

Preface

David Griffiths' book *Introduction to Quantum Mechanics* is perhaps the most widely used book on its subject, and manages to be accessible and conversational without excessive simplification. Still, many readers—especially those who can handle a slightly higher level of mathematical abstraction simplifies many of the book's derivations, and who are studying independently with limited help from professors—will be helped by a study guide.

In writing this commentary, I had three principal goals:

1. Provide summaries of the main findings of each section that can be consulted without wading through Griffiths' long derivations. In these sections, I often provide abbreviated versions of Griffiths' derivations, leaving out straightforward algebraic manipulations. The summary should be enough for you to reconstruct the original argument.
2. Use abstract results from linear algebra and operator theory to give shorter and more memorable derivations of some key results, especially those in the first two chapters, as Griffiths defers introducing many parts of the linear algebra formalism until Chapter 3.
3. Clarify a handful of points at which Griffiths makes a leap of logic that may not be obvious.

The result is intended as a companion, not a substitute, for Griffiths' book, and should be read alongside it. Perhaps the best method is to read one section in the original, then one section in the guide; though if a section in Griffiths is confusing upon first reading, the guide may help you to get unstuck.

The opening Chapter 0 presents the core elements of the mathematical formalism for QM (which are worth reading in full before beginning the book) as well as a handful of basic results on inner product spaces and Hermitian operators (which should be a review; if not, you may find it profitable to study abstract linear algebra first before trying to apply it to the messier concrete settings of QM).

Section titles and page references correspond to the second edition (2005).

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Chapter 0

Formalism and mathematical preliminaries

Griffiths defers the discussion of formalism until chapter 3, but if you've studied linear algebra (if you haven't, you're well advised to do that first!), seeing the basics first may help. This discussion is unavoidably a bit vague, but the next chapters will fill more details in. The advantage of discussing the formalism at the beginning is that we can start connecting Griffiths' discussions of specific systems to more general results, as well as provide generalizations.

0.1 States as elements of complex vector spaces

In QM, the state of a particle or a system can be described as an element of a vector space over \mathbb{C} . Different systems require different vector space models. For instance, the spin of a spin-1/2 particle such as an electron can be modeled as \mathbb{C}^2 , with $\mathbf{e}_1 = (1, 0)$ corresponding to a particle with spin up along the specified axis (for instance, the z -axis), and $\mathbf{e}_2 = (0, 1)$ corresponding to a particle with spin down along the same axis. Other linear combinations, such as $0.8\mathbf{e}_1 + 0.6\mathbf{e}_2$ or $\frac{i}{2}\mathbf{e}_1 + \frac{1+\sqrt{2}i}{2}\mathbf{e}_2$, correspond to other states, which could have definite spin along some other axis or no definite spin at all. (For reasons that we'll see later, a state $(k_1, k_2) = k_1\mathbf{e}_1 + k_2\mathbf{e}_2$ only corresponds to an actual physical state if $|k_1|^2 + |k_2|^2 = 1$.)

The state of a system determines physical properties such as momentum and energy, but not quite in the same way as in classical mechanics. In classical mechanics, these properties are continuous: that is, their allowable values are intervals of real numbers; and they're determinate: a particle always has an exact position, an exact energy, and so forth. But in quantum mechanics, these quantities are typically quantized and probabilistic. If you try to measure a system's state, you may get, you'll get one of a set of possible answers, and the same state won't always give you the same results.

For instance, if you test the spin of a spin-1/2 particle along the z -axis, you will get one of two results: either the particle's full spin points up along the z -axis, or it points down—you will never find only part of the spin along the z -axis, with another component in some unmeasured direction. And except for the states represented by \mathbf{e}_1 and \mathbf{e}_2 for particles with definite z -aligned spins, every state could yield spin-up or spin-down along z , with a larger first component of the state's vector representation corresponding to higher probability of spin-up. (In particular, the state (k_1, k_2) has

probability $|k_1|^2$ of being measured spin-up along the z -axis and probability $|k_2|^2$ of being measured spin-down. Probabilities have to add to 1, hence the comment before that real states need to have $|k_1|^2 + |k_2|^2 = 1$.)

Griffiths starts with a different simple system: a particle, with no relevant properties other than mass, moving in one dimension. To model this particle's possible states, we use (more or less¹) the space of complex-valued functions on \mathbb{R} , with vector addition and scalar multiplication determined point-by-point: the sum of two functions f and g is the function $x \mapsto f(x) + g(x)$, and the scalar product cf for some complex value c is the function $x \mapsto cf(x)$. The function that represents a particular particle state is called a *wavefunction*.

Ordinarily, we'll denote quantum states with symbols between a vertical line on the left and an angle bracket on the right as in $|\phi\rangle$ or $|1\rangle$. The whole symbol is called a *ket*, and the system of notation is *bra-ket notation* (or sometimes *Dirac notation*, the term that Griffiths prefers).

In Griffiths' book, a Greek letter in a ket typically mean the state whose wavefunction also has that letter: $|\Psi\rangle$ is the state with wavefunction $\Psi(x)$.

0.2 Inner products

Vector spaces in quantum mechanics also have a sesquilinear *inner product*. In linear algebra, a function $S : V^2 \rightarrow \mathbb{C}$ (where V is a complex vector space) is sesquilinear if it satisfies the following requirements:

1. If you fix the first argument, then varying the second argument gives a linear function: $S(\mathbf{v}, k_1\mathbf{w}_1 + k_2\mathbf{w}_2) = k_1S(\mathbf{v}, \mathbf{w}_1) + k_2S(\mathbf{v}, \mathbf{w}_2)$ for all vectors $\mathbf{v}, \mathbf{w}_1, \mathbf{w}_2 \in V$ and $k_1, k_2 \in \mathbb{C}$
2. If you fix the second argument, then varying the first argument gives an *antilinear* function: $S(k_1\mathbf{v}_1 + k_2\mathbf{v}_2, \mathbf{w}) = k_1^*S(\mathbf{v}_1, \mathbf{w}) + k_2^*S(\mathbf{v}_2, \mathbf{w})$, where k_1^* and k_2^* denote complex conjugates. (This asterisk notation for complex conjugates instead of $\overline{k_1}, \overline{k_2}$ is nearly universal in QM.)

Some books in pure mathematics make the first argument linear and the second antilinear, but antilinearity in the first argument is the convention in QM. To be an inner product, a sesquilinear form S also has to be *positive definite* (that is, $S(\mathbf{v}, \mathbf{v})$ is always a positive real number for all $\mathbf{v} \neq \mathbf{0}$), and *conjugate symmetric* (that is, $S(\mathbf{v}, \mathbf{w})$ and $S(\mathbf{w}, \mathbf{v})$ are conjugates).

In pure mathematics, the product of two elements on an inner product space is often denoted as $\langle \psi_1, \psi_2 \rangle$. In quantum mechanics, the convention is to use a very similar notation: *bra-ket notation* or *Dirac notation*. A state with wavefunction Ψ is denoted $|\Psi\rangle$, and the inner product of two such states $|\Psi_1\rangle$ and $|\Psi_2\rangle$ with the notation $\langle \Psi_1 | \Psi_2 \rangle$. The $\langle \Psi_1 |$ part is called a *bra* (that is, the other half of a bra-ket), and it can be treated as its own mathematical object closely related to, but different from, the state $|\Psi_1\rangle$. More on this later.

¹"More or less" because \mathbb{R} doesn't have units of distance attached, but a coordinate system that represents actual space does. Values of these functions themselves have units as well: as we'll see soon, the units of a one-dimensional wave function are $(\text{length})^{-1/2}$, because the integral of a squared wavefunction over a distance interval is the probability that the particle is located in that interval, and probabilities are dimensionless.

So how do we define inner products on QM vector spaces? For finite-dimensional spaces, the typical definition is a dot product. For instance, in a two-dimensional space like our spin-1/2 particle example, we might have one state $|\alpha\rangle$ represented as the vector $(a_1, a_2) \in \mathbb{C}^2$, and another state $|\beta\rangle$ is represented by (b_1, b_2) , then the inner product of two states $|\alpha\rangle = a_1|1\rangle + a_2|2\rangle$ and $|\beta\rangle = b_1|1\rangle + b_2|2\rangle$ is just $a_1^*b_1 + a_2^*b_2$.

Wavefunctions, though, are elements of infinite-dimensional function spaces. Instead of a sum over a finite number of basis states, we need to use an integral: the inner product of two wave functions Φ, Ψ as $\int_R \Phi(x)^*\Psi(x) d^n x$. The normalization requirement for wave functions, note, means that $\int_R |\Psi(x)|^2 d^n x = 1$.

These inner products have physical interpretations. One of the most important is the meaning of *orthogonal* states: that is, those with inner product zero. If $\langle\Phi|\Psi\rangle = 0$, then $|\Phi\rangle$ and $|\Psi\rangle$ are (to put it vaguely) physically independent: a system that's actually in state $|\Phi\rangle$ could never be measured to be in state $|\Psi\rangle$.

When we define inner products, we need to make sure that orthogonal states are in fact physically independent. Otherwise, our mathematical deductions won't correspond to physical facts. Using spin- $+z$ and spin- $-z$ as a basis for the space of spin-1/2 particle states, for instance, is fine, because a spin- $+z$ particle will never behave as though it has spin $-z$. Particles with a definite spin $+x$, on the other hand, could behave as though they had spin $-z$ if they were put through an experiment to measure magnetic moment along the z -axis, so $+x$ and $-z$ are not physically independent spin states, and if we constructed a vector space representation of spin-1/2 particles that made these orthogonal, we would run into trouble.

