{(p-1)}(t)$$

We assume that the state starts in some energy eigenstates $|\phi_m\rangle$ so that

$$c_n(0) = \delta_{nm}$$

This gives the 0th order coefficients

$$c_k^{(0)}(t) = c_k(0) = \delta_{nm}$$

The 1st order correction is given by

$$i\hbar \dot{c}_k^{(1)}(t) = \sum \langle \phi_k | H' | \phi_n \rangle e^{i\omega_{kn}t} c_n^{(0)}(t) = \langle \phi_k | H' | \phi_m \rangle e^{i\omega_{km}t}$$

which can be solved to get

$$c_k^{(1)}(t) = \frac{1}{i\hbar} \int_0^t \langle \phi_k | H'(t') | \phi_m \rangle e^{i\omega_{km}t'} dt'$$

Similarly we can solve the 2nd order condition to get

$$c_k^{(2)}(t) = \frac{1}{\hbar^2} \int_0^t dt' \int_0^{t'} dt'' \sum_n \langle \phi_k | H'(t') | \phi_n \rangle e^{i\omega_{kn}t} \langle \phi_n | H'(t'') | \phi_m \rangle e^{i\omega_{nm}t''}$$

Note that the validity of this approximation requires

$$|c_k^{(1)}|, |c_k^{(2)}|, \ldots \ll 1$$

Example. Consider a 1D simple harmonic oscillator at initial time $t_0 = -\infty$ and the perturbation

$$H'(t) = -|e|Exe^{-t^2/\tau^2}$$

Given that the initial state is the ground state, we would like to find the state at time $t = \infty$. To first order, coefficients are given by

$$c_n(\infty) = \delta_{n,0} + \frac{1}{i\hbar} \int_{-\infty}^{\infty} \langle n | i|e|E | 0 \rangle e^{-t^2/\tau^2} e^{in\omega_{n,0}t'} dt'$$

In particular, the probability that the particle ends up in the first excited state can be found using the first coefficient

$$c_1^{(1)}(\infty) = \frac{i}{\hbar}|e|E\sqrt{\frac{\hbar\pi}{2m\omega}}\tau e^{-\omega^2\tau^2/4}$$

Example. Suppose we have the time dependent Hamiltonian for a two state system

$$H = H_0 + H'f(t)$$

where

$$H_0 = \begin{pmatrix} E_1^{(0)} & 0 \\ 0 & E_2^{(0)} \end{pmatrix} \qquad H' = \begin{pmatrix} 0 & b \\ b & 0 \end{pmatrix} \qquad f(t) = \begin{cases} e^{\lambda t} & t < 0 \\ 1 & t > 0 \end{cases}$$

Assume that λ is a positive constant, b is real, positive, and "small," and that $0 < E_1^{(0)} < E_2^{(0)}$. Furthermore, suppose the system begins in the state $|1\rangle$ with energy $E_1^{(0)}$ at time $t = -\infty$. Using time dependent perturbation theory to first order

$$c_2^{(1)}(t) = \frac{1}{i\hbar} \int_{-\infty}^{t} \langle 2| H' |1\rangle f(t') e^{i\omega_{21}t'} dt'$$

$$= \frac{b}{i\hbar} \left[\int_{-\infty}^{0} e^{\lambda + i\omega_{21}t'} dt' + \int_{0}^{t} e^{i\omega_{21}t'} dt' \right]$$

$$= -\frac{ib}{\hbar} \left[\frac{1}{\lambda + i\omega_{21}} - \frac{i}{\omega_{21}} (e^{i\omega_{21}t} - 1) \right]$$

to get a transition probability of

$$P_{1\to2}(t) = \frac{b^2}{\hbar^2} \left[\left(\frac{\lambda}{\lambda^2 + \omega_{21}^2} + \frac{\sin(\omega_{21}t)}{\omega_{21}} \right)^2 + \left(\frac{\omega_{21}}{\lambda^2 + \omega_{21}^2} + \frac{\cos(\omega_{21}t) - 1}{\omega_{21}} \right)^2 \right]$$

In the limit $\lambda \to \infty$, we find

$$c_2^{(1)}(t) \to \frac{b}{\hbar\omega_{21}} (1 - e^{i\omega_{21}t})$$

and in the limit $\lambda \to 0$, we get

$$c_2^{(1)}(t) \to -\frac{b}{\hbar\omega_{21}} e^{i\omega_{21}t}$$

7.4.2   The Sudden Approximation

Suppose that the Hamiltonian can be represented

$$H = H_1\theta(t_0 - t) + H_2\theta(t - t_0) \qquad \theta(t) = \begin{cases} 0 & t < 0 \\ 1 & t > 0 \end{cases}$$

Define two states

$$|\psi_i\rangle = |\psi(-\epsilon)\rangle \qquad |\psi_f\rangle = |\psi(\epsilon)\rangle$$

By integrating, we find

$$|\psi_f\rangle = |\psi_i\rangle + \int_{-\epsilon}^{\epsilon} \frac{d}{dt} |\psi(t)\rangle \, dt = |\psi_i\rangle - \frac{i}{\hbar} \int_{-\epsilon}^{\epsilon} H(t) |\psi(t)\rangle \, dt$$

In the limit $\epsilon \to 0$, we see that $|\psi_f\rangle = |\psi_i\rangle$ as long as $H(t)$ is finite around $t = 0$. Thus the sudden approximation states that if H changed suddenly enough (say at $t = 0$), then the state won't have enough time to react and won't change

$$|\psi(0^+)\rangle = |\psi(0^-)\rangle$$

However, while the state doesn't change, the Hamiltonian still does so there is no guarantee that the state remains in an eigenstate of the the new Hamiltonian.

Example. Consider the last example in the previous section. If the change is sudden enough ($\lambda \to \infty$), then the state across the $t = 0$ boundary won't change, that is

$$|\psi(0)\rangle = |1\rangle$$

To time evolve this, we need to write it in terms of the new eigenstates which can be found with time independent perturbation theory

$$|\psi(0)\rangle = |1'\rangle + \frac{b}{\hbar\omega_{21}} |2'\rangle$$

Thus the state will evolve

$$
\begin{aligned}
|\psi(t)\rangle &= \exp\left(-\frac{iE_1 t}{\hbar}\right) |1'\rangle + \frac{b}{\hbar\omega_{21}} \exp\left(-\frac{iE_2 t}{\hbar}\right) |2'\rangle \\
&= \exp\left(-\frac{iE_1^{(0)} t}{\hbar}\right) |1\rangle + \frac{b}{\hbar\omega_{21}} (1 - e^{i\omega_{21} t}) \exp\left(-\frac{iE_2^{(0)} t}{\hbar}\right) |2\rangle
\end{aligned}
$$

So the probability of transition will be given by the coefficient

$$c_2^{(1)}(t) = \frac{b}{\hbar\omega_{21}} (1 - e^{i\omega_{21} t})$$

in agreement with the previous example (at the appropriate limit).

7.4.3   The Adiabatic Approximation

In the adiabatic approximation we assume that the Hamiltonian $H(t)$ varies slowly from H_1 to H_2. In this case it's useful to define instantaneous eigenstates

$$H(t) |\phi_n(t)\rangle = E_n(t) |\phi_n(t)\rangle$$

When we say that $H(t)$ changes "slowly," what we really mean is

$$\frac{\partial H}{\partial t} \ll \frac{H}{\tau} \qquad \tau \sim \frac{1}{\omega_{ij}}$$

If a system starts in some state $|\phi_n(t_0)\rangle$, then it will end up in $|\phi_n(t)\rangle$ at some later time t. In other words, the system will remain in the eigenstate it started in, though the eigenstate will evolve to remain an instantaneous eigenstate.

Suppose we have some (discrete and nondegenerate) initial state and take the ansatz

$$|\psi(t)\rangle = \sum_n c_n(t) |\phi_n(t)\rangle \exp\left(-\frac{i}{\hbar} \int_0^t E_n(t') dt'\right)$$

The time dependent Schrodinger equation gives

$$\sum_n (\dot{c}_n |\phi_n\rangle + c_n |\dot{\phi}_n\rangle) \exp\left(-\frac{i}{\hbar} \int_0^t E_n(t') dt'\right) = 0$$

By taking the inner product with $\langle \phi_k |$, we find

$$\dot{c}_k = -\sum_n \left\langle \phi_k \middle| \dot{\phi}_n \right\rangle \exp\left(-\frac{i}{\hbar}\int_0^t E_n(t')dt'\right)$$

The inner product $\left\langle \phi_k \middle| \dot{\phi}_n \right\rangle$ can be computed with

$$\frac{d}{dt}\left[H(t)\left|\phi_n(t)\right\rangle = E_n(t)\left|\phi_n(t)\right\rangle\right]$$

$$\frac{\partial H}{\partial t}\left|\phi_n\right\rangle + H(t)\left|\dot{\phi}_n\right\rangle = \dot{E}_n\left|\phi_n\right\rangle + E_n\left|\dot{\phi}_n\right\rangle$$

$$\langle\phi_k|\frac{\partial H}{\partial t}\left|\phi_n\right\rangle + E_k\left\langle\phi_k\middle|\dot{\phi}_n\right\rangle = E_n\left\langle\phi_k\middle|\dot{\phi}_n\right\rangle$$

$$\therefore \left\langle\phi_k\middle|\dot{\phi}_n\right\rangle = \frac{\langle\phi_k|\,\partial H/\partial t\,|\phi_n\rangle}{E_n - E_k} \qquad k \neq n$$

Thus the complete solution is

$$\dot{c}_k = -\sum_{n\neq k} c_n \frac{\langle\phi_k|\,\partial H/\partial t\,|\phi_n\rangle}{E_n - E_k} \exp\left(-\frac{i}{\hbar}\int_0^t E_n(t')dt'\right) - c_k\left\langle\phi_k\middle|\dot{\phi}_k\right\rangle$$

Suppose we start in some eigenstate $|\phi_m(t)\rangle$ so that $c_n(0) = \delta_{nm}$. Then for $k \neq m$, we get

$$\dot{c}_k = -\frac{\langle\phi_k|\,\partial H/\partial t\,|\phi_m\rangle}{E_m - E_k} \exp\left(-\frac{i}{\hbar}\int_0^t (E_m - E_k)dt'\right)$$

The inner product term can be treated as roughly constant while the exponential is slowly varying, this means we can write

$$c_k(t) \approx \frac{\langle\phi_k|\,\partial H/\partial t\,|\phi_m\rangle}{i/\hbar(E_m - E_k)^2}\left(\exp\left(-\frac{i}{\hbar}(E_m - E_k)t\right) - 1\right)$$

We see that the probability that the initial state transition to a different state is negligible if

$$\left|\langle\phi_k|\frac{\partial H}{\partial t}\,|\phi_m\rangle\right| \ll \frac{(E_m - E_k)^2}{\hbar} = \hbar\omega_{km}^2$$

This gives the necessary conditions for the adiabatic approximation to hold. In particular it breaks down if $E_m \approx E_k$ (hence why we assume nondegenerate and discrete energies).

Example. Returning again to the example from the last two sections, suppose that the Hamiltonian is slowly varying, which is the case $\lambda \to 0$. The adiabatic approximation claims the system will remain in the (evolving) ground state, so that

$$|\psi(t)\rangle = e^{-iE_1 t/\hbar}\,|1'\rangle = \left(|1\rangle - \frac{b}{\hbar\omega_{21}}\,|2\rangle\right)e^{-iE^{(0)}t/\hbar}$$

and to leading order we find

$$c_2^{(1)}(t) = -\frac{b}{\hbar\omega_{21}}e^{i\omega_{21}t}$$

again in agreement with the time dependent perturbation result (at the appropriate limit).

Note that we don't actually get the coefficient for the $k = m$ term, which should satisfy

$$\dot{c}_m = -c_m \left\langle \phi_m \middle| \dot{\phi}_m \right\rangle$$

The reason comes from the normalization condition

$$\frac{d}{dt}(\langle \phi_m | \phi_m \rangle = 1)$$

$$\left\langle \dot{\phi}_m \middle| \phi_m \right\rangle + \left\langle \phi_m \middle| \dot{\phi}_m \right\rangle = 0$$

$$\therefore \text{Re} \left\langle \phi_m \middle| \dot{\phi}_m \right\rangle = 0$$

Since it is pure imaginary, we might be led to believe that the eigenstate develops an overall global phase factor. Indeed, if we integrate to try an get the coefficient

$$c_m(t) = c_m(0) \exp\left(-\int \left\langle \phi_m \middle| \dot{\phi}_m \right\rangle dt \right) = c_m(0) e^{i\gamma_m(t)}$$

where

$$\gamma_m(t) = i \int_0^t \left\langle \phi_m \middle| \dot{\phi}_m \right\rangle dt$$

Is a real (as in not imaginary) phase factor. Naively we can try to phase this away by redefining the states

$$|\phi_m'\rangle = e^{i\chi(t)} |\phi_m\rangle \qquad i \left\langle \phi_m' \middle| \dot{\phi}_m' \right\rangle = -\dot{\chi} + i \left\langle \phi_m \middle| \dot{\phi}_m \right\rangle$$

$$\gamma_m(t) = i \int \left\langle \phi_m \middle| \dot{\phi}_m \right\rangle dt - \int \dot{\chi} dt$$

But there is some subtlety. Suppose that $H(t)$ is periodic, that is

$$H(t_f) = H(0)$$

Then integrating around the closed loop gives

$$i \oint \left\langle \phi_m' \middle| \dot{\phi}_m' \right\rangle dt = i \oint \left\langle \phi_m \middle| \dot{\phi}_m \right\rangle dt - (\chi(t_f) - \chi(0))$$

$$\therefore \chi(t_f) - \chi(0) = 2\pi n$$

which is not always possible. This phenomenon is not at all obvious

$$e^{i\gamma_m(t)} = e^{i \oint i \left\langle \phi_m \middle| \dot{\phi}_m \right\rangle dt}$$

is not eliminated by rephasing $\chi(t)$, in fact we must have a geometric phase

$$\gamma_m(t) = \oint \langle \phi_m | \frac{d}{dt} |\phi_m\rangle \, dt$$

Formally, suppose $H(t)$ depends on time through some set of parameters $R_i(t)$ where $I = 1, \ldots, k$ (we will drop the subscript i for convenience).

$$H(R(t)) \, |\phi(R(t))\rangle = E_n(R(t)) \, |\phi_n(R(t))\rangle$$

As usual, suppose $|\psi(0)\rangle = |\phi_m(R(0))\rangle$. We expect an ansatz

$$|\psi(t)\rangle = \exp\left(-\frac{i}{\hbar} \int_0^t E_m(R(t'))dt'\right) |\phi_m(R(t))\rangle$$

but this actually does not satisfy the Schrodinger equation since the time derivative now acts om E_m. Thus we must include an additional phase factor

$$|\psi(t)\rangle = \exp\left(i\gamma_m(t) - \frac{i}{\hbar} \int_0^t E_m(R(t'))dt'\right) |\phi_m(R(t))\rangle$$

allowing us to write down the phase

$$\gamma_m(t) = i \int_0^t \langle \phi_m(R(t'))| \, \frac{d}{dt'} \, |\phi_m(R(t'))\rangle \, dt'$$

$$= - \int_{R(0)}^{R(t)} \langle \phi_m(R)| \nabla_R \, |\phi_m(R)\rangle \, dR$$

If $R(t) = R(0)$ (so it's periodic), then

$$\gamma_m = i \oint \langle \phi_m(R)| \nabla_R \, |\phi_m(R)\rangle \, dR$$

where the ∇_R and dR are shorthand for a sum over all R_i. This is known as Berry's phase.

For the period case, we can also note that

$$i \langle \phi_m(R)| \, D_r \, |\phi_m(R)\rangle = A_\mu dR^\mu \qquad \gamma_m = \oint A_\mu dR^\mu$$

and A_μ is known as the Berry connection.

7.4.4   Fermi's Golden Rule

Returning to normal time dependent perturbation theorem with

$$H(t) = H_0 + H'(t) \qquad H_0 \, |\phi_n\rangle = E_n \, |\phi_n\rangle$$

The probability of a state transition (to state k) is

$$\text{Prob}_{m \to k}(t) = |c_k^{(1)}(t)|^2$$

where the coefficient is given by

$$c_k^{(1)} = \frac{1}{i\hbar} \int_0^t \langle \phi_k| \, H'(t') \, |\phi_m\rangle \, e^{i\omega_{km}t'} dt'$$

Suppose that $H'(t)$ is constant in time, but only switch on for the interval 0 to t. Then

$$\text{Prob}_{m \to k}(t) = \frac{1}{\hbar^2} |\langle \phi_k | H' | \phi_m \rangle|^2 \left| \int_0^t e^{i\omega_{km} t'} dt' \right|^2 = \frac{1}{\hbar^2} |\langle \phi_k | H' | \phi_m \rangle|^2 f(t, \omega_{km})$$

where we've defined the integral as it's own function

$$f(t, \omega) = \frac{2(1 - \cos(\omega t))}{\omega^2} = \frac{\sin^2(\omega t/2)}{(\omega/2)^2}$$

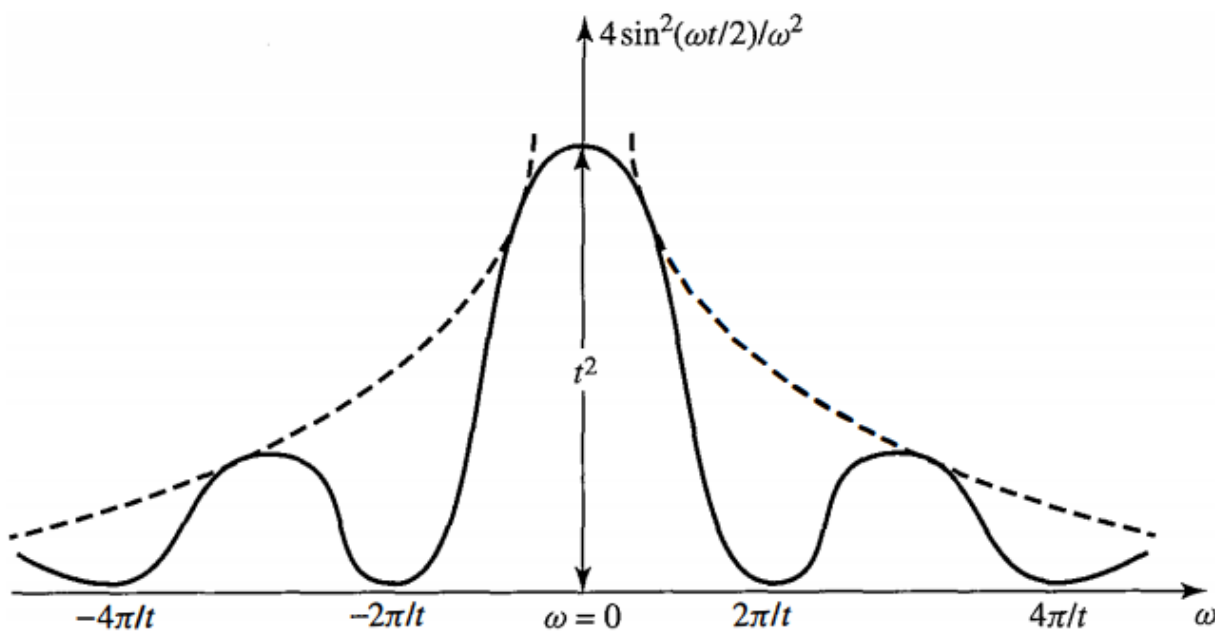This function has several useful properties

1.
$$\int_{-\infty}^{\infty} f(t, \omega) d\omega = 2\pi t$$

2.
$$\lim_{t \to \infty} f(t, \omega) = 2\pi t \delta(\omega)$$

3.
$$\lim_{\omega \to 0} f(t, \omega) = t^2$$

From the graph we see that energy conserving transitions ($\delta E \sim 2\pi\hbar/t$ thus $\omega_{km} \approx 0$) are favored. Consider transitions from $|\phi_m\rangle$ to neighboring states (e.g. to a continuum). Define the rate

$$\Gamma_{m \to \text{group}} = \frac{d\text{Prob}_{m \to \text{group}}}{dt} = \frac{\text{probability of transition}}{\text{unit time}}$$

For notation convenience, denote the continuum states as $|b\rangle$ with energies $E(b)$. The continuum states are normalized

$$\langle b | b' \rangle = \frac{\delta(b - b')}{n(b)}$$

and have the projection operator

$$\Lambda_B = \int_B n(b) |b\rangle \langle b| \, db = \int_{B(E)} |b\rangle \langle b| \, \rho_b(E) dE$$

where we've define the density of states

$$\rho_b(E) = n(b)\frac{db}{dt} \qquad \rho_b(E)dE = n(b)db$$

Then the transition probability is (to first order)

$$\text{Prob}_{m \to B} = \int_{B(E)} \text{Prob}_{m \to b}\rho_b(E)dE = \int_{B(E)} \frac{|\langle \phi_m | H' | b \rangle|^2}{\hbar^2}\rho_b(E)f(t, \omega_{bm})dE$$

Consider the situation where there are transitions to a small energy interval ϵ about some central value E. If ϵ is sufficiently small, then we can consider $\rho_b(E)$ and $\langle \phi_m | H' | b \rangle$ are roughly constant on the interval. Furthermore we consider large values of t, such that $\epsilon \gg 2\pi\hbar/t$. Under these assumptions

$$\text{Prob}_{m \to B} = \frac{|\langle \phi_m | H' | b \rangle|^2}{\hbar^2}\rho_b(E)\int_\epsilon f(t, \omega_{bm})dE_b$$

and there are two possibilities:

1. If the central peak of $f(t, \omega_{bm})$ is outside the domain of integration, so that transitions do not conserve energy, then we replace f with it's average

$$\text{Prob}_{m \to B} \approx \frac{2\epsilon\rho_b(E)}{(E - E_m)^2}|\langle \phi_m | H' | b \rangle|^2$$

2. If the central peak does lie in the domain of integration, then it will be the dominant contribution. Thus we can extend the limits of integration

$$\text{Prob}_{m \to B} = \frac{|\langle \phi_m | H' | b \rangle|^2}{\hbar^2}\rho_b(E)\int_{-\infty}^{\infty} f(t, \omega_{bm})dE_b = \frac{2\pi}{\hbar}|\langle \phi_m | H' | b \rangle|^2\rho_b(E_m)t$$

Thus the transition rate is

$$\boxed{\Gamma_{m \to B} = \frac{\text{Prob}_{m \to B}}{dt} = \frac{2\pi}{\hbar}|\langle \phi_m | H' | b \rangle|^2\rho_b(E_m)t}$$

This is an example of Fermi's golden rule and can be written

$$\Gamma_{m \to B} = \frac{2\pi}{\hbar} |\langle \phi_m | H' | b \rangle|^2 \delta(E_b - E_m)$$

to make energy conservation more apparent. It is understood that this form is to be multiplied by the density of states function and integrated over all energy.

