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# Chapter 11

# Quantum mechanics of vector- and matrix-states

Traditionally, the first encounter with quantum mechanics (QM) theory and its applications is through the state vector formalism, maybe just because it is the simpler choice (but not simple) conceptually. On a practical level, it is vastly the most economical one. The central concepts in this formulation for a physical system are (i) the physical states represented by the vector *state*, $|\psi\rangle$, (ii) the observables $\mathcal{Q}$ represented by operators, $\hat{Q}$, and (iii) 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 (the Schrödinger equation) and the other probabilistic (the measurement). All the predictions about a QM system are derived from these two central concepts, the abstract vector states $|\psi\rangle$ and the observable operators, $\hat{Q}$.

In the following, a set of QM axioms are listed, representing a merged version of the full set of postulates stated in [1], where a more detailed discussion can be found.

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**States.** The physical state of a system is represented by a vector $(|\psi\rangle)$ belonging to some linear vector space $\mathcal{V}$.

**Operators.** A physical quantity $(\mathcal{Q})$ is represented by an operator $(\hat{Q})$. Their action on a vector state, $\hat{Q}|\psi\rangle$, is also a vector state of $\mathcal{V}$.

**Time evolution.** The time evolution of the vector state $|\psi\rangle$ is governed by the system's total energy operator, $\hat{H}$, as

$$d|\psi\rangle = -\iota dt \hat{H}|\psi\rangle. \tag{11.1}$$

**Measurement.** A measurement of $\mathcal{Q}$ changes the state $|\psi\rangle$ to an eigenstate $|q_n\rangle$ of $\hat{Q}$ with probability dependent on the eigenstate $|q_n\rangle$ and the state $|\psi\rangle$. The measurement returns the value $q_n$.

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## 11.1 Vectors and operators

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

The fact that the space $\mathcal{V}$ is a linear vector space has many important consequences with the most fundamental being that any linear combination of vector states belonging to $\mathcal{V}$ also belongs to $\mathcal{F}$, 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 orthonormalized states $|\phi_n\rangle$ is defined when all $|\psi\rangle$ in $\mathcal{V}$ can be expressed in a unique way as

$$|\psi\rangle = \sum_n c_n|\phi_n\rangle, \qquad c_n = \langle\phi_n|\psi\rangle. \tag{11.2}$$

The above expansion is also known as a *superposition expansion*. This set is called orthonormalized when $\langle\phi_n|\phi_m\rangle = \delta_{nm}$. In analogy to the vector algebra learned in high school, the role of $|\psi_n\rangle$ is very similar to the Cartesian components of the familial spatial vector (see figure 11.1); namely, if $\mathbf{A}$ is a vector in the three-dimensional 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

$$\mathbf{A} = \sum_{i=1}^{3} A_i\hat{x}_i, \qquad A_i = \mathbf{A} \cdot \hat{x}_i, \qquad \hat{x}_i \cdot \hat{x}_j = \delta_{ij}. \tag{11.3}$$

An additional formulation of equation (11.3) is obtained if we identify the three-element column basis, satisfying

$$x_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \qquad x_2 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \qquad x_3 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \longrightarrow \mathbf{A} = \begin{pmatrix} A_1 \\ A_2 \\ A_3 \end{pmatrix}. \tag{11.4}$$

The generalization of the familiar three-dimensional algebra is slightly more involved, mainly for two reasons: (i) the dimensionality is higher (now it is not so easy to visualize an $n$-orthogonal vector, $|\phi_n\rangle$) and (ii) the inner product is complex valued, thus introducing the dual space basis vectors of $\mathcal{V}^\star$. For an $N$-dimensional state space,
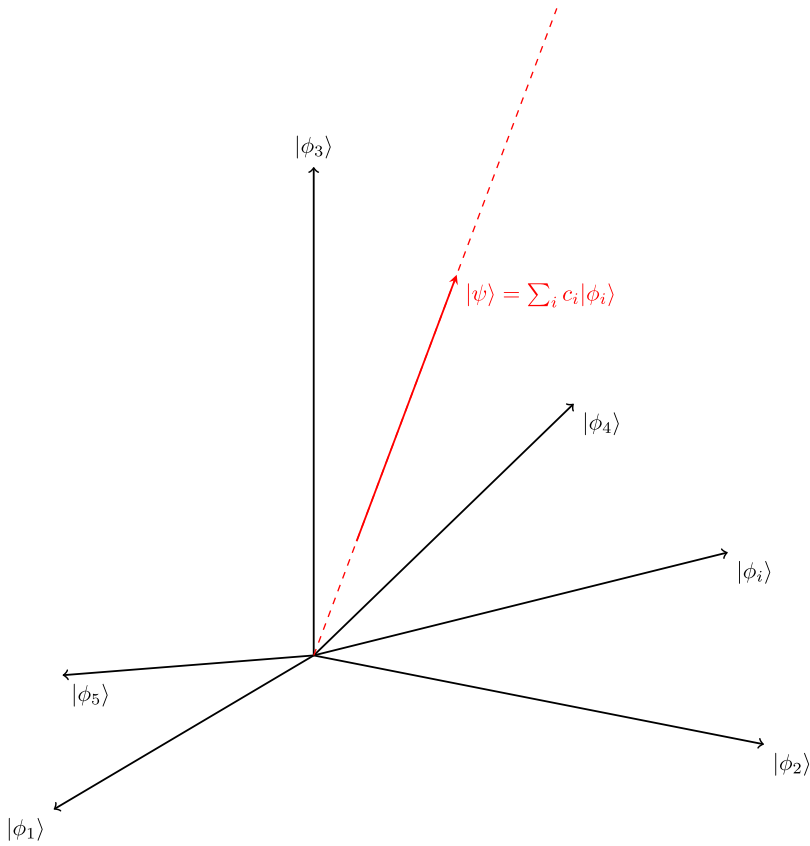
**Figure 11.1.** In QM a physical state can be thought of as a vector of the (abstract) Hilbert space spanned by the orthogonal eigenstates $|\phi_i\rangle$ of some observable operator, $\hat{Q}$. In accordance with this geometrical picture any change of the state can be analyzed in terms of the observable's eigenstates, which play the role of familiar components of the linear algebra. In other words, any observable defines its own 'coordinate system' for the vector state, known as the *representation*.

