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Quantum Mechanics II

2019-20 class

L. Nikolopoulos *

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Dublin City University- School of Physical Sciences

* DCU

These notes are not yet fully endorsed by myself and should be used with some caution. Note that lots of typos should be present. Also, please, do not hesitate to communicate such suspected typos or possible inaccuracies (Nov 2019)

Contents

List of Figures

List of Tables

Quantum mechanics vector formulation

1

Let's postulate the below:

QM postulates

1 **States.** *A physical state* of a system is represented by a normalized *vector* $|\psi\rangle$ belonging in some multidimensional linear complex vector space $\mathcal{V}$:

$$|\psi\rangle = \sum_n \lambda_n |v_n\rangle, \qquad \lambda_n = \langle v_n|\psi\rangle, \tag{1.1}$$

where $|v_n\rangle$ is a basis for $\mathcal{V}$ and λ_n generally complex. The latter property is known as *superposition principle*.

2 **Operators.** *A physical quantity* ($\mathbb{Q}$) is represented by an *observable* $\hat{Q}$, which defines a *complete, orthonormalized*, eigenbasis $|q_n\rangle$ of $\mathcal{V}$ via its *eigenvalue equation*:

$$\hat{Q}|q_n\rangle = q_n|q_n\rangle \qquad \rightarrow \qquad \begin{cases} q_n & \text{real,} \\ \sum_n |q_n\rangle\langle q_n| & = \mathbb{1}, \\ \langle q_n|q_m\rangle & = \delta_{nm} \end{cases} \tag{1.2}$$

The latter two equations are known as *completeness* and *orthonormalization* conditions, respectively[1].

3 **Dynamics.** The time evolution of the state $|\psi\rangle$ is governed by the system's Hamiltonian, $\hat{H}$,

$$|\psi(t+\tau)\rangle = e^{-\frac{\imath}{\hbar}\hat{H}\tau}|\psi(t)\rangle \quad \leftrightarrow \quad \imath\hbar\frac{d}{dt}|\psi\rangle = \hat{H}|\psi\rangle, \tag{1.3}$$

The latter form is known as Schrödinger Equation .

4 **Measurement.** A measurement[2] of an observable $\mathbb{Q}$ in state $|\psi\rangle$ gives one of its eigenvalues q_n with probability:

$$|\psi\rangle = \sum_n c_n|q_n\rangle \qquad \rightarrow \qquad P_\psi(\mathbb{Q} = q_n) = |c_n|^2 \tag{1.4}$$

The post-measurement state is then $|q_n\rangle$ with certainty. This QM process is also known as *reduction (or collapse)* of the state.

Traditionally, the first encounter with QM theory and its applications is through the state vector formalism, may be just

1: An adjustment of the formulation should be made in the case where the observables are of continuous nature (e.g. position,momentum, etc), namely, when the eigenvalues q_n are no longer discrete.

2: The measurement process is of particular importance as it departs from a purely QM deterministic description of nature (the first three postulates) toward an inherently probabilistic description due to interaction with the (external) measurement device. This postulate has been the subject of continuous debate from the inception of QM. The present *statistical* interpretation (also known as the *Copenhagen* interpretation) was put forward by N. Bohr, W. Heisenberg, Max Born and their coleagues during the years of 1925-27.

because it is the simpler choice (but not simple) conceptually; On a practical level, vastly, is the most economical one. The central concepts in this formulation for a physical system are (a) the physical states represented by the vector *state*, $|\psi\rangle$, (b) the observables $\mathbb{Q}$ represented by operators,$\hat{Q}$, and (c) the transformation rules when operators act on the vector states $\hat{Q}|\psi\rangle$, with the chief rule being the time-evolution laws, one deterministic (Schrödinger equation) and the other probabilistic (Measurement). All the predictions about a QM system are derived from two central concepts, namely, the abstract vector-states $|\psi\rangle$ and the observables-operators, $\hat{Q}$. The particular set of the presented QM postulates, represents a merged version of the QM postulates as stated in [**tanoujdi:1977**].

1.1 QM states (Vectors)

The abstract state $|\psi\rangle$ follows the Dirac convention and is also known as *ket* vector state. Associated (isomorphically) with the vector space $\mathcal{V}$ there is the dual (abstract) vector space ($\mathcal{V}^\star$) containing all *bra* state ($\langle\psi|$) associated with each $|\psi\rangle$ of $\mathcal{V}$.

The fact that the space $\mathcal{V}$ is a linear vector space has lots of important consequences with the most fundamental that *any linear combination of vector states belonging in $\mathcal{V}$ also belongs to $\mathcal{V}$, thus representing a physical state of the system.*

$$\text{if } |\chi\rangle, |\phi\rangle \text{ in } \mathcal{V} \text{ then} \qquad |\psi\rangle = c_1|\chi\rangle + c_2|\phi\rangle \text{ in } \mathcal{V}$$

Moreover, as $\mathcal{V}$ is a linear vector space a complex-valued inner product between $|\chi\rangle$ and $|\phi\rangle$ is defined.This way one is ready to define the scalar inner product between two arbitrary states of $\mathcal{V}$ as the complex value, expressed as,

$$c(\chi, \phi) = \langle\chi|\phi\rangle$$

The practical consequences of the above abstract (and general) definitions become more evident when $\mathcal{F}$ is specialized.

A *complete* set of orthonormalised states $|\phi_n\rangle$ is defined when all $|\psi\rangle$ in $\mathcal{V}$ can be expressed in a unique way as,

$$|\psi\rangle = \sum_n c_n|\phi_n\rangle, \qquad c_n = \langle\phi_n|\psi\rangle \tag{1.5}$$

The above expansion is also known as *superposition expansion*. This set is named orthonormalized when $\langle\phi_n|\phi_m\rangle = \delta_{nm}$. In analogy with the childhood vector algebra learned in high-school the role of $|\psi_n\rangle$ is very similar with the Cartesian components of a the familial spatial vector [see Fig:(1.1)]; namely, if $\mathbf{A}$ is a vector in the 3D space, then its (Cartesian) coordinates (A_1, A_2, A_3) can be expressed along three - orthogonal directions $(\hat{x}_1, \hat{x}_2, \hat{x}_3)$ as,

$$\mathbf{A} = \sum_{i=1}^{3} A_i \hat{x}_i, \qquad A_i = \mathbf{A} \cdot \hat{x}_i, \qquad \hat{x}_i \cdot \hat{x}_j = \delta_{ij} \tag{1.6}$$

An additional formulation (meaning reexpressing the same thing) of (1.6) is obtained if we identify the 3-elements column basis,

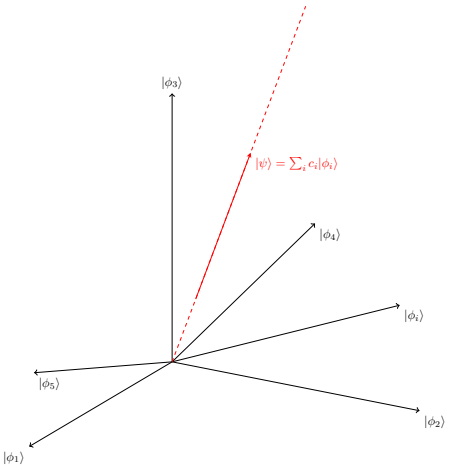


Figure 1.1: In quantum mechanics a physical state can be thought as a vector of the (abstract) Hilbert space spanned by the orthogonal eigenstates $|\phi_i\rangle$ of some observable operator, $\hat{Q}$. In accord to this geometrical picture any change of the state can be analyzed in terms of the observable's eigenstates which play the role of familiar components of linear algebra. In other words any observable defines its own 'coordinate system' for the vector state, known as *representation*.

satisfying,

$$\hat{x}_1 \longrightarrow |x_1\rangle = \begin{pmatrix}1\\0\\0\end{pmatrix}, \qquad \hat{x}_1 \rightarrow |x_2\rangle = \begin{pmatrix}0\\1\\0\end{pmatrix}, \qquad \hat{x}_1 \longrightarrow |x_3\rangle = \begin{pmatrix}0\\0\\1\end{pmatrix} \tag{1.7}$$

$$\hat{x}_1^T \longrightarrow \langle x_1| = \begin{pmatrix}1,0,0\end{pmatrix}, \qquad \hat{x}_1^T \longrightarrow \langle x_2| = \begin{pmatrix}0,1,0\end{pmatrix}, \qquad \hat{x}_1^T \longrightarrow \langle x_3| = \begin{pmatrix}0,0,1\end{pmatrix} \tag{1.8}$$

Given the above a physical 3D vector $\mathbf{A} = (A_1, A_2, A_3)$ with A_i real, $(A_i = A_i^*), i = 1,2,3$ may be expressed as,

$$\mathbf{A} \longrightarrow |A\rangle = A_1|x_1\rangle + A_2|x_2\rangle + A_3|x_3\rangle = \begin{pmatrix}A_1\\A_2\\A_3\end{pmatrix}, \tag{1.9}$$

$$\mathbf{A}^T \longrightarrow \langle A| = A_1^*\langle x_1| + A_2^*\langle x_2| + A_3^*\langle x_3| = \begin{pmatrix}A_1^*, A_2^*, A_3^*\end{pmatrix} \tag{1.10}$$

The generalization of the familiar 3D algebra is slightly more involved mainly for two reasons: (a) the dimensionality is higher (now it is not so easy to visualize a n-orthogonal vectors, $|\phi_n\rangle$, and (b) Inner product is complex valued, thus introducing the dual space basis vectors of $\mathcal{V}^\star$. For an $N-$dimensional state space [3] ,

$$|v_1\rangle = \begin{pmatrix}1\\0\\..\\0\end{pmatrix}, \qquad |v_2\rangle = \begin{pmatrix}0\\1\\0\\..\end{pmatrix}, ..., \quad |v_n\rangle = \begin{pmatrix}0\\0\\..\\1\\..\\0\end{pmatrix}, \tag{1.13}$$

$$\langle v_1| = \begin{pmatrix}1,..,0\end{pmatrix}, \qquad \langle v_2| = \begin{pmatrix}0,1,..\end{pmatrix}, ..., \quad \langle v_n| = \begin{pmatrix}0,0,..,1,..0\end{pmatrix}, \tag{1.14}$$

where we set $\mathbf{v}_i = |v_i\rangle$ and $\mathbf{v}_i^T = \langle v_i|,\ i = 1,2,...$ for the column and row vectors. For later reference let's call this (column) basis $(\{|v\rangle\} = |v_1\rangle, |v_2\rangle, ...)$ *fundamental ket basis* and its dual (row) basis as the *fundamental bra basis*. The above definitions help to express [4] :

$$|\psi\rangle = \mathbf{C} = \begin{pmatrix}c_1\\c_2\\..\\c_n\\..\\c_N\end{pmatrix} \qquad \langle\psi| = \mathbf{C}^T = \begin{pmatrix}c_1^*, c_2^*, ..., c_N^*\end{pmatrix} \tag{1.16}$$

3: For a two-dimensional basis (e.g. electron's spin 1/2),

$$|v_1\rangle = \begin{pmatrix}1\\0\end{pmatrix}, \qquad |v_2\rangle = \begin{pmatrix}0\\1\end{pmatrix}. \tag{1.11}$$

and,

$$\langle v_1| = \begin{pmatrix}1,0\end{pmatrix}, \quad \langle v_2| = \begin{pmatrix}0,1\end{pmatrix}. \tag{1.12}$$

The orthonormalization property, $\langle v_i|v_j\rangle = \delta_{ij}$ is easily checked. For example,

$$\langle v_1|v_1\rangle = \begin{pmatrix}1,0\end{pmatrix} \cdot \begin{pmatrix}1\\0\end{pmatrix} = 1.$$

4: For a two-dimensional basis,

$$|\psi\rangle = \begin{pmatrix}c_1\\c_2\end{pmatrix}, \qquad \langle\psi| = \begin{pmatrix}c_1^*, c_2^*\end{pmatrix}. \tag{1.15}$$

This way one can use matrix algebra to work out compactly and efficiently (suitable for numerical calculations) the (initially) abstract algebraic relations. For example, it is now immediately seen that the inner product of $|\psi\rangle$ with itself (multiplication of its bra with the ket state) is[5],

$$\langle\psi|\psi\rangle = \mathbf{C}^T \cdot \mathbf{C} = \left(c_1^*, ..., c_n^*, .., c_N^*\right) \begin{pmatrix} c_1 \\ ... \\ c_n \\ .. \\ c_N \end{pmatrix} = \sum_{n=1}^{N} |c_n|^2 \qquad (1.17)$$

Note that for normalized states the following is true:

$$\langle\psi|\psi\rangle = \sum_{n=1}^{N} |c_n|^2 = 1. \qquad (1.18)$$

Quantum states should have finite magnitude ('length') if their projections to an arbitrary vector space are to intepreted as probability values.

5: For a two-dimensional basis,

$$\langle\psi|\psi\rangle = \left(c_1^*, c_2^*\right) \cdot \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = |c_1|^2 + |c_2|^2$$

1.2 QM observables (Operators)

Operators act on states. In QM operators are used to represent physical quantities, also known as *observables*. Examples are energy, position, translational and angular momentum, spin and generally any combination of them is also an observable. The mathematical expression of the observables arises quite easily when the corresponding classical operator exists e.g. position ($\mathbf{r}$), translational momentum ($\mathbf{p}$), by following the quantization rules, $\mathbf{x} \to \hat{x}$ and $\mathbf{p} \to -\imath\nabla$. If one thinks that most of the classical mechanics quantities can be expressed in terms of these two fundamental quantities (e.g. angular momentum, $\mathbf{L} = \mathbf{r} \times \mathbf{p}$) then this approach is sufficient. Not always though, as one can conclude from the case of the spin operator, a purely quantum operator with no classical counterpart.

In any case, when the observable is chosen, an associated operator exists which in turn defines a *complete set* of eigenvectors and eigenvalues as:

Eigenspectrum of an observable

$$\hat{Q}|q_n\rangle = q_n|q_n\rangle, \tag{1.19}$$

$$\sum_n |q_n\rangle\langle q_n| = \mathbb{1}, \tag{1.20}$$

$$\langle q_n|q_m\rangle = \delta_{nm} = \begin{cases} 1 & n = m \\ 0 & n \neq m. \end{cases} \tag{1.21}$$

Noting that the eigenstate basis set of an observable (actually this is the requirement for a physical quantity to be an observable) is complete according to the superposition expansion (1.5) the ket state $|\psi\rangle$ can be expanded in terms of this eigenset:

Superposition principle

$$|\psi\rangle = \sum_n c_n|q_n\rangle, \qquad c_n = \langle q_n|\psi\rangle. \tag{1.22}$$

Coefficient c_n has a very precise physical meaning upon a measurement of $\mathbb{Q}$. For now, it is needed to note that the observable $\mathbb{Q}$ is associated with the operator $\hat{Q}$ which acts in $|\psi\rangle$. However, for each $|\psi\rangle$ ket we have a $\langle\psi|$ bra and it is normal to wonder what kind of operator (associated with the observable $\mathbb{Q}$) acts to these states. It turns out that for an observable the conjugate

(dual) operator acting in $\mathcal{V}^\star$ satisfies the conjugate eigenvalue equation* ,

$$\langle q_n|\hat{Q} = q_n\langle q_n|, \qquad \langle q_n|q_m\rangle = \delta_{nm}. \tag{1.23}$$

This means that for an arbitrary $|\psi\rangle$ ket or $\langle\psi|$ the action of an observable in the system if fully determined by the use of (1.22) and (1.19) and (1.23). For example:

$$\hat{Q}|\psi\rangle = \hat{Q}\sum_n c_n|q_n\rangle = \sum_n c_n\hat{Q}|q_n\rangle = \sum_n c_n q_n|q_n\rangle$$

Vector spaces of finite dimension are named as Hilbert spaces. A further level of generalization arises when the basis is of infinite dimension. The complication is that that eigenvectors $|q_n\rangle$ are not normalized and vector spaces resulting from such bases via (1.22) should have inner products that result to probabilities lying necessarily between 0 and 1.

Algebraic (Matrix) representation of operators Along similar lines as for the algebraic representation of the $|\psi\rangle$ and $\langle\psi|$ as 1-dimensional matrices (rows and columns) we can extend this to two-index vectors, represented as matrices. If the fundamental basis is defined as $\hat{\mathcal{U}}_{ij} = |v_i\rangle\langle v_i|$ and its matrix representation as $\mathcal{U}_{ij} = \mathbf{v}_i\mathbf{v}_j^T$,

$$\hat{\mathcal{U}}_{ij} = |v_i\rangle\langle v_j| \quad \leftrightarrow \quad \mathcal{U}_{ij} = \mathbf{v}_i\mathbf{v}_j^T = \begin{bmatrix} 0 & 0 & 0 & 0 & ... & 0 \\ 0 & 0 & 0 & 0 & ... & 0 \\ ... & ... & ... & ... & ... & 0 \\ 0 & 0 & ... & 1 & ... & 0 \\ ... & ... & ... & ... & ... & 0 \end{bmatrix} \tag{1.24}$$

then an arbitrary operator/matrix, $\hat{M}, \mathbf{M}$ can be expressed in the fundamental basis as,

$$\hat{M} = \sum_{ij} M_{ij}|v_i\rangle\langle v_j| = \sum_{ij} M_{ij}\hat{\mathcal{U}}_{ij} \tag{1.25}$$

$$\mathbf{M} = \sum_{ij} M_{ij}\mathcal{U}_{ij} \tag{1.26}$$

It is straightforward to confirm that

$$M_{ij} = \langle v_i|\hat{M}|v_j\rangle \tag{1.27}$$

* For an arbitrary operator (not necessarily an observable) if $\hat{A}|\psi_n\rangle = a_n|\psi_n\rangle$ then $\langle\psi_n|A^\dagger = a_n^\star\langle\psi_n|$.

Representation of an observable on its own basis . From the above algeraic expressions for the matrix elements of an matrix is quite straightforward to show that the representation of an observable, $\hat{Q}$ on its eigenbasis $|q_n\rangle, n = 1, 2, ..$ is a diagonal matrix with entries its eigenvalues, properly ordered:

$$\hat{Q} = \sum_n q_n |q_n\rangle\langle q_n| = \begin{bmatrix} q_1 & 0 & 0 & 0 & ... & 0 \\ 0 & q_2 & 0 & 0 & ... & 0 \\ ... & ... & ... & ... & ... & 0 \\ 0 & 0 & ... & q_n & ... & 0 \\ ... & ... & ... & ... & ... & 0 \end{bmatrix} \tag{1.28}$$

1.3 Dynamics

The time-development of a quantum state, expressed in (1.3), assigns to the system's Hamiltonian operator a special role. For this reason this operator (of the energy observable) is the most important among all the observables. As long as the system evolves in an isolated fashion, its time development is fully deterministic and its calculation is only of practical matter; exactly of the same type as the one encountered in non-quantum theories (Newton/Einstein mechanics and electrodynamics) where it is the huge number of variables required that prevents us from following the time-evolution of physical systems (hence the emergence of the statistical mechanics theories).

*Assume a quantum system, with Hamiltonian $\hat{H}(t)$, described by the vector state $\hat{\psi}(t)$. QM postulates the following time-evolution law for the state $\hat{\psi}(t)$:

$$\imath\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \hat{H}(t)|\psi(t)\rangle, \qquad |\psi_0\rangle \equiv |\psi(t=t_0)\rangle, \tag{1.29}$$

known as time-dependent Schrödinger equation (TDSE). Since the TDSE includes the first derivative in time of the state, as a consequence, determination of $\hat{\psi}(t)$ requires the knowledge of the state at a particular time t_0. For only one initial state a well defined (mathematical) problem is in place to solve. Usually the initial state is lower in energy, unless prepared to a different one. If, however, for example, the initial state is degenerate, then arises the problem which one among all these initial states one should be using. Then the solution procedure followed goes by other means not discussed at this stage.

Time-Independent Schrödinger Equation

In the present chapter will examine these type of problems where the Hamiltonian operator does not depend explicitly on time [6],

$$\frac{d}{dt}\hat{H}(t) = 0. \tag{1.30}$$

Then the TDSE (1.29) simplifies considerably as eventually is turned to an algebraic equation rather than a ODE. The goal is to find the time-development of the system's state, $|\psi\rangle(t)$. The calculational method goes as follows: (a) apply the QM (1.2)

6: Hamiltonians dependent on time are examined in Chapter 3.

* By now it is assumed familiarity with the abstract Hilbert formulation of QM states. If not, a brief account of this QM's viewpoint is presented in the on-line supplements. Also, for convenience, the notation for the ket $|\psi\rangle$ will be used interchangeably with $\hat{\psi}$.

postulate to find the Hamiltonian's spectrum (eigenvectors and eigenvalues) and then (b) the postulate (1.1) is used to expand the system states on the Hamiltonian's eigenbasis; finally (c) the postulate (1.3) is used to find how the state evolutes in time.

Step (a): is usually the hard part. As our focus is not of our interest (at this point of development) we assume temporarily that the spectrum is known; the eigenvectors $|E\rangle$ with corresponding eigenvalues E satisfy:

$$\hat{H}|E\rangle = E|E\rangle. \tag{1.31}$$

Since the Hamiltonian of the system doesn't change with time, the eigenvectors $|E\rangle$ also don't change.

Step (b): allows the expansion of any quantum state of the system in terms of the Hamiltonian's eigenstates,

$$|\Psi(t)\rangle = \sum_E c_E(t)|E\rangle, \tag{1.32}$$

??

where we are using $c_E(t)$ to represent the expansion coefficients. Since $|E\rangle$ are constant quantities all of the evolution of the quantum state will be in the coefficients.

Step (c): We now use this expansion with the TDSE to determine how the coefficients $a_E(t)$ evolve with time.

$$\begin{aligned}
\imath\hbar\frac{d}{dt}|\Psi(t)\rangle &= \hat{H}|\Psi(t)\rangle \\
&\rightarrow \imath\hbar\frac{d}{dt}\left[\sum_E c_E(t)|E\rangle\right] = \hat{H}\left[\sum_E c_E(t)|E\rangle\right] \\
&\rightarrow \imath\hbar\sum_E \frac{dc_E(t)}{dt}|E\rangle = \sum_E c_E(t)\hat{H}|E\rangle = \sum_E c_E(t)E|E\rangle.
\end{aligned}$$

Bringing all to one side,

$$\sum_E \left[\imath\hbar\frac{dc_E(t)}{dt} - Ec_E(t)\right]|E\rangle = 0. \tag{1.33}$$

The conclusion is that every term in the square brackets is zero:

$$\imath\hbar\frac{dc_E(t)}{dt} - Ec_E(t) = 0 \qquad \rightarrow \qquad c_E(t) = c_E(0)e^{-\imath Et/\hbar}, \tag{1.34}$$

where $c_E(0)$ is a constant determined by the initial conditionsl. So, for time-independent the solution is:

$$|\Psi(t)\rangle = \sum_E c_E(0)e^{-\imath Et/\hbar}|E\rangle. \tag{1.35}$$

Time evolution for time-independent Hamiltonians

To find $|\Psi(t)\rangle$ when $\hat{H}$ time-independent:

(i) Find the eigenvalues E and eigenvectors $|E\rangle$ of the Hamiltonian $\hat{H}$:

$$\hat{H}|E\rangle = E|E\rangle \tag{1.36}$$

(ii) Expand the quantum state in terms of the Hamiltonian eigenvectors:

$$|\Psi(0)\rangle = \sum_E c_E(0)|E\rangle, \qquad c_E(0) = \langle E|\Psi(0)\rangle\,. \tag{1.37}$$

(iii) Multiply c_E with the factors $e^{-\imath Et/\hbar}$ to obtain $|\Psi(t)$:

$$|\Psi(t)\rangle = \sum_E c_E(0)e^{-\imath Et/\hbar}|E\rangle. \tag{1.38}$$

1.4 Ehrenfrest theorem and Commutators

An alternative method of calculating time-dependent properties (in particular here, mean values) of a quantum system is through *Ehrenfrest theorem*.