Example. Consider a harmonic perturbation with frequency ω

$$H'(t) = 2H' \sin(\omega t)$$

which is switched on at time $t = 0$ and off at time $t = \tau$ with initial state $|\phi_m\rangle$. The probability of a transition to some state $|\phi_k\rangle$ to first order is

$$c_k^{(1)}(t) = -\frac{\langle \phi_k | H' | \phi_m \rangle}{i\hbar} \left(\frac{e^{i(\omega_{km} + \omega)\tau} - 1}{\omega_{km} + \omega} - \frac{e^{i(\omega_{km} - \omega)\tau} - 1}{\omega_{km} - \omega} \right)$$

The amplitudes of transition are only noticeable when $\omega_{km} = \pm\omega$, which means $E_k \approx E_m \pm \hbar\omega$ (in which either the first or second term dominates). This means that, to first order, the perturbation causes a state to either transfer or receive a quanta $\hbar\omega$ of energy.

As with before, we are interested from a transition from a discrete state $|\phi_m\rangle$ to some continuum $|b\rangle$ with $E_b > E_m$. Thus the second term dominates, allowing us to write

$$|c_b^{(1)}(t)|^2 = \frac{4}{\hbar^2} |\langle b | H' | \phi_m \rangle|^2 f(\tau, \omega_{bm} - \omega)$$

and the transition rate is given by Fermi's golden rule

$$\Gamma_{m \to B} = \frac{2\pi}{\hbar} |\langle b | H' | \phi_m \rangle|^2 \rho_b(E_b)$$

where $E_b = E_m + \hbar\omega$. Again, this can be written to make the energy conservation explicit

$$\Gamma_{m \to B} = \frac{2\pi}{\hbar} |\langle b | H' | \phi_m \rangle|^2 \delta(E_b - E_m - \hbar\omega)$$

where it's understood that this is to be multiplied by the density of states and integrated.

It is also possible to use box normalization to reduce the problem from a continuum of states to just a discrete set. Essentially we impose periodic boundary conditions on a plane wave

$$e^{i\mathbf{k} \cdot \mathbf{x}}|_{\mathbf{xL}} = 1 \longrightarrow k_i = \frac{2\pi n_i}{L}$$

where n_i is an integer and L is the box length. The states then are given by

$$\langle \mathbf{x} | \mathbf{p} \rangle = \frac{1}{L^{3/2}} e^{i\mathbf{k} \cdot \mathbf{x}}$$

Thus we can go ahead and calculate

$$n(b)db = dn_x dn_y dn_z = \left(\frac{L}{2\pi}\right)^3 dk_x dk_y dk_z = \left(\frac{L}{2\pi}\right)^3 k^2 dk d\Omega_k$$

$$dE_k = \frac{\hbar^2 k dk}{m} \longrightarrow k^2 dk = \frac{mk}{\hbar} dE_k$$

to get the density of states as

$$\rho(E_k) = \left(\frac{L}{2\pi}\right)^3 \frac{mk}{\hbar} d\cos(\theta_k) d\phi_k$$

If done properly, the final answer will be independent of L (as required).

7.5   Application: Semiclassical Radiation Theory

This is a description of a charge particle (treated quantum mechanically) interacting with a classical electromagnetic field. Let's consider an electron in a Coulomb potential which interacts with an external field

$$H_0 = \frac{p^2}{2m} - \frac{e^2}{r} \qquad H' = \frac{|e|}{mc}\mathbf{A}\cdot\mathbf{p} + \frac{e^2}{2mc^2}\mathbf{A}^2 - \gamma\mathbf{S}\cdot\mathbf{B}$$

As usual, we will work in the Coulomb gauge

$$\nabla\cdot\mathbf{A} = 0 \qquad \Phi = 0$$

so that we can write the vector potential as

$$\mathbf{A} = \mathbf{A}_0 \cos(\mathbf{k}\cdot\mathbf{x} - \omega t) \qquad \omega = c|\mathbf{k}|$$

where $\mathbf{k}$ is the direction of propagation. The two fields then are

$$\mathbf{E} = -\frac{\omega\mathbf{A}_0}{c}\sin(\mathbf{k}\cdot\mathbf{x} - \omega t)$$

$$\mathbf{B} = -\mathbf{k}\times\mathbf{A}_0 \sin(\mathbf{k}\cdot\mathbf{x} - \omega t)$$

and the Poynting vector is

$$\langle\mathbf{S}\rangle = \frac{\omega^2}{8\pi c}|\mathbf{A}_0|^2\hat{k}$$

For a weak field, we have

$$\frac{|e||\mathbf{A}_0|}{c} \ll p_0 \sim \frac{\hbar}{a_0} \longrightarrow \frac{\hbar k}{p_0} \sim ka_0 \sim \frac{e^2}{\hbar c} = \alpha$$

In other words $ka_0 \ll 1$, which means we can drop the $\mathbf{A}^2$ term as well as the $\mathbf{S}\cdot\mathbf{B}$ in the first order since

$$\frac{\mathbf{S}\cdot\mathbf{B}}{\mathbf{A}\cdot\mathbf{p}} \sim \frac{\hbar}{2}\left(\frac{\sigma\cdot\nabla\times\mathbf{A}}{\mathbf{A}\cdot\mathbf{p}}\right) \sim \frac{\hbar k}{p_0} \ll 1$$

Thus we can write the interaction Hamiltonian as

$$H'(t) = \frac{|e|\mathbf{A}_0}{mc}\cos(\mathbf{k}\cdot\mathbf{x} - \omega t) = \frac{|e|\mathbf{A}_0}{2mc}\left(e^{i(\mathbf{k}\cdot\mathbf{x}-\omega t)} + e^{-i(\mathbf{k}\cdot\mathbf{x}-\omega t)}\right)\cdot\mathbf{p}$$

Suppose the electron starts in the ground state, so that

$$E_f - E_i = \frac{p_f^2}{2m} + R_y \geq 0$$

and thus only the first term of H' matters. Using Fermi's golden rule, the absorption rate is

$$\Gamma_{i\to f} = \frac{2\pi}{\hbar}\left|\frac{|e|}{2mc}\int d^3x\,\psi_f^*(\mathbf{x})e^{i\mathbf{k}\cdot\mathbf{x}}\mathbf{A}_0\cdot(-i\hbar\nabla)\psi_i(\mathbf{x})\right|^2\delta(E_f - E_i - \hbar\omega)$$

For simplicity we will take ψ_f to have the form of a free particle wavefunction (though this is not rigorous since the Coulomb potential is long range).

$$\psi_i(\mathbf{x}) = \frac{e^{-r/a_0}}{\sqrt{\pi a_0^3}} \qquad \psi_f(\mathbf{x}) = \frac{e^{i\mathbf{p}_f\cdot\mathbf{x}/\hbar}}{(2\pi\hbar)^{3/2}}$$

Using the weak field approximation $e^{i\mathbf{k}\cdot\mathbf{x}} \approx 1$, we can write

$$\Gamma_{i\to f} = N\int d^3x\,e^{-i\mathbf{k}_f\cdot\mathbf{x}}\mathbf{A}_0\cdot(-i\hbar\nabla)e^{-r/a_0}$$

$$= N\mathbf{A}_0\cdot\mathbf{p}_f\int d^3x\,e^{-i\mathbf{k}_f\cdot\mathbf{x}}e^{-r/a_0}$$

where we've pulled out the coefficient

$$N = \frac{|e|}{2mc}\frac{1}{(2\pi\hbar)^{3/2}}\frac{1}{(\pi a_0^3)^{1/2}}$$

The integral evaluates to

$$\Gamma_{i\to f} = \frac{2\pi}{\hbar}\frac{64\pi^2 N^2}{a_0^2}\frac{|\mathbf{A}_0\cdot\mathbf{p}_f|^2}{(k_f^2 + 1/a_0^2)^4}\delta(E_f - E_i - \hbar\omega)$$

$$= \frac{4e^2 a_0^3}{m^2\pi^2\hbar^4 c^2}\frac{|\mathbf{A}_0\cdot\mathbf{p}_f|^2}{(1 + (k_f a_0)^2)4}\delta(E_f - E_i - \hbar\omega)$$

The rate of electrons deflected in a solid angle Ω would be

$$\frac{d\Gamma}{d\Omega} = \int_0^\infty p_f^2\Gamma_{i\to p_f}\,dp_f$$

$$= \frac{4e^2 a_0^3}{m^2\pi^2\hbar^4 c^2}\frac{\tilde{p}_f|\mathbf{A}_0\cdot\mathbf{p}_f|^2}{(1 + (\tilde{p}_f a_0/\hbar)^2)4}$$

where $\tilde{p}_f = \sqrt{2m(E_i + \hbar\omega)}$. The total rate then is

$$\Gamma = \int\frac{d\Gamma}{d\Omega}d\Omega = frac163\frac{e^2 a_0^3\tilde{p}_f^3 A_0^2}{3m\hbar^4 c^2(1 + (\tilde{p}_f a_0/\hbar)^2)^4}$$

Another useful quantity is the cross section, the absorption rate divide by incident flux

$$\sigma = \frac{dE_{abs}/dt}{\langle 0 \rangle \, \mathbf{S}} = \frac{128 a_0^3 e^2 \tilde{p}_f^3 \pi}{3 m \hbar^3 \omega c (1 + (\tilde{p}_f a_0/\hbar)^2)^4}$$

Similarly we can define the differential cross section

$$\frac{d\sigma}{d\Omega} = \frac{1}{\langle \mathbf{S} \rangle} \hbar \omega \frac{d\Gamma}{d\Omega} = \frac{32 a_0^3 e^2 \tilde{p}_f^3 \cos^2(\theta)}{m \hbar^3 \omega c (1 + (\tilde{p}_f a_0/\hbar)^2)^4}$$

In the limit $\tilde{p}_f a_0/\hbar \gg 1$, this becomes

$$\frac{d\sigma}{d\Omega} = \frac{32 e^2 \hbar^5 \cos^2(\theta)}{m \omega c \tilde{p}_f^5 a_0^5}$$

Example. Suppose linear polarized light of angular frequency ω is incident on a one-electron "atom" which we approximate with the ground state of a 3D isotropic oscillator of angular frequency ω_0. Suppose that the ejected photoelectron of momentum $\hbar \mathbf{k}_f$ can be approximated with a plane-wave. Here, the propagation of the electromagnetic wave is take to be along $\hat{z}$, so that $\mathbf{k} = \omega \hat{z}/c$ and the direction of polarization is to be along $\hat{x}$.

To summarize all the conditions given in the problem, we have

$$H'(t) = H' e^{-i\omega t} = \frac{|e|}{2mc} \mathbf{A}_0 \cdot \mathbf{p} e^{ikz} e^{-\omega t}$$

with states

$$\psi_i(\mathbf{x}) = \left(\frac{m\omega_0}{\pi\hbar} \right)^{3/4} e^{-m\omega_0 r^2/2\hbar} \qquad \psi_f(\mathbf{x}) = \frac{1}{(2\pi\hbar)^{3/2}} e^{i\mathbf{k}_f \cdot \mathbf{x}}$$

The matrix element is

$$\langle f | H' | i \rangle = \frac{|e| \mathbf{A}_0 \cdot \mathbf{p}_f}{2mc} \frac{1}{(2\pi\hbar)^{3/2}} \left(\frac{m\omega_0}{\pi\hbar} \right)^{3/4} \int e^{i\mathbf{q}\cdot\mathbf{x}} e^{-m\omega^0 r^2/2\hbar} d^3 x$$

$$= (\mathbf{A}_0 \cdot \hbar\mathbf{k}_f) \frac{|e|}{2mc} \left(\frac{m\omega_0}{\pi\hbar} \right)^{3/4} \frac{e^{-q^2\hbar/(2m\omega_0)}}{(m\omega_0)^{3/2}}$$

where $\mathbf{q} = \mathbf{k}_f - k\hat{z}$. Thus by using Fermi's golden rule, we get the transition rate

$$\Gamma_{i \to f} = \frac{2\pi}{\hbar} (\mathbf{A}_0 \cdot \mathbf{p}_f)^2 \frac{e^2}{4m^2 c^2} \frac{e^{-q^2\hbar/(m\omega_0)}}{(\pi\hbar m\omega_0)^{3/2}} \delta(p_f^2/2m - E_i - \hbar\omega)$$

$$\therefore \frac{d\Gamma}{d\Omega} = \int_0^\infty \Gamma_{i \to p_f} p_f^2 dp_f = \frac{2\pi p_f}{\hbar} (\mathbf{A}_0 \cdot \mathbf{p}_f)^2 \frac{e^2}{4mc^2} \frac{e^{-q^2\hbar/(m\omega_0)}}{(\pi\hbar m\omega_0)^{3/2}}$$

The differential cross section is given by

$$\frac{d\sigma}{d\Omega} = \frac{\hbar\omega}{F} \frac{d\Gamma}{d\Omega} = \frac{8\pi\hbar\omega}{A_0^2 \omega^2} \frac{d\Gamma}{d\Omega}$$

This can be evaluated using the fact

$$\mathbf{A}_0 \cdot \mathbf{p}_f = \hbar A_0 k_f \sin\theta \cos\phi$$

and simplified to get

$$\frac{d\sigma}{d\Omega} = \frac{4\alpha\hbar^2 k_f^3}{m^2 \omega\omega_0} \sqrt{\frac{\pi\hbar}{m\omega_0}} \exp\left[-\frac{\hbar}{m\omega_0} \left(k_f^2 + (\omega/c)^2 \right) \right] \sin^2\theta \cos^2\phi \exp\left[\left(\frac{2\hbar k_f \omega}{m\omega_0 c} \right) \cos\theta \right]$$

7.6   The Interaction Picture

We've already discussed two pictures already:

1. The Schrodinger picture: State kets evolve over time according to the Schrodinger equation, operators with no explicit time dependence are fixed

2. The Heisenberg picture: State kets are fixed in time and operators evolve according to the Heisenberg equations of motion

The third picture, the interaction picture, is useful when the Hamiltonian in the Schrodinger equation has the form

$$H(t) = H_0 + H'(t)$$

The states and operators are given by

$$|\psi_I(t)\rangle = U_S^{0\dagger}(t, t_0) |\psi_S(t)\rangle$$

$$A_i = U_S^{0\dagger} A_S U_S^0$$

where the time evolution operator is

$$U_S^0(t, t_0) = \exp\left(-\frac{iH_0(t - t_0)}{\hbar}\right)$$

The time evolution of kets in the interaction picture is given by

$$
\begin{aligned}
i\hbar \frac{d}{dt} |\psi_I(t)\rangle &= i\hbar \left(\frac{d}{dt} U_S^{0\dagger}\right) |\psi_S(t)\rangle + U_S^{0\dagger} i\hbar \frac{d}{dt} |\psi_S(t)\rangle \\
&= \left(-U_S^{0\dagger} H_0 + U_S^{0\dagger}(H_0 + H')\right) |\psi_S(t)\rangle \\
&= U_S^{0\dagger} H' |\psi_S(t)\rangle \\
&= U_S^{0\dagger} H' U_S^0 U_S^{0\dagger} |\psi_S(t)\rangle = H_I' |\psi_I\rangle
\end{aligned}
$$

We can define U_I by

$$|\psi_I(t)\rangle = U_I(t, t_0) |\psi_I(t_0)\rangle$$

and write

$$H_I' U_I(t, t_0) = i\hbar \frac{\partial}{\partial t} U_I(t, t_0)$$

Given U_I, it is possible to recover U_S with

$$|\psi_I(t)\rangle = U_I(t, t_0) |\psi_I(t_0)\rangle = U_I |\psi_S(t_0)\rangle$$

$$|\psi_I(t)\rangle = U_S^{0\dagger}(t, t_0) |\psi_S(t)\rangle = U_S^{0\dagger}(t, t_0) U_S(t, t_0) |\psi_S(t_0)\rangle$$

so that

$$U_S(t, t_0) = U_S^0(t, t_0) U_I(t, t_0)$$

We can then compute U_I subject to the boundary condition $U_I(t_0, t_0) = 1$. It's best to write interaction picture evolution as

$$U_I(t, t_0) = \mathbb{1} + \frac{1}{i\hbar} \int_0^t H_I'(t') U_I(t', t_0) dt'$$

If H' is a small perturbation, then we can expand U_I and solve this iteratively

$$U_I(t, t_0) = \mathcal{T} \exp\left[\frac{1}{i\hbar} \int_{t_0}^{t} H_I(t')dt'\right]$$

where the time ordering operator is

$$\mathcal{T}(H'_I(t_1)H'_I(t_2)\cdots H'_I(t_N)) = H'_I(t_N)\cdots H'_I(t_1) \qquad t_N > t_{N-1} > \cdots > t_1$$

8 Identical Particles

8.1 Symmetric States

So far we've assumes particles are distinguishable, in particular if we have two particles

$$|a\rangle \otimes |b\rangle = |ab\rangle \qquad |ab\rangle \neq |ba\rangle$$

But if the particles are identical, then $|ab\rangle$ and $|ba\rangle$ actually describe the same quantum state. In this case, we say that the Hamiltonian which describes these particles have permutation symmetry and its states will have exchange/permutation degeneracy.