$$|v_1\rangle = \begin{pmatrix} 1 \\ 0 \\ \cdots \\ 0 \end{pmatrix}, \quad |v_2\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \\ \cdots \end{pmatrix}, \quad \ldots, \quad |v_n\rangle = \begin{pmatrix} 0 \\ 0 \\ \cdots \\ 1 \\ \cdots \\ 0 \end{pmatrix}, \tag{11.5}$$

$$\langle v_1| = (1, \ldots, 0), \quad \langle v_2| = (0, 1, \ldots), \quad \ldots, \quad \langle v_n| = (0, 0, \ldots, 1, \ldots 0), \tag{11.6}$$

where we set $\mathbf{v}_i = |v_i\rangle$ and $\mathbf{v}_i^T = \langle v_i|$, $i = 1, 2, \ldots$ for the column and row vectors. For later reference let us call this (column) basis $(\{|v\rangle\} = |v_1\rangle, |v_2\rangle, \ldots)$ the *fundamental ket basis* and its dual (row) basis the *fundamental bra basis*. The above definitions help to express

$$|\psi\rangle = \mathbf{C} = \begin{pmatrix} c_1 \\ c_2 \\ \cdots \\ c_n \\ \cdots \\ c_N \end{pmatrix} \qquad \langle\psi| = \mathbf{C}^T = \begin{pmatrix} c_1^* \cdots c_N^* \end{pmatrix}. \tag{11.7}$$

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

$$\langle\psi|\psi\rangle = \mathbf{C}^T \cdot \mathbf{C} = \begin{pmatrix} c_1^*, & \ldots, & c_n^*, & \ldots, & c_N^* \end{pmatrix} \begin{pmatrix} c_1 \\ \cdots \\ c_n \\ \cdots \\ c_N \end{pmatrix} = \sum_{n=1}^{N} |c_n|^2, \tag{11.8}$$

and that

$$c_n = \langle v_n|\psi\rangle = (0, \ldots, 1, \ldots 0) \begin{pmatrix} c_1 \\ \cdots \\ c_n \\ \cdots \\ c_N \end{pmatrix}. \tag{11.9}$$

Finally, an important mathematical object arises when one multiplies a ket of a state with its bra, namely, $P_\psi = |\psi\rangle\langle\psi|$,

$$\mathbf{P}_\psi = \mathbf{C} \cdot \mathbf{C}^T = \begin{pmatrix} c_1 \\ \cdots \\ c_n \\ \cdots \\ c_N \end{pmatrix} \begin{pmatrix} c_1^*, & \ldots, & c_n^*, & \ldots, & c_N^* \end{pmatrix} = \begin{bmatrix} |c_1|^2 & c_1 c_2^* & \ldots & c_1 c_n^* & \cdots \\ c_2 c_1^* & |c_2|^2 & \ldots & c_2 c_n^* & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ c_n c_1^* & c_n c_2^* & \ldots & |c_n|^2 & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \end{bmatrix}. \tag{11.10}$$

The above object, $\hat{P}_\psi$, is known as the projection operator of $|\psi\rangle$ for reasons that will be explained shortly. Obviously, the projection operators have the algebraic structure of a matrix, but what is more interesting is that it appears to be an alternative construction for the physical state represented by $|\psi\rangle$. In this particular case $|\psi\rangle$ and $\hat{P}_\psi$ are completely equivalent and one can use either $|\psi\rangle$ or $\hat{P}_\psi$ to represent the state of the system. In such a context (where $\hat{P}_\psi$ is chosen to describe the state of the system) $\hat{P}_\psi$ is also known as the density-operator state with $\mathbf{P}_\psi$ the corresponding density-matrix state expanded in an arbitrary basis. $|\psi\rangle$ is of course more economical, as knowledge of the $N$ components is needed while for $\hat{P}_\psi$ one needs $N^2$ numbers for a complete determination[1]. Obviously, the use of $|\psi\rangle$ is preferred.

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[1] For normalized states since $\langle\psi|\psi\rangle = 1$ the number of unknowns is reduced by one.

Along similar lines as for the algebraic representation of $|\psi\rangle$ and $\langle\psi|$ as one-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 $\mathcal{U}_{ij} = \mathbf{v}_i\mathbf{v}_j^T$,

$$\hat{\mathcal{U}}_{ij} = |v_i\rangle\langle v_j| \quad \leftrightarrow \quad \mathcal{U}_{ij} = \mathbf{v}_i\mathbf{v}_j^T = \begin{bmatrix} 0 & 0 & 0 & 0 & \cdots & 0 \\ 0 & 0 & 0 & 0 & \cdots & 0 \\ \cdots & \cdots & \ldots & \cdots & \cdots & 0 \\ 0 & 0 & \cdots & 1 & \cdots & 0 \\ \cdots & \cdots & \ldots & \cdots & \cdots & 0 \end{bmatrix}, \tag{11.11}$$

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

$$\hat{M} = \sum_{ij} M_{ij}|v_i\rangle\langle v_j| = \sum_{ij} M_{ij}\hat{\mathcal{U}}_{ij} = \sum_{ij} \mathrm{Tr}(\mathbf{M} \cdot \mathcal{U}_{ji})\hat{\mathcal{U}}_{ij}, \tag{11.12}$$

$$\mathbf{M} = \sum_{ij} M_{ij}\mathcal{U}_{ij} = \sum \mathrm{Tr}(\mathbf{M} \cdot \mathcal{U}_{ji})\mathcal{U}_{ij}. \tag{11.13}$$

It is straightforward to confirm that

$$M_{ij} = \mathrm{Tr}(\mathbf{M} \cdot |v_j\rangle\langle v_i|) = \mathrm{Tr}(\mathbf{M} \cdot \mathcal{U}_{ji}). \tag{11.14}$$

With this notation the fundamental $\mathbb{1}_i$ projection operator is defined as $\mathbb{1}_i = |v_i\rangle\langle v_i|$ (obviously $\mathbb{1}_i = \mathbb{1}_i^T$ and $\sum_i \mathbb{1}_i = \mathbb{1}$).