Let's define the commutator operator defined as a special combination of operators $\hat{A}, \hat{B}$[7]:

$$\left[\hat{A}, \hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A}. \tag{1.39}$$

7: The multiplication order of the operators matters (recall its matrix representation to convince yourself that this should be the case).

Let's now try to calculate the average value of an arbitrary observable $\hat{Q}$; Its expectation value is,

$$\left\langle \hat{Q} \right\rangle = \langle \Psi(t)|\hat{Q}|\Psi(t)\rangle. \tag{1.40}$$

We aim to find its time-evolution in terms of a differential equation (to be solved). Let's take its time-derivative,

$$\begin{aligned}
&\frac{d}{dt}\left\langle \hat{L} \right\rangle \\
&= \underbrace{\left[\frac{d}{dt}\langle \Psi(t)|\right]}\hat{Q}|\Psi(t)\rangle + \langle \Psi(t)|\left(\frac{\partial}{\partial t}\hat{Q}\right)|\Psi(t)\rangle + \langle \Psi(t)|\hat{Q}\underbrace{\left[\frac{d}{dt}|\Psi(t)\rangle\right]}.
\end{aligned}$$

$$\frac{d}{dt}\langle \Psi(t)| = \frac{i}{\hbar}\hat{H} \qquad\qquad \frac{d}{dt}|\Psi(t)\rangle = -\frac{i}{\hbar}\hat{H}$$

Combining all the above the two operator terms and writing the middle term as an average value:

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

We then end up to the Ehrenfrest theorem for the mean values of observables,

Ehrefrenst Theorem

$$\imath\hbar\frac{d}{dt}\left\langle \hat{Q} \right\rangle = \left\langle \left[\hat{Q}, \hat{H}\right] \right\rangle + \imath\hbar\left\langle \frac{\partial}{\partial t}\hat{Q} \right\rangle \tag{1.41}$$

1.5 Measurement

The deterministic QM time-evolution law is interrupted from a probabilistic QM time-evolution law when an observation is realized (e.g. an external interaction, not included in the Hamiltonian, $\hat{H}(t)$). A typical example is the process of measurement, a central concept in QM). Observation is purely probabilistic and constitutes the essence of any QM theory. The state $|\psi(t)\rangle$ following an observation process entails in another quantum state $|\psi(t')\rangle$ with some probability. Both $|\psi(t')\rangle$ and its probability to show up depend on the $|\psi(t)\rangle$ and the type of the observation [8] .

That said, let's now consider a system in a state $|\psi\rangle$ and an observable $\mathbb{Q}$. In this case the state can be expanded according the superposition principle (1.22). Then the measurement of $\mathbb{Q}$ will give the real eigenvalue q_n with probability, $P(q_n)$,

Measurement probabilities of observable $\hat{Q}$

$$|\psi\rangle = \sum_n c_n |q_n\rangle \rightarrow P_\psi(\mathbb{Q} = q_n) = |\langle q_n|\psi\rangle|^2, \tag{1.42}$$

The state of the system immediately after the measurement is proportional to $|q_n\rangle$.

A more formal defintion. If we define the *projection* operator $\hat{Q}_n$ as:

$$\hat{Q}_n = |q_n\rangle\langle q_n| \tag{1.43}$$

then the following measurement process can be formally stated as below as well:

Measurement of $\hat{Q}$

Measurement of $\mathbb{Q}$ in state $|\psi\rangle$ gives the value q_n with probability $P(q_n)$ and leaves the system in state

$$P(\mathbb{Q} = q_n) = \langle\psi|\hat{Q}_n|\psi\rangle \quad \rightarrow \quad |\psi_n\rangle = \frac{\hat{Q}_n|\psi\rangle}{\sqrt{\langle\psi|\hat{Q}_n|\psi\rangle}}, \tag{1.44}$$

with the probabilities given by[9],

$$P_\psi(\mathbb{Q} = q_n) = \langle\psi|\hat{Q}_n|\psi\rangle = \langle\psi|\left(|q_n\rangle\langle q_n|\right)|\psi\rangle = \langle q_n|\psi\rangle^\star\langle q_n|\psi\rangle = |\langle q_n|\psi\rangle|^2$$

8: The action of an arbitrary operator, $\hat{Q}$, on a state $|\psi\rangle$ generally results to a different state, $\hat{Q}|\psi\rangle \rightarrow |\phi\rangle$. A measurement can be seen as a special type of time-evolution of a quantum system; the system changes abruptly state following its interaction with an external system (the measurement device). The measurement enforces a probabilistic time evolution of the system that is abrupt with a devastating effect in the system (known as '*collapse of the wavefunction*'); Following measurement, regardless the state, only one state will survive. No deterministic predictions are possible within the generally accepted interpretation of a quantum measurement. It leads to inconsistencies if pushed further, still a matter of debate, but it is not of concern here. Also, it is exactly this postulate that makes QM theory an inherently probabilistic theory with no way to escape. A readable discussion about the various interpretations of quantum mechanics can be found in **[weinberg:2015]** and references therein.

9: Therefore the appearance probabilities can be calculated as the averages of the projection operator, $\hat{Q}_n$.

Uncertainty in Measurement

It is should be fairly obvious now that the QM measurement model is probabilistic and we can't predict the outcome of any specific measurement, though the average can be predicted when many identical measurements will be. So the next question is: what is the uncertainty in that measurement? A measure of the randomness is the standard deviation [10] Within the QM the uncertainty in the measurement of an observable $\hat{Q}$ of quantum state $|\Psi\rangle$ is defined as

10: In statistics:

$$\sigma_x = \left[\sum_{i=1}^{N}(x_i - \bar{x})^2\right]^{1/2} \tag{1.45}$$

where $\bar{x}$ is the average of the measurements.

Uncertainty

$$\Delta Q_\Psi \equiv \left[\langle\Psi|(\hat{Q} - \langle\hat{Q}\rangle)^2|\Psi\rangle\right]^{1/2} = \sqrt{\langle\hat{Q}^2\rangle - \langle\hat{Q}\rangle^2} \tag{1.46}$$

The uncertainty in the measurement is a measure of the range of possible measurements of our quantum state.

Measurement of an arbitrary observable $\hat{Q}$. In this case one should distinguish between the cases where the commutator $[\hat{Q}, \hat{H}]$ vanishes or not:

(i) $[\hat{Q}, \hat{H}] = 0$.
In this case the $|\phi_n\rangle$ are also eigenstates of $\hat{Q}$ and the following relation is true:

$$\hat{Q}|\phi_n\rangle = q_n|\phi_n\rangle$$

(ii) $[\hat{Q}, \hat{H}] \neq 0$
Now it is required to solve the eigenvalue problem for $\hat{Q}$ and then to express the energy eigenstates in terms of the $\hat{Q}$ eigenstates (say $|q_n\rangle$). At this point one can extract information about the probability distribution of measurements of the $\hat{Q}$ observable among its eigenvalues (which according to QM are the only ones realized.)

1.6 Examples

Example 1.6.1

Assume a constant magnetic field along the $\hat{z}$ direction. The total mechanical energy (ignoring the kinetic energy) of the system is due to the interaction of the system's spin with the magnetic field. This is given to be

$$H = -\hat{M} \cdot \hat{B} = -\frac{q}{2m} B S_z = \gamma S_z. \tag{1.47}$$

Then, the system's Hamiltonian is modelled as

$$\hat{H} = \gamma B \hat{S}_z = \omega_0 S_z. \tag{1.48}$$

For a system where initial is in the state,

$$|\psi(0)\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle)$$

Solution.

(i) Assume the eigenvalues and eigenvectors of the Hamiltonian:

$$\hat{H}|1\rangle = \omega_0 \hat{S}_z |1\rangle = \omega_0 \frac{\hbar}{2}|1\rangle$$
$$\hat{H}|2\rangle = \omega_0 \hat{S}_z |2\rangle = -\omega_0 \frac{\hbar}{2}|2\rangle.$$

So our eigenvalues are $\pm\hbar\omega_0/2$ for the $|1\rangle$ and $|2\rangle$ eigenstates.

(ii) The next step is to write the initial states in terms of the Hamiltonian's eigenbasis

$$|\psi(0)\rangle = \frac{1}{\sqrt{2}}|1\rangle + \frac{1}{\sqrt{2}}|2\rangle \tag{1.49}$$

and $c_1(0) = c_2(0) = 1/\sqrt{2}$.

(iii) So the time evolution of the state is [11]

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}} e^{-\imath\omega_0 t/2}|1\rangle + \frac{1}{\sqrt{2}} e^{\imath\omega_0 t/2}|2\rangle. \tag{1.50}$$

11: You may check whether the state is still normalized.

Example 1.6.2

Normalization and energy measurements of a state $|\psi_0\rangle$

Assume a quantum system with three possible states with two of them doubly degenerate ($\omega_0 = \epsilon_1 < \epsilon_2 = \epsilon_3 = 2\omega_0$), initially in the normalized (coherent) superposition,

$$|\psi_0\rangle = \sum_{n=1}^{3} c_n |\phi_n\rangle = c_1|\phi_1\rangle + \frac{1}{2}|\phi_2\rangle + \frac{1}{2}|\phi_3\rangle, \tag{1.51}$$

Let's set $\epsilon_1 = \hbar\omega_0$ and $\epsilon_2 = \epsilon_3 = 2\hbar\omega_0$. Next we consider the energy observable $\mathscr{H}$.
(a) Assume that the energy measurement takes place at time $t_0 = 0$. What results one should expect and how probable they are.
(b) What are the expectation values for the energy and its standard deviation?
(c) Assume that we had let first the system evolve for time t and then to perform the energy measurements. What the results of (b) question would then be?
(a)
The operator of the energy observable $\mathscr{H}$ is (of course) the Hamiltonian operator, $\hat{H}$ and the following QM postulates hold,

$$\hat{H}|\phi_n\rangle = \epsilon_n|\phi_n\rangle, \qquad n, m = 1-3 \tag{1.52}$$

$$\langle\phi_n|\phi_m\rangle = \delta_{nm}, \qquad \sum_{n=1}^{3} |\phi_n\rangle\langle\phi_n| = \mathbb{1}. \tag{1.53}$$

Normalization. First things first, is to normalize the state at the time of observation, which, of course is given by (1.51). The absolute value of c_1 is easily calculated by,

$$\sum_{n=1}^{3} |c_n|^2 = 1 \quad \rightarrow \quad |c_1|^2 + |\frac{1}{2}|^2 + |\frac{1}{2}|^2 = 1 \quad \rightarrow \quad c_1 = \frac{e^{\imath\theta}}{\sqrt{2}},$$

where θ is a real arbitrary number. Despite the fact that is unknown[a] a good amount of information can still be extracted. So the initial state is,

$$|\psi_0\rangle = \frac{e^{\imath\theta}}{\sqrt{2}}|\phi_1\rangle + \frac{1}{2}|\phi_2\rangle + \frac{1}{2}|\phi_3\rangle. \tag{1.54}$$

Energy measurement outcomes. According to the QM postulates an *energy measurement* can provide only the eigenvalues of $\hat{H}$. In the present case only two eigenenergies will be realized, namely $\epsilon_1 = \omega_0$ and $\epsilon_2 = \epsilon_3 = 2\omega_0$ with some probability.
These probabilites can be found by using the QM postulate for the expansion of a state in an eigenbasis of a physical observable, $\hat{Q}|q_n\rangle = q_n|q_n\rangle$.

$$|\psi\rangle = \sum_n c_n|q_n\rangle, \qquad c_n = \langle q_n|\psi\rangle.$$

Here $\hat{Q} = \hat{H}$ and $|q_n\rangle = |\phi_n\rangle$ and and $|\psi\rangle = \rangle\psi_0$. Therefore we have,

$$P(E = \epsilon_n) = |\langle\phi_n|\psi_0\rangle|^2 = |c_n|^2.$$

[b] In the present case,

$$\boxed{P(\epsilon_1 = \hbar\omega_0) = |\langle\phi_1|\psi_0\rangle|^2 = \left|\frac{e^{\imath\theta}}{\sqrt{2}}\right|^2 = \frac{1}{2}.}$$

Similarly, for the second energy eigenvalue we obtain:

$$\boxed{P(\epsilon_2 = 2\hbar\omega_0) = |\langle\phi_2|\psi_0\rangle|^2 + |\langle\phi_3|\psi_0\rangle|^2 = \frac{1}{4} + \frac{1}{4} = \frac{1}{2}.}$$

[a] Note that the (relative) phase of a quantum state in linear superposition matters (in contrast with a global phase e.g. $e^{\imath\phi}|\psi_0\rangle$).
[b] These probabilities can also be found from the generalized definition of the projection operator, $\hat{Q}_n = |\phi_n\rangle\langle\phi_n| \quad \longrightarrow \quad P(q_n) = \langle\psi|\hat{Q}_n|\psi\rangle = \langle\psi|(|\phi_n\rangle\langle\phi_n|)|\psi\rangle = \langle\psi|\phi_n\rangle\langle\phi_n|\psi\rangle|\langle\psi|\phi_n\rangle|^2$.

Example 1.6.3

Energy mean value and standard deviation of a state $|\psi_0\rangle$

It is relatively trivial to calculate the expectation value of the Hamiltonian operator (mean energy of the system) by invoking the general expression for the expectation value of an operator, $\hat{Q}$

$$\langle Q\rangle_\psi = \langle\psi|\hat{Q}|\psi\rangle.$$

Accordingly in the current case $\hat{Q}=\hat{H}$ and $|\psi\rangle = |\psi_0\rangle$. Then we arrive at,

$$\begin{aligned}
\langle\hat{H}\rangle_{\psi_0} = \langle\psi_0|\hat{H}|\psi_0\rangle &= \left(\frac{e^{-\imath\theta}}{\sqrt{2}}\langle\phi_1| + \frac{1}{2}\langle\phi_2| + \frac{1}{2}\langle\phi_3|\right)\hat{H}\left(\frac{e^{\imath\theta}}{\sqrt{2}}|\phi_1\rangle + \frac{1}{2}|\phi_2\rangle + \frac{1}{2}|\phi_3\rangle\right)\\
&= \left(\frac{e^{-\imath\theta}}{\sqrt{2}}\langle\phi_1| + \frac{1}{2}\langle\phi_2| + \frac{1}{2}\langle\phi_3|\right)\left(\frac{e^{\imath\theta}}{\sqrt{2}}\hat{H}|\phi_1\rangle + \frac{1}{2}\hat{H}|\phi_2\rangle + \frac{1}{2}\hat{H}|\phi_3\rangle\right)\\
&= \left(\frac{e^{-\imath\theta}}{\sqrt{2}}\langle\phi_1| + \frac{1}{2}\langle\phi_2| + \frac{1}{2}\langle\phi_3|\right)\left(\frac{e^{\imath\theta}}{\sqrt{2}}\epsilon_1|\phi_1\rangle + \frac{1}{2}\epsilon_2|\phi_2\rangle + \frac{1}{2}\epsilon_3|\phi_3\rangle\right)\\
&= \frac{1}{2}\epsilon_1 + \frac{1}{4}\epsilon_2 + \frac{1}{4}\epsilon_3 = \frac{1}{2}\omega_0 + \frac{1}{4}(2\omega_0) + \frac{1}{4}(2\omega_0) = \frac{3}{2}\hbar\omega_0,
\end{aligned}$$

where the orthonormalization condition were used for the calculation of the inner products $\langle\phi_n|\phi_m\rangle$ according the orthonormality rules of (1.53),

$$\begin{aligned}
\langle\phi_1|\phi_1\rangle = \langle\phi_2|\phi_2\rangle = \langle\phi_3|\phi_3\rangle = 1\\
\langle\phi_1|\phi_2\rangle = \langle\phi_1|\phi_3\rangle = \langle\phi_2|\phi_3\rangle = 0.
\end{aligned}$$

An alternative method. An alternative, fast track, calculation of the mean energy value can be obtained by relying in matrix operations if we decide to represent operators and vectors on the (fundamental) vector basis (1.13)]. Then,

$$\hat{H} = \hbar\omega_0\begin{pmatrix}1&0&0\\0&2&0\\0&0&2\end{pmatrix}, \qquad |\psi\rangle = \frac{1}{2}\begin{pmatrix}e^{\imath\theta}\sqrt{2}\\1\\1\end{pmatrix} \tag{1.55}$$

We then immediately get,

$$\langle\hat{H}\rangle_{\psi_0} = \langle\psi_0|\hat{H}|\psi_0\rangle = \underbrace{\frac{1}{2}\left(\sqrt{2}e^{-\imath\theta},1,1\right)}_{\langle\psi_0|}\cdot\underbrace{\hbar\omega_0\begin{pmatrix}1&0&0\\0&2&0\\0&0&2\end{pmatrix}}_{\mathbf{H}}\cdot\underbrace{\frac{1}{2}\begin{pmatrix}\sqrt{2}e^{\imath\theta}\\1\\1\end{pmatrix}}_{|\psi_0\rangle} = \frac{3}{2}\hbar\omega_0$$

Example 1.6.4

Standard deviation of a state $|\psi_0\rangle$

The standard deviation of the system's energy at that particular time may be found by calculating ΔE using the well known statistical formula,

$$\Delta Q_\psi = \sqrt{\langle\psi|(\hat{Q}-\langle Q\rangle_\psi)^2|\psi\rangle} = \sqrt{\langle \mathbb{Q}^2\rangle_\psi - \langle\mathbb{Q}\rangle_\psi^2} \neq 0. \tag{1.56}$$

Replacing $\hat{Q}$ by $\hat{H}$ and using $|\psi_0\rangle$ followed by the calculation using either the abstract vector formulation in terms of bra and kets, or the matrix representation formulation on should end to $\Delta E = \hbar\omega_0/2$, shown below. It is relatively trivial to calculate the expectation value of the Hamiltonian operator (mean energy of the system) by invoking the general expression for the expectation value of an operator, $\hat{Q}$

$$\Delta H_\psi = \sqrt{\langle\psi|(\hat{H}-\langle H\rangle_\psi)^2|\psi\rangle} = \sqrt{\langle\hat{H}^2\rangle_\psi - \langle\hat{H}\rangle_\psi^2}. \tag{1.57}$$

Accordingly in the current case $\hat{Q}=\hat{H}$ and $|\psi\rangle = |\psi_0\rangle$. Then we arrive at,

$$\begin{aligned}
\langle\hat{H}^2\rangle_{\psi_0} = \langle\psi_0|\hat{H}^2|\psi_0\rangle &= \left(\frac{e^{-\imath\theta}}{\sqrt{2}}\langle\phi_1| + \frac{1}{2}\langle\phi_2| + \frac{1}{2}\langle\phi_3|\right)\hat{H}\hat{H}\left(\frac{e^{\imath\theta}}{\sqrt{2}}|\phi_1\rangle + \frac{1}{2}|\phi_2\rangle + \frac{1}{2}|\phi_3\rangle\right)\\
&= \left(\frac{e^{-\imath\theta}}{\sqrt{2}}\langle\phi_1|\hat{H} + \frac{1}{2}\langle\phi_2|\hat{H} + \frac{1}{2}\langle\phi_3|\hat{H}\right)\left(\frac{e^{\imath\theta}}{\sqrt{2}}\hat{H}|\phi_1\rangle + \frac{1}{2}\hat{H}|\phi_2\rangle + \frac{1}{2}\hat{H}|\phi_3\rangle\right)\\
&= \left(\frac{e^{-\imath\theta}}{\sqrt{2}}\langle\phi_1|\epsilon_1 + \frac{1}{2}\langle\phi_2|\epsilon_2 + \frac{1}{2}\langle\phi_3|\epsilon_3\right)\left(\frac{e^{\imath\theta}}{\sqrt{2}}\epsilon_1|\phi_1\rangle + \frac{1}{2}\epsilon_2|\phi_2\rangle + \frac{1}{2}\epsilon_3|\phi_3\rangle\right)\\
&= \frac{1}{2}\epsilon_1^2 + \frac{1}{4}\epsilon_2^2 + \frac{1}{4}\epsilon_3^2 = \frac{1}{2}\omega_0^2 + \frac{1}{4}(2\omega_0)^2 + \frac{1}{4}(2\omega_0)^2 = \frac{5}{2}\hbar^2\omega_0^2,
\end{aligned}$$

where (again) the orthonormalization condition were used for the calculation of the inner products $\langle\phi_n|\phi_m\rangle$ according the orthonormality rules of (1.53),

$$\begin{aligned}
\langle\phi_1|\phi_1\rangle = \langle\phi_2|\phi_2\rangle = \langle\phi_3|\phi_3\rangle = 1\\
\langle\phi_1|\phi_2\rangle = \langle\phi_1|\phi_3\rangle = \langle\phi_2|\phi_3\rangle = 0.
\end{aligned}$$

An alternative method. Along similar lines as in the calculation of the mean value one may use matrix operations by representing the $\hat{H}^2$ observable in the (fundamental) vector basis (1.13)]. Then,

$$\hat{H}^2 = \hbar\omega_0\begin{pmatrix}1&0&0\\0&2&0\\0&0&2\end{pmatrix}\hbar\omega_0\begin{pmatrix}1&0&0\\0&2&0\\0&0&2\end{pmatrix} = (\hbar\omega_0)^2\begin{pmatrix}1&0&0\\0&4&0\\0&0&4\end{pmatrix}, \qquad |\psi\rangle = \frac{1}{2}\begin{pmatrix}e^{\imath\theta}\sqrt{2}\\1\\1\end{pmatrix} \tag{1.58}$$

We then immediately get,

$$\langle\hat{H}\rangle_{\psi_0} = \langle\psi_0|\hat{H}^2|\psi_0\rangle = \underbrace{\frac{1}{2}\left(\sqrt{2}e^{-\imath\theta},1,1\right)}_{\langle\psi_0|}\cdot\underbrace{(\hbar\omega_0)^2\begin{pmatrix}1&0&0\\0&4&0\\0&0&4\end{pmatrix}}_{\mathbf{H}}\cdot\underbrace{\frac{1}{2}\begin{pmatrix}\sqrt{2}e^{\imath\theta}\\1\\1\end{pmatrix}}_{|\psi_0\rangle} = \frac{5}{2}(\hbar\omega_0)^2$$

Finally the standard deviation is

$$\Delta H_0 = \sqrt{\langle\hat{H}^2\rangle_0 - \langle\hat{H}\rangle_0^2} = \sqrt{\frac{5}{2}(\hbar\omega_0)^2 - \frac{9}{4}(\hbar\omega_0)^2} = \frac{1}{2}\hbar\omega_0 \tag{1.59}$$

1.7 Summary and discussion

So far, the discussion has been exclusively referred to a formulation of the quantum mechanics with the physical states as elements of an abstract Hilbert space. In the case of familiar 3D space vectors*, the choice of a particular coordinate system, say $\mathscr{C}$ provides the means for the practical calculations turning abstract vector relation (as is for example the 2-nd Newton's law) to down-to-earth numerical relations between physical quantities. Translation and/or rotation of the coordinate system ($\mathscr{C} \rightarrow \mathscr{C}'$) transforms the original set of component, expressed in $\mathscr{C}$), in a controlled way, to another set of components (expressed now in $\mathscr{C}'$)†. The choice of the coordinate systems can greatly facilitate (or not) the numerical computations. Even more, the proper choice can offer an improved insight about the process under question or it can obscure it all. Recall the calculation of the electrostatic potential of a motionless uniformly charged spherical ball in the spherical and orthogonal coordinate systems. What would be the wiser choice? Seems that the identification of physical symmetries, possessed by the system, is a fairly reasonable starting point to choose a suitable coordinate system.

