# Contents

**1 Quantum States** **1**

1.1 Quantum mechanics describes physical systems using states. . . . 2

1.1.1 A set of basis states describes the possible states of a system. 2

1.2 Quantum states can be represented concisely using Dirac ("bra-ket") notation. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 3

1.2.1 A "ket", $|\psi\rangle$, represents assertions about a state. . . . . . 3

1.2.2 A "bra", $\langle\phi|$, represents questions about a state. . . . . . 5

1.2.3 Arbitrary quantum states are described by linear combinations of basis states. . . . . . . . . . . . . . . . . . . . . 6

1.2.4 Bras and kets are related by Hermitian conjugation. . . . 8

1.2.5 Arithmetic on bra and ket pairs for arbitrary states can be determined in terms of a shared basis. . . . . . . . . . 10

1.2.6 Combinations of system can be expressed using tensor products of states. . . . . . . . . . . . . . . . . . . . . . 11

1.2.7 Entangled states describe unfactorizable multi-state systems 12

1.3 Chemical systems are described using quantum states. . . . . . . 12

1.3.1 A two-state model describes spin-1/2 particles such as electron and nuclear spins. . . . . . . . . . . . . . . . . . 12

1.3.2 Atomic orbitals are basis states describing an electron in an atom. . . . . . . . . . . . . . . . . . . . . . . . . . . 13

1.3.3 Hybrid atomic orbitals are linear combinations of atomic orbital basis states. . . . . . . . . . . . . . . . . . . . . . . 14

1.3.4 Molecular orbitals describe an electron in a molecule using a linear combination of atomic orbital basis functions. . . 16

1.3.5 The set of possible position basis states describes the location of a particular particle. . . . . . . . . . . . . . . . 17

1.3.6 There is no unique set of basis states for describing a physical system. . . . . . . . . . . . . . . . . . . . . . . . 18

**2 Measurement** **25**

2.1 Quantum states express knowledge about the actual state of a system. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 25

2.1.1 Quantum states can be interpreted as guesses about actual state of a system. . . . . . . . . . . . . . . . . . . . . . 26

2.1.2 Quantum states can be constructed from probabilistic prior knowledge. 28
2.1.3 Learning the system's actual state updates the best possible guess. 28
2.1.4 The same strategy is generalizable to any number of possible answer states. 29
2.2 Projectors express general questions about quantum states and measurements. 29
2.2.1 Sums of projectors represent arbitrary queries about quantum states. 31
2.2.2 Multiple applications of a projector leaves the state unchanged. 32
2.2.3 Applying the sum of all projectors leaves the system unchanged. 33
2.2.4 Projectors for multi-particle systems can be composed using the tensor product. 33
2.3 Quantum states may express indeterminacy of the physical system. 34
2.3.1 The $\psi$-ontic and $\psi$-epistemic interpretations make the same predictions. 34
2.3.2 In the $\psi$-ontic interpretation, measurement collapses the system's state to the observed state. 35
2.4 Classic examples of quantum measurement 36
2.4.1 The Stern-Gerlach Experiment 36
2.4.2 Schrödinger's Cat 40
2.4.3 The Two Slit Experiment 41
2.4.4 Bell Inequalities 41
2.4.5 Quantum Pseudo-Telepathy 41
2.5 Appendix: The Born Postulate is a consequence of probability and the definition of states. 42

**3 Operators** **47**
3.1 Operators define relationships between states. 47
3.1.1 Operators can be described as a set of rules. 48
3.1.2 Valid operators are linear. 49
3.1.3 Valid operators are Hermitian. 50
3.1.4 Operators describing a transformation are unitary. 51
3.1.5 Operators are often non-commutative. 52
3.1.6 Operators have characteristic eigenstates and eigenvalues. 53
3.2 Operators can be expressed using projectors. 54
3.2.1 Eigenstates and eigenvalues provide an alternative description of the operator. 55
3.3 Every experimentally observable property has a corresponding quantum operator. 56
3.3.1 Only the eigenvalues and eigenstates of the corresponding operator are observed when performing an experimental measurement. 57

3.3.2 Expectation values, $\langle\psi|\hat{O}|\psi\rangle$, describe the average value of an observable attribute for a state $|\psi\rangle$ . . . . . . . . . . 58
3.4 Operators for chemical systems . . . . . . . . . . . . . . . . . . . . 59
3.4.1 Spin-1/2 . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 59
3.4.2 Single spin in a magnetic field . . . . . . . . . . . . . . . . 59
3.4.3 The sequential Stern-Gerlach experiment described in terms of measurement operators. . . . . . . . . . . . . . . . . . . . 61
3.4.4 Two non-interacting, distinguishable spins. . . . . . . . . . 61
3.4.5 Two weakly-interacting, distinguishable spins . . . . . . . 62
3.4.6 Atomic orbitals are energy eigenstates for free atoms. . . 64
3.4.7 Molecular orbitals are energy eigenstates for molecules. . 66
3.4.8 Position operator . . . . . . . . . . . . . . . . . . . . . . . . 68
3.5 Appendix: The No-Cloning Theorem is a consequence of operator linearity. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 68

**4 Representations of States and Operators 75**

4.1 Linear algebra provides a natural representation of discrete states. 75
4.1.1 Vectors represent states. . . . . . . . . . . . . . . . . . . . 75
4.1.2 The vector dot-product performs overlap calculations for states with orthonormal basis states. . . . . . . . . . . . 77
4.1.3 Matrices represent operators. . . . . . . . . . . . . . . . . 77
4.1.4 Matrix eigenvalues and eigenvectors can be computed efficiently. . . . . . . . . . . . . . . . . . . . . . . . . . . . . 77
4.1.5 The outer (Kronecker) product of two vectors or matrices represents multi-particle systems . . . . . . . . . . . . . . 78
4.2 Functions provide a natural representation of continuous states. . 78
4.2.1 Functions represent states . . . . . . . . . . . . . . . . . . 78
4.2.2 Integrals perform overlap calculations. . . . . . . . . . . . 78
4.2.3 Derivatives and functions represent operators. . . . . . . . 79
4.2.4 Differential equations have eigenvalues and eigenfunctions. 79
4.2.5 The product of functions represents combined multi-state systems. . . . . . . . . . . . . . . . . . . . . . . . . . . . . 79
4.3 Continuous and discrete representations can be used together to solve problems of interest. . . . . . . . . . . . . . . . . . . . . . 79

# Chapter 1

# Quantum States

> Zi Lu said: “The ruler of Wei is anticipating your assistance in the administration of his state. What will be your top priority?”
> Confucius said, “There must be a correction of terminology.”
> Zi Lu said, “Are you serious? Why is this so important?”
> Confucius said, “You are really simple, aren’t you? A noble man is cautious about jumping to conclusions about that which he does not know.”
> “If terminology is not corrected, then what is said cannot be followed. If what is said cannot be followed, then work cannot be accomplished. ... Therefore, the noble man needs to have his terminology applicable to real language, and his speech must accord with his actions. The speech of the noble man cannot be indefinite.”
>
> Analects of Confucius [13:3]

Quantum mechanics provides a theoretical framework for making statements about physical systems, such as an atom or molecule. We can distinguish several types of statements:

1. What is a valid description of the system?
2. What properties does the described system have?
3. How do descriptions change over time?
4. Given some set of constraints, what are the best possible descriptions of the system?

Each question builds upon the previous questions. So to begin, we must develop a language for describing systems, and a way of separating valid and invalid descriptions.

## 1.1 Quantum mechanics describes physical systems using states.

A **state** describes our knowledge about a quantum system. This is not far removed from our ordinary use of the word. Consider the following examples:

- A coin can be described as having the state of "heads" or "tails".
- A light-switch can be described as having the state of "on" or "off", which is indicated by the switch pointing "up" or "down".
- A six-sided die can be described as having the state of 1, 2, 3, 4, 5, or 6 facing upwards.
- A ball can be described as a position.
- A wheel can be described by its rotational direction (clockwise/counterclockwise) and angular momentum.
- A classroom can be described by the number of teachers and the number of students that are within it.

Observe how these state descriptions *imply* assumptions about the material composition. The aspects of the coin's state that we care about ("heads"/"tails") is unambiguously described, but the metal alloy composition and the design stamped on its surface are not specified. The classroom's state can be unambiguously described without knowledge of the ages or species of the teachers and students. This is advantageous for several reasons. First, it gives us the ability to generalize and compare different systems (e.g., a kindergarten class versus a college seminar, or a class with human students versus a dog-training class). Any good physical theory should expose common underlying unifying patterns. Second, leaving the composition implicit allows us to specify what we do know about a system, without necessarily understanding everything about its parts (e.g., the metal alloy composition used in the coin, or the anatomical and metabolic details of entities in the classroom). This is helpful in a physical theory, because it allows us to reason about what a collection of parts "do" without having to know precisely what the parts "are." More explicitly, the precise nature of elementary particles, such as quarks and electrons is rather mysterious. Quantum mechanics provides us with a mechanism for describing the states of these particles, and how they interact to form more complicated structures such as protons and neutrons, and in turn to form atoms and molecules.

### 1.1.1 A set of basis states describes the possible states of a system.

The state that a particular system *actually* has is distinct from the possible states that it *could* adopt. The set of the possible states defines a *basis* within which the actual state can be described. In ordinary language, we might say that a particular system has a state that can be described in terms of its possible **basis states**. For example:

- A coin has possible basis states of heads and tails, but *this* coin is heads.
- A light switch has possible basis states of on or off, but *this* switch is off.
- A six-sided die has possible basis states of $\{1, 2, 3, 4, 5, 6\}$, but *this* die shows the number 5.
- A ball has the possible basis states of position, $\{x_0, x_1, x_2, x_3, \cdots\}$, (where we describe the continuous variables as a set of discrete values arranged in a number line, like pixels on a computer screen), but *this* ball is located at one of those positions, $x_j$.
- A wheel has the possible basis states of rotating { clockwise, counter-clockwise}, and angular momenta $l_0, l_1, l_2, \cdots$, but *this* wheel is rotating clockwise with angular momentum $l_2$.
- A classroom has possible basis states of $n_S = \{0, 1, 2, 3, \cdots\}$ students and $n_T = \{0, 1, 2, 3, \cdots\}$ teachers, but *this* classroom has exactly 12 students and one teacher.

## 1.2 Quantum states can be represented concisely using Dirac ("bra-ket") notation.

We need a way to write and performed structured reasoning about quantum states. A standardized notation allows us to verify that are making internally consistent manipulations and to communicate our work to others.

The English physicist Paul Dirac (1902-1984) introduced a standard way to denote quantum states that is almost universally used in quantum mechanics. **Dirac notation**, also referred to as **"bra-ket" notation**, uses a set the angle brackets $\langle|$ and $|\rangle$ to denote quantum states. The convention is to use the Greek letters $\psi$ ("psi") and $\phi$ ("phi") as the variable names for arbitrary quantum states, and we will do so below. The system named $\phi$ is described as having the "ket" $|\psi\rangle$ and the "bra" $\langle\psi|$, that describe its state. The quantum states denoted in this system can be manipulated following the ordinary rules of algebra, with a few special restrictions that will be discussed below.

### 1.2.1 A "ket", $|\psi\rangle$, represents assertions about a state.

The **ket** symbol, $|\psi\rangle$, denotes the *statement* "the system named $\psi$ is in state $\psi$." In other words, it is an assertion that the state of $\psi$ *is* $\psi$, which also carries the logical implication that it is *and not* "not-$\psi$". Despite the conceptual distinction between the actual state of the system and its possible basis states, we may use the same $|\rangle$ symbol for both the actual state and the basis states. Later we will see that this distinction is not necessarily so clear, and so using the same notation will more easily allow us to move between different representations of states.

Consider the example of a two-sided coin. The two basis states consist of the mutually exclusive possibilities of "heads" ($|H\rangle$) and "tails" ($|T\rangle$). These two basis states are mutually exclusive; one observes either $|H\rangle$ *or* $|T\rangle$. Mutually exclusive states are said to be **orthogonal** to each other; in this case $|H\rangle$ is orthogonal to $|T\rangle$ (and vice versa). One is free to define the state of a coin named "psi" ($\psi$) to have $|\psi\rangle = |T\rangle$ or $|\psi\rangle = |H\rangle$; and as we shall see below, quantum mechanics also allows us to make other, more general definitions for the $\psi$'s state.

**Your turn:** Consider the example of the light switch. Define a set of basis functions in Dirac notation. Are these basis states mutually exclusive? (Hint: Use the $\uparrow$ and $\downarrow$ symbols as names.)

A system described by multiple pieces of information, must have kets that represent this unambiguously. For example, consider the case of a system comprised of one small coin, $s$, and one large coin, $l$. We might choose the convention of writing the label for the state of the small coin first and the large coin last in the ket, $|s, l\rangle$. There are four possibilities comprising the basis states for the system, $|H, H\rangle, |H, T\rangle, |T, H\rangle, |H, H\rangle$. We could also unambiguously write this without the commas, for brevity, as $|HH\rangle, |HT\rangle, |TH\rangle, |TT\rangle$. Alternatively, we could choose another consistent order (e.g., $|l, s\rangle$), so long as we stick to this convention throughout our calculation.

**Your turn:** Define a set of possible basis states for a collection of *three* light switches, using kets.

In general, we want to describe all possible basis states. Any convenient, unambiguous label may be used to name these states. When there are many basis states, it is often convenient to pick some ordered series. For example, it might be convenient to define the basis states describing the six-sided die by naming as $|1\rangle, |2\rangle, |3\rangle, |4\rangle, |5\rangle, |6\rangle$. For cases where writing all of the possibilities explicitly is too tedious, one may specify the general pattern using the first few basis states (and perhaps the last one to designate the end), and then denote the missing elements in the set using an ellipsis ($\cdots$). Often the choice of systematic numerical names is sufficient for these general cases. For example, the discretized positions of a ball can be described using a set of basis states $|x_0\rangle, |x_1\rangle, |x_2\rangle, |x_3\rangle, \cdots$ and the number of students in the classroom described using the basis states $|0\rangle, |1\rangle, |2\rangle, \cdots$. In cases like these, it is often convenient to describe an arbitrary state using a variable name. For example, the $j$th position state of the ball is $|x_j\rangle$ and the case of exactly $n_S$ students in the classroom is $|n_S\rangle$, respectively. These are merely labels, and we would be free to use other labels such as $|x_k\rangle$ and $|s\rangle$, if desired.

It is a good practice to describe either in words or as an equation, any upper and lower bounds that these values may take, as some values may not be acceptable (e.g., a room cannot have a negative number of students, and there is probably some upper bound that depends upon the size of the room).

**Your turn:** Define a set of kets for the complete basis state description (including all variables) for the examples of the wheel and classroom examples.

### 1.2.2 A "bra", $\langle\phi|$, represents questions about a state.

The **bra** symbol, $\langle\phi|$, denotes the *question*, "Is the system in state $\phi$?" On its own, a bra, $\langle\phi|$, represents this question independent of any specific entity we might ask it about. To ask this question about a specific state $|\psi\rangle$, is described by the **overlap** of the two states, $\langle\phi|\psi\rangle$. This can be read as "Is the system (that says it is $\psi$) in the state $\phi$?" This is simply the sandwich of $\langle\phi||\psi\rangle$, but with the extra internal vertical line has been removed so that it looks nicer.) The answer to this question is a numerical value for the overlap $\langle\phi|\psi\rangle$, describing the truth of the statement. Two extreme values are one (denoting "entirely the same") and zero (denoting "entirely different"). More generally, the overlap $\langle\phi|\psi\rangle$ can be any number whose *magnitude* is between zero and one. We'll return to this more general case later in this chapter.

Returning to the two-sided coin example, consider a coin in the state "heads", $|H\rangle$. The first question one may ask about a system described by state $|H\rangle$ is: "Are you heads?", denoted as $\langle H|$. The answer to this question is $\langle H|H\rangle = 1$ ("Yes entirely."). This seems self evident; a state had better be what is! This is a requirement for logical self-consistency, as stated by Aristotle's Law of Identity whereby a thing is the same as itself ("A is A", or "whatever is, is"). To enforce this requirement for logically consistency, quantum mechanics requires that all states $|\psi\rangle$ must obey $\langle\psi|\psi\rangle = 1$. A state $\psi$ is **normalized** if $\langle\psi|\psi\rangle = 1$.

The second possible question to ask about the state $|H\rangle$ is: "Are you tails?"(denoted $\langle T|$). The answer to this question is $\langle T|H\rangle = 0$ ("Not at all."). Again, this seems self evident; the basis states of heads and tails are mutually exclusive of one another, and both mutually exclusive alternatives cannot simultaneously be true ("A is not not-A"). This is related to the classical logic principal of non-contradiction.[1] Two states $\phi$ and $\psi$ are **orthogonal** if $\langle\phi|\psi\rangle = 0$. Furthermore, a basis set of states is said to be **orthonormal** if the states are both normalized and orthogonal to each other. For example, the basis states

---

[1] And, in the case of states defined as mutually exclusive, this also invokes the law of the excluded middle ("A is either true or false.") This holds only for mutually exclusive states in quantum mechanics, but in general quantum mechanics admits the possibility of states for which the calculation is not entirely true or false.

$|H\rangle$ and $|T\rangle$ are orthonormal, because

$$\begin{aligned}\langle H|H\rangle &= 1\\ \langle T|T\rangle &= 1\\ \langle H|T\rangle &= 0\\ \langle T|H\rangle &= 0.\end{aligned}$$

Enumerating the various bra-ket combinations for the basis states in this way is helpful, as we can use these results to perform calculations on arbitrary states. However, explicit enumerations can become quite tedious for examples like the six-sided die, and perhaps not even possible for problems like the position states of a ball. A more concise way to write this is by using a mathematical function called the **Kronecker delta**, having the properties:

$$\delta_{ij} = \begin{cases} 1, & \text{if } i = j \\ 0, & \text{if } i \neq j \end{cases} \tag{1.1}$$

Defining the basis state bras as $\langle i|$ and the basis state kets as $|j\rangle$, then the orthonormality of these mutually-exclusive states can be written as $\langle i|j\rangle = \delta_{ij}$. Similarly, each of the pixelated positions of the ball, described using the basis state bras $\langle x_i|$ and basis set kets $|x_j\rangle$, has the orthonormality relationship $\langle x_i|x_j\rangle = \delta_{ij}$.

For descriptions that contain multiple parts, it is often useful to define orthonormality conditions for each part of the description independently. Consider the two coin example discussed above. The statement about the pair of the small and large coin is written as $|s, l\rangle$, the corresponding question about whether it has the small coin in state $s'$ and large coin in state $l'$ is $\langle s', l'|$. The state of the two-coin system only matches when both the small coins match ($s = s'$ and the large coins match ($l = l'$), which can be represented by the product of two Kronecker delta functions,

$$\langle s', l'|s, l\rangle = \delta_{s's}\delta_{l'l}. \tag{1.2}$$

**Your turn:** Write a series of bra-ket overlaps, $\langle|\rangle$ that describe the wheel and classroom examples. Include a brief narrative description of your state definitions and notations.

### 1.2.3 Arbitrary quantum states are described by linear combinations of basis states.

Basis states describe the possibilities for the system. A description of any arbitrary actual state can be constructed by combining the basis states. These descriptions can be more general than simple "either-or" choices between the basis states, provided that they follow some basic requirements needed for logical consistency.

A general state can be defined as a **linear combination** of other states. For example, an arbitrary state for a coin may be expressed as a sum of $|H\rangle$ and $|T\rangle$ states, where each of these terms appear only to first-order in the sum. To be concrete, the following expression is *not valid*:

$$|\psi\rangle = \alpha |H\rangle^2,$$

because $|H\rangle$ appears to second order, rather than first (linear) order. An example of a *valid* linear combination is:

$$|\psi\rangle = \alpha|H\rangle + \beta|T\rangle, \tag{1.3}$$

where $\alpha$ and $\beta$ are numerical coefficients describing the relative contributions made by $|H\rangle$ and $|T\rangle$ to $|\psi\rangle$. We can see this by taking the overlap of $\langle H|$ with Eq.(1.3),

$$\begin{aligned}
\langle H|\psi\rangle &= \langle H|\Big(\alpha|H\rangle + \beta|T\rangle\Big) \\
&= \langle H|\Big(\alpha|H\rangle\Big) + \langle H|\Big(\beta|T\rangle\Big) \\
&= \alpha\langle H|H\rangle + \beta\langle H|T\rangle \\
&= \alpha(1) + \beta(0) \\
&= \alpha,
\end{aligned}$$

where we have taken advantage of the fact that multiplication by the scalar numerical coefficients $\alpha$ and $\beta$ commutes, and the orthonormality of the basis states to evaluate the bra-ket overlaps.

**Your turn:** Demonstrate that $\langle T|\psi\rangle = \beta$.

The overlap between the state, $|\psi\rangle$ and the basis states $|H\rangle$ and $|T\rangle$ can be given a geometric interpretation, as depicted in Figure 1.1. If each of the two basis states is a vector of length one and mutually orthogonal (i.e. at right angles to one another), then $|\psi\rangle$ can be expressed as a combination of those two vectors, with $\alpha$ describing the contribution from $|H\rangle$ and $\beta$ describing the contribution from $|T\rangle$. The overlap, e.g., $\langle H|\psi\rangle = \alpha$ describes the coefficient as the projection that $\psi$ has on the $|H\rangle$ axis. This might suggest to you a natural representation of quantum mechanical states as vectors; we will return to this suggestion and describe a linear algebraic representation of quantum mechanics in Chapter 4.