**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, and 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, $\mathbf{x} \rightarrow \hat{x}$ and $\mathbf{p} \rightarrow -\imath\nabla$. 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, however, as one can conclude from 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

$$\hat{Q}|q_n\rangle = q_n|q_n\rangle, \qquad \langle q_n|q_m\rangle = \delta_{nm}. \tag{11.15}$$

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 (11.2), the ket state $|\psi\rangle$ can be expanded in terms of this eigenset:

$$|\psi\rangle = \sum_n c_n |q_n\rangle, \qquad c_n = \langle q_n|\psi\rangle. \tag{11.16}$$

Coefficient $c_n$ has a very precise physical meaning upon measurement of $\mathcal{Q}$. For now, it is necessary to note that the observable $\mathcal{Q}$ is associated with the operator $\hat{Q}$, which acts on $|\psi\rangle$. 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 $\mathcal{Q}$) acts on these states. It turns out that for an observable the conjugate (dual) operator acting in $\mathcal{V}^\star$ satisfies the conjugate eigenvalue equation[2],

$$\langle q_n|\hat{Q} = q_n\langle q_n|, \qquad \langle q_n|q_m\rangle = \delta_{nm}. \tag{11.17}$$

This means that for an arbitrary $|\psi\rangle$ ket or $\langle\psi|$ the action of an observable in the system is fully determined by the use of equations (11.15), (11.16) and (11.17). 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 called Hilbert spaces. A further level of generalization arises when the basis is of infinite dimension. The complication is that eigenvectors $|q_n\rangle$ are not normalized and vector spaces resulting from such bases via equation (11.16) should have inner products that result in probabilities lying necessarily between 0 and 1.

**Deterministic time evolution.** The time development of a quantum state is expressed in equation (11.1) and assigns a special role to the system's Hamiltonian operator. 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 interest; 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). Since a large fraction of the present text refers to this time-evolution law, no further comments will be made here apart from the fact that the Hamiltonian operator is the generator of time displacements and its form guarantees that the state becomes normalized as the system evolves.

**Probabilistic time evolution (measurement).** The action of an arbitrary operator, $\hat{Q}$, on a state $|\psi\rangle$ generally results in a different state, $\hat{Q}|\psi\rangle \to |\phi\rangle$. A measurement can be seen as a special type of time evolution of a quantum system; the system abruptly changes 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 on the system (known as 'collapse of the wavefunction'). Following the measurement, regardless of the state, only one state

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

will survive. No deterministic predictions are possible within the generally accepted interpretation of a quantum measurement. It leads to inconsistencies if pushed further, which is still a matter of debate, but it is not of concern here. Also, it is exactly this postulate that makes QM an inherently probabilistic theory with no way to escape. A readable discussion about the various interpretations of QM can be found in [2] and references therein.

That said, let us now consider a system in a state $|\psi\rangle$ and an observable $\mathcal{Q}$. A measurement of $\mathcal{Q}$ will give the real eigenvalue $q_n$ with probability $P_n$. If $\hat{Q}_n = |q_n\rangle\langle q_n|$,

$$P(q_n) = \langle\psi|\hat{Q}_n|\psi\rangle = \langle\psi|(|q_n\rangle\langle q_n|)|\psi\rangle = \langle q_n|\psi\rangle^\star\langle q_n|\psi\rangle = |\langle q_n|\psi\rangle|^2. \qquad (11.18)$$

The state of the system immediately afterwards is proportional to $|q_n\rangle$. The matrix representation of the projection operator (projector) $\hat{Q}_n$ on the fundamental basis $(\mathcal{U}_{ij})$ is

$$\mathbf{Q}_n = q_n \mathbb{1}_n = \begin{bmatrix} 0 & 0 & 0 & \cdots & \cdots \\ 0 & 0 & 0 & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & q_n & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \end{bmatrix}, \qquad (11.19)$$

where $\mathbb{1}_n$ is the basis projection matrix (see the definition following equations (11.12) and (11.13)). Accordingly, the matrix representation of the operator $\hat{Q}_n$ is given by

$$(Q_n)_{ij} = \langle v_i|\hat{Q}_n|v_j\rangle. \qquad (11.20)$$

The measurement process can be put on a more formal basis as follows[3]:

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

$$P(q_n) = \langle\psi|\hat{Q}_n|\psi\rangle \quad \rightarrow \quad |\psi_n\rangle = \frac{\hat{Q}_n|\psi\rangle}{\sqrt{\langle\psi|\hat{Q}_n|\psi\rangle}}. \qquad (11.21)$$

So far, the discussion has exclusively referred to a formulation of QM with the physical states as elements of an abstract Hilbert space. In the case of familiar three-dimensional space vectors[4], the choice of a particular coordinate system, say $\mathcal{C}$, provides the means for the practical calculations turning the abstract vector relation (such as Newton's second law) into down-to-earth numerical relations between physical quantities. Translation and/or rotation of the coordinate system ($\mathcal{C} \rightarrow \mathcal{C}'$) transforms the original set of components, expressed in ($\mathcal{C}$), in a controlled way, to

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[3] The below definition is suitable for both degenerate and non-degenerate eigenvalue spectra, provided a proper definition of the projection operator, $\hat{Q}_n$, is introduced.

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

another set of components (expressed now in $C'$)[5]. The choice of the coordinate system can greatly facilitate (or not) the numerical computations. Furthermore, the proper choice can offer improved insight on 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? It 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 QM problems as well. The key is that quantum physical states (and operators) live in linear vector spaces and dealing with QM systems, more often than not, a suitable complete basis set must be chosen. The abstract quantum basis set is used to expand the abstract vectors corresponding to the (spatial) coordinate system of classical mechanics. Also, the basis is often dictated by the observable ($Q$) in question and the type of measurement to be performed, and not only the system itself. Fortunately, the operator associated with the observable offers 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.

## 11.2 Statistical matrix state (or density matrix)

It was seen previously that for a quantum system, $\mathcal{S}$, in the state $|\psi\rangle$, the associated projector $\hat{P}_\psi$ contains the exact same information about the system as the state $|\psi\rangle$. This was seen during the derivation of equation (11.10). In this case one can calculate the expectation value of an observable $Q$ as $\langle Q \rangle_\psi$ together with its variance $\langle (\Delta Q)^2 \rangle$ (11.55). That is to say that, despite the fact that the $\mathcal{S}$ system is in a definite state $|\psi\rangle$, generally the measurements of an arbitrary observable are expected to be distributed in a statistical sense[6]. The outcome of a measurement of $\hat{Q}$ on one quantum system in state $|\psi\rangle$ can result in different values. The causality principle does not always apply in QM since cause and effect do not have a one-to-one relation; these quantum events can only be described statistically. This is an inherent obstacle, that it cannot be lifted within the current form of QM. Apart from this fundamental issue of the theory, more often than not the system's state is not *a priori* surely known; one may know that the system is in state $|\psi_1\rangle$ with probability $w_1$, in state $|\psi_2\rangle$ with probability $w_2$, and so on. This more general case cannot be written as a linear combination of $|\psi_n\rangle$, $n = 1, 2, \ldots$; so a question arises: how is a system in this *mixture* of states treated quantum mechanically? We can discriminate between the two different levels of knowledge we have for the system by saying that the system is in a *pure* state (where the system can be characterized by a single vector of the Hilbert space) while in the second case the system is in a *mixed* state (where the

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[5] Of course, the relations between the involved set of components remain as dictated by the laws of physics. For example, for a particle of mass $m$ subject to a force governed by Newton's second law, the ratio between acceleration and force will still be equal to the particle's mass, regardless of which coordinate system happens to be in use, ($C$) or $C'$.