One final purely mathematical property of inner products is the *Schwarz* or *Cauchy-Schwarz inequality*

$$|\langle\mathbf{v}, \mathbf{w}\rangle|^2 \leq \langle\mathbf{v}, \mathbf{v}\rangle \langle\mathbf{w}, \mathbf{w}\rangle.$$

Proof sketch: let z be some complex number such that $|z| = 1$ and $\langle\mathbf{v}, z\mathbf{w}\rangle$ is real (and thus $\langle\mathbf{v}, z\mathbf{w}\rangle = \langle z\mathbf{w}, \mathbf{v}\rangle$). Then $\langle\mathbf{v} + xz\mathbf{w}, \mathbf{v} + xz\mathbf{w}\rangle$ is a nonnegative real quantity. Expanding it for real x gives

$$\langle\mathbf{w}, \mathbf{w}\rangle x^2 + 2\langle\mathbf{v}, z\mathbf{w}\rangle x + \langle\mathbf{v}, \mathbf{v}\rangle \geq 0$$

which is a quadratic inequality that can only hold for all real x if the discriminant $4\langle\mathbf{v}, z\mathbf{w}\rangle^2 - 4\langle\mathbf{v}, \mathbf{v}\rangle \langle\mathbf{w}, \mathbf{w}\rangle$ is not positive, and $|\langle\mathbf{v}, z\mathbf{w}\rangle| = |z| |\langle\mathbf{v}, \mathbf{w}\rangle|$.

0.3 Product rule for derivatives of inner products

The linearity of inner products gives us a "product rule" for the inner product of vectors (or functions) that vary with time: for an infinitesimal increment dt where dt^2 can be neglected,

$$\langle\mathbf{u}(t) + \mathbf{u}'(t) dt, \mathbf{v}(t) + \mathbf{v}'(t) dt\rangle = \langle\mathbf{u}(t), \mathbf{v}(t)\rangle + (\langle\mathbf{u}(t), \mathbf{v}'(t)\rangle + \langle\mathbf{u}'(t), \mathbf{v}(t)\rangle) dt$$

so

$$\frac{d}{dt} \langle\mathbf{u}(t), \mathbf{v}(t)\rangle = \langle\mathbf{u}(t), \mathbf{v}'(t)\rangle + \langle\mathbf{u}'(t), \mathbf{v}(t)\rangle.$$

0.4 Bras as elements of the dual space

In linear algebra, if V is a vector space over \mathbb{F} , then the *dual* space of V , denoted V^* , is $\text{Hom}(V, \mathbb{F})$, or the set of linear maps from V to its base field. (For instance, the functions

$f_1, f_2 : \mathbb{R}^2 \rightarrow \mathbb{R}$ defined by $f(x_1, x_2) = 2x_1 - 3x_2$ and $f(x_1, x_2) = 4x_1$ are both elements of the dual space of \mathbb{R}^2 .)

In the inner product $\langle \Phi | \Psi \rangle$, we can identify $\langle \Phi |$ as an element of the dual space, namely the linear map that takes every state $|\Psi\rangle$ to its inner product with $|\Phi\rangle$. For instance, if $|\Phi\rangle$ is the state of a particle with the wavefunction f , then $\langle \Phi |$ is the map from any other wavefunction g to $\int f(x)^* g(x) dx$. This means that $\langle \Phi |$ is an element of the dual of the space of particle states. According to this formula, if $|\Phi\rangle = a_1 |\Psi_1\rangle + a_2 |\Psi_2\rangle$ (which means literally that $|\Phi\rangle$'s wavefunction is a_1 times $|\Psi_1\rangle$'s wavefunction plus a_2 times $|\Psi_2\rangle$'s wavefunction), then the corresponding bra $\langle \Phi |$ is $a_1^* \langle \Phi_1 | + a_2^* \langle \Phi_2 |$. We'll use this formula a lot.

Finally, elements of dual spaces (including bras) can be added just like any linear maps: if $f, g \in V^*$, then $f+g$ is the map that sends every vector $\mathbf{v} \in V$ to $f(\mathbf{v})+g(\mathbf{v}) \in \mathbb{F}$. This lets us expand products of sums of bras and kets: for instance, $(\langle a| + \langle b|)(|c\rangle + |d\rangle) = \langle a|c\rangle + \langle a|d\rangle + \langle b|c\rangle + \langle b|d\rangle$.

0.5 Observations as operators

In classical physics, quantities such as energy and the directional components of momentum are scalars. In quantum mechanics, the analogous quantities are actually *operators* on the vector space, which take one wavefunction (or similar) and produce another wavefunction (or similar) in the same space² These operators typically have explicit formulas, so if you have a formula for an input wavefunction, you can (at least theoretically) produce a formula for the output “energy” or “ x -component of momentum” wavefunction.

But how do you get from the output of an operator to a value of the corresponding quantity? The answer is that certain wavefunctions are eigenvectors—in QM, the more common word is *eigenstates*—of the corresponding operator, and the eigenvalue is the value of the physical quantity. That is: applying the operator just multiplies the original wavefunction by a constant factor, and this factor is the value of the physical quantity in question.

0.6 Expected values as inner products

For states $|\phi\rangle$ that aren't eigenfunctions of an operator \hat{Q} that measures some quantity Q (in QM, we usually mark operators with the hat symbol), we can at least calculate a mean expected value of Q with the formula $E(Q) = \langle \phi | \hat{Q} | \phi \rangle$. For instance, suppose \hat{Q} has orthogonal eigenstates $|1\rangle$ and $|2\rangle$ with eigenvalues Q_1 and Q_2 : that is, $\langle 1|1\rangle = \langle 2|2\rangle = 1$, $\langle 1|2\rangle = \langle 2|1\rangle = 0$, and $\hat{Q}|1\rangle = Q_1|1\rangle$ and $\hat{Q}|2\rangle = Q_2|2\rangle$. Suppose we have some hybrid state $|\phi\rangle = c_1|1\rangle + c_2|2\rangle$ (where for normalization $|c_1|^2 + |c_2|^2 = 1$). Then $\langle \phi | = c_1^* \langle 1| + c_2^* \langle 2|$ and $\hat{Q}|\phi\rangle = \hat{Q}(c_1|1\rangle + c_2|2\rangle) = c_1\hat{Q}|1\rangle + c_2\hat{Q}|2\rangle = c_1Q_1|1\rangle + c_2Q_2|2\rangle$. (Remember: \hat{Q} is a linear operator!)

So the expected value is $\langle \phi | \hat{Q} | \phi \rangle = (c_1^* \langle 1| + c_2^* \langle 2|)(c_1Q_1|1\rangle + c_2Q_2|2\rangle)$, which we can expand to $c_1^*c_1Q_1 \langle 1|1\rangle + c_1^*c_2Q_2 \langle 1|2\rangle + c_2^*c_1Q_1 \langle 2|1\rangle + c_2^*c_2Q_2 \langle 2|2\rangle$, and the orthonormality

²Again, ignoring the fact that the input and output may have different units, so you couldn't technically add them together the way you could add wavefunctions in a vector space.

of $|1\rangle$ and $|2\rangle$ simplifies this to $|c_1|^2 Q_1 + |c_2|^2 Q_2$. So $|\phi\rangle$'s value of Q is a weighted average of the value of Q in the constituent eigenstates $|1\rangle$ and $|2\rangle$, scaled by the contribution of each eigenstate to the overall state.

0.7 Hermitian and skew-Hermitian operators

Operators that correspond to observable quantities have an additional valuable property: they are *Hermitian*. Remember from linear algebra that a Hermitian matrix (by definition) one that equals its own conjugate transpose, and that a result called the *spectral theorem* guarantees that you can choose an orthogonal basis for the underlying vector space made up entirely of the eigenvectors of a Hermitian matrix.

In general complex vector spaces V with an inner product $\langle \cdot, \cdot \rangle : V^2 \rightarrow \mathbb{C}$, a Hermitian operator $H : V \rightarrow V$ is one that satisfies the equation $\langle H\mathbf{v}, \mathbf{w} \rangle = \langle \mathbf{v}, H\mathbf{w} \rangle$.³ You might also see the term *self-adjoint*: more generally, the *adjoint* of an operator T is the operator T^\dagger that satisfies $\langle T^\dagger \mathbf{v}, \mathbf{w} \rangle = \langle \mathbf{v}, T\mathbf{w} \rangle$.

The spectral theorem does generalize in a way to infinite-dimensional spaces. In particular, we have these two important results:

1. *Eigenstates of a Hermitian operator are real.* Proof: if \mathbf{v} is a nonzero eigenstate of H with eigenvalue λ , then $\langle H\mathbf{v}, \mathbf{v} \rangle = \langle \lambda\mathbf{v}, \mathbf{v} \rangle = \lambda^* \langle \mathbf{v}, \mathbf{v} \rangle$ and $\langle \mathbf{v}, H\mathbf{v} \rangle = \langle \mathbf{v}, \lambda\mathbf{v} \rangle = \lambda \langle \mathbf{v}, \mathbf{v} \rangle$. So $\lambda = \lambda^*$; that is, λ is real.
2. *Eigenstates of a Hermitian operator with different eigenvalues are orthogonal.* Proof: if $H\mathbf{v} = \lambda\mathbf{v}$ and $H\mathbf{w} = \mu\mathbf{w}$ (where λ and μ must be real, then $\langle H\mathbf{v}, \mathbf{w} \rangle = \langle \lambda\mathbf{v}, \mathbf{w} \rangle = \lambda \langle \mathbf{v}, \mathbf{w} \rangle$ and $\langle \mathbf{v}, H\mathbf{w} \rangle = \langle \mathbf{v}, \mu\mathbf{w} \rangle = \mu \langle \mathbf{v}, \mathbf{w} \rangle$. If these are equal, then either $\lambda = \mu$ or $\langle \mathbf{v}, \mathbf{w} \rangle = 0$.