Since H respects permutation symmetry, we can define the exchange operator

$$P_{12} |a\rangle |b\rangle = |b\rangle |a\rangle$$

so that $[H, P_{12}] = 0$, thus we can consider simultaneous eigenstates. Note that

$$P_{12} = P_{21} \qquad P_{12}^2 = \mathbb{1}$$

Example. As an example, suppose the labels a, b correspond to positions for two identical particles.

$$X_1 |a\rangle |b\rangle = a |a\rangle |b\rangle \qquad X_2 |a\rangle |b\rangle = b |a\rangle |b\rangle$$

Note that

$$P_{12} X_1 |a\rangle |b\rangle = P_{12} X_1 P_{12}^2 |a\rangle |b\rangle = P_{12} X_1 P_{12} |b\rangle |a\rangle$$

$$P_{12} X_1 |a\rangle |b\rangle = a P_{12} |a\rangle |b\rangle = a |b\rangle |a\rangle = X_2 |b\rangle |a\rangle$$

which gives a relationship between $X_{1,2}$ and the permutation operator

$$P_{12} X_{1,2} P_{12} = X_{2,1}$$

If $P_{12} H P_{12} = H$, then H respects permutation symmetry and the eigenstates of H can be labeled by the eigenstates of P_{12}. Since $P_{12}^2 = 1$ the eigenvalues are $\lambda = \pm 1$ and the eigenstates can easily be found by diagonalizing

$$P_{12} |\lambda_\pm\rangle = \pm |\lambda_\pm\rangle \qquad |\lambda_\pm\rangle = \frac{|a\rangle |b\rangle \pm |b\rangle |a\rangle}{\sqrt{2}}$$

These states can be labeled as either symmetric or antisymmetric based on how the permutation operator acts on them

$$P_{12} |ab\rangle_S = |ab\rangle_S \longrightarrow |ab\rangle_S = |\lambda_+\rangle = \frac{|a\rangle |b\rangle + |b\rangle |a\rangle}{\sqrt{2}}$$

$$P_{12} |ab\rangle_A = - |ab\rangle_A \longrightarrow |ab\rangle_A = |\lambda_-\rangle = \frac{|a\rangle |b\rangle - |b\rangle |a\rangle}{\sqrt{2}}$$

For a two state system, all states are either symmetric or antisymmetric but for a normal system we cannot do not know which combination to take. The rule of which state to use is given by the spin-statistics theorem which we take to be a postulate in (non-relativistic) quantum mechanics but can be proved in relativistic quantum field theory.

The selection rule is:

- For integer spins (bosons), the state is symmetric

- For half integer spins (fermions), the state is antisymmetric

The theorem could also be used for composite particles by considering the total spin. If the total spins is an integer (half integer), then the particle is bosonic (fermionic) and its state is symmetric (antisymmetric).

For the two particle case it is useful to factorize the state so that space and spin are separated

$$|\psi\rangle = |\psi_{space}\rangle \otimes |\psi_{spin}\rangle$$

We can use either $|m_1 m_2\rangle$ or $|s m_s\rangle$ as the basis for the spin state but the latter basis is usually better since it's already and eigenstate of the permutation operator. This only works on two particles because if there were any more then the set of symmetric/antisymmetric states are not enough to specify the basis due to the presence of mixed symmetry.

Example. Suppose we have two spin $1/2$ particles. Following the suggestion above, we factorize the states so that space and spin are separate. P_{12} acts on the position part by swapping position coordinates, while for the spins it swaps the spin states. This can be represented with

$$P_{12}^{spin} = \frac{1}{2}(\mathbb{1} + \sigma_1 \cdot \sigma_2) = \frac{1}{2}\left(\mathbb{1} + \frac{4\mathbf{S}_1 \cdot \mathbf{S}_2}{\hbar^2}\right)$$

We see that the $|1 m_s\rangle$ states will be symmetrical while $|0 0\rangle$ is antisymmetrical. This is further verified by rewriting them in the $|m_1 m_2\rangle$ basis and explicitly swapping the spin states. Thus the two particle states are linear combinations of

$$|\psi\rangle = \begin{cases} |\psi_{space}\rangle \otimes |0\,0\rangle_A & \text{(triplet)} \\ |\psi_{space}\rangle \otimes |1\,m_s\rangle_S & \text{(singlet)} \end{cases}$$

Suppose the particles are in an infinite well

$$|\psi_{space}\rangle = \begin{cases} \frac{1}{\sqrt{a}}\cos\left(\frac{n\pi x}{2a}\right) & n = 1, 3, 5, \ldots \\ \frac{1}{\sqrt{a}}\sin\left(\frac{n\pi x}{2a}\right) & n = 2, 4, 6, \ldots \end{cases}$$

$$E_n = \frac{\pi^2 \hbar^2 n^2}{8ma^2} = E_0 n^2$$

with a spin interaction

$$\lambda \mathbf{S}_1 \cdot \mathbf{S}_2 |s m_s\rangle = \begin{cases} \frac{\lambda \hbar^2}{4} |1\,m_s\rangle \\ -\frac{3\lambda \hbar^2}{4} |0\,0\rangle \end{cases}$$

Which means the states can be represented with the basis

$$|\psi\rangle = |n_1\,n_2\rangle \otimes |s\,m_s\rangle$$

Since we are working with fermions (spin $1/2$), the total state must be antisymmetric. Thus if the spatial state is antisymmetric then the spin state is symmetric and vice versa. There are two categories of state

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- For a symmetric spatial state and antisymmetric spin state there is no degeneracy

$$|1\,1\rangle_S \otimes |0\,0\rangle_A \qquad E = 2E_0 - \frac{3\lambda\hbar^2}{4}$$

$$|1\,2\rangle_S \otimes |0\,0\rangle_A \qquad E = 5E_0 - \frac{3\lambda\hbar^2}{4}$$

$$|2\,2\rangle_S \otimes |0\,0\rangle_A \qquad E = 8E_0 - \frac{3\lambda\hbar^2}{4}$$

$$\vdots$$

- For an antisymmetric spatial state and symmetric spin state there will be 3-fold symmetry (due to the triplet spin state)

$$|1\,2\rangle_A \otimes |1\,m_s\rangle_S \qquad E = 5E_0 - \frac{\lambda\hbar^2}{4}$$

$$|2\,3\rangle_A \otimes |1\,m_s\rangle_S \qquad E = 13E_0 - \frac{\lambda\hbar^2}{4}$$

$$|1\,4\rangle_A \otimes |1\,m_s\rangle_S \qquad E = 17E_0 - \frac{\lambda\hbar^2}{4}$$

$$|3\,4\rangle_A \otimes |1\,m_s\rangle_S \qquad E = 25E_0 - \frac{\lambda\hbar^2}{4}$$

$$\vdots$$

Actually normalizing these states gets difficult due to various "nuisance factors" that may arise. First we deal with just two particles, suppose there's some operator

$$\Omega\,|\omega_i\rangle = \omega_i\,|\omega_i\rangle$$

and we construct some two particle states

$$|\omega_1\omega_2\rangle = |\omega_1\rangle \otimes |\omega_2\rangle = |\omega_1\rangle\,|\omega_2\rangle$$

with the wavefunctions

$$\langle a|\omega\rangle = \psi_\omega(a) \qquad \langle ab|\omega_1\omega_2\rangle = \psi_{\omega_1}(a)\psi_{\omega_2}(b)$$

The symmetric and antisymmetric linear combinations are

$$|\omega_1\omega_2\rangle_S = c_S(|\omega_1\omega_2\rangle + |\omega_2\omega_1\rangle) \qquad |\omega_1\omega_2\rangle_A = c_A(|\omega_1\omega_2\rangle - |\omega_2\omega_1\rangle)$$

We need both states to be normalized, furthermore $_S\langle\psi|\psi\rangle_A = 0$ for $\omega_1 \neq \omega_2$. This gives $c_S = c_A = 1/\sqrt{2}$ and

$$_S\langle\omega_1'\omega_2'|\,|\omega_1\omega_2\rangle_S = \delta_{\omega_1'\omega_1}\delta_{\omega_2'\omega_2} + \delta_{\omega_1'\omega_2}\delta_{\omega_2'\omega_1}$$

$$_A\langle\omega_1'\omega_2'|\,|\omega_1\omega_2\rangle_A = \delta_{\omega_1'\omega_1}\delta_{\omega_2'\omega_2} + \delta_{\omega_1'\omega_2}\delta_{\omega_2'\omega_1}$$

For the symmetric case it's also possible that we have $\omega_1 = \omega_2 = \omega$, in which case the normalized state is just
$$|\omega\omega\rangle_S = |\omega\omega\rangle$$
If we measure Ω on a state $|\psi\rangle_S$, the probability of finding a state in $|\omega_1\omega_2\rangle_S$ is
$$P_S(\omega_1, \omega_2) = |\,_S\langle\omega_1\omega_2|\psi\rangle_S|^2$$
and similarly for the antisymmetric case
$$P_A(\omega_1, \omega_2) = |\,_A\langle\omega_1\omega_2|\psi\rangle_A|^2$$
Normalization requires that the probabilities over all physically distinct states sum to unity
$$_S\langle\psi|\psi\rangle_S = \frac{1}{2}\sum_{\omega_1\neq\omega_2}\sum_{\omega_2}P_S(\omega_1,\omega_2) + \sum_{\omega}P_S(\omega,\omega) = 1$$
$$_A\langle\psi|\psi\rangle_A = \frac{1}{2}\sum_{\omega_1\neq\omega_2}\sum_{\omega_2}P_A(\omega_1,\omega_2) = 1$$
If we consider the position wavefunctions, they are defined
$$\begin{aligned}\psi_{S,A}(x_1, x_2) &= \frac{1}{\sqrt{2}}\,_{S,A}\langle x_1 x_2|\omega_1\omega_2\rangle_{S,A}\\ &= \frac{1}{2}(\psi_{\omega_1}(x_1)\psi_{\omega_2}(x_2) \pm \psi_{\omega_2}(x_1)\psi_{\omega_1}(x_2))\\ &= \frac{1}{\sqrt{2}}\begin{vmatrix}\psi_{\omega_1}(x_1) & \psi_{\omega_2}(x_1)\\ \psi_{\omega_1}(x_2) & \psi_{\omega_2}(x_2)\end{vmatrix}_{\pm}\end{aligned}$$
The last expression is known as the Slater determinant, the label indicates that signs are positive for the symmetric case and given by the normal determinant for the antisymmetric case.

The additional $1/\sqrt{2}$ factor suggests that the probability density should instead be defined
$$P_{S,A}(x_1, x_2) = 2|\psi_{S,A}(x_1, x_2)|^2$$
so the normalization is
$$\int dx_1 dx_2|\psi_{S,A}(x_1, x_2)|^2 = \frac{1}{2}\int dx_1 dx_2 P_{S,A}(x_1, x_2) = 1$$
If the x_1, x_2 are far apart and ψ_{ω_1} is nonzero only in a small neighborhood about x_1 that does not include x_2 (and vice versa for ψ_{ω_2} about x_2), then the probability density is simplified
$$P_{S,A}(x_1, x_2) = |\psi_{\omega_1}(x_1)|^2|\psi_{\omega_2}(x_2)|^2$$
which is just the distinguishable particle case. In other words, the effects of exchange symmetry is only nonzero for overlapping spatial wavefunctions.

Now we consider a more complicated scenario, the case of three identical particles. If the three states $\omega_1, \omega_2, \omega_3$ are all distinct, the symmetric state is

$$|\omega_1\omega_2\omega_3\rangle_S = \sum_{\text{permutations}} \frac{1}{\sqrt{3!}}|\omega_1\omega_2\omega_3\rangle$$

$$= \frac{1}{\sqrt{6}}(|123\rangle + |132\rangle + |213\rangle + |231\rangle + |312\rangle + |321\rangle)$$

where the ω was dropped to simplicity.

If two of the three ω_i are equal, then

$$|\omega_1\omega_1\omega_2\rangle_S = \frac{1}{\sqrt{3}}(|\omega_1\omega_1\omega_2\rangle + |\omega_1\omega_2\omega_1\rangle + |\omega_2\omega_1\omega_1\rangle)$$

and if all three are equal, then as with before we have

$$|\omega\omega\omega\rangle_S = |\omega\omega\omega\rangle$$

There is only one antisymmetric state, given by

$$|\omega_1\omega_2\omega_3\rangle_A = \frac{1}{\sqrt{3!}}(|123\rangle + |231\rangle + |312\rangle - |132\rangle - |213\rangle - |321\rangle)$$

As usual the wavefunctions are

$$\psi_{S,A}(x_1, x_2, x_3) = \frac{1}{\sqrt{3!}}\,_{S,A}\langle x_1 x_2 x_3|\psi\rangle_{S,A}$$

with probability densities

$$P_{S,A} = 3!|\psi_{S,A}(x_1, x_2, x_3)|^2$$

and thus the normalization condition is

$$\int dx_1 dx_2 dx_3 |\psi_{S,A}|^2 = \frac{1}{3!}\int dx_1 dx_2 dx_3 P_{S,A} = 1$$

The spatial wavefunctions can be written with the Slater determinant as

$$\psi_{S,A} = \frac{1}{\sqrt{3!}}\begin{vmatrix} \psi_{\omega_1}(x_1) & \psi_{\omega_2}(x_1) & \psi_{\omega_3}(x_1) \\ \psi_{\omega_1}(x_2) & \psi_{\omega_2}(x_2) & \psi_{\omega_3}(x_2) \\ \psi_{\omega_1}(x_3) & \psi_{\omega_2}(x_3) & \psi_{\omega_3}(x_3) \end{vmatrix}$$

In general, for N particles the spatial wavefunctions are

$$\psi_{S,A}(x_1, \ldots, x_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_{\omega_1}(x_1) & \cdots & \psi_{\omega_N}(x_1) \\ \vdots & & \vdots \\ \psi_{\omega_1}(x_N) & \cdots & \psi_{\omega_N}(x_N) \end{vmatrix}_{\pm}$$

This can be modified to include both space and spin labels

$$\psi_{S,A}(x_1\, m_1, \ldots, x_N\, m_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_{\omega_1}(x_1\, m_1) & \cdots & \psi_{\omega_N}(x_1\, m_1) \\ \vdots & & \vdots \\ \psi_{\omega_1}(x_N\, m_N) & \cdots & \psi_{\omega_N}(x_N\, m_N) \end{vmatrix}_{\pm}$$

where $\psi_{\omega_i}(x_i\, m_i) = \langle x_i\, m_i|\omega_i\rangle$

8.2 Multi-electron Atoms

Since there's obviously no way to distinguish between different electrons of an atom, to discuss atoms with more electrons than hydrogen we must use methods introduced in this chapter. First we discuss the next case up: helium.

We will neglect all spin interactions and consider spin only as a counting tool, to first order

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}} = H_{0_1} + H_{0_2} + \frac{e^2}{r_{12}}$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ and the last term is the Coulomb repulsion term. Due to the presence of that term, the Schrodinger equation is not solvable exactly, instead we must approximate. We will consider three successive levels of approximation.

1) The most naive: ignore the repulsion term.

The energy levels if we ignore the Coulomb repulsion is simple

$$E_{n_1,n_2} = -4R_y \left(\frac{1}{n_1^2} + \frac{1}{n_2^2} \right)$$

giving us a ground state of energy

$$E_{11} \approx -8R_y$$

The observed ground level energy for helium is actually $-5.8R_y$, so this is a terrible approximation. Note that the naive estimate is actually lower than the observed value, thus the repulsion term will raise the energy levels of the state.

2) Take screening into account (crudely)

For a $n_1 = 1, n_2 = 2$ state, the $n = 1$ electron will have $Z = 2$ as usual but the $n = 2$ state will actually have $Z = 1$ because it is "further" from the nucleus and thus screened by the other electron. This gives a value of

$$E_{12} \approx -4.25R_y$$

which is actually decently close to experimental results, but we can't arrive at the ground level using this approach.

3) Variational method with Fermi statistics

Let the trial wavefunction by

$$\psi_{Z_{eff}} = Ce^{-Z_{eff}(r_1+r_2)/a_0}$$

where Z_{eff} is the variational parameter. The functional is

$$E[Z_{eff}] = \frac{\langle \psi_{Z_{eff}} | H | \psi_{Z_{eff}} \rangle}{\langle \psi_{Z_{eff}} | \psi_{Z_{eff}} \rangle} = -2R_y \left(4Z_{eff} - Z_{eff}^2 - \frac{5}{8}Z_{eff} \right)$$

Thus at the minimal value of this function, we have

$$Z_{eff} = 2 - \frac{5}{16} < 2 \qquad E[Z_{eff}] \approx -5.7R_y$$

Note that the effective atomic number is less than the actual atomic number. The ground level energy computed within this approach is only about 1.7% higher than experiment.

Now for the $n_1 = 1, n_2 = 2$ states, which there are many of since we can have $\ell_2 = 0, 1$ and $S = 0, 1$ (S being the total spin). The $1s, 2s$ states ($\ell_1 = \ell_2 = 0$) with $S = 0$ are just radial excitations of the ground state so the variational method isn't particularly useful. Instead we consider the $1s, 2p$ ($\ell_1 = 0, \ell_2 = 1$) states, which can have $S = 0$ or $S = 1$. These states can be more easily labeled with spectroscopic notation, in particular we have for this configuration the two states (for the $n = 2$ electron)

$$2^1P: \qquad S = 0, \ell = 1 \text{ with a symmetric spatial state}$$
$$2^3P: \qquad S = 1, \ell = 1 \text{ with an antisymmetric spatial state}$$

In general a quantum state is labeled as

$$N^{2S+1}L_J$$

where N is the principal quantum number ($n_2 = 2$ in our case), S is the spin quantum number (resulting in $2S+1$ total spin states), L refers to ℓ and is written with the orbital letter $S, P, D, F, \ldots$ for $\ell = 0, 1, 2, 3, \ldots$. Finally, J is the total angular momentum and has the range $J = L + S, L + S - 1, \ldots, |L - S|$ (this should look familiar).

This notation is particularly common in atomic physics. [5] We'll take the following variational states for the two electrons

$$1s: \qquad u(\mathbf{x}) = \frac{1}{\sqrt{\pi}} \left(\frac{\alpha}{a_0} \right)^{3/2} e^{-\alpha r/a_0}$$

$$2p: \qquad v_{m_\ell}(\mathbf{x}) = \frac{\sqrt{6}}{12} \left(\frac{\beta}{a_0} \right)^{3/2} e^{-\beta r/2a_0} Y_{1,m_\ell}(\theta, \phi)$$

where α, β are the variational parameters. Thus the two particle states are

$$|+\rangle = \psi(2^3P, m_\ell) = \frac{1}{\sqrt{2}} \left[u(\mathbf{x}_1)v_{m_\ell}(\mathbf{x}_2) + v_{m_\ell}(\mathbf{x}_1)u(\mathbf{x}_2) \right] \otimes |0\,0\rangle_A$$

$$|-\rangle = \psi(2^3P, m_\ell) = \frac{1}{\sqrt{2}} \left[u(\mathbf{x}_1)v_{m_\ell}(\mathbf{x}_2) - v_{m_\ell}(\mathbf{x}_1)u(\mathbf{x}_2) \right] \otimes |1\,m_s\rangle_S$$

There are 3 2^1P states (for the 3 choices of m_ℓ) and 9 2^3P states (3 choices for m_ℓ plus 3 choices for spin). Since H is independent of spin and furthermore rotationally invariant, we can set $m_s = m_\ell = 0$ without loss of generality.

---

[5]Spectroscopic notation was never actually explained in class for me and was really confusing. I found Gottfried and Yan Chapter 6.1 along with this link to be pretty helpful.