[6] Only when the state $|\psi\rangle$ is an eigenstate of $\hat{Q}$ do we have a sure value or equivalently $\langle \Delta Q^2 \rangle = 0$.

system has a probability distribution over a possible set of Hilbert-state vectors). We ask for a formulation of the quantum mechanics where these fundamentally different states are treated on an equal footing. The solution to this is to generalize the projection operator ($\hat{P}_\psi$) to a more general physical quantity, known as the density operator (or statistical operator), introduced by von Neumann [3]. This operator is generally used to describe all the (statistical) properties of any arbitrary operator within the QM theory. Based on this observation, the density-state operator $\hat{\rho}$ and the above formulation is an alternative to the 'traditional' *vector state* $|\psi\rangle$. The interested reader can find relevant information in the textbooks [1, 3–7].

### 11.2.1 Density-state operator

As there are a few different ways of defining the density-state operator for a QM system[7], one needs to choose. For pedagogical reasons, the current choice is to introduce the density-state operator in two ways, dependent on the quantum system in question. If the system is in a known state $\mathcal{S}$ state $|\psi\rangle$ (a *pure* state), as was the case so far, then the density-state operator will be defined in terms of vector states of a Hilbert space. Here, this approach is called *quantum mechanical*. However, when the system is initially in a state that is known only in a statistical sense (the system can possess a range of states with some probability) then the choice is to introduce the density-state operator as a method of calculating the statistical properties of an ensemble of identical quantum systems[8]. This latter approach will be called *statistical*, and most likely this is the reason that the density-state operator is also called the *statistical* operator. This particular method has its origin in the methods developed in statistical mechanics prior to QM. The third method, introduced by Fano [4], known as the *operational approach*, relies on the measurement of the mean values of some properly chosen physical quantities for the determination of the density operator. A detailed and comparative discussion of these three methods can be found in the early work by Ter Haar [5].

**Pure state.** Assume a system $\mathcal{S}$ in a particular state $|\psi_i\rangle$. Next, assume a set of orthogonal eigenstates of some *complete set of physical operators* (CSOP)[9], say $\hat{\Omega}_k$, $k = 1, 2, \ldots$, such as

$$\langle\phi_n|\phi_m\rangle = \delta_{nm}, \qquad \sum_n |c_n|^2 = 1, \qquad n = 1, 2, \ldots, N.$$

We take the general case where the state $|\psi_i\rangle$ is not in any of the states $|\phi_n\rangle$; however, it can still be expressed in terms of the eigenstates, $|\phi_n\rangle$,

$$|\psi_i\rangle = \sum_n c_n^{(i)}|\phi_n\rangle. \tag{11.22}$$

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[7] Of course all these different definitions should lead to the same predictions when the same problem is treated.
[8] As was first introduced by von Neumann in his monograph [3].
[9] The CSOP includes all observables with a common eigenstate basis.

Obviously the use of the superscript $i$ is to declare that the expansion coefficients $c_n^{(i)}$ are associated with the state $|\psi_i\rangle$. The expectation value (or equivalently mean value) of a physical quantity $\mathcal{Q}$ is calculated as

$$\langle\hat{Q}\rangle_i = \langle\psi_i|\hat{Q}|\psi_i\rangle = \sum_{m,n} c_m^{(i)\star} c_n^{(i)} Q_{mn}, \qquad Q_{mn} = \langle\phi_m|\hat{Q}|\phi_n\rangle. \tag{11.23}$$

The above (purely quantum) averaging (expectation value of $\hat{Q}$) of a physical observable ($\mathcal{Q}$) for a quantum system ($\mathcal{S}$) in a particular state $|\psi_i\rangle$ is a (*coherent*) summation over the eigenstate members of the $\hat{\Omega}_k$ set of operators. *Coherent* here is used in the sense that knowledge of the (complex) amplitudes $c_n$ is necessary for the averaging to be performed. In this context, the use of *incoherent* would mean that knowledge of the (real) absolute square of amplitudes, $|c_n|^2$, would suffice to perform the averaging. So quantum averaging is a *coherent* process.

**Mixed state.** Now, assume that there is lack of knowledge as to whether the system is in state $|\psi_i\rangle$ or not[10]. Therefore, the system has a probability $w_i$ to be in state $|\psi_i\rangle$. Let us now denote the mixture state by $(\psi_i, w_i)$ $i = 1, 2, \ldots, N$. The ensemble average of the QM expectation value (11.23) results in an overall expectation value for $\hat{Q}$:

$$\langle\hat{Q}\rangle = \sum_i w_i \langle\hat{Q}\rangle_i. \tag{11.24}$$

The above, with the help of equation (11.14), maybe re-written as

$$\langle\hat{Q}\rangle = \sum_i w_i \langle\hat{Q}\rangle_i = \sum_i w_i \langle i|\hat{Q}|i\rangle$$

$$= \sum_i w_i \, \mathrm{Tr}(\hat{Q}|i\rangle\langle i|) = \mathrm{Tr}\left(\hat{Q}\sum_i w_i|i\rangle\langle i|\right).$$

Now, if we define the density-state operator as

$$\hat{\rho} = \sum_i w_i|\psi_i\rangle\langle\psi_i|, \tag{11.25}$$

the expectation value of any physical operator is obtained by[11]

$$\langle\hat{Q}\rangle = \mathrm{Tr}(\boldsymbol{\rho} \cdot \mathbf{Q}), \tag{11.26}$$

where $\mathrm{Tr}(\mathbf{M})$ denotes the trace of the matrix $\mathbf{M}$. The above property of the density operator encapsulates two types of averaging into one: a quantum coherent

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[10] This is the most common case, of course. Nevertheless, one can obtain a certain knowledge at this level by preparing the system through the measurement of the observable of which that state is an eigenstate. For example, to prepare an electron in a plane-wave state $|\mathbf{k}m_s\rangle$ we must perform a measurement of its momentum (in three directions) together with a measurement of its spin projection along some axis.

[11] This relation can also be considered as a definition of the density operator of a system.

averaging in state $|i\rangle$ followed by a classical incoherent weighted (with $w_i$) averaging over the states $|i\rangle$, $i = 1, \ldots, N$.