Having said the above one should realize that these lines of thinking are valid in quantum mechanical problems as well. The key is that quantum physical states (and operators) live in linear vector spaces and dealing with quantum mechanical systems more often than not a suitable complete basis set must be chosen. The abstract quantum basis set used to expand the abstract vectors corresponds to the (spatial) coordinate system of classical mechanics. Also, often the basis is dictated by the observable ($\mathbb{Q}$) under question and the type of the measurement to be performed and not only the system itself. Fortunately, the operator associated with the observable offer through its eigenvalue equation a recipe to generate a complete basis set. Picking the right observable and solving the eigenvalue equation is a step that one needs to go through in most cases.

* You may imagine for example the vectors representing the position, momentum and angular momentum of a particle, or the force acting on the particle.

† Of course the relations between the involved set of components remain as dictated by the Physics laws. For example for a particle of mass m subject to a force governed by the Newton's 2nd law the ratio between acceleration and force still will be equal to particle's mass regardless what coordinate system happens to be in use ($\mathscr{C}$) or $\mathscr{C}'$

1.8 Questions

Question 1.8.1

Suppose initially an atom is in the state

$$|\psi(0)\rangle = \frac{1}{2}|E_1\rangle + i\frac{\sqrt{3}}{2}|E_2\rangle, \tag{1.60}$$

where $|E_1\rangle$ and $|E_2\rangle$ are two energy eigenstates of the system's Hamiltonian $\hat{H}$.

(a) What is $|\psi(t)\rangle$ for $t > 0$?
(b) If the energy is measured at $t > 0$, find the probability of obtaining E_2. Does this probability depend on time?

Question 1.8.2

Consider the time-evolved state of the latest example of measurement ($|\psi_0\rangle$).Following the general QM postulate for the time-evolution of a state, we have,

$$|\psi(t)\rangle = \sum_n c_n(0)e^{-\imath\epsilon_n t/\hbar}|\phi_n\rangle.$$

Since the $c_n(0)$ are known and $n = 1 - 3$ we end up to the following expression for the state of the current system:

$$\begin{aligned}|\psi(t)\rangle &= \frac{e^{\imath\theta}}{\sqrt{2}}e^{-\imath\epsilon_1 t/\hbar}|\phi_1\rangle + \frac{1}{2}e^{-\imath\epsilon_2 t/\hbar}|\phi_2\rangle + \frac{1}{2}e^{-\imath\epsilon_2 t/\hbar}|\phi_3\rangle \\ &= \frac{e^{\imath\theta}}{\sqrt{2}}e^{-\imath\omega_0 t}|\phi_1\rangle + \frac{1}{2}e^{-\imath 2\omega_0 t}|\phi_2\rangle + \frac{1}{2}e^{-\imath 2\omega_0 t}|\phi_3\rangle.\end{aligned}$$

You may try to repeat the calculations as in the case of $|\psi_0\rangle$ in example (1.6.4).

Question 1.8.3

A Hamiltonian $\hat{H}$ and an observable $\hat{Q}$ is given (represented in the the same eigenbasis):

$$\hat{H} = E_1\begin{pmatrix}1 & 0 & 0\\ 0 & 2 & 0\\ 0 & 0 & 3\end{pmatrix} \quad \hat{Q} = a_1\begin{pmatrix}1 & 0 & 0\\ 0 & 2 & 0\\ 0 & 0 & 1\end{pmatrix}, \tag{1.61}$$

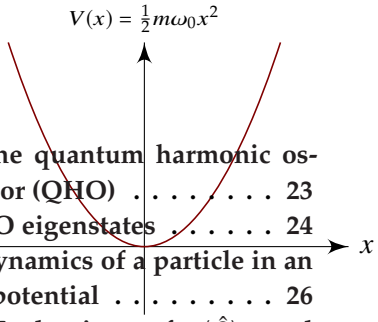
and a system in state,

$$|\Psi(0)\rangle \Rightarrow \frac{1}{3}\begin{pmatrix}1\\0\\0\end{pmatrix} - \frac{i}{3}\begin{pmatrix}0\\1\\0\end{pmatrix} + \frac{\sqrt{7}}{3}\begin{pmatrix}0\\0\\1\end{pmatrix}. \tag{1.62}$$

(a) What is $|\Psi(t)\rangle$ for $t > 0$?
(b) If $\hat{A}$ is measured at $t > 0$, what are the possible results and the associated probabilities for obtaining those results? What is the state of the system after each of the possible measurements?
(c) What is the average results of $\hat{Q}$?

The quantum harmonic oscillator

2



Let's consider a particle of mass m moving in a potential field of an harmonic oscillator. According to classical mechanics its potential energy outside its equillibrium position (assumed to be at $x = 0$) is $V(x) = m\omega_0 x^2/2$.

EOM for classical HO

For a classical HO the equation of motion is and its solutions are,

$$\ddot{x}(t) + \omega_0^2 x(t) = 0$$

Defining $m\dot{x} = p(t)$ the above 2nd-order ODE is written as,

$$\dot{p}(t) = -m\omega_0^2 x(t)$$
$$\dot{x}(t) = p(t)/m$$

For a given set of initial conditions, $x(0) = x_0$ and $v(0) = v_0$ the solutions are,

$$x(t) = x_0 \cos\omega_0 t + \frac{p_0}{m\omega_0}\sin\omega_0 t = A_0 \sin(\omega_0 t + \phi_0)$$
$$p(t) = p_0 \cos\omega_0 t - m x_0 \omega_0 \sin\omega_0 t = m A_0 \cos(\omega_0 t + \phi_0)$$

Energy is *constant of motion* and equal to,

$$E = \frac{1}{2}mv^2 + \frac{1}{2}m\omega_0^2 x^2 = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2 = \frac{1}{2}m\omega_0^2 A_0^2 \qquad (2.1)$$

2.1 The quantum harmonic oscillator (QHO)

The analogue of the quantum harmonic oscillator (QHO) is obtained as follows

(1) The starting point is the classical expression for the system's energy in terms of the momentum and position, which here is (2.1). The Hamiltonian is obtained by assuming that position and momentum are quantum observables, satisfying,

$$[\hat{x}, \hat{p}] = \imath\hbar,$$

Then the system's Hamiltonian is expressed by,

$$\hat{H}_{ho} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega_0^2\hat{x}^2. \tag{2.2}$$

The above expression for the Hamiltonian observable is given in the abstract algebraic formulation of QM.

(2) Second step is to choose a working representation for the $\hat{H}_{ho}$; here we choose the *position-representation* where the position- and the-momentum observables are expressed as below:

$$\hat{x} = x \qquad \hat{p} = -\imath\hbar\frac{d}{dx}. \tag{2.3}$$

By replacing expressions (2.3) into (2.2) we obtain:

$$H_{ho} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega_0^2x^2 \tag{2.4}$$

At this stage, it is obvious that the Hamiltonian in the position-representation becomes a differential operator with respect to the position, 'x'.

(3) In order to predict the outcome of the measurements of an arbitrary observable $\hat{Q}$ we need to determine the associated eigenvalues/eigenstates for the corresponding measured observable (e.g. energy, momentum, position,..).

(4) The dynamics of the system is given by the Schrödinger equation, [13]

$$\imath\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \hat{H}_{ho}|\psi(t)\rangle \qquad \longrightarrow \qquad \imath\hbar\frac{\partial}{\partial t}\psi(x,t) = \hat{H}_{ho}\psi(x,t) \tag{2.5}$$

13: where, $\psi(x,t) = \langle x|\psi(t)\rangle$

2.2 HO eigenstates

Starting from the formal QM expression for eigenvalue problem of the Hamiltonian we arrive at the conclusion that the HO's spectrum is discretized [14] and bounded from below. So, we have, [15]

$$\hat{H}_{ho}|\phi_n\rangle = E|\phi_n\rangle \qquad \Longrightarrow \qquad \hat{H}_{ho}\phi_n(x) = E\phi_n(x)$$

Substituting the HO hamiltonian (2.4) gives,

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega_0^2 x^2\right)\phi_n(x) = E_n\phi_n(x) \tag{2.6}$$

Defining,

$$\beta \equiv \sqrt{\frac{m\omega_0}{\hbar}} \tag{2.7}$$

the HO eigenfunctions and the corresponding eigenenergies are expressed as, [16]

Harmonic oscillator spectrum

$$\phi_n(x) = N_n H_n(\beta x)e^{-\frac{1}{2}\beta^2 x^2}, \qquad E_n = \hbar\omega\left(n + \frac{1}{2}\right), \quad n = 0, 1, 2, \cdots \tag{2.8}$$

$$\beta = \left(\frac{m\omega}{\hbar}\right)^{\frac{1}{2}}, \qquad N_n = \sqrt{\frac{\beta}{2^n n!\sqrt{\pi}}}$$

The QM orthonormalization and completeness relations for the $|\phi_n\rangle$,

$$\langle\phi_n|\phi_m\rangle = \delta_{nm} \qquad \mathbb{1} = \sum_n |\phi_n\rangle\langle\phi_n| \tag{2.9}$$

in the position representation the orthogonality condition become [17],

$$\langle\phi_n|\phi_m\rangle = \int_{-\infty}^{\infty} dx\, \phi_n^*(x)\phi_m(x) = \delta_{nm} = \begin{cases} 1 & n = m \\ 0 & n \neq m. \end{cases} \tag{2.10}$$

$$\sum_n \phi_n(x)\phi(x') = \delta(x - x') \tag{2.11}$$

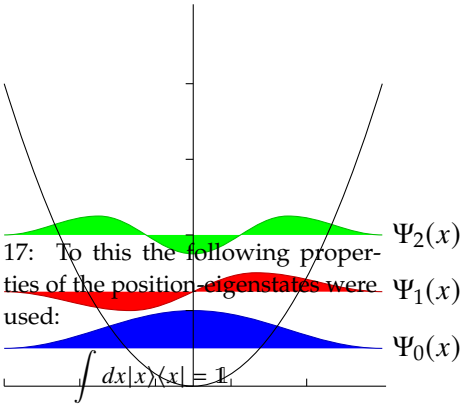
We also see that any physical state (say $|\psi\rangle$) of the particle in the HO potential can be expressed in terms of the HO eigenstates. This can be seen by taking the completeness relation and by

14: *Spectrum* in this context is used to de[illegible] e eigenstates/eigenergies of an observable. The detailed derivation is given in section (2.6

15: where, as usual $\phi_n(x) = \langle x|\phi_n\rangle$

$\hat{H}_{ho}\phi_n(x) = \langle x|\hat{H}_{ho}|\phi_n\rangle$

16:).



17: To this the following properties of the position-eigenstates were used:

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

multiplying from the left to obtain,

$$|\psi\rangle = \sum_n |\phi_n\rangle\langle\phi_n|\psi\rangle = \sum_n c_n|\phi_n\rangle, \qquad c_n = \langle\phi_n|\psi\rangle \tag{2.12}$$

Now by assuming the position-representation, we can multiple again from the left with $\langle x|$ to obtain:

$$\psi(x) = \sum_n c_n\phi_n(x), \qquad c_n = \int_{-\infty}^{\infty} dx\, \phi_n^*(x)\psi(x), \tag{2.13}$$

where $\psi(x) = \langle x|\psi\rangle$ and $\phi_n = \langle x|\phi_n\rangle$.

Energy measurement. The standard QM interpretation of the expansion coefficients, as the probability that an energy measurement will result to an eigenvalue E_n with probability:

$P(E = E_n, t) = |c_n(t)|^2 = |c_n e^{-\imath\omega_0(n+1/2)}| = |c_n|^2.$ **(constant in time)**

2.3 Dynamics of a particle in an HO potential

There are few different approaches to determine the relevant dynamics, depending on the available information. If the state of the system is known then one can calculate $\langle\hat{Q}\rangle$ directly. If the state of the system is known by its mean values then one could use the Ehrenfrest theorem. Or alternatively one could solve directly the time-dependent Schrödinger equation without relying in the knowledge of the eigenenergies/states. Let's discuss these approaches in a bit more detail.[18]

18: Note that the expectation (mean) value as the 'average result of many measurements' does not apply lightly for a QM system. Since, following a measurement, the system will end to one of its eigenstate, a subsequent measurement will give the corresponding eigenvalue with certainty. So, within QM the mean value is not practically obtained by measuring the same single system over many times. Instead, one performs the same type of measurement (once) on an number of identical copies of the same system prepared in the same state ψ. This is known as *ensemble* average

Evaluation of $\langle\hat{Q}\rangle$ and $\langle\Delta Q\rangle$

First one needs to calculate the time-evolution of an arbitrary state by expanding on the Hamiltonian's eigenstate basis:

$$|\psi\rangle = \sum_n c_n(0)|\phi_n\rangle \qquad \rightarrow \qquad |\psi(t)\rangle = \sum_n c_n(0)e^{-\imath E_n t/\hbar}|\phi_n\rangle \tag{2.14}$$

In the position representation by recalling (2.15) one has,

$$\psi(x,0) = \sum_n c_n\phi_n(x) \qquad \Longrightarrow \qquad \psi(x,t) = \sum_n c_n e^{-\imath\omega_0(n+1/2)}\phi_n(x). \tag{2.15}$$

Mean values For an arbitrary observable $\hat{Q}$ and when the particle is in an arbitrary state $|\psi(t)\rangle = \sum_n c_n|\phi_n\rangle$, QM gives for the expectation value (or mean value from a probabilistic point of view):

$$\langle\hat{Q}(t)\rangle_\psi = \langle\psi(t)|\hat{Q}|\psi(t)\rangle = \sum_{nm} c_n^*(0)c_m(0)e^{\imath(E_n-E_m)t/\hbar}Q_{nm}, \tag{2.16}$$

$$Q_{nm} = \langle\phi_n|\hat{Q}|\phi_m\rangle. \tag{2.17}$$

In the case of the HO (and again within the chosen position representation) the QM expression for mean values of observables (2.16) specializes to,

$$\langle\hat{Q}\rangle(t) = \langle\psi(t)|\hat{Q}|\psi(t)\rangle = \sum_{nm} c_n^* c_m e^{\imath\omega_0(n-m)t}Q_{nm}, \tag{2.18}$$

$$Q_{nm} = \int_{-\infty}^{\infty} dx\, \phi_n^*(x)\hat{Q}\phi_m(x) \tag{2.19}$$

Mean value of energy, $\langle \hat{H} \rangle$. For the special case of the energy mean value, $\hat{Q} = \hat{H}$, since $\hat{H}\phi_n(x) = E_n\phi_n(x)$ we end up to: [19]

$$H_{nm} = E_m \int_{-\infty}^{\infty} dx\, \phi_n^*(x)\phi_m(x) = E_m\delta_{nm} \qquad \rightarrow \qquad \langle H(t) \rangle = \sum_n E_n |c_n|^2$$

19: Which has the standard appearance of a (classical) mean value, $\langle E \rangle = \sum_n E_n P_n$, with $P_n = P(E = E_n)$ the probability distribution among energies E_n.

Mean value of position and momentum, $\langle \hat{x} \rangle$ and $\langle \hat{p} \rangle$. Let's specialize the above in the case of the classical mechanics dynamical variables, $\hat{x}$ and $\hat{p}$. From (2.18) and (2.19) it is seen that the matrix elements x_{nm} and p_{mn} over the HO energy eigenstates are needed for the calculation of $\langle \hat{x} \rangle$ and $\langle \hat{p} \rangle$ [20].

Fortunately, with the help of the properties of the Hermite polynomials these matrix elements can be calculated quite straightforward for arbitrary n and m:

20: Or equivalently the expression of the $\hat{x}$ and $\hat{p}$ in the *energy*-representation, $|\phi_n\rangle$.

(i)

$$x_{nm} = \langle \phi_n | \hat{x} | \phi_m \rangle = \int_{-\infty}^{\infty} dx\, \phi_n^*(x) x \phi_m(x) \tag{2.20}$$

(ii)

$$p_{nm} = \langle \phi_n | \hat{p} | \phi_m \rangle = \int_{-\infty}^{\infty} dx\, \phi_n^*(x)) \left(-\imath \frac{d}{dx} \right) \phi_m(x) \tag{2.21}$$

2.4 Equation of motion (EOM) for $\langle \hat{Q} \rangle$

To simplify the discussion we'll consider the Ehrenfrest theorem for observables that are not dependent on time explicitly [21] . Examples of such observables are the usual operators such as the position, momentum, energy, etc.. Then we have,

$$\imath\hbar \frac{d}{dt}\langle \hat{Q} \rangle = \langle [\hat{Q},\ \hat{H}_{ho}] \rangle \frac{1}{2m} \langle [\hat{Q},\ \hat{p}^2] \rangle + \frac{1}{2} m\omega_0^2 \langle [\hat{Q},\ \hat{x}^2] \rangle.$$

From the above we see that the commutation relations $[\hat{p},\ \hat{Q}]$ and $[\hat{x},\ \hat{Q}]$ are required in order to establish the EOM for $\langle \hat{Q} \rangle$. At this point one needs to know the explicit expression for

21: So $\frac{\partial \hat{Q}}{\partial t} = 0.$

2.5 Examples

Example 2.5.1

Assume an HO quantum system ($V(x) = m\omega_0^2/2$) initially prepared in the state,

$$\psi_0 = \frac{1}{\sqrt{6}}(\phi_0 + 2\phi_1 + i\phi_4).$$

The *non-zero* expansion coefficients are

$$c_0 = \frac{1}{\sqrt{6}}, \quad c_1 = \frac{2}{\sqrt{6}}, \quad c_4 = \frac{\imath}{\sqrt{6}}$$

First one checks that the state is correctly normalized to unity:

$$\langle\psi_0|\psi_0\rangle = \sum_n |c_n|^2 = |c_0|^2 + |c_1|^2 + |c_4|^2 = 1.$$

Energy measurement will give the following results with the corresponding probabilities:

Energy	Probability
$E_0 = \frac{1}{2}\hbar\omega_0$	$P_0 = \lvert c_0\rvert^2 = \frac{1}{6}$
$E_1 = \frac{3}{2}\hbar\omega_0$	$P_1 = \lvert c_1\rvert^2 = \frac{2}{3}$
$E_4 = \frac{9}{2}\hbar\omega_0$	$P_4 = \lvert c_4\rvert^2 = \frac{1}{6}$

Note that, according to QM, if a measurement gives E_4, then the system's state immediately after measurement is ϕ_4. Of course a subsequent *energy* measurement will give E_4 with certainty.

The mean energy, $\langle\hat{H}\rangle$, in the initial state, ψ_0, may be evaluated as,

$$\langle\hat{H}\rangle_0 = \sum_n E_n|c_n|^2 = \left(\frac{1}{2}\cdot\frac{1}{6} + \frac{3}{2}\cdot\frac{2}{3} + \frac{9}{2}\cdot\frac{1}{6}\right)\hbar\omega_0 = \frac{11}{6}\hbar\omega_0.$$

To calculate the standard deviation, $\Delta H_0 = \sqrt{\langle\hat{H}^2\rangle_0 - \langle\hat{H}\rangle_0}$ one needs, in addition, to calculate $\langle\hat{H}^2\rangle$:

$$\langle\hat{H}^2\rangle_0 = \sum_n E_n^2|c_n|^2 = \left((\frac{1}{2})^2\cdot\frac{1}{6} + (\frac{3}{2})^2\cdot\frac{2}{3} + (\frac{9}{2})^2\cdot\frac{1}{6}\right)(\hbar\omega_0)^2 = \frac{59}{12}(\hbar\omega_0)^2.$$

Therefore the standard deviation is,

$$\Delta H_0 = \hbar\omega_0\sqrt{\frac{59}{12} - (\frac{11}{6})^2} = \frac{\sqrt{14}}{3}\hbar\omega_0 \approx 1.247\hbar\omega_0.$$

Note: You may calculate the same quantities but for the state at a later time.

$$\psi(t) = \frac{1}{\sqrt{6}}(\phi_0 e^{-\imath\omega_0 t/2} + 2\phi_1 e^{-3\imath\omega_0 t/2} + i\phi_4 e^{-9\imath\omega_0 t/2}).$$

Example 2.5.2

Example: Mean value, standard deviation of $\hat{x}$ in state $|\phi_n\rangle$

$$\begin{aligned}
\langle x\rangle_n &= x_{nn} = \int_{-\infty}^{\infty} dx\, \phi_n^*(x) x \phi_n(x) = \int_{-\infty}^{\infty} dx\, N_n e^{-\beta^2x^2/2} H_n(\beta x) x N_n e^{-\beta^2x^2/2} H_n(\beta x) = N_n^2 \int_{-\infty}^{\infty} dx\, x e^{-\beta^2x^2} H_n^2(\beta x) \\
&= \frac{N_n^2}{\beta^2}\left[\int_{-\infty}^{0} d(\beta x)\,(\beta x) e^{-(\beta x)^2} H_n^2(\beta x) + \int_{0}^{\infty} d(\beta x)\,(\beta x) e^{-(\beta x)^2} H_n^2(\beta x)\right] \\
&= \frac{N_n^2}{\beta^2}\left[\int_{-\infty}^{0} d(-\beta x)\,(-\beta x) e^{-(-\beta x)^2} [(-1)^n H_n(-\beta x)]^2 + \int_{0}^{\infty} d(\beta x)\,(\beta x) e^{-(\beta x^2)} H_n^2(\beta x)\right] \\
&= \frac{N_n^2}{\beta^2}\left[\int_{-\infty}^{0} du\, u e^{-u^2} H_n^2(u) + \int_{0}^{\infty} dv\, v e^{-v^2} H_n^2(v)\right] = \frac{N_n^2}{\beta^2}\left[-\int_{\infty}^{0} du\, u e^{-u^2} H_n^2(u) + \int_{0}^{\infty} dv\, v e^{-v^2} H_n^2(v)\right] = 0
\end{aligned}$$

since the last two integrals have the same value. Note that set $u = -\beta x$ and $v = \beta x$ and used the (parity) property of the Hermite polynomials $H_n(x) = (-1)H_n(-x)$. The standard deviation of is now given by

$$\Delta x_n = \sqrt{\langle x^2\rangle_n - \cancelto{0}{\langle x\rangle_n}} \qquad \rightarrow \qquad \Delta x_n = \sqrt{\langle x^2\rangle_n}$$

The calculation now proceeds along similar steps as for $\langle x\rangle_n$, to have,

$$\begin{aligned}
\langle x^2\rangle_n &= x_{nn}^2 = \int_{-\infty}^{\infty} dx\, \phi_n^*(x) x^2 \phi_n(x) = N_n^2 \int_{-\infty}^{\infty} dx\, x e^{-\beta^2x^2} H_n^2(\beta x) = \frac{N_n^2}{\beta^2}\int_{-\infty}^{+\infty} dx\, e^{-\beta^2x^2}\,(\beta x H_n(\beta x))^2 \\
&= \frac{N_n^2}{\beta^2}\int_{-\infty}^{+\infty} dx\, e^{-\beta x^2}\left(\frac{1}{2}H_{n+1}^2(\beta x) + nH_{n-1}(\beta x)\right)^2 = \frac{N_n^2}{\beta^2}\int_{-\infty}^{+\infty} dx\, e^{-\beta x^2}\left[\frac{1}{4}H_{n+1}^2(\beta x) + n^2 H_{n-1}^2(\beta x) + nH_{n+1}(\beta x)H_{n-1}(\beta x)\right] \\
&= \frac{N_n^2}{\beta^2}\int_{-\infty}^{+\infty} dx\, e^{-\beta^2x^2}\left[\frac{1}{4N_{n+1}^2}N_{n+1}^2 H_{n+1}^2(\beta x) + \frac{n^2}{N_{n-1}^2}N_{n-1}^2 H_{n-1}^2(\beta x) + \frac{n}{N_{n+1}N_{n-1}}N_{n+1}H_{n+1}(\beta x)N_{n-1}H_{n-1}(\beta x)\right] \\
&= \frac{1}{\beta^2}\left[(\frac{N_n}{2N_{n+1}})^2 \cancelto{1}{\langle\phi_{n+1}|\phi_{n+1}\rangle} + (\frac{nN_n}{N_{n-1}})^2 \cancelto{1}{\langle\phi_{n-1}|\phi_{n-1}\rangle} + \frac{nN_n}{N_{n+1}N_{n-1}}\cancelto{0}{\langle\phi_{n+1}|\phi_{n-1}\rangle}\right] = \frac{1}{\beta^2}\left[(\frac{N_n}{2N_{n+1}})^2 + (\frac{nN_n}{N_{n-1}})^2\right] \\
&= \frac{1}{\beta^2}\left[\frac{n+1}{2} + \frac{n}{2}\right] = \frac{1}{\beta^2}(n+\frac{1}{2}) = \frac{\hbar}{m\omega_0}(n+\frac{1}{2}) = \frac{E_n}{m\omega_0^2}.
\end{aligned}$$

To perform the above integrals the following relations were used,

$$xH_n(x) = H_{n+1}(x) + nH_{n-1}(x), \qquad \langle\phi_n|\phi_m\rangle = \delta_{nm}, \qquad N_n = \sqrt{\frac{\beta}{2^n n!\sqrt{\pi}}}$$

Finally we end up to following general properties for an HO in its eigenstate:

$$\langle x\rangle_n = 0, \qquad \langle x^2\rangle_n = \frac{E_n}{m\omega_0^2} \qquad \Delta x_n = \sqrt{\frac{E_n}{m\omega_0^2}} \qquad (2.22)$$

Example 2.5.3

Example: Mean value, standard deviation of $\hat{p}$ in the HO state $|\phi_n\rangle$.