Often it's more convenient to represent a state as a weighted sum of eigenstates of a particular operator than to work with raw wavefunctions directly. Eigenstates of the energy operator, called the *Hamiltonian*, are especially convenient because they evolve through time in an especially simple way, and time evolution is another linear operator: to find how the sum of states changes through time, you can find how all of the constituent states change and then add the results.

This result will be helpful for determining if an operator is Hermitian.

Proposition. *Sums and real multiples of Hermitian operators are all Hermitian, as are the compositions of commuting Hermitian operators.*

Proof. Notation: all operators are defined on some complex vector space V with arbitrary elements \mathbf{v}, \mathbf{w} . Now we'll address in turn:

1. *Sums:* Suppose H_1, H_2 are two operators. Then $\langle (H_1 + H_2)\mathbf{v}, \mathbf{w} \rangle = \langle H_1\mathbf{v}, \mathbf{w} \rangle + \langle H_2\mathbf{v}, \mathbf{w} \rangle$ and $\langle \mathbf{v}, (H_1 + H_2)\mathbf{w} \rangle = \langle \mathbf{v}, H_1\mathbf{w} \rangle + \langle \mathbf{v}, H_2\mathbf{w} \rangle$. If H_1 and H_2 are Hermitian, then $\langle H_1\mathbf{v}, \mathbf{w} \rangle = \langle \mathbf{v}, H_1\mathbf{w} \rangle$ and likewise for H_2 , so $\langle (H_1 + H_2)\mathbf{v}, \mathbf{w} \rangle = \langle \mathbf{v}, (H_1 + H_2)\mathbf{w} \rangle$, so $H_1 + H_2$ is Hermitian.

³To see that the notions of Hermitian matrix and Hermitian operator correspond, note that if \mathbf{a} and \mathbf{b} are column vector representations of \mathbf{v}, \mathbf{w} and M is the Gram matrix of H (all relative to a basis that's orthonormal with respect to the inner product), then $\langle \mathbf{v}, H\mathbf{w} \rangle = \mathbf{a}^\dagger(M\mathbf{b})$ and $\langle H\mathbf{v}, \mathbf{w} \rangle = (M\mathbf{a})^\dagger\mathbf{b} = \mathbf{a}^\dagger M^\dagger\mathbf{b}$, where the symbol \dagger indicates the conjugate transpose. These quantities are equal for every possible \mathbf{a}, \mathbf{b} only if $M = M^\dagger$; that is, if M is Hermitian.

2. *Multiples:* Suppose H is a Hermitian operator and c is a real number. Then $\langle (cH)\mathbf{v}, \mathbf{w} \rangle = c^* \langle H\mathbf{v}, \mathbf{w} \rangle = c \langle H\mathbf{v}, \mathbf{w} \rangle$ (because c is real) and $\langle \mathbf{v}, (cH)\mathbf{w} \rangle = c \langle \mathbf{v}, H\mathbf{w} \rangle$. As H is Hermitian, these quantities are equal, so cH is Hermitian.
3. *Compositions of commuting operators:* Let H_1, H_2 be Hermitian operators such that $H_1H_2 = H_2H_1$. Then $\langle (H_1H_2)\mathbf{v}, \mathbf{w} \rangle = \langle H_1(H_2\mathbf{v}), \mathbf{w} \rangle = \langle H_2\mathbf{v}, H_1\mathbf{w} \rangle = \langle \mathbf{v}, H_2H_1\mathbf{w} \rangle$. So if $H_1H_2 = H_2H_1$, then H_1H_2 is Hermitian.

□

Remark. The requirement that H_1 and H_2 commute is vital! If they don't, then $H_1H_2 - H_2H_1$ is a nonzero operator that is guaranteed to be *skew-Hermitian* (see below for what this means).

There's a related notion of *skew-Hermitian operators* which satisfy $\langle \mathbf{v}, S\mathbf{w} \rangle = -\langle S\mathbf{v}, \mathbf{w} \rangle$. Here are some properties of skew-Hermitian operators; they can all be proved easily using very similar proof techniques.

1. Sums and real multiples of skew-Hermitian operators are skew-Hermitian.
2. Multiples of Hermitian operators by *purely imaginary* scalars are skew-Hermitian, and vice versa.
3. Skew-Hermitian operators have purely imaginary eigenvalues. (Proof: if \mathbf{v} is an eigenvector of the skew-Hermitian operator S with eigenvalue λ , then it's also an eigenvector of the Hermitian operator iS with necessarily real eigenvalue $i\lambda$.)
4. If A and B commute, then the composition $AB = BA$ is Hermitian if A and B are both Hermitian or both skew-Hermitian, and it's skew-Hermitian if one of A and B is Hermitian and the other is skew-Hermitian.

0.8 Adjoint operators

An operator $B : V \rightarrow V$ is an *adjoint* of an operator A on a vector space V with an inner product $\langle \cdot, \cdot \rangle$ if $\langle \mathbf{v}, A\mathbf{w} \rangle = \langle B\mathbf{v}, \mathbf{w} \rangle$ for all $\mathbf{v}, \mathbf{w} \in V$. (Hermitian operators, as defined above, are the operators that are adjoints of themselves.)

A few properties of adjoints, which Griffiths implicitly on in a few spots but doesn't prove, will come in handy later:

1. *If the inner product is nondegenerate—that is, there's no nonzero vector \mathbf{v} such that $\langle \mathbf{v}, \mathbf{w} \rangle = 0$ for all $\mathbf{w} \in V$ —then the adjoint of an operator is unique.*⁴ Proof: suppose A has two adjoints B_1, B_2 . Let \mathbf{v} be some vector such that $B_1\mathbf{v} \neq B_2\mathbf{v}$, and define $\mathbf{x} = B_1\mathbf{v} - B_2\mathbf{v}$. Then $\langle \mathbf{v}, A\mathbf{w} \rangle = \langle B_1\mathbf{v}, \mathbf{w} \rangle = \langle B_2\mathbf{v}, \mathbf{w} \rangle$ and thus $\langle B_1\mathbf{v}, \mathbf{w} \rangle - \langle B_2\mathbf{v}, \mathbf{w} \rangle = 0$ for all $\mathbf{w} \in V$. But by antilinearity of the inner product in the first argument, $\langle B_1\mathbf{v}, \mathbf{w} \rangle - \langle B_2\mathbf{v}, \mathbf{w} \rangle = \langle B_1\mathbf{v} - B_2\mathbf{v}, \mathbf{w} \rangle = \langle \mathbf{x}, \mathbf{w} \rangle$, so $\langle \cdot, \cdot \rangle$ is degenerate.

Every inner product that we work with in QM is nondegenerate, so we're guaranteed uniquely defined adjoints.

⁴The symmetry properties of inner products guarantee that this condition for nondegeneracy is equivalent to the condition defined the other way around: there's no \mathbf{w} such that $\langle \mathbf{v}, \mathbf{w} \rangle = 0$ for all \mathbf{v} .

2. If A is an adjoint of B , then B is an adjoint of A . Proof: we have $\langle \mathbf{v}, A\mathbf{w} \rangle = \langle A\mathbf{w}, \mathbf{v} \rangle^*$ and $\langle B\mathbf{v}, \mathbf{w} \rangle = \langle \mathbf{w}, B\mathbf{v} \rangle^*$ for any operators A, B by the symmetry properties of inner products. So if $\langle \mathbf{v}, A\mathbf{w} \rangle = \langle B\mathbf{v}, \mathbf{w} \rangle$ for arbitrary $\mathbf{v}, \mathbf{w} \in V$ (showing that B is an adjoint of A), then $\langle \mathbf{w}, B\mathbf{v} \rangle = \langle A\mathbf{w}, \mathbf{v} \rangle$ for arbitrary $\mathbf{v}, \mathbf{w} \in A$ (showing that A is an adjoint of B).
3. If B is an adjoint of A , then the composition AB is Hermitian. Proof: $\langle \mathbf{v}, AB\mathbf{w} \rangle = \langle \mathbf{v}, A(B\mathbf{w}) \rangle = \langle B\mathbf{v}, B\mathbf{w} \rangle = \langle AB\mathbf{v}, \mathbf{w} \rangle$.
4. If A_1, A_2 are operators with adjoints B_1, B_2 , then an adjoint of $k_1A_1 + k_2A_2$ for scalars k_1, k_2 is $k_1^*B_1 + k_2^*B_2$.

We use the special dagger notation for adjoints: $B = A^\dagger$.

0.9 Differential equations as linear operators

The set of functions in one or more variables with values in \mathbb{R} or \mathbb{C} is a vector space with pointwise addition and multiplication: $f + g$ is the map $x \mapsto f(x) + g(x)$ and cf for constant c is the map $x \mapsto cf(x)$. (The same thing can be said for functions with multiple values.) It also has an inner product defined on it, typically by integration along the lines of $\langle f, g \rangle = \int_a^b f(x)^*g(x) dx$.