In the special case of a system in a pure state $|k\rangle$ (a mixed state where $w_i = \delta_{ik}$), the grand average is reduced to include only the quantum average,

$$\langle \hat{Q} \rangle = \sum_i \delta_{ki} \langle \hat{Q} \rangle_i = \langle \hat{Q} \rangle_k = \langle k | \hat{Q} | k \rangle,$$

while the expression of the density operator in this pure state takes the form of a projection operator:

$$\hat{\rho}_k = |k\rangle\langle k|. \tag{11.27}$$

Below are given some general properties of the density operator which are useful to keep in mind:

$$\rho = \rho^*, \quad \mathrm{Tr}(\rho) = 1, \quad 0 \leqslant \mathrm{Tr}(\rho^2) \leqslant 1, \quad (\rho^2 = \rho, \quad \text{for a pure state}).$$

Transformation of the density matrix via the change of the CSOP representation (or base representation) follows the standard transformation rule:

$$\rho' = S^{-1}\rho S, \qquad S \text{ is unitary}, \tag{11.28}$$

where $\rho'$ is the representation of the density-operator state in the basis $|\phi'_n\rangle$ (the basis of a CSOP $\hat{Q}'_k$, $k = 1, 2, \ldots$), while $\rho$ is the corresponding representation in the basis $|\phi_n\rangle$ of the $\hat{Q}_k$ CSOP and $S$ is a unitary transformation matrix[12].

**Time development.** Within the Schrödinger picture the state of the system is time-dependent (TD), while the operator of a physical observable is constant. A similar property should be true for the density-operator state of the system. It has to be, in general, TD since it actually represents the state of the system. It is straightforward to show that the time evolution of the density-operator state $\hat{\rho}$ is given by

$$\iota \frac{d}{dt}\hat{\rho}(t) = [\hat{H}, \hat{\rho}(t)]. \tag{11.29}$$

The above equation replaces the time-dependent Schrödinger equation (TDSE) as a dynamical equation. In contrast to the operators of a physical observable, the density-operator state of a system in the Schrödinger picture (SP) is, in the general case, a TD quantity. In the Heisenberg picture, since the state vector $|\psi\rangle$ is time-independent, the same should hold (and can be shown to be true) for the density-operator state. It is worth noting that the time-evolution law of the density operator has the same form as the equation of motion of the observable operators in the Heisenberg picture, *but with the opposite sign*.

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[12] Unitarity is imposed by the fact that $\mathrm{Tr}(\rho') = \mathrm{Tr}(\rho) = 1$.

## 11.3 Position representation

We can specialize the above discussion and take as $|i\rangle$ the eigenstates of the position quantum operator, $\hat{\mathbf{r}}$.[13] The position operator is, genuinely, a continuous-spectrum operator. For our purposes we have to adopt a continuum notation for the index $i$, assuming that $|i\rangle \to |\mathbf{r}_i\rangle \to |\mathbf{r}\rangle$, we have

$$\hat{\mathbf{r}}|\mathbf{r}\rangle = \mathbf{r}|\mathbf{r}\rangle, \qquad \int d\mathbf{r}\, |\mathbf{r}\rangle\langle\mathbf{r}| = \mathbb{1} \qquad \langle\mathbf{r}'|\mathbf{r}\rangle = \delta(\mathbf{r}' - \mathbf{r}). \qquad (11.30)$$

Multiplying the completeness relation from the right by the ket $|\psi\rangle$ we obtain

$$|\psi\rangle = \int d\mathbf{r}\, |\mathbf{r}\rangle\langle\mathbf{r}|\psi\rangle = \int d\mathbf{r}\, \psi(\mathbf{r})|\mathbf{r}\rangle. \qquad (11.31)$$

Direct comparison of the above expansion on the $|\mathbf{r}\rangle$ basis, with the abstract state vector expansion of equation (11.2), relates the basis coefficients $c_i(t)$ as $c_i \to \psi(\mathbf{r})$ and, as such,

$$\psi(\mathbf{r}) = \langle\mathbf{r}|\psi\rangle. \qquad (11.32)$$

This equation, apart from a formal definition of a system's wavefunction in the position representation, is also a confirmation that the wavefunction values $\psi(\mathbf{r})$ can also be interpreted as the expansion coefficients of the state vector in the position's operator basis [2]. For the above function to have a legal role within QM it is vital to obey

$$\int d\mathbf{r}\, |\psi(\mathbf{r})|^2 < \infty. \qquad (11.33)$$

It is only then that $|\psi(\mathbf{r})|^2$ can be interpreted as a probability distribution of the particle's position[14]. It is desirable now to derive the evolution law in this representation. Since the spectrum of the position operator is continuous, there are no any discrete sums in the expressions for the state vector's TDSE. For quantum systems with a classical analogue, the Hamiltonian will be some function of the particle's position and momentum. The classical expression turns into a quantum mechanical operator by assigning the transformations[15]

$$\mathbf{r} \to \hat{\mathbf{r}}, \qquad \mathbf{p} \to -\imath\nabla_{\mathbf{r}}. \qquad (11.34)$$

We then have for the overlap matrix elements and the Hamiltonian matrix elements,

$$\langle\mathbf{r}|\hat{H}|\mathbf{r}'\rangle = \hat{H}(\mathbf{r}, -\imath\nabla_{\mathbf{r}})\delta(\mathbf{r}' - \mathbf{r}) = \hat{H}(\mathbf{r}', -\imath\nabla_{\mathbf{r}'})\delta(\mathbf{r}' - \mathbf{r}). \qquad (11.35)$$

Take the inner product of equation (11.1) with $|\mathbf{r}\rangle$ (in loose language, multiplying from the left by the bra $\langle\mathbf{r}|$), followed by integration all over the space by

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[13] Note the difference between $\hat{\mathbf{r}}$, $\hat{r}$ and $\mathbf{r}$. The first represents the position operator while the second represents the unit vector along the direction pointed to by the position vector $\mathbf{r}$.

[14] In fact, it is the integral that should be finite and not $|\psi(\mathbf{r})|^2$ itself.