For the mean value of the momentum we have $\langle p\rangle_n$, to have,

$$\begin{aligned}
\langle p\rangle_n &= \hat{p}_{nn} = \int_{-\infty}^{\infty} dx\, \phi_n^*(x)\hat{p}\phi_n(x) = N_n^2 \int_{-\infty}^{\infty} dx\, e^{-\beta^2x^2/2} H_n(\beta x)(-\imath\hbar\frac{d}{dx})\left[e^{-\beta^2x^2/2}H_n(\beta x)\right] \\
&= N_n^2 \int_{-\infty}^{\infty} dx\, e^{-\beta^2x^2/2} H_n(\beta x)\left[\imath\hbar x\beta^2 e^{-\beta^2x^2/2}H_n(\beta x) - \imath\hbar\beta e^{-\beta^2x^2/2}\frac{d}{d(\beta x)}H_n(\beta x)\right] \\
&= \imath\hbar \int_{-\infty}^{\infty} dx\, x N_n^2\beta^2 e^{-\beta^2x^2} H_n^2(\beta x) - \imath\hbar\beta \int_{-\infty}^{\infty} dx\, N_n e^{-\beta^2x^2/2} H_n(\beta x) e^{-\beta^2x^2/2}\,[2nH_{n-1}(\beta x)] \\
&= \imath\hbar \cancelto{0}{\langle\phi_n|x|\phi_n\rangle} - 2\imath\hbar\beta\frac{2n}{N_{n-1}}\int_{-\infty}^{\infty} dx\, \left(N_n e^{-\beta^2x^2/2}H_n(\beta x)\right)\left(N_{n-1}e^{-\beta^2x^2/2}H_{n-1}(\beta x)\right) \\
&= -2\imath\hbar\beta\frac{2n}{N_{n-1}}\cancelto{0}{\langle\phi_n|\phi_{n-1}\rangle} = 0
\end{aligned}$$

To perform the above integrals the following relations were used,

$$\frac{d}{dx}H_n(\beta x) = \beta\frac{d}{d(\beta x}H_n(\beta x) = \beta H'(u) = \beta 2nH_{n-1}(u) = 2n\beta H_{n-1}(\beta x) \quad \rightarrow \quad \frac{d}{dx}H_n(\beta x) = 2n\beta H_{n-1}(\beta x) \qquad \langle\phi_n|\phi_{n-1}\rangle = 0,$$

The standard deviation of the mean value is now given by,

$$\Delta p_n = \sqrt{\langle\hat{p}^2\rangle_n - \cancelto{0}{\langle\hat{p}\rangle_n}} \quad \rightarrow \quad \Delta p_n = \sqrt{\langle\hat{p}^2\rangle_n}$$

For the calculation of the required $\langle \mathrm{op}^2\rangle$ we can go ahead along the way already presented. Alternatively, at this point we can take advantage of the Hamiltonian expression for the HO in terms of $\langle\hat{x}^2\rangle$ and $\langle\hat{p}^2\rangle$. So using (2.2) we have,

$$\langle\hat{p}^2\rangle = 2m\langle\hat{H}\rangle - m^2\omega_0^2\langle x^2\rangle = 2mE_n - m^2\omega_0^2\frac{E_n}{m\omega_0^2} = mE_n, \tag{2.23}$$

where the mean value of $\langle\hat{x}^2\rangle$ used from (2.24) and that $\langle H\rangle = E_n$.

Finally we end up to following general properties for an HO in its eigenstate:

$$\langle p\rangle_n = 0, \qquad \langle p^2\rangle = mE_n, \qquad \Delta p_n = mE_n = \sqrt{mE_n}, \tag{2.24}$$

Based on the above results we can also evaluate the Heisenberg's relation for an HO in the state $|\phi_n\rangle$:

$$\Delta x_n\Delta p_n = \sqrt{\frac{E_n}{m\omega_0^2}}\sqrt{mE_n} = \frac{E_n}{\omega_0} = \hbar(n+\frac{1}{2}). \tag{2.25}$$

22

22: Therefore the uncertainty relation takes its minimum value when the system is in its ground state ($\phi_0(x)$):

$$\Delta x_0\Delta p_0 = \frac{\hbar}{2}$$

Example 2.5.4

EOMs for $\langle\hat{x}\rangle$ and $\langle\hat{p}\rangle$. As an example, we can specialize and try to find the equations of motions for the mean values of $\hat{x}$ and $\hat{p}$. This is done as below,

$$\imath\hbar\frac{d}{dt}\langle\hat{x}\rangle = \langle[\hat{x},\ \hat{H}_{ho}]\rangle = \langle[\hat{x},\ \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega_0^2\hat{x}^2]\rangle = \frac{1}{2m}\langle[\hat{x},\ \hat{p}^2]\rangle + \frac{1}{2}m\omega_0^2\langle[\hat{x},\ \hat{x}^2]\rangle$$
$$\imath\hbar\frac{d}{dt}\langle\hat{p}\rangle = [\hat{p},\ \hat{H}_{ho}] = \langle[\hat{p},\ \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega_0^2\hat{x}^2]\rangle = \frac{1}{2m}\langle[\hat{p},\ \hat{p}^2]\rangle + \frac{1}{2}m\omega_0^2\langle[\hat{p},\ \hat{x}^2]\rangle$$

Now, using $[\hat{x},\ \hat{p}] = \imath\hbar$ by noting that

$$[\hat{x},\ \hat{x}^2] = [\hat{p},\ \hat{p}^2] = 0,$$
$$[\hat{x},\ \hat{p}^2] = 2\imath\hbar\hat{p},$$
$$[\hat{p},\ \hat{x}^2] = -2\imath\hbar\hat{x},$$

resulting to,

$$[\hat{x},\ \hat{H}_{ho}] = \imath\hbar\frac{\hat{p}}{m}, \qquad [\hat{p},\ \hat{H}_{ho}] = -\imath\hbar m\omega_0^2\hat{x}.$$

The final EOM then become, [23]

$$\frac{d}{dt}\langle\hat{x}\rangle = \frac{\langle\hat{p}\rangle}{m}$$
$$\frac{d}{dt}\langle\hat{p}\rangle = -m\omega_0^2\langle\hat{x}\rangle$$

So given the mean values of the system's momentum and position at some time (say $t_0 = 0$) the corresponding solutions are,

$$\langle x\rangle(t) = x_0\cos\omega_0 t + \frac{p_0}{m\omega_0}\cos\omega_0 t, \qquad x_0 = \langle x\rangle(0) \tag{2.26}$$
$$\langle p\rangle(t) = p_0\cos\omega_0 t - m\omega_0 x_0\sin\omega_0 t, \qquad p_0 = \langle p\rangle(0) \tag{2.27}$$

Therefore the classical equations of motion are still valid in the quantum case, however for the corresponding expectation values! [24]

23: The first equation resembles the classical definition of momentum while the second one the equation of motion for the classical simple HO (after replacing $\frac{d}{dt}\langle\hat{x}\rangle = \langle\hat{p}\rangle$) :

$$\frac{d^2}{dt^2}\langle\hat{x}\rangle + \omega_0^2\langle\hat{x}\rangle = 0.$$

24: Nevertheless this reminiscinent of the classical motion it is only true if the HO's state is NOT an eigenstate. Then its behaviour is uniquely quantum!

2.6 Solution of the HO eigenvalue equation*

[25] The objective in this section is to provide the solution procedure for the HO's eigenvalue equation (). We have,

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+\frac{1}{2}m\omega_0^2x^2\right)\phi(x)=E\phi(x),$$

$$\rightarrow \quad \frac{d^2\phi(x)}{dx^2}-\left[(\frac{m\omega_0}{\hbar})^2x^2-\frac{2mE}{\hbar^2}\right]\phi(x)=0,$$

$$\rightarrow \quad \frac{d^2\phi(x)}{dx^2}-\frac{m\omega_0}{\hbar}\left[\frac{m\omega_0}{\hbar}x^2-\frac{2E}{\hbar\omega_0}\right]\phi(x)=0$$

$$\rightarrow \quad \frac{d^2\phi(x)}{d(\beta x)^2}-\left[(\beta x)^2-\frac{2E}{\hbar\omega_0}\right]\phi(x)=0,$$

where the β parameter (2.7) was introduced [26]. At this stage is convenient to introduce the scaled variables, X and $\mathscr{E}$ we end up to,

$$X=\left(\frac{m\omega_0}{\hbar}\right)^{\frac{1}{2}}x=\beta x, \qquad \mathscr{E}=\frac{E}{\hbar\omega}, \tag{2.28}$$

both of which is dimensionless. Then we are left with

$$\phi''(X)-(X^2-2\mathscr{E})\phi(X)=0, \tag{2.29}$$

with the differentiation with respect to X. This DE requires one more variable transformation before we end up to a familiar (in mathematical physics) DE. So the following transformation is introduced [27],

$$\Phi(X)=h(X)e^{-\frac{1}{2}X^2}. \tag{2.30}$$

Then the Schrödinger equation gives,

$$\boxed{h''(X)-2Xh'(X)+(2\mathscr{E}-1)=0.} \tag{2.31}$$

This is known as *Hermite's equation* a well-studied differential equation in the 19th century [28]

The series expansion and the normalization condition. A typical method of solving DEs with constant coefficients is to assume a power expansion of the solution in terms of the independent variable (here is X) with the task to find the unknown expansion coefficients:

$$h(X)=\sum_r c_rX^r, \qquad r=0,1,\cdots.$$

25: *__Not necessary for the final exams__

26:
$$\beta=\sqrt{\frac{m\omega_0}{\hbar}}$$

27: The rationale for this change goes as follows: For large X, such that $X^2 \gg \mathscr{E}$ the term $\mathscr{E}\phi(X)$ cannot offset $X^2\phi(X) \rightarrow \infty$. Therefore the DE will blow up, unless the $\phi''(X)$ term is of the same order as the $X^2\phi(X)$ term. The second derivative of a Gaussian exponential ($\sim e^{-X^2}$) produces down a factor X^2 and behaves as $\sim -X^2e^{-X^2}$.

28: Named after Charles Hermite (French, 1822-1902) despite that first were introduced by Pierre Simon Laplace in 1810 and later studies in detail by P. L. Chebyshev in 1859.

Direct substitution into the Hermite's equation gives,

$$\sum_{r\geq 0}\left[(r+2)(r+1)c_{r+2}+(2\mathscr{E}-1-2r)c_r\right]X^r=0.$$

In order the above to be true for all powers it is required that,

$$\frac{c_{r+2}}{c_r}=\frac{2r+1-2\mathscr{E}}{(r+2)(r+1)}\qquad r\geq 0.$$

Note that that this recursive expression relates coefficients which differ by 2 in their index. So two independent solutions are derived one including only even powers and the other only odd powers. Therefore this method gives the two independent solutions required from a 2nd-order differential equations.

From a physical point of view the expansion series cannot be of 'infinite order' since then the solution (again) will explode for large X. Simple inspection shows that the series terminates for some $r=n$ such that

$$2n+1-2\mathscr{E}=0\quad\rightarrow\quad\mathscr{E}_n=n+\frac{1}{2}\quad\rightarrow\quad\boxed{E_n=\hbar\omega_0(n+\frac{1}{2}),\quad n=0,1,2,..}$$

The latter relation gives the (now) quantized energies, E_n. For any given $n=0,1,2..$ the expansion solution is now given by, [29]

$$H_n(X)=\sum_r^n 2c_r\frac{r-n}{(r+2)(r+1)}X^r,\qquad r=\begin{cases}0,2,\cdots,n & \text{n even}\\ 1,3,\cdots,n & \text{n odd}\end{cases}\tag{2.32}$$

In the above it was assumed $c_0=1$ and $c_1=1$ (chosen independently) to get two linearly independent solutions.

For example, we have

$$\begin{aligned}H_0(X)&=c_0\\ H_1(X)&=c_1X\\ H_2(X)&=c_0(1-2X^2)\\ H_3(X)&=c_1\left(X-\frac{2}{3}X^3\right).\end{aligned}$$

These are known as the *Hermite polynomials*. [30] By combining (2.30) and (2.32) we obtain the HO eigenfunctions as ,

$$\phi_n(x)=N_nH_n(\beta x)e^{-\beta^2x^2/2}\tag{2.33}$$

with a slight change of notation ($\Phi_n(X)=\Phi_n(\beta x)=\phi_n(x)$).

29: Note the change of notation $h(X)\rightarrow H_n(X)$ to emphasize that one is restricted to Hermite polynomials H_n.

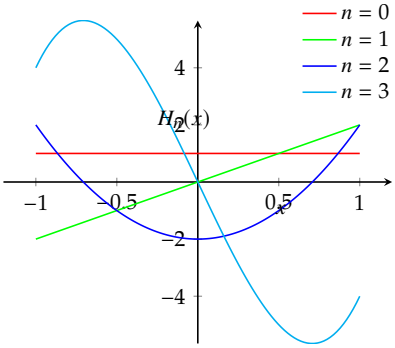


Figure 2.1: The graph of some Hermite polynomials.

30: There are numerous relations for the Hermite polynomials easily found in the print and digital literature. For our purposes and for the *normalized* $H_n(x)$ the following hold:

$$H_0(x)=1,\qquad H_1(x)=2x$$
$$H_2(x)=4x^2-2,\quad H_3(x)=8x^3-12x$$
$$\delta_{nm}(2^n n!\sqrt{\pi})=\int_{-\infty}^{\infty}dx\,e^{-x^2}H_n(x)H_m(x)$$
$$H_n(-x)=(-1)^nH_n(x)$$
$$H_n'(x)=2nH_{n-1}(x),$$
$$H_{n+1}(x)=2xH_n(x)-2nH_{n-1}(x)$$
$$H_{n+1}(x)=2xH_n(x)-H_n'(x)$$

2.7 Questions

Question 2.7.1

Virial theorem. In classical mechanics for a particle moving in a potential energy field of the form $V(x) = ax^n$ the following relation holds for the time-average of the total kinetic and potential energy:

$$\langle T \rangle_t = \frac{n}{2} \langle V \rangle_t, \qquad V(x) = ax^n. \tag{2.34}$$

This is known as *Virial theorem*.

(a) Specialize the above virial theorem for a particle of mass m ib the case of a classical HO.

(b) Show that for a particle in an quantum HO potential energy and in its eigenstate the following relations hold the mean values,

$$\langle T \rangle_n = \langle V \rangle_n = \frac{E_n}{2} \tag{2.35}$$

Question 2.7.2

Explicit calculations for the low-energy states. Consider the ground and the first excited state of a particle in an HO potential (m, ω_0). By explicit calculations of the relevant integrals: [31]

(a) Show that $\langle \hat{x} \rangle_0 = \langle \hat{x} \rangle_1 = 0$ and that $\langle \hat{p} \rangle_0 = \langle \hat{p} \rangle_1 = 0$

(b) Calculate the (dipole) matrix elements x_{01} and p_{01}

(The results are compatible with the general expressions given in the main text.)

31: You can use the following Gaussian Integrals:

$$\int_{-\infty}^{\infty} dx e^{-ax^2} = \sqrt{\frac{\pi}{a}},$$
$$\int_0^{\infty} dx\, x e^{-ax^2} = \frac{1}{2a},$$
$$\int_{-\infty}^{\infty} dx\, x^2 e^{-ax^2} = \frac{1}{2a}\sqrt{\frac{\pi}{a}},$$

Question 2.7.3

Matrix elements of $\hat{x}$, $x_{nn'}$.

(a) Use the properties of the Hermite polynomials to show that,

$$\hat{x}\phi_n(x) = \sqrt{\frac{\hbar}{2m\omega_0}} \left[\sqrt{n+1}\phi_n(x) + \sqrt{n}\phi_{n-1}(x) \right] \tag{2.36}$$

(b) Using the above calculate the arbitrary (dipole) matrix elements:

$$x_{nn'} = \langle \phi_n | \hat{x} | \phi_{n'} \rangle = ? \tag{2.37}$$

Question 2.7.4

Matrix elements of op, $p_{nn'}$.

(a) Use the properties of the Hermite polynomials to show that,

$$\hat{p}\phi_n(x) = \sqrt{\frac{m\omega_0}{2\hbar}}\left[\sqrt{n+1}\phi_n(x) - \sqrt{n}\phi_{n-1}(x)\right] \tag{2.38}$$

(b) Using the above calculate the arbitrary (dipole) matrix elements:

$$p_{nn'} = \langle\phi_n|\hat{p}|\phi_{n'}\rangle = ? \tag{2.39}$$

Question 2.7.5

Harmonic oscillator in an electric field Assume a particle of mass m and charge q, subject to an HO potential and and a constant electric field of amplitude $\mathscr{E}_0$. Therefore the potential energy of the particle is,

$$V(x) = \frac{1}{2}m\omega_0 x^2 + q_m\mathscr{E}_0\, x$$

(a) Provide an expression of its Hamiltonian in the position representation

(b) Assume that the particle is initially at a state where its mean position and momentum are zero. Using the Heisenber relations show that the corresponding mean values are time-dependent given by,

$$\langle x\rangle(t) = \frac{q\mathscr{E}_0}{m\omega_0^2}(1-\cos\omega_0 t) \qquad \langle p\rangle(t) = \frac{q\mathscr{E}_0}{\omega_0}\sin\omega_0 t \tag{2.40}$$

(c) Give the energy mean value $\langle H\rangle$.

Two-level systems 3

3.1 Two-level systems

at this point one should talk about the magnetic and electric dipole moments, defined as below:

$$V_B(t) = -\mathbf{m} \cdot \mathcal{B}(t), \tag{3.1}$$

$$V_E(t) = -\mathbf{d} \cdot \mathcal{E}(t). \tag{3.2}$$

3.2 Time-evolution of a TLS.

Let's take a quantum system, characterized by its hamiltonian, op_0, with only two eigenstates $|\phi_1\rangle$, $|\phi_2\rangle$ with energies E_1 and E_2. Then for this system the following relations hold:

$$\hat{H}_0|\phi_i\rangle = E_i|\phi_i\rangle, \qquad i = 1, 2. \tag{3.3}$$

$$\langle\phi_i|\phi_j\rangle = \delta_{ij}, \qquad \sum_i |\phi_i\rangle\langle\phi_i| = \mathbb{1}. \tag{3.4}$$

Undistorted TLS (isolated).

If the system initially is initially in the state $|\psi_0\rangle$ it is straightforward to find its state some time later (provided that no measurement has been performed): [33]

33: $$c_i(t) = c_i(0)e^{-\imath E_i t/\hbar}, \qquad i = 1, 2$$

$$|\psi_0\rangle = c_1(0)|\phi_1\rangle + c_2(0)|\phi_2\rangle \tag{3.5}$$

$$\Longrightarrow$$

$$|\psi(t)\rangle = c_1(0)e^{-\imath\frac{E_1}{\hbar}t}|\phi_1\rangle + c_2(0)e^{-\imath\frac{E_2}{\hbar}t}|\phi_2\rangle \tag{3.6}$$

One special case of the above is expressions is when the initial state is one of the system's eigenstate (e.g. say $|\phi_2\rangle$. In this case we have, $c_1(0) = 0$ and $c_2(0) = 1$ (since the states should be normalized and then,

$$|\psi(t)\rangle = e^{-\imath\frac{E_2}{\hbar}t}|\phi_2\rangle,$$

As it is has been shown according to QM $|\psi(t)\rangle$ and $|\phi_2\rangle$ represent the same state since they differ by a global phase factor of the form $e^{\imath\theta}$, with θ arbitrary real number (here $\theta = E_2/\hbar$). It's not difficult to see that the probability of an energy measurement to give energy E_2 (equal to unity) is constant in time:

$$P_{E=E_2}(t) = |c_2(t)|^2 = |c_2(0)e^{-\imath E_2/t}|^2 = |c_2(0)|^2 = 1 = P_{E=E_2}(0).$$

It's easy to see that they have the same length: [34]

34: Recall the rule:

$$|\psi\rangle = a|\phi\rangle \qquad \rightarrow \qquad \langle\psi| = \langle\phi|a^*$$

$$\langle\psi(t)|\psi(t)\rangle = \left(\langle\phi_2|e^{\imath E_2 t/\hbar}\right)\left(e^{-\imath E_2 t/\hbar}|\phi_2\rangle\right) = \langle\phi_2|\phi_2\rangle = 1.$$

In other words, if the system is in one of its eigenstates, unless it is perturbed, will stay there for ever! [35]

35: For this reason the Hamiltonian eigenstates are also known as 'stationary'.

Distorted TLS by a (weak) external field.

Let's know assume that the quantum system is distorted by an external interaction, represented by the operator $\hat{V}$ which in principle can be either time-dependent, $\hat{V}(t)$ or static $\hat{V}_0$, [36]. The condition that the external interaction should be 'weak' will be specified later in a quantitative context.

36: e.g for example one may think a particle with spin $s = 1/2$ in the presence of a magnetic field, $B(t)$ modelled as in (3.1) or an hydrogen in a electric field as in (3.2).