How should we interpret the state described by $|\psi\rangle$? The special case where $\alpha = 1$ and $\beta = 0$, is $|\psi\rangle = |H\rangle$. In this case, $\psi$ is merely an alias for “heads”, as $\psi$ is only heads and not at all tails. Similar reasoning can be applied for the case of $\beta = 1$ and $\alpha = 0$. These two limiting cases correspond to “only heads” and “only tails” descriptions of the state $|\psi\rangle$. However, there is no mathematical reason to limit ourself to these states. Any linear combinations of states, with

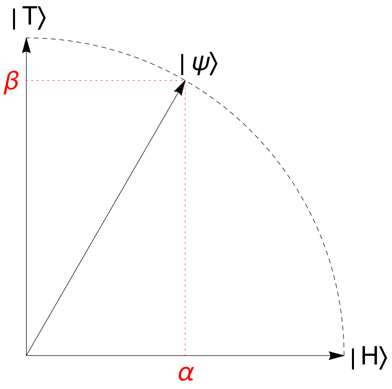

Figure 1.1: Geometric interpretation of the state $|\psi\rangle = \alpha|H\rangle + \beta|T\rangle$. The coefficients $\alpha = \langle H|\psi\rangle$ and $\beta = \langle T|\psi\rangle$ describe the overlap of the state $\psi$ on to the basis vectors. Any state with $|\alpha|^2 + |\beta|^2 = 1$ (indicated by the dashed arc) is satisfies the normalization conditions $\langle\psi|\psi\rangle = 1$

any choice of the values, such as $\alpha = 1/2$ and $\beta = \sqrt{3/4}$ are also permissible, so long as the state obeys the normalization condition $\langle\psi|\psi\rangle = 1$ (more on how to calculate this in the next section). These linear combinations are referred to as **superpositions** of the basis states and correspond to assertions that the state is intermediate between "pure heads" and "pure tails". Mathematically, there is no reason that $\alpha$ and $\beta$ must be positive—they may also be negative and still describe a valid state. Furthermore, there is no mathematical reason that they must be real numbers—**complex numbers** can also be used. (See Math Chapter A in McQ.) At first, this might seem to violate common sense: While we might describe an unfair coin as having a 25% chance of heads, and a 75% chance of tails—-or an ice-cream cone as being 25% vanilla and 75% chocolate—we would never say that it has a negative chance or a complex chance of one of the possible outcomes. However, quantum mechanics provides us with a way of interpreting these states in a logically consistent way, and thus there is no purely logical grounds for excluding them.

All of the comments above about the two-state system can be generalized to any number of possible basis states

$$|\psi\rangle = \alpha|A\rangle + \beta|B\rangle + \gamma|C\rangle + \cdots, \tag{1.4}$$

where, for concision we will only show the first three ($|A\rangle, |B\rangle, |C\rangle$), and use the ellipsis ($\cdots$) as a placeholder for as many other states (e.g., $|D\rangle, |E\rangle$, etc.) and their corresponding coefficients that may be present.

### 1.2.4 Bras and kets are related by Hermitian conjugation.

In Section 1.2.2, we introduced the requirement that all valid quantum mechanical states must be **normalized**, such that $\langle\psi|\psi\rangle = 1$, so as to satisfy the logical consistency of the Law of Identity. The applications in Section 1.2.2 only considered basis states for whom this was an *a priori* requirement. To do this for states that are superpositions of basis functions, requires a way of converting a state, $|\psi\rangle = \alpha|A\rangle + \beta|B\rangle + \gamma|C\rangle + \cdots$, into the corresponding bra, $\langle\psi|$. The **Hermitian conjugate**, denoted by the "dagger" (†) symbol, defines this process,

$$\begin{aligned}\langle\psi| &= \Big(|\psi\rangle\Big)^\dagger, \\ &= \alpha^*\langle A| + \beta^*\langle B| + \gamma^*\langle C|\cdots \qquad (1.5)\end{aligned}$$

The Hermitian conjugate generalizes the complex conjugate operation ($*$) on complex numbers—any number gets converted to its complex conjugate *and* any ket gets converted to a bra.

**Your turn:** Compute the bra form, $\langle\psi|$, of the following states of the two-sided coin example, expressed in the orthonormal basis $\{|H\rangle, |T\rangle\}$:

$$\begin{aligned}|\psi\rangle &= e^{i\pi/3}|H\rangle \\ |\psi\rangle &= \left(\frac{1}{2} + i\sqrt{\frac{3}{4}}\right)|H\rangle \\ |\psi\rangle &= \left(|H\rangle + |T\rangle\right)/\sqrt{2} \\ |\psi\rangle &= \left(|H\rangle - |T\rangle\right)/\sqrt{2} \\ |\psi\rangle &= \left(|H\rangle - i|T\rangle\right)/\sqrt{2} \\ |\psi\rangle &= \frac{1}{2}|H\rangle + i\sqrt{\frac{3}{4}}|T\rangle\end{aligned}$$

This is a bidirectional process, so the Hermitian conjugate also converts bras into kets, with $(\langle\psi|)^\dagger = |\psi\rangle$. It follows that first converting a ket to its corresponding bra, and then converting the resulting bra back into its corresponding ket by two applications of the Hermitian conjugate operator, is equivalent to the round-trip process of converting a ket back into itself, $(|\psi\rangle^\dagger)^\dagger = |\psi\rangle$. Furthermore, if applied to an overlap, each of the bras and kets should be interconverted, giving

$$\Big(\langle\phi|\psi\rangle\Big)^\dagger = \langle\psi|\phi\rangle, \qquad (1.6)$$

but the overlap is just a number, so this is equivalent to saying

$$\alpha^\dagger = \alpha^*, \qquad (1.7)$$

which implies that

$$\Big(\langle\phi|\psi\rangle\Big)^* = \langle\psi|\phi\rangle. \qquad (1.8)$$

### 1.2.5 Arithmetic on bra and ket pairs for arbitrary states can be determined in terms of a shared basis.

The definition of a Hermitian conjugate for converting $|\psi\rangle$ into $\langle\psi|$, combined with the normalization requirement that $\langle\psi|\psi\rangle = 1$ has several non-trivial consequences about the values that the $\alpha, \beta, \cdots$ coefficient values may take.

First, consider a state, described by only a single normalized basis function, $|\psi\rangle = \alpha|A\rangle$ (the coefficients for any other basis functions are all zero). Converting this to bra-form yields,

$$\langle\psi| = \Big(\alpha|A\rangle\Big)^{\dagger} = \alpha^*\langle A|. \tag{1.9}$$

The overlap between the two states is

$$\begin{aligned}\langle\psi|\psi\rangle &= \alpha^*\alpha\langle A|A\rangle \\ 1 &= \alpha^*\alpha \\ &= |\alpha|^2\end{aligned}$$

where both the left and right hand side substitutions follow from the requirement that the states are normalized (so $\langle\psi|\psi\rangle = 1$ and $\langle A|A\rangle = 1$). The **norm-square**, $|\alpha|^2 = \alpha^*\alpha$, is a shorthand. In general, any complex number of the form $\alpha = \exp[i\theta]$ satisfies this equation, because $\alpha^* = \exp[-i\theta]$ and $\exp[x]\exp[-x] = \exp[x]/\exp[x] = 1$. The consequence is that one is free to multiply the entire quantum state by an arbitrary **global phase** of $\exp[i\theta]$. Here we have only considered a single basis state, but the same would be true if we replaced $|A\rangle$ with an linear combination of states.

Second, consider a two state system, $|\psi\rangle = \alpha|A\rangle + \beta|B\rangle$ and $\langle\psi| = \alpha^*\langle A| + \beta^*\langle B|$. The overlap is:

$$\begin{aligned}\langle\psi|\psi\rangle &= \Big(\alpha^*\langle A| + \beta^*\langle B|\Big)\Big(\alpha|A\rangle + \beta|B\rangle\Big) \\ &= \alpha^*\alpha\langle A|A\rangle + \beta^*\alpha\langle B|A\rangle + \alpha^*\beta\langle A|B\rangle + \beta^*\beta\langle B|B\rangle, \end{aligned} \tag{1.10}$$

which follows simply by multiplying the terms in the sets of parentheses, as you learned in your elementary algebra classes. In the *general case* that where $|A\rangle$ and $|B\rangle$ are normalized (so that $\langle A|A\rangle = \langle B|B\rangle = 1$), but *not* orthogonal ($S_{AB} = \langle A|B\rangle = \langle B|A\rangle^* = S^*_{BA} \neq 0$), this simplifies to

$$1 = \alpha^*\alpha + \beta^*\beta + \beta^*\alpha S_{BA} + \alpha^*\beta S_{AB} \tag{1.11}$$

Further calculation would require knowledge of the specific value of $S_{AB}$. However, in the *special case* where $|A\rangle$ and $|B\rangle$ are an orthonormal basis, then $S_{AB} = S^*_{BA} = 0$, allowing a further simplification to

$$\begin{aligned}1 &= \alpha^*\alpha + 0 + 0 + \beta^*\beta \\ &= |\alpha|^2 + |\beta|^2, \end{aligned} \tag{1.12}$$

allowing us to solve for $\beta = \sqrt{1 - |\alpha|^2}$ to determine the valid choices for $\beta$ given a specification for $\alpha$.

Finally, calculations like these allow us to rescue states that are not-normalized by computing the correct normalization condition. Suppose that there is some not-normalized state $|\phi\rangle$ with $\langle\phi|\phi\rangle = a$. Then, we can always define a new state, $|\psi\rangle = |\phi\rangle/\sqrt{a}$, which will be correctly normalized.

**Your turn:** TODO: Write some problems

### 1.2.6 Combinations of system can be expressed using tensor products of states.

When introducing kets in Section 1.2.1, we included examples of systems described by several labels, in particular a system comprised of a small and large coin, and a classroom of students and teachers. You were left to devise your own enumeration of the possible states of the system. The bra-ket algebra provides a systematic way for us to generate these types of states by defining a **tensor product** of the two states, denoted by the operation $\otimes$, that combines the different system $|A\rangle$ and $|B\rangle$ into a single combined system, $|A, B\rangle$.

$$|A\rangle \otimes |B\rangle = |A, B\rangle \tag{1.13}$$

For example, if the small coin is in the state $|H\rangle$ and the large coin is in the state $|T\rangle$, then the state describing both coins is

$$|H\rangle \otimes |T\rangle = |H, T\rangle, \tag{1.14}$$

following our previous convention of listing the small coin first. The tensor product has the following algebraic properties:

$$\Big(a|A\rangle\Big) \otimes |B\rangle = a|A, B\rangle \tag{1.15}$$

$$\Big(|A_1\rangle + |A_2\rangle\Big) \otimes |B\rangle = |A_1, B\rangle + |A_2, B\rangle \tag{1.16}$$

$$|A\rangle \otimes \Big(|B_1\rangle + |B_2\rangle\Big) = |A, B_1\rangle + |A, B_2\rangle \tag{1.17}$$

$$|A\rangle \otimes \Big(|B\rangle \otimes |C\rangle\Big) = \Big(|A\rangle \otimes |B\rangle\Big) \otimes |C\rangle = |A, B, C\rangle \tag{1.18}$$

in other words, it commutes with a scalar multiplicative constant, $a$, and is distributive to the left and right, and is associative.

**Your turn:** Consider a system where one particle is $|A\rangle = \alpha|H\rangle + \beta|T\rangle$ and the other is $|B\rangle = |T\rangle$. What is $|A\rangle \otimes |B\rangle$ describing the combined system?

**Your turn:** Consider a system where the two particles are each described by $|A\rangle = |B\rangle = \Big(|H\rangle + |T\rangle\Big)/\sqrt{2}$. Is $|A\rangle \otimes |B\rangle$ properly normalized?

### 1.2.7 Entangled states describe unfactorizable multi-state systems

Not all states can be written as tensor products of two states. For example, none of following two-particle states can be written as a tensor product of two single-particle states:

$$|\Phi_+\rangle = \frac{|HH\rangle + |TT\rangle}{\sqrt{2}} \tag{1.19}$$

$$|\Phi_-\rangle = \frac{|HH\rangle - |TT\rangle}{\sqrt{2}} \tag{1.20}$$

$$|\Psi_+\rangle = \frac{|HT\rangle + |TH\rangle}{\sqrt{2}} \tag{1.21}$$

$$|\Psi_-\rangle = \frac{|HT\rangle - |TH\rangle}{\sqrt{2}}. \tag{1.22}$$

For example, the state described by Eqs.(1.19-1.20) always have the same state on the two subsystems (both heads or both tails). In contrast, the states described by Eqs.(1.21-1.22) always have a 'heads" on the first subsystem associated with a "tails" on the second subsystem, and vice versa. These types of specific correlations cannot be factored into a product of states of its local constituents; states having this type of non-factorizability are **entangled**. Yet they are clearly valid, correctly normalized states, and have a number of interesting properties, that will be discussed in Section 2.4.

## 1.3 Chemical systems are described using quantum states.

What is the relevance of this formalism to systems of chemical interest? Quantum mechanical states are the underlying language behind many of the concepts from your previous chemistry studies. Without knowing it, you have already learned and expressed these concepts in words and diagrams. In the examples below, we will review some of these basic problems and express them rigorously using the language of quantum states.

### 1.3.1 A two-state model describes spin-1/2 particles such as electron and nuclear spins.

Every introductory chemistry class introduces the concept that electrons have a property of "spin", and require drawing orbital diagrams that are filled in electrons as "spin up" and "spin down", indicated using up and down arrows,

$\{\uparrow, \downarrow\}$, to build up (German: *aufbau*) an atomic or molecular orbital energy diagram (more about those shortly). You may have assigned these states a **spin quantum number**, $m_s$, with values $m_s = \pm\frac{1}{2}$ corresponding to the up and down states Similarly, during your organic chemistry classes, you learned that certain nuclei, like $^1$H and $^{13}$C, have two allowed states observable during nuclear magnetic resonance (NMR) experiments.[2] The absorption of radio frequency photons causes transitions between the two states, and measuring the energy at which this is observed provides information about the local environment of the nuclear spins.

Both the electron and these nuclei are examples of two-state systems, like the coin and light switch examples discussed earlier in this chapter. Each particle has two possible orthogonal basis states, which can be named "up"/"down", $\uparrow$ / $\downarrow$, or $m_s = \pm\frac{1}{2}$, just as easily as they are named "heads"/"tails" or "on"/"off" in those previous examples. The states can be indicated in Dirac notation as $\{|\uparrow\rangle, |\downarrow\rangle\}$ or as $|m_s\rangle$ (specifically as $\{\left|+\frac{1}{2}\right\rangle, \left|-\frac{1}{2}\right\rangle\}$). Similarly, the basis states for a collection of spin-$\frac{1}{2}$ particles, such as the collection of electron and nuclear spins in a molecule, can be described by forming the possible combinations, as in the two-coin example of Section 1.2, labeling each of the spins in a defined order. So long as the spins are distinguishable from one another (e.g., two electrons with different spin, an electron and a nucleus or a nucleus of one type and a nucleus of another), the valid actual states can be described as we have done above. However, *indistinguishable* particles, such as two electrons with the same spin, have further requirements on the states which will be discussed in Section **??**.

As we have seen throughout this chapter, a two-state system is the simplest model for illustrating the properties of quantum mechanics. As such, we will often use the spin-1/2 particle, as an illustrative example when introducing a new topic for the remainder of the book. Conceptually this is no different from the two-sided coin examples, but will allow you to pretend that this is a book about chemistry and physics, rather than about gambling and probability.

### 1.3.2 Atomic orbitals are basis states describing an electron in an atom.

Every introductory chemistry course presents **atomic orbitals** as a description of where an electron is present around a central nucleus. Each type of atomic orbitals can be assigned a label, $1s, 2s, 2p_x, 3d_{x^2-y^z}$, etc. that describes a characteristic shape and symmetry of where the electron is more likely to be present relative to the nucleus. Alternatively, these labels correspond to a set of **quantum numbers**, namely the **principal quantum number**, $n = 1, 2, 3, \cdots$, the **orbital angular momentum quantum number**, $l = 0, 1, 2, \cdots$, the **magnetic quantum number**, $m_l = 0, \pm 1, \cdots \pm l$, and the **spin quantum number**, $m_s = \pm\frac{1}{2}$ (discussed above). These are identical sets of labels; the letters $s, p, d$

---

[2] Other nuclei, such as $^2$H and $^{12}$C are spin-1 particles, with three allowed states (+1, 0, -1). The presence of the intermediate state prevents direct observation in an NMR experiment. We will discuss spin in more detail in Section **??**.

describe the quantum numbers $l = 0, 1, 2$, and the labels $x, y, z$, etc. are related to the $m_l$ quantum numbers.

Each basis state $|n, l, m_l, m_s\rangle$ is a mathematical *function* describing the shape of where one might expect to find an electron having that state. A complete group of quantum numbers, $|n, l, m_l, m_s\rangle$ labels a unique states with a particular spatial shape, with the values of each individual quantum numbers indicating characteristics of that shape, such as the number of radial and angular nodes (in the case of $n, l, m_l$), or the spin of the electron (in the case of $m_s$). The atomic orbital basis states are orthonormal, and as such, two states $|n, l, m_l, m_s\rangle$ and $|n', l', m'_l, m'_s\rangle$ have the overlap

$$\langle n', l', m'_l, m'_s|n, l, m_l, m_s\rangle = \delta_{n'n}\delta_{l'l}\delta_{m'_l m_l}\delta_{m'_s m}. \tag{1.23}$$

The orthonormality of the bra-kets represents a similar orthonormality of the underlying mathematical functions describing the atomic orbitals. We will revisit quantum numbers for the hydrogenic atom in Chapter **??**.

### 1.3.3 Hybrid atomic orbitals are linear combinations of atomic orbital basis states.

Introductory and organic chemistry courses often use the concept of **hybrid atomic orbitals** to describe combinations of atomic orbitals that are oriented in the directions of chemical bonds. These are merely quantum states described by a linear combination of the atomic orbital basis states. When constructing these hybrid orbitals, we neglect the electron spin ($m_s$) and consider the spatial quantum numbers only. It is common to use the $1s, 2s, 2p$ labels instead of the $n, l, m_l$ quantum numbers when describing the spatial states.

For example, the two *sp*-hybrid orbitals, $|sp_a\rangle, |sp_b\rangle$ are linear combinations of the $|2s\rangle$ and $|2p_z\rangle$ atomic orbital basis functions:

$$|sp_a\rangle = \left(|2s\rangle + |2p\rangle\right)/\sqrt{2} \tag{1.24}$$

$$|sp_b\rangle = \left(|2s\rangle - |2p\rangle\right)/\sqrt{2}, \tag{1.25}$$

The other two atomic orbitals centered on that atom, $|2p_y\rangle$ and $|2p_z\rangle$ remain unhybridized.

**Your turn:** Using the atomic orbital basis function orthonormality relationship, Eq.(1.23) confirm that the hybrid atomic orbitals described above are valid states, such that $\langle sp_a|sp_a\rangle = 1$, $\langle sp_b|sp_b\rangle = 1$. Then show that these two states are orthogonal to each other (i.e., that $\langle sp_a|sp_b\rangle = 0$) and to the unhybridized atomic orbitals (i.e., $\langle sp_a|2p_y\rangle = 0$).

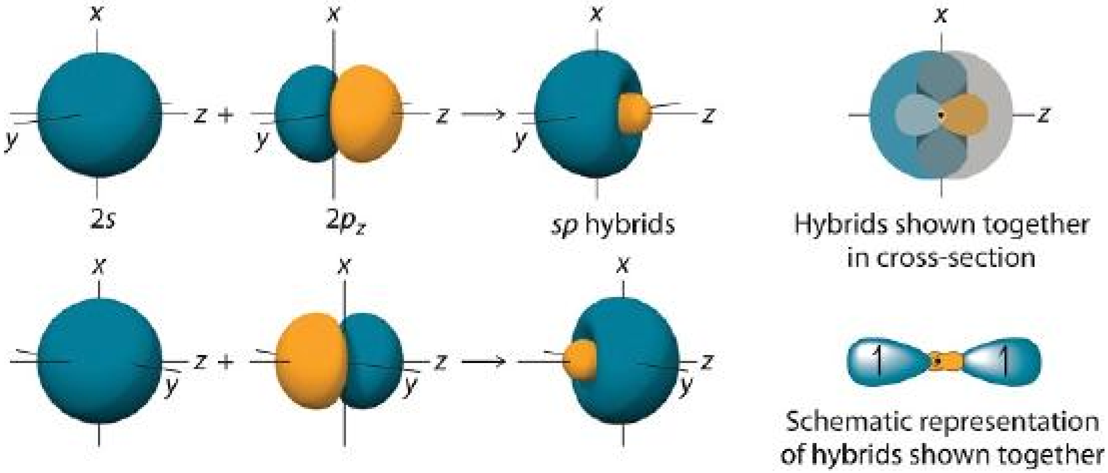
x
z +
y
2s
x
z ⟶
y
2p_z
x
z
y
sp hybrids
x
z
Hybrids shown together
in cross-section
x
z +
y
x
z ⟶
y
x
z
y
Schematic representation
of hybrids shown together

Figure 1.2: $sp$-hybrid orbitals are formed from adding and subtracting $|2s\rangle$ and $|2p_z\rangle$ atomic orbital hybrid functions. TODO: Remake graphic
Source: LibreText

Figure 1.3: TODO: Figure for $sp^2$ hybrid orbital linear combinations

Hybrid orbitals for $sp^2$:

$$\left|sp_a^2\right\rangle = \left(|2s\rangle - \sqrt{2}|2p_x\rangle\right)/\sqrt{3} \tag{1.26}$$

$$\left|sp_b^2\right\rangle = \left(\sqrt{2}|2s\rangle + |2p_x\rangle + \sqrt{3}|2p_y\rangle\right)/\sqrt{6} \tag{1.27}$$

$$\left|sp_c^2\right\rangle = \left(\sqrt{2}|2s\rangle + |2p_x\rangle - \sqrt{3}|2p_y\rangle\right)/\sqrt{6} \tag{1.28}$$

(and an unhybridized $|2p_z\rangle$)

Hybrid orbitals for $sp^3$:

$$\left|sp_a^3\right\rangle = \left(|2s\rangle + |2p_x\rangle + |2p_y\rangle + |2p_z\rangle\right)/2 \tag{1.29}$$

$$\left|sp_b^3\right\rangle = \left(|2s\rangle - |2p_x\rangle - |2p_y\rangle + |2p_z\rangle\right)/2 \tag{1.30}$$

$$\left|sp_c^3\right\rangle = \left(|2s\rangle + |2p_x\rangle - |2p_y\rangle - |2p_z\rangle\right)/2 \tag{1.31}$$

$$\left|sp_d^3\right\rangle = \left(|2s\rangle - |2p_x\rangle + |2p_y\rangle - |2p_z\rangle\right)/2 \tag{1.32}$$

Figure 1.4: TODO: Figure for $sp^3$ hybrid orbital linear combination

Figure 1.5: TODO: Graphical representation of H2 problem

**Your turn:** Pick one $sp^3$ hybrid orbital and compute the overlap with each of the atomic basis states, $\{|2s\rangle, |2p_x\rangle, |2p_y\rangle, |2p_z\rangle\}$.
**Your turn:** Pick two $sp^3$ atomic orbitals and show that they are orthonormal.
**Your turn:** What is the overlap $\langle sp_a^2 | sp_b^3 \rangle$?