The matrix element can be written

$$\langle H \rangle_{\pm} = \langle \pm | \, H \, | \pm \rangle = f(\alpha) + g(\beta) + I(\alpha, \beta) \pm J(\alpha, \beta)$$

where we've separated the matrix element into multiple parts:

- The nonperturbed matrix elements

$$f(\alpha) = \langle H_{0_1} \rangle = \int d^3 x \, u^*(\mathbf{x}) H_{0_1} u(\mathbf{x})$$

$$g(\beta) = \langle H_{0_2} \rangle = \int d^3 x \, v_0^*(\mathbf{x}) H_{0_2} v_0(\mathbf{x})$$

- The direct integral

$$I(\alpha, \beta) = \int d^3 x_1 d^3 x_2 \frac{e^2}{r_{12}} |u(\mathbf{x}_1) v_0(\mathbf{x}_2)|^2$$

- The exchange integral

$$J(\alpha, \beta) = \int d^3 x_1 d^3 x_2 \frac{e^2}{r_{12}} u^*(\mathbf{x}_1) v_0^*(\mathbf{x}_2) u(\mathbf{x}_2) v_0(\mathbf{x}_1)$$

The J integral was first discovered by Heisenberg and has no classical analogue, it is purely due to quantum statistics. The elements can all be computed using

$$\frac{1}{r_{12}} = \sum_{\ell, m_\ell} \frac{4\pi}{2\ell + 1} \frac{r_<^\ell}{r_>^{\ell+1}} Y_{\ell, m_\ell}^*(\hat{r}_1) Y_{\ell, m_\ell}(\hat{r}_2)$$

to evaluate the angular part where $r_<, r_>$ denote the lesser/greater of r_1, r_2. This results in

$$J(\alpha, \beta) > 0 \quad \longrightarrow \quad E(2^1 P) > E(2^3 P)$$

Since $2^1 P$ can be interpreted as the spins (of the two electrons) being antiparallel as opposed to the parallel spins of $2^3 P$, we conclude that the spins states have an effect on the energy despite H having no spin dependence. This is an example of Hund's rule, where higher spins states will have lower energy since antisymmetric spatial states imply that the electrons are further apart leading to less Coulomb repulsion. We find

$$
\begin{aligned}
2^1 P : & \quad \alpha = 2.003 \quad \beta = 0.965 \\
2^3 P : & \quad \alpha = 1.99 \quad \beta = 1.09
\end{aligned}
$$

with an energy difference of about 0.23 eV.

Now let's turn to the general case for an aton with N electrons and Z protons ($N = Z$ for a neutral atom and $N \neq Z$ for ions). For $N > 2$, it's better to use "effective" potentials rather than the full Hamiltonian (below)

$$H = \sum_{i=1}^{N} \left(-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{r_i} \right) + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{e^2}{r_{ij}}$$

There are many ways to replace the Coulomb repulsion terms with an effective potential, one way is the self-consistent central field approximation

$$V_i(\mathbf{x}_i) = -\frac{Ze^2}{r_i} + V_{eff}(\mathbf{x}_i)$$

Electron configurations are given by n for shells and ℓ for subshells (remember high school chemistry?), for instance

$$1s, \quad 2s, 2p, \quad 3s, 3p, 3d, \quad \ldots$$

Closed shells are necessarily singlet states but for configurations with valence electrons it is possible to have many distributions and thus many Slater determinants. We call valence electrons equivalent electrons if they have the same n, ℓ and they must obey the Pauli exclusion principle (thus antisymmetrical).

We've seen from studying the helium atom that the Coulomb repulsion term acts to align spin momenta. If it dominates, then the spin and orbital angular momenta will align for the lowest energy state, with

$$\mathbf{S} = \sum_i \mathbf{S}_i \qquad \mathbf{L} = \sum \mathbf{L}_i$$

and the total angular momentum is $\mathbf{J} = \mathbf{L} + \mathbf{S}$. This is called the Russell-Saunders (or LS) coupling scheme and applies for light atoms.

For heavier atoms where the spin-orbit coupling dominates over the Coulomb repulsion term, then the $\mathbf{L}_i$ and $\mathbf{S}_i$ individually couple to form $\mathbf{J}_i$ and instead the total angular momentum is $\mathbf{J} = \sum \mathbf{J}_i/$ This is the jj coupling scheme for heavy atoms.

For the LS coupling scheme, Hund's rules apply:

- For a given configuration, a higher S corresponds to lower energy

- For a given S (within it's multiplet), a larger L corresponds to lower energy

- For a given S, J, a lower J corresponds to:

    - Lower energy if the outermost shell is half or less filled
    - Higher energy if the outermost shell is more than half filled

---

For light atoms, ground states can be determined by looking at how the electrons fill the shells (according to the Pauli exclusion principle). Each shell is labeled by the principal quantum number n and the number of subshells given by $n - \ell - 1$ (so that $\ell = 0, \ldots, n - 1$). The subshells fill in increasing order with some exceptions (remember high school chemistry?).

Example. For instance in carbon ($N = Z = 6$), there are two equivalent outer electrons. There are 15 possible states, labeled

$$^1S_0 \quad ^3P_0, ^3P_1, ^3P_2, \quad ^1D_2$$

Using Hund's rules, we can identify $^3P_0$ as the ground state (outer shell half filled).

When we consider transitions between levels, previous discussions from symmetry tell us that $\Delta \ell = \pm 1$ and Δn can be anything. We can also discuss rules for S, L, J. From rotational invariance, we have that $\Delta J = 0, \pm 1$ though $0 \to 0$ is prohibited. For light atoms (LS coupling applies), we have $\Delta S = 0$ since the dipole operator is spin independent and thus $\Delta L = 0, \pm 1$ (again $0 \to 0$ is prohibited). For heavier atoms it is possible for transitions to have $\Delta S \neq 0$ since spin-orbit terms dominate.

To summarize the selection rules:

- $\Delta \ell = \pm 1$

- Δn can be anything

- $\Delta J = 0, \pm 1$, but we can't have $0 \to 0$

- For light atoms

  - $\Delta S = 0$

  - $\Delta L = 0, \pm 1$, but we can't have $0 \to 0$

- For heavy atoms, anything is possible (follow your dreams!)

Example. Suppose that the electron is actually a spin $3/2$ particle obeying Fermi-Dirac statistics (obeys the Pauli exclusion principle). Consider a hypothetical neon atom ($Z = 10$) made up of these electrons. We want to write down the electron configuration and identify a ground state.

The number of total spin states is $2S + 1 = 4$ for spin $3/2$ electrons, so the configuration is

$$1s^4 2s^4 2p^2$$

indicating that there are two electrons to concern ourselves with. The $2p$ subshell can hold $2\ell + 1 = 3$ electron, each with 4 possible spin states. Thus there are

$$\binom{12}{2} = \frac{12!}{2!10!} = 66$$

possible state, a highly degenerate configuration. We can choose from $L = 0, 1, 2$ and $S = 0, 1, 2, 3$ with $S = 0, 2$, $L = 1$ being the antisymmetric spin/spatial states and $S = 1, 3$, $L = 0, 2$ being the symmetric spin/spatial states. For half integer spin we require an overall antisymmetric state, so the possible states are

$$^1S_J, {}^5S_J, \quad {}^4P_J, {}^7P_J, \quad {}^5D_J, {}^5D_J$$

We see that the lower energy will be the ^7P_J states where $J = 2, 3, 4$. Thus the ground state is given by $^7P_2$, since the outermost shell is less than half filled.

9 Scattering Theory

9.1 The Lippmann-Schwinger Equation

The best way to understand particles is to smash them into each other. In fact, this is so useful that we've spent billions constructing large rings that allow us to smash things together better, faster, and stronger. In the immortal words of Jun J. Sakurai: "it is impossible to overemphasize the importance of this subject." Since this is not a particle physics course, we will only deal with simple scenarios.

First the simplest formalism: a spinless particle elastically collides with (scatters off) a structureless "invisible" target (a localized potential V). This is a good approximation for scattering a light particle off of a heavier one or for two-body collisions in the center of mass (CM) frame. The geometrical picture for how this is setup is below
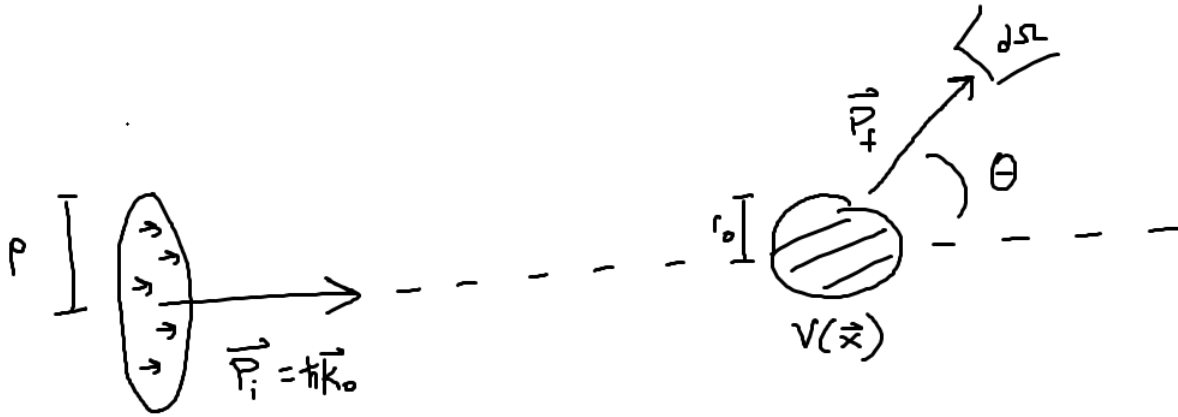
The incident particle initially propagates in the $\hat{z}$ direction and is scattering by the potential into a detector. The detector covers a solid angle $d\Omega$ which can be characterized by (θ, ϕ) where θ is (as usual) the angle from the z axis and ϕ is the azimuthal. We now also consider a beam of such particles distributed uniformly over ρ (a vector) perpendicular to the propagation direction $\hat{z}$ (imagine a flashlight of radius ρ shining in the $\hat{z}$ direction). Suppose the potential is localized to some range r_0 and that $\rho \gg r_0$.

Since the collision is elastic, we have

$$|\mathbf{p}_i| = |\mathbf{p}_f| \longrightarrow \hbar|\mathbf{k}_i| = \hbar|\mathbf{k}_f| = \hbar k$$

where

$$\mathbf{k}_i = k\hat{z} \qquad \mathbf{k}_f = k\hat{r}$$

and thus there is no change in the energy E.

A quantity of interest is the differential cross section, defined

$$\frac{d\sigma(k,\theta,\phi)}{d\Omega}d\Omega = \frac{\text{\# of particles scattered into } d\Omega \text{ per unit time}}{\text{\# of incoming particles per area per unit time}}$$

The total cross section then can also be defined

$$\sigma(k) = \int \frac{d\sigma}{d\Omega}d\Omega = \frac{\text{\# of scattered}}{\text{incident flux}}$$

and note that both quantities are proportional to area.

Calculating the differential cross section is best done using wavepackets. We take an initial wavepacket with mean momentum $\langle \mathbf{p} \rangle = \hbar \mathbf{k}_0$ and mean impact parameter $\langle \rho \rangle$ and expand in terms of continuum eigenstates

$$\psi_k = \psi_{inc} + \psi_{sc}$$

where ψ_{inc} is the incident (incoming) wave $e^{i\mathbf{k}\cdot\mathbf{x}} = e^{ik_0 z}$ and ψ_{sc} is a (purely outgoing) scattered wave. We then propagate this over time, identify the scattered wave as $t \to \infty$, and calculate its current density.

Note that we can integrate the probability current over a solid angle $d\Omega$ to get the probability that the incident particle goes into the detector. In particular, for our incident wave packet, this probability depends only on the initial momentum $\hbar \mathbf{k}_0$ (and thus just $\mathbf{k}_0$) and the mean impact parameter $\langle \rho \rangle$. Thus we can denote the probability as $\text{Prob}(\rho, \mathbf{k}_0 \to d\Omega)$. If we take a beam of $\eta(\rho)$ particles (per second) per unit area in the ρ plane, then the number of particles going into the detector is

$$\eta(d\Omega) = \int \text{Prob}(\rho, \mathbf{k}_0 \to d\Omega)d^2\rho$$

Since $\eta(\rho) = \eta$ is a constant, we can write down the differential cross section

$$\frac{d\sigma}{d\Omega}d\Omega = \frac{\eta(d\Omega)}{\eta} = \int \text{Prob}(\rho, \mathbf{k}_0 \to d\Omega)d^2\rho$$

Recall that in the 1D case, for sufficiently localized momentum packets we can use a time-independent approach by just taking one eigenstate

$$\psi_k(x) = \theta(-x)(Ae^{ikx} + Be^{-ikx}) + \theta(x)Ce^{ikx}$$

and identifying the transmission/reflection coefficients as just ratios of our probability currents

$$R = \left|\frac{B}{A}\right|^2 = \left|\frac{j_R}{j_I}\right| \qquad T = \left|\frac{C}{A}\right|^2 = \left|\frac{j_T}{j_I}\right|$$

A similar approach works in the 3D case as we take $\mathbf{x} \to \infty$, the differential cross section can be computed as

$$\frac{d\sigma}{d\Omega}d\Omega = \frac{\text{(prob. current density of scattered wave)} \cdot \text{(area of detector)}}{\text{prob. current density of incident wave}} = \frac{|\mathbf{j}_{sc}|r^2 d\Omega}{|\mathbf{j}_{inc}|}$$

Using this time-independent approach, the eigenstates of the Hamiltonian take the form

$$\psi_{\mathbf{k}}(\mathbf{x}) = \psi_{inc} + \psi_{sc} = e^{i\mathbf{k}_i \cdot \mathbf{x}} + \psi_{sc} = e^{ikz} + \psi_{sc}(r, \theta, \phi)$$

where we set $\mathbf{k}_i = k\hat{z}$ (incident beam in $\hat{z}$ direction). The form of the scattered wave ψ_{sc} depends on the details of the potential we are scattering off of. For now we assume that $r \to \infty$ gives a outgoing free particle solution (so V must be localized) which implies the condition

$$\lim_{r \to \infty} rV(r) = 0$$

In particular, the potential cannot be Coulomb. If this condition holds, then we can say that the particle is sufficiently localized and thus the scattered wave at $r \to \infty$ will satisfy the free particle equation

$$(\nabla^2 + k^2)\psi_{sc} = 0$$

which has the general solution (recall the angular momentum chapter)

$$\psi_{sc}(r \to \infty) \to \sum_{\ell,m}(A_\ell j_\ell(kr) + B_\ell n_\ell(kr))Y_{\ell,m}(\theta, \phi)$$

where j_ℓ, n_ℓ are the spherical Bessel and Neumann functions respectively. Since this is asymptotic behavior ($r \to \infty$), we can take asymptotic forms

$$j_\ell(kr) \to \frac{\sin(kr - \ell\pi/2)}{kr} \qquad n_\ell(kr) \to -\frac{\cos(kr - \ell\pi/2)}{kr}$$

An outgoing spherical wave we have the form e^{ikr}/r, for our solution to match we need $A_\ell/B_\ell = -i$ to get

$$\psi_{sc} = \frac{e^{ikr}}{kr}\sum_{\ell,m}(-i)^\ell(-B_\ell)Y_{\ell,m}(\theta, \phi) = \frac{e^{ikr}}{kr}f_k(\theta, \phi)$$

where $f_k(\theta, \phi)$ (sometimes denoted without the subscript, or just as f) is called the scattering amplitude. Thus the eigenstate can be written

$$\psi_{\mathbf{k}}(\mathbf{x}) = e^{ikz} + \frac{e^{ikr}}{kr}f(\theta, \phi)$$

Recall that probability densities are defined (in 1D) as

$$\mathbf{j} = \frac{\hbar}{2mi}(\psi^*\nabla\psi - \psi\nabla\psi^*)$$

But how do we extract $\mathbf{j}_{inc}, \mathbf{j}_{sc}$? This is actually a bit complicated since $\mathbf{j}$ actually includes cross terms so we cannot simply just separate the two. Instead we use various tricks to solve for the two currents. First we note that at $r \to \infty$, the scattered wave is negligible (due to the $1/r$ factor) and thus the incident current is

$$|\mathbf{j}_{inc}| = \frac{\hbar}{2mi}\left|e^{-ikz}\nabla e^{ikz} - e^{ikz}\nabla e^{ikz}\right| = \frac{\hbar k}{m}$$

This trick won't work for the scattered wave however because it never dominates over the incident wave. Instead, we claim that e^{ikz} is a wave which is limit in the transverse (perpendicular to propagation) by some $\rho \gg r_0$ and thus for $r \to \infty$ off-axis ($\theta \neq 0$), only the scattered wave should survive. This allows us to evaluate

$$|\mathbf{j}_{sc}| = \frac{\hbar}{2mi}|\psi_{sc}^*\nabla\psi_{sc} - \psi_{sc}\nabla\psi_{sc}^*|$$

Recall that the gradient operator in spherical is

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

As $r \to \infty$, all terms except $\hat{r}$ are irrelevant. So really the only piece we need is

$$\frac{\partial}{\partial r}\left(\frac{e^{ikr}}{r}f(\theta,\phi)\right) = f(\theta,\phi)ik\frac{e^{ikr}}{r} + O(1/r^2)$$

Neglecting higher order terms, we get the desired density

$$|\mathbf{j}_{sc}| = \frac{|f|^2}{r^2}\frac{\hbar k}{m}$$

which gives a differential cross section

$$\frac{d\sigma}{d\Omega}d\Omega = \frac{|\mathbf{j}_{sc}|r^2 d\Omega}{|\mathbf{j}_{inc}|} = |f(\theta,\phi)|^2$$

This last statement is a particularly important result, demonstrating that in the time-independent approach, the calculation of a cross section reduced to the problem of finding the scattering amplitude.

$$\boxed{\frac{d\sigma}{d\Omega} = |f(\theta,\phi)|^2}$$

To solve for the scattering amplitude, note that $\psi_k(\mathbf{x})$ (we drop the vector notation on $\mathbf{k}$ for simplicity) is a solution to the Schrodinger equation, which we can write

$$(\nabla^2 + k^2)\psi_k(\mathbf{x}) = \frac{2m}{\hbar^2}V(\mathbf{x})\psi_k(\mathbf{x})$$

This can be converted into an integral equation by looking for a Green's function

$$(\nabla_{\mathbf{x}}^2 + k^2)G^0(\mathbf{x}, \mathbf{x}') = \delta^3(\mathbf{x} - \mathbf{x}')$$

But this just gives the Green's function for a free particle [6]

$$G^0(\mathbf{x}, \mathbf{x}') = G^0(\mathbf{x} - \mathbf{x}') = G^0(|\mathbf{x} - \mathbf{x}'|)$$

Thus if we have

$$(\nabla_{\mathbf{x}}^2 + k^2)f(\mathbf{x}) = h(\mathbf{x})$$

then we can write down the general equation

$$f(\mathbf{x}) = g(\mathbf{x}) + \int d^3x' G^0(\mathbf{x} - \mathbf{x}')h(\mathbf{x}')$$

where $g(\mathbf{x})$ is a solution to the homogeneous equation and the integral expression gives a particular solution.

Applying this to the problem at hand, we derive what is called the Lippmann-Schwinger equation

$$\psi_k(\mathbf{x}) = \psi_k^0(\mathbf{x}) + \frac{2m}{\hbar^2} \int d^3x' G^0(\mathbf{x} - \mathbf{x}')V(\mathbf{x}')\psi_k(\mathbf{x}')$$

Note that since ψ_k appear both on the left and right side of the Schrodinger equation, this equation doesn't actually give the solutions. Instead we have converted the differential equation into an integral one (as we said we would), allowing us to expand ψ_k perturbatively.

The $\psi_k^0(\mathbf{x})$ is the solution to the homogeneous equation

$$(\nabla^2 + k^2)\psi_k^0(\mathbf{x}) = 0$$

which just gives the free particles. It can also be interpreted as the eigenstate to zeroth order in V (so we ignore V), which means that we just get the incident wave, which also makes sense since there's no potential to scatter off of. Thus we take $\psi_k^0 = e^{ikz}$ and start solving iteratively using the Neumann series method. In this context the series we get as a result is called the Born series.