The question is, if the system is in state $|\psi_0\rangle$ how now the system's state develops in time?

In other words we need to find $|\psi(t)\rangle$. QM's answer is the TDSE law about the state's time-evolution,

$$\imath\hbar\frac{\partial}{\partial t}\psi(t) = [\hat{H}_0 + \hat{V}(t)]\psi(t) \tag{3.7}$$

Also, we know that the time-dependent state may be written in terms of the $\hat{H}_0$ eigenbasis as,

$$|\psi(t)\rangle = c_1(t)|\phi_1\rangle + c_2(t)|\phi_2\rangle. \tag{3.8}$$

Since it is assumed that $|\phi_i\rangle,\ i = 1,2$ are known, to calculate $|\psi(t)\rangle$ is equivalent to calculate the coefficients, $c_1(t)$ and $c_2(t)$. This is done by inserting our TLS's wavefunction into (3.7):

$$\imath\hbar\frac{\partial}{\partial t}\left[c_1(t)|\phi_1\rangle + c_2(t)|\phi_2\rangle\right] = (\hat{H}_0 + \hat{V})\left[c_1(t)|\phi_1\rangle + c_2(t)|\phi_2\rangle\right].$$

The next step is to multiply from the left with $\langle\phi_1|$ and $\langle\phi_2|$ from the left to obtain, [37]

$$\begin{aligned}
\imath\hbar\frac{d}{dt}\left[c_1(t)\langle 1|1\rangle + c_2(t)\langle 1|2\rangle\right] &= \langle 1|(\hat{H}_0 + \hat{V}(t))\left[c_1(t)|1\rangle + c_2(t)|2\rangle\right] \\
\imath\hbar\frac{d}{dt}\left[c_1(t)\langle 2|1s\rangle + c_2(t)\langle 2|2\rangle\right] &= \langle 2|(\hat{H}_0 + \hat{V}(t))\left[c_1(t)|1\rangle + c_2(t)|2\rangle\right],
\end{aligned}$$

where $\langle i|j\rangle = \langle\phi_i|\phi_j\rangle$. These equations simplify since, by definition $\langle 1|1\rangle = \langle 2|2\rangle = 1$, $\langle 1|2\rangle = 0$ and by noticing that,

$$\begin{aligned}
\langle 1|\hat{H}_0|1\rangle &= \langle 1|E_1|1\rangle = E_1\langle 1|1\rangle = E_1, \\
\langle 2|\hat{H}_0|2\rangle &= \langle 2|E_2|2\rangle = E_2\langle 2|2\rangle = E_2, \\
\langle 1|\hat{H}_0|2\rangle &= \langle 1|E_2|2\rangle = E_2\langle 1|2\rangle = 0 \\
\langle i|\hat{V}|i\rangle &= V_{ii}(t), \qquad i = 1,2 \\
\langle 1|\hat{V}|2\rangle &= V_{12}(t) \\
\langle 2|\hat{V}|1\rangle &= V_{21}(t),
\end{aligned}$$

Substituting these value the following coupled system of ODEs is obtained:

37: To keep the notation simple we set:

$$|1\rangle \equiv |\phi_1\rangle, \qquad |2\rangle \equiv |\phi_2\rangle$$

$$\imath\hbar\dot{c}_1(t) = \hbar\omega_1(t)c_1(t) + V_{12}(t)\, c_2(t) \tag{3.9}$$
$$\imath\hbar\dot{c}_2(t) = \hbar\omega_2(t)c_2(t) + V_{21}(t)\, c_1(t), \tag{3.10}$$

where we have defined Rabi-frequency, Ω_0 and the eigen-frequencies, ω_i as,

$$\omega_i(t) = \frac{1}{\hbar}\left[E_i + V_{ii}(t)\right], \qquad i = 1, 2, \tag{3.11}$$

The later frequency based on the energy difference between the two states, ω_0, was defined for later convenience. At this point one can use any method to solve this system of equation. As first-order ODE, the solution is only possible when it is supplemented with the initial conditions for $c_1(t)$ and $c_2(t)$. For example, if the system is initially in its ground state which means that $P_{E=E_1}(0) = |c_1(0)| = 1$,[38]

$$c_1(0) = 1, \quad c_2(0) = 0. \tag{3.12}$$

At this point one cannot proceed further without specifying the form of the external interaction, $\hat{V}(t)$.

38: Strictly, speaking we should choose $c_1(0) = e^{\imath\phi}$ and $c_2(0) = 0$, but one may set $c_1(0) = 1$ with no loss of generality, as the observables depend on the phase difference between $c_1(t)$ and $c_2(t)$ and not the absolute phases of each state separately.)

Oscillating interaction, $\hat{V}(t) = \hat{V}e^{\imath\omega t}$.

[39]

In addition to this particular choice, we also assume the case where the external interaction has vanishing diagonal matrix elements (V_{ii} $i = 1, 2$). So we take,

$$V_{ii} = \langle\phi_i|\hat{V}|\phi_i\rangle = 0, \qquad i = 1, 2. \tag{3.13}$$

A matrix representation of the time-dependent Schrödinger equation (3.9) and (3.10) on the basis $|\phi_1\rangle, |\phi_2\rangle$ where,

$$|\psi(t)\rangle = \begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix}, \qquad \hat{H}_0 = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix}, \qquad \hat{V}(t) = \begin{pmatrix} 0 & V_{12}(t) \\ V_{21}(t) & 0 \end{pmatrix}$$

$$\imath\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \left[\begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} + \begin{pmatrix} 0 & V_{12}(t) \\ V_{21}(t) & 0 \end{pmatrix}\right]|\psi(t)\rangle \tag{3.14}$$

39: Note that for $\omega = 0$ we have the case of a static external interaction. Therefore by examining this more general case one can easily obtain the results for a constant external potential, $\hat{V}$, as well.

[40]

There are few ways that one can proceed further. The standard approach is to transform to another set of equations by setting, [41]

$$c_1(t) = u_1(t)e^{-\imath\omega_1 t}, \qquad c_2(t) = u_2(t)e^{-\imath\omega_2 t} \tag{3.15}$$

In this case

$$V_{ii}(t)$$

Upon inserting these transformations into (3.9)-(3.10) we are left with:

$$\imath\dot{u}_1(t) = \Omega_0\, e^{-\imath\delta t} u_2(t), \tag{3.16}$$
$$\imath\dot{u}_2(t) = \Omega_0^*\, e^{+\imath\delta t} u_1(t), \tag{3.17}$$

where δ is known as *detuning*, defined by, [42]

$$\delta \equiv \omega_0 - \omega = \omega_2 - (\omega_1 + \omega) \tag{3.18}$$

and Ω_0 is known as *Rabi-frequency*: [43]

$$\Omega_0(t) = \frac{V_{12}(t)}{\hbar} = \frac{\langle\phi_1|\hat{V}(t)|\phi_2\rangle}{\hbar}. \tag{3.19}$$

In the present case Ω_0 and δ are constants and the equations for $c_1(t)$ and $c_2(t)$ are ordinary differential equations (ODEs) with constant coefficients. Therefore any relevant method applies equally well. In one of these we can proceed as follows.

Solving the TDSE We can decouple this coupled system of ODEs by taking the time derivative of the second equation and then insert the expression for $\dot{u}_1(t)$ (first equation) into said derivative resulting to a second-order ODE describing a damped *harmonic oscillator* (DHO): [44]

$$\ddot{u}_2 - \imath\delta\dot{u}_2 + |\Omega_0|^2 u_2 = 0. \tag{3.20}$$

Following the same procedure for the amplitude $u_1(t)$ we arrive at,

$$\ddot{u}_1 + \imath\delta\dot{u}_1 + |\Omega_0|^2 u_1 = 0. \tag{3.21}$$

40: Or even more compactly,

$$\imath\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \begin{pmatrix} E_1 & V_{12} \\ V_{21} & E_2 \end{pmatrix}|\psi(t)\rangle$$

41: Going to a representation known as the *Interaction Picture* (IP). Essentially this results to remove the fast-oscillating part implicit in the coefficients $c_1(t), c_2(t)$ thus going to a slowly-varying coefficients $(u_1(t), u_2(t))$. This method is called as slowly-varying amplitudes transformation.

42:

$$\hbar\omega_0 = E_2 - E_1$$

43: Of course,

$$\Omega_0^* = \frac{V_{21}}{\hbar} = \frac{1}{\hbar}\langle\phi_2|\hat{V}(t)|\phi_1\rangle.$$

44: Reminder for the DHO:

$$\ddot{x}(t) + \gamma\dot{x}(t) + \omega_0^2 x(t) = 0.$$

It's solution for $\omega < \gamma/2$ is

$$x(t) = e^{-\frac{\gamma t}{2}}\left[A_1 e^{-\alpha t} + A_2 e^{\alpha t}\right]$$

with A_1, A_2 determined through the initial conditions.

Now the amplitude equations are decoupled and have the form of a DHO with damping parameter, $\imath\omega_0$ and 'eigen'-frequency, Ω_0! It's straightforward now to assume a solution of the form:

$$u_1(t) = Ae^{\sigma t},$$

which by substitution in (3.21) for the possible σ:

$$\sigma^2 + \imath\delta\sigma + |\Omega_0|^2\sigma = 0 \qquad \rightarrow$$
$$\sigma_{12} = \frac{-\imath\delta \pm \sqrt{(\imath\delta)^2 - 4|\Omega_0|^2}}{2} = \imath\frac{-\delta \pm \sqrt{\delta^2 + 4|\Omega_0|^2}}{2} = \imath\frac{-\delta \mp \tilde{\Omega}}{2}$$

where $\tilde{\Omega}$ is known as the *generalized* Rabi-frequency has now appeared,

$$\tilde{\Omega} = \sqrt{\delta^2 + 4|\Omega_0|^2} \tag{3.22}$$

Eventually we find for $u_2(t)$ the general solution,

$$u_1(t) = e^{-\imath\delta t/2}\left(A_1 e^{\imath\tilde{\Omega}/2} + A_2 e^{-\imath\tilde{\Omega}/2}\right). \tag{3.23}$$

Following a similar strategey, the ODE for the $u_2(t)$ amplitude is,

$$u_2(t) = e^{\imath\delta t/2}\left(B_1 e^{\imath\tilde{\Omega}/2} + B_2 e^{-\imath\tilde{\Omega}/2}\right). \tag{3.24}$$

The exact form of the solution depends on the initial state. [45] In the present case, two initial conditions needs to be set (since we have two unknown constants).

45: Note that alternatively one could express the general solution as,

$$u_1(t) = A_1 e^{-\imath\delta_i t}\cos(\Omega t + \phi_1),$$
$$u_2(t) = A_2 e^{\imath\delta_i t}\cos(\Omega t + \phi_2).$$

It's matter of preference which one to choose to apply the initial conditions.

Case: The system is initially in state $|\phi_1\rangle$. Assuming the system initially in this state and recalling (3.17), we have*,

$$u_1(0) = 1 \qquad \rightarrow \qquad \dot{u}_2(0) = -\imath\Omega_0^*(0).$$

So, we are going to specialize the general solution for $u_2(t)$ (3.24) with initial conditions:

$$\boxed{u_2(0) = 0, \qquad \dot{u}_2(0) = -\imath\Omega_0^*(0).}$$

Given the initial conditions, the solution is expressed as,

$$u_2(t) = -\frac{2\imath\Omega_0^*}{\tilde{\Omega}}e^{\imath\delta t/2}\sin(\frac{\tilde{\Omega}t}{2}) \tag{3.25}$$

* The initial conditions may be defined within an arbitrary phase constant. Any value of $u_1(0)$ is a legitimate one, as long as $|u_1(0)|^2 + |u_2(0)|^2 = 1$.

With $u_2(t)$ known, $u_1(t)$ can be found by substituting (3.25) into (**??**) followed by integration from $t' = 0$ to a $t > 0$:

$$u_1(t) = e^{-\imath\delta t/2}\left[\cos(\frac{\tilde{\Omega}t}{2}) + \imath\frac{\delta}{\tilde{\Omega}}\sin(\frac{\tilde{\Omega}t}{2})\right] \tag{3.26}$$

Having the $u_i(t), i = 1, 2$ available the $c_i(t)$ can be found from(3.15) and from (3.8),

$$c_1(t) = e^{-\imath(\bar{E}-\frac{\hbar\omega}{2})t}\left[\cos(\frac{\tilde{\Omega}t}{2}) + \imath\frac{\delta}{\tilde{\Omega}}\sin(\frac{\tilde{\Omega}t}{2})\right], \tag{3.27}$$

$$c_2(t) = -\frac{2\imath\Omega_0^*}{\tilde{\Omega}}e^{-\imath(\bar{E}+\frac{\hbar\omega}{2})t}\sin(\frac{\tilde{\Omega}t}{2}) \tag{3.28}$$

$$\bar{E} = \frac{E_1 + E_2}{2}, \quad \delta = E_2 - E_1 - \omega, \quad \tilde{\Omega} = \sqrt{\delta^2 + 4|\Omega_0|^2}.$$

Given the above solutions the probability of the system, upon energy measurement, is given by, [46]

$$P_{E=E_2}(t) = |c_2(t)|^2 = \frac{4|\Omega_0|^2}{|\tilde{\Omega}|^2}\sin^2(\frac{\tilde{\Omega}t}{2}),$$

$$P_{E=E_1}(t) = 1 - |c_2(t)|^2 = 1 - \frac{4|\Omega_0|^2}{|\tilde{\Omega}|^2}\sin^2(\frac{\tilde{\Omega}t}{2}).$$

46: Note that,

$$|c_i(t)|^2 = |u_i(t)|^2, \quad i = 1, 2$$

Note that the global exponent containing $\bar{E}$ plays no role, consistent with the fact that in physics only energy differences should matter on the results. A quick observation is that an off-resonant excitation shortens the oscillation period and reduces the excitation probability.

Time-dependent state $|\psi(t)\rangle$. Finally, the TD wavefunction $\psi(\mathbf{r}, t)$ results to,

$$|\psi(t)\rangle = \frac{e^{-\imath\bar{E}t}}{\tilde{\Omega}}\left[\left(\tilde{\Omega}\cos\frac{\tilde{\Omega}t}{2} + \imath\delta\sin\frac{\tilde{\Omega}t}{2}\right)e^{\imath\frac{\hbar\omega}{2}t}|\phi_1\rangle - 2\imath\Omega_0^*\sin\frac{\tilde{\Omega}t}{2}e^{-\imath\frac{\hbar\omega}{2}t}|\phi_2\rangle\right].$$

3.3 Questions

Question 3.3.1

Constant interaction $\hat{V}(t) = \hat{V}$. Specialize the findings of (3.27)-(3.28) when the interaction is constant.

Question 3.3.2

Exact resonance Specialize the findings of (3.27)-(3.28) for exact resonance conditions.

Question 3.3.3

Eliminating the interaction $\hat{V}(t)$. Specialize the findings of (3.27)-(3.28) when the interaction $V \to 0$. Does it comply with the results for $c_1(t), c_2(t)$ when the Hamiltonian is time-independent?

Hydrogen 4

In this chapter the eigenstates and eigenergies of the bound spectrum of the atomic hydrogen are discussed. The solution of the eigenvalue problem is sketched in some detail and the basic properties of the wavefunctions are presented.

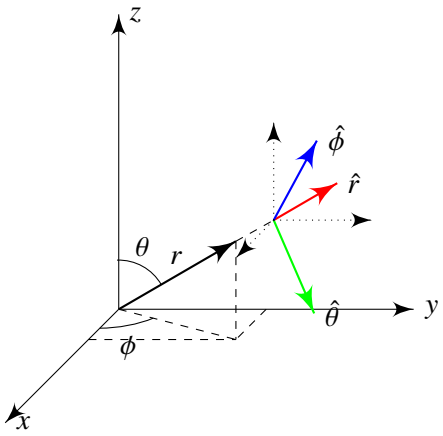
4.1 Orbital momentum

To take advantage of a spherically symmetric potential, $V = V(r)$, one needs to express the momentum operators in the position basis on a spherical-coordinate system:

$$\hat{\mathbf{p}} = -\imath\hbar\nabla. \tag{4.1}$$

The gradient (nabla) operator ∇ (the three-dimensional version of the derivative operator) is expressed as,

$$\begin{aligned}\boldsymbol{\nabla} &= \hat{x}\frac{\partial}{\partial x} + \hat{y}\frac{\partial}{\partial y} + \hat{z}\frac{\partial}{\partial z} \\ &= \hat{r}\frac{\partial}{\partial r} + \hat{\theta}\frac{1}{r}\frac{\partial}{\partial\theta} + \hat{\phi}\frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}\end{aligned}$$



Momentum

Therefore the momentum operator is given by,

$$\hat{\mathbf{p}} = -\imath\hbar(\frac{\partial}{\partial r},\ \frac{1}{r}\frac{\partial}{\partial\theta},\ \frac{1}{r\sin\theta}\frac{\partial}{\partial\phi})$$

Angular momentum.

The angular momentum is defined by $\mathbf{L} = \mathbf{r}\times\mathbf{p}$ and given that $\mathbf{r} = r\hat{r}$, the angular momentum operator in the position/spherical basis, is

$$\begin{aligned}\mathbf{L} = \mathbf{r}\times\mathbf{p} &= -\imath\hbar(r,0,0)\times(\frac{\partial}{\partial r},\ \frac{1}{r}\frac{\partial}{\partial\theta},\ \frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}) \\ &= -\imath\hbar\left[\hat{\phi}\frac{\partial}{\partial\theta} - \hat{\theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\phi'}\right]\end{aligned}$$

Therefore the angular momentum vector is

$$\hat{\mathbf{L}} = -\imath\hbar\left[\hat{\phi}\frac{\partial}{\partial\theta} - \hat{\theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\phi}\right] \tag{4.2}$$

The square of the angular momentum operator, $\hat{\mathbf{L}}^2$ (which is a scalar operator) can now be calculated to [48]:

$$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta'}\frac{\partial}{\partial\theta'}\left(\sin\theta'\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta'}\frac{\partial}{\partial\phi^2}\right]. \tag{4.4}$$

The operator of the squared angular momentum operator $\hat{L}^2$ appears in the eigenvalue equation for the hydrogen Hamiltonian.

48: Show that Eq. (4.4) is derived from Eq. (4.2). Use the dot product in polar coordinates:

$$\mathbf{U}\cdot\mathbf{V} = U_rV_r + U_\theta V_\theta + U_\phi V_\phi \tag{4.3}$$

and the derivatives of the unit vectors:

$$\begin{aligned}\frac{\partial\hat{\phi}}{\partial\theta} &= 0 \frac{\partial\hat{\theta}}{\partial\theta} = -\hat{r} \\ \frac{\partial\hat{\phi}}{\partial\phi} &= -\cos\theta\hat{\theta} - \sin\theta\hat{r} \\ \frac{\partial\hat{\theta}}{\partial\phi} &= \cos\theta\hat{\phi}.\end{aligned}$$

Its own eigenvalue equation can be solved to give as a solutions the so-called spherical harmonics, $Y_{lm}(\theta, \phi)$:

$$\hat{L}^2 Y_{lm_l}(\theta, \phi) = \hbar^2 l(l+1) Y_{lm}(\theta, \phi)$$

A more detailed exposition about the *spherical harmonics* is given at a later section where the eigenvalue problem is considered.

Example 4.1.1 (ssss) This is a test

4.2 Bound eigenstates

In the next sections it is shown the hydrogen eigenstates in the position basis are as below,

$$\phi_{nlm_l}(r,\theta,\phi) = R_{nl}(r)Y_{lm_l}(\theta,\phi), \quad \text{with} \begin{cases} n = & 1,2,\dots \\ l = & 0,1,\dots,n-1 \\ m_l = & -l,-l+1,\dots,l-1,l \end{cases} \tag{4.5}$$

These eigenfunctions constitute a complete orthonormal basis so that the following relations hold:

$$\int \mathbf{dr}\phi^*_{nlm_l}(\mathbf{r})\phi_{n'l'm'_l}(\mathbf{r}) = \delta_{nn'}\delta_{ll'}\delta_{m_lm'_l} \tag{4.6}$$

The hydrogen eigenfunctions are common eigenfunctions of the Hamiltonian, square angular-momentum operator and one of the angular-momentum components (here the z-component is chosen), namely of the $\hat{H}, \hat{L}^2, \hat{L}_z$. Therefore the following eigenvalue relations hold

$$\hat{H}\phi_{nlm_l}(\mathbf{r}) = E_n\phi_{nlm_l}(\mathbf{r}) \tag{4.7}$$
$$\hat{L}^2\phi_{nlm_l}(\mathbf{r}) = \hbar^2 l(l+1)\phi_{nlm_l}(\mathbf{r}) \tag{4.8}$$
$$\hat{L}_z\phi_{nlm_l}(\mathbf{r}) = \hbar m_l\phi_{nlm_l}(\mathbf{r}) \tag{4.9}$$

Where total energy is

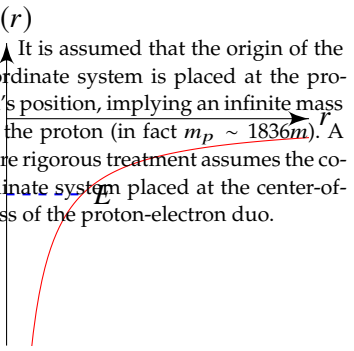
$$E_n = -\frac{E_1}{n^2}, \quad n = 1,2,3\dots, \quad \text{where } E_1 = \frac{me^4}{32\pi^2\epsilon_0^2\hbar^2}. \tag{4.10}$$

Radially Symmetric Potentials

As the methodology applies to any central potential (in the sense that the quantum particle is moving in a spherically symmetric potential field) we'll be using $V(r)$ to represent the potential field. For the atomic hydrogen the interaction between an electron (mass m and charge $-e$) and a proton (charge $+e$) in described by the electrostatic Coulombic potential

$$V(r) = -\frac{1}{4\pi\epsilon_0}\frac{e^2}{r}. \tag{4.11}$$

[49]



49: It is assumed that the origin of the coordinate system is placed at the proton's position, implying an infinite mass for the proton (in fact $m_p \sim 1836m$). A more rigorous treatment assumes the coordinate system placed at the center-of-mass of the proton-electron duo.