### 1.3.4 Molecular orbitals describe an electron in a molecule using a linear combination of atomic orbital basis functions.

Every introductory chemistry course discusses “bonding” and “antibonding” molecular orbitals. Molecular orbitals are merely linear combinations of the basis states of atomic orbitals centered on the two *different* atoms, in contrast to the hybrid atomic orbitals which are linear combinations of atomic orbitals of the *same* atom.

The hydrogen molecule, $H_2$, is useful example because it is the simplest diatomic molecule, and both atoms are the same, which introduces a symmetry that simplifies the analysis. Let us label each atom $A$ and $B$, and denote the $1s$ orbitals on each atom as $|1s_A\rangle$ and $|1s_B\rangle$. The two atomic orbital functions are each normalized, but are *not* orthogonal to one another, as shown in Figure 1.5. The precise amount of overlap between the two atomic orbitals will depend on their distance, and we’ll need to learn a bit more before we can calculate this, so for now let us simply call it $S_{AB}(R) = \langle 1s_A | 1s_B \rangle$. Furthermore, because the atomic orbital basis functions are real, we can assume that $S_{AB}$ is real, so that $S_{AB} = S_{BA}$. From Figure 1.5, we want the bonding ($b$) and antibonding ($a$) states should have the form,

$$|b\rangle = \beta\left(|1s_A\rangle + |1s_B\rangle\right) \tag{1.33}$$

$$|a\rangle = \alpha\left(|1s_A\rangle - |1s_B\rangle\right), \tag{1.34}$$

where $\alpha$ and $\beta$ are unknown parameters. The requirement that valid states are normalized is sufficient to determine these parameters. In the case of the bonding orbital,

$$\begin{aligned}
\langle b|b\rangle &= \beta^*\left(\langle 1s_A| + \langle 1s_B|\right)\beta\left(|1s_A\rangle + |1s_B\rangle\right) && (1.35)\\
&= \beta^*\beta\left(\langle 1s_A|1s_A\rangle + \langle 1s_A|1s_B\rangle + \langle 1s_B|1s_A\rangle + \langle 1s_B|1s_B\rangle\right) && (1.36)\\
&= |\beta|^2\left(1 + S_{AB} + S_{BA} + 1\right) && (1.37)\\
&= |\beta|^2\left(2 + 2S_{AB}\right), && (1.38)
\end{aligned}$$

Using the requirement that a valid state has $\langle b|b\rangle = 1$, allows us to solve for $\beta = 1/\sqrt{2 + 2S_{AB}}$. We are free to assume that $\beta$ is a real number (as well

Figure 1.6: TODO: Figure: pixels in a line, pixels in 2D, pixels in 3D with kets ; figure in 1D show a n=2 like state

as any arbitrary complex global phase, as discussed in Section 1.2.5, and the precise value of $\beta$ will depend on the value of $S_{AB}$, which will in turn depend on the distance between the nuclei.

What does this state description tell us about an electron in the bonding orbital? An electron having state $|b\rangle$ (Eq.(1.33) is described as equal contributions of both $|1s_A\rangle$ ("I am in the 1$s$ orbital on atom A.") and $|1s_B\rangle$ ("I am in the 1$s$ orbital on atom B.") Indeed, there is no reason to assume that it should prefer to be on one or the other atom, as they are both identical.

**Your turn:** Determine the proper normalized version of the antibonding molecular orbital, $|b\rangle$ for the $H_2$ molecule. Is this state also an equal contribution from the two atomic orbitals? Explain.

**Your turn:** The overlap, $S_{AB}$ is typically small, (e.g., $S_{AB} \approx 0.1$). Ignore the overlap by assuming $S_{AB} = 0$ and derive normalized expressions for the bonding and anti-bonding orbitals starting from Eqs.(1.33-1.34).

**Your turn:** Write a general formula for the the bonding and antibonding molecular orbital states of the LiH molecule, using the valence atomic orbitals on the two atoms, $|2s_{Li}\rangle$ and $|1s_H\rangle$ as basis states. What numerical values would you need to complete this definition? Given that the two atoms have different electronegativities, do you think that the states are equal superposition of the two basis states or an unequal superposition? If the latter, on which atom do you expect to find the electron more often when in the bonding state? The antibonding state?

### 1.3.5 The set of possible position basis states describes the location of a particular particle.

Spin-up and down basis states specify an abstract property that is independent of location; the statement $|\uparrow\rangle$ is equivalent to "I am up" and says nothing about where this is occurs. Atomic orbital basis states specify mathematical functions in three-dimensional space; the statement $|1s\rangle$ is equivalent to "I am generally found in this distribution of positions described by a 1$s$ atomic orbital." Therefore, a statement of the form "I am at position $x$" requires us to define possible basis states for position.

One way to construct these is by pixelating space as shown in Figure 1.6, and assigning a basis states to each pixel. For a particle located on a (one-dimensional) line, each position state can be assigned a single label from the set of position basis states, $\{|x_0\rangle, |x_1\rangle, |x_2\rangle, \cdots |x_j\rangle\}$. The basis state $|x_j\rangle$ corresponds to the statement "I am located at pixel $j$." The orthonormality of the position basis states,

$$\langle x_i|x_j\rangle = \delta_{ij}, \qquad (1.39)$$

Figure 1.7: TODO: Figure: n=1, n=2 like state expressions. Overlap?

follows from the necessity that each pixel is itself (normalization), and is not some different pixel (orthogonal). Generalizing to two- and three-dimensions merely requires assigning labels to each pixel. a natural way to do this is to assign labels to each axis, such as $|x_j, y_j, z_j\rangle$ or condensing the list of position labels as vector $|\vec{x_j}\rangle$.

Any state can be expressed as a linear combination of the position basis states,

$$\begin{aligned} |\psi\rangle &= c_0|x_0\rangle + c_1|x_1\rangle + c_2|x_2\rangle + \cdots \\ &= \sum_j c_j|x_j\rangle, \end{aligned} \tag{1.40}$$

provided that it satisfies the normalization condition for valid states, $\langle\psi|\psi\rangle = 1$. The orthonormality of the position basis functions (Eq.(1.39) makes it simple to evaluate overlaps of arbitrary position states. A few valid examples are shown in Figure 1.7.

One might argue that in the "real world" space is continuous and not pixelated.[3] On a practical level, the "rulers" used to measure positions in the laboratory have a finite resolution. Discretizing the state description below this threshold is a sufficient description of what can be observed and described in practice. Mathematically speaking, continuous functions can be discretized in a systematic way until a desired numerical precision threshold is reached, or until one reaches a limit of infinitesmal difference, which is foundational principle of calculus. We will discuss states in the position basis extensively in later chapters.

### 1.3.6 There is no unique set of basis states for describing a physical system.

The state of an electron in a molecule can be describing in many possible ways. One could describe its state in terms of its molecular orbital ("I am bonding." or "I am antibonding."). Alternatively, one could express the same state using a linear combination of atomic orbitals ("I am in a 1$s$ orbital on atom A.") In turn, the atomic orbitals can be expressed in terms of positions in space, and thus the electron's state can be described as contributions from a set of position states ("I am located at $\vec{x}$.") Each of these descriptions refers to the same individual electron, but the descriptive statement of the electron's state gets progressively more detailed as we proceed from molecular orbitals to atomic orbitals to position basis states.

---

[3] This is an active area of research in quantum gravity, but despite spurious folk-arguments based on misunderstandings of the Planck length, there is no evidence that space-time is fundamentally discrete. On the contrary, the continuous nature of space has been verified experimentally down to $10^{-16}$ cm, and there are theoretical, philosophical, and mathematical difficulties associated with a fundamental discretization. See Amit Hagar, *Discrete or Continuous?:The Quest for Fundamental Length in Modern Physics* (Cambridge Univ. Press, 2014) DOI:`https://doi.org/10.1017/CBO9781107477346`

The appropriate choice of a set of basis states is often about practical or rhetorical desires, rather than physics requirements. Some basis states may permit more facile calculations, or more detailed quantitative calculations than others. The appropriate level of description may depend on the scientific story one wishes to tell with those states, which may be most clearly expressed at a certain level of detail.

Even within a fixed level of detail, there remains an ambiguity of the correct choice of basis states. For example, consider the spin-1/2 particle. We have used the basis states $|{\uparrow}\rangle$ and $|{\downarrow}\rangle$ in the examples above, but we would be free to rotate this basis by 90°, and define a new set of basis states,

$$\begin{aligned} |{\rightarrow}\rangle &= \left(|{\uparrow}\rangle + |{\downarrow}\rangle\right)/\sqrt{2} \\ |{\leftarrow}\rangle &= \left(|{\uparrow}\rangle - |{\downarrow}\rangle\right)/\sqrt{2} \end{aligned}$$

and use these to express any $|\psi\rangle = \alpha|{\uparrow}\rangle + \beta|{\downarrow}\rangle$ in this new basis. That includes expressing the limiting cases themselves,

$$\begin{aligned} |{\uparrow}\rangle &= \left(|{\rightarrow}\rangle + |{\leftarrow}\rangle\right)/\sqrt{2} \\ |{\downarrow}\rangle &= \left(|{\rightarrow}\rangle - |{\leftarrow}\rangle\right)/\sqrt{2} \end{aligned}$$

Both basis choices comprise two orthonormal states, and can be used to construct any other state, including each other. There is no intrinsic reason to prefer one choice of basis states to another, but rather it is left to the scientist as a matter of taste or convention. Quantum mechanics provides a way of specifying the state of a physical system and guidelines on how to make those specifications logically self-consistent. Expressing these states using the bra-ket notation provides an algebraic way of defining transformations from descriptions specified using a certain set of basis states to descriptions in another set of basis states, allowing us to reason about these descriptions in a consistent way. This general mathematical framework only tells us if we are consistent, but not that a particular set of states are better or worse for describing the system of interest.

## Conclusion

This chapter introduced the concept of a state as a way to make statements and ask questions about a physical system. We introduced formal requirements on what makes a valid state, and have seen how to convert between different types of descriptions. As we will see in the coming chapters, quantum mechanics also provides us with a means of querying the properties of states and determine the most probable states given a set of interactions.

# Problems

1. As general guidance in this book, you are encouraged to complete all of the “Your turn” questions as you do the reading. Your first problem in every chapter should be completing any of those that you bypassed.

2. Devise 3 different equal superposition of the states of 6-sided die.

3. Consider the state:
$$|\psi\rangle = \frac{e^{i\theta}}{\sqrt{2}}\Big(|\uparrow\rangle - i|\downarrow\rangle\Big) \tag{1.41}$$
(a) What is the bra-form of this state? (b) What is $\langle\uparrow|\psi\rangle$ and $\langle\downarrow|\psi\rangle$? (c) Is $|\psi\rangle$ a valid state? Prove it.

4. The (invalid) state, $|\phi\rangle = (3i|\uparrow\rangle - 2|\downarrow\rangle)$ is an attempt to describe a state that is “more” up than down, but it is not normalized! (a) Compute $\langle\phi|\phi\rangle$ and use the result to define a new state $|\Phi\rangle$ that *is* correctly normalized. (b) What are the overlaps, $\langle\uparrow|\Phi\rangle$ and $\langle\downarrow|\Phi\rangle$ for this correctly normalized state?

5. Using the states $|\psi\rangle$ and $|\Phi\rangle$ from the previous two problems, compute $\langle\psi|\Phi\rangle$ and $\langle\Phi|\psi\rangle$. How are the two values related?

6. Construct your own valid quantum state for a two state system. Write both the bra and ket forms and demonstrate that it is correctly normalized. Do not be boring.

7. Consider the $sp^2$ hybrid orbital, $\left|sp^2{}_b\right\rangle$, (Eq.(1.26)): (a) What is $\langle 2s|sp^2_b\rangle$? $\langle 2p_x|sp^2_b\rangle$? $\langle 2p_y|sp^2_b\rangle$? $\langle 2p_z|sp^2_b\rangle$? (b) Suppose that when forming a chemical bond the $\left|sp^2_b\right\rangle$ hybrid is modified such that the $2s$ contribution is decreased by 10% causing the $2p_x$ and $2p_y$ to increase. Devise a new valid state assuming that the both $2p_x$ and $2p_y$ increase by the same fraction. (c) Using diagrams like those in Figure 1.3 reason about how the orientation of your new hybrid orbital from (b) will differ from the ordinary $sp^2$ hybrid.

8. The C-C bond is rotatable. (a) Consider the ethane molecule, $C_2H_6$. Describe the three conformational minima obtained by rotating about the C-C bond, using three basis states. Are any of these preferred? (b) Define a set of basis states for the same rotation, by described by the H-C-C-H dihedral angle.

9. TODO: Prove the Schwarz inequality. Assume $|A\rangle = |\psi\rangle + \lambda|\phi\rangle$. Compute $\langle A|A\rangle$ and prove that $|\langle\phi|\psi\rangle|^2 \leq \langle\psi|\psi\rangle\langle\phi|\phi\rangle$.

# Math Chapter: Complex numbers

McQuarrie Quantum Chemistry, Math Chapter A

# Computational Chapter: Arithmetic and Variables

(ICPC Appendix A)

- Entering expressions
- Arithmetic operations
- Boolean operators
- Variables (setting) and using

# Chapter 2

# Measurement

> Call to me, and I will answer you;
> I will tell you great things beyond the reach of your knowledge.
>
> Jeremiah 3:33

What can a quantum state description tell us? The requirements for a valid state introduced in Chapter 1 were limited to logical consistency—that a state be itself in all cases (normalization) and that mutually exclusive states not be each other (orthogonality). The overlap between a bra-ket pair, $\langle\phi|\psi\rangle$, describes a similarity between two states. The bra-ket algebra provides a means of computing these overlaps by expressing the states as a sum of underlying basis states with known orthonormality relationships. This chapter will discuss ways of asking more sophisticated questions about quantum states. Asking these questions in the laboratory corresponds to a **measurement** of the system. We will introduce a mathematical formalism for describing the measurement process, and discuss some of the practical and philosophical implications of this formalism for interpreting quantum states.

## 2.1 Quantum states express knowledge about the actual state of a system.

Consider a multiple choice test with possible answer-choices $\{|A\rangle, |B\rangle, |C\rangle, |D\rangle\}$. Only one answer-choice may be selected (and hence not another answer-choice), which corresponds to an orthonormal basis, $\langle i|j\rangle = \delta_{ij}$ for $i, j \in \{A, B, C, D\}$. There is only one correct answer, but a student taking the test does not know the correct answer. Because this is a quantum test, you may submit a quantum state $|\psi\rangle$ as your answer that describes what you know. The requirement that $\langle\psi|\psi\rangle = 1$ is equivalent to submitting exactly one answer. Assuming that your goal is to be correct, what is the best possible strategy for constructing your response?

### 2.1.1 Quantum states can be interpreted as guesses about actual state of a system.

The simplest test presents only a single possible choice $|A\rangle$. There is only one possible state to choose from, so the best response can only be $|\psi\rangle = |A\rangle$—and this cannot but be correct. This is equivalent to maximizing the overlap of $\langle A|\psi\rangle$—asking the question "Is the correct answer $|A\rangle$?" of the statement "I think the answer is $|\psi\rangle$."

A more difficult test presents two possible choices, $\{|A\rangle, |B\rangle\}$, only one of which is correct. If you knew for certain that the correct answer was $|A\rangle$, then you should always submit $|\psi\rangle = |A\rangle$ as your response; and similar reasoning applies if you were certain that the correct answer was $|B\rangle$. But if you had no knowledge about the correct answer, then from your perspective both $A$ and $B$ could equally likely be correct. Constructing a state $|\psi\rangle$ that was mostly $|A\rangle$ would not capture your knowledge that $|B\rangle$ was equally possible; and similar reasoning would argue against constructing a $|\psi\rangle$ that mostly $|B\rangle$. Rather, you would want to submit a state that was equally $|A\rangle$ and $|B\rangle$. One possible choice is

$$|\psi\rangle = \tfrac{1}{\sqrt{2}}\left(|A\rangle + |B\rangle\right), \tag{2.1}$$

which maximizes the values of both *overlaps* to the same value,

$$\begin{aligned}\langle A|\psi\rangle &= \tfrac{1}{\sqrt{2}}\\ \langle B|\psi\rangle &= \tfrac{1}{\sqrt{2}}.\end{aligned} \tag{2.2}$$

What is the *probability* that the correct answer actually is $|A\rangle$ or $|B\rangle$? If both answers are equally likely to be correct, then the probabilities, $p_A$ and $p_B$, must be equal ($p_A = p_B$). Furthermore, because there is a correct answer, the sum of the probabilities must be one ($p_A + p_B = 1$)—this is just the normalization of classical probabilities. Therefore, the *probabilities* must be

$$\begin{aligned}p_A &= \tfrac{1}{2}\\ p_B &= \tfrac{1}{2}.\end{aligned} \tag{2.3}$$

Comparing Eq.(2.2) and Eq.(2.3) suggests a *tentative* relationship,

$$\begin{aligned}p_A &= \left(\langle A|\psi\rangle\right)^2\\ p_B &= \left(\langle B|\psi\rangle\right)^2,\end{aligned}$$

but this is not completely correct, because as discussed in Section 1.2.5 valid quantum states can have an arbitrary **global phase** of $\exp[i\theta]$. Using the completely valid state,

$$|\psi\rangle = \tfrac{e^{i\theta}}{\sqrt{2}}\Big(|A\rangle + |B\rangle\Big) \tag{2.4}$$

and applying the squaring operation for the probability would *incorrectly* predict

$$p_A = \left(\langle A|\psi\rangle\right)^2 = \frac{e^{2i\theta}}{2},$$

which would imply negative real-valued and complex-valued probabilities. This cannot be correct, because probabilities are real numbers between zero and 1.[1] This suggests that we should generalize our procedure. The generalization of the square on real numbers is the *complex conjugate* of complex numbers, which suggests that the *correct* relationship is

$$\begin{aligned} p_A &= |\langle A|\psi\rangle|^2 \\ &= (\langle A|\psi\rangle)^* (\langle A|\psi\rangle) \\ &= \langle\psi|A\rangle\langle A|\psi\rangle. \end{aligned} \tag{2.5}$$

All of these are identical expressions, with the last following from the interconversion of bras and kets by the Hermitian conjugate operation,

$$\langle\phi|\psi\rangle = (\langle\psi|\phi\rangle)^\dagger = (\langle\psi|\phi\rangle)^*,$$

that was discussed in Section 1.2.4. A similar expression as Eq.(2.5) can also be written for $p_B$. The form chosen for Eq.(2.5) also returns valid probabilities $(0 \leq p_A \leq 1)$ for other choices for the state, such as

$$\begin{aligned} |\psi\rangle &= \tfrac{1}{\sqrt{2}}|A\rangle + \tfrac{1}{\sqrt{2}}|B\rangle \\ |\psi\rangle &= \tfrac{1}{\sqrt{2}}|A\rangle - \tfrac{1}{\sqrt{2}}|B\rangle \\ |\psi\rangle &= \tfrac{1}{\sqrt{2}}|A\rangle + i\tfrac{1}{\sqrt{2}}|B\rangle \\ |\psi\rangle &= \tfrac{1}{\sqrt{2}}|A\rangle - i\tfrac{1}{\sqrt{2}}|B\rangle \end{aligned}$$

**Your turn:** Compute $p_A = \langle\psi|A\rangle\langle A|\psi\rangle$ for these four states.

The expression relating the probabilities to the quantum state overlaps in Eq.(2.5) is known as the **Born postulate**, was proposed in 1926 by the German physicist Max Born (1882-1970).[2] However, in 2019, it was shown that this is a consequence of the nature of quantum states and the need for a valid probability.[3] Appendix 2.5 describes a simplified form of the proof.

---

[1] In retrospect, similar reasoning applies to the single-choice test discussed at the beginning of this section; there too, the answer presented could have included an arbitrary global phase $\exp[i\theta]$.

[2] Born won the 1954 Nobel Prize in Physics for his "fundamental research in quantum mechanics, especially in the statistical interpretation of the wave function," as exemplified by this postulate and other work in quantum mechanics. Born was the first to realize that the mathematics of linear algebra could be used to describe quantum mechanics (which we will discuss in Chapter **??**). Aside from contributions to relativity, quantum mechanics, and solid state physics, he is also known by chemists for the Born-Haber cycle—devised during a chance meeting with physical chemist Fritz Haber in 1918—that is a staple of introductory thermodynamics. Born is also the grandfather of the singer/actress Olivia Newton-John (1948-).

[3] L. Masanes, T. D. Galley, M. P. Müller, "The measurement postulates of quantum mechanics are operationally redundant" *Nature Commun*, 10, 1361 (2019) doi:10.1038/s41467-019-09348-x

### 2.1.2 Quantum states can be constructed from probabilistic prior knowledge.

Eq.(2.5) can be used "in reverse" to construct states that utilize pre-existing knowledge about the state. For example, suppose that we know that $p_A = \frac{1}{4}$ and $p_B = \frac{3}{4}$, and want to choose values of $\alpha$ and $\beta$ to construct a state $|\psi\rangle = \alpha|A\rangle + \beta|B\rangle$ that reflect that knowledge. Eq.(2.5) implies that any choices satisfying

$$\begin{aligned} \tfrac{1}{4} &= \langle\psi|A\rangle\langle A|\psi\rangle = \alpha^*\alpha \\ \tfrac{3}{4} &= \langle\psi|B\rangle\langle B|\psi\rangle = \beta^*\beta \end{aligned}$$

are valid choices. This includes:

$$\alpha = \begin{cases} +\sqrt{\frac{1}{4}} & = +\frac{1}{2} \\ -\sqrt{\frac{1}{4}} & = -\frac{1}{2} \\ +\sqrt{\frac{-1}{4}} & = +i\frac{1}{2} \\ -\sqrt{\frac{-1}{4}} & = -i\frac{1}{2}, \end{cases} \tag{2.6}$$

and by similar reasoning:

$$\beta = \begin{cases} \pm\sqrt{\frac{3}{4}} & = \pm\frac{\sqrt{3}}{2} \\ \pm\sqrt{\frac{-3}{4}} & = \pm i\frac{\sqrt{3}}{2} \end{cases} \tag{2.7}$$

**Your turn:** Choose two pairs of $\alpha$ and $\beta$ from above and use Eq.(2.5) to verify that these give the correct probabilities.
**Your turn:** Create a state $|\psi\rangle$ consistent with probabilities $p_A = 0.05$ and $p_B = 0.95$.

