QUANTUM MECHANICS I

G.H.

Contents

1. Introduction

These notes were taken in University of Delaware's PHYS811 (Quantum Mechanics I) course, taught by Dr. Alexei Kananenka in Spring 2022. I typed them based on handwritten notes taken during class each week- the hope was that a typed version would provide a better record in the future and be much more useful. Dr. Kananenka's lecture notes were self-contained, though we took material from:

- *Principles of Quantum Mechanics, R. Shankar*
- *Modern Quantum Mechanics, J.J. Sakurai & J. Napolitano*
- *Lectures of Quantum Mechanics, S. Weinberg*
- *Introduction to Quantum Mechanics, D.J. Griffiths*
- *Quantum Mechanics (Non-Relativistic Theory), L.D. Landau & E.M. Lifshitz*

Date: February 2022.

These notes are a work in progress; all mistakes are mine and mine alone (either through mistyping or a misunderstanding of the material). If you have any error corrections, tips, or general comments, please reach out to me at: ghoefer@udel.edu.

2. The foundations

2.1. **Basic concepts.** When we attempt to apply classical mechanics and electrodynamics to explain atomic phenomena, they lead to results which disagree with experimental results. As an example, consider the contradiction obtained when applying ordinary electrodynamics to a model of an atom in which electrons move around the nucleus in classical orbits: during such motion (as with any accelerated motion of charges), the electrons must emit electromagnetic waves continually and, therefore, must lose their energy. This would cause them to eventually fall into the nucleus; thus, according to classical electrodynamics, the atom would be unstable- a clear disagreement with reality.

This contradiction/gap between theory and experiment implies that any construction of a theory applicable to atomic phenomena requires a modification of the basic physical concepts and laws. Suppose we consider a well-known experiment on electron diffraction. It is found that when a homogeneous beam of electrons passes through a crystal, the emergent beam exhibits a pattern of alternate maxima and minima of intensity- similar to the diffraction pattern observed in the diffraction of electromagnetic waves. This means that under certain conditions, the behavior of material particles can display features belonging to wave processes. Through an abstraction of the previously described experiment where we pass electrons through a screen with two slits, we can show the exact results discussed above. Such an experiment shows that the mechanics which govern atomic phenomena- what we call *quantum mechanics*- must not allow for the idea that electrons move in paths. In quantum mechanics, as we shall see, there is no concept as the path of a particle.

There is a curious interrelation between quantum and classical mechanics: typically, the formulation of a more general physical theory can be done independently of a less general theory which forms a limiting case of the general. Therefore, relativistic quantum mechanics can be constructed from first principles, without reference or dependence on Newtonian mechanics. As an electron has no definite path, it must also have no dynamical characteristics (i.e. velocity, etc.). So, for a system composed only of quantum objects, it is entirely impossible to construct any logically independent mechanics. For a quantitative description of the motion of an electron to even be possible, we would need the presence of physical objects which obey classical mechanics to a "sufficient degree of accuracy". If an electron interacts with such an object (which we call *classical*), the state of the electron is (usually) altered. The nature and magnitude of this change depends on what state the electron was in, and can be used for a quantitative characterization of the electron.

In such a situation, the classical objection is typically called an *apparatus*, and the interaction with an electron is a *measurement*. However, we note that such a measurement does not necessarily involve an observer- in quantum mechanics, *any* process of interaction between classical and quantum objects is described as a measurement, and therefore oftentimes occurs apart from and independently of any observer.

Note: While we define an apparatus as a physical body which is governed (with sufficient accuracy) by classical mechanics, we do not necessarily assume the apparatus must be a non-microscopic object. The "with sufficient accuracy" condition allows for more variation than we might initially expect from such a classical object, which means we may sometimes include atomic particles.

What is a typical problem in quantum mechanics?

A typical problem in quantum mechanics consists of predicting the result of a subsequent measurement from known results of a previous measurement. As we shall see later, in comparison with classical mechanics, quantum mechanics (generally) restricts the range of values which can be obtained as a result of measuring a quantity under study. It is the methods of quantum mechanics which must enable us to determine these possible values.

The measuring process in quantum mechanics has a very important property: it always affects the electron subject to it, and is *in principle* impossible to make its effect arbitrarily small for a given accuracy of measurement. Essentially,

$$\text{The more exact the measurement} \quad \Rightarrow \text{The stronger the effect exerted by it.}$$

Only in measurements of very low accuracy can the effect on the measured object be small. This property of measurements is logically related to the fact that dynamical characteristics of an atomic particle- specifically, an electron- appear only as a result of the measurement itself. If we could make the effect of the measuring process arbitrarily small, this would suggest the measured quantity has a definite values independent of any measurement- a direct contradiction with the fact that any electron only has dynamical properties as a result of a measurement.

One measurement which plays an important role in quantum mechanics is the measurement of the coordinates of an electron. Within the limits of applicability of quantum mechanics, a measurement of the coordinates of an electron can always be performed with any desired accuracy. Suppose that at definite intervals Δt successive measurements of the coordinates of an electron are made. The results will, in general, not lie on a smooth curve (as an electron has no definite path). Indeed- the more accurate the measurement, the more discontinuous will be the variation in the results. If we leave the accuracy of the measurements unchanged, and diminish the intervals of Δt between measurements, the adjacent measurement should give neighboring values of coordinates. However, the results of a series of successive measurements, though lying in a physically small region of space, will be distributed within this region in an entirely random manner. As $\Delta t \to 0$, this implies that the quotient of the coordinates of a particle at two instances in time divided by Δt does not exist. Thus, a classical concept of velocity is not defined for a particle in quantum mechanics.

However, we shall see that we may still give a "reasonable" definition of the velocity of a particle at a given instant. The difference will lie in what this says about a quantitative definition of other characteristics of the particle: if velocity is well-defined at a given instance, the particle cannot have definite coordinates (as otherwise this would imply the existence of a definite path for the particle). Similarly, if we have (as the result of a measurement) definite coordinates for a particle, a definite velocity cannot be obtained. These two quantities cannot be simultaneously measured.

In classical mechanics, a complete description of the state of a physical system amounts to stating all coordinates and velocities at a given instant. Using the initial data from such a description, we can derive equations of motion which completely determine the system at all subsequent times. However, such a description in quantum mechanics is impossible (as coordinates and corresponding velocities cannot simultaneously exist). Therefore, a description of the state of a quantum system is limited to a smaller number of quantities than in classical mechanics. Additionally, even if we have a complete (within quantum mechanics) description of the state of a system, we are not able to determine with complete accuracy the future behavior of said system. This is what makes quantum *fundamentally* probabilistic.

All measuring processes in quantum mechanics may be divided into two classes. In one (which contains the majority of measurements), we find that they do not, in any state of

the system, lead to a unique result with certainty. The other class contains the measurements for which every possible result of measurement there exists a state in which said measurement leads with certainty to that result. These are known as "predictable".

Definition 2.1. *Suppose that a set of physical quantities S can be simultaneously measured, but if they all have definite values no other physical quantity which is not a function of quantities in S can have a definite value in that state. We say the set S is a complete set.*

Any description of the state of an electron arises as the result of some measurement. We say a state is completely described if it occurs as a result of the simultaneous measurement of a complete set of physical quantities. From the results of such a measurement, we can (in particular) determine the probability of various results of subsequent measurements, regardless of the history of the electron prior to the first measurement.

2.2. **Mathematical background.** We begin by reviewing the basics of vector spaces. We omit some of the more detailed (and elementary) explanations included in Shankar based on our mathematical background.

Definition 2.2. *A vector space V over a field $\mathbb{F}$ consists of the following:*

(i) *a collection of objects, called vectors;*

(ii) *a commutative, associative binary operation $+$ which associates any two $v_1, v_2 \in V$ to a vector $v_1 + v_2 \in V$ in such a way that*
- *there exists a unique vector $0 \in V$ such that $0 + v = v$ for all $v \in V$;*
- *for each $v \in V$ there exists a unique vector $-v \in V$ such that $v + (-v) = 0$.*

(iii) *a binary operation $\cdot$ which associates with any $v \in V$ and any scalar $c \in \mathbb{F}$ a vector $c \cdot v \in V$ in such a way that*
- *$1 \cdot v = v$ for all $v \in V$;*
- *$(c_1 c_2) \cdot v = c_1 \cdot (c_2 v)$;*
- *$c \cdot (v + w) = c \cdot v + c \cdot w$;*
- *$(c_1 + c_2) \cdot v = c_1 v + c_2 v$.*

Definition 2.3. *A set of vectors $\{v_1, \ldots, v_n\} \subseteq V$ is linearly independent if the only time there exists scalars $\lambda_1, \ldots, \lambda_n \in \mathbb{F}$ such that*

$$\sum_{i=1}^{n} \lambda_i v_i = 0,$$

then $\lambda_1 = \cdots = \lambda_n = 0$.

Definition 2.4. *We say that a set of vectors $\{v_1, \ldots, v_n\} \subseteq V$ forms a spanning set of V if any vector $v \in V$ may be written as a linear combination of the vectors $v_1, \ldots, v_n$.*

Definition 2.5. *If a set of vectors $\{v_1, \ldots, v_n\} \subseteq V$ are linearly independent and form a spanning set for V, we call the set a basis for V. We (furthermore) define $\dim(V)$ as the cardinality of any basis for V.*

Definition 2.6. *For any vector $v \in V$, the coefficients in the expansion of v with respect to a basis $\{v_1, \ldots, v_n\}$ of the space are called the components of the vector in that basis.*

Note: It is quite easy to verify that the components of a vector with respect to a basis are unique; however, if we change the basis we are using, the components necessarily change.

Definition 2.7. *Let $\mathbb{F}$ be a field, and V a vector space over $\mathbb{F}$. An inner product on V is a function which assigns to each ordered pair of vectors $v, w \in V$ a scalar $\langle v, w \rangle \in \mathbb{F}$ such that for all $v, w, u \in V$ and $c \in \mathbb{F}$:*

(i) $\langle v + w, u \rangle = \langle v, u \rangle + \langle w, u \rangle$;

(ii) $\langle cv, w \rangle = c\langle v, w \rangle$;

(iii) $\langle w, v\rangle = \overline{\langle v, w\rangle}$;
(iv) $\langle v, v\rangle > 0$ *if* $v \neq 0$.

Definition 2.8. *We call a vector space V over a field $\mathbb{F}$ endowed with an inner product an inner product space.*

Definition 2.9. *We say $v, w \in V$ are orthogonal if $\langle v, w\rangle = 0$. If $\mathcal{B} = \{v_1, \ldots, v_n\}$ is a basis for V, we say $\mathcal{B}$ is an orthonormal basis if the vectors in $\mathcal{B}$ are pairwise orthogonal and have norm 1.*

We pause here to briefly discuss a matter of notation that we will adopt for the remainder of the course- this is to introduce the notion of "Dirac notation". Up until the current moment, the standard notation to use for an inner product space (or any vector space in general) was to denote a vector using v in the space V; similarly, for elements of the dual space V^*, we denoted linear functionals typically using $\phi \in V^*$. Dirac notation is an alternative way of pairing vectors in a space V with functionals in V^*: in Dirac notation, we let $|v\rangle$ denote a vector in the space V, while $\langle w|$ denotes some linear functional in V^*. This notation is oftentimes clearer when showing the connection between vectors and functionals, along with the relationship between a linear operator and the adjoint in an inner product space.

Remark: To help us get a better grasp on Dirac notation, we will give the explicit formulation of how to switch between a representation of a vector with respect to some basis, and its adjoint. Let $|v\rangle \in V$, with $\mathcal{B} = \{|1\rangle, \ldots, |n\rangle\}$ an orthonormal basis for inner product space V. We have the following expansion for $|v\rangle$ with respect to $\mathcal{B}$:

$$|v\rangle = \sum_{i=1}^{n} v_i |i\rangle,$$
$$\Rightarrow v_i = \langle i|v\rangle, \quad i = 1, \ldots, n.$$

The adjoint of $|v\rangle$ is then given by

$$\langle v| = \sum_{i=1}^{n} \langle i| v_i^*.$$

If we recall that $v_i = \langle i|v\rangle, v_i^* = \langle v|i\rangle$, the equations above simplify to

$$|v\rangle = \sum_{i=1}^{n} \langle i| \langle i|v\rangle,$$
$$\langle v| = \sum_{i=1}^{n} \langle v|i\rangle \langle i|.$$

Theorem 2.10 (Cauchy-Schwarz Inequality)**.** *For an inner product space V and any vectors $|v\rangle, |w\rangle \in V$ we have*

$$|\langle v|w\rangle|^2 \leq \langle v|v\rangle \langle w|w\rangle.$$

Proof. Let

$$|z\rangle = |v\rangle - \frac{\langle w|v\rangle}{\|w\|^2} |w\rangle.$$

As $\langle z|z\rangle \geq 0$, we have

$$\langle z|z\rangle = \langle v - \frac{\langle w|v\rangle}{\|w\|^2} w | v - \frac{\langle w|v\rangle}{\|w\|^2} w\rangle$$
$$= \langle v|v\rangle - \frac{\langle w|v\rangle \langle v|w\rangle}{\|w\|^2} - \frac{\langle w|v\rangle^* \langle w|v\rangle}{\|w\|^2} + \frac{\langle w|v\rangle^* \langle w|v\rangle \langle w|w\rangle}{\|w\|^4} \geq 0.$$

As $\langle w|v\rangle^* = \langle v|w\rangle$, the above simplifies to

$$\langle v|v\rangle \geq \frac{\langle w|v\rangle \langle v|w\rangle}{\|w\|^2}$$
$$\Rightarrow |\langle v|w\rangle|^2 \leq \langle v|v\rangle \|w\|^2 = \langle v|v\rangle \langle w|w\rangle .$$

□

Theorem 2.11 (Triangle Inequality)**.** *In an inner product space V, for $|v\rangle, |w\rangle \in V$ we have*

$$\|v + w\| \leq \|v\| + \|w\|.$$

Proof. We shall provide a proof at a later date. □

Definition 2.12. *For a vector space V, we say a subset $W \subseteq V$ is a subspace if W is itself a vector space.*

Definition 2.13. *For a vector space V and $T, S \in \mathcal{L}(V)$, we define the commutator $[\cdot, \cdot]$ on $\mathcal{L}(V)$ as the operation*

$$[T, S] = TS - ST.$$

Remarks:

(i) Note that the commutator here is the same as we have seen in previous algebra courses, along with the commutator defined on a Banach algebra.

(ii) There are two identities related to the commutator that are oftentimes useful:

$$[T, SU] = S[T, U] + [T, S]U, \tag{1}$$
$$[ST, U] = S[T, U] + [S, U]T. \tag{2}$$

These are easy to verify by hand.

Shankar includes a large amount of exposition on the basics of linear operators and representing them as a matrix with respect to some basis, but we will skip including this material in these notes as we find it unnecessary.

Definition 2.14. *Let T be a linear operator on a vector space V. We say*

(i) T is Hermitian (or self-adjoint) if $T^* = T$;

(ii) T is skew-Hermitian if $T^* = -T$.

Remark: As we might expect, we have a "Jordan"-like decomposition of any operator into self-adjoint and skew-self-adjoint parts:

$$T = \frac{T + T^*}{2} + \frac{T - T^*}{2}.$$

Definition 2.15. *An operator U is unitary if $U^*U = UU^* = I$.*

Remarks:

(i) Unitary operators preserve the inner product on a vector space.

(ii) If U is a unitary operator acting on a finite dimensional dimensional vector space, the columns of a matrix representation of U will be orthonormal vectors.

Active versus passive transformations

We will spend a brief amount of time spent discussing the difference between what is called an "active transformation" of an operator, versus a "passive transformation". Suppose we subject all vectors $|v\rangle$ in a finite-dimensional space V to a unitary transformation

$$|v\rangle \mapsto U|v\rangle .$$

For any operator T, the matrix elements of this operator will be modified as follows:

$$\langle v'|Tv\rangle \to \langle Uv'|T(Uv)\rangle = \langle v'|U^*TUv\rangle\,.$$

This change will remain the same if we instead left the vectors in V alone, and conjugated all operators via

$$T \mapsto U^*TU.$$

The first case is an example of an *active transformation*, while the second is a *passive transformation*.

In what follows, we list a few theorems involving the spectral theory of operators on finite dimensional vector spaces; we shall omit the proofs, as it is ultimately unnecessary (and we have already seen extensive proofs in MATH672).

Theorem 2.16. *The eigenvalues of a Hermitian operator are real.*

Theorem 2.17. *If T is a Hermitian operator on a finite dimensional vector space V, there exists a basis for V consisting entirely of orthonormal eigenvectors. Furthermore, the matrix representation of T with respect to this basis is diagonal, with eigenvalues as its entries.*

Theorem 2.18. *The eigenvalues of a unitary operator are complex numbers which lie on $\mathbb{S}$, the unit circle (i.e. they all have unit modulus).*

Theorem 2.19. *The eigenvectors of a unitary operator are mutually orthogonal (assuming no degeneracy).*

Theorem 2.20. *If T, S are two commuting Hermitian operators, there exists a basis of common eigenvectors which diagonalizes them both.*

Derivatives of operators with respect to parameters

In what follows, we assume T is Hermitian unless specified otherwise. Using the continuous functional calculus, we know that applying continuous functions to T is well-defined-specifically, power series of T (when convergent), and powers of T will give us other operators on V. A very important function of an operator in quantum mechanics (as we shall see in the future) is the exponential function

$$e^T = \sum_{n=1}^{\infty} \frac{T^n}{n!}.$$

Suppose we define an operator $\theta(\lambda)$ which depends on the parameter λ. The derivative of $\theta(\lambda)$ with respect to λ is written as one might expect:

$$\frac{d\theta(\lambda)}{d\lambda} = \lim_{\Delta\lambda\to 0}\left[\frac{\theta(\lambda+\Delta\lambda)-\theta(\lambda)}{\Delta\lambda}\right].$$

If $\theta(\lambda)$ is written in some basis, the matrix representing the operator $\frac{d\theta(\lambda)}{d\lambda}$ is obtained by differentiating the entries of $\theta(\lambda)$.

We will consider the special case of the operator $\theta(\lambda) = e^{\lambda T}$, for T as above. Going by the eigenbasis of T (as T is Hermitian), we have

$$\frac{d\theta(\lambda)}{d\lambda} = Te^{\lambda T} = \theta(\lambda)T.$$

In fact, the same may be said even if T is not Hermitian but assuming the power series $\sum_{n=1}^{\infty} \frac{\lambda^n T^n}{n!}$ exists (I think a sufficient condition for this to occur is if T is normal- the functional calculus should still apply).

Conversely, we can say if we are given the differential equation

$$\frac{d\theta(\lambda)}{d\lambda} = \theta(\lambda)T,$$

the solution is given by

$$\theta(\lambda) = ce^{\left(\int_0^\lambda T d\lambda'\right)} = ce^{\lambda T}.$$

In the above, c stands for a constant operator. If we specifically choose $c = I$, then the solution is exactly what we started with originally- $\theta(\lambda) = e^{\lambda T}$.

The rest of the material in the first chapter of Shankar is a discussion of the generalization of operators to infinite dimensions, which we will not include here; for a more detailed description, see the notes written for MATH806.

We will finish this section with a few examples which integrate the concepts we have discussed above.

Example: We will derive the standard relationship between an operator and its adjoint, but using the braket notation. Suppose Ω is an operator on a Hilbert space, with adjoint $\Omega^\dagger$. If we assume Ω has a matrix representation (Ω_{ij}) with respect to some basis, we want to try and determine $(\Omega^\dagger)_{ij}$ with respect to the same basis. By definition, we have

$$(\Omega^\dagger)_{ij} = \langle i|\Omega^\dagger|j\rangle = \langle \Omega i|j\rangle = \langle j|\Omega i\rangle^* = \Omega^*_{ji}.$$

As this holds for any of our indices, we have the result we would expect: if $\Omega^\dagger$ is expressed in the same basis as Ω, its matrix representation is the conjugate transpose of the matrix representation for Ω.

Example: In this example, we will find a matrix representation of the operator $\hat{H} = \overrightarrow{S_1} \cdot \overrightarrow{S_2}$ with respect to the basis $\{|\uparrow\rangle, |\downarrow\rangle\}$. Here $|\uparrow\rangle, |\downarrow\rangle$ denote upward and downward spin. We recall that in a single system, the operator $\overrightarrow{S}$ is defined via

$$\overrightarrow{S} = \hat{S}_x + \hat{S}_y + \hat{S}_z,$$

where

$$\hat{S}_x = \frac{\hbar}{2}\hat{\sigma}_x, \quad \hat{S}_y = \frac{\hbar}{2}\hat{\sigma}_y, \quad \hat{S}_z = \frac{\hbar}{2}\hat{\sigma}_z$$

and

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

Let

$$|\uparrow\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \quad |\downarrow\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix}.$$

The operator $\overrightarrow{S}_1 \cdot \overrightarrow{S}_2$ is the product of individual operators $\overrightarrow{S_i}$ which act on their own respective systems, for $i = 1, 2$. To describe the joint system, we use the tensor product of states in the individual systems; this will form the basis

$$\{|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle\}$$

where

$$|\uparrow\uparrow\rangle = |\uparrow\rangle \otimes |\uparrow\rangle = \begin{bmatrix}1\\0\\0\\0\end{bmatrix}, \quad |\uparrow\downarrow\rangle = |\uparrow\rangle \otimes |\downarrow\rangle = \begin{bmatrix}0\\1\\0\\0\end{bmatrix},$$

$$|\downarrow\uparrow\rangle = |\downarrow\rangle \otimes |\uparrow\rangle = \begin{bmatrix}0\\0\\1\\0\end{bmatrix}, \quad |\downarrow\downarrow\rangle = |\downarrow\rangle \otimes |\downarrow\rangle = \begin{bmatrix}0\\0\\0\\1\end{bmatrix}.$$

As we wish to find the matrix representation of

$$\overrightarrow{\hat{S}}_1 \cdot \overrightarrow{\hat{S}}_2 = \hat{S_{1x}}\hat{S_{2x}} + \hat{S_{1y}}\hat{S_{2y}} + \hat{S_{1z}}\hat{S_{2z}}$$

with respect to the basis above, we may determine the matrix coefficients by figuring out how the individual operators act on the spin vectors.