Two types of expression that often show up in differential equations encountered in quantum mechanics can be expressed as linear operators on this space, and they are often (skew-)Hermitian. This fact often simplifies analysis of differential equations:

1. *Multiplication by given functions.* The map that sends a function f to its pointwise product with another (possibly constant) given function $k(x)$: that is, the map $f \mapsto k(x)f(x)$. (Why is this linear? It should be pretty clear that $k(x)(c_1f_1(x) + c_2f_2(x)) = c_1(k(x)f_1(x)) + c_2(k(x)f_2(x))$ for all constants c_1, c_2 and functions f_1, f_2 .)

With the inner product $\langle f, g \rangle = \int_I f(x)^*g(x) dx$ where I is some interval, this is Hermitian if k is real-valued: both $\langle kf, g \rangle$ and $\langle f, kg \rangle$ equal $\int_I f^*(x)k(x)g(x) dx$ (presuming either integral converges in the first place).

This operator is also linear (and Hermitian, if k is real-valued) if f and k are functions of multiple variables. (In this case, the inner product would usually be defined as a multiple integral.)

2. *Differentiation.* The differentiation operator $\frac{d}{dx}$ is linear: $\frac{d}{dx}(c_1f_1(x) + c_2f_2(x)) = c_1f_1'(x) + c_2f_2'(x)$.

If f is defined on the interval $[a, b]$ (we could have $a = -\infty$ or $b = \infty$), then the set of functions f that satisfy $f(a) = f(b) = 0$ (with $f(\pm\infty)$ interpreted as $\lim_{x \rightarrow \pm\infty} f(x)$ when we have an endpoint at ∞) is a linear subspace of the space of functions. On this subspace, the differentiation operator is skew-Hermitian. Remember that the derivative of the complex conjugate of a complex-valued function is also the complex conjugate of the derivative, and the product rule

$$\frac{d}{dx}f(x)^*g(x) = f(x)^*g'(x) + f'(x)^*g(x)$$

when integrated from $x = a$ to $x = b$ becomes the integration by parts formula

$$f(b)^*g(b) - f(a)^*g(a) = \int_a^b f(x)^*g'(x) dx + \int_a^b f'(x)^*g(x) dx = \langle f, g' \rangle + \langle f', g \rangle.$$

If the value of this equation is zero (for instance, because $a = -\infty, b = \infty$, and f and g asymptotically go to zero), then $\frac{d}{dx}$ is skew-Hermitian.

Wave functions representing particle density typically go to zero at each endpoint of their domain (or if they're defined over all of space, they go to zero at $x = \pm\infty$: you can't have a particle spread thickly over all of the universe), so this result is often useful.

3. *Iterated and partial differentiation.* As $\frac{d}{dx}$ is skew-Hermitian, so $ic\frac{d}{dx}$ is Hermitian for any real value c , and $\frac{d^2}{dx^2}$, as the composition of $\frac{d}{dx}$ with itself (and all operators commute with themselves), is Hermitian on the subspace of functions f that satisfy $f(a) = f(b) = 0$ and $f'(a) = f'(b) = 0$. (Even if f vanishes at a and b , $\frac{d}{dx}$ won't be skew-Hermitian on f' if $f'(a) \neq 0$ or $f'(b) \neq 0$, so the result that the composition of two skew-Hermitian operators is Hermitian isn't applicable.)

Similar results apply to partial derivatives. In general, the n th derivative operator is skew-Hermitian if n is odd and Hermitian if n is even when it's applied to the space of functions that vanish at a and b along with their first $n - 1$ derivatives.

To see how this theory, plus some basic results on abstract linear maps, can apply to differential equations, consider the important differential equation

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

defined on functions $\Psi(x, t)$ whose values (and all orders of derivatives) go to zero at $x \rightarrow \pm\infty$. We can express this as

$$\left(i\hbar\frac{\partial}{\partial t} + \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\Psi(x, t) = 0.$$

Taking derivatives by t and x , and multiplying by a fixed function V or constant such as $\frac{\hbar^2}{2m}$, are all linear operators, so the big expression in parentheses is a linear operator. We've reframed the differential equation as a statement that Ψ is in the *kernel* of a linear operator. Kernels are linear subspaces of their enclosing vector space: that is, if Ψ_1 and Ψ_2 are differential equations, then so is $c_1\Psi_1 + c_2\Psi_2$ for any constants c_1, c_2 .

Furthermore, it turns out that if initial conditions $\Psi(x, 0)$ for Ψ are given, then $\Psi(x, t)$ is uniquely determined: knowing $\Psi(x, 0)$ uniquely determines the initial value of $\frac{\partial^2\Psi}{\partial x^2}$ and therefore also of $\frac{\partial\Psi}{\partial t}$. So if $\Psi_1(x, t), \Psi_2(x, t)$ have initial conditions $\psi_1(x) = \Psi_1(x, 0)$ and $\psi_2(x) = \Psi_2(x, 0)$, then the solution with initial conditions $c_1\psi_1 + c_2\psi_2$ couldn't be anything other than $c_1\Psi_1 + c_2\Psi_2$. This means that the *time evolution operators* that take an input state $\psi_{t=0}$ at one time to an output state $\psi_{t=t_0}$ at some other time are also linear.

So on functions $\Psi(x, t)$ with $\lim_{x \rightarrow \pm\infty} \Psi(x, t) = \lim_{x \rightarrow \pm\infty} \frac{\partial}{\partial x} \Psi(x, t) = 0$, the map from Ψ to $\left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)\right) \Psi(x)$ is a Hermitian operator. This fact will come in handy later, letting us prove several properties about this operator using generic results on Hermitian operators without resorting to making explicit integrals. In fact, there are several important results that Griffiths derives using clunky integration by parts where the core insight turns out to be a lightly disguised “ $\frac{d}{dx}$ is skew-Hermitian”, and if we remember the general result on $\frac{d}{dx}$, we can derive these results without doing integrals in a specific setting again.

Chapter 1

The wave function

1.1 The Schrödinger equation

The equation that Griffiths presents as the Schrödinger equation is actually just the equation for one specific class of systems: a particle moving in a one-dimensional potential field V . Any interactions between the particle and external forces, such as between its charge and an external electric field, are encapsulated in V , so the only property that appears explicitly in the Schrödinger equation is V .

The fully generic form of the Schrödinger equation, which Griffiths doesn't present off the bat, is that if the state of a system at time t can be represented by some element $s(t)$ of a vector space called the *state space*, then

$$i\hbar s'(t) = \hat{H}s(t)$$

where s' denotes a derivative with respect to time, and \hat{H} is a particular (and always Hermitian) operator called the *Hamiltonian operator*.

As \hat{H} has units of energy \times time and the units of s' , like any time derivative, are the units of \hat{H} times time^{-1} , it follows that \hat{H} must have units of energy. It turns out, in fact, that if s is an eigenstate of \hat{H} , then the eigenvalue is the energy of \hat{H} .

s' could be a vector with a finite number of complex components, as in the spin-1/2 particle example that we discussed in Section 0.1. For the case of particles in one dimension, the state space is the set of complex-valued functions of one space coordinate. If we write $\Psi(x, t)$ to represent this state at any particular time t , then we get

$$i\hbar \frac{\partial \Psi(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V(x)\Psi(x, t)$$

(and its generalizations, which we'll get to later) is the most important equation in quantum mechanics. As we discussed in section 0.9, the operator $H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$ is a Hermitian operator, and we can use this fact to give some proofs of its properties that, unlike Griffiths' proofs, don't require juggling integrals.

Planck's constant. Griffiths calls \hbar *Planck's constant*, but some other books call it the *reduced Planck's constant* in some other books which reserve the term *Planck's constant*, without an adjective, for the quantity $h = 2\pi\hbar$. Planck's constant is a fundamental, experimentally determined constant of the universe, just like the speed of light or the mass of a proton; there's no way to derive it from other quantities.

The energy operator in the Schrödinger equation. Both sides of the Schrödinger equation have units of energy times units of the wavefunction (which, for particles in one dimension, is length^{-1/2}).

In fact, the right-hand side is actually the energy operator $\left(-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\right)$ applied to the function Ψ : that is, if Ψ is a wavefunction with some definite energy E , then $\left(-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\right) \Psi$ is just the scalar multiple $E\Psi$. The first term $-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2}$ represents kinetic energy, and the second term is the potential energy. The potential energy V could depend on a potential gradient that varies over space, so $V\Psi$ is really the function $x \mapsto V(x)\Psi(x)$. (For this reason, you'll often see V written with an operator hat \hat{V} .)

It's not obvious that $-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2}$ is actually the kinetic energy of Ψ . Ultimately, we believe that it is the kinetic energy because it agrees with experiment, but we can give (somewhat handwaving) derivations of this result from other experimental results, in particular *wave-particle duality*—the fact that small particles demonstrate wavelike phenomena such as interference. One example of this is the double-slit experiment: if you fire electrons through a barrier with two parallel slits at a screen that lights up where an electron hits it, the screen will display a pattern of diffraction and interference characteristic of wave phenomena, with alternating light and dark fringes. The distance between the fringes lets you calculate the “wavelength” of the electrons.