### 2.1.3 Learning the system's actual state updates the best possible guess.

If state $|\psi\rangle$ describes the best guess about the true state of the system, then it should be adjusted as new information is gathered about the system. *Before* taking the test the correct answer is not known with complete certainty. A best guess about the correct answer, $|\psi\rangle = \alpha|A\rangle + \beta|B\rangle$, corresponds to an estimate that the correct answer will be $|A\rangle$ with $p_A = \alpha^*\alpha$ and $|B\rangle$ with $p_B = \beta^*\beta = 1 - p_A$. *After* the test, the correct answer is revealed to be $|A\rangle$. There remains no uncertainty about the correct state, so if given the opportunity to take the same test again, the best guess should be updated to $|\psi\rangle = |A\rangle$ (within some arbitrary global phase, which does not change the probability). The correct answer, $|A\rangle$, remains the same—what changes is your guess $|\psi\rangle$ about what that correct answer could be.

### 2.1.4 The same strategy is generalizable to any number of possible answer states.

The same approach used for the two choice example can be extended to tests with an arbitrary number of possible choices. For a system with $N$ different possible basis states, a complete lack of knowledge about the correct state can be expressed by equal superposition,

$$|\psi\rangle = \tfrac{1}{\sqrt{N}}|A\rangle + \tfrac{1}{\sqrt{N}}|B\rangle + \tfrac{1}{\sqrt{N}}|C\rangle + \cdots \tfrac{1}{\sqrt{N}}|N\rangle, \tag{2.8}$$

as well as other states where the coefficients have negative signs, the imaginary $i = \sqrt{-1}$, and an arbitrary global phase, $\exp[i\theta]$. This equal superposition corresponds to a **uniform prior** assumption that all states are equally likely to be true. In general, the probability with which we believe that a particular state $|J\rangle$ to be correct is

$$p_J = \langle\psi|J\rangle\langle J|\psi\rangle = |\langle J|\psi\rangle|^2, \tag{2.9}$$

and in the specific case of the Eq.(**??**), a probability $1/N$ is assigned to every possible state. Alternatively, any information about the true state of the system—obtained by performing measurements of the system or from other constraints—can be incorporated then Eq.(2.5) can be used to compute values of the coefficients that are consistent with this information.

## 2.2 Projectors express general questions about quantum states and measurements.

Bra-ket overlaps can be grouped and evaluated in any order. Thus, there is no mathematical distinction between

$$\begin{aligned} p_J &= \langle\psi|J\rangle\langle J|\psi\rangle \\ &= \Big(\langle\psi|J\rangle\Big)\Big(\langle J|\psi\rangle\Big) \\ &= \langle\psi|\Big(|J\rangle\langle J|\Big)|\psi\rangle \end{aligned} \tag{2.10}$$

This algebraic identity provides an interesting perspective on the measurement process. In Chapter 1, the bra, $\langle J|$, was described as the question, "Are you $J$?" and the ket, $|J\rangle$ as the statement, "I am $J$." When viewed in this way, the term $|J\rangle\langle J|$ can be read as a question-answer relationship about the state that pairs the answer "I am $J$" ($|J\rangle$) with the question "Are you $J$?" ($\langle J|$). Like a stencil, $|J\rangle\langle J|$ passes along the correct answers of $J$, but discards all of the other answers that are not-$J$. Ket-bra pairs of the form $|J\rangle\langle J|$ are called **projectors**; the analogy being that they project out the state $J$ from an input state. To see this, suppose that we have a state

$$|\psi\rangle = \alpha|A\rangle + \beta|B\rangle + \gamma|C\rangle + \cdots \tag{2.11}$$

Applying the projector, $|B\rangle\langle B|$ to $|\psi\rangle$ returns only the portion of that state matching $|B\rangle$,

$$\begin{aligned}
|\phi\rangle &= \Big(|B\rangle\langle B|\Big)|\psi\rangle \\
&= |B\rangle\ \Big(\langle B|\psi\rangle\Big) \\
&= \alpha|B\rangle\ \Big(\langle B|A\rangle + \beta|B\rangle\langle B|B\rangle + \gamma|B\rangle\langle B|C\rangle + \cdots\Big) \\
&= \alpha|B\rangle(0) + \beta|B\rangle(1) + \gamma|C\rangle(0) + \cdots \\
&= \beta|B\rangle. \qquad (2.12)
\end{aligned}$$

The projector, $|B\rangle\langle B|$, can be used to compute the probability of $B$,

$$\begin{aligned}
p_B &= \langle\psi|\ \Big(|B\rangle\langle B|\Big)\ |\psi\rangle \\
&= \langle\psi|\ \Big(|B\rangle\langle B|\psi\rangle\Big) \\
&= \Big(\alpha^*\langle A| + \beta^*\langle B| + \gamma^*\langle C| + \cdots\Big)\ \Big(\beta|B\rangle\Big) \\
&= \alpha^*\beta\langle A|B\rangle + \beta^*\beta\langle B|B\rangle + \gamma^*\beta\langle C|B\rangle + \cdots \\
&= \alpha^*\beta(0) + \beta^*\beta(1) + \gamma^*\beta(0) + \cdots \\
&= \beta^*\beta, \qquad (2.13)
\end{aligned}$$

in agreement with the earlier result.

The projector formalism can also be used to update $|\psi\rangle$ in accordance with this measurement outcome. Applying the projector $|B\rangle\langle B|$ to $|\psi\rangle$ yields a new state $|\phi\rangle$,

$$\begin{aligned}
|\phi\rangle &= \Big(|B\rangle\langle B|\Big)\ |\psi\rangle \\
&= |B\rangle\langle B|\ \Big(\alpha|A\rangle + \beta|B\rangle + \gamma|C\rangle + \cdots\Big) \\
&= |B\rangle\Big(\alpha\langle A|B\rangle + \beta\langle B|B\rangle + \gamma\langle C|D\rangle + \cdots\Big) \\
&= |B\rangle\Big(0 + \beta + 0 + \cdots\Big) \\
&= \beta|B\rangle. \qquad (2.14)
\end{aligned}$$

This is *almost* correct: the new state $|\phi\rangle$ has been correctly updated to consist solely of $|B\rangle$ (and not any other possible states), but fails to satisfy the normalization condition, $\langle\phi|\phi\rangle = 1$, required for a valid state description. However, as seen in Chapter 1, this can be correct by dividing by $\sqrt{\langle\phi|\phi\rangle}$. To rephrase this using projectors,

$$|\psi_{\text{new}}\rangle = \frac{|\phi\rangle}{\sqrt{\langle\phi|\phi\rangle}} \tag{2.15}$$

$$= \frac{\Big(|B\rangle\langle B|\Big)|\psi\rangle}{\sqrt{\Big(\langle\psi|\,|B\rangle\langle B|\Big)\,\Big(|B\rangle\langle B|\,|\psi\rangle\Big)}}$$

$$= \frac{\Big(|B\rangle\langle B|\Big)\,|\psi\rangle}{\sqrt{\langle\psi|B\rangle\langle B|\psi\rangle}}$$

$$= |B\rangle\frac{\langle B|\psi\rangle}{|\langle B|\psi\rangle|}, \tag{2.16}$$

which for the specific example of Eq.(2.12), is $|\psi_{\text{new}}\rangle = \Big(\beta/|\beta|\Big)|B\rangle$ or simply $|B\rangle$ to within a global phase.

### 2.2.1 Sums of projectors represent arbitrary queries about quantum states.

Instead of assessing a single target state, suppose that we are interested in learning about a collection of states. For example, perhaps there are two correct possible answers. This is equivalent to our measurement process not distinguishing between those two outcomes. For concreteness, suppose we are interested in the probability assigned to either states $|A\rangle$ and $|C\rangle$ (i.e, $p_A + p_C$), but not $|B\rangle$ or any other state. One could compute this using the process above, applying each of the projectors one at a time to derive

$$p_A = \langle\psi|\Big(|A\rangle\langle A|\Big)|\psi\rangle = |\alpha|^2 \tag{2.17}$$

$$p_C = \langle\psi|\Big(|C\rangle\langle C|\Big)|\psi\rangle = |\gamma|^2, \tag{2.18}$$

following the same process as above, and then computing the probability of either $|A\rangle$ or $|C\rangle$ as $p_{A\vee C} = p_A + p_C$. Alternatively, we could simply use a sum of projectors $|A\rangle\langle A| + |C\rangle\langle C|$, to compute the probability,

$$p_{A\vee C} = \langle\psi|\,\Big(|A\rangle\langle A| + |C\rangle\langle C|\Big)\,|\psi\rangle$$

$$= \Big(\langle\psi|A\rangle\langle A|\psi\rangle\Big) + \Big(\langle\psi|C\rangle\langle C|\psi\rangle\Big)$$

$$= (\alpha^*\alpha + 0 + 0 + \cdots) + (0 + 0 + \gamma^*\gamma + \cdots)$$

$$= |\alpha|^2 + |\gamma|^2 \tag{2.19}$$

$$= p_A + p_C, \tag{2.20}$$

and obtain the same result.

Projection operators allow us to pose questions that are not necessarily in the language of the basis states. Suppose we want the probability associated with the state $|\phi\rangle = (|A\rangle - |B\rangle)/\sqrt{2}$. Before we begin, let us state an intermediate result,

$$\begin{aligned}
\langle A|\phi\rangle &= \left(\langle A|A\rangle - \langle A|B\rangle\right)/\sqrt{2} = \tfrac{1}{\sqrt{2}} \\
\langle B|\phi\rangle &= \left(\langle B|A\rangle - \langle B|B\rangle\right)/\sqrt{2} = -\tfrac{1}{\sqrt{2}} \\
\langle C|\phi\rangle &= 0.
\end{aligned}$$

The corresponding projection operator corresponding for $\phi$ is $|\phi\rangle\langle\phi|$, and the probability associated with that outcome for the state $|\psi\rangle = \alpha|A\rangle + \beta|B\rangle + \gamma|C\rangle + \cdots$ is

$$\begin{aligned}
p_\phi &= \langle\psi|\ \left(|\phi\rangle\langle\phi|\right)\ |\psi\rangle \\
&= \left(\alpha^*\langle A|\phi\rangle + \beta^*\langle B|\phi\rangle + \gamma^*\langle C|\phi\rangle + \cdots\right)\left(\alpha\langle\phi|A\rangle + \beta\langle\phi|B\rangle + \gamma\langle\phi|C\rangle + \cdots\right) \\
&= \left(\alpha^*/\sqrt{2} - \beta^*/\sqrt{2} + 0 + \cdots\right)\left(\alpha/\sqrt{2} - \beta/\sqrt{2} + 0 + \cdots\right) \\
&= \left(|\alpha|^2 + \alpha^*\beta + \beta^*\alpha + |\beta|^2\right)/2. \qquad (2.21)
\end{aligned}$$

Let us examine two special cases. If $\alpha$ and $\beta$ are real number ($\alpha = \alpha^*$ and $\beta = \beta^*$) then this simplifies to

$$p_\phi = \left(|\alpha|^2 + 2\alpha\beta + |\beta|^2\right)/2,$$

The product of the $\alpha$ and $\beta$ coefficients in Eq.(2.22) get added in the intermediate cross term, resulting in a **constructive interference** between the two states $|A\rangle$ and $|B\rangle$. In contrast, if one is real ($\alpha = \alpha^*$) and the other is purely imaginary ($\beta = -\beta^*$), then

$$\begin{aligned}
p_\phi &= \left(|\alpha|^2 + \alpha\beta - \beta\alpha + |\beta|^2\right)/2 \\
&= \left(|\alpha|^2 + 0 + |\beta|^2\right)/2. \qquad (2.22)
\end{aligned}$$

then the two cross terms formed by the products have the opposite sign in Eq.(2.22), resulting in a **destructive interference** between their states in the final probability calculation.

### 2.2.2 Multiple applications of a projector leaves the state unchanged.

Measuring a state once returned a definite answer. Measuring the same state again should return the same answer—our knowledge does not change each time we look at the same state. If projectors are a valid description of the measurement process, they should also have this property of giving the same result if we apply them repeatedly. An operation with this property is said to be

**idempotent**—from the Latin *idem*: same, *potent*: being. It is straightforward to demonstrate that projectors have this property. Consider a single projector, $|A\rangle\langle A|$ and some state $\Psi$. Applying the projector once yields,

$$\left(|A\rangle\langle A|\right)\,\psi = |A\rangle\,\left(\langle A|\psi\rangle\right). \tag{2.23}$$

Applying it twice yields,

$$\begin{aligned}\left(|A\rangle\langle A|\right)\,\left(|A\rangle\langle A|\right)\,\psi &= |A\rangle\,\left(\langle A|A\rangle\right)\,\left(\langle A|\psi\rangle\right)\\ &= |A\rangle\,(1)\,\langle A|\psi\rangle,\end{aligned} \tag{2.24}$$

where the second step relies upon the normality of $|A\rangle$ such that $\langle A|A\rangle = 1$; the final result is identical to Eq.(2.23). Subsequent application of $|A\rangle\langle A|$ to Eq.(2.24) will also give the same result.

**Your turn:** Demonstrate that sums of projectors, e.g., $(|A\rangle\langle A| + |C\rangle\langle C|)$ are also idempotent by applying to a general state $\psi$. Assume that $|A\rangle$ and $|C\rangle$ are orthonormal.

### 2.2.3 Applying the sum of all projectors leaves the system unchanged.

A single projector, $|A\rangle\langle A|$ extracts only the portion of the system having the state $|A\rangle$, and evaluates a probability $p_A$. We've seen that a sum of projectors, e.g., $|A\rangle\langle A| + |C\rangle\langle C|$, extracts only those parts, and is correct with the sum of the probabilities, $p_A + p_C$, corresponding to the two projectors. What if we considered the sum of all projectors

$$\hat{I} = |A\rangle\langle A| + |B\rangle\langle B| + |C\rangle\langle C| + \cdots \tag{2.25}$$

for a system? Applying $\hat{I}$ to the system will project out every state, excluding none, and thus leaving the system unchanged, $\hat{I}|\psi\rangle = |\psi\rangle$. Approaching this from the perspective of a probability calculation, it corresponds to a correct guess every time, because $p_A + p_B + p_C + \cdots = 1$ by the normalization of classical probability. This is referred to as the **identity operator**, because it is the projector equivalent of multiplying by one, leaving the state unchanged.

### 2.2.4 Projectors for multi-particle systems can be composed using the tensor product.

The language of projectors can also be used to ask questions about the subsystems that comprise a composite quantum state, by using the **tensor product** operation defined in Section 1.2.6. The question, "is the first part in state $\psi$ *and* the second part in state $\phi$?" can be represented by taking the tensor product of the two questions, where as with the formation of product states we assume the particles have some defined ordering.

$$|\psi\rangle\langle\psi| \otimes |\phi\rangle\langle\phi| = |\psi,\phi\rangle\langle\psi,\phi| \tag{2.26}$$

Including the identity operator (Eq.(2.25)) for one of the subsystems is equivalent to just ignoring that subsystems in the measurement, as

$$
\begin{aligned}
|\psi\rangle\langle\psi| \otimes \hat{I} &= |\psi\rangle\langle\psi| \otimes \left(|A\rangle\langle A| + |B\rangle\langle B| + |C\rangle\langle C| + \cdots\right) \\
&= |\psi\rangle\langle\psi| \otimes |A\rangle\langle A| + |\psi\rangle\langle\psi| \otimes |B\rangle\langle B| + |\psi\rangle\langle\psi| \otimes |C\rangle\langle C| + \cdots \\
&= |\psi, A\rangle\langle\psi, A| + |\psi, B\rangle\langle\psi, B| + |\psi, C\rangle\langle\psi, C| + \cdots \,, \qquad (2.27)
\end{aligned}
$$

as one can see that any of the possibilities for the second subsystem will be carried forward by the projector.

## 2.3 Quantum states may express indeterminacy of the physical system.

Our discussion has supposed that there is a pre-existing correct answer, and $|\psi\rangle$ expresses a guess based on incomplete knowledge about that correct answer. This **epistemological** interpretation—from the Greek ἐπιστήμη, *episteme*, knowledge—posits that $|\psi\rangle$ expresses knowledge (or lack thereof) about the system. A mathematically identical, but philosophically distinct, **ontological** interpretation—from the Greek ὄντος, *ontos*, being, that which is—posits that $|\psi\rangle$ describes what the system actually is.[4] Rather than the single pre-existing correct answer in the epistemological interpretation, in the ontological interpretation the system is more like a die and asking a question is like rolling that die. Each roll of a new die yields a different, randomly selected answer, whose probability is determined by the die's quantum state. This is a subtle distinction. In the $\psi$-epistemic interpretation the *experimenter* does not know the answer; in the $\psi$-ontic interpretation the *system* does not know the answer the measurement is performed. This leads to a very different implied world view: A $\psi$-epistemic interpretation posits that there is a single definite state, which might be known by an omniscient deity, but as non-omniscient beings, we often are limited to making guesses about that state. In contrast, the $\psi$-ontic interpretation posits that even God plays dice.[5]

### 2.3.1 The $\psi$-ontic and $\psi$-epistemic interpretations make the same predictions.

Philosophy aside, the two interpretations are mathematically identical. In Eq.(2.5), we expressed the probability of the true state of the system $|A\rangle$ correspond to the experimenter's guess $|\psi\rangle$ as

---

[4] People believing this interpretation are $\psi$-ontologists.

[5] "God doesn't play dice," is the frequent paraphrase of a statement made by Albert Einstein in a 04 Dec 1926 letter to Max Born. The full quote is more informative and reveals the unease with which a physicist might view the epistemic interpretation: *„Die Quantenmechanik ist sehr actunggebietend. Aber eine innere Stimme sagt mir, dass das noch nicht der wahre Jakob ist. Die Theorie liefert viel, aber dem Geheimnis des Alten bringt sie uns kaum näher. Jedenfalls bin ich überzeugt, dass* der *nicht würfelt."* ("Quantum mechanics is a rather awe-inspiring theory. But an inner voice tells me that it is not the real McCoy. The theory yields much, but it hardly brings us close to the Old One's secrets. In any case, I am convinced He does not play dice.")

$$p_A = \langle\psi|A\rangle\langle A|\psi\rangle. \tag{2.28}$$

But alternatively, we could just swap the order of the two overlaps

$$p_A = \langle A|\psi\rangle\langle\psi|A\rangle, \tag{2.29}$$

where now $|\psi\rangle$ is the true state of the system, measured using the projector $|\psi\rangle\langle\psi|$ and $|A\rangle$ is our guess about about its state. This "guess" is only a single definite outcome, so a more natural interpretation is to consider this as the definite readout on some measurement apparatus. In this interpretation, $p_A$ is the probability that the detector reads out "A" when measuring the particle. The detector either reads out "A" when it detects $|A\rangle$ or it does not (when it does not detect $|A\rangle$). We learn the probability by generate many copies of the system $|\psi\rangle$, measuring each of them, and performing a statistical analysis of the results. Thus the $\psi$-ontic interpretation assigns a **frequentist** interpretation of probability as the limit of an event's relative frequency over a large number of experimental trials. In contrast, the $\psi$-epistemic interpretation assigns a **Bayesian** interpretation of probability, in which it quantifies belief and expectation.

The frequentist approach suggests an interpretation of the projectors as computing average properties of the state $\psi$. Eq.(2.28) can be rewritten as

$$\begin{aligned} p_A &= \langle\psi|\Big(|A\rangle\langle A|\Big)|\psi\rangle, \\ &= \langle\psi|\hat{Q}|\psi\rangle \end{aligned} \tag{2.30}$$

in which $\hat{Q} = |A\rangle\langle A|$ defines a query about a system ("Is this thing $A$?") and $\langle\psi|\hat{Q}|\psi\rangle$ is the average value of that query ("On average value $|\psi\rangle$ is $A$ with probability $p_A$.) when repeated many times. These average values are also described as an **expectation value** for the query, and in the $\psi$-epistemic approach, this is simply an expectation about what will occur. In the next chapter, we will see that Eq.(2.30) provides a way for expressing more general questions about the properties of quantum states.

### 2.3.2 In the $\psi$-ontic interpretation, measurement collapses the system's state to the observed state.

Both interpretations trust the veracity of the measurement. If the system is observed to have state $|A\rangle$, then the system must now be in state $|A\rangle$—about this there can be no doubt. The two interpretations differ in how the system came to have that state. A $\psi$-epistemic interpretation posits that the system was *already* in state $|A\rangle$; the measurement merely updates our *subjective* knowledge, $|\psi\rangle$, about the system's true state. In contrast, a $\psi$-ontic interpretation posits that the system was actually in the state $|\psi\rangle$ before measurement, and the measurement process changed the *objective* state of the system to become $|A\rangle$

(with some probability $p_A$). This offers the counterfactual alternative that it *could* have become some different state with probability $1 - p_A$. In the $\psi$-ontic interpretation the observation causes the pre-measurement state, $|\psi\rangle$ to **collapse** into the observed state, $|A\rangle$. Measuring a system—merely looking at it—changes the system in an abrupt, non-deterministic way.

The $\psi$-ontic **Copenhagen interpretation** of measurement (developed by Niels Bohr and Werner Heisenberg, at Bohr's institute in Copenhagen in 1925-1927) is one of the most commonly taught interpretations of quantum mechanics. This may seem strange, given the fundamental indeterminacy it assigns to the behavior of the world. (And let us not forget, that quantum mechanics is not only a theory of strange little things like electrons and atoms and molecules, but by extension of the entire physical world.) Proponents argue that physics should be about the actual things of the world—and so to speak of the state of a system should be to describe the actual thing in itself. The price paid for assigning a reality to the state is that it has this unusual behavior. In contrast, the $\psi$-epistemic world view discussed earlier in this chapter limits itself to describing subjective knowledge *about* the world, not the world itself. Subjective knowledge is usually considered a branch of psychology or economics, rather than physics, and it seems that this gets us no closer to knowledge about what the world actually is. Which interpretation you prefer is a matter of taste, and you should feel uncomfortable about both alternatives, but at the same time, free to use them interchangeably.[6]

## 2.4 Classic examples of quantum measurement

### 2.4.1 The Stern-Gerlach Experiment

The Stern-Gerlach experiment was the first experiment to study a spin-1/2 system, specifically by probing the interaction of an unpaired electron with an externally applied magnetic field, and is the paradigmatic example of quantum measurement. The original version, conceived by Otto Stern (an assistant to Max Born) in 1921, and conducted together with Walther Gerlach in Frankfurt in 1922, used silver atoms; as you will recall from your general chemistry course work, these atoms have an unpaired *s*-electron in their valence shell. However, the principle is entirely general and applies to any spin-1/2 system: T. E. Phipps and J. Taylor reproduced the effect using hydrogen atoms in 1927, and Isidore Rabi performed related studies using nuclear spin-1/2 systems ( measuring the outcome using radio wave absorption) that were a precursor to the principles used in NMR spectroscopy, about which we will have more to say in the following

---

[6] "Interpretations of quantum mechanics, unlike Gods, are not jealous, and thus it is safe to believe in more than one at the same time. So if the many-worlds interpretation makes it easier to think about the research you're doing in April, and the Copenhagen interpretation makes it easier to think about the research you are doing in June, the Copenhagen interpretation is not going to smite you for praying to the many-worlds interpretation. At least I hope it won't because otherwise I'm in big trouble." –Peter Shor, comment on Shtetl Optimized (`TODO` in 2007.