We have

$$\hat{S_x}\,|\uparrow\rangle = \frac{\hbar}{2}\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}\begin{bmatrix}1\\0\end{bmatrix} = \frac{\hbar}{2}\,|\downarrow\rangle\,.$$

Using basic rules of tensor product multiplication, we then have

$$\hat{S_{1x}}\hat{S_{2x}}\,|\uparrow\uparrow\rangle = \frac{\hbar^2}{4}\,|\downarrow\downarrow\rangle\,.$$

Similarly,

$$\hat{S_y}\,|\uparrow\rangle = \frac{\hbar}{2}\begin{bmatrix}0 & -i\\i & 0\end{bmatrix}\begin{bmatrix}1\\0\end{bmatrix} = \frac{i\hbar}{2}\,|\downarrow\rangle\,.$$

Thus,

$$\hat{S_{1y}}\hat{S_{2y}}\,|\uparrow\uparrow\rangle = \frac{\hbar^2}{4}\,|\downarrow\downarrow\rangle\,.$$

Finally,

$$\hat{S_z}\,|\uparrow\rangle = \frac{\hbar}{2}\begin{bmatrix}1 & 0\\0 & -1\end{bmatrix}\begin{bmatrix}1\\0\end{bmatrix} = \frac{\hbar}{2}\,|\uparrow\rangle\,,$$

and therefore

$$\hat{S_{1z}}\hat{S_{2z}}\,|\uparrow\uparrow\rangle = \frac{\hbar^2}{4}\,|\uparrow\uparrow\rangle\,.$$

We work out the others similarly, using direct computation:

$$\hat{S_x}\,|\downarrow\rangle = \frac{\hbar}{2}\,|\uparrow\rangle\,, \quad \hat{S_y}\,|\downarrow\rangle = -\frac{i\hbar}{2}\,|\uparrow\rangle\,, \quad \hat{S_z}\,|\downarrow\rangle = -\frac{\hbar}{2}\,|\downarrow\rangle\,.$$

Then

$$\hat{S_{1x}}\hat{S_{2x}}\,|\uparrow\downarrow\rangle = \frac{\hbar^2}{4}\,|\downarrow\uparrow\rangle\,, \quad \hat{S_{1y}}\hat{S_{2y}}\,|\uparrow\downarrow\rangle = \frac{\hbar^2}{4}\,|\downarrow\uparrow\rangle\,, \quad \hat{S_{1z}}\hat{S_{2z}}\,|\uparrow\downarrow\rangle = -\frac{\hbar^2}{4}\,|\uparrow\downarrow\rangle\,.$$

This means

$$\hat{S}_1 \cdot \hat{S}_2\,|\uparrow\downarrow\rangle = -\frac{\hbar^2}{4}\,|\uparrow\downarrow\rangle + \frac{\hbar^2}{2}\,|\downarrow\uparrow\rangle\,.$$

While we omit the rest of the computations directly, we have the matrix representation of $\hat{S}_1 \cdot \hat{S}_2$ with respect to $\{|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle\}$ given via

$$\hat{S}_1 \cdot \hat{S}_2 = \begin{bmatrix}\frac{\hbar^2}{4} & 0 & 0 & 0\\0 & -\frac{\hbar^2}{4} & \frac{\hbar^2}{2} & 0\\0 & \frac{\hbar^2}{2} & -\frac{\hbar^2}{4} & 0\\0 & 0 & 0 & \frac{\hbar^2}{4}\end{bmatrix}.$$

Example: Suppose we wish to find a matrix representation of $e^{\hat{S_1}\cdot\hat{S_2}}$ (which is well-defined, as $\hat{S_1}\cdot\hat{S_2}$ is self-adjoint). The general process in this case would be to first find the unitary matrix U which diagonalizes $\hat{S_1}\cdot\hat{S_2}$; once we have it, we can directly write out the expression

$$e^{\hat{S_1}\cdot\hat{S_2}} = U^\dagger \begin{bmatrix} e^{\lambda_1} & 0 & 0 & 0 \\ 0 & e^{\lambda_2} & 0 & 0 \\ 0 & 0 & e^{\lambda_3} & 0 \\ 0 & 0 & 0 & e^{\lambda_4} \end{bmatrix} U,$$

where $\lambda_1, \ldots, \lambda_4$ are the eigenvalues for $\hat{S_1}\cdot\hat{S_2}$. For alternative manipulations of $e^{\hat{S_1}\cdot\hat{S_2}}$, we can use the standard power series expansion.

Remark: On the first homework assignment, Problem 3(f), the operator $\hat{L}$ defined via

$$\hat{L}\hat{P} = \hat{H}\hat{P} - \hat{P}\hat{H}$$

acts on operators $\hat{P}$, sending it to the commutator with a fixed element $\hat{H}$. This operator $\hat{H}$ is not specifically the Hamiltonian, just another fixed operator. If we specifically pick $\hat{H}$ as a Hamiltonian, the operator $\hat{L}$ is known as the *Liouvillian operator.*

Definition 2.21. *For an operator Ω, the expectation value of Ω when a system is in state $|\psi\rangle$ is denoted $\langle\Omega\rangle$ and defined via*

$$\langle\Omega\rangle = \langle\psi|\Omega|\psi\rangle\,.$$

Note: The standard interpretation of the expectation value for an operator is that it represents the measurement of said operator on the system in state $|\psi\rangle$.

Example: Suppose we have a system in state $|\psi\rangle = c_1\,|\uparrow\rangle + c_2\,|\downarrow\rangle$, and we consider the operator

$$\hat{\sigma_z} = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

with respect to the basis $\{|\uparrow\rangle, |\downarrow\rangle\}$. The expectation value is computed as

$$\langle\hat{\sigma_z}\rangle = \langle\psi|\hat{\sigma_z}|\psi\rangle = \begin{bmatrix} c_1^* & c_2^* \end{bmatrix} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = |c_1|^2 - |c_2|^2.$$

2.3. **Introducing important operators.**

A brief aside on Poisson brackets

In classical mechanics, if we have a system of N particles, the state of this system is determined by the position and momentum $(\mathbf{q}, \mathbf{p})$ where $\mathbf{p} = (p_1, \ldots, p_N)$ and $\mathbf{q} = (q_1, \ldots, q_N)$. The classical equations of motion are described via

$$\frac{dq_k}{dt} = \frac{\partial H}{\partial p_k}, \quad \frac{dp_k}{dt} = -\frac{\partial H}{\partial q_k}$$

for $k = 1, \ldots, N$ where H is the Hamiltonian. If we have a function $F(q_1, \ldots, q_N, p_1, \ldots, p_N, t)$ of coordinates, momenta and time we write

$$\frac{dF}{dt} = \frac{\partial F}{\partial t} + \sum_{i=1}^{N} \left(\frac{\partial F}{q_k}\frac{dq_k}{dt} + \frac{\partial F}{\partial p_k}\frac{dp_k}{dt} \right) = \frac{\partial F}{\partial t} + \{H, F\}.$$

We get this using the relations for the equations of motion above, and by the definition of the Poisson bracket:

$$\{H, F\} = \sum_{k=1}^{N} \left(\frac{\partial F}{\partial p_k}\frac{\partial H}{\partial q_k} - \frac{\partial F}{\partial q_k}\frac{\partial H}{\partial p_k} \right).$$

Note that for $k \neq \ell$, we have

$$\{q_k, q_\ell\} = \{p_k, p_\ell\} = 0, \quad \{p_k, q_\ell\} = \delta_{k\ell}.$$

Dirac attempted to find some sort of analog operation which relates operators in a similar way, when developing the foundations of quantum mechanics. The analog we settle on is the commutator $[\cdot, \cdot]$.

Recall that

$$\{F_1 F_2, G\} = F_1\{F_2, G\} + \{F_1, G\}F_2.$$

If we suppose $\hat{F}, \hat{G}$ are operators, using the above equation we can write

$$\{\hat{F}_1\hat{F}_2, \hat{G}\} = \hat{F}_1\{\hat{F}_2, \hat{G}\} + \{\hat{F}_1, \hat{G}\}\hat{F}_2,$$
$$\{\hat{F}, \hat{G}_1\hat{G}_2\} = \hat{G}_1\{\hat{F}_1, \hat{G}_2\} + \{\hat{F}_1, \hat{G}_1\}\hat{G}_2.$$

If we let $\hat{G} = \hat{G}_1\hat{G}_2$, using the relations above we can derive

$$\{\hat{F}_1\hat{F}_2, \hat{G}_1\hat{G}_2\} = \hat{F}_1\hat{G}_1\{\hat{F}_2, \hat{G}_2\} + \hat{F}_1\{\hat{F}_2, \hat{G}_1\}\hat{G}_2 + \hat{G}_1\{\hat{F}_1, \hat{G}_2\}\hat{F}_2 + \{\hat{F}_1, \hat{G}_1\}\hat{G}_2\hat{F}_2.$$

Similarly, if we instead let $\hat{F} = \hat{F}_1\hat{F}_2$ we find

$$\{\hat{F}_1\hat{F}_2, \hat{G}_1\hat{G}_2\} = \hat{G}_1\hat{F}_1\{\hat{F}_2, \hat{G}_2\} + \hat{G}_1\{\hat{F}_1, \hat{G}_2\}\hat{F}_2 + \hat{F}_1\{\hat{F}_2, \hat{G}_1\}\hat{G}_2 + \{\hat{F}_1, \hat{G}_1\}\hat{F}_2\hat{G}_2.$$

These together imply

$$(\hat{F}_1\hat{G}_1 - \hat{G}_1\hat{F}_1)\{\hat{F}_2, \hat{G}_2\} = \{\hat{F}_1, \hat{G}_1\}(\hat{F}_2\hat{G}_2 - \hat{G}_2\hat{F}_2).$$

This is true only if

$$\{\hat{F}, \hat{G}\} = c(\hat{F}\hat{G} - \hat{G}\hat{F})$$

for some constant c. Additionally,

$$\{\hat{F}, \hat{G}\}^\dagger = c^*(\hat{G}^\dagger\hat{F}^\dagger - \hat{F}^\dagger\hat{G}^\dagger) = -c^*\{\hat{F}\hat{G} - \hat{G}\hat{F}\}.$$

Thus, if we require that the Poisson bracket of two physical quantities to be real, we need $c^* = -c$- so $c = i$ (or specifically, $c = \frac{i}{\hbar}$ where $\hbar$ was determined via experimental verification). This shows that we have the following relationship between the classical Poisson bracket and the commutator:

$$\{\hat{F}, \hat{G}\} = \frac{i}{\hbar}\left(\hat{F}\hat{G} - \hat{G}\hat{F}\right) = \frac{i}{\hbar}[\hat{F}, \hat{G}].$$

The Hamiltonian

Assume we have a system, and that our system is described by a state $|\psi\rangle$. To determine the "characteristics" of our system (i.e., most, if not all, of the relevant information about it), we will use this state to compute the expectation value of various operators which measure quantities in our system. If the state a system is described via some $|\psi\rangle$, it must tell us not only all properties of the system at a given moment in time, but also the properties at all subsequent times. This means that the time derivative $\frac{\partial|\psi\rangle}{\partial t}$ (denoted $|\dot{\psi}\rangle$) must be well defined, and via the superposition principle the relation between $|\dot{\psi}\rangle$ and $|\psi\rangle$ must be linear. In other words, suppose our state also has a well-defined derivative with respect to time, which satisfies the equation

$$\frac{\partial}{\partial t}|\psi\rangle = |\dot{\psi}\rangle = -\frac{i}{\hbar}\hat{H}|\psi\rangle$$

where $\hat{H}$ is some linear operator. This equation is known as the *Time-Dependent Schrödinger Equation*; it connects the state of the system to its derivative.

Question: What are some properties of the operator $\hat{H}$?

We wish to determine some of the properties of the operator $\hat{H}$, if at all possible. We will start from the fact that

$$\frac{\partial}{\partial t}\langle\psi|\psi\rangle = 0,$$

as the inner product $\langle\cdot|\cdot\rangle$ is a scalar. Using basic derivative properties, we expand the equation directly above and write

$$0 = \frac{\partial}{\partial t}\langle\psi|\psi\rangle = \langle\dot{\psi}|\psi\rangle + \langle\psi|\dot{\psi}\rangle\,.$$

As

$$|\dot{\psi}\rangle = -\frac{i}{\hbar}\hat{H}\,|\psi\rangle\,, \quad \langle\dot{\psi}| = \frac{i}{\hbar}\,\langle\psi|\,\hat{H}^*,$$

if we substitute these equalities into our derivative above we find

$$0 = \frac{i}{\hbar}\,\langle\psi|\hat{H}^*|\psi\rangle - \frac{i}{\hbar}\,\langle\psi|\hat{H}|\psi\rangle\,.$$

This implies $\hat{H}$ is a Hermitian operator.

Before continuing with our initial investigation into the Hamiltonian $\hat{H}$, we will pause to develop the *time-derivative of an expectation value*. The time-derivative of an expectation value for an operator $\hat{\Omega}$ is defined via

$$\frac{d}{dt}\langle\hat{\Omega}\rangle = \langle\frac{d\hat{\Omega}}{dt}\rangle.$$

We wish to find an explicit formula for this derivative. If our system is in state $|\psi\rangle$, again using basic derivative properties we can expand the expectation value to find

$$\frac{d}{dt}\,\langle\psi|\hat{\Omega}|\psi\rangle = \langle\dot{\psi}|\hat{\Omega}|\psi\rangle + \langle\psi|\dot{\hat{\Omega}}|\psi\rangle + \langle\psi|\hat{\Omega}|\dot{\psi}\rangle\,.$$

If we again substitute in the formula $i\hbar\,|\dot{\psi}\rangle = \hat{H}\,|\psi\rangle$ into the equation above, after simplification we find

$$\begin{aligned}\frac{d}{dt}\,\langle\psi|\hat{\Omega}|\psi\rangle &= \langle\psi|\left(\frac{\partial\hat{\Omega}}{\partial t} + \frac{i}{\hbar}(\hat{H}\hat{\Omega} - \hat{\Omega}\hat{H})\right)|\psi\rangle \\ &= \langle\psi|\left(\frac{\partial\hat{\Omega}}{\partial t} + \frac{i}{\hbar}[\hat{H},\hat{\Omega}]\right)|\psi\rangle\,.\end{aligned}$$

Then as $\frac{d}{dt}\langle\hat{\Omega}\rangle = \langle\frac{d\hat{\Omega}}{dt}\rangle$, this implies

$$\frac{d\hat{\Omega}}{dt} = \frac{\partial\hat{\Omega}}{\partial t} + \frac{i}{\hbar}[\hat{H},\hat{\Omega}].$$

This equation is known as the *Heisenberg equation of motion* for an operator $\hat{\Omega}$. Operators $\hat{\Omega}$ which satisfy

$$\frac{d\hat{\Omega}}{dt} = \frac{\partial\hat{\Omega}}{\partial t} + \frac{i}{\hbar}[\hat{H},\hat{\Omega}] = 0$$

correspond to quantities which are called "conserved". Consider the Hamiltonian operator for a closed system; the Hamiltonian $\hat{H}$ cannot explicitly depend on time, as for a closed system all times are equivalent. As any operator always commutes with itself, we see in this closed system

$$\frac{d\hat{H}}{dt} = 0 + \frac{i}{\hbar}[\hat{H},\hat{H}] = 0.$$

Thus, $\hat{H}$ is conserved.

In general, if the operator for some quantity is conserved, it commutes with the Hamiltonian; this means that any physical quantity which is conserved can be measured simultaneously with energy. Therefore, the Hamiltonian measures some conserved quantity in our system- specifically, *the energy of the system.* The law of conservation of energy means

that if we prepare a system with a definite value of energy, its value remains constant in time. States in which energy has definite values are called *stationary states*; we will consider them in further detail later on.

Remark: There is a classical mechanical analogue to Heisenberg's Equation of Motion: for some function F of position and momentum, we have

$$\frac{dF}{dt} = \frac{\partial F}{\partial t} + \{H, F\}$$

where H is the classical Hamiltonian, and $\{\cdot, \cdot\}$ is the Poisson bracket.

Theorem 2.22 (Ehrenfest Theorem)**.** *For a particle with position operator x and momentum operator p moving in a scalar potential $V(x)$, we have*

$$m\frac{d\langle x\rangle}{dt} = \langle p\rangle,$$
$$\frac{d\langle p\rangle}{dt} = -\langle V'(x)\rangle.$$

Proof. Using the Heisenberg Equation of Motion, we see

$$\frac{d\langle x\rangle}{dt} = \frac{i}{\hbar}\langle[\hat{H}, x]\rangle = \frac{i}{\hbar}\langle[(p^2/2m), x]\rangle = \left\langle \frac{p}{m} \right\rangle,$$

while

$$\frac{d\langle p\rangle}{dt} = \frac{i}{\hbar}\langle[\hat{H}, p]\rangle = \frac{i}{\hbar}\left\langle \left[V(x), \frac{\hbar}{i}\frac{d}{dx}\right] \right\rangle = -\left\langle \frac{dV(x)}{dx} \right\rangle.$$

□

The Momentum Operator

Consider a system of particles free from any external fields; all positions in space of such a system are equivalent. Equivalently, we can say that the Hamiltonian (energy) of such a system does not change when the system undergoes a parallel displacement. Consider the arbitrarily small displacement $\delta\mathbf{r}$ changing the radius vectors $\mathbf{r}_\alpha$ of all particles via

$$\mathbf{r}_\alpha \mapsto \mathbf{r}_\alpha + \delta\mathbf{r}.$$

An arbitrary function of the coordinates then becomes

$$\Psi(\mathbf{r}_1 + \delta\mathbf{r}, \mathbf{r}_2 + \delta\mathbf{r}, \ldots) = \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots) + \delta\mathbf{r} \cdot \sum_\alpha \nabla_\alpha \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots) + \cdots$$
$$= \left(1 + \delta\mathbf{r} \cdot \sum_\alpha \nabla_\alpha\right)\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots),$$

where ∇_α denotes a vector with components $\left\{\frac{\partial}{\partial x_\alpha}, \frac{\partial}{\partial y_\alpha}, \frac{\partial}{\partial z_\alpha}\right\}$ and the expression in parenthesis can be understood as a displacement operator:

$$\hat{O} = \left(1 + \delta\mathbf{r} \cdot \sum_\alpha \nabla_\alpha\right).$$

Suppose we look at how $\hat{O}, \hat{H}$ act on some state. Since $\hat{O}$ changes only position in the system but <u>not</u> the energy (as a displacement operator), we have

$$\hat{O}(\hat{H}\,|\psi\rangle) = \hat{H}(\hat{O}\,|\psi\rangle) \Rightarrow [\hat{H}, \hat{O}] = 0.$$

We can even simplify the operator $\hat{O}$ slightly: as we are already perturbing each individual coordinate by a fixed amount (i.e., $1 + \delta r_\alpha$), we may without loss of generality drop the

1 from our perturbation, as it commutes with everything anyways. If we substitute just the sum $\delta\mathbf{r}\sum_\alpha \nabla_\alpha$ into the commutator with $\hat{H}$, we know

$$\left(\delta\mathbf{r}\sum_\alpha \nabla_\alpha\right)\hat{H} - \hat{H}\left(\delta\mathbf{r}\sum_\alpha \nabla_\alpha\right) = 0.$$

Since this is 0 for any choice of perturbation $\delta\mathbf{r}$, we may also without loss of generality drop this shift. This leaves us with $\sum_\alpha \nabla_\alpha$, which "corresponds" to momentum in a system.

The momentum operator (for a specific scalar α) is written as

$$\hat{p}_\alpha = c\nabla_\alpha,$$

while the general momentum operator is

$$\hat{p} = c\nabla.$$

In both cases, the constant c above is $c = -i\hbar$ (which we have yet to show why this must be the case). We can write the components of $\hat{p}$ via

$$\hat{p}_x = -i\hbar\frac{\partial}{\partial x}, \quad \hat{p}_y = -i\hbar\frac{\partial}{\partial y}, \quad \hat{p}_z = -i\hbar\frac{\partial}{\partial z}.$$

Exercise: Check that $\hat{p}$ is a Hermitian operator.