We can derive (with a bit of handwaving) formulas for the momentum and thereby kinetic energy operators along these lines (discussion here is adapted from Frank J. Pilar, *Elementary Quantum Chemistry*):

1. In one dimension,¹ the energy E , momentum p , wavelength λ , and frequency ν of a particle follow the experimentally determined relations $p\lambda = h = 2\pi\hbar$ (the *de Broglie relation*).
2. If particles are modeled by complex wavefunctions, it's reasonable to suppose that a particle with wavelength λ and definite momentum in the positive x -direction might have the wavefunction

$$\Psi(x, t) = C \exp\left(\frac{2\pi i}{\lambda}x - vt\right)$$

where C is some constant and v is the particle's velocity, which is positive if the particle is moving in the positive x -direction.

If we differentiate Ψ with respect to x , we get $\frac{\partial \Psi}{\partial x} = \frac{2\pi i}{\lambda}C \left(\frac{2\pi i}{\lambda}x - vt\right) = \frac{2\pi i}{\lambda}\Psi$:

that is, Ψ is an eigenstate of $\frac{\partial}{\partial x}$ with eigenvalue $\frac{2\pi i}{\lambda}$. And the de Broglie relation gives $\frac{2\pi i}{\lambda} = \frac{ip}{\hbar}$, so the operator $\frac{\hbar}{i} \frac{\partial}{\partial x}$ would simply extract p , the momentum of the wave, as an eigenvalue.

(Griffiths gives another derivation of the momentum operator in section 1.5, but his derivation takes the Schrödinger equation for granted.)

¹In one dimension, we can treat vector quantities such as momentum as just other scalar quantities.

3. The classical equations $p = mv$ and $E = mv^2/2$, giving momentum and kinetic energy in terms of mass and velocity, can be combined to give kinetic energy in terms of mass and momentum $E = p^2/2m$. Applying the momentum operator $\frac{\hbar}{i} \frac{\partial}{\partial x}$ twice (equivalent to applying $-\hbar^2 \frac{\partial^2}{\partial x^2}$ once) extracts p^2 as an eigenvalue from a momentum eigenstate, so $-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$ gives the kinetic energy.

1.2 The statistical interpretation

This section merely spells out in detail things that we mentioned prior: in particular, that the squared amplitude of a wave function can be interpreted as a probability. (This isn't really something that you can work out a priori, but again, the ultimate test is that it agrees with experiment.)

The takeaway of wavefunction collapse is also important: if you measure a particle or system to have some value of a quantity, then the system changes state to the state with that definite value of that quantity (i.e. to the eigenstate of the corresponding operator for that quantity). This is unavoidably weird and there's a lot of philosophical speculation about what actually happens.

1.3 Probability

This is a review of basic techniques for working with expected values and variances. There's not much here if you remember basic statistics, but the formula $\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2$ for variance is worth memorizing: you'll use it a lot.

1.4 Normalization

We covered the concept of normalization in the prefatory discussion, but to reemphasize: squared amplitudes of a wavefunction represent probability densities, and the integral of a probability density has to equal 1. Often you'll find that a formula for a particle's wavefunction includes some scalar constant, and you have to set the constant so that this normalization criterion is satisfied.

Griffiths offers a proof that a state that's normalized at time $t = 0$ stays normalized for all t by directly working with the Schrödinger equation. There's another argument that works directly from the fact that \hat{H} is Hermitian. We have the generic form of the Schrödinger equation

$$i\hbar s'(t) = \hat{H}s$$

or

$$s'(t) = -\frac{i}{\hbar} \hat{H}s(t)$$

If \hat{H} is Hermitian, then

$$\begin{aligned}
 \frac{d}{dt} \langle \mathbf{s}(t), \mathbf{s}(t) \rangle &= \langle \mathbf{s}(t), \mathbf{s}'(t) \rangle + \langle \mathbf{s}'(t), \mathbf{s}(t) \rangle && \text{(product rule; see section 0.3)} \\
 &= \left\langle \mathbf{s}(t), -\frac{i}{\hbar} \hat{H} \mathbf{s}(t) \right\rangle + \left\langle -\frac{i}{\hbar} \hat{H} \mathbf{s}(t), \mathbf{s}(t) \right\rangle && \text{(Schrödinger equation)} \\
 &= -\frac{i}{\hbar} \langle \mathbf{s}(t), \hat{H} \mathbf{s}(t) \rangle + \frac{i}{\hbar} \langle \hat{H} \mathbf{s}(t), \mathbf{s}(t) \rangle \\
 &\quad \text{(inner product is antilinear in first argument and linear in second)} \\
 &= 0 && (\hat{H} \text{ is Hermitian})
 \end{aligned}$$

so $\langle \mathbf{s}(t), \mathbf{s}(t) \rangle$ is constant.

1.5 Momentum

This section develops formulas for velocity and momentum operators—or, more precisely, formulas for the expected values of velocity and momentum that follow the format $\langle \Psi | \hat{A} | \Psi \rangle = \int \Psi(x)^* \hat{A}(\Psi)(x) dx$, from which we can extract a formula for the operator \hat{A} . (The notation $\hat{A}(\psi)(x)$ may seem confusing; what it says is “apply the operator \hat{A} to the whole wavefunction ψ , producing another wavefunction that we then evaluate at x .”) We gave a handwaving development of a momentum operator in section 1.1, but that version started from more basic experimental considerations, whereas Griffiths’ development here takes the Schrödinger equation as granted.

1.6 The uncertainty principle

Nothing to add here.

Chapter 2

Time-independent Schrödinger equation

2.1 Stationary states

Griffiths' basic method in this chapter, put slightly more abstractly, is the following:

1. Start with the Schrödinger equation $i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$. Look for solutions of the form $\Psi(x, t) = \psi(x)\phi(t)$. If \hat{H} does not have any derivatives with respect to t ,¹ then we can treat the $\phi(t)$ component on the right as a constant, getting

$$i\hbar\psi(x)\phi'(t) = \phi'(t).$$

Similarly, we can treat ψ as a constant with respect to differentiation by t , getting the result

$$i\hbar\psi(x)\phi'(t) = \phi(t)\hat{H}\psi(x).$$

2. This equation can be rearranged to

$$i\hbar \frac{\phi'(t)}{\phi(t)} = \frac{1}{\psi(x)} \hat{H}\psi(x).$$

Now if \hat{H} has no time dependence at all, the LHS depends only on t and the right only on x . Both sides must therefore be equal to some constant E .

3. On the RHS, $E = \frac{1}{\psi(x)} \hat{H}\psi(x)$ says that $\psi(x)$ (and thus $\Psi(x)$) is an eigenfunction of \hat{H} with eigenvalue (i.e. energy) E . Now, \hat{H} is some differential operator, so setting the RHS equal to E gives a differential equation that we can solve to get

¹Griffiths says that this step is possible as long as \hat{H} is completely independent of t , but this condition is actually stronger than necessary: even if \hat{H} involves t -dependent terms, as long as those terms are only getting multiplied with Ψ rather than being differentiated or integrated, they can be treated as constants with respect to differentiation and integration by other variables, and we can still rewrite $\hat{H}(\psi(x)\phi(t))$ as $\phi(t)\hat{H}\psi(x)$. This slight generalization isn't of much practical use, though, because we need complete time-independence of \hat{H} for the next step.

the corresponding values of ψ ; the physically attainable values of E will be whatever values give a normalizable state that matches the boundary conditions (for instance, $\phi(x) = 0$ at either end of an infinite well).

The LHS, meanwhile, is $i\hbar \frac{d}{dt} \ln \phi(t)$, with general solution $\phi(t) = Ce^{-iEt/\hbar}$. So stationary states are $\phi(x)e^{-iEt/\hbar}$ for any eigenstate ϕ of \hat{H} .

4. The solutions to $i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$ are elements of the kernel of the linear operator $i\hbar \frac{\partial}{\partial t} - \hat{H}$, which must be a linear subspace of the state space, so we can get (at least some) solutions as a linear combination of the separable solutions. (It's harder to prove that *every* solution is a linear combination of the separable solutions, and Griffiths handwaves this.)

Time evolution of energy eigenstates. If Ψ is an eigenstate of \hat{H} (that is, it's a state with definite energy E), then the Schrödinger equation (reintroducing explicit notation for the space and time inputs to Ψ) becomes

$$i\hbar \frac{\partial \Psi(x, t)}{\partial t} = E\Psi(x, t)$$

with no derivative with respect to x involved. The solution to this equation is

$$\Psi(x, t) = e^{-iEt/\hbar} \Psi(x, 0);$$

that is, an energy eigenstate keeps the same wavefunction shape, only changing by an overall complex phase $e^{-iEt/\hbar}$ that revolves around the unit circle at a rate proportional to E .

This is true for any eigenstate Ψ of \hat{H} , even if \hat{H} has time-dependence. That is, every eigenstate of \hat{H} is also a stationary state. Griffiths' separation-of-variables technique proved that the converse is true if \hat{H} is time-independent: every solution that can be separated as $\phi(x)\phi(t)$, in this case, is also an energy eigenstate.

Normalized linear combinations of energy eigenstates stay normalized. As a linear combination of energy eigenstates evolves through time (and remember that time evolution is linear, so we can look separately at the time evolution of each constituent eigenstate of an arbitrary state and then add the results), the associated coefficients will change complex phase but not absolute value, so the sum of squared absolute values of their coefficients—which must equal 1 for a normalized state—won't change, either. We already proved this without reference to decomposing states into eigenstates, but it may help to see it spelled out again in a different context.