The first step is to actually calculate the Green's function. Since it depends only on the separation $\mathbf{x} - \mathbf{x}'$ (technically $|\mathbf{x} - \mathbf{x}'|$ due to symmetry), we can write without loss of generality

$$(\nabla_{\mathbf{x}}^2 + k^2)G^0(\mathbf{x}) = \delta^3(\mathbf{x})$$

There are many solutions to the homoegeneous equation but we want one that gives an our outgoing wave ψ_{sc} in the $r \to \infty$ limit. In position space, the Green's function is invariant, so we write

$$G^0(r) = \frac{U(r)}{r} \longrightarrow \left(\frac{d^2}{dr^2} + k^2\right)U = 0$$

---

[6]Source: trust me on this

We get general solutions

$$U(r) = Ae^{ikr} + Be^{-ikr}$$

and since we want purely outgoing solutions, we take $B = 0$. Since e^{ikr} solves the homogeneous equation, we're just left with the particular solution. Note that

$$\nabla^2 \left(\frac{1}{r} \right) = -4\pi \delta^3(\mathbf{x})$$

so that the full solution is

$$G^0(\mathbf{x}, \mathbf{x}') = -\frac{1}{4\pi} \frac{e^{ik|\mathbf{x}-\mathbf{x}'|}}{|\mathbf{x} - \mathbf{x}'|}$$

Even if we didn't correctly guess the form of the Green's function, we can arrive at the result by converting into momentum space.

$$G^0(\mathbf{q}) = \frac{1}{(2\pi)^{3/2}} \int e^{-i\mathbf{q}\cdot\mathbf{x}} G^0(\mathbf{x}) d^3x$$

$$G^0(\mathbf{x}) = \frac{1}{(2\pi)^{3/2}} \int e^{i\mathbf{q}\cdot\mathbf{x}} G^0(\mathbf{q}) d^3q$$

Since position and momentum space are related by a Fourier transform, we can Fourier transform the entire differential equation

$$\frac{1}{(2\pi)^{3/2}} \int e^{-i\mathbf{q}\cdot\mathbf{x}} (\nabla^2 + k^2) G^0(\mathbf{x}) d^3x = \frac{1}{(2\pi)^{3/2}} \int e^{-i\mathbf{q}\cdot\mathbf{x}} \delta^3(\mathbf{x}) d^3x$$

$$\frac{1}{(2\pi)^{3/2}} \int (-q^2 + k^2) e^{-i\mathbf{q}\cdot\mathbf{x}} G^0(\mathbf{x}) d^3x = \frac{1}{(2\pi)^{3/2}}$$

$$\therefore (-q^2 + k^2) G^0(\mathbf{q}) = \frac{1}{(2\pi)^{3/2}}$$

$$\therefore G^0(\mathbf{x}) = \frac{1}{(2\pi)^3} \int \frac{e^{i\mathbf{q}\cdot\mathbf{x}}}{k^2 - q^2} d^3q$$

But this integral diverges at $q = k$, we must regulate the integrate using the $i\epsilon$ prescription. We can define the integral as a limit

$$G^0_\pm(\mathbf{x}) = \frac{1}{(2\pi)^3} \lim_{\epsilon\to 0^+} \int \frac{e^{i\mathbf{q}\cdot\mathbf{x}}}{k^2 - q^2 \pm i\epsilon} d^3q$$

Since we want an outgoing spherical wave, we take G^0_+ as our desired Green's function. The integral is done by choosing coordinates $\mathbf{q}$ such that

$$G^0_+(\mathbf{x}) = \lim_{\epsilon\to 0^+} \frac{1}{(2\pi)^3} \int \frac{e^{iqr\cos\theta} q^2 dq \, d\cos\theta \, d\phi}{k^2 - q^2 + i\epsilon}$$

$$= \lim_{\epsilon\to 0^+} \frac{2\pi}{(2\pi)^3} \int_0^\infty \frac{e^{iqr} - e^{-iqr}}{iqr(k^2 - q^2 + i\epsilon)} q^2 dq$$

$$= \lim_{\epsilon\to 0^+} -\frac{i}{(2\pi)^2 r} \int_0^\infty \frac{e^{iqr} - e^{-iqr}}{k^2 - q^2 + i\epsilon} q \, dq$$

$$= \lim_{\epsilon\to 0^+} -\frac{i}{(2\pi)^2 r} \int_{-\infty}^\infty \frac{e^{iqr} q \, dq}{k^2 - q^2 + i\epsilon}$$

This last integral can be done using contour integration to get

$$G_+^0 = -\frac{e^{ikr}}{2\pi r}$$

which is the same result we got earlier.

Thus the Lippmann-Schwinger equation is

$$\psi_k(\mathbf{x}) = \psi_k^0(\mathbf{x}) - \frac{2m}{4\pi\hbar^2} \int d^3x' \frac{e^{ik|\mathbf{x}-\mathbf{x}'|}}{|\mathbf{x}-\mathbf{x}'|} V(\mathbf{x}')\psi_k(\mathbf{x}')$$

Since the potential $V(\mathbf{x})$ is localized, consider the limit in which $r \gg r'$ so that we can expand

$$|\mathbf{x} - \mathbf{x}'| \approx r - \hat{r}\cdot\mathbf{x}' + \cdots$$

Using these approximations, the Lippmann-Schwinger equation becomes

$$\psi_k(\mathbf{x}) = e^{i\mathbf{k}_i\cdot\mathbf{x}} - \frac{2m}{4\pi\hbar^2}\frac{e^{ikr}}{kr} \int d^3x' e^{-i\mathbf{k}_f\cdot\mathbf{x}'} V(\mathbf{x}')\psi_k(\mathbf{x}')$$

where we use $\mathbf{k}_f = k\hat{r}$ so that the scattering amplitude is

$$f(\theta,\phi) = -\frac{2m}{4\pi\hbar^2} \int d^3x' e^{-i\mathbf{k}_f\cdot\mathbf{x}'} V(\mathbf{x}')\psi_k(\mathbf{x}') = -\frac{2m}{4\pi\hbar^2} \left\langle \mathbf{k}_f^0 \right| V \left| \mathbf{k}_i \right\rangle$$

In this equation we use the shorthand

$$\left\langle \mathbf{x}|\mathbf{k}_f^0 \right\rangle = e^{i\mathbf{k}_f\cdot\mathbf{x}} \qquad \left\langle \mathbf{x}|\mathbf{k}_f \right\rangle = \psi_k(\mathbf{x})$$

This solution is exact in the large r limit as long as $rV(r) \to 0$ as $r \to \infty$. Note the lack of normalization, it's not particularly worrying because they will drop out when we calculate the differential cross section.

9.2 Born Approximations

We can replace the initial state $|\mathbf{k}_i\rangle$ with a plane wave approximation $|\mathbf{k}_i^0\rangle$ to get the first Born approximation

$$f^{(1)}(\theta,\phi) = -\frac{2m}{4\pi\hbar^2} \int e^{-i\mathbf{q}\cdot\mathbf{x}'} V(\mathbf{x}') d^3x'$$

where $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$ so that $\hbar\mathbf{q}$ is the momentum transferred in the collision. Note that

$$q^2 = |\mathbf{k}_f - \mathbf{k}_i|^2 = k_f^2 - k_i^2 - 2\mathbf{k}_i\cdot\mathbf{k}_f$$

and since $\mathbf{k}_i = k\hat{z}$ and $\mathbf{k}_f = k\hat{r}$, we have a useful formula

$$q^2 = 2k^2(1 - \cos\theta) = 4k^2\sin^2(\theta/2) \qquad q = 2l\sin(\theta/2)$$

We can note that the first Born approximation is just the Fourier transform of the potential (with some additional factors) with respect to $\mathbf{q}$. We can use this result to get higher order approximations and obtain the Born series

$$\psi_k(\mathbf{x}) = \psi_k^{(0)}(\mathbf{x}) + \psi_k^{(1)}(\mathbf{x}) + \cdots$$

$$f(\theta,\phi) = f^{(1)} + f^{(2)} + \cdots$$

Born Summarized

The 0th order approximation is just the incoming wave

$$\psi_k^{(0)} = e^{ikz}$$

The 1st approximation is done with a plane wave $|\mathbf{k}_i^0\rangle = e^{i\mathbf{k}_i \cdot \mathbf{x}}$

$$f^{(1)}(\theta, \phi) = -\frac{2m}{4\pi\hbar^2} \langle \mathbf{k}_f^0| V |\mathbf{k}_i^0\rangle = -\frac{2m}{4\pi\hbar^2} \int e^{-i\mathbf{q}\cdot\mathbf{x}'} V(\mathbf{x}') d^3 x'$$

$$\psi_k^{(1)}(\mathbf{x}) = \frac{2m}{\hbar^2} \int G^0(\mathbf{x} - \mathbf{x}') V(\mathbf{x}') \psi_k^0(\mathbf{x}') d^3 x'$$

where $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$ and can be represented

$$q^2 = 2k^2(1 - \cos\theta) = 4k^2 \sin^2(\theta/2) \qquad q = 2l\sin(\theta/2)$$

The 2nd born approximation is

$$f^{(2)}(\theta, \phi) = \left(\frac{2m}{4\pi\hbar^2}\right)^2 \int e^{i\mathbf{k}_f\cdot\mathbf{x}'} V(\mathbf{x}') \frac{e^{ik|\mathbf{x}'-\mathbf{x}''|}}{|\mathbf{x}'-\mathbf{x}''|} V(\mathbf{x}'') e^{i\mathbf{k}_i\cdot\mathbf{x}''} d^3 x' d^3 x''$$

$$\psi_k^{(2)}(\mathbf{x}) = \left(\frac{2m}{\hbar^2}\right)^2 \int G^0(\mathbf{x} - \mathbf{x}'') V(\mathbf{x}') G^0(\mathbf{x}' - \mathbf{x}'') V(\mathbf{x}'') \psi_k^0(\mathbf{x}'') d^3 x' d^3 x''$$

and the differential cross section is

$$\frac{d\sigma}{d\Omega} = \left| f^{(1)} + f^{(2)} + \cdots \right|^2$$

Recall that the probability current is

$$\mathbf{j} = \frac{\hbar}{2mi}(\psi^*\nabla\psi - \psi\nabla\psi^*) = \frac{\hbar}{m}\text{Im}(\psi^*\nabla\psi)$$

Given that $\psi_k = \psi_{inc} + \psi_{sc}$, we can relate the (forward) scattering amplitude and total cross section with

$$\text{Im}[f(\theta = 0)] = \frac{k}{4\pi}\sigma$$

Note that if $\theta = 0$, then ϕ is meaningless. This famous relationship is known as the optical theorem and is actually quite general, it holds regardless of whether the potential is spherically symmetric or not. In the context of the Born approximation, it relates different orders of the Born series, equating powers of V.

To better understand how this all works, suppose we scatter off the Yukawa potential

$$V(r) = \frac{qe^{-\mu_0 r}}{r}$$

where g is a coupling parameter and μ_0 indicates the range (it's actually inversely proportional to effective range). For $\mu = 0$ we get the Coulomb potential while for $\mu_0 \neq 0$, then potential is localized. This potential is used to describe nucleon-nucleon interactions.

Note that for spherically symmetric potentials we can do the angular integration right away and the scattering amplitude will depend only on θ (technically q)

$$f^{(1)}(\theta) = -\frac{2m}{\hbar^2 q} \int_0^\infty r \sin(qr) V(r) dr$$

For the Yukawa potential this is

$$f^{(1)}(\theta) = -\frac{2mg}{\hbar^2 q} \int_0^\infty r \sin(qr) \frac{e^{-\mu_0 r}}{r} dr$$

This integral can be done by noting

$$f^{(1)}(\theta) = -\frac{2mg}{\hbar^2 q} \text{Im} \left[\int_0^\infty e^{iqr - \mu_0 r} \right] = -\frac{2mg}{\hbar^2(q^2 + \mu_0^2)}$$

giving a ifferential cross section

$$\frac{d\sigma}{d\Omega} = \frac{4m^2 g^2}{\hbar^4 (q^2 + \mu_0^2)^2} = \frac{4m^2 g^2}{\hbar^4(4k^2 \sin^2(\theta/2) + \mu_0^2)^2}$$

where we recall $q = 2k\sin(\theta/2)$. Let's consider some various limits:

- Low energies: $k \to 0, q \to 0$
$$\frac{d\sigma}{d\Omega} = \frac{4m^2 g^2}{\hbar^4 \mu_0^4}$$

  which is isotropic (not dependent on direction)

- High energies: k large, $mu_0^2 \ll 4k^2 \sin^2(\theta/2)$

$$\frac{d\sigma}{d\Omega} \approx \frac{m^2 g^2}{4\hbar^4 k^4 \sin^4(\theta/2)}$$

  which is increasingly peaked in the forward direction.

Note that we can attempt $\mu_0 = 0$ and $g = -Ze^2$ with $p = \hbar k$ to try and model the Coulomb potential. We get

$$\frac{d\sigma}{d\Omega} = \frac{m^2(Ze^2)^2}{4p^4 \sin^4(\theta/2)} = \frac{(Ze^2)^2}{16E^2 \sin^4(\theta/2)}$$

which is actually the correct answer for Rutherford scattering, but our formalism does not apply for the Coulomb potential. This is an example of a false derivation.

Let's further investigate the two energy regimes. For the low energy regime, we have

$$k \to 0 \quad \longrightarrow \quad q = 2k\sin(\theta/2) \to 0$$

The scattering amplitude in this case can be written

$$\lim_{k\to 0} f^{(1)} = -\frac{2m}{4\pi\hbar^2}\int V(\mathbf{x})d^3x = -\frac{2m}{\hbar^2}V(r)r^2dr$$

To characterize these further for arbitrary potentials, we can define an effective magnitude and range for any potential as

$$\int V(\mathbf{x})d^3x = V_0\frac{4\pi r_0^3}{3}$$

This definition isn't necessarily unique but is good enough for estimating magnitudes. For the Yukawa potential, these are $r_0 = 1/m_0$ and $V_0 \sim g\mu_0$, giving

$$\lim_{k\to 0} f^{(1)}(\theta,\phi) = -\frac{2m}{3\hbar^2}V_0 r_0^3$$

and indicating that the cross section is isotropic in low energies.

For higher energies $k \to \infty$, we will have $q \to \infty$ unless $\sin(\theta/2) \to 0$. Since the exponential oscillates rapidly for large q, it will integrate to 0 unless $\theta \to 0$. Thus we expect the cross section to be strongly forward peaked $\theta \leq 1/kr_0$. As a general remark, it's sometimes useful to remember that $f(\theta,\phi)$ is a function of q only and is always real.

Since the Born series is essentially expanding in powers of the potential, the validity of it should depend on the strength of the potential. In particular we need the potential to be weak which can be characterised by the incident wave not being strongly disturbed. In particular, at $r = 0$ the ratios between the scattered and incident waves should be minuscule, giving the condition

$$\left|\frac{\psi_{sc}(0)}{\psi_k^0(0)}\right| \ll 1 \quad \longrightarrow \quad |\psi_{sc}(0)| \ll 1$$

We can actually calculate the scattered wave using the Lippmann-Schwinger equation. For simplicity assume a spherically symmetric potential

$$\psi_{sc} = -\frac{2m}{4\pi\hbar^2}\int \frac{e^{ikr}}{r}V(r)e^{ikr\cos\theta}d^3x = \frac{2m}{\hbar^2 k}\int_0^\infty e^{ikr}\sin(kr)V(r)dr$$

and we get the condition

$$\frac{2m}{\hbar^2 k}\left|\int_0^\infty e^{ikr}\sin(kr)V(r)dr\right| \ll 1$$

Since this also depends on k, the $k \to 0$ low energy limit gives the most strict condition, by expanding we get

$$\frac{2m}{\hbar^2 k} \left| \int_0^\infty krV(r)dr \right| \ll 1 \qquad \longrightarrow \qquad \left| \frac{mV_0 r_0^2}{\hbar^2} \right| \ll 1$$

Let's try an provide some physics interpretation to this condition. Suppose we have a potential well of depth V_0 and rage r_0. For a bound state of size r_0, the momentum is $\hbar/r_0$ and thus kinetic energy is $\hbar^2/2mr_0^2$. For a bound state we need the potential to dominate the kinetic energy but instead we have the opposition, the criteria is

$$\left| \frac{V_0}{\langle KE \rangle} \right| \ll 1$$

In other words, the potential must be too weak to bind a state in order for the Born approximation to be valid.

Example. Suppose that we scatter off a spherical well of depth V_0 and radius r_0. This calculation is straightforward, we take the first Born approximation

$$f^{(1)}(\theta) = -\frac{2m}{\hbar^2 q} \int rV(r)\sin(qr) = \frac{2mV_0}{\hbar^2 q} \int_0^{r_0} r\sin(qr)dr = \frac{2mV_0}{\hbar q^3}(\sin(qr_0) - qr_0\cos(qr_0))$$

giving a differential cross section of

$$\frac{d\sigma}{d\Omega} = 4r_0^2 \left(\frac{mV_0 r_0^2}{\hbar} \right)^2 \frac{(\sin(qr_0) - qr_0\cos(qr_0))^2}{(qr_0)^6}$$

In the limit $k \to 0$, this becomes

$$\frac{d\sigma}{d\Omega} = \frac{4r_0^2}{9} \left(\frac{mV_0 r_0^2}{\hbar^2} \right)^2$$

which is isotropic. The total cross section is

$$\sigma = \frac{16\pi r_0^2}{9} \left(\frac{mV_0 r_0^2}{\hbar^2} \right)^2$$

9.3 Partial Wave Expansions

For a spherically symmetrical potential $V(\mathbf{x}) = V(r)$, we have $[H, L_i] = 0$ and can thus expand the incoming wave as

$$\psi_{inc} = \psi_k^0 = e^{ikz} = e^{ikr} \sum_{\ell=0}^{\infty} i^\ell (2\ell + 1) j_\ell(kr) P_\ell(\cos\theta)$$

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Since the scattering amplitude for a spherically symmetric potential depends only on θ (and k), it can also be expanded

$$f(\theta) = \sum_{\ell=0}^{\infty} a_\ell(k)(2\ell+1)P_\ell(\cos\theta)$$

and the problem are determining the scattering amplitude has been reduced to finding the coefficients $a_\ell(k)$.

The usefulness of this method comes at low energies $k \to 0$ since only a few values of ℓ are important, namely

$$\ell \sim k\rho \sim kr_0$$

where ρ is the impact parameter and r_0 the potential range.[7]

In the large r limit, note that

$$\lim_{r\to\infty} j_\ell(kr) = \frac{\sin(kr - \ell\pi/2)}{kr}$$

and we can write the expansion

$$\psi_k^0 = e^{ikz} \to \sum_{\ell=0}^{\infty} i^\ell(2\ell+1)\frac{\sin(kr - \ell\pi/2)}{kr}P_\ell(\cos\theta)$$

$$= \sum_{\ell=0}^{\infty} i^\ell \frac{2\ell+1}{2ik}\left[\frac{e^{i(kr-\ell\pi/2)}}{r} - \frac{e^{-i(kr-\ell\pi/2)}}{r}\right]P_\ell(\cos\theta)$$

$$= \sum_{\ell=0}^{\infty} \frac{2\ell+1}{2ik}\left[\underbrace{\frac{e^{ikr}}{r}}_{\text{outgoing}} - \underbrace{\frac{e^{-i(kr-\ell\pi)}}{r}}_{\text{incoming}}\right]P_\ell(\cos\theta)$$

So we can think of the incoming plane wave as a superposition of states of definite ℓ, each of which consists on an incoming and outgoing spherical wave at a $\ell\pi$ phase difference.