Suppose we wish to determine the eigenvalues of the operator $\hat{p}$- i.e., we solve

$$\hat{p}\,|p\rangle = p\,|p\rangle\,.$$

For the ease of derivation, assume our system is one-dimensional. Projecting into the coordinate basis, we have

$$\langle x|\hat{p}|p\rangle = p\,\langle x|p\rangle$$
$$\Rightarrow \langle x|\hat{p}|p\rangle = \int \langle x|\hat{p}|x'\rangle\,\langle x'|p\rangle\,dx'.$$

Note that in the above equation, we used the completeness relations, where

$$\sum_\alpha |\alpha\rangle\,\langle\alpha| = I,$$
$$\int |x'\rangle\,\langle x'|\,dx' = I$$

for either the discrete (former) or the continuous (latter) case. Write $\psi_p(x') = \langle x'|p\rangle$. As our system is one-dimensional, the momentum operator in the coordinate basis is

$$\hat{p} = -i\hbar\frac{\partial}{\partial x}.$$

If we substitute this into the integral above, everything simplifies to

$$\int \langle x|\hat{p}|x'\rangle\,\langle x'|p\rangle\,dx' = \int [-i\hbar\delta'(x-x')]\psi_p(x')dx' = -i\hbar\frac{\partial\psi_p(x)}{dx}.$$

Recall that $\delta'(x-x')$ denotes the derivative of the Dirac-delta function. Reframing our original eigenvalue equation, this means

$$-i\hbar\frac{\partial\psi_p(x)}{\partial x} = p\psi_p(x).$$

Our solution to the differential equation given above is

$$\psi_p(x) = ce^{i\hat{p}_x x/\hbar}$$

(where $c = f(y,z)$ is potentially some constant additional function of y and z). For three-dimensions, we can easily generalize the above and get

$$\psi_{\mathbf{p}}(\mathbf{r}) = Ce^{i\mathbf{p}\cdot\mathbf{r}/\hbar}.$$

Suppose we try and determine the constant C above. We can do so using the normalization of our basis:

$$\delta(\mathbf{p}-\mathbf{p'}) = \int \psi^*_{\mathbf{p}}(\mathbf{r})\psi_{\mathbf{p'}}(\mathbf{r})d\mathbf{r} = C^2 \int e^{i(\mathbf{p}-\mathbf{p'})\cdot\mathbf{r}/\hbar}d\mathbf{r} = C^2(2\pi\hbar)^3\delta(\mathbf{p}-\mathbf{p'}).$$

This implies $C = (2\pi\hbar)^{-3/2}$. The wave function is then given by

$$\psi_{\mathbf{p}}(\mathbf{r}) = \langle \mathbf{r}|\mathbf{p}\rangle = \frac{1}{(2\pi\hbar)^{3/2}} e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}.$$

Notes:

(i) This derivation of the wave function is for a representation of the momentum operator in the position basis.

(ii) Through the completeness relation in position space,

$$\psi(\mathbf{r}) = \langle \mathbf{r}|\psi\rangle = \int \langle \mathbf{r}|\mathbf{p}\rangle \langle \mathbf{p}|\psi\rangle \, d\mathbf{p} = \int \langle \mathbf{r}|\mathbf{p}\rangle \, \psi(\mathbf{p}) d\mathbf{p}$$
$$= \frac{1}{(2\pi\hbar)^{3/2}} \int e^{i(\mathbf{p}\cdot\mathbf{r})/\hbar} \psi(\mathbf{p}) d\mathbf{p}.$$

We can then switch between representations in position or momentum space via the Fourier transform.

Suppose now we wish to derive an explicit expression for the operator $\hat{\mathbf{r}}$ in momentum space. We start by looking at the expectation value, and use the fact that it should be the same regardless of which space we represent $\hat{\mathbf{r}}$ in:

$$\langle \mathbf{r} \rangle = \int \psi^*(\mathbf{r}) \mathbf{r} \psi(\mathbf{r}) d\mathbf{r} = \int \psi^*(\mathbf{p}) \hat{\mathbf{r}} \psi(\mathbf{p}) d\mathbf{p},$$

where $\hat{\mathbf{r}}$ is a position operator in momentum space. We know that

$$\mathbf{r}\psi(\mathbf{r}) = \frac{1}{(2\pi\hbar)^{3/2}} \int \mathbf{r}\psi(\mathbf{p}) e^{i(\mathbf{p}\cdot\mathbf{r})/\hbar} d\mathbf{p}.$$

Note that we may write the above as

$$\frac{1}{(2\pi\hbar)^{3/2}} \int \mathbf{r}\psi(\mathbf{p}) e^{i(\mathbf{p}\cdot\mathbf{r})/\hbar} d\mathbf{p}. = \frac{1}{(2\pi\hbar)^{3/2}} \int i\hbar e^{i(\mathbf{p}\cdot\mathbf{r})/\hbar} \left[\frac{\partial \psi(\mathbf{p})}{\partial \mathbf{p}} \right] d\mathbf{p}.$$

From this, we have

$$\int \psi^*(\mathbf{r}) \hat{\mathbf{r}} \psi(\mathbf{r}) d\mathbf{r} = \frac{i\hbar}{(2\pi\hbar)^{3/2}} \int d\mathbf{r} \int \psi^*(\mathbf{r}) e^{i(\mathbf{p}\cdot\mathbf{r})/\hbar} \left[\frac{\partial \psi(\mathbf{p})}{\partial \mathbf{p}} \right] d\mathbf{p}$$
$$= i\hbar \int \psi^*(\mathbf{p}) \frac{\partial \psi(\mathbf{p})}{\partial \mathbf{p}} d\mathbf{p} = \int \psi^*(\mathbf{p}) \hat{\mathbf{r}} \psi(\mathbf{p}) dp.$$

This, of course, implies $\hat{\mathbf{r}} = i\hbar \frac{\partial}{\partial \mathbf{p}}$. We summarize the relationship between the operators and representations in these spaces with the following table:

Position	Momentum
$\hat{\mathbf{r}}$	$i\hbar \frac{\partial}{\partial \mathbf{p}}$
$-i\hbar\nabla\mathbf{r}$	$\hat{\mathbf{p}}$

The Parity Operator

(In short- it changes the sign of your variable in the discrete case.) Suppose we have an inversion transformation which consists of simultaneously changing the sign of all coordinates. This is a reversal of the direction of each coordinate axis. The invariance of the Hamiltonian under this transformation expresses the symmetry of space under mirror reflection; such a transformation is known as a *parity operator*. Unlike other space transformations like rotation, parity is a discrete transformation. Classically, the parity operation corresponds to reflecting the state of the particle through the origin $x \mapsto -x,\ p \mapsto -p$.

Suppose we have a parity operator $\hat{P}$ where

$$\hat{P} \left| \mathbf{r} \right\rangle = \left| -\mathbf{r} \right\rangle .$$

It is clear that

$$\langle \mathbf{r}|\hat{P}|\psi\rangle = \langle \mathbf{r}| - \psi\rangle = \psi(-\mathbf{r})$$

for a wave function ψ. We claim that $\hat{P}$ is Hermitian. To see how, note

$$\langle\psi|\hat{P}|\psi\rangle = \int \langle\psi|\mathbf{r}\rangle \langle\mathbf{r}|\hat{P}|\psi\rangle \, d\mathbf{r} = \int \langle\psi|\mathbf{r}\rangle \langle -\mathbf{r}|\psi\rangle \, d\mathbf{r}$$
$$= \int \langle\psi|\mathbf{r}\rangle \langle\mathbf{r}|\hat{P}^\dagger|\psi\rangle \, d\mathbf{r} = \langle\psi|\hat{P}^\dagger|\psi\rangle .$$

As this holds for any wavefunction, we have $\hat{P} = \hat{P}^\dagger$. It is also easy to see that $\hat{P}$ is idempotent, and thus $\hat{P} = \hat{P}^{-1}$. This implies that the only eigenvalues of $\hat{P}$ are ± 1.

How might we understand the eigenvectors associated to $\hat{P}$? If ψ_+, ψ_- are the eigenvectors of $\hat{P}$, we shall see they must satisfy

$$\hat{P}\psi_+(\mathbf{r}) = \psi_+(-\mathbf{r}) = \psi_+(\mathbf{r}), \tag{3}$$

$$\hat{P}\psi_-(\mathbf{r}) = \psi_-(-\mathbf{r}) = -\psi_-(\mathbf{r}). \tag{4}$$

Functions which satisfy (3) are called even, and those which satisfy (4) are odd. Clearly, ψ_+ corresponds to the eigenvalue $\lambda_1 = 1$, while ψ_- corresponds to $\lambda_2 = -1$. We may also compute

$$\langle\psi_-|\psi_+\rangle = \int \psi_-^*(-\mathbf{r})\psi_+(\mathbf{r})d\mathbf{r} = -\int \psi_-^*(\mathbf{r})\psi_+(\mathbf{r})d\mathbf{r} = -\langle\psi_-|\psi_+\rangle .$$

This implies $\langle\psi_-|\psi_+\rangle = 0$; other orthogonality relations can be deduced in this way as well. These orthogonality relations lead to

$$\psi_+(\mathbf{r}) = \frac{1}{2}[\psi(\mathbf{r}) + \psi(-\mathbf{r})], \quad \psi_-(\mathbf{r}) = \frac{1}{2}[\psi(\mathbf{r}) - \psi(-\mathbf{r})].$$

Note: Since $\hat{P}^2 = I$, we have $\hat{P}^n = \hat{P}$ if n is odd, and $\hat{P}^n = I$ if n is even. The invariance of the Hamiltonian under inversion expresses what is known as the law of conservation of parity: if the state of a closed system has definite parity (i.e., either even or odd) then this parity is conserved with time.

2.4. **The Heisenberg Uncertainty Principle.** We will start by trying to derive an expression of

$$[x, p_x].$$

Suppose the commutator acts on the wave function ψ:

$$[x, p_x]\psi = (xp_x - p_x x)\psi = -i\hbar x\frac{\partial\psi}{\partial x} + i\hbar\frac{\partial}{\partial x}(x\psi)$$
$$= -i\hbar x\frac{\partial\psi}{\partial x} + i\hbar x\frac{\partial\psi}{\partial x} + i\hbar\psi = i\hbar\psi.$$

Thus, $[x, p_x] = i\hbar$. Considering the other operators in 3D-space, it is not hard to see how we can generalize this to state

$$[\hat{x}_k, \hat{p}_j] = i\hbar\delta_{kj}.$$

Additionally, we have

$$[f(x), p_x] = i\hbar = [x, g(p_x)]$$

for any continuous function f of x or g of p_x.

We will spend a bit of time discussing what's known as the Heisenberg Uncertainty Principle; we present the proof in its general form, but for a more potentially practical interpretation of the H.U.P. we focus on just the momentum and position operators. The principle roughly states that if we think of the spread of values we get measuring by x and the spread on the values measuring by p, their product must be bound below by a certain value dependent on the operators.

Definition 2.23. *For an operator $\hat{A}$, the uncertainty (denoted $\Delta\hat{A}$) is defined via*

$$\Delta\hat{A} = \sqrt{\langle(\hat{A} - \langle\hat{A}\rangle)^2}.$$

Notation: For an operator $\hat{A}$ and state $|v\rangle$, we use the notation $|v_A\rangle$ for the vector

$$|v_A\rangle = (\hat{A} - \langle\hat{A}\rangle)\,|v\rangle\,.$$

Theorem 2.24 (The Heisenberg Uncertainty Principle)**.** *For any two Hermitian operators $\hat{A}, \hat{B}$ we have*

$$\Delta\hat{A}\Delta\hat{B} \geq \frac{1}{2}|\langle[\hat{A}, \hat{B}]\rangle|.$$

Proof. By the Cauchy-Schwarz Inequality, we have

$$\|v_A\|\|v_B\| \geq |\,\langle v_A|v_B\rangle\,|.$$

If we write out the inner product, we see

$$\begin{aligned}\langle v_A|v_B\rangle &= \langle v|\left[\hat{A}\hat{B} - \langle\hat{A}\rangle\hat{B} - \hat{A}\langle\hat{B}\rangle + \langle\hat{A}\rangle\langle\hat{B}\rangle\right]|v\rangle \\ &= \langle v|\left[\hat{A}\hat{B} - \langle\hat{A}\rangle\langle\hat{B}\rangle\right]|v\rangle\,.\end{aligned}$$

Write $\alpha := \langle v_A|v_B\rangle$. We also see

$$\langle v_A|v_B\rangle^* = \langle v|\left[\hat{B}\hat{A} - \langle\hat{A}\rangle\langle\hat{B}\rangle\right]|v\rangle = \alpha^*.$$

As $\langle v_A|v_B\rangle \in \mathbb{C}$, we may write

$$\begin{aligned}\langle v_A|v_B\rangle &= \mathrm{Re}\alpha + i\mathrm{Im}\alpha = \langle v|\hat{A}\hat{B}|v\rangle - \langle\hat{A}\rangle\langle\hat{B}\rangle\|v\|^2, \\ \langle v_A|v_B\rangle^* &= \mathrm{Re}\alpha - i\mathrm{Im}\alpha = \langle v|\hat{B}\hat{A}|v\rangle - \langle\hat{A}\rangle\langle\hat{B}\rangle\|v\|^2.\end{aligned}$$

This implies $\alpha - \alpha^* = 2i\mathrm{Im}\alpha = \langle v|[\hat{A}, \hat{B}]|v\rangle$, and so

$$\mathrm{Im}\,\langle v_A|v_B\rangle = \frac{\langle v|[\hat{A}, \hat{B}]|v\rangle}{2i}.$$

If we take any complex $z \in \mathbb{C}$, we may say $|\mathrm{Im}z| \leq |z|$. Thus,

$$|\,\langle v_A|v_B\rangle\,| \geq \frac{1}{2}|\langle[\hat{A}, \hat{B}]\rangle|.$$

It is easy to verify that that

$$|\,\langle v_A|v_B\rangle\,| = \Delta\hat{A}\Delta\hat{B}.$$

This directly implies

$$\Delta\hat{A}\Delta\hat{B} \geq \frac{1}{2}|\langle[\hat{A}, \hat{B}]\rangle|.$$

□

Corollary 2.25. *We have*

$$\Delta x\Delta p \geq \frac{\hbar}{2}.$$

2.5. **Density operators.**

Definition 2.26. *Suppose we have an ensemble of states $|i\rangle$ for $1 \leq i \leq k$, where each state $|i\rangle$ is prepared with probability p_i. The density operator for the ensemble, denoted $\hat{\rho}$, is defined as*

$$\hat{\rho} = \sum_i p_i \left|i\right\rangle \left\langle i\right| .$$

If $p_i = 0$ for all but one $1 \leq i \leq k$, we call $\hat{\rho}$ a pure state.

Note: Up until now, we have considered the equation for the expectation value of an operator on a pure state- this can be easily generalized for an equation for the ensemble expectation:

$$\langle \Omega \rangle = \sum_i p_i \langle i|\hat{\Omega}|i\rangle .$$

Indeed, by completeness relations we may even say that

$$\mathrm{Tr}(\hat{\Omega}\hat{\rho}) = \sum_j \langle j|\hat{\Omega}\hat{\rho}|j\rangle = \sum_j \sum_i \langle j|\hat{\Omega}|i\rangle \langle i|\hat{\rho}|j\rangle$$
$$= \sum_j \sum_i \langle j|\hat{\Omega}|i\rangle \langle i|j\rangle p_i = \sum_i p_i \langle i|\hat{\Omega}|i\rangle = \langle \Omega \rangle.$$

Properties of a density operator:

(i) $\hat{\rho}^\dagger = \hat{\rho}$ for any density operator $\hat{\rho}$.
(ii) $\mathrm{Tr}(\hat{\rho}) = 1$.
(iii) $\hat{\rho}^2 = \hat{\rho}$ only for pure states.
(iv) $\mathrm{Tr}(\hat{\rho}^2) \leq 1$, and is equal only for pure states.

Proof. Exercise! □

Example: Suppose $\{|\alpha_1\rangle, |\beta_1\rangle\}$ describes spin up (respectively, down) for one system and $\{|\alpha_2\rangle, |\beta_2\rangle\}$ describe spin up (down) for a second system. For any element in our first system $\mathcal{H}_1$, it must be of the form

$$c_\alpha |\alpha_1\rangle + c_\beta |\beta_1\rangle$$

while any element in our second system $\mathcal{H}_2$ is of the form

$$d_\alpha |\alpha_2\rangle + d_\beta |\beta_2\rangle .$$

If we take the composite system $\mathcal{H}_1 \otimes \mathcal{H}_2$ of our two individual systems, any element in the composite system is a linear combination of the states $\{|\alpha_1\rangle \otimes |\alpha_2\rangle, |\alpha_1\rangle \otimes |\beta_2\rangle, |\beta_1\rangle \otimes |\alpha_2\rangle, |\beta_1\rangle \otimes |\beta_2\rangle\}$. More explicitly, we have

$$\xi = \gamma_{\alpha\alpha} |\alpha_1\rangle \otimes |\alpha_2\rangle + \gamma_{\alpha\beta} |\alpha_1\rangle \otimes |\beta_2\rangle + \gamma_{\beta\alpha} |\beta_1\rangle \otimes |\alpha_2\rangle + \gamma_{\beta\beta} |\beta_1\rangle \otimes |\beta_2\rangle , \tag{5}$$

$$|\gamma_{\alpha\alpha}|^2 + |\gamma_{\alpha\beta}|^2 + |\gamma_{\beta\alpha}|^2 + |\gamma_{\beta\beta}|^2 = 1. \tag{6}$$

Question: Suppose we take the tensor product of $(c_\alpha |\alpha_1\rangle + c_\beta |\beta_1\rangle)$ and $(d_\alpha |\alpha_2\rangle + d_\beta |\beta_2\rangle)$. Are there relations we can determine on the coefficients $c_\alpha, c_\beta, d_\alpha, d_\beta$?

One way to approach the above is to consider the following state:

$$|\psi_{12}\rangle = \frac{1}{\sqrt{2}}(|\alpha_1\rangle \otimes |\beta_2\rangle + |\beta_1\rangle \otimes |\alpha_2\rangle).$$

This is a valid state in our composite system $\mathcal{H}_1 \otimes \mathcal{H}_2$. If we try to connect $|\psi_{12}\rangle$ with the general tensor product in (5), we end up finding that we would need

$$c_\alpha d_\alpha = 0, \quad c_\beta d_\alpha = \frac{1}{\sqrt{2}}, \quad c_\alpha d_\beta = \frac{1}{\sqrt{2}}, \quad c_\beta d_\beta = 0.$$

This is found by expanding the tensor product directly. However, we note that if all four relations hold, they are mutually contradicting: for example, if $c_\alpha d_\alpha = 0$, this forces either $c_\alpha = 0$ or $d_\alpha = 0$. Then either $c_\alpha d_\beta = 0$, or $c_\beta d_\alpha = 0$.

What this shows is that we cannot always take an arbitrary element in our composite system $\mathcal{H}_1 \otimes \mathcal{H}_2$ and describe it solely in terms of the elements in our individual systems. This property in quantum composite systems is known as quantum entanglement.

Remark: In what follows, we will use the (easy to show) identity without establishing it fully:

$$\langle\psi|\hat{O}|\psi\rangle = \mathrm{Tr}(|\psi\rangle\langle\psi|\hat{O}).$$

Suppose we start with the same set up as given in the previous example, and let $\hat{A}_1$ be an operator which acts exclusively on $\mathcal{H}_1$. We may augment this operator to get an operator which acts on $\mathcal{H}_1 \otimes \mathcal{H}_2$ via

$$\hat{A}_1 \to \hat{A}_1 \otimes I_{\mathcal{H}_2}.$$

Suppose we take the maximally entangled state $|\psi_{12}\rangle$ given above; through direct computation, we find

$$\begin{aligned}
&\langle\psi_{12}|\hat{A}_1 \otimes I_{\mathcal{H}_2}|\psi_{12}\rangle \\
&= \frac{1}{2}\Big(\langle\alpha_1|\hat{A}_1|\alpha_1\rangle\langle\beta_2|\beta_2\rangle + \langle\beta_1|\hat{A}_1|\beta_1\rangle\langle\alpha_2|\alpha_2\rangle + \langle\alpha_1|\hat{A}_1|\beta_1\rangle\langle\beta_2|\alpha_2\rangle + \langle\beta_1|\hat{A}_1|\beta_1\rangle\langle\alpha_2|\beta_2\rangle \Big) \\
&= \frac{1}{2}\Big(\langle\alpha_1|\hat{A}_1|\alpha_1\rangle + \langle\beta_1|\hat{A}_1|\beta_1\rangle \Big)
\end{aligned}$$

using the relations $\langle\alpha_i|\beta_i\rangle = 0, \langle\alpha_i|\alpha_i\rangle = \langle\beta_i|\beta_i\rangle = 1$ for $i = 1, 2$.