A conventional way to study the QM of a system is to start from the classical expression for the system's energy, which typically is the sum of the kinetic and potential energy $T + V(r)$:

$$E = \frac{1}{2}mv^2 + V(r) = \frac{p^2}{2m} + V(r)$$

In the present case the system will be studied in the position representation which calls for the following quantization rules for the momentum and position:

$$\hat{\mathbf{r}} = \mathbf{r}, \qquad \hat{\mathbf{p}} = -\imath\hbar\nabla.$$

Therefore the system's Hamiltonian operator is modeled,

$$\hat{H}_a = \frac{\hat{p}^2}{2m} + V(\hat{r}) = -\frac{\hbar^2}{2m}\nabla^2 + V(r) \tag{4.12}$$

Hydrogen Schrödinger Equation It is our task now to solve the hydrogen eigenvalue problem for the hydrogen:

$$\hat{H}_a|\phi\rangle = E|\phi\rangle. \tag{4.13}$$

Projecting the abstract Schrödinger Equation onto the position basis, $|\mathbf{r}\rangle$ in spherical coordinates we obtain: [50]

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\phi(\mathbf{r}) = E\phi(\mathbf{r}) \tag{4.14}$$

The next step is to expand the nabla (or Laplace) differential operator in a suitable coordinate system. Here, the spherically symmetrical potential calls for the spherical one. In this case the where the differential operator is

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]. \tag{4.15}$$

We notice that the Laplace operator can be re-written in terms of two differential operators; one that acts exclusively on radially-dependent functions and the other acting only on angularly dependent functions; namely an radial (square)-momentum, $\hat{p}_r^2$

50:

$$\langle\mathbf{r}|\hat{H}_a|\phi\rangle = E\langle\mathbf{r}|\phi\rangle \qquad \rightarrow \qquad \hat{H}_a\phi(\mathbf{r}) = E\phi(\mathbf{r})$$

and an angular (square)-momentum, $\hat{L}^2$ operator,

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial}{\partial\phi^2} \right], \tag{4.16}$$

$$\hat{p}_r^2 = -\hbar^2 \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right). \tag{4.17}$$

[51]The Schrödinger Equation becomes

$$\left[\frac{1}{2m} \left(\hat{p}_r^2 + \frac{1}{r^2} \hat{L}^2 \right) + V(r) \right] \phi(\mathbf{r}) = E\phi(\mathbf{r}) \tag{4.18}$$

51: At present, this radial 'momentum'-operator is used as short-hand for the radial derivatives. A more rigorous definition is,

$$\langle \mathbf{r} | \hat{p}_r^2 | \mathbf{r}' \rangle = -\hbar^2 \delta(\mathbf{r} - \mathbf{r}') \frac{1}{r'^2} \frac{\partial}{\partial r'} \left(r'^2 \frac{\partial}{\partial r'} \right).$$

Separation of variables method. To solve the above (partial) differential equation we seek a solution of the following product form:

$$\phi(\mathbf{r}) = R(r)Y(\theta, \phi) \tag{4.19}$$

We then have,

$$\begin{aligned} ER(r)Y(\theta,\phi) &= \left[\frac{1}{2m} \left(\hat{p}_r^2 + \frac{1}{r^2} \hat{L}^2 \right) + V(\hat{R}) \right] R(r)Y(\theta,\phi) \\ &= Y(\theta,\phi) \left[\frac{\hat{p}_r^2}{2m} R(r) + V(r)R(r) \right] + R(r) \left[\frac{1}{2mr^2} \hat{L}^2 Y(\theta,\phi) \right] \end{aligned}$$

The next step is to divide by $R(r)Y(\theta,\phi)$ and bring the-radial and angle-dependent terms to different sides of the equation:

$$\underbrace{\frac{\hat{L}^2 Y(\theta,\phi)}{Y(\theta,\phi)}}_{\hbar^2 l(l+1)} = \underbrace{\frac{2mr^2}{R(r)} \left[E - V(r) - \frac{\hat{p}_r^2}{2m} \right]}_{\hbar^2 l(l+1)}. \tag{4.20}$$

The equation above can only be true for all values of r, θ, ϕ only if its RHS and LHS are separately equal to a constant. In a later section it is shown that this constant has the form of $\hbar^2 l(l+1)$. [52]. The end result is that the initial partial differential equation is splitted to two 'simpler' ones dependend on the radial coordinate and the other on the angles coordinates:

52: This constant is nothing else than the discretized orbital angular momentum of the electron, with $l = 0, 1, 2, ..$ integer, with some maximum value (for the bound hydrogen eigenstates)

$$\hat{L}^2 Y_{lm_l}(\theta,\phi) = \hbar l(l+1) Y_{lm_l}(\theta,\phi), \tag{4.21}$$

$$\left[\frac{\hat{p}_r^2}{2m} + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r) \right] R(r) = ER(r). \tag{4.22}$$

For the radial equation we need to specify the quantum system by choosing the central potential $V = V(r)$ in order to proceed

further. The angle-dependent equation is common for all central potentials.

4.3 Radial Schrödinger Equation

For the hydrogen the electrostatic potential is given by (4.11). The radial-momentum operator $\hat{p}_r^2$ is replaced as,

$$\hat{p}_r^2\left(R(r)\right) = -\frac{\hbar^2}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right) = -\frac{\hbar^2}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}(R(r))\right)$$

The radial wave equation then becomes,

$$\left[-\frac{\hbar^2}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}(\cdot)\right) + \frac{\hbar^2 l(l+1)}{2mr^2} - \frac{1}{4\pi\epsilon_0}\frac{e^2}{r}\right]R(r) = ER(r). \quad (4.23)$$

The physically acceptable [53] (normalized to unity) solution for the radial functions is given as,

$$\begin{aligned} R_{nl}(r) &= N_{nl}e^{-\frac{r}{na_0}}\left(\frac{2r}{na_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right). \\ N_{nl} &= \sqrt{\left(\frac{2}{na_0}\right)^3\frac{(n-l-1)!}{2n\left[(n+l)!\right]^3}} \\ E_n &= -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2}\frac{1}{n^2} \\ n &= 1,2,3,\ldots \quad \text{and} \quad l = 0,1,2,3,\ldots,n-1. \end{aligned}$$

with known a_0 known as the *Bohr radius*

$$a_0 \equiv \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529077\times10^{-10}\ \text{m}. \quad (4.24)$$

Alternative expressions for the hydrogen's energy eigenvalues appear in the various text. A frequent one is expressed in term of the *Rydberg* unit of energy Ry: [54]

$$\begin{aligned} E_n &= -\frac{Ry}{n^2} \\ Ry &= \frac{me^4}{32\pi^2\epsilon_0^2\hbar^2} = -13.605693122994\ \text{eV} \sim 2.179\times10^{-19}\ \text{J}. \end{aligned}$$

The first few radial functions $R_{nl}(r)$

In table (**??**) the radial eigenfunctions for $n = 1,2,3$ are listed along with the corresponding plots

53: Since $E < 0$ for bound states we can define $k^2 = -2mE/\hbar^2 > 0$ and the general solution is a linear combination of the two-independent solutions (second-order in the r-variable), which are the (hypergeometric) $U_a^b(z)$ and the (Laguerre) $L_n^a(z)$ functions:

$$R(r) = e^{-kr}r^l\left[AL_\lambda^{2l+1}(2kr) + BU_{-\lambda}^{2l+1}(2kr)\right]$$

with

$$\lambda = \frac{me^2}{k\hbar^2}\frac{1}{4\pi\epsilon_0} - l - 1.$$

The solution is specialized by applying the boundary conditions. The hypergeometric is rejected since $\lim_{r\to0}U_{-\lambda}^{2l+1}(2kr)\to\infty$ (unacceptable, since $R(r)$ will be interpreted as a probability distribution). On the other hand the Laguerre function at the infinity takes finite values, $\lim_{r\infty\infty}L_\lambda^{2l+1}(2kr) < \infty$ only if λ is an integer, which is customary to be defined as.

$$\lambda = n - l - 1, \quad n \equiv \frac{me^2}{k\hbar^2}\frac{1}{4\pi\epsilon_0}$$

From $k^2 = -2mE/\hbar^2$ and the latter definition of n the discrete (quantized) energies are predicted. Finally the constant A (we rename it as N_{nl}) is calculated by the requirement that $R(r)$ should be normalized to unity.

$$\int_0^\infty dr r^2R^2(r) = 1.$$

54: The Rydberg unit of energy is related with the Rydberg constant R_∞ by,

$$R_\infty = \frac{1}{hc}Ry = 10973731.568160(21)\ \text{m}^{-1}$$

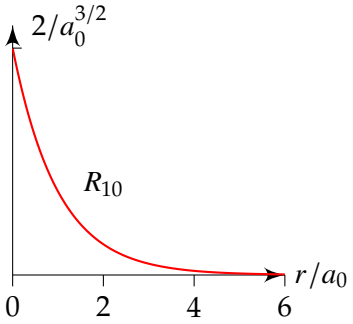
$n = 1$	$l = 0$: $R_{10}(r) = \dfrac{2}{a_0^{3/2}} e^{-r/a_0}$
$n = 2$	$l = 0$: $R_{20}(r) = \dfrac{1}{\sqrt{2}a_0^{3/2}} \left[1 - \dfrac{1}{2}\left(\dfrac{r}{a_0}\right)\right] e^{-r/(2a_0)}$
	$l = 1$: $R_{21}(r) = \dfrac{1}{\sqrt{24}a_0^{3/2}} \left(\dfrac{r}{a_0}\right) e^{-r/(2a_0)}$
$n = 3$	$l = 0$: $R_{30}(r) = \dfrac{2}{\sqrt{27}a_0^{3/2}} \left[1 - \dfrac{2}{3}\left(\dfrac{r}{a_0}\right) + \dfrac{2}{27}\left(\dfrac{r}{a_0}\right)^2\right] e^{-r/(3a_0)}$
	$l = 1$: $R_{31}(r) = \dfrac{8}{27\sqrt{6}a_0^{3/2}} \left(\dfrac{r}{a_0}\right) \left[1 - \dfrac{1}{6}\left(\dfrac{r}{a_0}\right)\right] e^{-r/(3a_0)}$
	$l = 2$: $R_{32}(r) = \dfrac{4}{81\sqrt{30}a_0^{3/2}} \left(\dfrac{r}{a_0}\right)^2 e^{-r/(3a_0)}$

To check the normalization of the given radial functions one needs to evaluate the orthonormalization condition:

$$\int_0^\infty r^2 R_{nl}(r) R_{n'l'}(r) dr = \delta_{nn'}.$$

For example,

$$\int_0^\infty dr r^2 R_{10}(r) R_{10}(r) = \int_0^\infty \frac{4r^2}{a_0^3} e^{-2r/a_0} dr = 1$$



It is left to the reader to confirm that:

$$\int_0^\infty r^2 R_{20}(r) R_{20}(r) dr = \int_0^\infty \left(\frac{1}{\sqrt{2}a_0^{3/2}} \left[1 - \frac{1}{2}\left(\frac{r}{a_0}\right)\right] e^{-r/(2a_0)}\right)^2 r^2 dr = 1$$

$$\int_0^\infty r^2 R_{10}(r) R_{20}(r) dr = \int_0^\infty \frac{2r^2}{a_0^{3/2}} e^{-r/a_0} \left(\frac{1}{\sqrt{2}a_0^{3/2}} \left[1 - \frac{1}{2}\left(\frac{r}{a_0}\right)\right] e^{-r/(2a_0)}\right) dr = 0$$

4.4 Spherical Harmonics

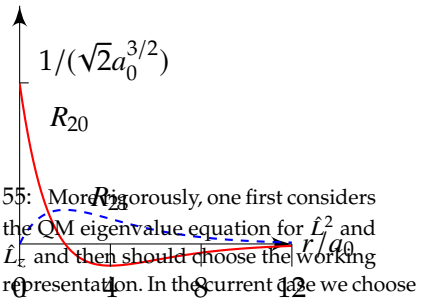
In the position representation the eigenvalue problem for the $\hat{L}^2$ and $\hat{L}_z$ operators transforms to partial differential equation problem in the angular variables $\Omega = (\theta, \phi)$ [55] :

$$-\imath\hbar\frac{\partial}{\partial\phi}Y_{lm_l}(\theta,\phi) = m_l\hbar Y_{lm_l}(\theta,\phi)$$

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

where we've defined the angular wavefunction $\langle\mathbf{r}|lm_l\rangle \equiv Y_{lm_l}(\theta,\phi)$. These are two differential equations that have known solutions. Here we'll be use the separation-of-variables method and will be seeking solutions of the following type: Assuming solutions of the form,

$$Y_{lm_l}(\theta,\phi) = \Theta(\theta)\Phi(\phi) \tag{4.25}$$



55: More rigorously, one first considers the QM eigenvalue equation for $\hat{L}^2$ and $\hat{L}_z$ and then should choose the working representation. In the current case we choose the position basis, so we project with $\langle\mathbf{r}|$:

$$\langle\mathbf{r}|\hat{L}^2|lm_l\rangle = l(l+1)\hbar^2\langle\mathbf{r}|lm_l\rangle$$
$$\langle\mathbf{r}|\hat{L}_z|lm_l\rangle = m_l\hbar\langle\mathbf{r}|lm_l\rangle$$

Then it is inserted the completeness relationship on the left and project out of the integrals using the Dirac delta function. For example,

$$\begin{aligned}\langle\mathbf{r}|\hat{L}^2\left(\int d\mathbf{r}'|\mathbf{r}'\rangle\langle\mathbf{r}'|\right)|lm_l\rangle &= \int d\mathbf{r}'\langle\mathbf{r}|\hat{L}^2|\mathbf{r}'\rangle\langle\mathbf{r}'|lm_l\rangle \\ &= \int d\mathbf{r}'\delta(\mathbf{r}-\mathbf{r}')\hat{L}^2(\Omega')Y_{lm_l}(\Omega') \\ &= \hat{L}^2(\Omega)Y_{lm_l}(\Omega)\end{aligned}$$

Following similar reasoning for the $\hat{L}_z$ operator and that $\langle\mathbf{r}|lm_l\rangle \equiv Y_{lm_l}(\Omega)$ we arrive at the position-representation eigenvalue equations,

$$\hat{L}^2Y_{lm_l}(\Omega) = l(l+1)\hbar^2Y_{lm_l}(\Omega)$$
$$\hat{L}_zY_{lm_l}(\Omega) = m_l\hbar Y_{lm_l}(\Omega)$$

$\hat{L}_z$ eigenvalue solution

The eigenvalue equation for the $\hat{L}_z$ operator is defined as,

$$\hat{L}_zY_{lm_l}(\Omega) = m_l\hbar Y_{lm_l}(\Omega), \qquad \hat{L}_z = -\imath\hbar\frac{\partial}{\partial\phi}. \tag{4.26}$$

substitution of the differential form of the $\hat{L}_z$ operator results to

$$-\imath\frac{\partial}{\partial\phi}\Theta(\theta)\Phi(\phi) = \imath m_l\Theta(\theta)\Phi(\phi) \quad\Longrightarrow\quad -\imath\Theta(\theta)\frac{d}{d\phi}\Phi(\phi) = \imath m_l\Theta(\theta)\Phi(\phi). \tag{4.27}$$

This means that the $\Theta(\theta)$ functions dissappear and the partial diffentiation becomes total [56] :

$$\Phi'_{m_l}(\phi) = \imath\Phi_{m_l}(\phi) \quad\rightarrow\quad \Phi(\phi) = \Phi(0)e^{\imath m_l\phi}$$

where $\Phi(0)$ is determined by the initial conditions of the state. The conditions require that the wavefunction should be *continuous and single-valued*, thus requiring

$$\Phi(\phi) = \Phi(\phi+2\pi) \quad\Longrightarrow\quad \Phi(0)e^{\imath m_l\phi} = \Phi(0)e^{\imath m_l(\phi+2\pi)} \tag{4.28}$$

56: Note that now the $\Phi(\phi)$ is indexed with the m_l parameter.

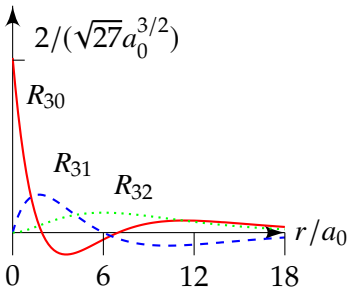
This means that

$$e^{\imath m_l 2\pi} = 1 \quad\rightarrow\quad 2m_l\pi = 2k\pi \quad\rightarrow\quad m_l = k \quad \text{(integer)}.$$

so m_l must be an integer.

Next, it'll be shown that m_l is allowed to range from $-l$ to l, so that implies that l must also be an integer. We therefore have

$$\begin{aligned} m_l &= -l, -l+1, -l+2, \ldots l-2, l-1, l \quad \text{and} \\ l &= 0, 1, 2, 3, \ldots . \end{aligned} \tag{4.29}$$



$\hat{L}^2$ eigenvalue solution

The eigenvalue equation for the $\hat{L}_z$ operator is defined as,

$$\hat{L}^2 Y_{lm_l}(\theta,\phi) = l(l+1)\hbar^2 Y_{lm_l}(\theta,\phi) \tag{4.30}$$

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial}{\partial\phi^2} \right]. \tag{4.31}$$

Using the separated-variables form of Y_{lm_l} (4.25) followed by the substitution of the differential form of the $\hat{L}^2$ operator we have:

$$\Phi_{m_l}(\phi)\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta(\theta) - \Theta(\theta)\frac{m_l^2}{\sin^2\theta}\Phi_{m_l}(\phi) = -l(l+1)\Theta(\theta)\Phi_{m_l}(\phi).$$

where (4.26) was used. Now it is $\Phi_{m_l}(\phi)$ that cancels from both sides of the above equation which makes it an ODE equation for the $\Theta(\theta)$ part of the Y_{lm_l} solution [57] :

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}(\Theta_{lm_l}(\theta))\right) - \frac{m_l^2}{\sin^2\theta}\Theta_{m_l}(\theta) = -l(l+1)\Theta_{lm_l}(\theta).$$

$$\Theta''_{lm_l}(\theta) - \frac{1}{\tan\theta}\Theta'_{lm_l}(\theta) + \left[l(l+1) - \frac{m_l^2}{\sin^2\theta} \right]\Theta_{lm_l}(\theta) = 0$$

Since it is a 2nd-order ODE its general solution is written as a linear combination of two independent solutions, known as *Legendre* polynomials $P_l^{m_l}(\theta)$ and $Q_l^{m_l}(\theta)$:

$$\Theta_{lm_l}(\theta) = AP_l^{m_l}(\cos\theta) + BQ_l^{m_l}(\cos\theta) \tag{4.32}$$

By recalling the boundary conditions the Legendre, $Q_l^{m_l}$-polynomials do not converge and are exclued. Therefore we left as an acceptable solution only with the first-member of the Legendre polynomials,

$$\Theta_{lm_l}(\theta) = AP_l^{m_l}(\cos\theta)$$

Finally, recalling (4.25) and substituting the found solutions for the θ-and -ϕ part of the spherical harmonics we arrive to the following (normalized expression for the $Y_{lm_l}(\theta,\phi)$ [58]:

57: Here it is anticipated that the $\Theta(\theta)$ functions will depend on the l, m_l variables, given that appear in the relevant ODE.

58: Some caution is required here. There is an alternative normalization of the spherical harmonics which adds an extra negative factor $(-1)^{m_l}$.

Table 4.1: The first handful of spherical harmonics.

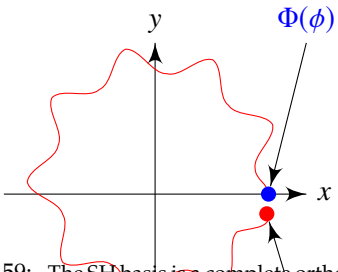
	$m_l = 0$	$m_l = \pm 1$	$m_l = \pm 2$
$l = 0$	$Y_0^0 = \sqrt{\frac{1}{4\pi}}$		
$l = 1$	$Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta$	$Y_1^{\pm 1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm\imath\phi}$	
$l = 2$	$Y_2^0 = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)$	$Y_2^{\pm 1} = \mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{\pm\imath\phi}$	$Y_2^{\pm 2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{\pm\imath 2\phi}$

$$Y_{lm_l}(\theta,\phi) = N_{lm_l}P_l^{m_l}(\cos\theta)e^{\imath m_l\phi},$$
$$N_{lm_l} = \sqrt{\frac{(2l+1)(l-m_l)!}{4\pi(l+m_l)!}}$$

The normalization integral for the spherical harmonics is given by [59] :

$$\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta {Y_{lm_l}}^*(\theta,\phi)Y_{lm_l}(\theta,\phi) = \delta_{ll'}\delta_{m_l m_l'} \tag{4.33}$$

Few of the lowest member of the spherical harmonics basis is shown in Table 4.1.



59: The SH basis is a complete orthornormal set. Practically means that any function $f(\theta,\phi)$ can be expanded in terms of the spherical harmonics,

$$f(\theta,\phi) = \sum_{l=0}^{\infty}\sum_{m_l=-l}^{l} c_{lm_l}Y_{lm_l}(\theta,\phi)$$

where the coefficients c_{l,m_l} are constants.

4.5 Questions

(i) **Orthonormalization conditions** Define,

$$\left\langle lm_l | l'm_l' \right\rangle = \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \, Y^*_{lm_l}(\theta,\phi) Y_{l'm_l'}(\theta,\phi).$$

Calculate explicitly the following integrals,

$$\langle 00|00\rangle = 1, \qquad \langle 00|10\rangle = 0, \qquad \langle 10|10\rangle = 1, \qquad \langle 11|10\rangle = 0.$$

(ii) **Radial averaged values** Define [60] ,

$$\langle Q(\mathbf{r})\rangle_{nlm_l} = \int_{-\infty}^{\infty} \mathbf{dr} \phi^*_{nlm_l}(\mathbf{r}) \hat{Q}(\mathbf{r}) \phi_{nlm_l}(\mathbf{r})$$

Calculate in terms of the Bohr radius a_0 the following mean values [61] :

$$\langle r\rangle_{100}, \quad \langle r^2\rangle_{100}, \quad \langle 1/r\rangle_{100}, \quad \langle 1/r^2\rangle_{100}$$
$$\langle r\rangle_{210}, \quad \langle r^2\rangle_{210}, \quad \langle 1/r\rangle_{210}, \quad \langle 1/r^2\rangle_{210}$$

(iii) **Probabilities for position measurement**
Find the probability of finding the electron in the ground state of hydrogen is There's no need to do an integral. (Hint: Does the probability vary significantly in this region?
(a) At a distance less the Bohr radius ($r \leq a_0$).

(b) Inside the nucleus ($r \leq r_{nucleus} \sim 10^{-15}$ m).

(iv) **Energy measurement** A hydrogen atom is excited (e.g. with a near-resonant laser field) in the following state.

$$\Psi(\mathbf{r}, t=0) = \frac{1}{2}\psi_{1,0,0}(\mathbf{r}) + \imath\frac{\sqrt{3}}{2}\psi_{2,1,0}(\mathbf{r}). \qquad (4.34)$$

(a) If energy is measured, what results are possible and with what probabilities?
(b) Following the measurement, what is the wave function after each possible result?

(v) **Angular momentum measurements**
For the same state as above and at time $t = 0$ the angular momentum is measured.
(a) What values of $\hat{L}_z$ are possible and with what probabilities?
(b) What values of $\hat{L}^2$ are possible and with what probabilities?

60: where,

$$\mathbf{dr} = r^2 dr d\Omega = r^2 dr \sin\theta d\theta d\phi$$

61: Compare your results with the following general formulas (for $Z = 1$):

$$\langle r\rangle_{nlm_l} = \frac{1}{2Z}[3n^2 - l(l+1)]a_0$$
$$\langle r^2\rangle_{nlm_l} = \frac{n^2}{2Z^2}[5n^2 + 1 - 3l(l+1)]a_0^2$$
$$\langle \frac{1}{r}\rangle_{nlm_l} = \frac{Z}{n^2 a_0}$$
$$\langle \frac{1}{r^2}\rangle_{nlm_l} = \frac{2Z^2}{n^2(2l+1)a_0}$$

(vi) **Dynamics**
If the excited state of the previous question is let to evolve freely:
(a) Find the state at a later time $t > 0$.
(b) Calculate the possible results and the corresponding probabilities for energy and angular momentum measurements, namely for the operators $\hat{H}, \hat{L}^2, \hat{L}_z$.
(c) Calculate the corresponding mean values of $\hat{H}, \hat{L}^2, \hat{L}_z$:

$$\langle H \rangle_\psi, \qquad \langle \hat{L}^2 \rangle_\psi, \qquad \langle \hat{L}^2 \rangle_\psi$$

CAs 5

QM postulates (again)

1 **States.** *A physical state* of a system is represented by a normalized *vector* $|\psi\rangle$ belonging in some multidimensional linear complex vector space $\mathcal{V}$:

$$|\psi\rangle = \sum_n \lambda_n |v_n\rangle, \qquad \lambda_n = \langle v_n|\psi\rangle, \tag{5.1}$$

where $|v_n\rangle$ is a basis for $\mathcal{V}$ and λ_n generally complex. The latter property is known as *superposition principle*.