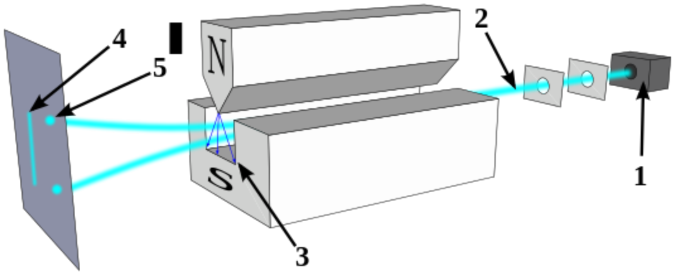

Figure 2.1: Stern–Gerlach experiment: Silver atoms traveling through an inhomogeneous magnetic field, and being deflected up or down depending on their spin; (1) furnace, (2) beam of silver atoms, (3) inhomogeneous magnetic field, (4) classically expected result, (5) observed result. Image Source: Theresa Knott, CC A-SA 4.0 `https://commons.wikimedia.org/wiki/File:Stern-Gerlach_experiment_svg.svg`

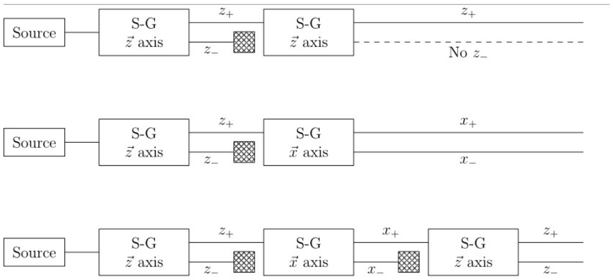

Figure 2.2: Top: Measurement when $|z+\rangle = |\uparrow\rangle$ is passed through a second, identical S-G apparatus, resulting in only $|z+\rangle = |\uparrow\rangle$ being output, as expected. Middle: Sending the $|\uparrow\rangle$ states through an apparatus that measures either $|x+\rangle = |\leftarrow\rangle$ or $|x-\rangle = |\rightarrow\rangle$. Bottom: Feeding the $|x+\rangle = |\leftarrow\rangle$ output results in both $|\uparrow\rangle$ and $|\downarrow\rangle$ output, suggesting that the measurement must be altering the states of the particles. Image Source: Francesco Versaci, public domain `https://commons.wikimedia.org/wiki/File:Sg-seq.svg`

chapters.

The basic setup of the experiment is illustrated in Figure 2.1. A hot furnace is used to produce a gas of silver atoms, and a small pinhole in the furnace allows those atoms to escape in the form of a beam. As you will recall from your general chemistry class (e.g. during the discussion of paramagnetism), an unpaired electron behaves like a little bar magnet. When placed in an inhomogeneous external magnetic field, the spin will align with the magnetic field—in other words, its energy is lower when aligned against the magnetic field (N-S) and higher when aligned with the magnetic field (N-N). This is the same principle used by a magnetic compass, in which a magnetized needle orients itself with the external magnetic field of the Earth. A (classical) compass can have any state between north and south, each with a characteristic energy. On the other hand, a spin-1/2 particle only has *two* states, $|\uparrow\rangle$ and $|\downarrow\rangle$, and this is precisely what Stern and Gerlach observed in their experiment. The magnetic field causes splits the beam into those spins aligned with and opposed to the field (the two states), and collision with a plate *measures* the state of the system, either as $|\uparrow\rangle\langle\uparrow|$ or $|\downarrow\rangle\langle\downarrow|$, resulting in two two observed "spots" observed. This is the fundamental experimental demonstration that the system is described by the two-state spin-1/2 model. Typically the $z$-axis is chosen to correspond to the up-down basis, but one is free to rotate the magnets by 90°, corresponding to a measurement of $|\leftarrow\rangle = (|\uparrow\rangle + |\downarrow\rangle)/\sqrt{2}$ and $|\rightarrow\rangle = (|\uparrow\rangle - |\downarrow\rangle)/\sqrt{2}$.

This first version is sufficient to know that the system is a spin-1/2, but the Stern-Gerlach experiment gets especially interesting when we consider multiple measurements. We'll consider three possible variations depicted in Figure 2.2. In all cases, the silver atoms emerge from the oven with some unknown possible initial state, $|\psi\rangle = \alpha|\uparrow\rangle + \beta|\downarrow\rangle$. We'll begin by measuring along the $z$-axis, and allowing the $|\uparrow\rangle$ states to continue through (the unlucky $|\downarrow\rangle$ states collide with a barrier). This first measurement produces a beam of purely $|{\uparrow}\rangle$ atoms for use during the subsequent experiments. The first scenario (top inset) considers the case where re-measure that resulting beam. What is the probability associated with observing $|{\uparrow}\rangle$? The state was $|{\uparrow}\rangle$ after the initialization step, so it must still be up with probability one. The second scenario (middle inset), considers the case where the $|{\uparrow}\rangle$ beam is sent through a Stern-Gerlach apparatus along the $x$-axis. The projectors for the $|{\leftarrow}\rangle$ and $|{\rightarrow}\rangle$ are used to calculate the probabilities associated with each of these measurement outcomes. The projector for measuring $x+$ is,

$$\begin{aligned} |{\leftarrow}\rangle\langle{\leftarrow}| &= \left(|{\uparrow}\rangle + |{\downarrow}\rangle\right)\left(\langle{\uparrow}| + \langle{\downarrow}|\right)/2 \\ &= \left(|{\uparrow}\rangle\langle{\uparrow}| + |{\downarrow}\rangle\langle{\uparrow}| + |{\uparrow}\rangle\langle{\downarrow}| + |{\downarrow}\rangle\langle{\downarrow}|\right)/2, \end{aligned} \tag{2.31}$$

and the probability associated with observing this outcome for the initial state $|{\uparrow}\rangle$ is

$$\begin{aligned} p_{\leftarrow} &= \langle{\uparrow}|\Big(|{\leftarrow}\rangle\langle{\leftarrow}|\Big)|{\uparrow}\rangle \\ &= \langle{\uparrow}|\Big(|{\uparrow}\rangle\langle{\uparrow}| + |{\downarrow}\rangle\langle{\uparrow}| + |{\uparrow}\rangle\langle{\downarrow}| + |{\downarrow}\rangle\langle{\downarrow}|\Big)|{\uparrow}\rangle/2 \\ &= \Big((1)(1) + (0)(1) + (1)(0) + (0)(0)\Big)/2 \\ &= 1/2, \end{aligned} \tag{2.32}$$

and the state of the system observed to have this outcome must now be $|{\leftarrow}\rangle$.

**Your turn:** What is $p_{\leftarrow}$ when the initial state is $|{\downarrow}\rangle$?
**Your turn:** Expand $|{\rightarrow}\rangle\langle{\rightarrow}|$ into an expression into $|{\uparrow}\rangle$ and $|{\downarrow}\rangle$ basis expression.
**Your turn:** Compute $p_{\rightarrow}$ for the state $|{\uparrow}\rangle$.

So far this seems reasonable. The first measurement asked whether the particle was in the state $z+$, and the second measurement asks whether it is $x+$. It is plausible that these two different questions give different answers. Where it gets interesting is the variant of the experiment shown in the bottom inset of Figure 2.2. The beam of $|{\leftarrow}\rangle$ atoms that emerge from the $x+$ measurement are measured *again* along the $z$-axis. Previously these *same* atoms had been measured to be $|{\uparrow}\rangle$, so we would naïvely expect them to be $|{\uparrow}\rangle$ in this measurement as well. Except, that's *not* what Stern-Gerlach observed, nor what quantum mechanics predicts. Using the $|{\uparrow}\rangle\langle{\uparrow}\,|$ measurement applied to the $|{\leftarrow}\rangle$ state,

$$\begin{aligned} p_\uparrow &= \langle\leftarrow|\Big(|{\uparrow}\rangle\langle{\uparrow}|\Big)|{\leftarrow}\rangle \\ &= \Big(|{\uparrow}\rangle + |{\downarrow}\rangle\Big)|{\uparrow}\rangle\langle{\uparrow}|\Big(|{\uparrow}\rangle + |{\downarrow}\rangle\Big)/2 \\ &= \Big(\langle\uparrow|\uparrow\rangle\langle\uparrow|\uparrow\rangle + \langle\uparrow|\uparrow\rangle\langle\uparrow|\downarrow\rangle + \langle\downarrow|\uparrow\rangle\langle\uparrow|\uparrow\rangle + \langle\downarrow|\uparrow\rangle\langle\downarrow|\uparrow\rangle\Big)/2 \\ &= \Big((1)(1) + (1)(0) + (0)(1) + (0)(0)\Big)/2 \\ &= 1/2, \end{aligned} \tag{2.33}$$

indicating that only *half* of the particles are observed to be $|{\uparrow}\rangle$, with the other half measured to be $|{\downarrow}\rangle$. What happened here? This seems at odds with the $\psi$-epistemic picture, as we should not have lost knowledge about the system. On the other hand, it seems to support the $\psi$-ontic picture, as the process of measuring $|{\leftarrow}\rangle$ has lead to an actual change in the state of the atom.

**Your turn:** Verify that $p_\downarrow = 1/2$ by performing an explicit calculation.

### 2.4.2 Schrödinger's Cat

Adopting the $\psi$-ontic interpretation presents other problems when we think about measurement. A classic example is the *gedanken*-experiment—from the German: *Gedanken*:thought—proposed by Schrödinger. Don't worry, no actual cats are harmed, as this is purely a thought experiment to show why the $\psi$-ontic interpretation is questionable. However, lest you should think this is merely a speculation, know that Serge Haroche (1944-) and David J. Wineland (1944-) were awarded the 2012 Nobel Prize in physics for *experimental* tests of this process, albeit with photons and atoms instead of cats. Here's what Schrödinger wrote:[7]

> One can even set up quite ridiculous cases. A cat is penned up in a steel chamber, along with the following device (which must be secured against direct interference by the cat): in a Geiger counter, there is a tiny bit of radioactive substance, so small, that perhaps in the course of the hour one of the atoms decays, but also, with equal probability, perhaps none; if it happens, the counter tube discharges and through a relay releases a hammer that shatters a small flask of hydrocyanic acid. If one has left this entire system to itself for an hour, one would say that the cat still lives if meanwhile no atom has decayed. The first atomic decay would have poisoned it. The

---

[7] E. Schrödinger, "Die gegenwärtige Situation in der Quantenmechanik," *Naturwissenschaften* **23**, 807–812 (1935) doi:10.1007/BF01491891; J. D. Trimmer, "The Present Situation in Quantum Mechanics: A Translation of Schrödinger's "Cat Paradox" Paper". *Proc. Am. Phil. Soc.* **124**, 323–338 (1980). JSTOR 986572

> psi-function of the entire system would express this by having in it the living and dead cat (pardon the expression) mixed or smeared out in equal parts.
>
> It is typical of these cases that an indeterminacy originally restricted to the atomic domain becomes transformed into macroscopic indeterminacy, which can then be resolved by direct observation. That prevents us from so naively accepting as valid a "blurred model" for representing reality. In itself, it would not embody anything unclear or contradictory. There is a difference between a shaky or out-of-focus photograph and a snapshot of clouds and fog banks.

For simplicity, we will describe the atom and the cat as spin-1/2 particles, as they both have two states in this story. The atom is either undecayed ($\uparrow$) or decayed ($\downarrow$) and the cat is either alive ($\uparrow$) or dead ($\downarrow$). The state of indeterminacy is one where we are equally uncertain about the atom's state (which should be the same as the cat's state)

$$|atom, cat\rangle = \left(|{\uparrow\uparrow}\rangle + |{\downarrow\downarrow}\rangle\right)/\sqrt{2} \tag{2.34}$$

In a sense, this is not a problem of measurement, *per se*. Observing the atom as decayed corresponds to a measurement of $|{\downarrow}\rangle\langle{\downarrow}| \otimes (|{\uparrow}\rangle\langle{\uparrow}| + |{\downarrow}\rangle\langle{\downarrow}|) = |{\downarrow\uparrow}\rangle\langle{\downarrow\uparrow}| + |{\downarrow\downarrow}\rangle\langle{\downarrow\downarrow}|$, which always gives a consistent answer. The real trouble is interpreting what Eq.(2.34) means. Most of us have an experience with live cats, and can at least imagine the experience of a dead cat. These are two clearly distinct states, but it is unclear how we should interpret the cat's portion of $|atom, cat\rangle$. Schrödinger found it implausible that a macroscopic, wet, fuzzy mammal is in a superposition state between alive ($|{\uparrow}\rangle$) and dead ($|{\downarrow}\rangle$)—and you might agree. This presents a problem for the $\psi$-ontic perspective, and there are many possible escape paths that have been posited. From the $\psi$-epistemic perspective it presents no problem—we simply do not know the answer, and the superposition attributed to the cat's state is simply our best bet in the absence of other knowledge. This is an interpretative puzzle at the heart of quantum mechanics, but whether we like the interpretation or not, it appears to be the way that nature works.

### 2.4.3 The Two Slit Experiment

### 2.4.4 Bell Inequalities

See `https://en.wikipedia.org/wiki/Bell%27s_theorem`

### 2.4.5 Quantum Pseudo-Telepathy

See `https://en.wikipedia.org/wiki/Quantum_pseudo-telepathy`

## 2.5 Appendix: The Born Postulate is a consequence of probability and the definition of states.

See `https://www.nature.com/articles/s41467-019-09348-x`

## Problems

1. Consider the $sp^2$ hybrid orbitals defined in Eqs.(1.26-1.28). Supposing that you could measure which (non-hybrid) atomic orbital the electron was present in, what are the probabilities of finding the electron in the $2s$, $2p_x$ and $2p_y$ orbitals for each of the hybrid orbitals?

2. Consider the HeH$^+$ molecule, in which the two electrons (one with spin up and one with spin down) are described as being in a molecular orbital expressed in the basis of atomic orbitals on the two atoms $|1s_{He}\rangle$ and $|1s_H\rangle$. The *bonding* molecular orbital has the form $|b\rangle = \alpha|1s\ _{He}\rangle + \beta|1s_H\rangle$, where $\alpha$ and $\beta$ are both positive real scalars.For simplicity, let us assume that the two atomic orbital basis functions are orthonormal. (a) Derive an expression for the probability of finding one electron on the Helium atom using the Born probability rule, Eq.(2.5), as a function of $\alpha$ (b) Your expression from part (a) gives the expected value of finding each electrons in that molecular orbital on the helium atom; because there are two electrons in the molecule, what is the *total* expected number of electrons on the helium atom? (c) Derive an expression for the *net charge* on the helium atom, i.e., the number of (positively-charged) protons minus the number of (negatively-charged) electrons. (d) Given the *net* charges 0.698 and 0.302 on the He and H nuclei respectively,[8], determine the values of $\alpha$ and $\beta$ that describe the bonding molecular orbital, $|b\rangle$. (e) Using your bonding orbital, devise an *antibonding* molecular orbital, of the form $|a\rangle = \alpha'|1s_{He}\rangle - \beta'|1s_H\rangle$, by using the orthogonality relationship, $\langle a|b\rangle = 0$, and the requirement of normalization $\langle a|a\rangle = 0$.

3. The $x$-axis measurement described for the Stern-Gerlach experiment is a rotation by 90° degrees of the magnet, but might also be conducted with the second magnet rotated by 45°, corresponding to a measurement along along the $|\nwarrow\rangle = \left(|\uparrow\rangle + \sqrt{3}|\downarrow\rangle\right)/2$ measurement. Compute the outcome probabilities for observing this state (given an initial state of $|\uparrow\rangle$), and for measuring $|\uparrow\rangle$ (given this state as the initial state).

4. TODO: Multiple particle measurement problem

5. TODO: Bell-Inequality type measurement

---

[8] Hartree-Fock/6-311+G(2d,p) level Mulliken charges.

# Math Chapter: Probability & Statistics

McQuarrie Math Chapter B

# Computational Chapter: Functions

(ICPC Appendix A)

A function is just an input-output relationship, e.g., f(x)
Built-in functions
Defining your own functions
Plot[]
Minimum[] / Maximum[]

# Chapter 3

# Operators

> To encounter the quantum is to feel like an explorer from a faraway land who has come for the first time upon an automobile. It is obviously meant for use, and an important use, but what use? One opens the door, cranks the window up and down, flashes the lights on and off, and perhaps even turns over the starter, all the time without knowing the central point of the thing. The quantum is the automobile. We use the quantum in a transistor to control machinery, in a molecule to design an anesthetic, in a superconductor to make a magnet. Could it be that all the time we have been missing the central point, the use of the quantum phenomenon in the construction of the universe itself?
>
> ---
>
> John Archibald Wheeler, "Law without Law"

Chapter 1 described the requirements for a valid quantum mechanical state, and Chapter 2 described how to learn about that state by asking mathematical questions corresponding to laboratory measurements. Yet nothing in this world is static—everything appears to be in motion, changing from one state to another, either as a result of experimental interventions or as a natural process in time. A complete theory must therefore describe how states evolve into other states. The evolution from an initial state to some final state (but not to others) can be viewed as a relationship between the initial and final states. More generally, the relationships between states can include timeless intrinsic relations that are independent of any external intervention. The relationships between states define the questions and answers about the properties of the states.

## 3.1 Operators define relationships between states.

Quantum **operators** describe functions relating an input state to an output state. Functions can be defined by a set of rules describing an explicit transformation process for each input. Not all functions are valid operators, as logical consistency constrains the possibilities for valid functions operating on quantum states.

### 3.1.1 Operators can be described as a set of rules.

By convention, an operator named "$O$", is indicated by a "hat", $\hat{O}$. Operators apply to the right; $\hat{O}|\psi\rangle$ corresponds to applying the operator to the state $\psi$. By this convention, $\hat{O}_2\hat{O}_1|\psi\rangle$ should be interpreted as $\hat{O}_2(\hat{O}_1|\psi\rangle)$, i.e., first apply $\hat{O}_1$ to $|\psi\rangle$ and then apply $\hat{O}_2$ to the resultant state.[1]

Operators may be defined as a set of rules in terms of the possible basis states of the system. The number of rules is the same as the number of basis states. As an example, consider the spin-$\frac{1}{2}$ system discussed in Section 1.3.1, with basis states $|\uparrow\rangle$ and $|\downarrow\rangle$. Everyday experience with other two state systems, such as coins and switches, suggests a few possible operators that change the system from one state to another. The *identity* operator, $\hat{I}$, transforms a state into itself:

$$\begin{aligned}\hat{I}|\uparrow\rangle &= |\uparrow\rangle \\ \hat{I}|\downarrow\rangle &= |\downarrow\rangle. \qquad (3.1)\end{aligned}$$

This may not seem particularly exciting, but it is one possible transformation of a state into another state, and is useful for constructing other operators.

**Your turn:** Define an identity operator for a system with basis states $|A\rangle, |B\rangle, |C\rangle$.

The *flip* operator, $\hat{\sigma}_x$, converts up to down and vice versa. One can define this operator in terms of its consequences on the state it operates upon:

$$\begin{aligned}\hat{\sigma}_x|\uparrow\rangle &= |\downarrow\rangle \\ \hat{\sigma}_x|\downarrow\rangle &= |\uparrow\rangle. \qquad (3.2)\end{aligned}$$

**Your turn:** Define a three-way flip operator that converts $|A\rangle \rightarrow |B\rangle$, converts $|B\rangle \rightarrow |C\rangle$ and converts $|C\rangle \rightarrow |A\rangle$.

Operators can also be defined that assign multiplicative constants on different states. For example, suppose we play a coin-flip game together using the spin-1/2 system. You win the game with up, and your opponent wins on down. One can describe the payout (from your perspective) as $+1$ when you win and $-1$ when you lose. The operator $\hat{\sigma}_Z$ encodes this payout information by multiplying the state by $\pm 1$ accordingly, but otherwise leaves the state unchanged:

$$\begin{aligned}\hat{\sigma}_z|\uparrow\rangle &= (+1)|\uparrow\rangle \\ \hat{\sigma}_Z|\downarrow\rangle &= (-1)|\downarrow\rangle. \qquad (3.3)\end{aligned}$$

---

[1] Operators are also **associative**, meaning that $\hat{O}_2\left(\hat{O}_1|\psi\rangle\right) = \left(\hat{O}_2\hat{O}_1\right)|\psi\rangle$, which will become more apparent when we define the operators in terms of projectors in Section 3.2.

Operators are not restricted to output only basis states; in general they may output arbitrary quantum states. For example, one may define the following operator that outputs an equal superposition with a relative phase that depends on what the input state is:

$$\begin{aligned}\hat{S}|\uparrow\rangle &= \left(|\uparrow\rangle + |\downarrow\rangle\right)/\sqrt{2} \\ \hat{S}|\downarrow\rangle &= \left(|\uparrow\rangle - |\downarrow\rangle\right)/\sqrt{2}. \end{aligned} \tag{3.4}$$

Notice that the relative phase is different for the two input states, and the two output states $(|\uparrow\rangle \pm |\downarrow\rangle)/\sqrt{2}$ are orthonormal.