If we let

$$|\psi_1\rangle = \frac{1}{\sqrt{2}}(|\alpha_1\rangle + |\beta_1\rangle),$$

consider

$$\langle\psi_1|\hat{A}_1|\psi_1\rangle = \frac{1}{2}\Big(\langle\alpha_1|\hat{A}_1|\alpha_1\rangle + \langle\beta_1|\hat{A}_1|\beta_1\rangle + \langle\alpha_1|\hat{A}_1|\beta_1\rangle + \langle\beta_1|\hat{A}_1|\alpha_1\rangle \Big).$$

Clearly, $\langle\psi_1|\hat{A}_1|\psi_1\rangle \neq \langle\psi_{12}|\hat{A}_1 \otimes I_{\mathcal{H}_2}|\psi_{12}\rangle$. This implies that "somehow", the presence of the second spin (in our composite system) affects the measurement, even if we only consider an augmented operator which changes behavior on a single system.

Using the expression for $\langle\psi_{12}|\hat{A}_1 \otimes I_{\mathcal{H}_2}|\psi_{12}\rangle$ given above and the identity cited after the example, we may rewrite to find

$$\begin{aligned}
\langle\psi_{12}|\hat{A}_1 \otimes I_{\mathcal{H}_2}|\psi_{12}\rangle &= \frac{1}{2}\Big(\mathrm{Tr}(|\alpha_1\rangle\langle\alpha_1|\hat{A}_1) + \mathrm{Tr}(|\beta_1\rangle\langle\beta_1|\hat{A}_1) \Big) \\
&= \mathrm{Tr}\left(\frac{1}{2}(|\alpha_1\rangle\langle\alpha_1| + |\beta_1\rangle\langle\beta_1|)\hat{A}_1 \right) \\
&= \mathrm{Tr}(\hat{\rho}_1\hat{A}_1),
\end{aligned}$$

where $\hat{\rho}_1$ is the density operator for the state ψ_1 in $\mathcal{H}_1$.

Remark: The density operator $\hat{\rho}_1$ in the $\{|\alpha_1\rangle, |\beta_1\rangle\}$ basis has the matrix representation

$$\hat{\rho}_1 = \begin{bmatrix} 1/2 & 0 \\ 0 & 1/2 \end{bmatrix}.$$

Note that $\hat{\rho}_1$ is a pure state.

Deriving equations of motion for a time-independent pure state:
Suppose we have a time-independent pure state $\hat{\rho} = |\psi\rangle\langle\psi|$. We have

$$\frac{\partial\hat{\rho}}{\partial t} = |\dot{\psi}\rangle\langle\psi| + |\psi\rangle\langle\dot{\psi}| = -\frac{i}{\hbar}\hat{H}|\psi\rangle\langle\psi| + \frac{i}{\hbar}|\psi\rangle\langle\psi|\hat{H} = -\frac{i}{\hbar}[\hat{H},\hat{\rho}].$$

If we compare the above to what we derived with the Heisenberg Equations of Motion, we note that the above has a negative sign while for a general time-independent operator, the sign of $\frac{i}{\hbar}$ is positive.

Question: Why?

Answer: It's because in order for Heisenberg's equation to hold, our operator must correspond to some actual measurement/observable. In our case, $\hat{\rho}$ is not a measurement; in fact, in general if you have something which is not a measurement your sign for $\frac{i}{\hbar}$ will always be negative.

Matrix elements of the density matrix $\rho = (\rho_{nm})$ satisfy the properties

$$\rho_{nn}\rho_{mm} \geq |\rho_{mn}|^2, \quad \rho_{nn}\rho_{mm} = |\rho_{mn}|^2 \text{ for pure states.}$$

Definition 2.27. *For a density operator ρ, the von Neumann entropy of ρ is defined as*

$$S[\rho] = -k_B \operatorname{Tr}(\rho\ln\rho) = -k_B\sum_i p_i\ln(p_i).$$

Note: For mixed states, $S > 0$ while for pure states, $S = 0$.

3. The time-dependent Schrödinger equation

Suppose we consider a free particle in some space- the free particle has the interesting property that the measurement of its energy is independent of position; such a system is known as *isotropic*. As the Hamiltonian measures energy, this means that in an isotropic system the Hamiltonian can only depend on momentum.

In three-dimensions, as we most likely have seen the Hamiltonian can be written as

$$\hat{H} = \frac{p^2}{2m} = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) = -\frac{\hbar}{2m}\nabla^2,$$

where

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}.$$

For a system of N interactive particles, we may write it as

$$\hat{H} = -\frac{\hbar^2}{2}\sum_\alpha \frac{1}{m_\alpha}\nabla_\alpha^2.$$

If we consider a quantum system of N interactive particles, we now have the additional term involving some potential:

$$\hat{H} = -\frac{\hbar^2}{2}\sum_\alpha \frac{1}{m_\alpha}\nabla_\alpha^2 + \hat{U}(\mathbf{r}_1,\ldots,\mathbf{r}_N).$$

The latter part $\hat{U}$ of the sum above is known as the potential energy, while the former is the kinetic energy. Note that the potential energy is not included for $\hat{H}$ in the case of a free particle, as $\hat{U}(x) = 0$ everywhere.

We're going to look at solving the time-dependent Schrödinger Equation; if we consider first the time-dependent equation for the free particle, it takes the form

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + \hat{U}\psi.$$

As $\hat{U} = 0$ for a free particle, the solution for ψ is easily seen to be

$$\psi(t) = Ce^{-i(Et+\mathbf{p}\cdot\mathbf{r})/\hbar}$$

where $\frac{E}{\hbar}$ is the angular frequency.

Notes:

(i) For the free particle, the energy spectrum is continuous.

(ii) In the homework, we specified that a "well-defined" eigenfunction must be continuous, injective, and its first derivative must be continuous. However, this is only true for when the potential energy of a system is finite- if there is a "point" where the potential becomes infinite, we do not continue to impose continuity of the first derivative for a potential eigenfunction.

If we look at the most general (at least for our purposes) solution for the time-dependent equation

$$i\hbar\,|\dot{\psi}\rangle = \hat{H}\,|\psi\rangle\,,$$

it must be of the form $|\psi(t)\rangle = \hat{U}(t)\,|\psi(0)\rangle$. So our real goal will be to use the time-independent equation to solve for $\hat{U}(t)$; we build up our solution by looking first at the solutions for

$$\hat{H}\,|E\rangle = E\,|E\rangle\,.$$

That is, we look at stationary states.

Assuming the stationary states form an orthonormal basis for the space, if we let $a_E(t) = \langle E|\psi(t)\rangle$ we see

$$|\psi(t)\rangle = \sum_E |E\rangle\,\langle E|\psi(t)\rangle = \sum_E a_E(t)\,|E\rangle$$

(i.e., we've just expanded $|\psi(t)\rangle$ in terms of the basis). As

$$0 = (i\hbar\frac{\partial}{\partial t} - \hat{H})\,|\psi(t)\rangle\,,$$

using the expansion above we find

$$0 = (i\hbar\frac{\partial}{\partial t} - \hat{H})\,|\psi(t)\rangle = \sum_E (i\hbar\dot{a_E}(t) - Ea_E(t))\,|E\rangle$$
$$\Rightarrow it\dot{a_E}(t) = Ea_E(t).$$

The solution to the differential equation above is

$$a_E(t) = a_E(0)e^{-iEt/\hbar}.$$

With this, we substitute back to find

$$|\psi(t)\rangle = \sum_E |E\rangle\,\langle E|\psi(t)\rangle = \sum_E a_0\,|E\rangle\,e^{-iEt/\hbar} = \sum_E |E\rangle\,\langle E|\psi(0)\rangle\,e^{-iEt/\hbar}.$$

This implies that the propagator takes the form

$$\hat{U}(t) = \sum_E |E\rangle\,\langle E|\,e^{-iEt/\hbar}.$$

Thus, if we are looking for a solution of the time-dependent equation, if we either first find the stationary states or we are given the stationary states, we can immediately determine the time propagator $\hat{U}(t)$ necessary to determine the solution at any time t.

Remarks:

(i) $\hat{U}(t)$ is a unitary operator, which is not hard to show.

(ii) We can think of $\hat{U}(t)$ acting on $|\psi(0)\rangle$ as a rotation of $|\psi(0)\rangle$ in our space throughout time. As $\hat{U}(t)$ is unitary, the state $|\psi(0)\rangle$ does not stretch or expand in time.

Consider now a time-dependent expectation value for an operator $\hat{\Omega}$: based on our previous work, we see

$$\langle\Omega\rangle = \langle\psi(t)|\hat{\Omega}|\psi(t)\rangle = \langle\psi(0)|U^{\dagger}\hat{\Omega}U|\psi(0)\rangle = \langle\psi(0)|\hat{\Omega}(t)|\psi(0)\rangle\,.$$

Notes:

(i) In the Schrödinger picture of quantum mechanics, states change in time while operators do not.

(ii) In the Heisenberg picture of quantum mechanics, states do *not* change in time, while operators do.

(iii) It is often of practical use to switch between pictures, as one may find a solution easier depending on whether our states or operators change in time. Both formulations, notice, are equivalent- we pass from one to the other via

$$\hat{\Omega}_H(t) = U^{\dagger}\hat{\Omega}_S U$$

(note the lack of dependence on time for $\hat{\Omega}_S$). Their equivalence holds from the fact that $\hat{U}$ is unitary.

Looking at $\frac{\partial}{\partial t}\hat{\Omega}(t)$, we see

$$\frac{\partial}{\partial t}\hat{\Omega}(t) = \frac{\partial}{\partial t}[U^{\dagger}(t)\hat{\Omega}U(t)]$$
$$= \frac{i}{\hbar}\hat{H}e^{i\hat{H}t/\hbar}\hat{\Omega}e^{-i\hat{H}t/\hbar} + e^{i\hat{H}t/\hbar}\left(\frac{\partial\Omega}{\partial t}\right)e^{-i\hat{H}t/\hbar} - \frac{i}{\hbar}e^{i\hat{H}t/\hbar}\hat{\Omega}\hat{H}e^{-i\hat{H}t/\hbar}.$$

Note that we are using the form of $\hat{U}(t)$ given via

$$\hat{U}(t) = e^{-i\hat{H}t/\hbar}.$$

As $[\hat{H}, f(\hat{H})] = 0$ for any continuous function of $\hat{H}$, we can commute $\hat{H}$ and $e^{i\hat{H}t/\hbar}$ to get

$$e^{i\hat{H}t/\hbar}\left(\frac{\partial\Omega}{\partial t}\right)e^{-i\hat{H}t/\hbar} + \frac{i}{\hbar}e^{i\hat{H}t/\hbar}[\hat{H},\hat{\Omega}]e^{-i\hat{H}t/\hbar}$$
$$= \left(\frac{\partial\Omega}{\partial t}\right)_H + \frac{i}{\hbar}[\hat{H},\hat{\Omega}_H].$$

This gives an equation of motion through time for the Heisenberg picture.

Remark: A nice property of the propagator $\hat{U}(t)$ allows for breaking down an evolution in time in the following way: if we have a propagation $\hat{U}(t_1t_3)$ from t_1 to t_3, we may instead take the propagation $\hat{U}(t_1t_2)\hat{U}(t_2t_3)$ from t_1 to t_2, and then from t_2 to t_3.

4. Problems in one-dimension

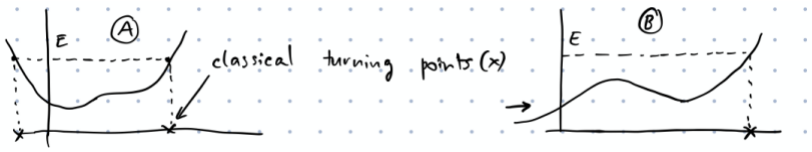
4.1. **Basic examples.** Suppose we have a potential $U(x)$ of a system in a state with total energy E. If we can show that

$$U(-\infty) > E, \quad U(\infty) > E$$

we say that our state is *bound*. If instead we have

$$U(-\infty) < E, \quad U(\infty) > E$$

our state is known as a *scattering* state. The picture directly below (on the next page) illustrates both a bound state (A), and a scattering state (B).



If we think intuitively of "throwing in" a particle into a system which is in a bound state where the particle has energy less than E, it will remain in the region bounded by E and the potential $U(x)$ and won't escape. The same is not true for a particle in a scattering state.

Note: The behavior of $U(x)$ at $\pm\infty$ is quite important for a system. For a potential $U(x)$ which satisfies $U(x) \to 0$ as $x \to \pm\infty$, if $E < 0$ our state is bound. Otherwise, if $E > 0$ it is scattering.

4.2. **Free particle in one dimension.** For a free particle in one-dimension, the potential $U(x) = 0$ everywhere. The (time-dependent) Schrödinger equation in this case is written as

$$i\hbar\,|\dot{\psi}\rangle = \hat{H}\,|\psi\rangle = \frac{p^2}{2m}\,|\psi\rangle\,.$$

For the time-independent equation, we have

$$\hat{H}\,|E\rangle = \frac{p^2}{2m}\,|E\rangle = E\,|E\rangle\,.$$

Rewriting the equation above, we see

$$\frac{p^2}{2m}\,|E\rangle = E\,|E\rangle \Rightarrow \left(\frac{p^2}{2m} - E\right)|E\rangle = 0.$$

As $|E\rangle$ is non-zero, this clearly forces $p = \pm(2mE)^{1/2}$. As the operator is Hermitian, the corresponding eigenstates are orthogonal. That we have both positive and negative eigenvalues just means that our particle can move to the left or right with momentum $|p| = (2mE)^{1/2}$. This holds for any non-zero E.

Suppose we try to determine $\hat{U}(t) = e^{-\hat{H}t/\hbar}$ for this case. As $U(x) = 0$, the only operator we have associated to our particle is $\hat{p}$ (note that we have been implicitly using this fact so far). Via completeness relations, we write

$$\hat{U}(t) = \int |p\rangle\,\langle p|\,e^{-i\hat{H}t/\hbar}dp = \int |p\rangle\,\langle p|\,e^{-iEt/\hbar}dp = \int |p\rangle\,\langle p|\,e^{-\frac{ip^2t}{2m\hbar}}dp.$$

Note that this is the momentum representation for the propagator $\hat{U}(t)$. We now will try to determine the position representation. In what follows, we use the notation

$$\hat{U}(x, x', t) = \langle x|\hat{U}(t)|x'\rangle\,.$$

We see

$$\hat{U}(x, x', t) = \langle x|\hat{U}(t)|x'\rangle = \int \langle x|p\rangle\,\langle p|x'\rangle\,e^{-\frac{ip^2t}{2m\hbar}}dp.$$

Recall that in the one-dimensional case,

$$\langle x|p\rangle = (2\pi\hbar)^{-1/2}e^{ipx/\hbar}.$$

With this, the integral above may be written as

$$\int \langle x|p\rangle \langle p|x'\rangle e^{-\frac{ip^2t}{2m\hbar}}dp = \frac{1}{2\pi\hbar}\int e^{ip(x-x')\hbar}e^{-\frac{ip^2t}{2m\hbar}}dp$$
$$= \left(\frac{m}{2\pi\hbar it}\right)^{1/2} e^{im(x-x')/2\hbar t}.$$

Remark: If we were to start with a state ψ which is Gaussian, to find its position at time t we only need to multiply the state of the system at time $t = 0$ (i.e. $\psi(0)$) by the above. Note that in the derivation above, we consider the particle in point x' at time $t = 0$, and are propagating to point x at time t.

$$(x', 0) \to (x, t)$$

Then

$$\psi(x, t) = \int U(x, t;\ x', 0)\psi(x', 0)dx'.$$

4.3. **Gaussian wave packet.** Let

$$\psi(x,0) = e^{ip_0 x/\hbar}\frac{e^{-x^2/2\Delta^2}}{(\pi\Delta)^{1/4}}.$$

As we have (partially) seen on the homework,

$$\langle x\rangle = 0, \quad \langle x^2\rangle = \frac{\Delta^2}{2}.$$

Suppose we wish to say something about $\hat{p}$. For a momentum representation of ψ, using the Fourier transform we find

$$\psi(p,0) = \frac{1}{(2\pi\hbar)^{1/2}}\int \psi(x,0)e^{-ipx/\hbar}dx = \left(\frac{\Delta}{\pi\hbar^2}\right)^{1/4} e^{-(p-p_0)^2\Delta^2/2\hbar^2}.$$

Clearly, $\langle\hat{p}\rangle = p_0$ here. Additionally, $\Delta\hat{p} = \frac{\hbar}{\Delta\sqrt{2}}$. Using $\langle x^2\rangle$, we have $\Delta X = \frac{\Delta}{\sqrt{2}}$, and thus

$$\Delta X\Delta\hat{p} = \frac{\hbar}{2}.$$

This means our state has minimum uncertainty. In terms of classical mechanics, a state of minimum uncertainty is "most classical", i.e. close to a classical state. The wave function $\psi(x,0)$ as defined above is known as a minimum uncertainty wave packet. To determine an expression for the packet at time t, we use the propagator and derive

$$\psi(x,t) = \int U(x,t;x',t')\psi(x',t')dx'$$

$$= \left[\pi^{1/2}\left(\Delta + \frac{i\hbar t}{m\Delta}\right)\right]^{-1/2}\exp\left[-\frac{((x-p_0t)/m)^2}{2\Delta^2((1+i\hbar t)/m\Delta^2)}\right]\exp\left[\frac{ip_0}{\hbar}\left(x - \frac{p_0t}{2m}\right)\right].$$

We immediately see that

$$\langle x\rangle = \frac{p_0t}{m} = \frac{\langle p\rangle t}{m}$$

as $\langle p\rangle = p_0$. Recall that in classical mechanics, we have the relationship

$$x = \frac{pt}{m}.$$

This is, thus, a quantum analog for a classical relationship; in fact, Ehrenfest's Theorem "essentially" says to formulate quantum equations of motion, we may replace dynamical variables in classical equations with their expectation values (considering the variables as operators).

We include (without deriving) the expression for ΔX over time:

$$\Delta X(t) = \frac{\Delta}{\sqrt{2}}\left(1 + \frac{\hbar^2t^2}{m^2\Delta^4}\right)^{1/2},$$

where $\Delta X(0) = \Delta X$. Note that this implies $\Delta X(t) \geq \Delta X(0)$ for all t. Physically, this says that if we start with a Gaussian wave packet, propagation over time does not change the essential form of the wave function (i.e., it remains a Gaussian wave-packet); the uncertainty essentially just "spreads out" over time. This is a reflection of the fact that if we have any initial uncertainty in velocity (i.e., momentum), this will be reflected as a growing uncertainty in position over time.

4.4. **A particle in a box.** Consider a free particle, and add the potential $V(x)$ where

$$V(x) = \begin{cases} \infty, & |x| > \frac{L}{2}, \\ 0, & x \in [-L/2, L/2]. \end{cases}$$

Here $L \in \mathbb{R}^+$ is some arbitrary constant. The goal here is to solve the time-independent Schrödinger equation in the position representation for the Hamiltonian associated to $V(x)$. This means we wish to solve

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

for some wave-function ψ. If we let Region I denote space when $x < -L/2$, Region II denote the space when $x \in [-L/2, L/2]$, and Region III denote the space when $x > L/2$, we will solve in each individual region and bring them together for the general solution.

We consider the solution for Regions I and III together, as the behavior of the particle is essentially the same here. Let ψ_I (resp. ψ_{III}) denote the wave function in these regions. We have

$$\frac{d^2}{dx^2}\psi_{I/III} - \frac{2m}{\hbar}(V_0 - E)\psi_{I/III} = 0,$$

where V_0 is arbitrarily large but finite. Based on the above, we know that $\psi_{I/III}$ must be of the form

$$\psi_{I/III}(x) = Ae^{-kx} + Be^{kx}, \quad k = \sqrt{2m(V_0 - E)}.$$

As $\psi_{I/III}$ must be a valid eigenfunction, we need $\psi_{I/III}(x) \to 0$ as $x \to \pm\infty$. Noting that if $x \to \infty$, $Be^{kx} \to \infty$ unless $B = 0$, this forces $B = 0$. Similarly, if $A \neq 0$, then as $x \to -\infty$ the term $Ae^{-kx} \to \infty$ which is not possible. Therefore, $A = B = 0$, and so $\psi = 0$ in these regions.

In Region II, the potential of our particle is 0. Let ψ_{II} denote the wave-function in this region. At this point, we already know that the behavior of ψ in Region II is identical to the behavior of a free particle; however, we cannot state that ψ is a free particle everywhere, as we have the additional requirements

$$\psi_I(-L/2) = \psi_{II}(-L/2) = 0,$$
$$\psi_{II}(L/2) = \psi_{III}(L/2) = 0.$$

This means the behavior as $x \to \pm\infty$ is different for ψ than a typical free particle. Instead, we write

$$\psi_{II}(x) = Ae^{ikx} + Be^{-ikx}$$

and try to solve for A and B. By our boundary conditions, we know

$$A^{-ik(L/2)} + Be^{ik(L/2)} = 0,$$
$$Ae^{ik(L/2)} + Be^{-ik(L/2)} = 0.$$

Solving, we find that

$$e^{-ikL} - e^{ikL} = 2i\sin(kL).$$

This has a non-trivial solution for $k = \frac{n\pi}{L}$, where $n \in \mathbb{Z}$. This means

$$Ae^{-in\pi/2} + Be^{in\pi/2} = 0 \Rightarrow A = e^{-in\pi}B.$$

We can use these relations to get a final solution for the stationary states $\psi_n(x)$ of the wave-function, where

$$\psi_n(x) = \begin{cases} \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right), & n \text{ even}, \\ \left(\frac{2}{L}\right)^{1/2} \cos\left(\frac{n\pi x}{L}\right), & n \text{ odd}. \end{cases}$$

Recalling that $k = \sqrt{2m(V_0 - E)}$, and we have non-trivial solutions only when $k = \frac{n\pi}{L}$ where $n \in \mathbb{Z}$, this implies

$$E_n = \frac{\hbar k^2}{2m} = \frac{\hbar^2 n^2 \pi^2}{2mL^2}.$$

Notes:

(i) All states here are bound states, as the potential at the boundary of the box is infinite and thus the particle cannot "escape".