Potential energy and meaninglessness of overall phase. You may note something questionable about potential energy V in the Schrödinger equation: potential energy can only be defined relative to some arbitrarily chosen baseline of zero potential. But if we changed the baseline—a change purely in mathematical convention that shouldn't affect the physics—then we also change the Schrödinger equation solutions as well.

The resolution to this seeming paradox is that not all wavefunctions correspond to meaningfully different states. In particular, the *amplitude* of a wavefunction has

physical meaning (corresponding to the probability of finding a particle in a particular location), and the *difference between complex phases* of two wavefunctions also has physical meaning (this is what gives rise to interference phenomena: the amplitude of a sum of wavefunctions of different particles at a particular point is different from the sum of the individual wavefunctions' amplitudes if the wavefunctions don't have matching phases). But the complex phase has no meaning by itself. In particular, if you multiply every wavefunction (or other state) in a system by some complex phase $e^{i\theta}$, amplitudes and phase differences between wavefunctions—and, therefore, the actual physics of the system—remain unchanged.

Now let's remember the time evolution for energy eigenstates:

$$\Psi(x, t) = e^{-iEt/\hbar}\Psi(x, 0);$$

If we redefined the potential energy baseline down by some quantity E' (equivalent to adding E' to the energy of every eigenstate), the solution becomes

$$\Psi(x, t) = e^{-i(E+E')t/\hbar}\Psi(x, 0) = e^{-iE't}e^{-iEt/\hbar}\Psi(x, 0).$$

That is, every energy eigenstate, regardless of its own energy, simply picks up an overall phase $e^{-iE't/\hbar}$. At any moment of time, this phase is the same for every eigenstate, so the phase differences between eigenstates—and, therefore, the overall amplitudes of any state constructed out of a linear combination of eigenstates—remain unaffected.

Infinite sums in vector spaces. In pure linear algebra, vector spaces only have concepts of finite sums, while Griffiths is using infinite sums. You can define infinite sums on vector spaces that have an idea of a norm or an inner product: in this case, an infinite sum $\mathbf{v}_1 + \mathbf{v}_2 + \mathbf{v}_3 + \dots$ can be said to converge to a limit \mathbf{w} if $\|\mathbf{v}_1 - \mathbf{w}\|$, $\|\mathbf{v}_1 + \mathbf{v}_2 - \mathbf{w}\|$, $\|\mathbf{v}_1 + \mathbf{v}_2 + \mathbf{v}_3 - \mathbf{w}\|$ converges (as a sequence of real numbers) to zero—that is, if for every positive real number ϵ you can find some index N such that $\|\mathbf{v}_1 + \dots + \mathbf{v}_n - \mathbf{w}\| < \epsilon$ whenever $n > N$.

In real analysis classes, you'll learn all about the hazards of extending common-sense results on finite sums to infinite sums. For instance, an infinite sum of elements of a vector subspace (defined as a subset of vectors closed under scalar multiplication and *finite* vector sum) doesn't necessarily converge to an element of that subspace.² Similarly, it's possible to construct linear operators $T : V \rightarrow V$ that are topologically discontinuous, to the effect that even if $\mathbf{v}_1 + \mathbf{v}_2 + \dots$ is defined, $T\mathbf{v}_1 + T\mathbf{v}_2 + \dots$ may not be.

In QM, though, you can generally ignore these difficulties: in particular, an infinite sum of solutions to a differential equation (which, remember, make up a vector subspace of functions) is also a solution.

²Example: consider a space that we'll denote ℓ^2 , the set of infinite sequences (x_1, x_2, x_3, \dots) of real numbers such that $\sum_{i=1}^{\infty} x_i^2 < \infty$, with addition and multiplication defined component-by-component and inner product $\langle (x_1, x_2, \dots), (y_1, y_2, \dots) \rangle = \sum_{i=1}^{\infty} x_i y_i$ (which, by the Cauchy-Schwarz inequality, must be finite if $\sum x_i^2$ and $\sum y_i^2$ are both finite), and let W be the subspace of ℓ^2 with only a finite number of nonzero entries. Then you can construct infinite sums of elements of W , such as $(1, 0, 0, 0, \dots) + (0, 1/2, 0, 0, \dots) + (0, 0, 1/4, 0, \dots) + (0, 0, 0, 1/8, \dots) + \dots$, whose values are defined in ℓ^2 but not in W .

2.2 The infinite square well

In this section, Griffiths presents a simple physical system: the infinite square well (sometimes also called “particle in a box”). The box has flat potential inside but infinite potential outside, so the particle is free to move inside but can’t cross outside.

The stationary states of the particle in the box are sinusoids with one-half, one, three-halves, etc. periods contained in the box’s length. (This is a good time to mention a general rule of thumb: wavefunctions with graphs that have more and sharper curves are higher-energy.) Griffiths makes the following claims about the stationary states:

1. The stationary states are all orthogonal to each other (and offers a proof).
2. Any wavefunction at all can be constructed as an infinite linear combination of these stationary states; that is, the stationary states are mathematically *complete*. (This is not proved.)
3. As a result of (1), we can extract the coefficient of such a linear combination for a given stationary state by taking inner products of the wavefunction on the right with the stationary state in question on the left.

These properties are true of most quantum systems (for some of them, we have to replace a sum over a countable number of stationary solutions with an integral over an uncountable number). It’s worth elaborating on them in a slightly more general setting.

Coefficient extraction with inner products. Suppose that V is some vector space (real or complex) with an inner product defined on it and $\mathbf{v}_1, \dots, \mathbf{v}_n$ are some linearly independent basis vectors. If $\mathbf{v}_1, \dots, \mathbf{v}_n$ are orthonormal (that is, $\langle \mathbf{v}_i, \mathbf{v}_j \rangle$ is 1 if $i = j$ and 0 if $i \neq j$), and we have some other vector $\mathbf{w} = c_1 \mathbf{v}_1 + \dots + c_n \mathbf{v}_n$, then

$$\langle \mathbf{v}_i, \mathbf{w} \rangle = \langle \mathbf{v}_i, c_1 \mathbf{v}_1 + \dots + c_n \mathbf{v}_n \rangle = c_1 \langle \mathbf{v}_1, \mathbf{w} \rangle + \dots + c_n \langle \mathbf{v}_n, \mathbf{w} \rangle = c_i.$$

That is, we can extract a coefficient out of \mathbf{w} by taking an inner product that puts \mathbf{w} on the right and the basis vector whose coefficient we want on the left. Some books will call $(|\mathbf{v}_1\rangle \langle \mathbf{v}_1|) + \dots + (|\mathbf{v}_n\rangle \langle \mathbf{v}_n|)$ an “identity operator”, that is, $\mathbf{w} = (|\mathbf{v}_1\rangle \langle \mathbf{v}_1| + \dots + |\mathbf{v}_n\rangle \langle \mathbf{v}_n|)\mathbf{w}$, and expanding the right-hand side of this equation gives a decomposition of \mathbf{w} into orthogonal components. And if we can decompose a state into a sum of stationary states at time $t = 0$, we know the total time evolution of the series.

Griffiths’ discussion of orthogonal states of the infinite square well is just a specialization of this: the wavefunctions $\psi_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right)$ all satisfy

$$\langle \psi_m, \psi_n \rangle = \int_0^a \psi_m(x)^* \psi_n(x) dx = \begin{cases} 1 & m = n \\ 0 & m \neq n \end{cases}$$

so they’re orthonormal, and given any state $\psi = \sum_{n=1}^{\infty} c_n \psi_n$, you can extract the coefficient c_n as $\langle \psi_n, \psi \rangle = \int_0^a \psi_n(x)$.

Bigger box = lower energy. Griffiths presents the formula $E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}$ for the energy level of the stationary state with n half-periods (where, again, a is the size of the box). One consequence of this formula, with important qualitative implications in other fields, is that the energy of the particle decreases as the size of the well increases. This turns out to be a general fact: giving particles more space decreases their energy.

This fact is important in chemistry: molecules with lower-energy electrons are more stable and less reactive. You may have learned that molecules that have multiple resonance structures are more stable because of “electron delocalization.” For instance, formic acid (HCOOH) is acidic because when the proton on the -OH group leaves, the resulting formate ion has two resonance structures: one lone pair on the newly deprotonated oxygen atom can form a pi bond to the carbon atom.

The p orbitals on the carbon atom and the two oxygens form a large “box” for two electrons that extends from one oxygen atom to the other, lowering their energy compared to a lone pair confined to a single oxygen atom. This makes the formate ion lower-energy and less reactive—in particular, less prone to recombine with one of its lost protons to form a formic acid molecule.

By contrast, in chemicals such as methanol, if the hydrogen from the hydroxyl group leaves, the remaining structure does not have any resonance stabilization: its electrons are roughly as reactive as they were before. This is why, unlike formic acid and other chemicals with the carboxylic acid radical -COOH, methanol and other alcohols are not acidic.

2.3 The harmonic oscillator

Commutator bracket. Griffiths introduces the notation $[A, B] = AB - BA$ for the commutator of two operators A and B . Seeing a few properties of the commutator presented abstractly may make Griffiths’ discussion easier to follow.