**Your turn:** Define an operator that acts on three orthonormal basis states, $\{|A\rangle, |B\rangle, |C\rangle\}$ and outputs three orthonormal equal superpositions of those states, analogous to Eq.(3.4)

Finally, operators can also apply to multiple particles at the same time. For example, consider the following operator that acts on two spins (denoted $|\uparrow\uparrow\rangle = |\uparrow\rangle \otimes |\uparrow\rangle$, etc., as introduced in Section 1.2.6). If the first spin is ↑, then it flips the state of the second spin; otherwise it leaves the state unchanged. The rules corresponding to this process are

$$\begin{aligned}\hat{C}|\uparrow\uparrow\rangle &= |\uparrow\downarrow\rangle \\ \hat{C}|\uparrow\downarrow\rangle &= |\uparrow\uparrow\rangle \\ \hat{C}|\downarrow\uparrow\rangle &= |\downarrow\uparrow\rangle \\ \hat{C}|\downarrow\downarrow\rangle &= |\downarrow\downarrow\rangle \end{aligned} \tag{3.5}$$

**Your turn:** Define an operator that acts on two spins; if they are both up, then multiply by $-1$, otherwise multiply by $+1$.

### 3.1.2 Valid operators are linear.

The operator definitions in Eqs.(3.1-3.5) describe changes to the $|\uparrow\rangle$ and $|\downarrow\rangle$ basis states. How are they applied to an arbitrary quantum state, $|\psi\rangle = \alpha|\uparrow\rangle + \beta|\downarrow\rangle$? This is made unambiguous by requiring valid quantum mechanical operators to be **linear functions**. An operator, $\hat{O}$ is linear if it has both of the following properties:

$$\hat{O}\Big(|x\rangle + |y\rangle\Big) = \hat{O}|x\rangle + \hat{O}|y\rangle \tag{3.6}$$

$$\hat{O}\Big(c|x\rangle\Big) = c\hat{O}|x\rangle \tag{3.7}$$

for all valid states $\{|x\rangle, |y\rangle\}$, and for any scalar $c$. Stated in words, operators should distribute across sums of states (Eq.(3.6)) and should commute with scalar constants (Eq.(3.7)). These two properties are sufficient to apply a linear operator, $\hat{O}$ across any general state:

$$\begin{aligned}\hat{O}|\psi\rangle &= \hat{O}\Big(\alpha|A\rangle + \beta|B\rangle + \cdots\Big)\\ &= \hat{O}\Big(\alpha|A\rangle\Big) + \hat{O}\Big(\beta|B\rangle\Big) + \cdots\\ &= \alpha\hat{O}|A\rangle + \beta\hat{O}|B\rangle + \cdots\,, \end{aligned}\tag{3.8}$$

invoking each of the two linearity properties to reach the last line. Then the relevant operator definitions can be used to evaluate the each of the $\hat{O}|A\rangle, \hat{O}|B\rangle, \cdots$ terms individually using the relevant set of rules.

**Your turn:** Apply the operators $\hat{I}, \hat{\sigma}_x, \hat{\sigma}_z, \hat{S}$ defined in Eqs.(3.1-3.4) to the state $|\psi\rangle = \alpha|\uparrow\rangle + \beta|\downarrow\rangle$, by invoking linearity. Identify the cases for which the final state after applying the operator is different from the initial state (apart from a global phase), including any special choices of the $\alpha$ and $\beta$ parameters that would remove that difference.
**Your turn:** Apply the operator $\hat{C}$ defined in Eq.(3.5) to the states: (i) $|\psi\rangle = (\alpha|\uparrow\uparrow\rangle + \beta|\downarrow\uparrow\rangle)$; and (ii) $|\psi\rangle = (\alpha|\uparrow\uparrow\rangle + \beta|\uparrow\downarrow\rangle)$. Identify the cases for which the final state is different from the initial state (apart from the global phase), and any special choices of the parameters that would remove the difference.

The requirement that operators act linearly restricts the types of transformations that can occur for quantum states. A particularly interesting consequence is the "No-Cloning" theorem stating that arbitrary quantum states cannot be copied , discussed in the Appendix to this chapter.[2]

### 3.1.3 Valid operators are Hermitian.

Until now, the operator rule definitions have been expressed as transformations of *kets* into other kets, which is sufficient for most practical calculations. However, for the purposes of mathematical proofs, it may also be relevant to describe how operators apply to *bras*. First, consider an operator $\hat{O}$ that transforms a state $|\psi\rangle$ into a new state $|\phi\rangle$,

$$|\phi\rangle = \hat{O}|\psi\rangle \tag{3.9}$$

We know from Section 1.2.4 that kets and bras can be interconverted by taking the **Hermitian conjugate**, expressed by the † (dagger) symbol, so let us take the Hermitian conjugates of both sides

---

[2] See `https://en.wikipedia.org/wiki/No-cloning_theorem` and W. Wootters, W. Zurek "A Single Quantum Cannot be Cloned," *Nature.* **299**, 802–803 (1982). `http://dx.doi.org/10.1038/299802a0`

$$\begin{aligned}\Big(|\phi\rangle\Big)^\dagger &= \Big(\hat{O}|\psi\rangle\Big)^\dagger \\ \langle\phi| &= \langle\psi|\hat{O}^\dagger \end{aligned} \tag{3.10}$$

In place of the former definition of the operator $\hat{O}$ acting on the *ket* to its *right*, the operator's Hermitian conjugate $\hat{O}^\dagger$ describes acts on the *bra* to its *left*.

An **Hermitian operator** has the property $\hat{O} = \hat{O}^\dagger$. In the mathematical literature, this is alternatively referred to as being **self-adjoint**. We will require that valid operators *must* be Hermitian.[3] The requirement that operators be Hermitian has the important consequence of making the experimentally observed properties real numbers, for reasons that will be discussed in Section 3.2.

### 3.1.4 Operators describing a transformation are unitary.

Operators convert an initial quantum state, $|\psi\rangle$ to another state, $|\phi\rangle$. If the initial state is valid—which demands that it at least satisfies $\langle\psi|\psi\rangle = 1$—then the final state $|\phi\rangle$ must also satisfy $\langle\phi|\phi\rangle = 1$. In other words, a valid operator should always transform a valid normalized state into another valid normalized state, and never produce an (invalidly) unnormalized state.

**Your turn:** For the state $|\psi\rangle = \alpha|\uparrow\rangle + \beta|\downarrow\rangle$ with $|\alpha|^2 + |\beta|^2 = 1$, show that operators $\hat{I}, \hat{\sigma}_x, \hat{\sigma}_z, \hat{S}$ defined in Eqs.(3.1-3.4) preserve this normalization. That is, for $|\phi\rangle = \hat{O}|\psi\rangle$, show that $\langle\phi|\phi\rangle = 1$ in all cases.

This suggests that a single projector, $|\phi\rangle\langle\phi|$ is in general *not* a valid operator, unless it also normalizes the state (as described in Section 2.2).[4] However the sum of all projectors for a system, because it leaves the system unchanged (as discussed in Section 2.2.3) *is* a valid unitary operator.

---

[3] Entry-level course, like the one supported by this textbook, require that valid operators *must* be Hermitian, but strictly speaking, a weaker condition that the operator is invariant with respect to simultaneous parity inversion and time reversal (PT-symmetry) is sufficient to provide real valued observables. Processes involving resonance states and dissipative processes can sometimes be more readily calculated using an appropriately constructed non-Hermitian approach. For more details see the book-length introduction with applications to atomic and molecular problems by Nimrod Moiseyev, *Non-Hermitian Quantum Mechanics* (Cambridge Univ. Press, 2011).

[4] This is the origin of some of the philosophical disputes about the interpretation of quantum measurement. It seems unusual that a measurement process (as conducted by a single projector) breaks this requirement of unitarity in the $\psi$-ontic Copenhagen interpretation. One possible alternative is that the state of the entire universe branches unitarily whenever a measurement is performed. This "Many Worlds" interpretation of quantum mechanics was put forward by Hugh Everett (1930-1982). In this interpretation the Born rule emerges as the credence one should attach to being an observer in a particular branch of the universes wavefunction. Like all quantum mechanical interpretations, the results of the calculations are identical to the other interpretations, and it has a number of vocal proponents and critics. For a brief overview, see `https://en.wikipedia.org/wiki/Many-worlds_interpretation`; for a recent book-length presentation for a general audience by a proponent see Sean Carroll,

Another way to state this property: An operator is unitary if $\hat{O}^\dagger \hat{O} = \hat{I}$, where $\hat{I}$ is the **identity operator** introduced in Section 2.2.3. That is to say, $\hat{O}$ has the interpretation of applying a transformation, and $\hat{O}^\dagger$ has the interpretation that it undoes that transformation. A **unitary transformation** is thus reversible, and as such is important for describing the time-evolution of quantum systems, as will be discussed in Chapter **??**.

### 3.1.5 Operators are often non-commutative.

Operators describe processes performed on quantum states. Like ordinary life, sometimes the order in which processes are performed is important and sometimes it is not. For example, first putting on your *left* shoe and then putting on your *right* shoe results in the same outcome as first putting on your *right* shoe and then your *left* shoe. If we define these processes as operators, $\hat{L}$ and $\hat{R}$, respectively, and the state of your discalced feet as $|f\rangle$, the left-then-right process is $\hat{R}\hat{L}|f\rangle$—recall that operators apply to the ket on the right, so the implied order of operations is $\hat{R}\left(\hat{L}|f\rangle\right)$. Similarly, the right-then-left process is described by $\hat{L}\hat{R}|f\rangle$. From our experience of these operations, we know that they result in the same outcome state (both shoes on), so they must be equal:

$$\hat{R}\hat{L}|f\rangle = \hat{L}\hat{R}|f\rangle \tag{3.11}$$

Two operators having this property that they can be applied in either order are said to **commute** with one another. This is analogous to the commutation of ordinary scalar arithmetic, where $ab = ba$; multiplication of scalar numbers is commutative.

However, many processes depend upon the order in which they are performed. For example, first putting on *socks* and then *shoes* results in a different outcome than first putting on *shoes* and then *socks*! If we define these processes as $\hat{C}$ (Spanish: *calcetines*, socks) and $\hat{Z}$ (Spanish: *zapatos*, shoes), then it follows that

$$\hat{C}\hat{Z}|f\rangle \neq \hat{Z}\hat{C}|f\rangle \tag{3.12}$$

The operators do not commute, so the two processes are **non-commutative**.

**Your turn:** Which pairs of $\hat{I}, \hat{\sigma}_x, \hat{\sigma}_z, \hat{S}$ defined in Eqs.(3.1-3.4) commute with each other, when applied to an arbitrary state $|\psi\rangle = \alpha|\uparrow\rangle + \beta|\downarrow\rangle$? Determine this by computing $\hat{O}_1\hat{O}_2|\psi\rangle$ and $\hat{O}_2\hat{O}_1|\psi\rangle$ and seeing if they match.
**Your turn:** Does an operator always commute with itself? Explain.

---

*Something Deeply Hidden: Quantum Worlds and the Emergence of Spacetime* (Publisher, 2019) ; for a book-length discussion of the historical process of this interpretation, see TODO-AUTHOR/PUBLISHER *The Many Worlds of Hugh Everett*.

In general, the processes described by quantum operators are complicated and we will typically not have experiences or intuitions about whether they commute or not. Therefore, one should always assume that the operators are non-commutative, and conduct the operator evaluations in the specific order they are written, unless there is specific knowledge otherwise.

It is useful to be able to detect the difference. Returning to the first example of right and left shoes, in Eq.(3.11),

$$\begin{aligned}\hat{R}\hat{L}|f\rangle - \hat{L}\hat{R}|f\rangle &= 0 \\ \left(\hat{R}\hat{L} - \hat{L}\hat{R}\right)|f\rangle &= 0 \qquad (3.13)\end{aligned}$$

obtained by first subtracting $\hat{L}\hat{R}|f\rangle$ from both sides and then by using the property of linearity described in Section 3.1.2 to factor out $|f\rangle$. This must be true for any state $|f\rangle$. Thus, while we could only learn about this commutation by acting upon some state $|f\rangle$, *that* they commute is intrinsic to the relationship between the two operators $\hat{L}$ and $\hat{R}$, without reference to any particular state $|f\rangle$. For this reason it is convenient to define the **commutator** of two operators,

$$\left[\hat{A}, \hat{B}\right] \equiv \hat{A}\hat{B} - \hat{B}\hat{A} \qquad (3.14)$$

to more concisely describe this relationship. For the example of left and right shoes in Eq.(3.13),

$$\left[\hat{R}, \hat{L}\right]|f\rangle = 0$$

implying that

$$\left[\hat{R}, \hat{L}\right] = 0 \qquad (3.15)$$

In contrast, let us consider the shoes-and-socks example. Eq.(3.12) indicates that $\left[\hat{C}, \hat{Z}\right]|f\rangle \neq 0$. If we had a more detailed mathematical descriptions of these processes, we might be able to make a more specific statement about the value of $\left[\hat{C}, \hat{Z}\right]$.

**Your turn:** Compute the commutators, $[\hat{A}, \hat{B}]$, for operator pairs chosen from $\hat{I}, \hat{\sigma}_x, \hat{\sigma}_z, \hat{S}$.

### 3.1.6 Operators have characteristic eigenstates and eigenvalues.

Operators have special characteristic states that are unchanged when the operator is applied to that state. For example, the $\hat{\sigma}_z$ operator in Eq.(3.3) leaves the $|\uparrow\rangle$ and $|\downarrow\rangle$ states unchanged, but merely multiplies them by a scalar number, $\pm 1$. That is, (per our earlier definition)

$$\begin{aligned}\hat{\sigma}_z|\uparrow\rangle &= (+1)|\uparrow\rangle \\ \hat{\sigma}_z|\downarrow\rangle &= (-1)|\downarrow\rangle\end{aligned}$$

These special unchanged states are called **eigenstates** of the operator. Applying an operator to one of its eigenstates gives a number—an **eigenvalue**—times the same eigenstate back again. The eigenstates and eigenvalues are characteristic to the operator itself (from the German: *eigen*: self, own)

In general, there are as many eigenstates as there are basis functions describing the operator. However, the eigenstates need not—and typically are not—the basis states used to define the operator. For example, the flip operator $\hat{\sigma}_x$ (Eq.(3.2)) is defined in the basis of $|\uparrow\rangle$ and $|\downarrow\rangle$ states, but neither of these are eigenstates of $\hat{\sigma}_x$, because neither $\hat{\sigma}_x|\uparrow\rangle = |\downarrow\rangle$ and $\hat{\sigma}_x|\downarrow\rangle = |\uparrow\rangle$ yields the *same* state back again.

**Your turn:** Determine the two eigenstates and corresponding eigenvalues of $\hat{\sigma}_x$. Hint: Consider states composed of both $|\uparrow\rangle$ and $|\downarrow\rangle$.

## 3.2 Operators can be expressed using projectors.

Section 2.2 introduced a limited example of operators in the form of the **projectors**, $|\phi\rangle\langle\phi|$. The action of the projector can be thought of as a rule that asks about the existence of an input state $\langle\phi|$ and returns the output state $|\phi\rangle$—in this case they happen to be the same. When applying this rule to some general input state $|\psi\rangle$, the projector returns the answer $|\phi\rangle\,(\langle\phi|\psi\rangle)$ as output—the term in parentheses is just a number describing the overlap between the $\psi$ and $\phi$ states, and the new state is $|\phi\rangle$.

A generalized version of the projectors, $|f\rangle\langle i|$, can be used to express operators. The bra, $\langle i|$, selects out the input state, and the ket, $|f\rangle$, defines the output final state. In general, an operator will consist of a sum of projector terms, each term describing a particular input-output mapping.

Let's begin by considering the identity operator, Eq.(3.1). We need to convert $|\uparrow\rangle \to |\uparrow\rangle$ and $|\downarrow\rangle \to |\downarrow\rangle$. We can rewrite this as

$$\hat{I} = |\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow|. \tag{3.16}$$

Observe how this consists of a sum of the projectors for the two possible states. However, the input and output states need not be the same. For example, to write an expression for the $\hat{\sigma}_x$ ("flip") operator, we need to convert $|\uparrow\rangle \to |\downarrow\rangle$ and $|\downarrow\rangle \to |\uparrow\rangle$, as follows

$$\hat{\sigma}_x = |\uparrow\rangle\langle\downarrow| + |\downarrow\rangle\langle\uparrow|. \tag{3.17}$$

We are also free to define operators where each projector term is multiplied by a constant. For example, the $\hat{\sigma}_z$ ("payout") operator,

$$\begin{aligned}\hat{\sigma}_z &= (+1)|\uparrow\rangle\langle\uparrow| + (-1)|\downarrow\rangle\langle\downarrow| \\ &= |\uparrow\rangle\langle\uparrow| - |\downarrow\rangle\langle\downarrow| \end{aligned} \tag{3.18}$$

**Your turn:** Verify that the projector-based operator definitions for $\hat{I}, \hat{\sigma}_x, \hat{\sigma}_z$ yield the same results as the ones defined previously, by computing the effects on a general state $|\psi\rangle = \alpha|\uparrow\rangle + \beta|\downarrow\rangle$.
**Your turn:** Define the operators $\hat{S}$ (Eq.(3.4)) and $\hat{C}$ (Eq.(3.5)) using projections. For the latter, you will need to work in a basis of spin pairs.

Expressing operators as a sum of projections reduces the evaluation of an operator's effect on a state to the bra-ket overlap algebra introduced in Chapter 1. This also allows us to verify that the operator satisfies the validity requirements. By construction, any operator written as a sum of projections satisfies the linearity requirement. Furthermore, it is easy to verify that the operator is Hermitian by applying the Hermitian conjugate, †, to each projection. As discussed in Section 1.2.4, the † operator interconverts bras and kets and converts scalar constants into their complex conjugate. For a single projection, this has the form

$$\Big(c|X\rangle\langle Y|\Big)^\dagger = c^*|Y\rangle\langle X|, \tag{3.19}$$

and for a sum of projection operators, the Hermitian conjugation, †, acts linearly on each term,

$$(c|X\rangle\langle Y| + d|Y\rangle\langle Z|)^\dagger = c^*|Y\rangle\langle X| + d^*|Z\rangle\langle Y|. \tag{3.20}$$

As described in Section 3.1.3, a **Hermitian operator** have the property $\hat{O} = \hat{O}^\dagger$. Stated in the language of projectors, this means that every term $c|X\rangle\langle Y|$ in the sum must also have a corresponding term $c^*|Y\rangle\langle X|$ in the sum. This implies that $c|X\rangle\langle X| = c^*|X\rangle\langle X|$, i.e., that that the multiplicative constants for these terms must be real-valued so that $c = c^*$.

**Your turn:** Verify that $\hat{\sigma}_y = +i|\uparrow\rangle\langle\downarrow| - i|\downarrow\rangle\langle\uparrow|$ is a Hermitian operator.
**Your turn:** Verify that $\hat{I}, \hat{\sigma}_x, \hat{\sigma}_z, \hat{S}$, and $\hat{C}$ are Hermitian by expressing them as projectors and taking the Hermitian conjugate.

### 3.2.1 Eigenstates and eigenvalues provide an alternative description of the operator.

The complete set of eigenvalues and eigenstates is equivalent to knowledge of the operator, and vice versa. This allows us to redefine any operator[5] in terms of its eigenvalues and eigenstates. Mathematicians refer to this as a **spectral decomposition**. Let's begin with $\hat{\sigma}_z$. The eigenvalue-eigenstate pairs are $\{+1, |\uparrow\rangle\}$ and $\{-1, |\downarrow\rangle\}$. We can use these either to write the operator

$$\hat{\sigma}_z|\uparrow\rangle = (+1)|\uparrow\rangle$$
$$\hat{\sigma}_z|\downarrow\rangle = (-1)|\downarrow\rangle$$

---

[5] Not all functions can be decomposed in this way, but the requirements imposed for valid quantum mechanical operators makes this possible.

or as sums of projections,

$$\hat{\sigma}_z = (+1)|\uparrow\rangle\langle\uparrow| + (-1)|\downarrow\rangle\langle\downarrow|, \tag{3.21}$$

which is identical to the previous definition in Eq.(3.18).

In general, given a list of eigenvalues, $\epsilon_j$ and corresponding eigenstates $|j\rangle$ for an operator $\hat{O}$,

$$\begin{aligned}\hat{O}|1\rangle &= \epsilon_1|1\rangle \\ \hat{O}|2\rangle &= \epsilon_2|2\rangle \\ &\cdots \\ \hat{O}|j\rangle &= \epsilon_j|j\rangle\end{aligned}$$

or

$$\begin{aligned}\hat{O} &= \epsilon_1|1\rangle\langle 1| + \epsilon_2|2\rangle\langle 2| + \cdots + \epsilon_j|j\rangle\langle j| + \cdots \\ &= \sum_j \epsilon_j|j\rangle\langle j| \end{aligned} \tag{3.22}$$

For example, $\hat{\sigma}_x$ (Eq.(3.2)) has the eigenvalues ±1 and corresponding eigenstates $\left(|\uparrow\rangle \pm |\downarrow\rangle\right)/\sqrt{2}$. Let us call these two eigenstates $|{\rightarrow}\rangle$ and $|{\leftarrow}\rangle$. The operator can thus be described in this spectral form as

$$\hat{\sigma}_x = (+1)|{\rightarrow}\rangle\langle{\rightarrow}| + (-1)|{\leftarrow}\rangle\langle{\leftarrow}|. \tag{3.23}$$

**Your turn:** Demonstrate that the two expressions for $\hat{\sigma}_x = |\uparrow\rangle\langle\downarrow| + |\downarrow\rangle\langle\uparrow|$ and Eq.(3.23) are identical by operating both of them on the state $|\psi\rangle = \alpha|\uparrow\rangle + \beta|\downarrow\rangle$ and converting the result to a common basis.

## 3.3 Every experimentally observable property has a corresponding quantum operator.

Chapter 2 discussed questions about *what state* was present. Operators organize questions about the *attributes* of the state, expressed in terms of the attributes and relationships amongst the collection of possible basis states. Some examples of physical property attributes of a state include position, momentum, and energy. Experimental measurements observe a particular attribute of a state. For example, the position of a particle is observed by the dark spot it forms when striking a piece of photographic film or the "click" registered by an electronic detector. Spectroscopic measurements—the absorption of a photon with a particular energy—observe a *transition* from one energy state to another, and thus provides an indirect measurement of the energy. For historical reasons, the operator corresponding to the energy is called the **Hamiltonian**, after the Irish mathematician William Rowan Hamilton (1805-1865).[6] Because energy plays a an important role in physical theories, we will be devoting significant effort to the Hamiltonian operator in the remainder of the text.

### 3.3.1 Only the eigenvalues and eigenstates of the corresponding operator are observed when performing an experimental measurement.