2 **Operators.** *A physical quantity* ($\mathbb{Q}$) is represented by an *observable* $\hat{Q}$, which defines a *complete, orthonormalized*, eigenbasis $|q_n\rangle$ of $\mathcal{V}$ via its *eigenvalue equation*:

$$\hat{Q}|q_n\rangle = q_n|q_n\rangle \qquad \rightarrow \qquad \begin{cases} q_n & \text{real}, \\ \sum_n |q_n\rangle\langle q_n| & = \mathbb{1}, \\ \langle q_n|q_m\rangle & = \delta_{nm} \end{cases} \tag{5.2}$$

The latter two equations are known as *completeness* and *orthonormalization* conditions, respectively.

3 **Dynamics.** The time evolution of the state $|\psi\rangle$ is governed by the system's Hamiltonian, $\hat{H}$,

$$|\psi(t+\tau)\rangle = e^{-\frac{\imath}{\hbar}\hat{H}\tau}|\psi(t)\rangle \quad \leftrightarrow \quad \imath\hbar\frac{d}{dt}|\psi\rangle = \hat{H}|\psi\rangle, \tag{5.3}$$

The latter form is known as Schrödinger Equation .

4 **Measurement.** A measurement of an observable $\mathbb{Q}$ in state $|\psi\rangle$ gives one of its eigenvalues q_n with probability:

$$|\psi\rangle = \sum_n c_n|q_n\rangle \qquad \rightarrow \qquad P_\psi(\mathbb{Q} = q_n) = |c_n|^2 \tag{5.4}$$

The post-measurement state is then $|q_n\rangle$ with certainty. This QM process is also known as *reduction (or collapse)* of the state.

5.1 CA-1

Question 5.1.1

Assume, $|\psi\rangle = N(|1\rangle + |2\rangle + |3\rangle)$ with $|i\rangle, i = 1-3$ orthonormalized, complete basis. An acceptable value of N is,

Solution: In accord to (1.1) the state $|\psi\rangle$ must be normalized:

$$\langle\psi|\psi\rangle = \sum_{n=1}^{N} |c_n|^2 = 1$$

Here we have 3 states, $n = 3$, with, $c_1 = c_2 = c_3 = N$ and the above requirement gives,

$$3|N|^2 = 1 \qquad \rightarrow \qquad N = \frac{e^{\imath\phi}}{\sqrt{3}}.$$

Since a single quantum state can be defined up to an arbitrary phase factor one can simplify and chose $\phi = 0$ and therefore

$$\boxed{N = \frac{1}{\sqrt{3}}}.$$

Question 5.1.2

If,

$$\hat{S}_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{5.5}$$

is the representation of the spin observable along the axis $\hat{x}$ on the complete, orthonormalized basis $|1\rangle, |2\rangle$ then the value of $\langle 1|\hat{S}_x|2\rangle$ is,

Solution: The $\hat{S}_x$ observable is represented by a 2×2 matrix so the dimension of the vector space is $n = 2$. Then the fundamental basis for $n = 2$ is defined as in (1.13)

$$|v_1\rangle = |1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad |v_2\rangle = |2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{5.6}$$

If one consider the matrices $|v_i\rangle\langle v_j|$, from (1.25) we have for a matrix representation of an operator in the fundamental basis,

$$\begin{aligned}\hat{S}_x &= \sum_{i=1,2}\sum_{j=1,2} S_{ij}|v_i\rangle\langle v_j| \qquad \text{where} \qquad (S_x)_{ij} \equiv S_{ij} = \langle v_i|\hat{S}_x|v_j\rangle \\ &= S_{11}|v_1\rangle\langle v_1| + S_{12}|v_1\rangle\langle v_2| + S_{21}|v_2\rangle\langle v_1| + S_{22}|v_i\rangle\langle v_j| \\ &= S_{11}\begin{pmatrix}1 & 0\\ 0 & 0\end{pmatrix} + S_{12}\begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix} + S_{21}\begin{pmatrix}0 & 0\\ 1 & 0\end{pmatrix} + S_{22}\begin{pmatrix}0 & 0\\ 0 & 1\end{pmatrix} \\ &= \begin{pmatrix}S_{11} & S_{12}\\ S_{21} & S_{22}\end{pmatrix} \qquad \text{must be equal to} \qquad \frac{\hbar}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}.\end{aligned}$$

From the latter expression comparison with (5.5) gives [63]

$$\boxed{\langle 1|\hat{S}_x|2\rangle = S_{12} = \frac{\hbar}{2}.}$$

63: Of course it also holds,

$$\langle 2|\hat{S}_x|1\rangle = \frac{\hbar}{2}$$
$$\langle 1|\hat{S}_x|1\rangle = \langle 2|\hat{S}_x|2\rangle = 0$$

Question 5.1.3

A system is prepared in the state $|\psi\rangle = (e^{\imath\phi}|1\rangle + \imath|2\rangle)/\sqrt{2}$ on the eigenstate basis of the $\hat{S}_z$ observable. A measurement of $\hat{S}_z$ will provide the eigenvalue of state $|1\rangle$ with probability:

Solution. Comparing the expression of the state $|\psi\rangle$ on an eigenstate basis, (1.22), with the given expression (on the two-dimensional $\hat{S}_z$ eigenstate basis) we obtain the expansion c_1, c_2 coefficients:

$$|\psi\rangle = c_1|1\rangle + c_2|2\rangle \qquad \Longrightarrow \qquad \begin{cases} c_1 = \frac{e^{\imath\phi}}{\sqrt{2}} \\ c_2 = \imath/\sqrt{2}\end{cases}$$

Now the state $|\psi\rangle$ is expanded on the S_z eigenbasis. In accord to QM postulate, (1.4), a measurement of $\hat{S}_z$ will provide the eigenvalue of $|1\rangle$ with probability[64],

$$\boxed{P_1 = |c_1|^2 = \left|\frac{e^{\imath\phi}}{\sqrt{2}}\right|^2 = \frac{1}{2}}$$

(since $|e^{\imath\phi}|^2 = 1$)

64: Note that if the state $|1\rangle$ is associated with the positive value of the $\hat{S}_z$ according to,

$$\hat{S}_z|1\rangle = \frac{\hbar}{2}|1\rangle, \qquad \hat{S}_z|2\rangle = -\frac{\hbar}{2}|2\rangle.$$

we have that $P_1 = P_1(S_z = \frac{\hbar}{2})$

Question 5.1.4

A system is in the state $|\psi\rangle$ and a measurement of observable $\hat{Q}$ provides the eigenvalue q_1 with probability p_1. If the system is in the state $|\psi'\rangle = e^{\imath\pi/2}|\psi\rangle$ will provide the eigenvalue q_1 with probability:

Solution To find the probability to appear the value q_1 of the observable $\hat{Q}$ we'll assume the state $|\psi\rangle$ expanded on the eigenbasis of $\hat{Q}$:

$$|\psi'\rangle = e^{\imath\phi}\sum_i c_i|q_i\rangle = \sum_i \left(e^{\imath\phi}c_i\right)|q_i\rangle = \sum_i C_i|q_i\rangle.$$

where we set $\phi = \pi/2$. Therefore we have the expansion of $|\psi'\rangle$ on the eigenstate basis of $\hat{Q}$:

$$|\psi'\rangle = \sum_i C_i|q_i\rangle, \qquad \text{where} \qquad C_i = e^{\imath\phi}c_i.$$

According to QM postulate (1.4), a measurement of $\hat{Q}$ will give the eigenvalue q_i (associated with the eigenstate $|q_i\rangle$) with probability:

$$\boxed{P_{\psi'}(\mathbb{Q} = q_1) = |C_1|^2 = |e^{\imath\phi}c_1|^2 = |c_1|^2 = P_\psi(\mathbb{Q} = q_1) = p_1}$$

Note:

An alternative (and more direct) way is to substitute $|\psi'\rangle$ in (1.42):

$$\begin{aligned} P_{\psi'}(\mathbb{Q} = q_n) &= |\langle q_n|\psi'\rangle|^2 = |\langle q_n|e^{\imath\pi/2}\psi\rangle|^2 = |e^{\imath\phi}\langle q_n|\psi\rangle|^2 \\ &= |e^{\imath\phi}||^2\langle q_n|\psi\rangle|^2 = 1 \times P_\psi(\mathbb{Q} = q_n) = p_n \end{aligned}$$

Note:

A third way is to use the projection operator (**??**) and by noticing that $\langle\psi'| = \langle\psi|e^{-\imath\phi}$:

$$\begin{aligned} P_{\psi'}(\mathbb{Q} = q_n) &= \langle\psi'|\hat{Q}_n|\psi'\rangle = \langle\psi|e^{-\imath\phi}\hat{Q}_n e^{\imath\phi}|\psi\rangle \\ &= \langle\psi|\hat{Q}_n|\psi\rangle = P_{\psi'}(\mathbb{Q} = q_n) = p_n \end{aligned}$$

From the above we see that the measurements for all $P(\mathbb{Q} = q_n)$ probabilities remain the same regardless the value of ϕ and not just for $n = 1$ and $\phi = \pi/2$. *This is to emphasize, once more, that for QM the states $|\psi\rangle$ and $e^{\imath\phi}|\psi\rangle$ represent the same physical state.*

Question 5.1.5

A quantum system with Hamiltonian,

$$\hat{H} = E_0 \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}, \qquad E_0 > 0,$$

is in the state $|1\rangle$. An energy measurement will provide a negative value with probability,

Solution. To solve this question we should proceed by (a) finding the eigenspectrum of the Hamiltonian (eigenstates/eigenvalues) say $|\phi_1\rangle, |\phi_2\rangle$, (b) use QM postulate (1.4) and expand the *fundamental* state $|1\rangle$ on the Hamiltonian's eigenbasis to find the probability for an energy measurement resulting to a negative value.

1 *(Eigenstates/eigenvalues) of* $\hat{H}$.
The eigenvalue equation for the Hamiltonian is,

$$\hat{H}|\phi\rangle = \epsilon|\phi\rangle,$$

Representing $|\phi\rangle$ as a column vector, $|\phi\rangle = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$ the problem is turned to an 2×2 algebraic (matrix-diagonalization) problem. Its solution provides two eigenstates/eigenvalues, $|\phi_1\rangle, |\phi_2\rangle$ [65] :

$$|\phi_1\rangle = \sqrt{\frac{1}{2(2+\sqrt{2})}} \begin{pmatrix} 1 \\ -(\sqrt{2}+1) \end{pmatrix}, \qquad \epsilon_1 = -E_0\sqrt{2} \tag{5.7}$$

$$|\phi_2\rangle = \sqrt{\frac{1}{2(2-\sqrt{2})}} \begin{pmatrix} 1 \\ \sqrt{2}-1 \end{pmatrix}, \qquad \epsilon_2 = +E_0\sqrt{2} \tag{5.8}$$

The Hamiltonian's eigenstates are re-expressed on the fundamental basis as [66]:

$$|\phi_1\rangle = \sqrt{\frac{1}{2(2+\sqrt{2})}} \Big(|1\rangle - (\sqrt{2}+1)|2\rangle \Big), \tag{5.9}$$

$$|\phi_2\rangle = \sqrt{\frac{1}{2(2-\sqrt{2})}} \Big(|1\rangle + (\sqrt{2}-1)|2\rangle \Big) \tag{5.10}$$

(i) *Measurement of energy*. We know the system is at state $|1\rangle$. Since the results of an energy measurement are required we need to expand this state on the Hamiltonian's eigenbasis and interpret the expansion coefficients according to

65: One can easily check that these states are orthonormalized and that:

$$\hat{H}|\phi_1\rangle = -E_0\sqrt{2}|\phi_1\rangle$$
$$\hat{H}|\phi_2\rangle = E_0\sqrt{2}|\phi_2\rangle$$

and that,

$$\langle\phi_1|\phi_1\rangle = \langle\phi_2|\phi_2\rangle = 1, \langle\phi_1|\phi_2\rangle \quad = 0$$

66:

$$|v_1\rangle = |1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix},$$
$$|v_2\rangle = |2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

measurement postulate (1.4). From (5.9)-(5.10) it is straightforward to find:

$$|1\rangle = \left(\frac{1}{2}\sqrt{2-\sqrt{2}}\right)|\phi_1\rangle + \left(\frac{1}{2}\sqrt{2+\sqrt{2}}\right)|\phi_2\rangle$$
$$|2\rangle = \left(-\frac{1}{2}\sqrt{2+\sqrt{2}}\right)|\phi_1\rangle + \left(\frac{1}{2}\sqrt{2-\sqrt{2}}\right)|\phi_2\rangle.$$

So, at this point we have expanded the system's state $|1\rangle$ onto the Hamiltonian's eigenbasis according to (1.4). Since the eigestate $|\phi_1\rangle$ has as an eigenvalue $\epsilon_1 = -E_0\sqrt{2}$ an energy measurement will give this value with probability,

$$P_{|1\rangle}(E = -\frac{E_0}{\sqrt{2}}) = |c_1|^2 = \left|\frac{1}{2}\sqrt{2-\sqrt{2}}\right|^2 = \frac{2-\sqrt{2}}{4},$$

Note: The above solution is re-written as,

$$P(E<0) = \frac{2-\sqrt{2}}{4} = \frac{(\sqrt{2}-1)}{2\sqrt{2}} = \frac{(\sqrt{2}-1)(\sqrt{2}-1)}{2\sqrt{2}(\sqrt{2}-1)} = \frac{1}{2}\frac{(1-\sqrt{2})^2}{(2-\sqrt{2})}$$

5.2 CA-2

Consider the spin-observable, $\mathbf{S}$, with its projections, $\hat{S}_x, \mathrm{op}S_y, \hat{S}_z$ represented on the complete, orthonormalized basis $|1\rangle, |2\rangle$ of the $\hat{S}_z$ as

$$\hat{S}_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \hat{S}_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -\imath \\ \imath & 0 \end{pmatrix}, \qquad \hat{S}_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

$$\hat{S}_z|1\rangle = -\frac{\hbar}{2}|1\rangle, \qquad \hat{S}_z|2\rangle = \frac{\hbar}{2}|2\rangle,$$

A particle with spin 1/2 has a Hamiltonian given by $\hat{H} = \omega_0 \hat{S}_y,\ \omega_0 > 0$. Its state at $t = 0$ is $|\psi(0)\rangle = |2\rangle$. The particle's spin state evolves at time t to a state $|\psi(t)\rangle$. Answer the below:

Some preparation is needed before we go to the answers. We need to identify $|\psi(0)\rangle$ and $|\psi(t)\rangle$.

(i) **Calculation of** $|\psi(0)\rangle$. First, we have to check what is the state $|2\rangle$. We see that if we define,

$$|2\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad |1\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{5.11}$$

then indeed ,

$$\hat{S}_z|2\rangle = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2}|2\rangle$$

Therefore,

$$|\psi(t)\rangle = |2\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}. \tag{5.12}$$

(ii) **Calculation of** $|\psi(t)\rangle$. Now we go on to find the state at the later time t.
One method is the following: We'll be writing the initial state in terms of the Hamiltonian eigenbasis $|\phi_1\rangle, |\phi_2\rangle$ and then will find $|\psi(t)\rangle$ by,

$$|\psi(0)\rangle = c_1|\phi_1\rangle + c_2|\phi_2\rangle \tag{5.13}$$

$$\rightarrow \qquad |\psi(t)\rangle = c_1 e^{-\imath\epsilon_1/\hbar}|\phi_1\rangle + c_2 e^{-\imath\epsilon_2/\hbar}|\phi_2\rangle. \tag{5.14}$$

So we need first to find all $c_i, \epsilon_i, |\phi_i\rangle\ i = 1, 2$. One approach is to solve the eigenvalue problem for the Hamiltonian, $\hat{H} = \omega_0 \hat{S}_y$:

$$\hat{H}|\phi\rangle = \epsilon|\phi\rangle \qquad \rightarrow \qquad \begin{pmatrix} 0 & -\imath E_0 \\ \imath E_0 & 0 \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \epsilon\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}, \qquad E_0 = \frac{\hbar\omega_0}{2}$$

But, another method can be followed since the system's Hamiltonian is proportonial to the spin $\hat{S}_y$ operator; so they have the same eigenstates given by, [67] ,

$$|\phi_1\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-\imath\end{pmatrix} = \frac{1}{\sqrt{2}}(|2\rangle - \imath|1\rangle) \tag{5.15}$$

$$|\phi_2\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\+\imath\end{pmatrix} = \frac{1}{\sqrt{2}}(|2\rangle + \imath|1\rangle) \tag{5.16}$$

where the expressions (5.11) were assumed. Now re-write the eigenstates $|1\rangle$ and $|2\rangle$ as,

$$|1\rangle = \frac{\imath}{\sqrt{2}}(|\phi_1\rangle - |\phi_2\rangle), \qquad |2\rangle = \frac{1}{\sqrt{2}}(|\phi_1\rangle + |\phi_2\rangle)$$

Eventually we are able to apply (5.13),(5.14) since $|\psi(0)\rangle = |2\rangle$:

$$|\psi(0)\rangle = \frac{1}{\sqrt{2}}(|\phi_1\rangle + |\phi_2\rangle) \tag{5.17}$$

$$|\psi(t)\rangle = \frac{e^{\imath\omega_0/2}}{\sqrt{2}}|\phi_1\rangle + \frac{e^{-\imath\omega_0/2}}{\sqrt{2}}|\phi_2\rangle, \tag{5.18}$$

where the state of the system is expanded on the eigenbasis of the Hamiltonian (and of course the eigenstates of the spin-operator $\hat{S}_y$).

67: It is not difficult to confirm that

$$\hat{H}|\phi_1\rangle = -\frac{\hbar\omega_0}{2}|\phi_1\rangle$$
$$\hat{H}|\phi_2\rangle = \frac{\hbar\omega_0}{2}|\phi_2\rangle$$

Question 5.2.1

Consider the commutator $\hat{C}_2 = [\hat{S}_x, \hat{S}_y] = \hat{S}_x\hat{S}_y - \hat{S}_y\hat{S}_x$. The result of $\hat{C}_2|\psi(0)\rangle$ is,

Solution. First one needs to find the matrix representation of $\hat{C}_2$. This straightforward to calculate since the matrix representations of $\hat{S}_x, \hat{S}_y$ are given; so,

$$\hat{C}_2 = \hat{S}_x\hat{S}_y - \hat{S}_y\hat{S}_x = \frac{\hbar}{2}\begin{pmatrix}0&1\\1&0\end{pmatrix}\frac{\hbar}{2}\begin{pmatrix}0&-\imath\\\imath&0\end{pmatrix} - \frac{\hbar}{2}\begin{pmatrix}0&-\imath\\\imath&0\end{pmatrix}\frac{\hbar}{2}\begin{pmatrix}0&1\\1&0\end{pmatrix}$$
$$= \frac{\hbar^2}{4}\begin{pmatrix}\imath&0\\0&-\imath\end{pmatrix} - \begin{pmatrix}-\imath&0\\0&\imath\end{pmatrix} = \imath\frac{h^2}{2}\begin{pmatrix}1&0\\0&-1\end{pmatrix} = \imath\hbar\hat{S}_z$$

This will give the following result:

$$\boxed{\hat{C}_2|\psi(0)\rangle = \hat{C}_2|2\rangle = \imath\hbar\hat{S}_z|2\rangle = \imath\hbar\frac{\hbar}{2}|2\rangle = \frac{\imath\hbar^2}{2}|2\rangle.}$$

Question 5.2.2

The square of the spin observable is $\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$. Consider the commutator $\hat{C}_1 = [\hat{S}^2, \hat{S}_y] = \hat{S}^2\hat{S}_y - \hat{S}_y\hat{S}^2$. The result of $\hat{C}_1|\psi(t)\rangle$ is,

Solution. Let's again find the matrix representation of $\hat{C}_1$. First we need to calculate, $\hat{S}^2$ matrix-representation:

$$\begin{aligned}\hat{S}^2 &= \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 \\ &= (\frac{\hbar}{2})^2 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + (\frac{\hbar}{2})^2 \begin{pmatrix} 0 & -\imath \\ \imath & 0 \end{pmatrix}\begin{pmatrix} 0 & -\imath \\ \imath & 0 \end{pmatrix} + (\frac{\hbar}{2})^2 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \\ &= (\frac{\hbar}{2})^2 \left(\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \right) = \frac{3\hbar^2}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\end{aligned}$$

So the $\hat{S}^2$ is proportional to the diagonal matrix. Now it is straightforward to see that,

$$\hat{C}_1 = \hat{S}^2\hat{S}_y - \hat{S}_y\hat{S}^2 = ... = 0.$$

This will give the following result:

$$\boxed{\hat{C}_1|\psi(0)\rangle = 0.}$$

Question 5.2.3

An energy measurement at time t will provide positive eigenvalue with probability:

Solution. The state $|\psi(t)\rangle$ in (5.18) is expanded on the eigenbasis of the Hamiltonian so according to postulate (1.4) the positive eigevalue $(\hbar\omega_0/2)$ which is associated with the eigenstate $|\phi_2\rangle$ will be realized with probability,

$$\boxed{P_\psi(E = \frac{\hbar\omega_0}{2}) = |c_2|^2 = |\frac{1}{\sqrt{2}}e^{-\imath\omega_0/2}|^2 = \frac{1}{2}.}$$

Note

Of course the probability to get the negative value is [68],

$$P_\psi(E = \frac{-\hbar\omega_0}{2}) = |c_1|^2 = |\frac{1}{\sqrt{2}}e^{\imath\omega_0/2}|^2 = \frac{1}{2}.$$

68: or equivalently,

$$P_\psi(E = \frac{-\hbar\omega_0}{2}) = 1 - P_\psi(E = \frac{\hbar\omega_0}{2}) = 1 - \frac{1}{2} = \frac{1}{2}.$$

Question 5.2.4

A measurement of $\hat{S}_y$ at time t will provide the eigenvalue $\hbar/2$ with probability:

Solution. Noticing that the Hamiltonian and the spin-$\hat{S}_y$ observable share the same eigenbasis, means that the state $|\psi(t)\rangle$ in (5.18) is also expanded on the eigenbasis of the $\hat{S}_y$ operator. Therefore, once more, according to postulate (1.4) the positive eigevalue of $\hat{S}_y$ ($\hbar/2$) which is associated with the eigenstate[69] $|\phi_2\rangle$ will be realized with probability,

$$\boxed{P_\psi(S_y = \frac{\hbar}{2}) = |c_2|^2 = |\frac{1}{\sqrt{2}} e^{-\imath\omega_0/2}|^2 = \frac{1}{2}.}$$

69: Just check that,

$$\hat{S}_y|\phi_1\rangle = -\frac{\hbar}{2}|\phi_1\rangle$$
$$\hat{S}_y|\phi_2\rangle = +\frac{\hbar}{2}|\phi_2\rangle$$

Question 5.2.5

A measurement of $\hat{S}_x$ at time t will provide the eigenvalue $\hbar/2$ with probability:

Solution. In order to answer this question, as usual, we need to expand the state $|\psi(t)\rangle$ in terms of the eigenbasis of the operator $\hat{S}_x$ (say $|s_1\rangle, |s_2\rangle$ and interpret the expansion coefficients in accord to postulate (1.4).