(ii) The lowest energy in the system- i.e., E_1- is non-zero.

Q: Why?

A: We will give another way to arrive at the conclusion in the previous note. Consider the Hamiltonian $\hat{H} = \frac{\hat{p}^2}{2m}$ (there is no $+V(x)$ term here, as the potential is 0 inside the box). We have

$$\langle H \rangle = \frac{\langle \hat{p}^2 \rangle}{2m}.$$

Recalling that $\langle \hat{p} \rangle = 0$ for bound states (**exercise:** try and prove it!), we see

$$\langle H \rangle = \frac{\langle \hat{p}^2 \rangle}{2m} = \frac{(\Delta p)^2}{2m} = \frac{\langle (\hat{p} - \langle p \rangle)^2 \rangle}{2m}.$$

By the Heisenberg uncertainty principle, $\Delta x \Delta p \geq \frac{\hbar}{2}$; so

$$\langle H \rangle \geq \frac{\hbar^2}{8m(\Delta x)^2}.$$

What is a reasonable approximation we can take for Δx? Considering we are in a box of length L, we can assume $\Delta x \leq \frac{L}{2}$. Then

$$\langle H \rangle \geq \frac{\hbar^2}{2mL^2}.$$

I.e., the energy levels are bound below by a non-zero value.

Note: We have $\Delta p \sim \frac{\hbar}{L}$ (using the previous equations). The ground state corresponds to $n = 1$ in the equation for E_n derived above. As we have mentioned, if the particle has zero energy, it will be at rest inside the well- violating Heisenberg's uncertainty principle. By localizing or confining the particle to a limited region in space, it will acquire a finite momentum- leading to a minimum kinetic energy. As the momentum uncertainty is inversely proportional to the width of the well, a decrease in L will correspond to increasing uncertainty on p. This makes the particle move faster and faster, so the *zero-point energy* increases. Conversely, if the width of the well increases, the zero-point energy decreases without vanishing. The zero-point energy, therefore, reflects the necessity of a minimum motion of a particle due to localization.

The zero-point energy occurs in all bound state potentials. In the case of binding potentials, the lowest energy state has an energy which is higher than the minimum of the potential energy. This is in sharp contrast to classical mechanics, where lowest potential energy is always equal to the minimum potential energy (when we have zero kinetic energy). This has far-reaching physical consequences in the microscopic world- for instance,

without zero-point motion, atoms would not be stable, for the electrons would fall into the nuclei.

If we study this case as a time-dependent problem, the propagator is given by

$$\hat{U}(t) = \sum_{n=1}^{\infty} |n\rangle \langle n| \, e^{-i/\hbar \left(\frac{\hbar^2 n^2 \pi^2}{2mL^2} \right) t}.$$

4.5. **Delta function potential.** Consider the potential $V(x)$ defined via $V(x) = -\alpha\delta(x)$ (technically should just be $-\delta(x)$, but we use constant α for unit purposes). We'll solve for the bound states using the equation

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

Let Region I denote when $x < 0$, Region II denote when $x > 0$, and Region III denote when $x = 0$. In Region I, the equation above simplifies to

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar} = k^2\psi,$$

where $k = \frac{\sqrt{-2mE}}{\hbar}$ is real (as $E < 0$ for bound states).

The general solution is of the form

$$\psi(x) = Ae^{-kx} + Be^{kx}$$

(as $k \in \mathbb{R}$). As before, if $x \to -\infty$ then $Ae^{-kx} \to \infty$ if $A \neq 0$; this forces $A = 0$. So,

$$\psi_I(x) = Be^{kx}.$$

Using a similar argument for Region II, we can say

$$\psi_{II}(x) = Fe^{-kx}$$

for $k \in \mathbb{R}$.

In order for $\psi(x)$ to be continuous (as a potential eigenfunction), as $\psi_I(x) = Be^{kx}$ for $x < 0$ while $\psi_{II}(x) = Fe^{-kx}$ for $x > 0$, we also should have $\psi_I(0) = \psi_{II}(0)$. This implies $B = F$- so we reduce the problem to solving for B.

Let $\epsilon > 0$ be given. Looking at the integral of our general equation in a small interval around zero, we see

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

$$\Rightarrow -\frac{\hbar^2}{2m}\frac{d\psi}{dx}\bigg|_{-\epsilon}^{\epsilon} + \int_{-\epsilon}^{\epsilon}V(x)\psi(x)dx = 0.$$

Note that the latter integral is 0, as we are integrating a finite value over an interval of arbitrarily small length. Taking limits, we find

$$\lim_{\epsilon\to 0}\left[\frac{d\psi}{dx}\bigg|_{\epsilon} - \frac{d\psi}{dx}\bigg|_{-\epsilon}\right] = \frac{2m}{\hbar^2}\lim_{\epsilon\to 0}\int_{-\epsilon}^{\epsilon}V(x)\psi(x)dx = -\frac{2m}{\hbar^2}\alpha\psi(0).$$

Taking $\psi(x) = Be^{-kx}$ in the above, we get

$$\lim_{\epsilon \to 0} \Big[-Bk - Bk \Big] = -\frac{2m}{\hbar^2}\alpha\psi(0)$$
$$\Rightarrow -2Bk = -\frac{2m}{\hbar^2}\alpha B$$
$$\Rightarrow k = \frac{m\alpha}{\hbar^2} = \frac{\sqrt{-2mE}}{\hbar}$$
$$\Rightarrow E = -\frac{m\alpha^2}{2\hbar^2}.$$

We use these to solve for B, where the resulting equation for the wave function (in its normalized form) is

$$\psi(x) = \frac{\sqrt{m\alpha}}{\hbar} e^{-\frac{m\alpha|x|}{\hbar^2}}.$$

Now, we consider stattering states with $E > 0$. For $x < 0$, the Schrödinger equation becomes

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2} = -k^2\psi,$$

which is almost the same as above except now we take $k = \sqrt{2mE}/\hbar$ (as $E > 0$ here). The solution to this equation is given by $\psi(x) = Ae^{ikx} + Be^{-ikx}$; similarly, for $x > 0$ the solution is given by $\psi(x) = Fe^{ikx} + Ge^{-ikx}$. Continuity of the wave function (specifically at $x = 0$) tells us that we must have

$$A + B = F + G.$$

If we repeat the same process as we have done for bound states, for the derivative of the wave function at $x = 0$ we have

$$\frac{d\psi}{dx} = ik(Fe^{ikx} - Ge^{-ikx}), \text{ for } x > 0 \Rightarrow \left.\frac{d\psi}{dx}\right|_+ = ik(F - G),$$
$$\frac{d\psi}{dx} = ik(Ae^{ikx} - Be^{-ikx}) \text{ for } x < 0 \Rightarrow \left.\frac{d\psi}{dx}\right|_- = ik(A - B).$$

Thus,

$$\left.\frac{d\psi}{dx}\right|_+ - \left.\frac{d\psi}{dx}\right|_- = ik(F - G - A + B).$$

As $\psi(0) = A + B$, via the same limiting process as before we know

$$ik(F - G - A + B) = -2m\alpha(A + B)/\hbar^2,$$

which we may rewrite as

$$F - G = A(1 + 2i\beta) - B(1 - 2i\beta)$$

for $\beta = m\alpha/(k\hbar^2)$.

We note that we have four unknowns, but only two equations to determine them. To help us solve this apparent issue, consider the wave function

$$\psi(x) = Ae^{ikx} + Be^{-ikx}$$

and recall that we build any time dependent wave-function from the wave function $\psi(x)$ by adding $e^{(-iEt/\hbar)}$. Therefore, the time-dependent wave function has two waves: one propagating tow the right e^{ikx}, and one to the left e^{-ikx} with corresponding coefficients A, B and F, G. In a typically scattering experiment, we shoot particles from one side- so in this case, we may assume without loss of generality that we can set certain coefficients to zero to fix the direction we are doing in our experiment.

Let $G = 0$; in this case, Ae^{ikx} propagates to the right, as does Fe^{ikx}- however, Be^{-ikx}

propagates to the left. These are known as the incident, transmitted, and reflected waves (respectively) for the situation. Using that $G = 0$, we can solve our two equations

$$A + B = F + G,$$
$$F - G = A(1 + 2i\beta) - B(1 - 2i\beta)$$

to get

$$B = \frac{i\beta}{1 - i\beta}A, \quad F = \frac{1}{1 - i\beta}A.$$

We can use these to define two coefficients: the first of the two is the reflection coefficient R, defined via

$$R = \frac{|B|^2}{|A|^2} = \frac{\beta^2}{1 + \beta^2}.$$

The second is the transmission coefficient T, defined via

$$T = \frac{|F|^2}{|A|^2} = \frac{1}{1 + \beta^2}.$$

The coefficient R tells us essentially fraction of particles which will come back, while T tells us the fraction of which will be transmitted.

Remarks:

(i) $T + R = 1$, which makes sense according to physical intuition.

(ii) If we plug $k = \sqrt{2mE}/\hbar$ into $\beta = m\alpha/(k\hbar^2)$ we see

$$\beta^2 = \frac{m\alpha^2}{2E\hbar^2}.$$

The transmission and reflection coefficients may then be written as

$$R = \frac{1}{1 + 2\hbar^2 E/m\alpha^2}, \quad T = \frac{1}{1 + m\alpha^2/2\hbar^2 E}.$$

Note that the greater the energy (our value E), the higher the probability is that our particle will be transmitted. Similarly, a particle with a lower mass has a higher transition probability than a heavier particle.

(iii) If we turn the potential over by sending $\alpha \mapsto -\alpha$, we note that R and T as written above do not change, as they depend only on α^2. This means in quantum mechanics, for this given potential, a particle is just as likely to pass through a barrier as to cross over a well. Classically, if $E > V_{\max}$ then $T = 1$ while $R = 0$. If $E < V_{\max}$ then $T = 0$ while $R = 1$. What we have just shown above, however, is that in quantum mechanics a particle has a non-zero probability of passing through the potential regardless of our energy level. This phenomenon is known as tunneling.

4.6. **A slightly more complicated potential.** Consider the following one-dimensional potential:

$$V(x) = V_0(e^{-2x/c} - be^{-x/c})$$

where $V_0, b, c > 0$. We wish to search for bound states. The Schrödinger equation has the following form:

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V_0 e^{-2x/c} + V_0 be^{-x/c})\psi = 0.$$

To solve this equation, we introduce the variable $z = 2\beta e^{-x/c}$ where $\beta = (2mV_0c^2/\hbar^2)^{1/2}$. Via the chain rule, we get

$$\frac{d^2\psi}{dx^2} = \frac{d^2\psi}{dz^2}\left(\frac{dz}{dx}\right)^2 + \frac{d\psi}{dz}\frac{d^2z}{dx^2} = \left(\frac{d^2\psi}{dz^2}\frac{4\beta^2}{c^2} + \frac{d\psi}{dz}\frac{2\beta}{c^2}\right)e^{-x/c}.$$

If we let $\psi' = \frac{d\psi}{dz}$ and $\psi'' = \frac{d^2\psi}{dz^2}$, the above equation becomes

$$\psi'' + \frac{\psi'}{z} + \left(-\frac{s^2}{z^2} - \frac{1}{4} + \frac{b\beta}{2z}\right)\psi = 0,$$

where $s = c\sqrt{-2mE}/\hbar$.

One important tool (which we should try to use for future problems as well) is to look at limiting behavior of z. If we first let $z \to \infty$, the equation above roughly becomes

$$\psi'' - \frac{1}{4}\psi = 0$$

which has the solutions $\psi = e^{\pm z/2}$; we choose $\psi = e^{-z/2}$. If we instead let $z \to 0$, the equation above roughly becomes

$$\psi'' - \frac{s^2}{z^2}\psi = 0$$

(compare the rate at which z, z^2 approach 0). This equation has the solution $\psi = e^{-z/2}z^s w(z)$, where $w(z)$ is some function of z. Plugging this into our original equation, we get (after much derivation)

$$zw'' + w'(1 + 2s - z) + w\left(\frac{\beta b}{2} - \frac{1}{2} - s\right) = 0.$$

The equation above is a specific form of a more general equation

$$zw'' + (b - z)w' - aw = 0$$

known as "Kummer's equation". As a second order differential equation, it has two linearly independent solutions: one can be written in terms of a hypergeometric function

$$M(a, b, z) = 1 + \frac{az}{b} + \frac{(a)_2 z^2}{(b)_2 2!} + \cdots + \frac{(a)_n z^n}{(b)_n n!} + \cdots$$

where

$$(a)_n = a(a + 1)(a + 2)\cdots(a + n - 1), \quad (a)_0 = 1$$

is the rising factorial. This solution is valid as long as b is not an integer less than 1.

The other solution for Kummer's equation is

$$z^{1-b}M(a + 1 - b, 2 - b, z)$$

which is valid as long as b is not an integer greater than 1.

Note that for our purposes, considering $c > 0, E > 0$ and $m > 0$, then $b = 1 + 2s$ is a valid choice corresponding to the first solution. Thus,

$$w(z) = gM\left(s + \frac{1}{2} - \frac{\beta b}{2}, 1 + 2s, z\right)$$

where g is some constant. The solution given above satisfies the condition that a wave function must be finite only when the infinite series $M(a, b, z)$ truncates at some term. What this means is, we must have $a = -n$ for some $n \in \mathbb{N}$. Therefore, we may write

$$-n = s_n + \frac{1}{2} - \frac{\beta b}{2}, \quad n = 0, 1, \ldots, \left(\frac{\beta b}{2} - \frac{1}{2}\right)$$

where the upper bound on n corresponds to $s_n = 0$ (as we must have bound states where $E < 0$). Note here that

$$s_n = c\sqrt{2mE_n}/\hbar.$$

We may then write energy in terms of the variables above, to find

$$E_n = -\frac{\hbar^2 s_n^2}{2mc^2} = -\frac{\hbar^2}{2mc^2}\left[\left(\frac{mb^2c^2V_0}{2\hbar^2}\right)^{1/2} - \left(n+\frac{1}{2}\right)\right]^2.$$

Note: For $b = 2$, the potential $V(x)$ takes the familiar form of a Morse potential (apart from a constant factor of V_0).

5. The harmonic oscillator

5.1. **An analytic approach.** The problem which we will now consider is of such importance to the wider physical world that we wish to point it out- this is the harmonic oscillator problem. Any system fluctuating by a small amount "near" equilibrium may be described by the harmonic oscillator, or by a collection of decoupled harmonic oscillators. As we shall see, their Hamltonians take on a nice form, and many systems which occur naturally may be described by harmonic oscillators.

Example: Say we have a mass m coupled to a string with force constant k. For small deformations of x, Hooke's law tells us $F = -kx$; this gives rise to the potential $V = kx^2/2$. This is potentially the simplest example one can give of a harmonic oscillator. The Hamiltonian for this system is

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

where $\omega = \sqrt{k/m}$ is the classical frequency of oscillation. In general, any Hamiltonian that is quadratic in coordinate x and momentum p will be called a harmonic oscillator Hamiltonian.

Consider a general potential $V(x)$. We expand it into a Taylor series around its minimum x_0 to get

$$V(x) = V(x_0) + \left.\frac{dV}{dx}\right|_{x_0}(x-x_0) + \frac{1}{2!}\left.\frac{d^2V}{dx^2}\right|_{x_0}(x-x_0)^2 + \cdots$$

As $V(x_0)$ is a fixed value for $V(x)$, and x_0 acts as an arbitrary reference point, without loss of generality we may drop the first term in $V(x)$. Furthermore, as x_0 is a minimum of $V(x)$, the term $\left.\frac{dV}{dx}\right|_{x_0}(x-x_0) = 0$. Shifting the origin to x_0 (which we again are allowed to do without loss of generality), we get

$$V(x) = \frac{1}{2!}\left.\frac{d^2V}{dx^2}\right|_{x_0}(x-x_0)^2 + \cdots$$

As we are considering a system where only small perturbations around equilibrium occur, higher order terms are dropped. Therefore, we arrive at the potential

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

for the harmonic oscillator. The extension to a system of N uncoupled harmonic oscillators is fairly easy to derive:

$$\hat{H} = \sum_{i=1}^{N}\left(\frac{p_i^2}{2m_i} + \frac{1}{2}m_i\omega_i^2x_i^2\right).$$

For coupled harmonic oscillators, V cannot just be written as a sum of uncoupled potentials- it must depend on $x_1, \ldots, x_N$ simultaneously. Near an equilibrium point of V, we may expand to find

$$V(x_1, \ldots, x_N) = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left. \frac{\partial^2 V}{\partial x_i \partial x_j} \right|_0 x_i x_j + \cdots .$$

For small oscillations, therefore, we have

$$\hat{H} = \sum_{i=1}^{N} \sum_{j=1}^{N} \left(\frac{p_i p_j \delta_{ij}}{2m} + \frac{1}{2} x_i V_{ij} x_j \right)$$

where $V_{ij} = \left. \frac{\partial^2 V}{\partial x_i \partial x_j} \right|_0 = V_{ji}$ (assuming all masses are equal).

If we then diagonalize the matrix (V_{ij}), using the eigenvectors for the diagonalized matrix we can transform the Hamiltonian into one describing N uncoupled oscillators- we can then use this to reduce to our first case in order to solve.

Consider the expectation value of the harmonic oscillator Hamiltonian: we see

$$\begin{aligned} \langle H \rangle &= \frac{1}{2m} \langle \psi | \hat{p}^2 | \psi \rangle + \frac{1}{2} m\omega^2 \langle \psi | \hat{x}^2 | \psi \rangle \\ &= \frac{1}{2m} \langle \psi | \hat{p}^\dagger \hat{p} | \psi \rangle + \frac{1}{2} m\omega^2 \langle \psi | \hat{x}^\dagger \hat{x} | \psi \rangle \\ &= \frac{1}{2m} \langle \hat{p}\psi | \hat{p}\psi \rangle + \frac{1}{2} m\omega^2 \langle \hat{x}\psi | \hat{x}\psi \rangle \geq 0. \end{aligned}$$

So the energy values for $\hat{H}$ are non-negative.

Suppose we try and solve the Schrödinger equation, by considering the stationary states. In the coordinate basis, we have

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

and we only consider solutions ψ which lie in the Hilbert space. Use the substitution $\zeta = x\sqrt{m\omega/\hbar}$, where ζ is dimensionless. If we plug that into the equation above, we find

$$\frac{d^2\psi}{d\zeta^2} + \frac{2E}{\hbar\omega} \psi - \zeta^2 \psi = 0.$$

If we set $\epsilon = \frac{E}{\hbar\omega}$, we obtain

$$\psi'' + (2\epsilon - \zeta^2)\psi = 0.$$

To help determine a solution, we'll consider the asymptotic behavior. If we first let $|\zeta| \to \infty$, then ζ^2 tends to ∞ much faster than the term 2ϵ; so without loss of generality, we may reduce the equation to

$$\psi'' - \zeta^2 \psi = 0.$$

This has the general solution $\psi = Ae^{\zeta^2/2} + Be^{-\zeta^2/2}$. As $Ae^{\zeta^2/2} \to \infty$ when $|\zeta| \to \infty$ if $A \neq 0$, this forces $A = 0$ (as we only consider solutions in the Hilbert space). Therefore, one solution is given by $\psi = Be^{-\zeta^2/2}$.

If we instead let $|\zeta| \to 0$, the equation we began with reduces to

$$\psi'' + 2\epsilon\psi = 0.$$

This has solutions which are written in the form

$$\psi = A\cos(\sqrt{2\epsilon}\zeta) + B\sin(\sqrt{2\epsilon}\zeta).$$

When $|\zeta| \to 0$, the left part of the sum tends to A, while the right part of the sum tends to $B\sqrt{2\epsilon}$. Thus,

$$\psi \to A + B\sqrt{2\epsilon} + \mathcal{O}(\zeta^2)$$

which is constant. This, unfortunately, means that our limit case here is not very helpful. To circumvent this, we'll try and consider instead a general solution of the form $\psi = H(\zeta)e^{-\zeta^2/2}$ where $H(\zeta)$ must be chosen so that as $|\zeta| \to \infty$, the term $e^{-\zeta^2/2}$ dominates. If we take this choice of ψ and plug it into our equation, we obtain

$$H'' - 2\zeta H' + (2\epsilon - 1)H = 0$$

(note here that H is not the Hamiltonian). There are two ways to solve this equation- for the first, read the relevant section in Shankar.