1. The commutator is linear in each argument: that is, $[c_1A_1 + c_2A_2, B] = c_1[A_1, B] + c_2[A_2, B]$, and likewise for the second argument.
2. Because the commutator is linear in each argument, the expression $[A + B, A - B]$ can be expanded as $[A, A] + [B, A] - [A, B] - [B, B]$. Every operator commutes with itself, so this expression equals $[B, A] - [A, B] = 2[B, A] = -2[A, B]$. Similarly, $[A - B, A + B] = 2[A, B]$.
3. The commutator appears as an additional term as the “factoring” of $A^2 - B^2$ (where squaring, remember, just means operator composition: the square of $\frac{d}{dx}$ is the second derivative operator $\frac{d^2}{dx^2}$). If we expand $(A + B)(A - B)$, we get $A^2 - AB + BA + B^2 = A^2 + B^2 - [A, B]$, so $A^2 - B^2 = (A + B)(A - B) + [A, B]$. Similar logic gets us the alternate factoring $A^2 - B^2 = (A - B)(A + B) + [B, A] = (A - B)(A + B) - [A, B]$.

Two important operators are x (that is, the map that takes a function f to the func-

tion $x \mapsto xf(x)$ and $\frac{d}{dx}$. This means:

$$\begin{aligned} \left[x, \frac{d}{dx} \right] f(x) &= x \frac{d}{dx} f(x) - \frac{d}{dx} (xf(x)) \\ &= xf'(x) - (xf'(x) + f(x)) \\ &= -f(x) \end{aligned}$$

That is, $\left[x, \frac{d}{dx} \right]$ is the negative identity operator $-I$ (which we could also denote -1).

Definitions of ladder operators Eigenstates of the Harmonic oscillator are separable solutions to the 1D Schrödinger equation with $V = m\omega^2 x^2/2$; that is,

$$i\hbar \frac{\partial \Psi}{\partial t} = \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} m\omega^2 x^2 \right) \Psi$$

The term in parentheses is \hat{H} . Applying the factoring $A^2 - B^2 = (A+B)(A-B) + [A, B]$ with $A = m\omega x$ and $B = \hbar \frac{d}{dx}$ gets us

$$\begin{aligned} \hat{H} &= \frac{1}{2m} \left(\left(m\omega x + \hbar \frac{d}{dx} \right) \left(m\omega x - \hbar \frac{d}{dx} \right) + \left[m\omega x, \hbar \frac{d}{dx} \right] \right) \\ &= \frac{1}{2m} \left(\left(m\omega x + \hbar \frac{d}{dx} \right) \left(m\omega x - \hbar \frac{d}{dx} \right) \right) - \frac{\hbar\omega}{2} \\ &= \hbar\omega \left(\frac{m\omega x + \hbar d/dx}{\sqrt{2m\hbar\omega}} \frac{m\omega x - \hbar d/dx}{\sqrt{2m\hbar\omega}} - \frac{1}{2} \right) \end{aligned}$$

where in the step from the first equation to the second, we extracted the coefficients on x and $\frac{d}{dx}$ by using the fact that the commutation bracket is linear and then used $\left[x, \frac{d}{dx} \right] = -1$. The step from the second equation to the third is just shuffling coefficients around.

We can write this in terms of the momentum operator $p = -i\hbar \frac{d}{dx}$ (which still satisfies the classical relation $E = p^2/2m$ where E is the kinetic energy $-\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$), as

$$\hat{H} = \hbar\omega \left(\frac{m\omega x + ip}{\sqrt{2m\hbar\omega}} \frac{m\omega x - ip}{\sqrt{2m\hbar\omega}} - \frac{1}{2} \right)$$

The two large fractions are the operators that Griffiths gives the respective names a_- and a_+ . We could find the commutator $[a_-, a_+]$ by following Griffiths' suggestion on the bottom of page 43, tracing through the factoring of \hat{H} again using the formula $A^2 - B^2 = (A-B)(A+B) - [A, B]$ to get an expression for \hat{H} with a_+ on the left. But an easier way is to use the linearity of each argument of the commutator bracket and the relations $[A+B, A-B] = [B, A]$ and $\left[x, \frac{d}{dx} \right] = -1$ (so $[x, p] = \left[x, -i\hbar \frac{d}{dx} \right] = i\hbar$). The commutators end up being $[a_+, a_-] = -1$ and $[a_-, a_+] = 1$.

The ladder operators are each other's adjoints Griffiths mentions on p. 47 that the ladder operators a_+ and a_- are "hermitian conjugates" of each other (another term is *adjoint*): that is, $\langle f, a_{\pm}g \rangle = \langle a_{\mp}f, g \rangle$. One cleaner way to see this: remember that $\frac{d}{dx}$ is a skew-Hermitian operator (when acting on functions that vanish at each endpoint), so its imaginary multiple $p = -i\hbar\frac{d}{dx}$ is Hermitian. The operator x , which multiplies inputs by a fixed real-valued function, is also Hermitian. So a_+ and a_- have the form $A + iB$ and $A - iB$ where A and B are Hermitian.

If A and B are any two Hermitian operators on an arbitrary vector space, then

$$\langle \mathbf{v}, (A + iB)\mathbf{w} \rangle = \langle \mathbf{v}, A\mathbf{w} \rangle + i\langle \mathbf{v}, B\mathbf{w} \rangle$$

by linearity of the inner product in the first argument. Similarly,

$$\langle (A - iB)\mathbf{v}, \mathbf{w} \rangle = \langle A\mathbf{v}, \mathbf{w} \rangle + i\langle B\mathbf{v}, \mathbf{w} \rangle = \langle \mathbf{v}, A\mathbf{w} \rangle + \langle \mathbf{v}, B\mathbf{w} \rangle$$

by antilinearity of the inner product in the first argument and the fact that A and B are Hermitian. A similar argument establishes that $\langle \mathbf{v}, (A - iB)\mathbf{w} \rangle = \langle (A + iB)\mathbf{v}, \mathbf{w} \rangle$. So $A + iB$ and $A - iB$ are each other's Hermitian conjugates.

Other properties of ladder operators. Griffiths proves several properties of a_+ and a_- and the eigenstates ψ_n . Many of his proofs can be simplified if you recognize that he's just rederiving, in a specific context, several general properties of adjoint and Hermitian operators. It's useful to have these properties in an easy-to-consult list with a short sketch of the justification:

1. The commutation relation $[a_+, a_-] = -1$, as before.
2. If ψ is a nonzero eigenstate of \hat{H} with eigenvalue (i.e. energy) E , then $a_+\psi$ and $a_-\psi$ are (not necessarily normalized) eigenstates with respective energies $E + \hbar\omega$ and $E - \hbar\omega$. The proof involves starting with $\hat{H}(a_+\psi)$ and using the fact that \hat{H} has two expressions, one with an a_-a_+ term and one with an a_+a_- term, to rewrite it as $a_+(\hat{H} + \hbar\omega)\psi = a_+(E + \hbar\omega)\psi = (E + \omega)\hbar\psi$.
3. As $\hat{H}\psi = \hbar\omega(a_+a_- + \frac{1}{2})\psi = \hbar\omega(a_-a_+ - \frac{1}{2})\psi$ for any ψ and $\hat{H}\psi_n = \hbar\omega\left(n + \frac{1}{2}\right)\psi_n$ for the eigenstate ψ_n , it follows that $a_+a_-\psi_n = n$ and $a_-a_+\psi_n = n + 1$. (Note that this agrees with the commutator relation $[a_+, a_-] = -1$.) Some books call a_+a_- the "number operator," though Griffiths doesn't.
4. a_- has nonzero kernel: that is, there's some ψ_0 such that $a_-\psi_0 = 0$. To find ψ_0 , remember that $a_-\psi_0 = 0$ is just shorthand for the first-order differential equation $\frac{1}{\sqrt{2\hbar m\omega}}\left(\hbar\frac{d}{dx} + m\omega x\right)\psi_0$ which you can solve by separation of variables and then normalize to get

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

Any state that satisfies $a_-\psi_0 = 0$ must also satisfy $\hat{H}\psi_0 = \hbar\omega\left(a_+a_- + \frac{1}{2}\right)\psi_0 = \frac{\hbar\omega}{2}\psi_0$, so ψ_0 has energy $\frac{1}{2}\hbar\omega$.

5. Because the raising operator takes eigenstates of \hat{H} to eigenstates of \hat{H} , we get a whole series of eigenstates $\psi_n := A_n a_+^n \psi_0$ with energy $\left(n + \frac{1}{2}\right) \hbar\omega$, where the quantities A_n are some normalization constants and $A_0 = 1$.
6. We can get the constants A_n by noting that if ψ_n is a normalized eigenstate, then $\langle a_+ \psi_n, a_+ \psi_n \rangle = \langle \psi_n, a_- a_+ \psi_n \rangle = \langle \psi_n, (n+1) \psi_n \rangle = n+1$. So we have to divide $a_+ \psi_n$ by $\sqrt{n+1}$ to get a properly normalized eigenstate, so $A_{n+1} = \frac{A_n}{\sqrt{n+1}}$. As $A_0 = 1$, so $A_n = \frac{1}{\sqrt{n!}}$.
7. The eigenstates are orthonormal. Griffiths' proof here essentially boils down to proving two general facts about operators: the composition of adjoint operators such as a_+ and a_- is a Hermitian operator, and eigenstates of Hermitian operators with different eigenvalues are orthogonal (remember that $a_+ a_- \psi_n = n \psi_n$).