Let's take the eigenbasis of $\hat{S}_x$ in terms of the fundamental basis[70],

$$|s_1\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix} = \frac{1}{\sqrt{2}}(|2\rangle - |1\rangle) \tag{5.19}$$
$$|s_2\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix} = \frac{1}{\sqrt{2}}(|2\rangle + |1\rangle) \tag{5.20}$$

70: Just check that

$$\hat{S}_x|s_1\rangle = -\frac{\hbar}{2}|s_1\rangle$$
$$\hat{S}_x|s_2\rangle = +\frac{\hbar}{2}|s_2\rangle$$

Now the task is to write $|\psi(t)\rangle$ in (5.14) in terms of $|s_1\rangle$ and $|s_2\rangle$. For this, first the relations (5.16)-(5.15) together with (5.19)-(5.20) are used to find that,

$$|\phi_1\rangle = \frac{1+\imath}{2}|s_1\rangle + \frac{1-\imath}{2}|s_2\rangle \tag{5.21}$$
$$|\phi_2\rangle = \frac{1-\imath}{2}|s_1\rangle + \frac{1+\imath}{2}|s_2\rangle \tag{5.22}$$

Given the above expressions it is straightforward to write down

for $|\psi(t)\rangle$:

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}}\left[\frac{e^{\imath\omega_0 t/2}(1+\imath)+e^{-\imath\omega_0 t/2}(1-\imath)}{2}|s_1\rangle + \frac{e^{\imath\omega_0 t/2}(1-\imath)+e^{-\imath\omega_0 t/2}(1+\imath)}{2}|s_2\rangle\right]$$
$$= \frac{1}{\sqrt{2}}(\cos\frac{\omega_0 t}{2} - \sin\frac{\omega_0 t}{2})|s_1\rangle + \frac{1}{\sqrt{2}}(\cos\frac{\omega_0 t}{2} + \sin\frac{\omega_0 t}{2})|s_2\rangle,$$

where we used the identities $\cos x = (e^{\imath x} + e^{-\imath x})/2$ and $\sin x = (e^{\imath x} - e^{-\imath x})/2\imath$. At this point $|\psi(t)\rangle$ is expressed in terms of the eigenstates of $\hat{S}_x$, so we can use the postulate (1.4) and predict that a measurement of $\hat{S}_x$ will give the positive value $\hbar/2$ (eigenvalue of the $|s_1\rangle$ eigenvector):

$$\boxed{P_\psi(S_x = \frac{\hbar}{2}) = |c_2|^2 = |\frac{1}{\sqrt{2}}(\cos\frac{\omega_0 t}{2} + \sin\frac{\omega_0 t}{2})|^2 = \frac{1+\sin\omega_0 t}{2}.}$$

Note:

As usual the probability to get the negative value can be found by,

$$P_\psi(S_x = -\frac{\hbar}{2}) = |c_1|^2 = |\frac{1}{\sqrt{2}}(\cos\frac{\omega_0 t}{2} - \sin\frac{\omega_0 t}{2})|^2 = \frac{1-\sin\omega_0 t}{2}.$$

or it can be found by using the completeness condition,

$$P_\psi(S_x = -\frac{\hbar}{2}) = 1 - P_\psi(S_x = \frac{\hbar}{2}) = 1 - \frac{1+\sin\omega_0 t}{2} = \frac{1-\sin\omega_0 t}{2}$$

5.3 CA-3

The expression, eigenstates/eigenenergies of the position ($\hat{x}$), momentum ($\hat{p}$), free-Hamiltonian ($\hat{H}_f = \hat{p}^2/2m$) and harmonic oscillator ($\hat{H}_{ho} = \hat{p}^2/2m + m\omega_0^2\hat{x}^2/2$)-observables in the position-representation of a particle of mass m are as below,

$$\hat{x} = x, \qquad \phi_{x'}(x) = \delta(x - x'), \qquad \hat{x}\phi_{x'} = x\phi_{x'}, \qquad \delta(x) \text{ delta-Dirac function}$$

$$\hat{p} = -\imath\hbar\frac{d}{dx}, \qquad \phi_p(x) = \frac{1}{\sqrt{2\pi\hbar}}e^{\imath px/\hbar}, \qquad \hat{p}\phi_p(x) = p\phi_p(x)$$

$$\hat{H}_f = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}, \qquad \phi_p(x) = \frac{1}{\sqrt{2\pi\hbar}}e^{\imath px/\hbar}, \qquad \hat{H}_f\phi_p(x) = \frac{p^2}{2m}\phi_p(x)$$

$$\hat{H}_{ho} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega_0^2x^2, \qquad \phi_n(x) = N_n e^{-\beta^2x^2/2}H_n(\beta x), \qquad \hat{H}_{ho}\phi_n(x) = \hbar\omega_0(n + \frac{1}{2})\phi_n(x),$$

$$\beta = \sqrt{\frac{m\omega_0}{\hbar}}, \qquad H_n(x) \text{ Hermite polynomials}, \qquad n = 0, 1, 2...$$

Question 5.3.1

For each of the above observables write down the corresponding (a) completeness and (b) orthogonalization conditions.

Solution. One has to recall the (discrete) completeness and orthogonalization relations as given by (1.2) and extend to the case of observables with continuous spectrum:

$$\hat{Q}|q_n\rangle = q_n|q_n\rangle \tag{5.23}$$

$$\sum_n |q_n\rangle\langle q_n| = \mathbb{1}, \qquad \langle q_n|q_m\rangle = \delta_{nm} \tag{5.24}$$

The required (mathematical) adjustments in the formulation when the discrete state $|q_n\rangle$ (discreteness is characterized by the integer n) becomes continuous, namely, $|q_n\rangle \to |q\rangle$,

$$\sum_n = \sum_{q_n} \qquad \to \qquad \int dq,$$

$$\delta_{nm} = \delta_{q_n q_m} \qquad \to \qquad \delta_{qq'} \equiv \delta(q - q')$$

Let's specialize the above relations

(i) *position* $\hat{Q} = \hat{\mathbf{x}}$ *and* $q_n = x$. The eigenvalue equation for the position operator (which obviously takes continuous values) is [71],

$$\hat{\mathbf{x}} = x, \qquad \hat{\mathbf{x}}\phi_{x'}(x) = x\phi_{x'}(x) \qquad \to \qquad \phi_{x'}(x) = \delta(x - x'),$$

71: The abstract eigenvalue problem for the position operator is,

$$\hat{\mathbf{x}}|x\rangle = x|x\rangle.$$

In the position representation the state $|x\rangle$ takes the form of a wave-function,

$$\phi_{x'}(x) = \langle x'|x\rangle$$

Therefore the completeness relation (5.24) becomes,

$$\boxed{\int dx|x\rangle\langle x| = \mathbb{1}, \qquad \langle x|x'\rangle = \delta(x - x')}$$

(ii) *Momentum $\hat{Q} = \hat{\mathbf{p}}$ and $q_n = p$.* The eigenvalue equation for the position operator (which obviously takes continuous values) is [72],

$$\hat{\mathbf{p}} = -\imath\hbar\frac{d}{dx}, \quad \hat{\mathbf{p}}\phi_p(x) = p\phi_p(x) \qquad \rightarrow \qquad \phi_p(x) = \frac{e^{\imath\frac{px}{\hbar}}}{\sqrt{2\pi\hbar}},$$

Therefore the completeness relation (5.24) becomes,

$$\boxed{\int dp|p\rangle\langle p| = \mathbb{1}, \qquad \langle p|p'\rangle = \delta(p - p')} \tag{5.25}$$

(iii) *Free-particle Hamiltonian $\hat{H}_f = \hat{\mathbf{p}}/2m$ and $q_n = \epsilon = p^2/2m$.* Here we notice that the free-particle Hamiltonian is made of exclusively the momentum operator $\hat{\mathbf{p}}$, so it commutes,

$$[\hat{H}_f, \hat{\mathbf{p}}] = \hat{H}_f\hat{\mathbf{p}} - \hat{\mathbf{p}}\hat{H}_f = \frac{1}{2m}(\hat{\mathbf{p}}^3 - \hat{\mathbf{p}}^3) = 0.$$

This means that the eigenstates of the free-particle Hamiltonian has the same eigenstates as the momentum operator, albeit with different eigenvalues (ϵ_f). For the latter reason it is legal to switch the index p with the index $\epsilon \equiv p^2/2m$. So the understanding is that[73],

$$\phi_p(x) = \frac{e^{\imath\frac{px}{\hbar}}}{\sqrt{2\pi\hbar}} \qquad \rightarrow \qquad \phi_\epsilon(x) = \frac{e^{\imath\frac{\sqrt{2m\epsilon}}{\hbar}x}}{\sqrt{2\pi\hbar}}$$

Therefore we may write [74]:

$$\hat{H}_f = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}, \qquad \hat{H}_f\phi_\epsilon(x) = \epsilon_f\phi_\epsilon(x), \qquad \epsilon = \frac{p^2}{2m}$$

Now the completeness and the orthonormalization relation becomes,

$$\boxed{\int d\epsilon|\epsilon\rangle\langle\epsilon| = \mathbb{1}, \qquad \langle\epsilon|\epsilon'\rangle = \delta(\epsilon - \epsilon')} \tag{5.26}$$

(iv) *HO Hamiltonian $\hat{Q} = \hat{H}_{ho}$, $q_n = \epsilon_n = \hbar\omega_0(n + 1/2)$.* The HO spectrum is discrete which means that the discrete completeness and orthonormalization conditions hold as they are provided that the eigenstates/eigenvalues are

72: The abstract eigenvalue problem for the momentum operator is,

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

In the position representation the state $|p\rangle$ takes the form of a wavefunction,

$$\phi_p(x) = \langle x|p\rangle = \frac{e^{\imath\frac{px}{\hbar}}}{\sqrt{2\pi\hbar}}$$

73: Note that in the literature, usually, the notation $\phi_p(x)$ is used to denote the free-particle Hamiltonian instead the $\phi_\epsilon(x)$ notation.

74: Again, the abstract eigenvalue problem for the free-particle Hamiltonian is,

$$\hat{H}_f|\epsilon\rangle = \epsilon|\epsilon\rangle.$$

In the position representation the state $|p\rangle$ takes the form of a wavefunction,

$$\phi_\epsilon(x) = \langle x|\epsilon\rangle$$

those of the HO:

$$\hat{H}_{ho}\phi_n(x) = \epsilon_n\phi_n(x) \qquad \rightarrow \qquad \begin{cases} \phi_n(x) & = N_n e^{-\beta^2 x^2/2} H_n(\beta x), \\ \epsilon_n & = \hbar\omega_0(n+\frac{1}{2}) \\ \beta & = \sqrt{\frac{m\omega_0}{\hbar}}, \quad n = 0, 1, 2.. \end{cases} .$$

Since the spectrum is discretized by changing $q_n = \epsilon_n$ we have for the HO's completeness and orthonormalization conditions:

$$\boxed{\sum_n |\epsilon_n\rangle\langle\epsilon_n| = \mathbb{1}, \qquad \langle\epsilon_n|\epsilon_m\rangle = \delta_{nm}}$$

Question 5.3.2

Assume an electron moving freely and is in the state, $\psi(x) = N\frac{e^{\imath p_0 x/\hbar}}{\sqrt{x^2+a^2}}$ Calculate N, the probability that a position measurement will find the particle in the region $[-a/\sqrt{3}, a/\sqrt{3}]$ and the mean value of its momentum.

Solution.

(i) *Calculation of the normalization constant N.*
Wavefunctions needs to be normalized, namely to satisfy:

$$\int_{-\infty}^{\infty} dx|\psi(x)|^2 = 1. \tag{5.27}$$

Substitution of the given wavefunctions gives,

$$\begin{aligned} 1 &= |N|^2 \int_{-\infty}^{\infty} dx \left|\frac{e^{\imath p_0 x/\hbar}}{\sqrt{x^2+a^2}}\right|^2 = |N|^2 \int_{-\infty}^{\infty} \frac{dx}{x^2+a^2} \\ &= \frac{|N|^2}{a} \int_{-\infty}^{\infty} \frac{d(x/a)}{1+(x/a)^2} = \frac{|N|^2}{a} \int_{-\infty}^{\infty} \frac{du}{1+u^2} \\ &= \frac{|N|^2}{a} [\tan u]_{-\infty}^{\infty} = \frac{|N|^2}{a}\pi. \end{aligned}$$

From the last equation we easily find,

$$|N| = \sqrt{\frac{a}{\pi}} \qquad \rightarrow \qquad \boxed{N = e^{\imath\phi}\sqrt{\frac{a}{\pi}}, \qquad \phi \text{ arbitrary}} .$$

Since ϕ is freely chosen (without changing any physical prediction) we choose, $\phi = 0$ and the normalized wavefunction is,

$$\psi(x) = \sqrt{\frac{a}{\pi}}\frac{e^{\imath p_0 x/\hbar}}{\sqrt{x^2+a^2}} \tag{5.28}$$

(ii) *Calculation of the probability* $P_\psi(|x| < a/\sqrt{3})$.
Since the quantity $dP(x)$,

$$dP(x) = dx|\psi(x)|^2, \tag{5.29}$$

represents the *probability* that a measurement position will find the particle between the $[x, x+dx]$, by summing all the individual probabilities from $-\frac{a}{\sqrt{3}}$ to $\frac{a}{\sqrt{3}}$ will give us the desired probability:

$$\begin{aligned}
P_\psi(|x| < \frac{a}{\sqrt{3}}) &= \int_{-\frac{a}{\sqrt{3}}}^{+\frac{a}{\sqrt{3}}} dP(x) = \int_{-\frac{a}{\sqrt{3}}}^{+\frac{a}{\sqrt{3}}} dx|\psi(x)|^2 \\
&= \int_{-\frac{a}{\sqrt{3}}}^{+\frac{a}{\sqrt{3}}} dx \left|\sqrt{\frac{a}{\pi}}\frac{e^{\imath p_0 x/\hbar}}{\sqrt{x^2+a^2}}\right|^2 \\
&= \frac{a}{\pi}\int_{-\frac{a}{\sqrt{3}}}^{+\frac{a}{\sqrt{3}}} \frac{dx}{x^2+a^2} = \frac{1}{\pi}\int_{-\frac{1}{\sqrt{3}}}^{+\frac{1}{\sqrt{3}}} \frac{du}{1+u^2} \\
&= \frac{1}{\pi}[\tan u]_{-1/\sqrt{3}}^{1/\sqrt{3}} = \frac{1}{\pi}\left[\frac{\pi}{6} - (-\frac{\pi}{6})\right] = \frac{\pi}{3}.
\end{aligned}$$

Therefore the result is

$$\boxed{P_\psi(|x| < \frac{a}{\sqrt{3}}) = \frac{\pi}{3}}$$

(iii) *Calculation of the mean momentum* $\langle p\rangle$.
By QM rules the mean value of an observable, $\mathbb{Q}$, for a system in state $|\psi\rangle$, is defined by,

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

where the last expression holds when the observable and the state are expressed in the position representation. For the particular case of the momentum operator,

$$\begin{aligned}
\langle\hat{\mathbf{p}}\rangle &= \langle\psi|\hat{\mathbf{p}}|\psi\rangle = \int_{-\infty}^{\infty} dx\psi^*(x)\left(-\imath\hbar\frac{d}{dx}\right)\psi(x) \\
&= -\imath\hbar\int_{-\infty}^{\infty} dx\psi^*(x)\frac{d\psi(x)}{dx} \\
&= -\imath\hbar\frac{a}{\pi}\int_{-\infty}^{\infty} dx\frac{e^{-\imath p_0 x/\hbar}}{\sqrt{x^2+a^2}}\frac{d}{dx}\left(\frac{e^{\imath p_0 x/\hbar}}{\sqrt{x^2+a^2}}\right) \\
&= \ldots = \frac{a}{\pi}p_0\left[\int_{-\infty}^{\infty}\frac{dx}{x^2+a^2} + \imath\hbar\int_{-\infty}^{\infty}\frac{dx\ x}{x^2+a^2}\right] \\
&= \frac{a}{\pi}p_0\left[\frac{\pi}{a} + 0\right] = p_0.
\end{aligned}$$

Finally we have,

$$\boxed{\langle\hat{\mathbf{p}}\rangle = p_0}$$

Question 5.3.3

An electron is moving in the field of an harmonic oscillator (HO) potential with $\hbar\omega_0 = 0.04$ eV. Initially it is found in the state, $m = m_e$, $\omega_0 = 0.4$ eV.

$$\psi(x,0) = \phi_1(x), \qquad \phi_1, \text{ HO's first eigenstate.}$$

(a) Find the particle's mean position and momentum values at time $t = 0$. Find the corresponding mean values at a later time $t = \pi/\omega_0$.

(b) find the standard deviations Δx and Δp. What is the value $\Delta x \Delta p$? Is this value in accordance with Heisenberg's uncertainty relation?

Solution. The electron is in the first excited state of an HO potential,

$$\phi_1(x) = 2\beta^{3/2}\sqrt{\frac{1}{2\sqrt{\pi}}}xe^{-\frac{\beta^2x^2}{2}} = \lambda_1 xe^{-\frac{\beta^2x^2}{2}} \qquad \beta = \sqrt{\frac{m\omega_0}{\hbar}} \quad (5.30)$$

This is its initial state. Its state at a later time can be found by using (2.15) for $c_1 = 1$ and all other coefficients zero.:

$$\psi(x,0) = \phi_1(x) \qquad \rightarrow \qquad \psi(x,t) = e^{-\imath\frac{3\omega_0 t}{2}}\phi_1(x)$$

(i) *Mean position:*
According to (2.19) [75] :

$$\langle x\rangle_0 = \langle\psi_0|\hat{\mathbf{x}}|\psi_0\rangle = \int_{-\infty}^{\infty} dx\psi^\star(x,0)x\psi(x,0) = \int_{-\infty}^{\infty} dx x|\phi(x)|^2$$
$$= \lambda_1^2\int_{-\infty}^{\infty} dx\ x^3e^{-\beta^2x^2} = \ldots = 0.$$

At a later time, one finds the same answer since[76],

$$|\psi(x,t)|^2 = |\psi(x,0)|^2 = |\phi_1(x)|^2.$$

therefore,

$$\boxed{\langle x\rangle_0 = \langle x\rangle_t = 0.}$$

(ii) *Mean momentum:*

75: You can use the following Gaussian Integrals:

$$\int_{-\infty}^{\infty} dx x^{2k+1}e^{-ax^2} = 0,$$
$$\int_{-\infty}^{\infty} dx e^{-ax^2} = \sqrt{\frac{\pi}{a}},$$
$$\int_{-\infty}^{\infty} dx\ xe^{-ax^2} = \frac{1}{2a},$$
$$\int_{-\infty}^{\infty} dx\ x^2e^{-ax^2} = \frac{1}{2a}\sqrt{\frac{\pi}{a}},$$

76: Check it yourself

Similarly, according to (2.19):

$$\begin{aligned}\langle p\rangle_0 = \langle\psi_0|\hat{\mathbf{p}}|\psi_0\rangle &= \int_{-\infty}^{\infty} dx\psi^\star(x,0)\left(-\imath\hbar\frac{d}{dx}\right)\psi(x,0)\\ &= -\imath\hbar\lambda_1^2\int_{-\infty}^{\infty} dx x e^{-\frac{\beta^2x^2}{2}}\frac{d}{dx}\left(xe^{-\frac{\beta^2x^2}{2}}\right)\\ &= -\imath\hbar\lambda_1^2\int_{-\infty}^{\infty} dx\left[xe^{-\beta^2x^2}-\beta^2x^3e^{-\beta^2x^2}\right]\\ &= -\imath\hbar\lambda_1^2\int_{-\infty}^{\infty} dx x e^{-\beta^2x^2}+\imath\hbar\lambda_1^2\beta^2\int_{-\infty}^{\infty} dx x^3e^{-\beta^2x^2}\\ &= 0+0=0.\end{aligned}$$

The mean momentum at a later time is also zero since,

$$\begin{aligned}\langle p\rangle_t = \langle\psi_t|\hat{\mathbf{p}}|\psi_t\rangle &\int_{-\infty}^{\infty} dx\psi^\star(x,t)\left(-\imath\hbar\frac{d}{dx}\right)\psi(x,t)\\ &= \int_{-\infty}^{\infty} dx\psi^\star(x,0)e^{\imath\frac{3\omega_0t}{2}}\left(-\imath\hbar\frac{d}{dx}\right)e^{-\imath\frac{3\omega_0t}{2}}\psi(x,0)\\ &= \int_{-\infty}^{\infty} dx\psi^\star(x,0)\left(-\imath\hbar\frac{d}{dx}\right)\psi(x,0)=\langle p\rangle_0.\end{aligned}$$

So eventually we have,

$$\boxed{\langle p\rangle_0 = \langle p\rangle_t = 0.}$$

(iii) *Calculation of* Δx *and* Δp
For this one needs to calculate,

$$\Delta x_{\psi_0} = \sqrt{\langle x^2\rangle_0^2 - \langle x\rangle_0^2} = \langle x^2\rangle_0$$

and

$$\Delta p_{\psi_0} = \sqrt{\langle p_0^2\rangle^2 - \langle p\rangle_0^2} = \langle p^2\rangle_0$$

So the calculation entails to find the average values of the $\hat{x}^2$ and $\hat{p}^2$. Either one calculates directly the integrals using the Gaussian integrals or uses the general method exposed in detail in the HO chapter. Same conclusions are true for the same quantities at a later time.

Question 5.3.4

An electron is moving in the field of an harmonic oscillator (HO) potential with $\hbar\omega_0 = 0.04$ eV. Initially it is found in the state, $m = m_e$,$\omega_0 = 0.4$ eV.

$$\psi(x,0) = (\phi_0(x) + \imath\phi_1(x))/\sqrt{2}, \qquad \phi_0, \phi_1, \text{ HO's eigenstates.}$$

(a) Find the particle's mean position and momentum values

at time $t = 0$. Find the corresponding mean values at a later time $t = \pi/\omega_0$.

(b) find the standard deviations Δx and Δp initially and at the later time $t = \pi/\omega_0$. What is the value $\Delta x \Delta p$? Is this value in accordance with Heisenberg's uncertainty relation?

Solution The question below can be worked following the method of the Question 5.3.2 above with the $\phi_1(x)$ replaced with the given initial state which now is a linear combination of $\phi_0(x)$ and $\phi_2(x)$. The relevant integrals either are calculated directly as in the previous question or following the general methods in the HO chapter.

Question 5.3.5

(a) Calculate the expressions for N_0, N_1 for the two lower HO's eigenstates.

(b) Prove the Ehrenfest theorem

(c) if $\hat{H}_1 = x^2$ Show that $\langle x|\hat{H}_1|\phi\rangle = x^2\phi(x)$ where $\phi(x)$ is the the state's position representation. (Difficult)

(d)if $\hat{H}_2 = \hat{p}^2$, Show that $\langle x|\hat{H}_2|\phi\rangle = -\hbar^2(d^2/dx^2)\phi(x)$. (Difficult)

Solution (a) The calculation of N_n is based on the fulfilment of the normalization property:

$$\int dx|\phi_n(x)|^2 = 1 \qquad \rightarrow \qquad N_n = ...$$

The relevant integrals either are calculated directly as in the previous question or following the general methods in the HO chapter.

(b) Ignore

(c) Ignore.

Appendix