[15] Because the action of $\hat{\mathbf{r}}$ is to multiply the ket position vectors (11.30) by $\mathbf{r}$, one may use $\mathbf{r}$ to represent either the classical position vector or the quantum position operator.

$$\iota\frac{\partial}{\partial t}\langle\mathbf{r}|\psi(t)\rangle = \langle\mathbf{r}|\hat{H}|\psi\rangle = \langle\mathbf{r}|\hat{H}(\mathbb{1})|\psi(t)\rangle$$

$$= \langle\mathbf{r}|\hat{H}\left(\int d\mathbf{r}\,'|\mathbf{r}'\rangle\langle\mathbf{r}'|\right)|\psi(t)\rangle = \int d\mathbf{r}\,'\langle\mathbf{r}|\hat{H}|\mathbf{r}'\rangle\langle\mathbf{r}'|\psi(t)\rangle$$

$$= \int d\mathbf{r}\,'\hat{H}(\mathbf{r}', -\iota\nabla_{\mathbf{r}'})\delta(\mathbf{r}' - \mathbf{r})\psi(\mathbf{r}', t) = \hat{H}(\mathbf{r}, -\iota\nabla_{\mathbf{r}})\psi(\mathbf{r}, t),$$

where equations (11.30) and (11.35) were used. So, we arrived at the familiar TDSE expressed as a partial differential equation in space and time:

$$\iota\frac{\partial}{\partial t}\psi(\mathbf{r}, t) = \hat{H}(\mathbf{r}, -\iota\nabla_{\mathbf{r}})\psi(\mathbf{r}, t), \qquad \psi(\mathbf{r}, t_0) = \psi_0(\mathbf{r}). \qquad (11.36)$$

where by definition, $\psi_0(\mathbf{r}) \equiv \langle\mathbf{r}|\psi(t_0)\rangle$ is known. In the final expression for the TDSE, the time has been explicitly added to emphasize the fact that the Hamiltonian can be an explicit function of time as well. This is true when the quantum system is interacting with an external agent (e.g. the electro-magnetic field). The Hamiltonians of particular interest are those that can be split into a time-independent part plus a TD part. We will generally denote the former by $\hat{H}_0$ and the second by $\hat{V}(t)$, allowing us to write the full system's Hamiltonian as

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t). \qquad (11.37)$$

In the context of atomic and molecular physics, $\hat{H}_0$ could represent the atomic or molecular Hamiltonian, free from any external interactions. We call external interactions the interactions with the environment, either static or TD. For example, placing an atom in a region of a constant magnetic or electric field is a static external interaction. On the other hand, irradiation of an atom or molecule by a laser pulse represents an external TD interaction. Provided that such a separation is in place we arrive at our final form of the TDSE in the position representation,

$$\iota\frac{\partial}{\partial t}\psi(\mathbf{r}, t) = [\hat{H}_0(\hat{\mathbf{r}}, \hat{\mathbf{p}}, t) + \hat{V}(\hat{\mathbf{r}}, \hat{\mathbf{p}}, t)]\psi(\mathbf{r}, t), \qquad \psi(\mathbf{r}, t_0) = \psi_0(\mathbf{r}), \qquad (11.38)$$

with $\mathbf{p} = -\iota\nabla$ the momentum operator in the position representation. At last, it is mentioned here that the physical meaning of the wavefunction $\psi(\mathbf{r}, t)$ derives from Born's statistical interpretation of $|\psi(\mathbf{r}, t)|^2 dv_r$ as the probability for a particle to be observed in the elementary volume, $dv_r$, centered at position $\mathbf{r}$ at time $t$.

## 11.4 Degenerate systems

In the discussion of the time evolution and measurement(s) of a system no mention was made of the possibility that an operator's eigenvalue could correspond to different eigenstates of the system. For such cases some proper amendments are in place, however, these are not always trivial. It might be better to show how one can work with such systems by using a concrete example. In doing this, let us take a quantum system with three possible states with two of them doubly degenerate. We consider the degenerate states to be energetically higher than the non-degenerate states. If the system's Hamiltonian is $\hat{H}$, the above considerations are expressed as

$\hat{H}|\phi_i\rangle = \epsilon_i|\phi_i\rangle$, $i = 1 - 3$ with $\epsilon_2 = \epsilon_3$. For these states the following orthonormal relations hold,

$$\langle \phi_n^{(i)}|\phi_m^{(j)}\rangle = \delta_{ij}\delta_{nm}, \qquad \sum_{i=1}^{g_i}\sum_{n=1}^{N}|\phi_n^{(i)}\rangle\langle\phi_n^{(i)}| = \mathbb{1}. \qquad (11.39)$$

For our case, we have $N = 2$, $g_1 = 1$, $g_2 = 2$. To simplify the discussion let us set $\epsilon_i = \omega_0$ and $\epsilon_2 = \epsilon_3 = 2\omega_0$. Also, the system is initially in a normalized (coherent) superposition of the above states, for example

$$|\psi_0\rangle = \sum_n c_n|\phi_n\rangle, \qquad c_2 = c_3 = \frac{1}{2}. \qquad (11.40)$$

Next we consider the observables $\mathcal{H}$ and $\mathcal{Q}$. We wish to examine the results of some measurements made on this system.

**Energy measurement.** The operator of the energy observable $\mathcal{H}$ is the Hamiltonian operator, $\hat{H}$. Let us assume that the energy measurement takes place at time $t_0 = 0$. The question is what results one should expect and how probable they are. The first thing to do is to determine the state at the time of observation which is given by equation (11.40). Since the state is normalized the absolute value of $c_1$ is easily calculated by

$$\sum_n |c_n|^2 = 1 \quad \rightarrow \quad |c_1|^2 + 2\frac{1}{4} = 1 \quad \rightarrow \quad c_1 = \frac{e^{i\theta}}{\sqrt{2}},$$

where $\theta$ is of real value but unknown. Nevertheless, a good amount of information can still be extracted. So the initial state is

$$|\psi_0\rangle = \frac{e^{i\theta}}{\sqrt{2}}|\phi_1\rangle + \frac{1}{2}|\phi_2\rangle + \frac{1}{2}|\phi_3\rangle. \qquad (11.41)$$

Energy measurement can provide only the two eigenvalues of $\hat{H}$, $\omega_0$ and $2\omega_0$ with some probability. These probabilities can be found from the generalized definition of the projection operator, $\hat{Q}_n$,

$$\hat{Q}_n = \sum_i^{g_i}|\phi_n^{(i)}\rangle\langle\phi_n^{(i)}|, \qquad (11.42)$$

$$P(q_n) = \langle\psi|\hat{Q}_n|\psi\rangle = \sum_i^{g_i}|\langle\phi_n^{(i)}|\psi\rangle|^2. \qquad (11.43)$$