The next step is to decompose the exact solution

$$\psi_k(\mathbf{x}) = \sum_{\ell=0}^{\infty} R_\ell(r)P_\ell(\cos\theta)$$

In the large r limit, the radial function should reduce to the free particle solutions though there may be a phase shift due to the potential.

$$\lim_{r\to\infty} R_\ell(r) = 2iA_\ell \frac{\sin(kr - \ell\pi/2 + \delta_\ell)}{kr}$$

$$= 2iA_\ell\left[\cos(\delta_\ell)j_\ell(kr) - \sin(\delta_\ell)n_\ell(kr)\right]$$

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[7]A heuristic "proof" is given in Shankar 19.4

where $\delta_\ell(k) = \delta_\ell$ indicates the phase shift of a specific ℓ state and is dependent on k (though sometimes we drop this for simplicity). The $A_\ell(k)$ are some overall coefficients. This equation can be rewritten using asymptotic forms since $r \to \infty$

$$R_\ell(r) \to \frac{A_\ell}{k} \left[\frac{e^{i(kr - \ell\pi/2 + \delta_\ell)}}{kr} - \frac{e^{-i(kr - \ell\pi/2 + \delta_\ell)}}{kr} \right]$$

This can also be written in the form of an incident wave plus a scattered wave

$$R_\ell(r) = \psi_k^0 + f(\theta) \frac{e^{ikr}}{r} = \frac{2\ell + 1}{2ik} \left[\frac{e^{ikr}}{r} - \frac{e^{-i(kr - \ell\pi)}}{r} \right] + (2\ell + 1)a_\ell \frac{e^{ikr}}{r}$$

and equating the e^{-ikr}/r terms gives the overall coefficients

$$A_\ell(k) = \frac{2\ell + 1}{2i} e^{i(\ell\pi/2 + \delta_\ell)}$$

Putting this back into the general solution and equating them again allows us to determine the a_ℓ

$$a_\ell(k) = \frac{e^{2i\delta_\ell}}{2ik} = \frac{e^{i\delta_\ell} \sin(\delta_\ell)}{k} = \frac{1}{k \cot(\delta_\ell) - ik}$$

This is sometimes written in terms of the S matrix $S_\ell(k) = e^{2ik\delta_\ell}$

$$a_\ell(k) = \frac{1}{2ik}(S_\ell(k) - 1)$$

In our case of elastic scattering, the S matrix is just a complex number with modulus one. Yet again we've reduced the problem of find the differential cross section, this time to just finding the phase shifts δ_ℓ.

$$f(\theta) = \frac{1}{k} \sum (2\ell + 1)e^{i\delta_\ell} \sin(\delta_\ell) P_\ell(\cos\theta)$$

$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2 = \frac{1}{k^2} \sum_{\ell,\ell'} (2\ell + 1)(2\ell' + 1)e^{i(\delta_\ell - \delta_{\ell'})} \sin(\delta_\ell) \sin(\delta_{\ell'}) P_\ell(\cos\theta) P_{\ell'}(\cos\theta)$$

We can exploit the orthogonality of Legendre polynomials to obtain the total cross section

$$\int_{-1}^{1} d(\cos\theta) P_\ell(\cos\theta) P_{\ell'}(\cos\theta) = \frac{2}{2\ell + 1} \delta_{\ell,\ell'}$$

$$\therefore \sigma = \int \frac{d\sigma}{d\Omega} d\Omega = \sum_\ell \frac{4\pi}{k^2}(2\ell + 1) \sin^2(\delta_\ell)$$

In other words, the total cross section is the sum of smaller, independent cross sections

$$\sigma = \sum \sigma_\ell(k) \qquad \sigma_\ell(k) = \frac{4\pi}{k^2}(2\ell + 1) \sin^2(\delta_\ell)$$

Notably, there is not interference between different ℓ values. Furthermore there is a limit to how big the cross section can be

$$\sigma_\ell(k) \leq \frac{4\pi}{k^2}(2\ell + 1)$$

known as the unitarity bound, since it's a consequence of unitarity.

It's also easy to prove the optical theorem using the partial wave expansion

$$\text{Im}[f(\theta = 0)] = \text{Im}\left[\sum \frac{2\ell + 1}{k} e^{i\delta_\ell} \sin(\delta_\ell)\right]$$

$$= \sum \frac{2\ell + 1}{k} \sin^2(\delta_\ell)$$

$$= \frac{k}{4\pi}\left[\frac{4\pi}{k^2}(2\ell + 1)\sin^2(\delta_\ell)\right]$$

$$= \frac{k}{4\pi}\sigma$$

However this derivation is dependent on the fact that $V(\mathbf{x})$ is spherically symmetric. In general, the optical theorem holds for all potentials regardless of symmetry.

9.3.1 Hard Sphere Scattering

In the partial expansion method, the final goal is to compute the phase shifts to obtain the scattering cross section. This can be done by solving the radial Schrodinger equation

$$\left(\frac{d^2}{dr^2} + \frac{2m}{\hbar^2}\left(E - V(r) - \frac{\ell(\ell + 1)\hbar^2}{2mr^2}\right)\right)u_\ell(r) = 0$$

where $u_\ell(r) = rR_\ell(r)$ with boundary conditions

$$u_\ell(r \to 0) = 0 \qquad R_\ell(r \to \infty) = 2iA_\ell[\cos(\delta_\ell)j_\ell(kr) - \sin(\delta_\ell)n_\ell(kr)]$$

In general we will consider potentials which vanish outside a given range, the simplest case is the hard sphere.

$$V(r) = \begin{cases} \infty & r < r_0 \\ 0 & r > r_0 \end{cases}$$

The particle clearly vanishes inside the sphere and it's given by a free particle outside

$$R_\ell(r) = \begin{cases} 0 & r < r_0 \\ A_\ell j_\ell(kr) + B_\ell n_\ell(kr) & r > r_0 \end{cases}$$

Boundary conditions require that the wavefunctions match at $r = r_0$, that is

$$A_\ell j_\ell(kr_0) + B_\ell n_\ell(kr_0) = 0$$

$$\frac{B_\ell}{A_\ell} = -\frac{j_\ell(kr_0)}{n_\ell(kr_0)} = -\tan(\delta_\ell)$$

$$\therefore \tan(\delta_\ell) = \frac{j_\ell(kr_0)}{n_\ell(kr_0)}$$

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where we use asymptotic forms at $r > r_0$ to obtain the phase shifts. For $\ell = 0$ we have

$$\tan(\delta_0) = \frac{j_0(kr_0)}{n_0(kr_0)} = \tan(-kr_0)$$

so we have $\delta_0 = -kr_0$, indicating a repulsive potential. For an attractive potential, the phase shift will be positive, signifying that the wave function is pulled in. At the low energy regime $k \to 0$, for general values of ℓ

$$j_\ell(x \to 0) \to \frac{x^\ell}{(2\ell + 1)!!} \qquad n_\ell(x \to 0) \to -x^{-(\ell+1)}(2\ell - 1)!!$$

So that the phase shift at low energies is

$$\tan(\delta_\ell) \to -\frac{(kr_0)^{2\ell+1}}{(2\ell + 1)!!(2\ell - 1)!!}$$

$$\therefore \lim_{k \to 0} \delta_\ell = -(kr_0)^{2\ell+1}$$

For simple piecewise continuous finite potentials, the procedure is

1. Find $u\ell(r)$ or $R_\ell(r)$ in each region

2. Match wavefunctions and their 1st derivative at boundaries

3. Extract the phase shift δ_ℓ from $R_\ell(r \to \infty)$ condition. Note for $\ell = 0$

$$u(r \to 0) = 0 \qquad u(r \to \infty) = \sin(kr + \delta_0)$$

Returning to the hard sphere problem, the total cross section is

$$\sigma = \frac{4\pi}{k^2} \sum (2\ell + 1) \sin^2(\delta_\ell) = \frac{4\pi}{k^2} \sum \frac{(2\ell + 1)j_\ell^2(kr_0)}{k_\ell^2(kr_0) + n_\ell^2(kr_0)}$$

For sufficiently low energies, only the $\ell = 0$ partial wave is important, so

$$\lim_{k \to 0} \sigma = 4\pi r_0^2$$

which is actually four times the classical result, but this is ok since we are at low energies. However, at high energies we find for $kr_0 \gg 1$ that

$$\sigma \approx 2\pi r_0^2$$

which is still twice the classical result. This is because we are double counting due to diffraction around the hard sphere in the forward direction. The asymptotic form of our wavefunctions admits two contributions: one from actual scattering and another from the shadow of the sphere (diffraction). This can be better understood by writing the scattering amplitude as

$$f(\theta) = \frac{1}{2ik} \sum e^{2i\delta_\ell}(2\ell + 1)P_\ell + \frac{i}{2k} \sum (2\ell + 1)P_\ell = f_{refl} + f_{shadow}$$

If we evaluate these separately, we find

$$\int |f_{refl}|^2 d\Omega = \int |f_{shad}|^2 d\Omega = \pi r_0^2$$

with negligible overlap between the two contributions.

Now we return to the Lippmann-Schwinger equation using the partial wave formalism we've developed thus far

$$\psi_k(\mathbf{x}) = e^{ikz} + \frac{2m}{\hbar^2} \int d^3x' G^0(|\mathbf{x} - \mathbf{x}'|) V(r') \psi_k(\mathbf{x}')$$

The Green's function can be expanded as

$$G^0(|\mathbf{x} - \mathbf{x}'|) = -ik \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} Y_{\ell m}(\hat{r}) Y_{\ell m}^*(\hat{r}) j_\ell(kr_<) h_\ell(kr_>)$$

$$= -ik \sum_{\ell=0}^{\infty} P_\ell(\hat{r} \cdot \hat{r}') \frac{2\ell + 1}{4\pi} j_\ell(kr_<) n_\ell(kr_>)$$

where h_ℓ are the spherical Hankel functions (of the first kind), note that as $r \to \infty$

$$h_\ell(kr) = j_\ell(kr) + in_\ell(kr) \to \frac{(-i)^{\ell+1}}{k} \frac{e^{ikr}}{r}$$

By expanding the incoming wave and doing the angular integration, we get

$$R_\ell(r) = \frac{u_\ell(r)}{r} = i^\ell(2\ell + 1) j_\ell(kr) - \frac{2imk}{\hbar^2} \int j_\ell(kr_<) h_\ell(kr_>) V(r') u_\ell(r') dr'$$

Given that $V(r)$ is localized, we can take $r = r_>$ and $r' = r_<$. The second term is the scattered wave, allowing us to derive a formula for the phase shift

$$\boxed{\frac{e^{i\delta_\ell} \sin(\delta_\ell)}{k} = -\frac{2m}{\hbar^2} \frac{(-i)^\ell}{2\ell + 1} \int_0^\infty j_\ell(kr') V(r') u_\ell(r') r' dr'}$$

which is exact as $r \to \infty$. If $V(r)$ is small, then we can use the Born approximation and replace

$$\frac{u_\ell(r)}{r} \to i^\ell(2\ell + 1) j_\ell(kr)$$

and derive the phase shifts as

$$\boxed{\frac{e^{i\delta_\ell} \sin(\delta_\ell)}{k} = -\frac{2m}{\hbar^2} \int_0^\infty j_\ell^2(kr) V(r) r^2 dr}$$

Furthermore, if we are in the low energy regime, then we can derive

$$e^{i\delta_\ell} \sin(\delta_\ell) = -\frac{2m}{\hbar^2} \frac{k^{2\ell+1}}{((2\ell + 1)!!)^2} \int_0^\infty r^{2\ell+2} V(r) dr$$

which shows $\delta_\ell \to k^{2\ell+1}$ as $k \to 0$.

9.3.2 Scattering in a Spherical Well

Suppose we have an attractive spherical well

$$V(r) = \begin{cases} -V_0 & r < a \\ 0 & r > a \end{cases}$$

In the low energy limit, the $\ell = 0$ limit dominates

$$
\begin{aligned}
e^{i\delta_0} \sin(\delta_0) \approx \delta_0 &= \frac{2mV_0 k}{\hbar^2} \int_0^a j_0^2(kr) r^2 dr \\
&= \frac{2mV_0}{\hbar^2 k} \sin^2(kr) dr \\
&= \frac{mV_0}{\hbar^2 k^2} (ka - \cos(ka)\sin(ka)) \\
&\approx \frac{2mV_0 a^3 k}{3\hbar^2}
\end{aligned}
$$

Thus the cross section in this limit is isotropic

$$\lim_{k \to 0} \sigma = \frac{4\pi}{k^2} \delta_0^2 = \frac{16\pi}{9} \left(\frac{mV_0 a^3}{\hbar^2} \right)^2$$

For a general potential with range a and $V(r) \sim 0$ for $r > a$ there is a general procedure for finding the phase shifts. Let region I be $r < a$ and region II be $r > a$. We solve for the radial wavefunction on region I and define

$$\gamma_\ell(k) = \left. \frac{R_\ell^{(I)'}}{R_\ell^{(I)}} \right|_{r=a}$$

which should be constant in both regions. The radial wavefunction in region II is given by

$$R_\ell(r) = 2i A_\ell(k) [j_\ell(kr) \cos(\delta_\ell) - n_\ell(kr) \sin(\delta_\ell)]$$

and we define γ again as

$$\gamma_\ell(k) = \left. \frac{R_\ell^{(II)'}}{R_\ell^{(II)}} \right|_{r=a} = k \left[\frac{\cos(\delta_\ell) j_\ell'(ka) - \sin(\delta_\ell) n_\ell'(ka)}{\cos(\delta_\ell) j_\ell(ka) - \sin(\delta_\ell) n_\ell(ka)} \right]$$

By rearranging this, we find that the phase shift is given by

$$\boxed{\tan(\delta_\ell) = \frac{k j_\ell'(ka) - \gamma_\ell(k) j_\ell(ka)}{k n_\ell'(ka) - \gamma_\ell(k) n_\ell(ka)}}$$

which in the low energy regime becomes

$$\tan(\delta_\ell) = \frac{(ka)^{2\ell+1}}{(2\ell+1)!!(2\ell-1)!!} \frac{\ell - a\gamma_\ell(0)}{\ell + 1 + a\gamma_\ell(0)}$$

once again showing that $\gamma_\ell \sim k^{2\ell+1}$ at low energies. This is more general than the Born approximation, in fact we can recover it in the limit of small potentials.

For convenience then first two phase shifts are listed

$$\tan \delta_0 = -\frac{\gamma_0 ka^2}{1 + \gamma_0 a} \qquad \tan \delta_1 = \frac{(ka)^3}{3} \frac{1 - \gamma_1 a}{2 + \gamma_1 a}$$

Returning to the spherical well example, we can compute

$$\gamma_\ell(k) = \frac{k' j'_\ell(k'a)}{j_\ell(k'a)} \qquad k' = \sqrt{\frac{2m(E + V_0)}{\hbar^2}} = \sqrt{k^2 + \frac{2mV_0}{\hbar^2}}$$

For $\ell = 0$, we find

$$\gamma_0 a = k'a \cot(k'a) - 1$$

If we assume the denominators for $\tan(\delta_0), \tan(\delta_1)$ do not vanish, then $\ell = 0$ will dominate scattering to give a cross section

$$\sigma = \frac{4\pi}{k^2} \sin^2(\delta_0) = 2\pi a^2 \frac{\gamma_0 a^2}{(1 + \gamma_0 a)^2} = 4\pi a^2 \left(1 - \frac{\tan(k'a)}{k'a}\right)^2$$

Note that if $V_0 \to 0$, then

$$k'a \to \sqrt{\frac{2mV_0 a}{\hbar^2}}$$

is also small and thus

$$\gamma_0 a \to -\frac{1}{3}(k'a)^2 = -\frac{2mV_0 a^2}{3\hbar^2}$$

If both $V_0 \to 0$ and we are in the low energy limit,

$$\tan(\delta_0) \sim \delta_0 \sim -\gamma_0 ka^2 \sim \frac{2mV_0 a^3 k}{3\hbar^2}$$

in agreement with the result we obtained from the Born approximation earlier.

Example. Now suppose we scatter off of a repulsive potential well

$$V(r) = \begin{cases} V_0 & r < a \\ 0 & r > a \end{cases}$$

γ can be easily calculated, it's the same as the repulsive well case

$$\gamma_\ell(k) = \frac{k' j'_\ell(k'a)}{j_\ell(k'a)} \qquad k' = \sqrt{\frac{2m(E - V_0)}{\hbar^2}}$$

Using the fact $j_0(x) = \sin(x)/x$, we get the $\ell = 0$ phase shift

$$\delta_0 = -ka \left(1 - \frac{\tan(k'a)}{k'a}\right)$$

9.4 Scattering Resonances

When we calculate the phase shift using $\tan(\delta_\ell)$, it is possible for the denominator to vanish and thus $\tan(\delta_\ell) \to \infty$. In the low energy limit this occurs when

$$\ell + 1 + a\gamma_\ell(k_r) = 0$$

where k_r is the value of k at which the denominator vanishes. This phenomenon is called resonance where $\delta_\ell = \pi/2$ and so scattering is maximized. The resonance energy can be defined

$$E_r = \frac{\hbar^2 k_r^2}{2m}$$

We can redefine γ to depend on the energy instead of k, thus at resonance

$$\ell + 1 + a\gamma(E_r) = 0 \to a\gamma(E_r) = -\gamma - 1$$

By expanding the resonance conditions for energies near E_r

$$\gamma + 1 + a\gamma_\ell(E) \approx (E - E_r)a \left.\frac{d\gamma_\ell}{dE}\right|_{E_r}$$

This can be used to give near resonance phase shifts at low energies

$$\cos(\delta_\ell) = (ka)^{-(2\ell+1)}\frac{\ell + 1 + a\gamma_\ell}{\ell - a\gamma_\ell}(2\ell + 1)!!(2\ell - 1)!!$$

$$= (ka)^{-(2\ell+1)}\frac{a(E - E_r)\frac{\partial\gamma_\ell}{\partial E}}{2\ell + 1}(2\ell + 1)!!(2\ell - 1)!!$$

$$= k^{-(2\ell+1)}a^{-2\ell}((2\ell - 1)!!)^2(E - E_r)\left.\frac{\partial\gamma_\ell}{\partial E}\right|_{E_r}$$

which we can rewrite as

$$\boxed{\cot(\delta_\ell) = -\frac{2(E - E_r)}{\Gamma_k} \qquad \Gamma_k = -\frac{2k^{2\ell+1}a^{2\ell}}{((2\ell - 1)!!)^2\frac{\partial\gamma_\ell}{\partial E}|_{E_r}}}$$

Using this new quantity, the partial wave cross section near resonance is

$$\sigma = \frac{4\pi}{k^2}\frac{2\ell + 1}{\cot^2(\delta_\ell) + 1}$$

$$= \frac{4\pi}{k^2}\frac{(2\ell + 1)(\Gamma_k/2)^2}{(E - E_r)^2 + (\Gamma_k/2)^2}$$

This is called the Breit-Wigner form for scattering near resonance and the quantity Γ_k is the Breit-Wigner width. Note that this expression is peaked at $E = E_r$ with Γ_k being the full width at half maximum (characteristic width).

If we return to the phase shift formula, we can rewrite

$$\gamma_\ell(E) = \frac{\pi}{2} + \tan^{-1}\left(\frac{E - E_r}{\gamma_k/2}\right)$$

which means as $E \to E_r$, the phase shift approaches $\pi/2$ from below. There is a connection between scattering resonances and bound states of the potential. As an example consider the attractive spherical well again

$$V(r) = \begin{cases} -V_0 & r < a \\ 0 & r > a \end{cases}$$

For the $\ell = 0$ wave the resonance condition is

$$a\gamma_0 = k'a\cot(k'a) - 1 \qquad k' = \sqrt{k^2 + \frac{2mV_0}{\hbar^2}}$$

We'll fix $k = 0$ and vary V_0, the resonance condition is

$$1 + a\gamma_0 = 0 \to k'a\cot(k'a) = 0$$

which results in

$$\lambda \equiv k'a = \left(n + \frac{1}{2}\right)\pi$$

at resonance. Recall that the bound state conditions for a spherical well are

$$k'a\cot(k'a) = -\kappa a \qquad \kappa = \sqrt{-\frac{2mE}{\hbar^2}}$$

This means that for various values of λ

$$\lambda < \frac{\pi}{2} : \text{no solutions}$$

$$\lambda = \frac{\pi}{2} : \text{one } E = 0 \text{ state}$$

$$\frac{\pi}{2} < \lambda < \frac{3\pi}{2} : \text{one } E = 0 \text{ state}$$

$$\lambda = \frac{3\pi}{2} : \text{one } E = 0, \text{ one } E < 0 \text{ state}$$

$$\frac{3\pi}{2} < \lambda < \frac{5\pi}{2} : \text{two } E < 0 \text{ states}$$

$$\vdots$$

Thus we see the connection between resonance and bound states:

> A resonance at zero energy $(k = 0)$ scattering corresponds to the turning on of a bound state for a potential.

Here we consider $E = 0$ exactly, but realistically metastable $E > 0$ can also exist at resonance. They are not truly bound as they can tunnel out at some amplitude governed by the Breit-Wigner width.