The other solution is given by using the Hermite polynomials- they solve the differential equation above only for values of the form $2\epsilon = 2n + 1$ for $n = 0, 1, 2, \ldots$. The solution has the form

$$\psi_n(\zeta) = AH_n(\zeta)e^{-\zeta^2/2},$$

where A is the normalization constant and

$$H_n(\zeta) = (-1)^n e^{\zeta^2} \frac{d^n(e^{-\zeta^2})}{d\zeta^n}.$$

We have the following identities:

$$H_0 = 1, \quad H_1 = 2\zeta, \quad H_2 = 4\zeta^2 - 2.$$

These can be used to derive the general recurrence relation

$$H_{n+1}(\zeta) = 2\zeta H_n(\zeta) - 2nH_{n-1}(\zeta).$$

Recall that $\zeta = x\sqrt{m\omega/\hbar}$. Re substituting in to recover our original equation, we get

$$\psi_n(x) = Ae^{-\frac{m\omega x^2}{2\hbar}} H_n\left[\left(\frac{m\omega}{\hbar}\right)^{1/2} x\right]$$

where if we normalize, we may write

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

Note: The Hermite polynomials satisfy the following property (which we can use to help normalize):

$$\int_{-\infty}^{\infty} H_m(\zeta)H_n(\zeta)e^{-\zeta^2} d\zeta = \delta_{nm}\pi^{1/2}2^n n!,$$

for $n, m \in \mathbb{N}$.

We want an expression for the energy E as well- recalling that $\epsilon = \frac{E}{\omega\hbar}$, and $2\epsilon = 2n+1$, we have

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

for $n = 0, 1, 2, \ldots$.

Notes:

(i) Our energy is quantized (I think this has to do with the fact we only consider solutions in the Hilbert space, and not arbitrary solutions).

(ii) For any $n \in \mathbb{N}$, $E_{n+1} - E_n = \Delta E = \hbar\omega$. The lowest value of energy is for $n = 0$, where

$$E_0 = \frac{\hbar\omega}{2} > 0.$$

Note that this agrees with our previous observation that $\langle H\rangle \geq 0$. The 0^{th}-level energy state corresponds to zero-point energy of the system.

One question we may ask is: now that we have a countably infinite number of states (corresponding to the energy levels E_n), which state might minimize uncertainty? Say we begin with arbitrary state $|\psi\rangle$, and consider

$$\langle H\rangle = \langle\psi|\hat{H}|\psi\rangle = \frac{\langle\hat{p}^2\rangle}{2m} + \frac{1}{2}m\omega\langle\hat{x}^2\rangle.$$

Recall:

$$(\Delta p)^2 = \langle\hat{p}^2\rangle - \langle\hat{p}\rangle^2, \quad (\Delta x)^2 = \langle\hat{x}^2\rangle - \langle\hat{x}\rangle^2.$$

Using the definition of uncertainty, we substitute in the above to get

$$\langle H\rangle = \frac{(\Delta p)^2 + \langle\hat{p}\rangle^2}{2m} + \frac{1}{2}m\omega\Big[(\Delta x)^2 + \langle\hat{x}\rangle^2\Big].$$

In classical mechanics, $\Delta p = \Delta x = 0$. If we use classical mechanics as a guide, to find the "most classical" state then we aim to minimize the expression above with respect to the uncertainties $(\Delta p)^2, (\Delta x)^2$. To that end, we set $\langle p\rangle = \langle x\rangle = 0$. The expectation above then reduces to

$$\langle H\rangle = \frac{(\Delta p)^2}{2m} + \frac{1}{2}m\omega(\Delta x)^2.$$

As $\Delta x\Delta p \geq \hbar/2$, $\Delta p \geq \frac{\hbar}{2\Delta x}$. Thus,

$$\langle H\rangle \geq \frac{\hbar^2}{8m(\Delta x)^2} + \frac{1}{2}m\omega(\Delta x)^2.$$

To minimize, if we take $\frac{\partial\langle H\rangle}{\partial(\Delta x)} = 0$ we get

$$\frac{\partial\langle H\rangle}{\partial(\Delta x)} = 0 = -\frac{\hbar^2}{8m(\Delta x)^4} + \frac{1}{2}m\omega^2.$$

This implies $(\Delta x)^2 = \frac{\hbar^2}{2m\omega}$ is our minimum. So,

$$\langle H\rangle_{\min} = \frac{\hbar\omega}{2}$$

i.e., uncertainty is minimized at our ground state. The wave function for the ground state is

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

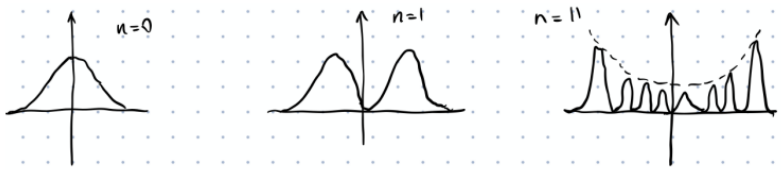
Note: This is a Gaussian wave function- which matches with previous results we have seen, showing that Gaussian wave packets minimize uncertainty.

Properties:

(i) We have

$$\psi_n(-x) = \psi_n(x) \text{ for } n \text{ even},$$
$$\psi_n(-x) = -\psi_n(x) \text{ for } n \text{ odd}.$$

(ii) The probability distribution for varying choices of n is shown below:



(iii) As $n \to \infty$, the probability distribution is proportional to

$$P_{\text{cl}}(x) \propto \frac{1}{v(x)} = \frac{1}{\omega(x_0^2 - x^2)^{1/2}}.$$

I.e., the classical probability distribution is proportional to an inverse velocity.

Example: Suppose we now start with the time-dependent case. We expand the wave function at $t = 0$ and write

$$\Psi(x, 0) = \sum_{n=0}^{\infty} c_n \psi_n(x)$$

where the c_n's are determined via

$$c_n = \int \psi_n^*(x)\Psi(x, 0)dx.$$

Using the propagator equation, we can derive the general expression for the wave function:

$$\Psi(x, t) = e^{-i\omega t/2} \sum_{n=0}^{\infty} c_n \psi_n(x) e^{-in\omega t}.$$

The identity above follows from the general propagator equation, and using the fact that $E_n = \hbar\omega\left(n + \frac{1}{2}\right)$.

5.2. **An algebraic approach.** We have previously seen a solution to the harmonic oscillator problem using analytic tools and special functions; in what follows, we will use a less common algebraic approach. Begin by rearranging the harmonic oscillator Hamiltonian as

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

Define the operator

$$\hat{a} = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} + i\frac{\hat{p}}{m\omega}\right).$$

We note that $\hat{a}$ is not Hermitian, as $\hat{a} \neq \hat{a}^\dagger$. If we use the canonical commutator relations between $\hat{x}$ and $\hat{p}$, where $[\hat{x}, \hat{p}] = i\hbar$, we can rewrite the equation for the Hamiltonian above as

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

The commutator relation between $\hat{a}, \hat{a}^\dagger$ is also easily shown to be

$$[\hat{a}, \hat{a}^\dagger] = \hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a} = 1.$$

As we were able to write $\hat{H}$ as a linear equation in terms of $\hat{a}^\dagger\hat{a}$, it is clear that $\hat{H}, \hat{a}^\dagger\hat{a}$ commute with each other. Thus, they have a common set of eigenvectors- so it will be

sufficient to solve the eigenvalue problem for $\hat{H}$ by solving it for the operator $\hat{a}^\dagger\hat{a}$.

We want to solve the eigenvalue problem

$$\hat{a}^\dagger\hat{a}\,|n\rangle = \lambda_n\,|n\rangle\,.$$

First, we note that if we multiply both sides of the equation above by $\langle n|$ on the left, we get

$$\langle n|\hat{a}^\dagger\hat{a}|n\rangle = \lambda_n\,\langle n|n\rangle \Rightarrow \langle \hat{a}n|\hat{a}n\rangle = \lambda\,\langle n|n\rangle = \lambda_n \geq 0.$$

We also notice that if $|n\rangle$ is an eigenvector of $\hat{a}^\dagger\hat{a}$, then $\hat{a}^\dagger\,|n\rangle$ is an eigenvector as well: to see why, note that

$$(\hat{a}^\dagger\hat{a})\hat{a}^\dagger\,|n\rangle = \hat{a}^\dagger(\hat{a}^\dagger\hat{a}+1)\,|n\rangle = (\lambda_n+1)\hat{a}^\dagger\,|n\rangle$$

where we take advantage of the commutator relation $\hat{a}\hat{a}^\dagger = \hat{a}^\dagger\hat{a}+1$. Using a similar argument, we can show that $\hat{a}\,|n\rangle$ is an eigenvector of $\hat{a}^\dagger\hat{a}$ with corresponding eigenvalue λ_n-1.

Note: The operators $\hat{a}, \hat{a}^\dagger$ are called ladder operators/raising and lowering operators.

As $\lambda_n \geq 0$ for all $n \in \mathbb{N}$, there is a lower bound on the number of times we can reduce λ_n using $\hat{a}^\dagger\hat{a}$ (as we cannot repeatedly subtract 1 indefinitely). If we label the "lowest step on the ladder" by setting $n = 0$, we have

$$\hat{a}^\dagger\hat{a}\,|0\rangle = \lambda_0\,|n\rangle\,, \quad 1 > \lambda_0 \geq 0,$$
$$\hat{a}\,|0\rangle = 0, \quad \lambda_0 = 0.$$

Starting from $|0\rangle$, we can then obtain all other eigenvectors and eigenvalues by repeated application of the operator $\hat{a}^\dagger$. The eigenvalues (as we have seen) increase in unit steps, and so we may write

$$|n\rangle = N_n(\hat{a}^\dagger)^n\,|0\rangle\,, \quad n = 0,1,2,\ldots, \quad \lambda_n = n$$

where N_n is some normalization constant which is yet to be determined. If we combine all of this information together, it is easy to see that

$$\hat{H}\,|n\rangle = \hbar\omega\left(n+\frac{1}{2}\right)|n\rangle\,,$$

and so the energy eigenvalues are given by

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

(where $\lambda_n = n$ in the above identification).

Notation:

(i) $\hat{a}^\dagger$ is called the raising operator.
(ii) $\hat{a}$ is called the lowering operator.
(iii) The operator $\hat{N} = \hat{a}^\dagger\hat{a}$ is called the number operator, as

$$\hat{N}\,|n\rangle = n\,|n\rangle$$

(i.e., it tells us the number of which state we are in). As a side note, the notion of a particle as an excitation of an oscillator-like dynamics system is quite important in quantum mechanics. An n^{th} excited state of a harmonic oscillator is interpreted as corresponding to the presence of n particles or quasiparticles, each carrying energy $\hbar\omega$. These particles/quanta are named photons, excitons, phonons, etc. (depending on the physical context). The eigenstate $|0\rangle$ is known as the ground-state, or the no-particle state of the system.

Suppose we try and determine the normalization constant N_n mentioned above. By the "ladder property" of the lowering and raising operators and the orthonormality of states $|n\rangle$, we can conclude that the matrix elements of $\hat{a}, \hat{a}^\dagger$ in the representation with basis $\{|n\rangle\}$ connect only neighboring basis states- i.e., we have:

$$\langle n-1|\hat{a}|n\rangle = C_n, \qquad \langle n+1|\hat{a}^\dagger|n\rangle = \langle n|\hat{a}|n+1\rangle = C_{n+1}^*.$$

To find C_n, we use the completeness relation- we see

$$\begin{aligned} |C_n|^2 &= \langle n-1|\hat{a}|n\rangle^* \langle n-1|\hat{a}|n\rangle = \langle n|\hat{a}^\dagger|n-1\rangle \langle n-1|\hat{a}|n\rangle \\ &= \sum_{n'} \langle n|\hat{a}^\dagger|n'\rangle \langle n'|\hat{a}|n\rangle = \langle n|\hat{a}^\dagger\hat{a}|n\rangle = n, \end{aligned}$$

which suggests $C_n = \sqrt{n}e^{i\theta}$ for some $\theta \in [0, 2\pi)$. Without loss of generality, we may assume $\theta = 0$, and thus we may set $C_n = \sqrt{n}$. From this, we have the relations

$$\begin{aligned} \hat{a}\,|n\rangle &= |n-1\rangle \langle n-1|\hat{a}|n\rangle = \sqrt{n}\,|n-1\rangle\,, \\ \hat{a}^\dagger\,|n\rangle &= |n+1\rangle \langle n+1|\hat{a}^\dagger|n\rangle = \sqrt{n+1}\,|n+1\rangle\,. \end{aligned}$$

From here, we get the normalized eigenfunctions of $\hat{a}^\dagger\hat{a}$:

$$|n\rangle = (n!)^{1/2}(\hat{a}^\dagger)^n\,|0\rangle\,.$$

If we tried to determine the matrix representation of $\hat{a}, \hat{a}^\dagger$ with respect to the eigenbasis $\{|n\rangle\}$, using the relations above it should be fairly easy to see that their matrices take the forms:

$$\hat{a} = \begin{bmatrix} 0 & \sqrt{1} & 0 & 0 & \cdots \\ 0 & 0 & \sqrt{2} & 0 & \cdots \\ 0 & 0 & 0 & \sqrt{3} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{bmatrix},$$

$$\hat{a}^\dagger = \begin{bmatrix} 0 & 0 & 0 & 0 & \cdots \\ \sqrt{1} & 0 & 0 & 0 & \cdots \\ 0 & \sqrt{2} & 0 & 0 & \cdots \\ 0 & 0 & \sqrt{3} & 0 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{bmatrix}.$$

This matches what we know about $\hat{a}, \hat{a}^\dagger$- i.e., they are not Hermitian operators. As $\hat{H} = \hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right)$, we can easily find the matrix representation for the Hamiltonian in this basis as well:

$$\hat{H} = \frac{\hbar\omega}{2}\begin{bmatrix} 1 & 0 & 0 & \cdots \\ 0 & 3 & 0 & \cdots \\ 0 & 0 & 5 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix}.$$

As the coordinate operator $\hat{x}$ can be expressed as a linear equation of $\hat{a}, \hat{a}^\dagger$, we can also use the matrix representations above to find the matrix representation for $\hat{x}$ in this basis:

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}\begin{bmatrix} 0 & \sqrt{1} & 0 & \cdots \\ \sqrt{1} & 0 & \sqrt{2} & \cdots \\ 0 & \sqrt{2} & 0 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix}.$$

Clearly, $\hat{x}$ is a Hermitian operator, as its matrix representation is real and symmetric. We can also easily show that the matrix representation for $\hat{p}$ will be real and symmetric as

well, using a similar argument as above.

To determine the eigenstates and eigenvalues of the position operator, we'll need to solve the problem

$$\sqrt{\frac{\hbar}{2m\omega}}\begin{bmatrix} 0 & \sqrt{1} & 0 & \cdots \\ \sqrt{1} & 0 & \sqrt{2} & \cdots \\ 0 & \sqrt{2} & 0 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix}\begin{bmatrix} c_0 \\ c_1 \\ c_2 \\ \vdots \end{bmatrix} = x'\begin{bmatrix} c_0 \\ c_1 \\ c_2 \\ \vdots \end{bmatrix}$$

where x' is an eigenvalue, and $c_n = \langle n|x'\rangle$ are the transformation coefficients. Multiplying out, we find the system of linear equations

$$\begin{gathered} \sqrt{1}c_1 = \sqrt{\frac{2m\omega}{\hbar}}x'c_0, \\ \sqrt{2}c_2 + \sqrt{1}c_0 = \sqrt{\frac{2m\omega}{\hbar}}x'c_1, \\ \cdots = \cdots \\ \sqrt{n+1}c_{n+1} + \sqrt{n}c_{n-1} = \sqrt{\frac{2m\omega}{\hbar}}x'c_n \\ \cdots = \cdots \end{gathered}$$

The recurrence relation can be solved, and has the solution

$$c_n(x') = \langle n|x'\rangle = 2^{-(n/2)}(n!)^{-1/2}H_n\left(\sqrt{\frac{m\omega}{\hbar}}x'\right)c_0$$

where H_n is the n^{th} Hermite polynomial. As everything can be written in terms of c_0, this is the only constant left to determine. Using the completeness relation inserted into $\langle x'|x''\rangle = \delta(x' - x'')$, we have

$$\sum_n \langle x'|n\rangle \langle n|x''\rangle = \delta(x' - x'').$$

Using this, we find

$$\langle n|x'\rangle = \psi_n(x') = \left(\frac{m\omega}{\pi\hbar 2^{2n}(n!)^2}\right)^{1/4}\exp\left[-\frac{m\omega x^2}{2\hbar}\right]H_n\left[\left(\frac{m\omega}{\hbar}\right)^{1/2}x'\right].$$

Note that this is exactly the solution we arrived at previously with the analytic method.

5.3. **Coherent states.** The general state of a harmonic oscillator can be expressed as a superposition of the energy eigenstates $|n\rangle$ (which is no surprise). However, there are other classes of eigenstates that we may wish to consider, even if they do not necessarily form a well-defined basis. One specific class are called coherent (or Glauber) states. These are states $|a\rangle$ which act as an eigenstate for the lowering operator $\hat{a}$: i.e., we have

$$\hat{a}\,|a\rangle = \alpha\,|a\rangle\,,$$

where α is some eigenvalue.

For any scalar α, consider the unitary shifting/displacement operator $\hat{D_\alpha}$ defined via

$$\hat{D}_\alpha = e^{\alpha\hat{a}^\dagger - \alpha^*\hat{a}}.$$

We call it a displacement operator, as

$$\hat{D}_\alpha^\dagger\hat{a}\hat{D}_\alpha = e^{\alpha^*\hat{a} - \alpha\hat{a}^\dagger}\hat{a}e^{\alpha\hat{a}^\dagger - \alpha^*\hat{a}} = \hat{a} - \alpha[\hat{a}^\dagger, \hat{a}] = \hat{a} + \alpha,$$

where we use the operator identity

$$e^{\lambda\hat{A}}\hat{B}e^{-\lambda\hat{A}} = \hat{B} + \lambda[\hat{A}, \hat{B}]$$

provided $[\hat{A},[\hat{A},\hat{B}]]=0$ (which is true in this case).

Note: For any $\alpha\in\mathbb{C}$, we have

$$\hat{D}_{-\alpha}=\hat{D}_{\alpha}^{\dagger}=\hat{D}_{\alpha}^{-1}.$$

Theorem 5.1. *The coherent state $|a\rangle$ is generated from the vacuum state $|0\rangle$ by the displacement operator $\hat{D}_a$.*

Proof. Applying a negative displacement to $|a\rangle$, we find

$$\hat{a}\hat{D}_{-a}|a\rangle=\hat{D}_{-a}\hat{D}_{-a}^{\dagger}\hat{a}\hat{D}_{-a}|a\rangle=\hat{D}_{-a}(\hat{a}-a)|a\rangle=a\hat{D}_{-a}|a\rangle-a\hat{D}_{-a}|a\rangle=0.$$

This implies $\hat{D}_{-a}|a\rangle=0$; that is, it is a vacuum state. We can also then write $\hat{D}_a|0\rangle=|a\rangle$, or

$$|a\rangle=e^{a\hat{a}^{\dagger}-a^{*}\hat{a}}|0\rangle=e^{-|a|^2/2}e^{a\hat{a}^{\dagger}}|0\rangle,$$

where we use the operator identity

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

which holds when $[[A,B],A]=[[A,B],B]=0$. □

6. Angular momentum and spin

Initially, when we derived the momentum operator and the law of conservation of momentum we considered a closed system of particles in the absence of any fields; we used the fact that all positions in space of such a system are equivalent. Additionally, we used the fact that such a space is isotropic- so all directions in space are equivalent as well. By using the fact that the Hamiltonian does not change when the system is translated as a whole, we found a "quantity" which commutes with the Hamiltonian- this is what we called momentum.

Now, we wish to derive the operator for angular momentum. We consider a closed system, and use the fact that the Hamiltonian of such a system cannot change when the system rotates as a whole through an arbitrary angle about an arbitrary axis. Consider an arbitrary rotation of a radius vector $\mathbf{r}_\alpha$ of a particle α around some rotation axis through an angle $\delta\theta$ with the corresponding $\delta\theta$ vector of infinitely small rotation. If we let $\mathbf{n}$ be a vector which points along the axis of rotation in the change in $\mathbf{r}_\alpha$, denoted $\delta\mathbf{r}_\alpha$, we may write it as

$$\delta\mathbf{r}_\alpha=\delta\theta\mathbf{n}\times\mathbf{r}_\alpha=\delta\theta\times\mathbf{r}_\alpha.$$

Any arbitrary function Ψ of coordinates is then transformed into

$$\begin{aligned}\Psi(\overrightarrow{r}_1+\delta\mathbf{r}_1,\ldots)&=\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots)+\sum_\alpha\delta\mathbf{r}_\alpha\cdot\nabla_\alpha\Psi\\&=\Psi(\mathbf{r}_1,\ldots)+\sum_\alpha\delta\theta\times\mathbf{r}_\alpha\cdot\nabla_\alpha\Psi\\&=\left(1+\delta\theta\cdot\sum_\alpha\mathbf{r}_\alpha\times\nabla_\alpha\right)\Psi(\mathbf{r}_1,\ldots).\end{aligned}$$

From the above, we see that $(1+\delta\theta\dot{\sum}_\alpha\mathbf{r}_\alpha\times\nabla_\alpha)$ is an expression for an infinitely small rotation.