In the particular case we examine we have

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

Similarly, for the second energy eigenvalue we obtain

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

It is relatively trivial to calculate the expectation value of the Hamiltonian operator (the mean energy of the system) by

$$\langle \hat{H} \rangle = \langle \psi_0 | \hat{H} | \psi_0 \rangle = \left( \frac{e^{-\iota\theta}}{\sqrt{2}} \langle \phi_1 | + \frac{1}{2} \langle \phi_2 | + \frac{1}{2} \langle \phi_3 | \right) \hat{H}$$

$$\times \left( \frac{e^{\iota\theta}}{\sqrt{2}} | \phi_1 \rangle + \frac{1}{2} | \phi_2 \rangle + \frac{1}{2} | \phi_3 \rangle \right)$$

$$= \cdots = \frac{1}{2} \epsilon_1 + \frac{1}{4} \epsilon_2 + \frac{1}{4} \epsilon_3$$

$$= \frac{1}{2} \omega_0 + \frac{1}{4} (2\omega_0) + \frac{1}{4} (2\omega_0) = \frac{3}{2} \omega_0.$$

The $\cdots$ in the above calculations represent the calculation of the inner products $\langle \phi_n^{(i)} | \phi_m^{(j)} \rangle$ according the orthonormality rules of equation (11.39). An alternative, fast track, calculation of the mean energy value can be obtained by relying on matrix operations if we decide to represent operators and vectors on the (fundamental) vector basis (11.5). Then,

$$\mathbf{H} = \omega_0 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix}, \qquad |\psi\rangle = \frac{1}{2} \begin{pmatrix} e^{\iota\theta} \sqrt{2} \\ 1 \\ 1 \end{pmatrix}. \tag{11.44}$$

We then immediately obtain

$$\langle \hat{H} \rangle = \langle \psi_0 | \hat{H} | \psi_0 \rangle$$

$$= \left[ \frac{1}{2} \left( \sqrt{2} e^{-\iota\theta}, 1, 1 \right) \right] \cdot \left[ \omega_0 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix} \right] \cdot \left[ \frac{1}{2} \begin{pmatrix} \sqrt{2} e^{\iota\theta} \\ 1 \\ 1 \end{pmatrix} \right] = \frac{3}{2} \omega_0.$$

The standard deviation of the system's energy at that particular time may be found by calculating $\Delta E$ using the well known statistical formula

$$(\Delta Q_\psi)^2 = \langle \psi | (\hat{Q} - \langle Q \rangle_\psi)^2 | \psi \rangle = \langle Q^2 \rangle_\psi - \langle Q \rangle_\psi^2 \neq 0. \tag{11.45}$$

Replacing $\hat{Q}$ by $\hat{H}$ followed by calculation either using the analytical approach or the matrix representation approach[16] should end up with $\Delta E = \omega_0/2$.

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[16] Left as an exercise for the reader to familiarize with the algebraic operations involved.

$\mathcal{Q}$ **measurement.** Now we repeat the same question for an observable $\mathcal{Q}$. As an example we specify its matrix representation on the fundamental ket basis and take it as

$$\mathbf{Q} = q \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}. \tag{11.46}$$

The measurement outcomes and the associated probabilities are determined from the corresponding eigenvalue problem (11.15). Since a matrix representation of the operator is available a standard matrix diagonalization suffices to find the observable's eigenvalues:

$$(\mathbf{Q} - q_n \mathbb{1})|q_n\rangle = 0, \qquad \rightarrow \qquad \begin{pmatrix} q - q_n & 0 & 0 \\ 0 & -q_n & q \\ 0 & q & -q_n \end{pmatrix} \cdot \begin{pmatrix} q_{n1} \\ q_{n2} \\ q_{n2} \end{pmatrix} = 0, \tag{11.47}$$

with $q_{ni}$ the $i$th component of the $n$th eigenvalue ($q_n$). The possible eigenvalues can be simply found as the roots of the $(\mathbf{Q} - q_n \mathbb{1})$ matrix:

$$det(\mathbf{Q} - q_n \mathbb{1}) = 0 \rightarrow (q - q_n)(q^2 - q_n^2) = 0$$
$$\rightarrow (q - q_n)^2(q + q_n) = 0 \rightarrow q_n = \pm q.$$

So one eigenvalue, $q_1 = -q$, is non-degenerate and this allows us to assign one single ket to it, say $|q_1\rangle$,

$$\hat{Q}|q_1\rangle = q|q_1\rangle.$$

The other eigenvalue, $q_2 = q$, is doubly degenerate and is associated with all kets belonging to a special two-dimensional Hilbert space (which is determined as long as we determine two kets belonging to this subspace). Let us call two of these states $|q_2\rangle = |u_2^{(1)}\rangle$ and $|q_3\rangle = |u_2^{(2)}\rangle$. Thus, for the second eigenvalue we have, for any complex values of $a$, $b$,

$$|u\rangle = a|q_2\rangle + b|q_3\rangle \qquad \rightarrow \qquad \hat{Q}|u\rangle = q|u\rangle. \tag{11.48}$$

At this point it is left as an exercise for the reader to calculate the normalized eigenvectors, $|q_1\rangle$, $|q_2\rangle$, $|q_3\rangle$, representing these quantum states on the fundamental vector set as[17]

$$|q_1\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix}, \qquad |q_2\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix}, \qquad |q_3\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}. \tag{11.49}$$

It is trivially seen that $\langle q_i|q_j\rangle = \delta_{ij}$ for any combination of $i, j = 1 - 3$. Now one is in a position to calculate the probabilities for the measurement outcomes of $\mathcal{Q}$ exactly

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[17] Unless explicitly stated, it will be assumed that matrix representations are on this basis.

the same way as used for the energy measurement. Nevertheless, for pedagogical reasons, the matrix form of equation (11.43) will be used. So first, using equation (11.42) the matrix representation of the projection operators are calculated as

$$\mathbf{Q}_1 = M(|q_1\rangle\langle q_1|) = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix}\frac{1}{\sqrt{2}}(0, 1, -1) = \frac{1}{2}\begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & -1 \\ 0 & -1 & 1 \end{pmatrix}, \qquad (11.50)$$

$$\mathbf{Q}_2 = M\left(\sum_{i=2,3}|q_i\rangle\langle q_i|\right) = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix}\frac{1}{\sqrt{2}}(0, 1, 1) + (1, 0, 0)\cdot\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$$

$$= \frac{1}{2}\begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 1 \\ 0 & 1 & 1 \end{pmatrix} + \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 2 & 0 & 0 \\ 0 & 1 & 1 \\ 0 & 1 & 1 \end{pmatrix}.$$