Formally, recall asymptotic behavior of the radial wavefunction

$$\lim_{r \to \infty} R_\ell(r) = 2iA_\ell \frac{\sin(kr - \ell\pi/2 + \delta_\ell)}{kr}$$
$$= \frac{A_\ell}{k} \left[\frac{e^{i\delta_\ell} e^{i(kr - \ell\pi/2)}}{r} - \frac{e^{-i\delta_\ell} e^{-i(kr - \ell\pi/2)}}{r} \right]$$

which consists of an outgoing and incoming wave. For unitarity the two components should have equal probabilities. Define the S matrix

$$S_\ell(k) = \frac{\text{amplitude of outgoing wave}}{\text{amplitude of incoming wave}}$$
$$= e^{2i\delta_\ell} = \frac{\cot(\delta_\ell) + i}{\cot(\delta_\ell) - i}$$

Near resonance, recall

$$\cot \delta_\ell = -\frac{2(E - E_r)}{\Gamma_k}$$

which gives an S matrix of

$$S_\ell(E = E_r) \approx \frac{(E - E_r) - i\Gamma_k/2)}{(E - E_r) + i\Gamma_k/2}$$

and so there is a pole at $E = E_r - i\Gamma_k/2$. Recall that a general bound state evolves as

$$|\psi_B(t)\rangle = e^{-iE_B t/\hbar} |\psi_B(0)\rangle$$

and thus the time dependence of a resonant state is

$$|\psi_r(t)\rangle = e^{-iE_r t/\hbar} e^{-\Gamma_k t/2\hbar} |\psi_r(0)\rangle$$

indicating that the resonances are metastable, with a tunnelling amplitude given by the decaying exponential. The lifetime of a resonant state is inversely proportional to the Breit-Wigner width $\tau \sim 1/\Gamma_k$.

To connect with true (not metastable) bound states, let $E < 0$ and take $k \to i\kappa$

$$R_\ell(r) \to \frac{A_\ell(i\kappa)}{i\kappa} \left[e^{i\delta_\ell(i\kappa)} \frac{e^{-\kappa r}}{r} e^{i\ell\pi/2} - e^{-i\delta_\ell(i\kappa)} \frac{e^{\kappa r}}{r} e^{i\ell\pi/2} \right]$$

For this to be normalizable, the growing exponential must vanish

$$e^{-i\delta_\ell(i\kappa)} = 0$$

which is just the same as saying $S_\ell(k)$ has a pole

$$S_\ell(i\kappa) = e^{2i\delta_\ell(i\kappa)} = \frac{e^{i\delta_\ell(i\kappa)}}{e^{-i\delta_\ell(i\kappa)}}$$

Thus poles in the S matrix corresponds to bound state energies.

9.5 Spin Scattering

So far we've been considering spinless particles when scattering. Now we want to investigate what happens when we throw spin into the mix. When scattering a spin $1/2$ particle off a spinless target, we have potentials of the form

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

$$V(\mathbf{x}) = V_1(\mathbf{x}) + V_2(\mathbf{x})\sigma \cdot \mathbf{B} + V_3(\mathbf{x})\mathbf{L} \cdot \sigma + \cdots$$

Thus V is a 2x2 matrix and we can factor our states as

$$|\psi\rangle = |\psi_{space}\rangle \otimes |\chi\rangle$$

where $|\chi\rangle$ is a spinor. The full solution to the Schrodinger equation is

$$\psi_k(\mathbf{x}) = e^{i\mathbf{k}_i \cdot \mathbf{x}}\chi_i + \psi_{sc}$$

with asymptotic form

$$\psi_k(\mathbf{x}) = \left(e^{i\mathbf{k}_i \cdot \mathbf{x}} + \frac{e^{ikr}}{r}\mathcal{M}\right)\chi_i$$

$\mathcal{M}$ is a 2x2 matrix, a generalization of the scattering amplitude and a function of k, θ, ϕ (just like the amplitude f). The differential cross section for $(\mathbf{k}_i, \chi_i)$ to $(\mathbf{k}_f, \chi_f)$ is given by the specific matrix element

$$\frac{d\sigma_{fi}}{d\Omega} = |\mathcal{M}_{fi}|^2$$

$$\mathcal{M}_{fi} = \langle \chi_f| \mathcal{M} |\chi_i\rangle = \chi_f^\dagger \begin{pmatrix} \mathcal{M}_1 1 & \mathcal{M}_1 2 \\ \mathcal{M}_2 1 & \mathcal{M}_2 2 \end{pmatrix} \chi_i$$

So now instead of finding f, the question now is to determine $\mathcal{M}$. From the Born approximation we have the expression

$$\mathcal{M} = -\frac{m}{2\pi\hbar^2}\int e^{-i\mathbf{q}\cdot\mathbf{x}}V(\mathbf{x})d^3x$$

where $V(\mathbf{x})$ is a 2x2 matrix with the spin interactions and $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$ represents momentum transferred.

In realistic (aka experimental) scenarios, we might not have a definite initial spin state, instead we have a polarized incident beam. It's also possible to have situations in which the final spin isn't actually measured, thus we can sum over all finals spins to get a (total) cross section.

$$\frac{d\sigma_i}{d\Omega} = \sum_f \frac{d\sigma_{fi}}{d\Omega} = \sum_f |\mathcal{M}_{fi}|^2 \qquad \sigma_i = \int \frac{d\sigma_i}{d\Omega} d\Omega$$

This still assumes we have a definite initial spin state, in general there may not be a preferred spin direction for the incident beam, i.e. we have an unpolarized beam. In such a case we must average over incoming spin states as well

$$\frac{d\sigma}{d\Omega} = \frac{1}{2}\sum_i \frac{d\sigma_i}{d\Omega} = \frac{1}{2}\sum_{fi} = \frac{d\sigma_{fi}}{d\Omega} = \sum_{fi} |\mathcal{M}_{fi}|^2$$

The prefractor of $1/2$ is due to the spin $1/2$, since half the particles are in $+z$ and the other half in $-z$. For higher spins, this generalizes to a factor of $1/2S + 1$. From this equation, we can derive

$$\frac{d\sigma}{d\Omega} = \frac{1}{2}\sum_{fi} |\mathcal{M}_{fi}|^2$$

$$= \frac{1}{2}\sum_f \sum)i| \langle \chi_f | \mathcal{M} | \chi_i \rangle |^2$$

$$= \frac{1}{2}\sum_f \sum_i \langle \chi_i | \mathcal{M}^\dagger | \chi_f \rangle \langle \chi_f | \mathcal{M} | \chi_i \rangle$$

$$= \frac{1}{2}\sum_i \langle \chi_f | \mathcal{M}^\dagger \mathcal{M} | \chi_i \rangle$$

and we get the useful result

$$\boxed{\frac{d\sigma}{d\Omega} = \frac{1}{2}\mathrm{Tr}(\mathcal{M}^\dagger \mathcal{M}) = \frac{1}{2}\mathrm{Tr}(\mathcal{M}\mathcal{M}^\dagger)}$$

Sometimes we get a detector which can record the spin direction of the final state, this gives a polarization vector $\mathbf{P}(k, \theta, \phi)$ defined as

$$P_j = \frac{(\text{Prob. final state in } +\hat{e}_j \text{ direction}) - (\text{Prob. final state in } -\hat{e}_j \text{ direction})}{\text{Prob. final state in } +\hat{e}_j \text{ direction}) + (\text{Prob. final state in } -\hat{e}_j \text{ direction})}$$

where $\hat{e}_j$ is the vector direction in which the final spin is measured. Thus P_j is just the expectation value of σ_j for all the final state particles.

Using this, for a polarized initial state, the polarization vector of the final state can be written

$$P_j = P_j(k, \theta, \phi) = \frac{\dfrac{d\sigma_{\hat{e}_{j+i}}}{d\Omega} - \dfrac{d\sigma_{\hat{e}_{j-i}}}{d\Omega}}{\dfrac{d\sigma_{\hat{e}_{j+i}}}{d\Omega} + \dfrac{d\sigma_{\hat{e}_{j-i}}}{d\Omega}}$$

If the initial spin state is unpolarized, then we must take averages

$$P_j = \left(\frac{1}{2}\sum_i \frac{d\sigma_{\hat{e}_{j+i}}}{d\Omega} - \frac{1}{2}\sum_i \frac{d\sigma_{\hat{e}_{j-i}}}{d\Omega}\right)\left(\frac{1}{2}\sum_i \frac{d\sigma_{\hat{e}_{j+i}}}{d\Omega} + \frac{1}{2}\sum_i \frac{d\sigma_{\hat{e}_{j-i}}}{d\Omega}\right)^{-1}$$

$$= \frac{\sum_i |\mathcal{M}_{\hat{e}_{j+1}}|^2 - \sum_i |\mathcal{M}_{\hat{e}_{j-1}}|^2}{\sum_i |\mathcal{M}_{\hat{e}_{j+1}}|^2 + \sum_i |\mathcal{M}_{\hat{e}_{j-1}}|^2}$$

which can be expressed more compactly (and usefully) as

$$P_j = \frac{\text{Tr}(\sigma_j \mathcal{M}\mathcal{M}^\dagger)}{\text{Tr}(\mathcal{M}\mathcal{M}^\dagger)}$$

Example. Consider a potential of the form

$$V(\mathbf{x}) = V_1(r) + V_2(r)\mathbf{L} \cdot \mathbf{S}$$

It can be shown that the scattering matrix takes the form

$$\mathcal{M} = A(\theta) + \mathbf{B}(\theta) \cdot \sigma$$

Let's assume $A, \mathbf{B}$ are real (and they are in the first Born approximation), then it's straightforward to calculate

$$\mathcal{M}\mathcal{M}^\dagger = A^2 + B^2 + 2A\mathbf{B} \cdot \sigma$$

$$\text{Tr}(\mathcal{M}\mathcal{M}^\dagger) = 2(A^2 + B^2) \qquad \text{Tr}(\sigma\mathcal{M}\mathcal{M}^\dagger) = 4A\mathbf{B}$$

so that the polarization of the final state is

$$\mathbf{P} = \frac{2A\mathbf{B}}{A^2 + B^2}$$

If there is a polarized initial beam, then we must turn to the density matrix formalism. Recall that the density matrices are

$$\rho_i = \sum_n |\chi_n\rangle p_{i_n} \langle\chi_n|$$

and that $\text{Tr}(\rho^2) < \text{Tr}(\rho) = 1$ where equality holds only for pure states (where only one $p_{i_n} = 1$, the rest are zero). For spine 1/2 particles the density matrix can be written

$$\rho_i = \frac{1}{2}(1 + \sigma \cdot \mathbf{P}_i)$$

$\mathbf{P}_i$ is the initial polarization vector and can be found as the ensemble average using the initial density matrix

$$\mathbf{P}_i = \text{Tr}(\rho_i \sigma) = [\sigma]$$

If we don't measure the final state polarization, then the cross section is

$$\frac{d\sigma_i}{d\Omega} = \sum_f \sum_n p_{i_n} |\mathcal{M}_{fn}|^2 = \sum_n p_{i_n} (\mathcal{M}\mathcal{M}^\dagger)_n n$$

which can be written as an ensemble average

$$\frac{d\sigma_i}{d\Omega} = \text{Tr}(\mathcal{M}\rho_i \mathcal{M}^\dagger)$$

If we do want to know the final state polarization then we must first calculate the final state density matrix before computing the ensemble average.

$$\rho_f = \frac{\mathcal{M}\rho_i \mathcal{M}^\dagger}{\text{Tr}(\mathcal{M}\rho_i \mathcal{M}^\dagger)}$$

$$\mathbf{P}_f = \text{Tr}(\sigma \rho_f) = \frac{\text{Tr}(\mathcal{M}\rho_i \mathcal{M}^\dagger)}{\text{Tr}(\mathcal{M}\rho_i \mathcal{M}^\dagger)}$$

Example. Suppose we have a potential of the form

$$V = V_0(r) + V_1(r)\mathbf{L} \cdot \sigma$$

This indicates the interaction is invariant under parity and time reversal symmetry as well as spherical symmetry. The scattering matrix takes the form

$$\mathcal{M} = g_1 + g_2 \sigma \cdot (\mathbf{k}_i \times \mathbf{k}_f) = g(k, \theta) + h(k, \theta)\sigma \cdot \hat{n}$$

where we've defined the unit normal

$$\hat{n} = \frac{\mathbf{k}_i \times \mathbf{k}_f}{|\mathbf{k}_i \times \mathbf{k}_f|}$$

For an unpolarized initial beam, we can compute

$$\frac{d\sigma}{d\Omega} = \frac{1}{2}\text{Tr}(\mathcal{M}\mathcal{M}^\dagger) = |g|^2 + |h|^2 \qquad \mathbf{P}_f = \frac{2\text{Re}(gh^*)}{|g|^2 + |h|^2}\hat{n}$$

which shows that final state polarization in the scattering plane is prohibited. In fact this occurs whenever an interaction is invariant under just parity.

For a general (spherically symmetric) potential

$$V(\mathbf{x}) = V_0(r) + V_1(r)\mathbf{L} \cdot \sigma + \frac{1}{2}\{V_2(r), \sigma \cdot \mathbf{p}\} + V_3(r)\sigma \cdot \mathbf{x}$$

the scattering matrix will be of the form

$$\mathcal{M} = g_1 + g_2\sigma \cdot (\mathbf{k}_i \times \mathbf{k}_f) + g_3\sigma \cdot (\mathbf{k}_i + \mathbf{k}_f) + g_4\sigma \cdot (\mathbf{k}_i - \mathbf{k}_f)$$

in which the coefficients are functions of k, θ, more precisely

$$g_i = g_i(k, \theta) = g_i(k_i \cos\theta)$$

where θ is the angle between the initial and final momenta

$$\cos\theta = \hat{k}_i \cdot \hat{k}_f$$

Example. Consider a spin $1/2$ particle with initial momentum $\mathbf{p}_i = \hbar k\hat{z}$ with spin oriented along it's direction of motion (so $\hat{z}$). Suppose it's scattered by an angle of θ in the xz plane by the spin-dependent potential

$$V(\mathbf{x}) = \lambda A(\mathbf{x})g(r)$$

where $\lambda \ll 1$ and $A(\mathbf{x})$ provide the spin dependence.

From the initial conditions, we have

$$\chi_i = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \longrightarrow \quad \rho_i = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

The scattering matrix is given by

$$\mathcal{M} = -\frac{m}{2\pi\hbar^2}\int d^3x e^{-i\mathbf{q}\cdot\mathbf{x}}\lambda A(\mathbf{x})g(r)$$

First, in the case $A(\mathbf{x}) = \mathbb{1}$, we see that $\mathcal{M}$ will be proportional to the identity matrix. We can go ahead and compute the final density matrix but it's easy to see that

$$\chi_f = \chi_i = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

so that the polarization hasn't changed. $\mathbf{P}_f = \mathbf{P}_i = \hat{z}$ and the final state is aligned with the initial momentum.

For the case $A(\mathbf{x}) = \sigma_x$, the scattering matrix is proportional to σ_x, it can be written as

$$\mathcal{M} = \begin{pmatrix} 0 & h(k, \theta) \\ h(k, \theta) & 0 \end{pmatrix}$$

and we can compute the polarization from here. Another way is to note that since the scattering matrix is proportional to σ_x, we will have

$$\chi_f = \sigma_x\chi_i = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Thus $\mathbf{P}_f = -\mathbf{P}_i = -\hat{z}$, so the final state is anti-aligned with the initial momentum.

A more complicated case is $A(\mathbf{x}) = \sigma \cdot \mathbf{x}$. In this case we'll have

$$\mathcal{M} = h(k,\theta)\sigma \cdot \mathbf{q}$$

We've been told that the particle is scattered by an angle θ in the xy plane and the initial particle is propagating in the $\hat{z}$ direction, so

$$\mathbf{k}_i = k\hat{z} = k(0,0,1) \qquad \mathbf{k}_f = k(\sin\theta, 0, \cos\theta)$$

indicating that the matrix is of the form

$$\mathcal{M} = h(k,\theta)(\sin(\theta)\sigma_x + (\cos\theta - 1)\sigma_z) = \begin{pmatrix} \cos\theta - 1 & \sin\theta \\ \sin\theta & 1 - \cos\theta \end{pmatrix}$$

We can now calculate the final density matrix

$$\begin{aligned}
\rho_f &= \frac{\mathcal{M}\rho_i\mathcal{M}^\dagger}{\mathrm{Tr}(\mathcal{M}\rho_i\mathcal{M}^\dagger)} \\
&= \frac{1}{2(1-\cos\theta)} \begin{pmatrix} (\cos\theta - 1)^2 & \sin\theta(\cos\theta - 1) \\ \sin\theta(\cos\theta - 1) & \sin^2\theta \end{pmatrix} \\
&= -\frac{1}{2} \begin{pmatrix} \cos\theta - 1 & \sin\theta \\ \sin\theta & -\cos\theta - 1 \end{pmatrix}
\end{aligned}$$

and obtain a polarization

$$\mathbf{P}_f = \mathrm{Tr}(\sigma\rho_f) = -(\sin\theta, 0, \cos\theta) = -\mathbf{k}_f$$

Thus the final spin is anti-aligned with the final momentum.

9.6   Two-Particle Scattering

Up until now, we've been scattering particles off of potentials. Now let's consider scattering particles off of each other. First we assume the two particles are spinless and distinguishable, with a Hamiltonian

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V(\mathbf{x}_1, \mathbf{x}_2)$$

we'll assume that the potential depend only on their separation (the relative coordinate) $V(\mathbf{x}_1, \mathbf{x}_2) = V(\mathbf{x}_1 - \mathbf{x}_2)$. It's easiest to work in the center of mass frame

$$\mathbf{x} = \mathbf{x}_1 - \mathbf{x}_2 \qquad \mathbf{x}_{CM} = \frac{m_1\mathbf{x}_1 + m_2\mathbf{x}_2}{M}$$

$$M = m_1 + m_2 \qquad \mu = \frac{m_1 m_2}{M}$$

With these substitutions the Schrodinger equation is

$$\left(-\frac{\hbar^2}{2M}\nabla^2_{\mathbf{x}_{CM}} - \frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{x}} + V(\mathbf{x}) \right) \psi(\mathbf{x}, \mathbf{x}_{CM}) = E_{tot}\psi(\mathbf{x}, \mathbf{x}_{CM})$$

The asymptotic form of the two particle wavefunction is

$$\psi(\mathbf{x}_1, \mathbf{x}_2) \to \psi_{CM}(\mathbf{x}_{CM})\psi(\mathbf{x}) = e^{i\mathbf{k}_{CM}\cdot\mathbf{x}_{CM}}\left(e^{ikz} + f(\theta, \phi)\frac{e^{ikr}}{r}\right)$$

Note that in f, we replace the mass with the reduced one $m \mapsto \mu$, which allows us to compute the cross section as

$$\left(\frac{d\sigma}{d\Omega}\right)_C M d\Omega_{CM} = |f(\theta, \phi)|^2 d\Omega_{CM}$$

The differential cross section in this frame will not be equal to that in the lab frame, however the total cross section will remain the same. The main issue between the two cross sections has to do with relating angles.
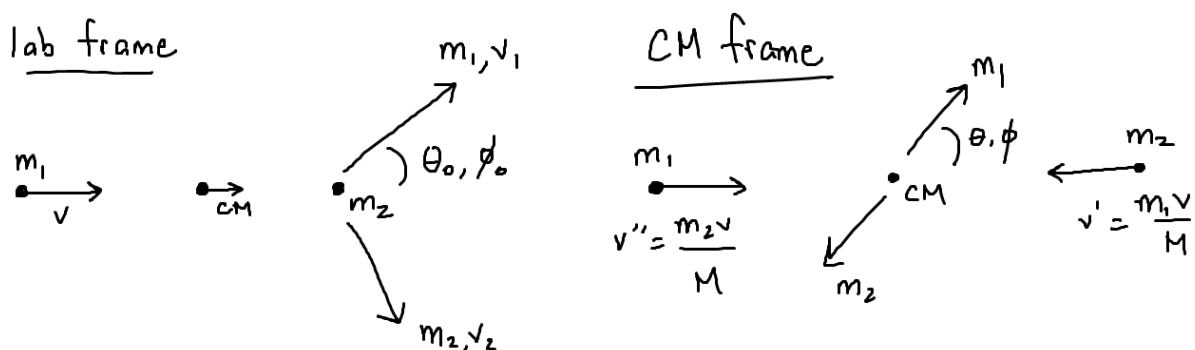
The relationship between the two sets of angles in the two frames is

$$\tan\theta_0 = \frac{\sin\theta}{m_1/m_2 + \cos\theta}$$

If the two particles have spin then we must compute a scattering matrix $\mathcal{M}$ which is 2x2 for a spin 1/2 and a spin 0, 4x4 for two spin 1/2, etc.