Experimental observation should report the attributes possessed by state. Suppose we have a perfect measurement apparatus and there is no experimental error. There should exist at least some states for which this measurement device gives a reliable answer, that is to say that it *always* gives the *same* answer for that state. These **fiducial** states—from the Latin: *fiducia*, trust—can be trusted to reveal the actual attributes of the state in question. There may also be other non-fiducial states that are less trustworthy, and give different answers each time they are observed. From the $\psi$-epistemic perspective, fiducial bets describe the best possible agreement between the system's state and the guess, and non-fiducial bets correspond to a mismatch between the actual and guessed descriptions. From the $\psi$-ontic perspective, the non-fiducial states must be collapsing into some or the other definite fiducial result, and not some other one.

We can get some insight into the nature of fiducial states by revisiting the two-choice test-taking example introduced in Section 2.1.1. Given two possible choices, $\{|A\rangle, |B\rangle\}$, the goal is to provide the best guess of the form $|\psi\rangle = \alpha|A\rangle + \beta|B\rangle$. According to the **Born postulate** (Eq.(2.5)), the probability the true value was $A$ is given by

$$\begin{aligned} p_A &= |\langle A|\psi\rangle|^2 \\ &= \langle\psi| \Big(|A\rangle\langle A|\Big) |\psi\rangle, \end{aligned}$$

described in terms of the projector $|A\rangle\langle A|$ as in Section 2.2. A similar expression holds for $p_B$. Suppose that we also assign scores of $a$ and $b$ points to each of the two answers, and define the test grading process as an operator,

$$\hat{T} = a|A\rangle\langle A| + b|B\rangle\langle B|, \tag{3.24}$$

which has the effect of assigning $a$ points to $A$ and $b$ points to $B$. There are at least three options to consider. Answering with $|\psi\rangle = |A\rangle$, should always result in getting $a$ points. We can verify this through the following bra-ket algebra,

---

[6] Hamilton died long before the conception of quantum mechanics, and he originally developed a mathematical formalism for *classical* mechanics that proved especially conducive to quantum mechanics. He is also known for inventing **quaternions**, a generalization of the idea of complex numbers.

$$\begin{aligned}\langle\psi|\hat{T}|\psi\rangle &= \langle\psi|\left(a|A\rangle\langle A|\right)|\psi\rangle + \langle\psi|\left(b|B\rangle\langle B|\right)|\psi\rangle && (3.25)\\ &= a|\langle A|A\rangle|^2 + b|\langle A|B\rangle|^2 && (3.26)\\ &= a(1) + b(0) && (3.27)\\ &= a && (3.28)\end{aligned}$$

Observe that Eq.(3.26) is equivalent to $ap_A + bp_B$; in this case $p_A = 1$. A similar calculation can be conducted for a guess $|\psi\rangle = |B\rangle$, which should always return $b$. In other words, $|A\rangle$ and $|B\rangle$ are fiducial states, that always ($p_A = 1$ or $p_B = 1$) report the values $a$ and $b$, respectively, when provided as inputs. This is unsurprising, as it is merely a generalization of the original result derived in Section 2.1.1, which assumed that there was one point assigned to a particular outcome and zero points to the other outcome. On the other hand, it takes on new relevance now that we know about operator properties—these *fiducial states are eigenstates of the operator, and observed values are the corresponding eigenvalues.*

What happens with $|\psi\rangle = (|A\rangle + |B\rangle)/\sqrt{2}$? This is not an eigenstate of $\hat{T}$, and by a similar algebraic process as above results in

$$\begin{aligned}\langle\psi|\hat{T}|\psi\rangle &= \langle\psi|\ (a|A\rangle\langle A|)\ |\psi\rangle + \langle\psi|\ (b|B\rangle\langle B|)\ |\psi\rangle\\ &= ap_A + bp_B\\ &= \tfrac{a}{2} + \tfrac{b}{2},\end{aligned}$$

The only difference is that the probability values are $p_A = p_B = 1/2$, rather than one or zero. It appears that we are *sampling* the two different fiducial outcomes with some probability. In the $\psi$-ontic interpretation, the $p_A$ and $p_B$ terms corresponds to a collapse of $\psi$ into one or the other fiducial states $A$ and $B$, and so it must be that we observe either $a$ or $b$, with the associated probability. In the $\psi$-epistemic interpretation, the operator has well-defined payouts, and $\psi$ describes the strategy used—sometimes trying $A$ and sometimes trying $B$, and getting different results as we change the strategy—in other words, it is not a *stable* strategy. The result describes the **expectation value** or average payout that is expected from playing this strategy.

### 3.3.2 Expectation values, $\langle\psi|\hat{O}|\psi\rangle$, describe the average value of an observable attribute for a state $|\psi\rangle$

One can ask what the *average* expected value of a property is for some arbitrary state $\psi$, even if it is not an eigenstate of the operator. As noted above, in the $\psi$-epistemic view, this corresponds to the **expectation value** associated with the guess $|\psi\rangle$—how do we expect that guess to "payout" values of the properties. In the $\psi$-ontic view, the expectation value corresponds to the **average** or **mean** value observed on a set of repeated property measurements for different copies of $|\psi\rangle$.

Figure 3.1: TODO: Energy eigenstates of a spin-1/2 particle in an external magnetic field, as a function of the the external magnetic field strength, $B_z$.

As discussed above, only the fiducial eigenstates of the operator are observed in any single experiment. The average value is unambiguously defined, even if it is never observed in any experiment. For example, there are always an integer number of students in a class (the fiducial outcome of the "how many students?" operator), but the average class size at the school may be some fractional value. One never observes a class with a student chopped in half!—the fractional value in the average merely describes an epistemic bet about class size or an ontic summary of a collection of observations.

Expectation values are computed using the same bra-ket algebra used in Eq.(**??**). It is irrelevant where the state is an eigenstate or not, and is generalizable to any operator definition (including those defined in terms of more generalized projections of the form $|f\rangle\langle i|$.

## 3.4 Operators for chemical systems

The business of quantum mechanics is defining operators that describe the relations and interactions between states in a physical system. Every observable physical property has a corresponding operator. The operator's eigenvalues correspond to the observation outcomes for the system. The operator's eigenstates are the best descriptions of the corresponding observation outcomes. Expectation values describe average quantities that might be observed in a collection of measurements.

### 3.4.1 Spin-1/2

As discussed in Section 1.3.1, the spin-1/2 model provides a natural description of electron and nuclear spins. To describe experimental observations about these systems—for example spectroscopy—we will need to devise operators acting on those states. Spectroscopic measurements describe measurement of energy, and hence the relevant operator is the **Hamiltonian**. In fact, we have already introduced all the relevant operators needed to describe the Hamiltonian for a spin-1/2 system earlier in this chapter.

### 3.4.2 Single spin in a magnetic field

The first step in the Stern-Gerlach experiment (Section 2.4.1) demonstrated that a spin-1/2 system, such as an unpaired electron in an atom or a nuclear spin, interacts with a magnetic field. The same type of interaction with a magnetic applies to any spin-1/2 system, including the nuclear spins present in a **nuclear magnetic resonance** (NMR) experiment or the unpaired electron spins present in an **electron paramagnetic resonance** (EPR) experiment.

The simplest NMR experiment has only a single spin that does not interact with any other spins. This hypothetical experiment closely corresponds to the typical $^{13}$C NMR experiments, as only 1.1% of natural carbon nuclei are $^{13}C$, making it rare that two $^{13}$C nuclei are close enough to interact; consequently the nuclei are non-interacting.[7] Another possible experimental realization of non-interacting spin-1/2 is $^{1}$H NMR with only one proton, e.g., of chloroform or some mostly-deuterated molecule. Each of these experiments can be modeled as a system with a single spin-1/2 particle.

The energy of a spin in a z-axis external magnetic field is described by the Hamiltonian operator

$$\hat{H} = -\gamma \frac{\hbar^2}{2} B_{eff} \Big( |\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow| \Big), \tag{3.29}$$

where $\gamma$ is the **gyromagnetic ratio** of the particle, $\hbar = h/2\pi$ is the reduced Planck constant (a fundamental unit of angular momentum) and $B_{eff} = (1-\sigma)B_z$ defines the effective magnetic field observed by the spin. For a nuclear spin like $^{1}$H or $^{13}$C, the surrounding electrons shield the nuclear spin from experiencing the actual applied magnetic field $B_z$, and it is typical to describe this in terms of a **shielding constant**, $\sigma$ that depends on the specific molecular electronic environment.[8]

A closer examination of Eq.(3.29) reveals that this is just the $\hat{\sigma}_z$ operator defined in Section 3.1.1, scaled by a multiplicative constant,

$$\hat{H} = -b\,\hat{\sigma}_z, \tag{3.31}$$

where $b = \gamma\hbar(1-\sigma)B_z/2$ describes the characteristic energy of the spin's state given its type and chemical environment in the particular external applied magnetic field, $b$. As discussed in Section 3.1.6, the eigenstates of $\hat{\sigma}_z$ are $|\uparrow\rangle$ and $|\downarrow\rangle$, with eigenvalues $\pm 1$, respectively. Hence, the observed energies are $\mp b$—which results from multiplying these by the constant above. As discussed in Section 3.3.1, these eigenstates are the *only* states observed in the energy measurement experiment. Spectroscopic experiments observe the absorption or emission of light corresponding to *differences* between the final and initial *energy* eigenstates. The difference between the two energy eigenstates is $\Delta E = +b - (-b) = 2b$. A single absorbance peak (or a single emission peak) in the spectrum corresponds to a transition between two energy levels, as illustrated in Figure 3.1.

---

[7] Provided one performs the experiment so as to decouple these spins from the protons, as is done in the basic types of $^{13}$C-NMR experiments used in organic chemistry lab.

[8] In the laboratory, the shieldings observed in NMR spectra are more commonly expressed as a **chemical shift**,

$$\delta = \left( \frac{\nu - \nu_{TMS}}{\nu_{NMR}} \right) \times 10^6 \tag{3.30}$$

expressed in parts-per-million (PPM) relative to the frequency of (radio wave) radiation absorbed by a standard (typically trimethylsilane, $\nu_{\mathrm{TMS}}$), and the characteristic frequency of the NMR machine, $\nu_{\mathrm{NMR}}$ (e.g. 400 Megahertz is $\nu_{\mathrm{NMR}} = 400 \times 10^6\,\mathrm{s}^{-1}$). This frequencies, $\nu$, correspond to the energy difference $h\nu$, between the energy eigenstates.

### 3.4.3 The sequential Stern-Gerlach experiment described in terms of measurement operators.

The Hamiltonian of Eq.(3.31) describes any single spin-1/2 system in an external magnetic field, and thus is equally applicable to the Stern-Gerlach experiment introduced in Section 2.4.1. Aside from the differences in the physical object being studied (unpaired electrons in silver atoms versus nuclear spins), the primary difference is what the measurement observes. The Stern-Gerlach experiment observes which *eigenstate*, $|\uparrow\rangle$ or $|\downarrow\rangle$, describes each atom in the beam of atoms, as measured by the deflection towards or away from the magnetic field direction and impingement on the background. In contrast, the spectroscopic experiment observes the amount of energy needed to go between the final and initial energy *eigenvalues*. They share the same Hamiltonian operator, and merely study these two different aspects.

Reframing the Stern-Gerlach experiment in terms of Hamiltonian eigenstates can help explain the origin of the sequential measurement experiments discussed in Section 2.4.1. Measurement along the $z$-axis corresponds to $\hat{H} = -b\hat{\sigma}_z$. Measurement along the $x$-axis corresponds to $\hat{H} = -b\hat{\sigma}_x$. The fact that we get different measurement outcomes follows from the non-commutation of the two operators, as evinced by the non-zero commutator $[\hat{\sigma}_z, \hat{\sigma}_x] \neq 0$, discussed in Section 3.1.5.

**Your turn:** Derive the commutation relation, $[\hat{\sigma}_z, \hat{\sigma}_x]$.

### 3.4.4 Two non-interacting, distinguishable spins.

Suppose there are *two* non-interacting spins in a system. Each spin experiences the magnetic field with its own characteristic shielding constant, and each spin's interaction is described by its own Hamiltonian, $\hat{H}_1$ and $\hat{H}_2$, respectively. When one spin interacts with the magnetic field, the other spin just does nothing...conveniently represented by the identity operator, $\hat{I} = |\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow|$, which is the sum of the projectors for all of the possible states of a single spin. The total Hamiltonian for both spins is constructed using the tensor product of the two operators, introduced in Section 2.2.4,

$$
\begin{aligned}
\hat{H}_{\text{non-int}} &= \hat{H}_1 \otimes \hat{I} + \hat{I} \otimes \hat{H}_2 && (3.32)\\
&= \Big( -b_1\hat{\sigma}_z \Big) \otimes \hat{I} + \hat{I} \otimes \Big( (-b_2)\hat{\sigma}_z \Big) && (3.33)\\
&= -b_1 \Big( |\uparrow\rangle\langle\uparrow| - |\downarrow\rangle\langle\downarrow| \Big) \otimes \Big( |\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow| \Big) \\
&\quad - b_2 \Big( |\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow| \Big) \otimes \Big( |\uparrow\rangle\langle\uparrow| - |\downarrow\rangle\langle\downarrow| \Big) && (3.34)\\
&= \Big( -b_1 - b_2 \Big) |\uparrow\uparrow\rangle\langle\uparrow\uparrow| + \Big( -b_1 + b_2 \Big) |\uparrow\downarrow\rangle\langle\uparrow\downarrow| \\
&\quad + \Big( +b_1 - b_2 \Big) |\downarrow\uparrow\rangle\langle\downarrow\uparrow| + \Big( +b_1 + b_2 \Big) |\downarrow\downarrow\rangle\langle\downarrow\downarrow| && (3.35)
\end{aligned}
$$

This looks rather complicated, but the physical meaning can be clarified by looking at the signs before each of the $b_1$ and $b_2$ terms. The state of the first spin determines whether the energy is raised or lowered by $b_1$, and the state of the second spin determines whether the energy is raised or lowered by $b_2$. The pluses and minus track the state of the relevant spin. Because the two spins are non-interacting, the total energy change is the sum of the independent contributions from the two spins.

Let us consider the case where the spins are distinguishable—for example, they are present in different parts of the molecule and have distinct environments, or are even different types of spins (e.g., one $^{13}$C and one $^{1}$H). We will have to wait to discuss cases where they are identical in later chapters. Of course, they *could* have an accidental degeneracy, but this is very unlikely if they have different chemical environments, and obscures the interpretation of the spectrum.[9]. Having assumed $b_1 \neq b_2$, one $b_i$ will be greater than the other, so without loss of generality[10] let us take $b_1 > b_2$.

What are the allowed transitions? A **selection rule** states that only one spin can change at a time when absorbing a photon. Therefore there are *two* spectral lines observed for this system, one corresponding to flipping the first spin ($2b_1$) and the other corresponding to flipping the second spin ($2b_2$). This is unsurprising if you think back to the $^{13}$C NMR spectra acquired in your organic chemistry studies; each (independent) nucleus has its own characteristic chemical shift ($\delta$) or screening constant ($\sigma$) describing its chemical environment, and each of these distinct spins undergoes a transition on its own. In the NMR case, these were distinct spins on different molecules, but there is nothing preventing this from being two spins on the same molecule, provided they did not interact.

### 3.4.5 Two weakly-interacting, distinguishable spins

Suppose we have two *interacting* spins, such as two nearby nuclei in a molecule. In an NMR experiment, this usually means that they are on the same molecule. There are of course $^{1}$H-$^{1}$H, $^{1}$H-$^{13}$C, and $^{13}$C-$^{13}C$ interactions possible, depending on the nuclei present; they all have the same *mathematical* description, although the coupling strength will vary. How does the energy change when the spins to interact? Continuing with the analogy that the spins behave like little bar magnets, the energy is increased by $J$ when they are aligned in the same direction, and decreased by $J$ when aligned in opposite directions, where the interaction or **spin-spin coupling** parameter $J$ is inddependent of the applied

---

[9] You may have encountered something like this when interpretting the NMR spectra of symmetric molecules.

[10] This is the stylized way that textbook writers say: "We need to give them arbitrary names, 1, 2, 3...., but we are free to change the names in any order so that this statement is true."

Figure 3.2: TODO: Energy levels (Eq.(3.37)) and observed spectrum of two weakly-interacting spin-1/2 particles.

magnetic field. That is, we want

$$\begin{aligned}\hat{H}_{int} &= +J|\uparrow\uparrow\rangle\langle\uparrow\uparrow| + +J|\downarrow\downarrow\rangle\langle\downarrow\downarrow| - J|\uparrow\downarrow\rangle\langle\uparrow\downarrow| - J|\downarrow\uparrow\rangle\langle\downarrow\uparrow| \\ &= J\hat{\sigma}_z \otimes \hat{\sigma}_z, \end{aligned} \tag{3.36}$$

and the total Hamiltonian of the system is then described by the sum of the non-interacting (Eq.(3.35)) and interacting (Eq.(3.36)) terms

$$\hat{H} = \hat{H}_{\mathrm{non-int}} + J\hat{\sigma}_z \otimes \hat{\sigma}_z \tag{3.37}$$

What are the eigenstates and eigenvalues? This weak interaction leaves the eigenstates unchanged—there are only projectors that go from each state to one like it, not to different states—but adds or subtracts values of J depending upon if the spins are aligned (high energy) or anti-aligned (low energy), respectively. More specifically, the energy of the $|\uparrow\uparrow\rangle$ and $|\downarrow\downarrow\rangle$ are raised by $+J$ and the energies of the $|\uparrow\downarrow\rangle$ and $|\downarrow\uparrow\rangle$ states are lowered by $-J$.

**Your turn:** Write the complete Hamiltonian for Eq.(3.37) by expanding out $\hat{\sigma}_z \otimes \hat{\sigma}_z$ and identify the eigenvalues that are as described below.

This results in a **splitting** of the observed spectrum as depicted in Figure 3.2. Whereas in the *absence* of the interaction term, the spectral transitions between energy levels were

$$\begin{aligned}\Delta E_1 &= 2b_1 \\ \Delta E_2 &= 2b_2 \\ \Delta E_3 &= 2b_1 = \Delta E_1 \\ \Delta E_4 &= 2b_2 = \Delta E_2,\end{aligned}$$

in the *presence* of the interaction, the degeneracy is broken,

$$\begin{aligned}\Delta E_1 &= 2b_1 - 2J \\ \Delta E_2 &= 2b_2 - 2J \\ \Delta E_3 &= 2b_1 + 2J \\ \Delta E_4 &= 2b_2 + 2J.\end{aligned}$$

The two peaks centered around the (hypothetical non-interacting) single peak are referred to as a **doublet**; this is the simplest example of the “$N+1$ splitting” rule in NMR spectroscopy. Observe that both $b_1$ and $b_2$ increase with the strength of the magnetic field, whereas the $J$ term is independent of the magnetic field strength.

### 3.4.6 Atomic orbitals are energy eigenstates for free atoms.

From introductory chemistry class, you'll recall that atomic ions have distinctive **line spectra** corresponding to transitions between various atomic states. The classic example of this is the hydrogen atom spectrum, but the same is true of other atoms as well. These characteristic line spectra result in the distinctive colors of golden Mercury-lamps used to illuminate stadiums and "neon" lights (whether or not they use neon or other gases). Furthermore they are observed in atomic absorption spectroscopy, the least sophisticated of these being the flame tests taught in qualitative analysis labs. Like all spectra, the atomic spectra correspond to transitions between energy levels, i.e., between the atom's energy eigenstates. The energy eigenstates of the atoms are nothing other than the **atomic orbital** basis states reviewed in Section 1.3.2.

A close observation of the experimental patterns reveals patterns. For now, let us treat these as empirical observations; in Chapter **??** we will derive these from the basic principles of quantum mechanics. For a **hydrogenic atom**, consisting of one electron and $Z$ protons, the eigenenergies can be shown to be

$$\varepsilon_{n,l,m_l} = \frac{-Z^2}{2n^2} E_H \tag{3.38}$$

where $n, l, m_l$ are the quantum numbers discussed in Section 1.3.2, and $E_H$ is the Hartree energy, the atomic unit of energy. Observe that the energies of Eq.(3.38) are not a function of $l$ or $m_l$ quantum numbers. This does not prohibit the existence of states having different values of these quantum numbers, it simply means that energy does not depend on the values of those quantum numbers. We say that two states that have the same energy (or other property) are **degenerate**—this is not a judgment about their moral character, but rather that we cannot distinguish one state from another based solely on the eigenvalues. Stated otherwise, a system is degenerate when two eigenstates have the same eigenvalue.

Knowledge of the eigenstates (atomic orbital states) and eigenenergies of those states (the energy levels) allow us immediately to write the Hamiltonian operator in this basis, by using the concept of **spectral decomposition** introduced in Section 3.2.1. Eq.(3.38) provides the energies for each eigenstate projector

$$\begin{aligned}\hat{H} =& \varepsilon_{n=1}|1s\rangle\langle 1s| + \varepsilon_{n=2}|2s\rangle\langle 2s| + \varepsilon_{n=2}|2p_x\rangle\langle 2p_x| \\ &+ \varepsilon_{n=2}|2p_y\rangle\langle 2p_y| + \varepsilon_{n=2}|2p_z\rangle\langle 2p_z| + \cdots\end{aligned} \tag{3.39}$$

**Your turn:** Are hybrid atomic orbitals (Section 1.3.3) eigenstates of the hydrogenic Hamiltonian (Eq.(3.39))?

As you may recall from introductory chemistry, the energy levels of multi-electron atoms are slightly more complicated. In fact, you may recall that when building up (German: *aufbau*) the energy level diagrams of multi-electron atoms,

Table 3.1: TODO: Include a table of effective nuclear charges `https://en.wikipedia.org/wiki/Effective_nuclear_charge`

the $2p$ orbitals tend to be slightly *higher* in energy than the $2s$ orbitals (so the $2s$ level gets filled first), and the $3d$ energy levels are usually higher in energy than the $4s$ energy levels, but lower than the $4p$ energy levels (so the filling proceeds $4s \to 3d \to 4p$). This resulted in the progression of occupied atomic states as proceeding through the periodic table. The energies and their change as the number of protons and electrons increases can be predicted quantitatively using quantum mechanics, but for now let us introduce a simplified model of the behavior. Analogous to how we described the energy change for the nuclear spin energy levels by a shielding constant, $\sigma$, in Section 3.4.2, we might explain the energy level changes for the electronic states in terms of a **shielding** or **screening** term, $S$, that describes how the other electrons present in the other atomic orbitals reduce the perceived Coulombic interaction that an electron in "this" atomic orbital experiences. Rather than the electron perceiving the total positive charge $Z$, it instead perceives a reduced **effective nuclear charge**, $Z_{eff} = Z - S$ that depends on the presence of those other electrons. Therefore a pragmatic approach is to generalize the hydrogenic atomic energy expression (Eq.(3.38)) by replacing $Z \to Z_{eff}$:

$$\varepsilon_n = \frac{-Z_{eff}^2}{2n^2} E_H \tag{3.40}$$

and allow $Z_{eff} = Z_{eff}(Z, n, l)$ to be a function that depends on the other variables. In Chapter **??** we will discuss how to calculate these effective nuclear charges directly from quantum mechanical calculations of the atoms; for now we can treat them as parameters. These can be looked up in tables, such as Table 3.1 or calculated using simple formulas, such as Slater's Rules (see Problem TODO)

Effective nuclear charges help rationalize a number of atomic properties. The **ionization potential** is the amount of energy needed to remove an electron; given the energies in Eq.(3.40) one can compute those values. Considering the energy level diagram, removing an electron requires us to put energy into the system, as it requires a change between an electron from a bound state ($\varepsilon < 0$) to an unbound state (non-interacting electron and nucleus, $\varepsilon = 0$). Similarly, the **electron affinity** is the amount of energy released when an electron is bound to an atom, and hence energy is released when this process occurs (the electron goes from a non-interacting state with $\varepsilon = 0$ to a bound state with $\varepsilon < 0$). Other periodic trends can also be rationalized using effective nuclear charge trends.