The fact that an infinitely small rotation does not alter the Hamiltonian implies (as discussed earlier) that the rotation operator must commute with the Hamiltonian. As $\delta\theta$ is a constant vector, we can simplify by dropping it without error. Therefore, we have

$$\left(\sum_\alpha\mathbf{r}_\alpha\times\nabla_\alpha\right)\hat{H}-\hat{H}\left(\sum_\alpha\mathbf{r}_\alpha\times\nabla_\alpha\right)=0.$$

This is again a conservation law for some quantity $\sum_\alpha \mathbf{r}_\alpha \times \nabla_\alpha$. Adjusting for a constant prefactor of $-i\hbar$, we let $\hat{\ell}$ denote this quantity, and call $\hat{\ell}$ the angular momentum. For a single particle, it can be written in condensed form as

$$\hat{\ell} = -i\hbar \mathbf{r} \times \nabla = \hat{\mathbf{r}} \times \hat{\mathbf{p}}.$$

Note: This is exactly as how it is defined in classical mechanics.

The angular momentum operator for a whole system is denoted by $\hat{L}$, and written as

$$\hat{L} = -i\hbar \sum_\alpha \mathbf{r}_\alpha \times \nabla_\alpha.$$

It may also be written in terms of its components $\hat{\ell}_i$, where

$$\hat{\ell}_i = -i\hbar \sum_{jk} \epsilon_{ijk} r_j \frac{\partial}{\partial r_k} = \sum_{jk} \epsilon_{ijk} \hat{r}_j \hat{p}_k$$

where i, j, k run over the three directions x, y and z and the coefficient ϵ_{ijk} is defined via

$$\epsilon_{ijk} = \begin{cases} +1, & i,j,k \text{ is an even permutation of } x,y,z, \\ -1, & i,j,k \text{ is an odd permutation of } x,y,z, \\ 0, & \text{otherwise.} \end{cases}$$

Note: As each component of the angular momentum operator is Hermitian, the angular momentum operator is Hermitian.

Remark: We have the following commutator relations, which are fairly easy to derive:

(i) $[\hat{\ell}_y, \hat{y}] = [\hat{\ell}_z, \hat{z}] = [\hat{\ell}_x, \hat{x}] = 0$.
(ii) $[\hat{\ell}_i, \hat{x}_j] = i\hbar\epsilon_{ijk}\hat{x}_k$.
(iii) $[\hat{\ell}_i, \hat{p}_j] = i\hbar\epsilon_{ijk}\hat{p}_k$.
(iv) $[\hat{\ell}_i, \hat{\ell}_j] = i\hbar\epsilon_{ijk}\hat{\ell}_k$.

For clarity, we give an example showing how to derive a specific case of the last relation. Consider $\hat{\ell}_x, \hat{\ell}_y$:

$$\begin{aligned} [\hat{\ell}_x, \hat{\ell}_y] &= \hat{\ell}_x(\hat{z}\hat{p}_x - \hat{x}\hat{p}_z) - (\hat{z}\hat{p}_x - \hat{x}\hat{p}_z)\hat{\ell}_x \\ &= (\hat{\ell}_x\hat{z} - \hat{z}\hat{\ell}_x)\hat{p}_x - \hat{x}(\hat{\ell}_x\hat{p}_z - \hat{p}_z\hat{\ell}_x) \\ &= [\hat{\ell}_x, \hat{z}]\hat{p}_x - \hat{x}[\hat{\ell}_x, \hat{p}_z] = -i\hbar\hat{y}\hat{p}_x + i\hbar\hat{x}\hat{p}_y \\ &= i\hbar(\hat{x}\hat{p}_y - \hat{y}\hat{p}_x) = i\hbar\hat{\ell}_z. \end{aligned}$$

We introduce three more important operators, connected to the angular momentum:

$$\begin{aligned} \hat{L}^2 &= \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2, \\ \hat{L}_+ &= \hat{L}_x + i\hat{L}_y, \\ \hat{L}_- &= \hat{L}_x - i\hat{L}_y. \end{aligned}$$

Proposition 6.1. *We have*

$$[\hat{L}^2, \hat{L}_x] = [\hat{L}^2, \hat{L}_y] = [\hat{L}^2, \hat{L}_z] = 0.$$

Proof. We will only prove one of them; the proof for the rest are almost identical. Considering $[\hat{L}^2, \hat{L}_z]$, we see

$$\begin{aligned}[\hat{L}_z, \hat{L}^2] &= [\hat{L}_x^2, \hat{L}_z] + [\hat{L}_y^2, \hat{L}_z] + [\hat{L}_z^2, \hat{L}_z] \\ &= [\hat{L}_x^2, \hat{L}_z] + [\hat{L}_y^2, \hat{L}_z] \\ &= [\hat{L}_z, \hat{L}_x]\hat{L}_x + \hat{L}_x[\hat{L}_z, \hat{L}_x] + [\hat{L}_z, \hat{L}_y]\hat{L}_y + \hat{L}_y[\hat{L}_z, \hat{L}_y] \\ &= i\hbar(\hat{L}_y\hat{L}_x + \hat{L}_x\hat{L}_y - \hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x) = 0.\end{aligned}$$

The others follow through similar computations. □

Remark: We note that $\hat{L}^2$ can be written in terms of $\hat{L}_x$ and $\hat{L}_y$ by taking

$$\hat{L}^2 = \hat{L}_-\hat{L}_+ + \hat{L}_z^2 + \hbar\hat{L}_z.$$

The proof of the equation above follows just through expansion and algebra.

We will try and find the eigenvalues for the momentum operator. For sake of simplicity, we consider a system with only a single particle, and focus on one component $\hat{\ell}_z$- i.e., we'll solve for

$$\hat{\ell}_z\psi = \ell_z\psi.$$

Switching to polar coordinates (r, θ, ϕ) where

$$x = r\sin\theta\cos\phi, \quad y = r\sin\theta\sin\phi, \quad z = r\cos\theta$$

the representation for $\hat{\ell}_z$ in the basis becomes

$$\hat{\ell}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \Rightarrow -i\hbar\frac{\partial}{\partial\phi}.$$

Therefore, we solve the differential equation $-i\hbar\frac{\partial}{\partial\phi}\psi = \ell_z\psi$; this clearly has a solution of the form $\psi = f(r,\theta)e^{i\ell_z\phi/\hbar}$, where $f(r,\theta)$ is some undetermined function of r and θ.

As we are looking for valid eigenstate solutions, we know any potential candidate wavefunction in our Hilbert space must be injective; considering our change in coordinate representation, this forces $\psi(0) = \psi(2\pi)$ if ψ is an eigenstate. Therefore,

$$1 = e^{2\pi\ell_z/\hbar} \Rightarrow \ell_z = m\hbar$$

where $m \in \mathbb{Z}$ is called the magnetic quantum number. For the total angular momentum of a system, we similarly have that the eigenvalues of $\hat{L}_z$ are $M\hbar$ with $M \in \mathbb{Z}$.

As the direction of the z-axis is in no way distinctive, we note that the same results as derived above must hold for $\hat{\ell}_x, \hat{\ell}_y$ as well (and thus for $\hat{L}_x, \hat{L}_y$). We are careful to note, however, that a common eigenstate for all three exists only when their corresponding eigenvalues are the same: there is no state in which two or three components of the angular momentum have definite values different from zero.

Question: Is there a limit to our values of m?

Suppose $|ab\rangle$ is a simultaneous eigenstate of $\hat{L}_z, \hat{L}^2$ with

$$\hat{L}_z|ab\rangle = b|ab\rangle, \quad \hat{L}^2|ab\rangle = a|ab\rangle.$$

Consider the operator $\hat{L}^2 - \hat{L}_z^2$; we have

$$\langle ab|\hat{L}^2 - \hat{L}_z^2|ab\rangle = a - b^2 \geq 0,$$

where the latter inequality follows from the fact that $\hat{L}^2 - \hat{L}_z^2 = \hat{L}_x^2 + \hat{L}_y^2$, which is positive definite. This means $b^2 \leq a$, and so there does indeed exist an upper bound for our eigenvalues of $\hat{L}_z$ (and $\hat{L}_x, \hat{L}_y$).

Suppose we now try to determine the eigenvalues of the operator $\hat{L}^2$. Let $|M\rangle$ be an eigenstate of $\hat{L}_z$, with corresponding eigenvalue $\hbar M$. Consider the operator $\hat{L}_+$; using the commutator relation $[\hat{L}_z, \hat{L}_+] = \hbar \hat{L}_+$, we note

$$\hat{L}_z \hat{L}_+ |M\rangle = \hbar(M+1)\hat{L}_+ |M\rangle .$$

This means that $\hat{L}_+ |M\rangle$ is an eigenstate of $\hat{L}_z$ as well. We let $|M+1\rangle = \lambda \hat{L}_+ |M\rangle$ for some $\lambda \in \mathbb{C}$. Let $|L\rangle$ denote the eigenstate corresponding to our upper limit on the eigenvalues of $\hat{L}_z$ (which we know exists, by our work above). We note that $\hat{L}_+ |L\rangle = 0$. If we now consider the operator $\hat{L}_-$, as $\hat{L}^2 = \hat{L}_- \hat{L}_+ + \hat{L}_z^2 + \hbar \hat{L}_z$, we see

$$\hat{L}_- \hat{L}_+ |L\rangle = (\hat{L}^2 - \hat{L}_z^2 - \hbar \hat{L}_z) |L\rangle = 0.$$

Therefore,

$$\begin{aligned} \hat{L}^2 |L\rangle &= \hat{L}_z^2 |L\rangle + \hbar \hat{L}_z |L\rangle \\ &= \hbar^2 L^2 |L\rangle + \hbar^2 L |L\rangle \\ &= \hbar^2 L(L+1) |L\rangle . \end{aligned}$$

This implies $\hbar^2 L(L+1)$ is an eigenvalue of $\hat{L}^2$. Therefore, for a fixed eigenvalue M of $\hat{L}_z$ (equivalently, $\hat{L}_x, \hat{L}_y$) we have $-L \leq M \leq L$ with $2L+1$ possible choices for the value M takes. Thus, the energy level corresponding to the angular momentum L has $2L+1$-fold degeneracy.

We'll return to the eigenvalue problem in the coordinate representation we initially started with: that is, we look for the eigenfunctions of $\hat{\ell}_z$. We know $\psi = f(r,\theta)e^{im\phi}$. Suppose we only consider the angular part of the wave function: we let

$$Y_{\ell m}(\theta, \phi) = \Phi_m(\phi)\Theta_{\ell m}(\theta)$$

where $\Phi_m(\phi) = Ae^{im\phi}$, where A is a potential normalization constant which we have yet to determine. To find A, we normalize $\Phi_m(\phi)$ over $[0, 2\pi]$; a standard application of the normalization process shows $A = (2\pi)^{-1/2}$.

Total normalization of the wavefunction is given by

$$\int_0^{\pi} d\theta \int_0^{2\pi} |Y_{\ell m}|^2 \sin\theta d\phi = 1.$$

As we have already normalized $\Phi_m(\phi)$, all that is left is to determine $\int_0^{\pi} |Y_{\ell m}|^2 \sin\theta d\theta = 1$. While $Y_{\ell m}(\theta, \phi)$'s are orthonormal (as the eigenfunction of a Hermitian operator), our functions $\Theta_{\ell m}(\theta)$ are not eigenfunctions of any of the angular momentum operators; furthermore, they are orthogonal for different values of ℓ, but not for m. Luckily for us, this last issue is taken care of by the corresponding $\Phi_m(\phi)$.

We want to determine the functions $\Theta_{\ell m}(\theta)$, solving the eigenvalue problem

$$\hat{\ell}^2 Y_{\ell m}(\theta, \phi) = \hbar^2 \ell(\ell+1) Y_{\ell m}(\theta, \phi).$$

Taking the representation of $\hat{\ell}^2$ in the polar coordinate basis, we have

$$\begin{aligned} &\hat{\ell}^2 Y_{\ell m}(\theta, \phi) \\ &= -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} Y_{\ell m}(\theta, \phi) \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} Y_{\ell m}(\theta, \phi) \right] = \hbar^2 \ell(\ell+1) Y_{\ell m}(\theta, \phi). \end{aligned}$$

Rewriting the above, we have

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}Y_{\ell m}(\theta,\phi)\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}Y_{\ell m}(\theta,\phi)+\ell(\ell+1)Y_{\ell,m}(\theta,\phi)=0.$$

If we substitute in $Y_{\ell m}(\theta,\phi)=\Phi_m(\phi)\Theta_{\ell m}(\theta)$, this reduces down to the equation

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\Theta_{\ell m}(\theta)\right)-\frac{m^2}{\sin^2\theta}\Theta_{\ell m}(\theta)+\ell(\ell+1)\Theta_{\ell m}(\theta)=0.$$

This solutions to this equation which also satisfy boundary conditions and injectivity for positive integer values $-\ell\leq m\leq\ell$ are called the associated Legendre polynomials $P_\ell^m(\cos\theta)$, which are polynomials in $\cos\theta$ and $\sin\theta$. A closed form expression for $\Theta_{\ell m}(\theta)$ is given by

$$\Theta_{\ell m}(\theta)=(-1)^m i^\ell\left[\frac{(2\ell+1)(\ell-m)}{2(\ell+m)!}\right]^{1/2}P_\ell^m(\cos\theta)$$

for $m\geq 0$. For $m<0$, we can use $\Theta_{\ell,-|m|}=(-1)^m\Theta_{\ell|m|}$ instead. We can then use these to determine

$$Y_{\ell m}(\theta,\phi)=(-1)^{(m+|m|)/2}i^\ell\left[\frac{2\ell+1(\ell-|m|)!}{4\pi(\ell+|m|)!}\right]^{1/2}P_\ell^{|m|}(\cos\theta)e^{im\phi}.$$

Examples:

(i) In the case where $m=0$,

$$Y_{\ell 0}=i^\ell\sqrt{\frac{2\ell+1}{4\pi}}P_\ell(\cos\theta).$$

For an example with a specific value of ℓ, consider

$$Y_{10}=\sqrt{\frac{3}{4\pi}}\cos\theta.$$

(ii) In the case where $m=\pm1$, if $\ell=1$ we have

$$Y_{11}=-i\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta e^{i\phi},$$
$$Y_{1,-1}=Y_{11}.$$

6.1. **Motion in a centrally symmetric field.** We now turn to a class of problems; specifically, those for which $V(r,\theta,\phi)=V(r)$. Recall that the Schrodinger equation in spherical coordinates is written as

$$\left[-\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\frac{1}{r^2}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)+V(r)\right]\psi(r,\theta,\phi)=E\psi(r,\theta,\phi).$$

For rotationally invariant problems, in a central field any motion in such a field preserves angular momentum.

Recall: $[\hat{H},\hat{\ell}]=0$; therefore, $\hat{H},\hat{\ell}^2,\hat{\ell}_z$ have simultaneous eigenfunctions of the form

$$\psi(r,\theta,\phi)=R(r)Y_{\ell m}(\theta,\phi).$$

Suppose we use the functions ψ of the form above, and plug them into the Schrodinger equation in spherical coordinates; as

$$\hat{\ell}^2=-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right],$$

we get

$$\left[-\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}-\frac{\ell(\ell+1)}{r^2}\right)+V(r)\right]R(r)=ER(r).$$

Note that in order to derive the above, we used the fact that $\hat{\ell}Y_{\ell m}(\theta,\phi) = \hbar^2\ell(\ell+1)Y_{\ell m}(\theta,\phi)$. We also pay close attention to the fact that our simplified equation above does not depend on m.

We can further rewrite the equation derived above, where

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{2m}{\hbar}\left[E - V - \frac{\hbar^2\ell(\ell+1)}{2mr^2}\right]R(r) = 0,$$

and introduce a new function χ defined so that $R = \chi/r$. With this, we rewrite our previous equation in terms of χ so that

$$\frac{d^2\chi}{dr^2} + \frac{2m}{\hbar}\left[E - V - \frac{\hbar^2\ell(\ell+1)}{2mr^2}\right]\chi = 0. \tag{7}$$

Notes:

(i) This equation is formally identical to the Schrodinger equation for one-dimensional motion along r.
(ii) The variable r goes from 0 to ∞.
(iii) Potential energy should now be redefined so that $V_\ell(r) = V(r) + \ell(\ell+1)/2mr^2$. Here the term $\ell(\ell+1)/2mr^2$ is called the centrifugal energy, and it is non-zero only for $\ell \neq 0$.
(iv) The wave function ψ is now completely determined by E, ℓ, and m. Therefore, the energy, square of the angular momentum, and the z component of angular momentum form a complete set of physical quantities for motion in a centrally symmetric field.

Suppose we now examine the limiting behavior using the previous equation. If $r \to 0$ for general V which satisfies $\lim_{r\to 0} V(r)r^2 = 0$, then our equation becomes dominated by the centrifugal term:

$$V_\ell \to \ell(\ell+1)/2mr^2.$$

Looking for R in terms of a power series expression, we have R has the approximate behavior of r^s. If we substitute this into the Schrodinger equation, we get $s(s+1) = \ell(\ell+1)$. Therefore, either $s = \ell$ or $s = -(\ell+1)$. However, the latter case does not guarantee a valid wave function, as $r^{-(\ell+1)}$ approaches infinity as $r \to 0$ when $\ell \geq 0$. Therefore, the only "physically" possible choice is when $s = \ell$. This indicates that near the origin, wave functions are proportional to r^ℓ.

If we instead consider $r \to \infty$, making the assumption that $\lim_{r\to\infty} rV(r) = 0$ our equation becomes

$$\frac{d^2\chi}{dr^2} = -\frac{2m}{\hbar}E\chi.$$

If $E > 0$, then $\chi = Ae^{ikr} + Be^{-ikr}$ where $k = (2mE/\hbar^2)^{1/2}$. We note this is precisely the scenario describing a free particle (as we have seen before). If $E < 0$, we use the change of variable $k \mapsto ik$ so that $k = (2m|E|/\hbar^2)^{1/2}$ with $\chi = Ae^{kr} + Be^{-kr}$. In this case, we have bound states when $B = 0$.

6.2. **A free particle in spherical potential.** If we suppose $V = 0$, the equation 7 reduces to

$$\frac{1}{r^2}\frac{d}{dr}r^2\frac{dR}{dr} + \frac{2m}{\hbar}\left[E - \frac{\ell(\ell+1)\hbar^2}{2mr^2}\right]R = 0.$$

If we suppose $k = \sqrt{2mE/\hbar^2}$, we can rewrite the reduced equation above as

$$R''_{k\ell} + \frac{2}{r}R'_{k\ell} + \left[k^2 - \frac{\ell(\ell+1)}{r^2}\right]R_{k\ell} = 0.$$

Note that now, R depends on both k and ℓ; additionally, we remark that the previous equation is precisely the radial part of the Helmholtz equation.

In order to help us solve the equation for $R_{k\ell}$, we will start by considering the specific case of $\ell = 0$. For this choice of ℓ, our equation becomes

$$\frac{d^2R_{k0}}{dr^2} + \frac{2}{r}\frac{dR_{k0}}{dr} + k^2R_{k0} = 0 \Rightarrow \frac{d^2(rR_{k0})}{dr^2} + k^2rR_{k0} = 0.$$

The equation has a solution $R_{k0} = \frac{2\sin(kr)}{r}$, where the constant term 2 arises from normalization. We can now use our expression for R_{k0} to find a general solution for all other values of ℓ: if we use the substitution $R_{k\ell} = r^\ell\chi_{k\ell}$, we can find

$$\chi''_{k\ell} + \frac{2(\ell+1)}{r}\chi'_{k\ell} + k^2\chi_{k\ell} = 0.$$

Differentiating the above with respect to r, we see

$$\chi'''_{k\ell} + \frac{2(\ell+1)}{r}\chi''_{k\ell} - \frac{2(\ell+1)}{r^2}\chi'_{k\ell} + k^2\chi'_{k\ell} = 0,$$
$$\Rightarrow \chi'''_{k\ell} + \frac{2(\ell+1)}{r}\chi''_{k\ell} + \left[k^2 - \frac{2(\ell+1)}{r^2}\right]\chi'_{k\ell} = 0.$$

If we then introduce $\chi'_{k\ell} = r\chi_{k,\ell+1}$, the above can be rewritten as

$$\chi''_{k,\ell+1} + \frac{2(\ell+2)}{r}\chi'_{k,\ell+1} + k^2\chi_{k,\ell+1} = 0.$$

In general, we use the previous methods to derive a recurrence relation where

$$\chi_{k\ell} = \left(\frac{1}{r}\frac{d}{dr}\right)^\ell \chi_{k0}.$$

The radial functions $R_{k\ell}$ can now be expressed using our $\chi_{k\ell}$'s:

$$R_{k\ell} = (-1)^\ell \frac{2r^\ell}{k^\ell}\left(\frac{1}{r}\frac{d}{dr}\right)^\ell \frac{2\sin(kr)}{r}.$$

We note that $k^{-\ell}$ arises via normalization, and we introduce the factor of $(-1)^\ell$ (without affecting the general solution) for our convenience.