Based on the above[18], using equation (11.43), we obtain

$$P(-q) = \langle\psi_0|\hat{Q}_1|\psi_0\rangle = \frac{1}{2}\left(\sqrt{2}e^{-\iota\theta}, 1, 1\right)\cdot\frac{1}{2}\begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & -1 \\ 0 & -1 & 1 \end{pmatrix}\cdot\frac{1}{2}\begin{pmatrix} \sqrt{2}e^{\iota\theta} \\ 1 \\ 1 \end{pmatrix} = 0$$

and

$$P(q) = \langle\psi_0|\hat{Q}_2|\psi_0\rangle = \frac{1}{2}\left(\sqrt{2}e^{-\iota\theta}, 1, 1\right)\cdot\frac{1}{2}\begin{pmatrix} 2 & 0 & 0 \\ 0 & 1 & 1 \\ 0 & 1 & 1 \end{pmatrix}\cdot\frac{1}{2}\begin{pmatrix} \sqrt{2}e^{\iota\theta} \\ 1 \\ 1 \end{pmatrix} = 1.$$

Of course, the last result could have been derived by noting that only two eigenvalues are possible and as such $P(-q) + P(q) = 1$. We could have predicted that a measurement of $Q$ will give the value $q$ with certainty since $|\psi_0\rangle$ belongs to the relevant subspace (11.48) with $a = 1/\sqrt{2}$ and $b = e^{\iota\theta}/\sqrt{2}$. Noting that the operator $\hat{Q}$ commutes with the Hamiltonian $\hat{H}$,[19] we may predict that if we had waited and performed the measurement not at time $t_0 = 0$ but at a later time $t$, then the outcome would have been again $q$ with certainty. This is because $|\psi_0\rangle$ belongs to the $q$-subspace.

## 11.5 Homework problems

**Problem 11.1.** *Probability distribution current.* Assume the state of a particle in position representation, $\psi(\mathbf{r}, t)$, and define the probability distribution as $\rho(\mathbf{r}, t) = \langle\psi|\psi\rangle = |\psi(\mathbf{r}, t)|^2$. Show that a continuity equation holds for the time evolution of the probability distribution leading to an associated probability current distribution

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[18] Note that we could have calculated $\mathbf{Q}_2$ more easily from $\mathbf{Q}_1 + \mathbf{Q}_2 = \mathbb{1}$ since $\sum_n \hat{Q}_n = \mathbb{1}$.

[19] It can be checked simply by confirming that for the corresponding matrices $\mathbf{HQ} = \mathbf{QH}$ holds.

$$\frac{\partial}{\partial t}\rho(\mathbf{r}, t) + \nabla\hat{\mathbf{j}}(\mathbf{r}, t) = 0, \qquad \hat{\mathbf{j}}(\mathbf{r}, t) = \text{Re}[\psi^\star(\mathbf{r}, t)\hat{\mathbf{p}}\psi(\mathbf{r}.t)]. \qquad (11.51)$$

**Problem 11.2.** *Calculation of eigenvectors.* Consider the matrices of the observables $\mathcal{H}$ and $\mathcal{Q}$ of section 11.4 and the initial state at time $t = 0$, $|\psi_0\rangle$ given by equation (11.41) with $\theta = 0$. In addition, consider the observable $\mathcal{Q}'$ defined by

$$\mathbf{Q}' = q'\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \qquad (11.52)$$

(a) Show that $[\hat{H}, \hat{Q}'] \neq 0$.
(b) What is the state vector at time $t$ and what are the expectation values for the system's energy and observables $\mathcal{Q}$ and $\mathcal{Q}'$? You may use the general QM formula $\langle Q\rangle(t) = \langle\psi|\hat{Q}|\psi\rangle$.
(c) A measurement of $\mathcal{Q}$ and $\mathcal{Q}'$ takes place at time $t = 0$. Find the possible outcomes for each of the observables and the corresponding probabilities.
(d) The above measurements, instead of being taken at time $t = 0$, take place at a later time $t > 0$. Similarly, find the possible outcomes for each of the observables and the corresponding probabilities. How do they differ from the results of question 11.2 (c) above? Comment on your observations.

**Problem 11.3.** *Calculation of eigenvectors.* Consider the matrices of the observables $\mathcal{H}$ and $\mathcal{Q}$ of section 11.4.

(a) Show that $[\hat{H}, \hat{Q}] = 0$.
(b) Determine their eigenvalues and the corresponding eigenvectors within an undetermined phase factor. For convenience, set the phase equal to zero for all eigenvectors.
(c) For the Hamiltonian operator name the three eigenkets $|e_i\rangle$, $i = 1 - 3$ and form the matrix, $\mathbf{S} = [\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3]$. Show that

$$\mathbf{H}_d = \mathbf{S}\mathbf{H}\mathbf{S}^{-1}$$

is a diagonal matrix. Similarly, show that $\mathbf{Q}_d = \mathbf{S}\mathbf{Q}\mathbf{S}^{-1}$. The above property of the matrices $\mathbf{S}$ formed by the eigenvectors of an operator provide a brute-force recipe for the transformation of an arbitrary matrix to a diagonal one.

**Problem 11.4.** *Expectation and variance of observables in a pure state.* Consider a system $\mathcal{S}$ in the pure state $|\psi\rangle$ and the observable $\mathcal{Q}$. Using the eigenvalue equations (11.2), (11.15) and (11.17) show that:
If the $|i\rangle$ is an eigenbasis of $Q$ then a simplified expression for the mean is

$$\langle Q \rangle_\psi = \sum_n \rho_{ii} q_i \tag{11.53}$$

and for the variance,

$$\Delta Q_\psi = \langle \psi | (\hat{Q} - \langle Q \rangle_\psi)^2 | \psi \rangle = \langle Q^2 \rangle_\psi - \langle Q \rangle_\psi^2 \neq 0. \tag{11.54}$$

**Problem 11.5.** *Expectation and variance of an observable in a mixture of states.* Consider a system $\mathcal{S}$ in the mixture of states $(|i\rangle, w_i)$ $i = 1, 2, \ldots, N$ and the observable $\mathcal{Q}$. Show that the expectation value for $\mathcal{Q}$ is

$$\langle Q \rangle = \sum_i w_i \langle Q \rangle_i, \tag{11.55}$$

where $\langle Q \rangle_i$ is given by equation (11.53) for $|\psi\rangle = |i\rangle$. The above results show that the mean value of any operator $\hat{Q}$ is a linear combination of the expectation values of the base operators $\hat{P}_i$.

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