**Your turn:** Write out the Hamiltonian for the effective nuclear charge model of the lithium atom, using the expression Eq.(3.40), and the tabulated effective nuclear charge values (Table 3.1).

**Your turn:** Compare and contrast the effective nuclear charge model Hamiltonian of a beryllium atom to that of a lithium atom.
**Your turn:** Are hybrid atomic orbitals of a carbon atom (Section 1.3.3) eigenstates of the generalized effective-nuclear charge atomic carbon Hamiltonian (Eq.(3.39))?

### 3.4.7 Molecular orbitals are energy eigenstates for molecules.

In addition to explaining spectroscopy, Hamiltonians can be used to describe chemical bonds. Section 1.3.4 reminded you that **molecular orbitals** are simply linear combinations of atomic orbitals located on *different* atomic centers. Whereas the atomic orbitals are energy eigenstates of the (isolated) atomic Hamiltonian, molecular orbitals are energy eigenstates of the **molecular** Hamiltonian.

As noted at the end of Section 1.3.4, although atomic orbitals on different atoms are in general *not* orthogonal to each other, the overlap tends to be relatively small, and so for the purposes of getting a *qualitative* understanding of the problem we will assume them to be orthogonal in the discussion below.[11].

#### $H_2$ molecule

A hydrogen molecule is comprised of two hydrogen atoms. The $1s$ atomic orbitals on each atom is may be labeled $|1s_A\rangle$ and $|1s_B\rangle$, and we know that energy of each of these non-interacting, independent hydrogen atom levels is described by Eq.(3.38).

What are the two non-interacting atomic orbital energies? Analogous to the non-interacting spin-1/2 particles discussed in Section 3.4.1, the two **non-interacting** atoms can (to a first approximation) be described as the sum of the contributions from each independent atom.

$$\hat{H}_{\text{non-int}} = \varepsilon_{H1s}|1s_A\rangle\langle 1s_A| + \varepsilon_{H1s}|1s_B\rangle\langle 1s_B|, \tag{3.41}$$

where $\varepsilon_{H1s}$ is the $1s$ orbital energy of an isolated hydrogen atom according to Eq.(3.38). The two degenerate eigenvalues are both $\varepsilon_{H1s}$, corresponding to an electron on atom A or an electron on atom B. The total energy is the sum of the energy of electron one and electron two, or $2\varepsilon_{H1s}$. We are of course free to define this as our "zero" of energy, i.e., to measure the interaction relative to the isolated atom; this is equivalent to setting $\varepsilon_{H1s} = 0$.

What is the interaction? Let's call it a "bond" of strength $t$, and describe the total Hamiltonian with this interaction as

$$\hat{H} = \hat{H}_{\text{non-int}} + t|1s_A\rangle\langle 1s_B| + t|1s_B\rangle\langle 1s_A|, \tag{3.42}$$

---

[11] This is the zero-differential overlap (ZDO) assumption that is made in Hückel and many of the semi-empirical Hartree-Fock molecular orbital theory methods; we'll discuss this and how to remove this assumption in Chapter **??**

where the two projectors are needed so that the Hamiltonian is Hermitian. Describing the energy relative to the zero of the free atoms, reduces to simply

$$\hat{H} = t\Big(|A\rangle\langle B| + |B\rangle\langle A|\Big) \tag{3.43}$$

Our goal is to find the energy eigenstates of this operator, satisfying

$$\hat{H}|\psi_i\rangle = \epsilon_i|\psi_i\rangle \tag{3.44}$$

for the bonding and antibonding molecular orbital eigenstates, respectively. Conveniently, $\hat{H}$ has the same structure as the "flip" operator, $\hat{\sigma}_x$, introduced in Eq.(3.2) of Section 3.1.1. So we already know the eigenstates, $|\psi_i\rangle = (|A\rangle \pm |B\rangle)/\sqrt{2}$, and corresponding eigenvalues $\epsilon_i = \pm t$. Furthermore, we know that the bonding orbital should be *lower* in energy than the antibonding orbital. This implies that $t$ is a negative number, implying that the energy decreases as the electron is **delocalized** across the two atoms. The total energy of the system is the sum of the energies of the two (spin-up and spin-down) electrons[12], and hence is $-2t$, relative to the free atoms. That is, the **bond dissociation energy** required to atomize the molecule is $-2t$.

We have thus far avoided assigning a precise numerical value for $t$. For a qualitative description, the precise value of $t$ is unimportant, and may be removed by using it as the unit of energy for the stability of the chemical bond relative to the two atoms. On the other hand, it is often useful to have a quantitative numerical estimate of the value, so as to perform thermochemical calculations and comparisons to other bonds. One approach to estimate $t$ is based on **thermochemical** estimation. If we know the experimental heat of atomization for dissociating a hydrogen molecule into two hydrogen atoms, we can use that to estimate the value of $2t$. Alternatively, we can estimate $t$ **spectroscopically** from the the energy associated with the observed transition between the bonding and antibonding molecular orbital $(t - (-t) = 2t$.

**Your turn:** The heat of atomization for the hydrogen molecule is 218 kJ/mol. What is $t$ in electron-volts? In Hartrees?
**Your turn:** The spectroscopic transition between the bonding and antibonding molecular orbitals of the hydrogen molecule is roughly 1100 nm. What is $t$ in electron-volts? In Hartrees?
**Your turn:** Why are these two values not the same?

### Heteronuclear diatomic molecule

What about a heteronuclear diatomic molecule? We will no longer be able to assume that the two atoms have the same energy, but one can certainly use an effective nuclear charge type model (Eq.(3.40)) to describe the isolated atomic orbital energies and introduce an empirical value for the bond interaction $t$.

---

[12] in the single electron model

But this can only be a first approximation of the system; as the electrons are redistributed across the atoms, the effective nuclear charges will increase or decrease until some equilibrium is reached. In practice, these are calculated using **self-consistent field** methods, that will be discussed in Chapter **??**.

### 3.4.8 Position operator

As we discussed in Section 1.3.5, the position basis states can be described as a discrete set of "pixels", $|x_0\rangle, |x_1\rangle, \cdots, |x_j\rangle$ describing an orthonormal basis. This basis is also a natural way to express a position *operator* that reports where the particle is located,

$$\hat{x} = x_0|x_0\rangle\langle x_0| + x_1|x_1\rangle\langle x_1| + x_2|x_2\rangle\langle x_2| \cdots x_j|x_j\rangle\langle x_j| + \cdots \tag{3.45}$$

Applying this operator to a state reports the *value* of the position associated with each *state*. Just like we have done in previous examples, we can use this operator to compute the *expectation value* or average position of a particle, given a description in terms of this set of basis states.

## 3.5 Appendix: The No-Cloning Theorem is a consequence of operator linearity.

## Problems

1. Consider three weakly-interacting spin-1/2 particles, labeled $A, B, C$. $A$ interacts with $B$ by the coupling $J\hat{\sigma}_{z_A} \otimes \hat{\sigma}_{z_B}$ and $J\hat{\sigma}_{z_B} \otimes \hat{\sigma}_{z_C}$. For simplicity, assume that $J$ is identical for the two interactions. Stated in words, $B$ interacts with both $A$ and $C$, but $A$ and $C$ do not interact directly with each other. (a) Define the 8 basis states. (b) Write the non-interacting Hamiltonian for the system and describe the eigenenergies and eigenstates, arranging the results into an energy level diagram. (c) Write the interaction Hamiltonian. (d) Find the eigenstates and eigenenergies of the complete (non-interacting + interaction) Hamiltonian and arrange these in an energy level diagram. (e) Sketch the spectrum.

2. Atomic orbitals are energy eigenstates of the individual atom's Hamiltonian operator. In general, *s*, *p*, *d*, etc. atomic orbitals have different energies. Are hybrid atomic orbitals also eigenstates of the atom's Hamiltonian? Explain.

3. Slater's rules. Implement a function for the algorithm described at `https://en.wikipedia.org/wiki/Slater%27s_rules` and compare your results to the effective nuclear charge values of Clementi and Roetti in Table 3.1.

   *The following problems use the effective nuclear charge model (see Table 3.1)*

4. Using the effective nuclear charge model, sketch (and compute numerical values for) the energy levels of the neon atom. Using the difference between the energy levels, predict what transitions could be responsible for the characteristic red/orange emission line of neon lighting (observed as roughly 1.65 - 2.10 eV or 590-740 nm).

5. Using the effective nuclear charge model, predict the energy associated with (a) removing an electron from a lithium atom; (b) adding an electron to a fluorine atom. (c) Moving an electron from a lithium atom to a fluorine atom.

6. Using the effective nuclear charge model, compute the average energy (expectation value of the Hamiltonian) of a carbon $sp^2$ hybrid atomic orbital. Is this greater than, less than, or the same as the lowest energy (non-hybridized) atomic orbital? Speculate on the consequences of your result.

   *The following two problems develop an effective nuclear charge model for the HeH$^+$ molecule as an example of a heteronuclear diatomic molecule.*

7. Qualitative trends: Consider two different atomic orbital energies for the HeH$^+$ molecule. Set up a series of equations that allow you to find the eigenenergies and eigenstates as a function of $t$, and compare how: (a) the molecular orbital energies change relative to the atomic orbital energies; and (b) the molecular orbital state's contribution from the two atomic orbitals change relative to an equal contribution in the small $t$ and large $t$ cases.

8. Quantitative calculations: Using the Effective nuclear charge model for the atomic orbital energies, (a) find a value of $t$ that reproduces the net charges for the HeH$^+$ molecule of +0.698 and +0.302, respectively; (b) Use your result to estimate the total energy (the lowest energy eigenvalue times two electrons) for the HeH$^+$. How much lower is this than the energy of one electron in each of the two atoms?

9. A particle is in the (unnormalized) state

   $$|\psi\rangle \propto |x_1\rangle + \frac{1+\sqrt{5}}{2}|x_2\rangle + \frac{1+\sqrt{5}}{2}|x_3\rangle + |x_4\rangle,$$

   described in the orthonormal position basis functions, $|x_j\rangle$. (a) Normalize $|\psi\rangle$ (and use it for the remaining parts of this problem). (b) What is the probability that the particle described by $|\psi\rangle$ is observed in the state $|x_1\rangle$? (c) What is the probability that the particle is described in state $|x_2\rangle$? (d) What is the probability it is observed in $|x_1\rangle$ or $|x_2\rangle$? (e) If $x_1 = 1, x_2 = 2, x_3 = 3, x_4 = 4$ along the position number line, evaluate the the expectation value of the position operator $\hat{x}$ (Eq.(3.45)).

10. Repeat the previous problem, but using the (unnormalized) state

$$|\psi\rangle \propto -|x_1\rangle + \frac{1-\sqrt{5}}{2}|x_2\rangle + \frac{-1+\sqrt{5}}{2}|x_3\rangle + |x_4\rangle,$$

(note the sign changes relative to the previous problem.)

# Math Chapter: Vectors

McQuarrie Math Chapter C

# Computational Chapter: Lists

(ICPC Appendix A)
  data structures
  making lists: Table
  using lists: as inputs Map (list to list)
  visualization (ListPlot, ListLinePlot)
  Statistics/Histograms

# Chapter 4

# Representations of States and Operators

> "It looks strange, and it looks strange and it looks very strange; and then suddenly it doesn't look strange at all and you can't understand what made it look strange in the first place.
>
> Gertrude Stein (on modern art)

## 4.1 Linear algebra provides a natural representation of discrete states.

We required that states and operators have a property of linearity. This suggests that **linear algebra** is an appropriate representation consistent with these constraints. The advantage of a linear algebraic representation is that it is amenable to large-scale numerical computation.

### 4.1.1 Vectors represent states.

Figure 4.1 shows a geometric interpretation of the state description.

We can assign each orthonormal basis function an axis or **unit vector**. By convention we assign kets as **column vectors**. For example the basis ket unit vectors are

$$|A\rangle = \begin{bmatrix} 1 \\ 0 \\ 0 \\ \cdots \end{bmatrix} \tag{4.1}$$

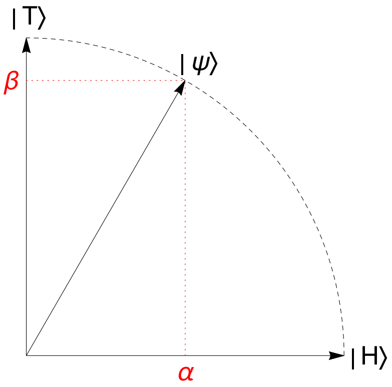

Figure 4.1: Geometric interpretation of the state $|\psi\rangle = \alpha|H\rangle + \beta|T\rangle$. The coefficie nts $\alpha = \langle H|\psi\rangle$ and $\beta = \langle T|\psi\rangle$ describe the ove rlap of the state $\psi$ on to the basis vectors.

and

$$|B\rangle = \begin{bmatrix} 0 \\ 1 \\ 0 \\ \cdots \end{bmatrix}. \tag{4.2}$$

Similarly, the convention is represent bras as **row vectors**, and the basis bra unit vectors are

$$\langle A| = \begin{bmatrix} 1 & 0 & 0 & \cdots \end{bmatrix} \tag{4.3}$$

and

$$\langle B| = \begin{bmatrix} 0 & 1 & 0 & \cdots \end{bmatrix} \tag{4.4}$$

Using the basis vectors, we can represent arbitrary states. An arbitrary ket $|\psi\rangle = \alpha|A\rangle + \beta|B\rangle + \gamma|C\rangle + \cdots$ is described as a the column vector

$$|\psi\rangle = \begin{bmatrix} \alpha \\ \beta \\ \gamma \\ \cdots \end{bmatrix} \tag{4.5}$$

where the first entry represents the contribution from $|A\rangle$, the second entry from $|B\rangle$, etc. Likewise the an arbitrary bra is represented as the row vector

$$\langle\psi| = \begin{bmatrix} \alpha^* & \beta^* & \gamma^* & \cdots \end{bmatrix} \tag{4.6}$$

From this definition, it is apparent that the **Hermitian conjugate** operation that interconverts kets and bras, † has the effect of turning columns into rows (and vice versa) and taking the complex conjugate of the values in the vector. This is referred to as the **conjugate transpose**.

### 4.1.2 The vector dot-product performs overlap calculations for states with orthonormal basis states.

Orthnormal basis function have the property $\langle i|j\rangle = \delta_{ij}$, where we have described the orthonormality relationship using the Kronecker Delta function introduced in Section **??**. Now this has an interesting property. The overlap $\mathbf{i}j$ is always a *scalar* value, whereas our states are represented as vectors. Therefore it is natural to use the **scalar product** of the two vectors—alternately called the **dot product** or **inner product** of the vectors. This was introduced in Math Chapter C in McQ.

**Your turn:** Go back to Chapter 1 and retry the problems as vector representations

### 4.1.3 Matrices represent operators.

Matrices (Math Chapter G in McQ) form a natural representation of the generalized projectors, $|f\rangle\langle i|$ (introduced in Section 3.2) that map some initial state $i$ into final state $f$. In terms of matrix algebra, each column describes an input state $i$ and each row describes the final output state $f$. For example, suppose that we want to represent $\hat{O} = a|A\rangle\langle B|$, using the vector representation discussed above. The corresponding matrix is

$$a|A\rangle\langle B| = \begin{bmatrix} 0 & a & 0 & \cdots \\ 0 & 0 & 0 & \cdots \\ 0 & 0 & 0 & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{bmatrix} \tag{4.7}$$

and applying this operator to the state corresponds to taking the **matrix-vector** product. That this is the correct representation can be verified by multiplying $|B\rangle$ vector defined in Eq.(**??**)...and observing that it gets converted into the $|A\rangle$

### 4.1.4 Matrix eigenvalues and eigenvectors can be computed efficiently.

As discussed in Section **??** we are often interested in finding the eigenstates of an operator, as this describes the measurement outcomes. The general representation makes this somewhat challenging; in contrast the change to the matrix-vector representation makes this tractable even for systems with thousands of basis states.

$$\hat{A}|\psi_i\rangle = a_i|\psi_i\rangle \tag{4.8}$$

corresponds to

$$\mathbf{A}\vec{\psi}_i = a_i\vec{\psi}_i \tag{4.9}$$

having the **eigenvectors** $\vec{\psi}_i$. In general, it can be challenging to derive exact symbolic expressions for systems with more than five basis states, however, efficient numerical algorithms exists for finding numerical solutions to arbitrary numerical precision.

### 4.1.5 The outer (Kronecker) product of two vectors or matrices represents multi-particle systems

## 4.2 Functions provide a natural representation of continuous states.

Position states were introduced in Section **??** as a pixelated set of discrete states, although we alluded to the fact that this is an inherently continuous property. Fortunately, the tools of calculus allow us to describe how we approach an infinitesmal limit of difference between these states

### 4.2.1 Functions represent states

$$\begin{aligned}
|\psi\rangle &= \psi_0|x_0\rangle + \psi_1|x_1\rangle + \psi_2|x_2\rangle + \cdots \psi_j|x_j\rangle + \cdots && (4.10)\\
&= \sum_j \psi_j|x_j\rangle && (4.11)\\
&= \psi(x) && (4.12)
\end{aligned}$$

Replace the discrete values $\psi_j$ with a function, $\psi(x)$ describing the value of each $\psi_j$ at the corresponding $|x_j\rangle$. In the function, we are using the value of $x$ itself as the index, and we allow these to vary continuously over an implied continuum of states $|x\rangle$.

What about the bras? By similar reasoning, we see

$$\begin{aligned}
\langle\psi| &= |\psi\rangle^\dagger \\
\langle\psi| &= \psi_0^*\langle x_0| + \psi_1^*\langle x_1| + \psi_2^*\langle x_2| + \cdots \psi_j^*\langle x_j| + \cdots && (4.13)\\
&= \sum_j \psi_j^*\langle x_j| && (4.14)\\
&= \psi^*(x) && (4.15)
\end{aligned}$$

which is to say that the bra form is simply the complex conjugate of the function.

### 4.2.2 Integrals perform overlap calculations.

As noted in Section 1.3.5, the basis states of position are orthonormal. In the linear-algebraic formulation, the overlap looked like the *sum* described by the dot product of the two states. When we move to the continuous picture, these sums become integrals

$$\langle\phi|\psi\rangle = \Big(\phi_0^*\langle x_0| + \phi_1^*\langle x_1| + \phi_2^*\langle x_2| + \cdots \phi_j^*\langle x_j| + \cdots\Big)\Big(\psi_0|x_0\rangle + \psi_1|x_1\rangle + \psi_2|x_2\rangle + \cdots \psi_j|x_j\rangle + \cdots\Big) \tag{4.16}$$

$$= \phi_0^*\psi_0 + \phi_1^*\psi_1 + \phi_2^*\psi_2 + \cdots + \phi_j^*\psi_j + \cdots \tag{4.17}$$

$$= \sum_{j=0}^{max} \phi_j^*\psi_j \,\langle x_j|x_j\rangle \tag{4.18}$$

$$= \int_0^{max} \phi^*(x)\psi(x)\,\mathrm{d}x \tag{4.19}$$

Comparison to our discussion of probability calculations with states in Chapter 2 and the theory of continuous probability in Math Chapter B in McQ also gives us a way to restate the **Born postulate** in the language of functions. The **probability density** for a state $|\psi\rangle = \psi(x)$ is given by,

$$p(x) = \psi^*(x)\psi(x) \tag{4.20}$$

and the probability of observing this continuous value between some $x_{\mathrm{min}}$ and $x_{\mathrm{max}}$ is

$$p = \int_{x_{\mathrm{min}}}^{x_{\mathrm{min}}} \psi^*(x)\psi(x)\,\mathrm{d}x \tag{4.21}$$

normalization

### 4.2.3 Derivatives and functions represent operators.

We know how to operate on functions—we can use other functions, including functions that contain derivatives—to perform operations that transform one function into another function.

**Expectation values** can be computed using the states

$$\langle A\rangle = \int_{-\infty}^{+\infty} \psi^*(x)\hat{A}\psi(x)\,\mathrm{d}x \tag{4.22}$$

### 4.2.4 Differential equations have eigenvalues and eigenfunctions.

### 4.2.5 The product of functions represents combined multistate systems.

## 4.3 Continuous and discrete representations can be used together to solve problems of interest.

**matrix element**

$$
\begin{aligned}
A_{rs} &= \langle \phi_r | \hat{O} | \phi_s \rangle && (4.23) \\
&= \int_{-\infty}^{+\infty} \phi_r^*(x) \hat{O} \phi_s(x) \ \mathrm{d}x && (4.24)
\end{aligned}
$$

can be used to evaluate an integral and then deposit the result into a matrix. This is particularly useful for evaluations involving atomic orbital functions, where the functions describe a spatial function, but we want the state to describe a particular orbital.

## Problems

1. TODO

# Math Chapter: Matrices

McQuarrie Math Chapter G

(and a few words from Matrix Eigenvalue Problems, but just forget about the secular determinant stuff)