We also note that the expression for $R_{k\ell}$ above can be simplified further; indeed, we have

$$R_{k\ell} = \sqrt{\frac{2\pi k}{r}}J_{\ell+1/2}(kr) = 2kj_\ell(kr),$$

where $j_\ell(x) = \sqrt{\pi/2x}J_{\ell+1/2}(x)$ are the spherical Bessel functions.

Examples: The first two spherical Bessel functions are given as follows:

$$j_0(x) = \frac{\sin x}{x}, \quad j_1 = \frac{\sin x}{x} - \frac{\cos x}{x}.$$

Recall: We originally solved the Schrodinger equation for a free particle using a Cartesian coordinate representation, and found that the wave function is given by

$$\psi_E(x, y, z) = Ce^{i\mathbf{p}\cdot\mathbf{r}/\hbar} = Ce^{i\mathbf{k}\cdot\mathbf{r}}$$

where $\mathbf{p} = \hbar\mathbf{k}$. Clearly, the solution in polar spherical coordinates is much more involved (both in its expression, and in the derivation); it also depends explicitly on the value ℓ. We can write it in the general form as $c_\ell j_\ell(kr)Y_{\ell m}(\theta, \phi)$ where c_ℓ is some constant. Both sets of eigenfunctions for the Hamiltonian of a free particle are complete- the plane waves $e^{i\mathbf{k}\cdot\mathbf{r}}$ and the spherical waves written above.

Note: For a given energy E, the number of plane waves is uncountable while the number of spherical waves is countable (based on the quantum numbers ℓ, m).

We wish to derive some sort of expression which shows how our two sets of eigenfunctions are related. Start by writing $e^{i\mathbf{k}\cdot\mathbf{r}} = e^{ikr\cos\chi}$, where χ is the angle between $\mathbf{k}$ and $\mathbf{r}$. Expanding this as a series of Legendre polynomials, we get

$$e^{ikr\cos\chi} = \sum_{\ell=0}^{\infty} c_\ell P_\ell(\cos\chi)$$

where the coefficients c_ℓ are found via

$$c_\ell = \frac{2\ell+1}{2}\int_{-1}^{1} e^{ikrt}P_\ell(t)dt$$

with $t = \cos\chi$. We rely on the orthonormality of the Legendre polynomials to get the expression above. Note that we also have an integral representation of a spherical Bessel function, where

$$j_\ell(x) = \frac{1}{2i^\ell}\int_{-1}^{1} e^{ixt}P_\ell(t)dt.$$

Using this representation, we can rewrite the above as

$$c_\ell = (2\ell+1)i^\ell j_\ell(kr),$$

and if we insert this expression for c_ℓ into our series decomposition we get

$$e^{ikr\cos\chi} = \sum_{\ell=0}^{\infty}(2\ell+1)i^\ell j_\ell(kr)P_\ell(\cos\chi).$$

Using the addition theorem for spherical harmonics (see) where

$$P_\ell(\cos\chi) = \frac{4\pi}{2\ell+1}\sum_{m=-\ell}^{\ell}[Y_{\ell m}(\Omega_1)]^* Y_{\ell m}(\Omega_2)$$

(so χ is an angle between Ω_1, Ω_2) we have the final expression

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 4\pi\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell} i^\ell j_\ell(kr)[Y_{\ell m}(\alpha,\beta)]^* Y_{\ell m}(\theta,\phi)$$

where α, β are the spherical polar coordinates of $\mathbf{k}$ and θ, ϕ are the spherical coordinates of $\mathbf{r}$. The previous equation is sometimes called the "resolution of a plane wave"; it expresses the connection between our two sets of eigenfunctions.

6.3. **Spin.** Quantum mechanics (as originally formulated) failed to account for multiplicity of atomic energy levels. As an example, for some alkali metals (lithium, sodium, etc.) we know the energy levels of such atoms depend on the angular momentum quantum number ℓ and the radial quantum number n (otherwise known as the principal quantum number). As these atoms are acting in a spherically symmetric field, absent of external fields we also know there should be no dependence on the quantum number m. If we are given a valid set of quantum numbers (n, ℓ, m), we would expect that there only be one energy level of the atom described by the triple; however, experimental verification showed that this is quite untrue.

As a potential solution to the problem, Pauli first proposed there existed a fourth quantum number which takes one of two values in all but s states. Then, in 1925 Goudsmith and Uhlenbeck proposed that the doubling of energy levels was due to some internal angular momentum whose component in a direction of $\mathbf{L}$ (when $\mathbf{L} \neq 0$) can only take two values; furthermore, its interaction with a weak magnetic field produced by orbital motion of the electron would split all but s states into nearly degenerate doubles. As with ℓ, we would need such a value s to satisfy the equation $2s + 1 = 2$- so s can have fractional

values. Experimental verification throughout the years convinced those in the field of the existence of such a fourth quantum number, which we know now as spin.

Whereas originally we discussed the existence of orbital angular momentum $\mathbf{L}$ by using invariance under spatial rotation, if we now add spin rotational invariance leads to the existence of a conserved quantity $\mathbf{J}$ known as the *total angular momentum*. It is the sum of its orbital and spin angular momentum, denoted $\mathbf{L}$ and $\mathbf{S}$ (respectively).

If a particle has spin, the wave function now must depend on both (x, y, z) (as before) but also on σ, which is a discrete variable (i.e., there are only a discrete number of potential values for it to take) which gives the value of the projection of the spin on a selected direction in space (usually the z-axis). We denote such a wave function by $\psi(x, y, z, \sigma)$. The integral

$$\int |\psi(x, y, z, \sigma)|^2 dxdydz$$

determines the probability that a particle has a certain value of σ. If instead we wanted to determine the probability that a particle is in volume region $dV = dxdydz$ with any value of σ, we compute

$$dV \sum_{\sigma} |\psi(x, y, z, \sigma)|^2.$$

Definition 6.2. *We define $\hat{\boldsymbol{j}}$ as an operator of the total angular momentum of a particle, and $\hat{\boldsymbol{J}}$ to be the total angular momentum operator; similarly, we define $\hat{\boldsymbol{s}}$ to be the spin angular momentum operator for an individual particle with $\hat{\boldsymbol{S}}$ the total spin operator for a system of many particles.*

Note: For particles with spin, $\hat{\mathbf{J}}$ is the generator of all rotations- so the commutator relations for $\hat{\mathbf{L}}$ also hold for $\hat{\mathbf{J}}$- for example, we can derive

(i) $[J_i, J_j] = i\hbar\epsilon_{ijk}J_k$;
(ii) $[s_i, x_j] = [s_i, p_j] = 0$;
(iii) $[s_i, \ell_j] = 0$;
(iv) $[j_i, j_j] = i\hbar\epsilon_{ijk}\ell_k + [s_i, s_j] = i\hbar\epsilon_{ijk}j_k$ (as $\hbar\mathbf{j} = \hat{\ell} + \hat{\mathbf{s}}$). This implies $[s_i, s_j] = i\hbar\epsilon_{ijk}s_k$.

Using our derivations for orbital angular momentum, we can say the eigenvalues for $\hat{S}_z$ form a sequence of numbers which differ by intervals of length 1- however, there is no requirement that they be integers. The sequence is still bound by $\pm s$, with the difference $2s$ between the greatest and least eigenvalues of $\hat{S}_z$ an integer. This implies the eigenvalues of $\hat{S}_z$ are of the form $0, \frac{1}{2}, \frac{3}{2}, \ldots$ (where we potentially factor out $\hbar$ for simplicity). This also implies the eigenvalues of $\hat{\mathbf{s}}$ are $\hbar^2 s(s+1)$. Clearly, the wave function of a particle with spin s has a total of $2s + 1$ possible values for s.

For the total angular momentum operator of a single particle (i.e., $\hat{\mathbf{j}}$), if ℓ, s are given eigenvalues for $\hat{\ell}, \hat{\mathbf{s}}$ then $\hat{\mathbf{j}}$ can possibly take values $\ell + s, \ell + s - 1, \ldots, |\ell - s|$.

We continue our initial investigation into spin by trying to determine the form of a spin operator for an electron. Such an operator would need to be composed of operators $\hat{s}_x, \hat{s}_y$, and $\hat{s}_z$ which satisfy the relations

(i) $[\hat{s}_x, \hat{s}_y] = i\hbar\hat{s}_z$;
(ii) $[\hat{s}_y, \hat{s}_z] = i\hbar\hat{s}_x$;
(iii) $[\hat{s}_z, \hat{s}_x] = i\hbar\hat{s}_y$;
(iv) Operator $\hat{s}_z$ has only two eigenvalues (which controls the dimension).

It can be shown (not here) that the following operators satisfy all of the conditions above:

$$\hat{s}_x = \frac{\hbar}{2}\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix},$$
$$\hat{s}_y = \frac{\hbar}{2}\begin{bmatrix}0 & -i\\ i & 0\end{bmatrix},$$
$$\hat{s}_z = \frac{\hbar}{2}\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}.$$

The matrices above (modulo the constant factor out in front) are in fact quite important in quantum mechanics- they are known as the Pauli matrices, where

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

Thus, we can write $\hat{\mathbf{s}} = \frac{\hbar}{2}\hat{\sigma}$ where $\hat{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$.

Remark: Pauli matrices have the following properties:

(i) $\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = 1$;
(ii) $\sigma_y\sigma_z = i\sigma_x, \sigma_z\sigma_x = i\sigma_y, \sigma_x\sigma_y = i\sigma_z$;
(iii) $\sigma_i\sigma_k + \sigma_k\sigma_i = 2\delta_{ik}$. This is sometimes called the anticommutator $[\sigma_i, \sigma_k]_+$- so Pauli matrices anti-commute with one another.
(iv) $\sigma^2 = 3$;
(v) $\mathrm{Tr}(\sigma_i) = 0$;
(vi) $(\hat{\sigma}\cdot\mathbf{a})(\hat{\sigma}\cdot\mathbf{b}) = \mathbf{a}\cdot\mathbf{b} + i\hat{\sigma}\cdot(\mathbf{a}\times\mathbf{b})$;
(vii) Together with the identity matrix, $\{I, \sigma_x, \sigma_y, \sigma_z\}$ form a linearly independent set.

Using the properties above, we can easily show that the eigenvectors of $\hat{s}_x, \hat{s}_y$ and $\hat{s}_z$ are

$$\hat{s}_x \to \frac{1}{\sqrt{2}}\begin{bmatrix}1\\ 1\end{bmatrix}, \quad \frac{1}{\sqrt{2}}\begin{bmatrix}1\\ -1\end{bmatrix},$$
$$\hat{s}_y \to \frac{1}{\sqrt{2}}\begin{bmatrix}1\\ i\end{bmatrix}, \quad \frac{1}{\sqrt{2}}\begin{bmatrix}1\\ -i\end{bmatrix},$$
$$\hat{s}_z \to \begin{bmatrix}1\\ 0\end{bmatrix}, \quad \begin{bmatrix}0\\ 1\end{bmatrix}.$$

As $\hat{s}_z, \mathbf{s}^2$ commute, the total set of physical quantities for the corresponding system can be described using the basis vectors $|s, s_z\rangle$ where $s = 1/2$ and s_z is either "+" or "−". The operator $\hat{s}_z$ is diagonal in this basis, so we may identify

$$|1/2, +\rangle = \begin{bmatrix}1\\ 0\end{bmatrix}, \quad |1/2, -\rangle = \begin{bmatrix}0\\ 1\end{bmatrix}.$$

As we should already know, any arbitrary ket can be written as $|\chi\rangle = \alpha\,|1/2, +\rangle + \beta\,|1/2, -\rangle$ by expanding in this basis.

6.4. **Addition of angular momenta.** It is often the case that a physical system contains angular momenta of two or more different types.

Examples:

(i) In the ground state of a helium atom, there are two elections- each with their own spin and no orbital momentum.
(ii) In the excited states of a hydrogen atom (with $\ell > 0$), there is both orbital and spin angular momentum.

In general, individual angular momenta are not separately conserved; in light of this, we instead focus on the total angular momentum operator for the whole system, which does still commute with the Hamiltonian. The problem we wish to consider is how to relate states labeled by the values of the total angular momentum, to states described in terms of the individual angular momenta.

As an example, suppose we start with two spin 1/2 particles and ignore orbital degrees of freedom. The total spin operator is given by $\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2$, where we have the commutator relations

(i) $[\hat{s}_{1i}, \hat{s}_{2j}] = 0$ for $i, j \in \{x, y, z\}$;
(ii) $[\hat{s}_{1i}, \hat{s}_{ij}] = i\hbar\epsilon_{ijk}\hat{s}_{1k}$.

To describe the states of such a composite system, we will need a total set of physical quantities- i.e., we need a set of mutually commuting operators. A potential choice is to use $\hat{s}_{z1}, \hat{s}_{z2}$; with this choice, the eigenkets for $\hat{s}_{z1}$ will be denoted via $|m_1\rangle$ and $|m_2\rangle$ for $\hat{s}_{z2}$. The basis for the composite system is spanned by the tensor products $|m_1\rangle$'s and $|m_2\rangle$'s, with a total of four vectors

$$|{+}{+}\rangle\,, \quad |{+}{-}\rangle\,, \quad |{-}{+}\rangle\,, \quad |{-}{-}\rangle\,.$$

This is, however, not the only possible choice for a basis- instead, we can consider the operators $\hat{S}_z = \hat{S}_{1z} + \hat{S}_{2z}$ and $\hat{\mathbf{S}}^2$. Their corresponding eigenkets will be denoted using $|sm\rangle$.

We wish to write $|sm\rangle$'s in terms of the basis vectors $|m_1 m_2\rangle$- i.e., we are hoping to change the basis we represent our system in. We first note that

$$\hat{S}_z\,|{+}{+}\rangle = \hbar\,|{+}{+}\rangle\,, \quad \hat{S}_z\,|{+}{-}\rangle = \hat{S}_z\,|{-}{+}\rangle = 0, \quad \hat{S}_z\,|{-}{-}\rangle = \hbar\,|{-}{-}\rangle\,.$$

As $m \in \{-s, \ldots, s\}$ in steps of size 1 (here we are discarding any factors of $\hbar$, as they are not relevant) we see the maximum values of $s = 1$ corresponds to $|{+}{+}\rangle$ with $m = 1$, while $|{-}{-}\rangle$ corresponds to $s = 1$ with $m = -1$. Therefore, we can associate

$$|11\rangle \cong |{+}{+}\rangle\,,$$
$$|1\,{-}1\rangle \cong |{-}{-}\rangle\,.$$

(Note that our association is not formal (yet) in any precise sense). We now will try to find a similar type of association between the remaining basis vectors in our two possible bases. Considering the lowering operator $\hat{S}_-$, we note that

$$\hat{S}_-\,|11\rangle = (\hat{S}_{1-} + \hat{S}_{2-})\,|{+}{+}\rangle = \hbar\,|{-}{+}\rangle + \hbar\,|{+}{-}\rangle\,.$$

We also note that the left hand side (in general) is described using the formula

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

When $s = 1, m = 1$ this reduces to $\hat{S}_- = \hbar\sqrt{2}\,|10\rangle$; therefore, we can rewrite the equation above as

$$\hbar\sqrt{2}\,|10\rangle = \hbar\,|{-}{+}\rangle + \hbar\,|{+}{-}\rangle$$
$$\Rightarrow |10\rangle = \frac{1}{\sqrt{2}}(|{-}{+}\rangle + |{+}{-}\rangle).$$

Using similar tactics, it is easy to show that we must then also have

$$|00\rangle \cong \frac{1}{\sqrt{2}}(|{+}{-}\rangle - |{-}{+}\rangle).$$

To summarize our previous discoveries, we have three states corresponding to s = 1- $|11\rangle\,, |10\rangle\,, |1\,{-}1\rangle$ (which are called triplet states), and one singlet state $|00\rangle$. The matrix

representation of the transformation T from the $\{|{+}{+}\rangle, \ldots, |{-}{-}\rangle\}$ basis to the $\{|11\rangle, \ldots, |1-1\rangle\}$ basis is easily found to be

$$[T] = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1/\sqrt{2} & 1/\sqrt{2} & 0 \\ 0 & -1/\sqrt{2} & 1/\sqrt{2} & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

when we order our original basis using $(|{+}{+}\rangle, |{-}{+}\rangle, |{+}{-}\rangle, |{-}{-}\rangle)$. The transformation (in general) may be written as

$$|sm\rangle = \sum_{m_1,m_2} C^{s_1 s_2 s}_{m_1 m_2 m} \, |s_1 s_2;\ m_1 m_2\rangle \, .$$

As the transformation matrix above is a change of basis, it must be unitary. The matrix coefficients in T- denoted by $C^{s_1 s_2 s}_{m_1 m_2 m}$ as above- are called the Clebsh-Gordan coefficients.

In general, if we have two spin particles s_1, s_2, when we combine them we get every spin in the range $s_2 - s_1, \ldots, s_2 + s_1$ (assuming without loss of generality that $s_2 \geq s_1$) in integer steps- i.e.,

$$s = (s_1 + s_2), (s_1 + s_2 - 1), \ldots, |s_1 - s_2|.$$

The matrix for the transformation we derived above will in general have dimension $(2s_1 + 1)(2s_2 + 1)$. For more than two particles, we can extend this to a matrix with dimension $(2s_1 + 1)(2s_2 + 1)(2s_3 + 1)\cdots$.

After the previous example, we now turn to the study of the theory of addition of angular momentum. Consider operators $\hat{j}_1, \hat{j}_2$ which act on separate Hilbert spaces. The components of $\hat{j}_1$ (resp., $\hat{j}_2$) satisfy the usual angular momentum commutator relations:

(i) $[\hat{j}_{1i}, \hat{j}_{1j}] = i\hbar\epsilon_{ijk}\hat{j}_{1k}$;
(ii) $[\hat{j}_{2i}, \hat{j}_{2j}] = i\hbar\epsilon_{ijk}\hat{2k}$;
(iii) $[\hat{j}_{1k}, \hat{2\ell}] = 0$.

We define the total angular momentum $\hat{\mathbf{J}} = \hat{j}_1 + \hat{j}_2$, which (as we recall) satisfies the commutator relation $[\hat{J}_i, \hat{J}_j] = i\hbar\epsilon_{ijk}\hat{J}_k$. As in our previous example, we can consider two different bases for our space:

(i) Begin with simultaneous eigenkets of $\hat{j}_1^2, \hat{j}_2^2$, $\hat{j}_{1z}$ and $\hat{j}_{2z}$. All of these operators are mutually commuting, and we have the following relations:

$$\begin{aligned} \hat{j}_1^2 \, |j_1 j_2;\ m_1 m_2\rangle &= \hbar^2 j_1(j_1+1) \, |j_1 j_2;\ m_1 m_2\rangle \, , \\ \hat{j}_2^2 \, |j_1 j_2;\ m_1 m_2\rangle &= \hbar^2 j_2(j_2+1) \, |j_1 j_2;\ m_1 m_2\rangle \, , \\ \hat{j}_{1z} \, |j_1 j_2;\ m_1 m_2\rangle &= \hbar m_1 \, |j_1 j_2;\ m_1 m_2\rangle \, , \\ \hat{j}_{2z} \, |j_1 j_2;\ m_1 m_2\rangle &= \hbar m_2 \, |j_1 j_2;\ m_1 m_2\rangle \, . \end{aligned}$$

(ii) Simultaneous eigenkets of $\hat{\mathbf{J}}^2$ and $\hat{J}_z$. We have the relations:

$$\begin{aligned} \hat{\mathbf{J}}^2 \, |j_1 j_2;\ jm\rangle &= \hbar^2 J(J+1) \, |j_1 j_2;\ jm\rangle \, , \\ \hat{J}_z \, |j_1 j_2;\ jm\rangle &= \hbar m \, |j_1 j_2;\ jm\rangle \, . \end{aligned}$$

As before, the transformation between the two bases is given by

$$|j_1 j_2;\ jm\rangle = \sum_{m_1,m_2} |j_1 j_2;\ m_1 m_2\rangle \, \langle j_1 j_2;\ m_1 m_2 | j_1 j_2;\ jm\rangle \, .$$

The Clebsh-Gordan (CG) coefficients are of course the scalar values in the latter part of the previous equation. They have many important properties:

(i) CG coefficients vanish, unless $m = m_1 + m_2$.
(ii) Additionally, they vanish unless $|j_1 - j_2| \leq j \leq j_1 + j_2$. For a complete proof, see the text in Sakurai.

(iii) CG coefficients must always be real, and they form a unitary matrix. Additionally, we know real unitary matrices are orthogonal, with

$$\sum_j \sum_m \langle j_1 j_2;\ m_1 m_2 | j_1 j_2;\ jm\rangle \langle j_1 j_2;\ m_1' m_2' | j_1 j_2;\ jm\rangle = \delta_{m_1 m_1'} \delta_{m_2 m_2'}.$$

Likewise,

$$\sum_{m_1} \sum_{m_2} \langle j_1 j_2;\ m_1 m_2 | j_1 j_2;\ jm\rangle \langle j_1 j_2;\ m_1 m_2 | j_1 j_2;\ j'm'\rangle = \delta_{jj'} \delta_{mm'}.$$

This allows us to derive the normalization condition

$$\sum_{m_1} \sum_{m_2} |\langle j_1 j_2;\ m_1 m_2 | j_1 j_2;\ jm\rangle|^2 = 1.$$

7. Perturbation theory