This immediately gets complicated if the particles are identical because the detector cannot distinguish between them, i.e. we'll get the same results for the two paths below

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For identical particles we must symmetrize the wavefunction

$$\psi(\mathbf{x}_1, \mathbf{x}_2) \to \psi(\mathbf{x}_1, \mathbf{x}_2) \pm \psi(\mathbf{x}_2, \mathbf{x}_1)$$

Note that the center of mass wavefunction ψ_{CM} is already symmetric.

We'll begin with the case of spin 0 particles (bosons), the symmetrized wavefunction is

$$\psi(\mathbf{x}_1, \mathbf{x}_2) = \psi_{CM}(\mathbf{x}_{CM})(\psi(\mathbf{x}) + \psi(-\mathbf{x})$$

Note that as $r \to \infty$

$$\psi(\mathbf{x}) + \psi(-\mathbf{x}) = e^{ikz} + e^{-ikz} + \psi_{sc}(\mathbf{x}) + \psi_{sc}(-\mathbf{x})$$

$$= e^{ikz} + e^{-ikz} + [f(\theta, \phi) + f(\pi - \theta, \pi + \phi)]\frac{e^{ikr}}{r}$$

and thus the differential cross section (in the CM frame) is

$$\left(\frac{d\sigma}{d\Omega}\right)_{CM} = |f(\theta, \phi) + f(\pi - \theta, \pi + \phi)|^2$$

for a total cross section of

$$\sigma = \frac{1}{2} \int \frac{d\sigma}{d\Omega} d\Omega$$

The 1/2 factor in front is to prevent double counting. If we introduce spin there are a bunch of cases depending on whether the spin state is symmetric or anti-symmetric

- For bosons (integer spin):

  - A symmetric spin state pairs with a symmetric spatial state

  $$\left(\frac{d\sigma}{d\Omega}\right)_{CM} = |f(\theta, \phi) + f(\pi - \theta, \pi + \phi)|^2$$

  - An antisymmetric spin state pairs with an antisymmetric spatial state

  $$\left(\frac{d\sigma}{d\Omega}\right)_{CM} = |f(\theta, \phi) - f(\pi - \theta, \pi + \phi)|^2$$

- For fermions (half-integer spin):

  - A symmetric spin state pairs with an antisymmetric spatial state

  $$\left(\frac{d\sigma}{d\Omega}\right)_{CM} = |f(\theta, \phi) - f(\pi - \theta, \pi + \phi)|^2$$

  - An antisymmetric spin state pairs with a symmetric spatial state

  $$\left(\frac{d\sigma}{d\Omega}\right)_{CM} = |f(\theta, \phi) + f(\pi - \theta, \pi + \phi)|^2$$

For instance consider the scattering two spin $1/2$ particles in which the interaction preserves total spin and is spin independent. For total spin $s = 0$

$$\psi_{sc} = \left[e^{ikz} + e^{-ikz} + (f(\theta, \phi) + f(\pi - \theta, \pi + \phi)) \frac{e^{ikr}}{r} \right] |s = 0, m_s = 0\rangle$$

$$\therefore \left(\frac{d\sigma}{d\Omega} \right)_{CM} = |f(\theta, \phi) + f(\pi - \theta, \pi + \phi)|^2$$

A similar approach works for total spin $s = 1$

$$\psi_{sc} = \left[e^{ikz} + e^{-ikz} + (f(\theta, \phi) + f(\pi - \theta, \pi + \phi)) \frac{e^{ikr}}{r} \right] |s = 1, m_s\rangle$$

$$\therefore \left(\frac{d\sigma}{d\Omega} \right)_{CM} = |f(\theta, \phi) - f(\pi - \theta, \pi + \phi)|^2$$

If the interaction preserves total spin but is spin dependent, then the f functions will not be the same, more on this later. In experimental situations there usually isn't correlations between the two initial spins (i.e. they're not all $s = 0$ or $s = 1$). Thus we generally must consider beams which may or may not have specific polarizations and use the density matrix polarization.

Note that for two unpolarized beams, first consider a heuristic argument: each beam has a $1/2$ probability of being up or down ($+$ or $-$). Clearly then, we have

$$P_{++} = P_{11} = \frac{1}{4} \qquad P_{--} = P_{1,-1} = \frac{1}{4}$$

For the mixed states, note that they are half as likely to be in $+-$ or $-+$

$$P_{10} = \frac{1}{2} P_{+-} + \frac{1}{2} P_{-+} = \frac{1}{2}\frac{1}{4} + \frac{1}{2}\frac{1}{4} = \frac{1}{4} \qquad P_{00} = \frac{1}{4}$$

Thus the unpolarized cross section is

$$\frac{d\sigma}{d\Omega} = \frac{1}{4} \left(\frac{d\sigma}{d\Omega} \right)_{s=0} + \frac{3}{4} \left(\frac{d\sigma}{d\Omega} \right)_{s=1} = \frac{1}{4}|f_+|^2 + \frac{3}{4}|f_-|^2$$

where we've defined, for convenience, the functions

$$f_+(\theta, \phi) = f(\theta, \phi) + f(\pi - \theta, \pi + \phi) \qquad f_-(\theta, \phi) = f(\theta, \phi) - f(\pi - \theta, \pi + \phi)$$

For more complicated initial states, we use the density matrix formalism. The initial (symmetrized) scattering matrix takes the form

$$\mathcal{M} = f_+(\theta, \phi)\mathcal{P}_{s=0} + f_-(\theta, \phi)\mathcal{P}_{s=1}$$

where $\mathcal{P}$ is the projection onto $s = 0, 1$ subspaces, given by

$$\mathcal{P}_{s=0} = |0\,0\rangle\,\langle 0\,0| = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} = \frac{1}{4}(\mathbb{1} - \sigma_1 \cdot \sigma_2)$$

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$$\mathcal{P}_{s=1} \sum_{m_s} |1\,m_s\rangle \langle 1\,m_s| = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = \frac{3}{4}(3\mathbb{1} + \sigma_1 \cdot \sigma_2)$$

Note that the matrix is ordered as $00, 11, 10, 1-1$ from top to bottom. For unpolarized initial spins we have

$$\rho_i = \frac{1}{4}\mathbb{1} = \frac{1}{4}\mathcal{P}_{s=0} + \frac{1}{4}\mathcal{P}_{s=1}$$

Thus the (unpolarized) cross section is

$$\frac{d\sigma}{d\Omega} = \mathrm{Tr}(\rho_i \mathcal{M}\mathcal{M}^\dagger) = \mathrm{Tr}\left[\frac{|f_+|^2}{4}\mathcal{P}_{s=0} + \frac{|f_-|^2}{4}\mathcal{P}_{s=1}\right] = \frac{1}{4}|f_+|^2 + \frac{3}{4}|f_-|^2$$

where we've used the fact

$$\mathcal{P}^2 = \mathcal{P} \qquad \mathcal{P}_{s=0}\mathcal{P}_{s=1} = 0$$

This result agrees with the previous result derived from the heuristic.

Now we consider a case with spin dependent interactions. For simplicity, let's just consider a potential of the form

$$V(\mathbf{x}) = V_1(r) + V_2(r)\sigma_1 \cdot \sigma_2$$

If we assume that the potential is small enough to be treated perturbatively, we can use the first Born approximation

$$f_{1,2}(\theta) = -\frac{m/2}{2\pi\hbar^2} \int e^{i\mathbf{q}\cdot\mathbf{x}} V_{1,2}(r) d^3 x$$

Note that

$$\sigma_1 \cdot \sigma_2 |00\rangle = -3 |00\rangle$$
$$\sigma_1 \cdot \sigma_2 |1m_s\rangle = 1 |1m_s\rangle$$

thus the scattering amplitudes are

$$f_{s=0} = f_1 - 3f_2$$
$$f_{s=1} = f_1 + f_2$$

The symmetrized scattering matrix takes the form

$$\mathcal{M} = (f_{s=0})_+ \mathcal{P}_{s=0} + (f_{s=1})_- \mathcal{P}_{s=1}$$

For notational simplicity define

$$\tilde{f}_i = f_i(\pi - \theta, \pi + \phi)$$

and the symmetrized scattering matrix is now

$$\mathcal{M} = (f_1 + \tilde{f}_1 - 3(f_2 + \tilde{f}_2))P_{s=0} + (f_1 - \tilde{f}_1 + f_2 - \tilde{f}_2)P_{s=1}$$

Example. Suppose two beams of identical spin $1/2$ particles of mass m initially moving in the $+\hat{z}$ and $-\hat{z}$ directions scatter via the potential

$$V(r) = \frac{\theta(a-r)}{r}[A + B\sigma_1 \cdot \sigma_2]$$

We'll calculate the cross section for various initial beams, first define

$$f(\theta) = -\frac{m}{\hbar^2 q}\int_0^\infty \sin(qr)\frac{\theta(a-r)}{r}r\,dr = -\frac{m}{\hbar^2 q^2}(1 - \cos(qa))$$

and for symmetry purposes define

$$\tilde{f}(\theta) = f(\pi - \theta)$$

First the case of unpolarized initial beams, the density matrix is just $\rho_i = 1/4\mathbb{1}$

$$\frac{d\sigma}{d\Omega} = \frac{1}{4}\left(\frac{d\sigma}{d\Omega}\right)_{s=0} + \frac{3}{4}\left(\frac{d\sigma}{d\Omega}\right)_{s=1} = \frac{1}{4}|(f + \tilde{f})(A - 3B)|^2 + \frac{3}{4}|(f - \tilde{f})(A + B)|^2$$

If the spins of the initial spins are parallel to the momentum, we have the initial state

$$|+-\rangle = \frac{1}{\sqrt{2}}(|00\rangle + |10\rangle)$$

which gives a cross section

$$\frac{d\sigma}{d\Omega} = \frac{1}{2}\left(\frac{d\sigma}{d\Omega}\right)_{s=0} + \frac{1}{2}\left(\frac{d\sigma}{d\Omega}\right)_{s=1} = \frac{1}{2}|(f + \tilde{f})(A - 3B)|^2 + \frac{1}{2}|(f - \tilde{f})(A + B)|^2$$

Finally, for a slightly more complicated example, suppose each beam has half it's particles in $+\hat{y}$ spin and the other half $-\hat{z}$ spin. The initial state for each beam is

$$|\psi\rangle = \frac{1}{\sqrt{2}}(|+\rangle_y + |-\rangle_z) = \frac{1}{2}(|+\rangle + (\sqrt{2} + i)|-\rangle)$$

We can compute a density matrix by first getting $|\psi\rangle_1 |\psi\rangle_2$ and then computing the matrix elements, this gives

$$|\psi_i\rangle = \frac{1}{4}[|++\rangle + (\sqrt{2} + i)(|+-\rangle + |-+\rangle) + (1 + 2i\sqrt{2})|--\rangle$$

Thus we get a density matrix

$$\rho_i = \frac{1}{16}\begin{pmatrix} 1 & -i & -i & -1 \\ i & 3 & 1 & -3i \\ i & 1 & 3 & -3i \\ -1 & 3i & 3i & 9 \end{pmatrix}$$

with the ordering $++, +-, -+, --$. This can be converted into the matrix

$$\rho_i = \frac{1}{16}\begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 1 & -i\sqrt{2} & -1 \\ 0 & i\sqrt{2} & 4 & -3i\sqrt{2} \\ 0 & 1 & 3i\sqrt{2} & 9 \end{pmatrix}$$

with the ordering $00, 11, 10, 1-1$. Thus the cross section is

$$\frac{d\sigma}{d\Omega} = |(f+\tilde{f})(A-3B)|^2 \text{Tr}(\rho_i \mathcal{P}_{s=0}) + |(f-\tilde{f})(A+B)|^2 \text{Tr}(\rho_i \mathcal{P}_{s=1})$$
$$= \frac{1}{8}|(f+\tilde{f})(A-3B)|^2 + \frac{7}{8}|(f-\tilde{f})(A+B)|^2$$

9.7   Inelastic Collisions

The final scattering situation we consider is that of a spinless free particle α off of another particle β which is bound in a potential.

The Hamiltonian in this situation is

$$H = \frac{p_\alpha^2}{2m_\alpha} + \frac{p_\beta^2}{2m_\beta} + V(|\mathbf{x}_\alpha - \mathbf{x}_\beta|) + U(\mathbf{x}_\beta)$$

where U is the binding potential for β.

Let ψ_n be the nth bound state of the potential $U(\mathbf{x}_\beta)$ with associated energies E_n, then there are three possibilities for this scattering process

$$\alpha + \psi_0 \to \begin{cases} \alpha + \psi_0 & \text{elastic scattering} \\ \alpha + \psi_n & \text{inelastic scattering} \\ \alpha + \beta & \beta \text{ ejected into continuum} \end{cases}$$

For now we consider the case of inelastic scattering,

$$|\mathbf{k}_f| \neq |\mathbf{k}_i| = k$$

Using Fermi's golden rules and integrating over final momenta, we can write down

$$\frac{d\sigma_n}{d\Omega} d\Omega = \frac{\Gamma_{\alpha \to d\Omega, x_0 \to x_n}}{j_{inc}} = \frac{k_f}{k_i} (2\pi)^4 m_\alpha^2 \hbar^2 |\langle \mathbf{k}_f \, n| V |\mathbf{k}_i \, 0\rangle| d\Omega$$

Note that when we integrate, the delta function imposes the condition

$$\frac{\hbar^2 k_i^2}{2m_\alpha} + E_0 = \frac{\hbar^2 k_f^2}{2m_\alpha} + E_n$$

and thus we define

$$k_f = \sqrt{k^2 - \frac{2m_\alpha}{\hbar}(E_n - E_0)} = \sqrt{k^2 - \gamma^2}$$

The matrix element is

$$\langle \mathbf{k}_f\, n | V | \mathbf{k}_i\, 0 \rangle = \frac{1}{(2\pi\hbar)^3} \int d^3x_\alpha dx_\beta e^{-i\mathbf{q}\cdot\mathbf{x}_\alpha} \psi_n^*(\mathbf{x}_\beta)\psi_0(\mathbf{x}_\beta) V(|\mathbf{x}_\alpha - \mathbf{x}_\beta|)$$

where $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$ as usual.

We'll change the variable of integration to $\mathbf{x}_\beta$ and $\mathbf{x} = \mathbf{x}_a - \mathbf{x}_\beta$, transforming the integral to

$$\langle \mathbf{k}_f\, n | V | \mathbf{k}_i\, 0 \rangle = \frac{1}{(2\pi\hbar)^3} \int d^3x e^{-i\mathbf{q}\cdot\mathbf{x}} V(r) \int d^3x_\beta e^{-i\mathbf{q}\cdot\mathbf{x}_\beta} \psi_n^*(\mathbf{x}_\beta)\psi_0(\mathbf{x}_\beta)$$

The last integral is called the form factor, we'll write it here again for clarity

$$F_n(\mathbf{q}) = \int d^3x_\beta e^{-i\mathbf{q}\cdot\mathbf{x}_\beta} \psi_n^*(\mathbf{x}_\beta)\psi_0(\mathbf{x}_\beta)$$

and we can write the cross section as

$$\frac{d\sigma_n}{d\Omega} = \left(\frac{k_f}{k_i}\right) |f^{(1)}(\mathbf{q})|^2 |F_n(\mathbf{q})|^2$$

where $f^{(1)}$ is just the scattering amplitude from the first Born approximation

$$f^{(1)}(\mathbf{q}) = \frac{m}{2\pi\hbar^2} \int d^3x e^{-i\mathbf{q}\cdot\mathbf{x}} V(r)$$

If $n = 0$ then we just have elastic scattering since

$$k_f = k_i = k$$

$$\frac{d\sigma_0}{d\Omega} = |f^{(0)}(\mathbf{q})|^2 |F_0(\mathbf{q})|^2$$

$$F_0(\mathbf{q}) = \int d^3x e^{-i\mathbf{q}\cdot\mathbf{x}} |\psi_0(\mathbf{x})|^2$$

so the form factor is just the Fourier transform of the number density.

Note that $F_0(\mathbf{q} = 0) = 1$. If the ground state is spherically symmetric (which is usually is), then for $\mathbf{q} \to q$, we can expand

$$F_0(\mathbf{q}) = \int d^3x |\psi_0(r)|^2 \left(1 - i\mathbf{q} \cdot \mathbf{x} - \frac{(\mathbf{q} \cdot \mathbf{x})^2}{2} + \cdots \right)$$

Note that upon integrating, the $\mathbf{q} \cdot \mathbf{x}$ term vanishes due to symmetry. The next term takes the form

$$(\mathbf{q} \cdot \mathbf{x})^2 = \sum_{i,j} \frac{q_i q_j}{2} \int x_i x_j |\psi_0(r)|^3 d^3x$$

Define

$$R^2 = \int r^2 |\psi_0(r)|^2 d^3x = \langle r_{op}^2 \rangle_0$$

and note that the integral will vanish unless $i = j$, in which case

$$(\mathbf{q} \cdot \mathbf{x})^2 = \frac{q^2 R^2}{6}$$

Thus for $qR \ll 1$, we get

$$F_0(\mathbf{q}) \to \int d^3x |\psi_0(r)|^2 \left(1 - \frac{(qR)^2}{6} + \cdots \right)$$

These results are correct to first order, if we want to improve on them we can do

$$\frac{d\sigma_0}{d\Omega} = \left(\frac{d\sigma}{d\Omega} \right)_{\text{elastic}} |F_0(\mathbf{q})|^2$$

which is known as the impulse approximation.

For the inelastic form factor, $n \neq 0$

$$F_n(\mathbf{q}) = \int d^3x e^{-i\mathbf{q} \cdot \mathbf{x}} \psi_n^*(\mathbf{x}) \psi_0(\mathbf{x})$$

and note that due to orthogonality

$$F_n(0) = \int d^3x \psi_n^*(\mathbf{x}) \psi_0(\mathbf{x}) = 0$$

Example. Suppose we scatter an electron off a neutral atom with atomic number Z, the process is

$$e^- + \psi_0(\mathbf{x}_1, \ldots, \mathbf{x}_Z) \to e^- + \psi_n(\mathbf{x}_1, \ldots, \mathbf{x}_Z)$$

Note that ψ_0, ψ_n are fully antisymmetrical due to Pauli's exclusion principle. We'll ignore any statistics between scattered and bound electrons. The potential is

$$V(\mathbf{x}) = -\frac{Ze^2}{r} + \sum_{i=1}^{Z} \frac{e^2}{|\mathbf{x} - \mathbf{x}_i|}$$

Using the fact
$$\int d^3x \frac{e^{-i\mathbf{q}\cdot\mathbf{x}}}{r} = \lim_{\mu_0 \to 0} \int d^3x \frac{e^{-i\mathbf{q}\cdot\mathbf{x}-\mu_0 r}}{r} = \frac{4\pi}{q^2}$$

we can derive

$$\frac{d\sigma_n}{d\Omega} = \frac{4m_e^2}{\hbar^4} \frac{(Ze^2)^2}{q^4} \frac{k_f}{k_i} |-\delta_{n,0} + F_n(\mathbf{q})|^2$$

$$F_n(\mathbf{q}) = \frac{1}{2} \langle n| \sum_{i=1}^{Z} e^{-i\mathbf{q}\cdot\mathbf{x}} |0\rangle$$

$$= \frac{1}{2} \int d^3x_1 \cdots d^3x_Z \psi_n^*(\mathbf{x}_1, \ldots, \mathbf{x}_Z) \left(\sum_{i=1}^{Z} e^{-i\mathbf{q}\cdot\mathbf{x}_i} \right) \psi_0(\mathbf{x}_1, \ldots, \mathbf{x}_Z)$$

Thus the inelastic cross section is

$$\frac{d\sigma_n}{d\Omega} = 4Z^2 a_0^2 \frac{k_f}{k_i} |F_n(\mathbf{q})|^2$$