Analytic method. An abbreviated description of Griffiths' method. Griffiths introduces the dimensionless coordinate $\xi = \sqrt{\frac{m\omega}{\hbar}} x$ and energy $K = \frac{2E}{\hbar\omega}$ with respect to which the Schrödinger equation becomes

$$\frac{d^2\psi}{d\xi^2} = (\xi^2 - K)\psi$$

and argues based on the behavior for $|\xi| \rightarrow \infty$ that the solution should have the form

$$\psi(\xi) = h(\xi)e^{-\xi^2/2}$$

with

$$\frac{d^2h}{d\xi^2} - 2\xi \frac{dh}{d\xi} + (K - 1)h = 0.$$

This has solutions $h_{\text{even}}(\xi) = a_0 + a_2\xi^2 + a_4\xi^4 + \dots$ and $h_{\text{odd}}(\xi) = a_1 + a_3\xi^3 + a_5\xi^5 + \dots$. Plugging either power series into the equation gives the recursion for the coefficients

$$a_{j+2} = \frac{2j+1-K}{(j+1)(j+2)} a_j$$

This equation gives us a non-normalizable solution with the coefficients $a_{2j}, a_{2j+1} = O\left(\frac{1}{j!}\right)$ and thus $h_{\text{odd}}, h_{\text{even}} = O(e^{\xi^2})$ unless K is an odd integer, in which case the power series at some point becomes 0.

The terminating power series are called *Hermite polynomials* H_n and the general formula is

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

2.4 The free particle

It's worth briefly tracing out Griffiths' discussion here and also emphasizing the physical meaning of all the variables that he defines.

Remember that if ψ is an eigenstate of the Hamiltonian with eigenvalue E , then $\Psi(x, t) = \psi(x) \exp(-iEt/\hbar)$ solves the Schrödinger equation $-i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$. This is what Griffiths means by $\exp(-iEt/\hbar)$ being the “standard time dependence.” Remember also that in a generic complex wave function of form $A \exp[i(kx - \omega t)]$:

- k is *wave number*: the number of radians in the wave per unit distance.
- ω is *angular frequency*: the number of radians that pass any point per unit time.
- The ratio $\frac{\omega}{k}$ is the *phase velocity* of the wave: the linear speed at which any peak or valley moves. (Note that if you use a space coordinate $\xi = x - \frac{\omega}{k}t$ that moves along with the wave, the formula for the wave becomes a time-invariant function of just ξ .)

For a one-dimensional particle, if $V = 0$ and $E > 0$, then the stationary states of \hat{H} solve

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

with general eigenstates

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

with wave number $k = \frac{\sqrt{2mE}}{\hbar}$. The corresponding time-dependent wave function is

$$\Psi(x, t) = A \exp\left[i\left(kx - \frac{E}{\hbar}t\right)\right] + B \exp\left[i\left(-kx - \frac{E}{\hbar}t\right)\right]$$

The first term is a wave traveling to the right; the second term is a wave traveling to the left. We can write the basis solutions as

$$\Psi(x, t) = \exp[i(\pm kx - \omega t)]$$

with the new variable $\omega = \frac{E}{\hbar} = \frac{\hbar k^2}{2m}$. The speed of both waves is

$$v = \frac{\omega}{k} = \frac{\hbar k}{2m} = \sqrt{E/2m}.$$

This is half the speed of a classical particle: $E = mv^2/2 \implies v = \sqrt{2E/m}$.

These solutions aren't normalizable, but we can represent any state of a free particle as a sum of some number of these solutions with infinitesimal coefficients (that is, as an integral). If $\frac{1}{\sqrt{2\pi}}\phi(k)$ is the infinitesimal contribution of e^{ikx} to a starting state $\psi(x)$, then we can get $\phi(k)$ by taking an “inner product” with e^{ikx} on the left:

$$\phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-ikx} dx$$

though this integral usually can't be evaluated symbolically.

We can evaluate the group velocity (movement of the “envelope” of the wave peaks, as opposed to any individual peak) by starting with a generic wave equation

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{i(kx - \omega t)} dk$$

where ω is a function of k . If the wavenumbers in a packet are concentrated around k_0 , then choose some point k_0 and write $\omega_0 = \omega(k_0)$, $\omega'_0 = \omega'(k_0)$. Adopting the new variable $s = k - k_0$, $ds = dk$ and using the Taylor approximation $\omega(k_0 + s) \approx \omega_0 + \omega'_0 s$ gives

$$\Psi(x, t) \approx \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k_0 + s) \exp[i((k_0 + s)x - (\omega_0 + \omega'_0 s)t)] ds$$

then factor out the terms in the integrand not dependent on x into an overall phase (which accounts for the difference between group and phase velocities), we can get the formula

$$\Psi(x, t) \approx \frac{1}{\sqrt{2\pi}} \underbrace{\exp[i(-\omega_0 t + k_0 \omega'_0 t)]}_{\text{overall phase}} \int_{-\infty}^{\infty} \phi(k_0 + s) \underbrace{\exp[i(k_0 + s)(x - \omega'_0 t)]}_{\text{envelope movement}} ds$$

If $\phi(k_0 + s)$ is very small except around $s = 0$, then the envelope will move with a velocity given by the ratio of t and x coefficients in the integrand, or ω'_0 . For the QM free particle dispersion relation $\omega = \frac{\hbar k^2}{2m}$, we have $\omega'_0 = \frac{\hbar k}{m} = \sqrt{\frac{2E}{m}}$, which is also the classical result.

2.5 The delta-function potential

Bound and scattering states Griffiths classifies states into two ways:

1. *Bound state*: energy is less than the potential at ∞ ; particle is confined to a finite region of space.
2. *Scattering state*: energy is greater than the potential at ∞ ; particle will eventually go (or spread) to infinity.

Scattering states include *quantum tunneling*: if a state has initially in some region surrounded by a potential barrier of finite height and width, but it has higher energy than the potential at ∞ , then it will eventually leak out of the barrier even if it has lower energy than the barrier.

Dirac delta function The Dirac delta function is a pseudo-function with $\delta(0) = +\infty$ and $\delta(x) = 0$ elsewhere, with the property that

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

Griffiths studies the potential $V(x) = -\alpha\delta(x)$ with $\alpha > 0$. This is mostly the same as the free particle potential, so we'd expect stationary solutions with exponentials: either $Ae^{\kappa x} + Be^{-\kappa x}$ for negative energy (and one or the other term has to have coefficient zero to get a normalizable state), or $Ae^{ikx} + Be^{-ikx}$ for positive energy.

Derivative discontinuity across the Dirac potential Griffiths relies on one result whose generality may be clearer if presented in isolation. Suppose that V is some potential that includes a multiple $k\delta(x)$ of the Dirac potential at zero, and ψ is a necessarily continuous eigenstate of the potential.³ Write $\psi'(0^+)$ and $\psi'(0^-)$ as shorthands for the one-sided limits $\lim_{x \rightarrow 0^+} \psi'(x)$ and $\lim_{x \rightarrow 0^-} \psi'(x)$.

Then if we integrate the Schrödinger equation

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

over an interval $[-\epsilon, \epsilon]$, then we get

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

As we take $\epsilon \rightarrow 0$, all the finite parts of the integrals become zero, so the RHS becomes zero and $\int_{-\epsilon}^{\epsilon} V(x)\psi(x) dx$ becomes $k\psi(0)$. So we're left with the equation

$$-\frac{\hbar^2}{2m}(\psi'(0^+) - \psi'(0^-)) + k\psi(0) = 0$$

or, rearranged

$$\psi'(0^+) - \psi'(0^-) = \frac{2mk}{\hbar^2}\psi(0).$$

That is, in crossing a delta potential with amplitude k from left to right, the derivative of an eigenstate ψ has to change by $\frac{2mk}{\hbar^2}\psi(0)$.

Griffiths' treatment of delta potential The summary of Griffiths' discussion (which doesn't need much clarification) is:

1. If $E < 0$, then taking solutions of the form $\psi(x)Ae^{\kappa x} + Be^{-\kappa x}$ where $\kappa = \frac{\sqrt{-2mE}}{\hbar}$, using normalizability considerations to conclude that $B = 0$ for $x < 0$ and $A = 0$ for $x > 0$, and using the fact that ψ must be continuous even at zero gives the solution $\psi(x) = Be^{-\kappa|x|}$.

Not every value of κ is allowable, though: substituting $\psi(0) = B$, $k = -\alpha$, and $\psi'(0^\pm) = \mp B\kappa$ into the equation for derivative discontinuity across a delta potential gives $\kappa = \frac{m\alpha}{\hbar^2}$, so $E = \frac{\hbar^2\kappa^2}{-2m} = -\frac{m\alpha^2}{2\hbar^2}$. The normalization constant $B = \frac{\sqrt{m\alpha}}{\hbar}$ is easy to compute.

2. For scattering states $E > 0$, take a solution of the form $Ae^{ikx} + Be^{-ikx}$ where $E = \frac{\sqrt{2mE}}{\hbar}$ at $x < 0$ and $F e^{ikx} + G e^{-ikx}$ at $x > 0$. This isn't a normalizable solution: it represents a current or beam of particles, not a single particle.

³Also assume there's some interval $[-\epsilon, \epsilon]$ around $x = 0$ with no Dirac terms in the potential except the one at $x = 0$.

There are four unknown constants with two equations relating them:

$$A + B = F + G \quad (\text{continuity at zero})$$

$$(iFk - iGk) - (iAk - iBk) = -\frac{2m\alpha}{\hbar^2}(A + B)$$

(derivative discontinuity across a Dirac potential)

The solution is a two-dimensional space. We can get basis solutions by setting:

- $G = 0$: this is a beam from the left (amplitude given by A) that splits into a reflected beam back to the left (amplitude given by B) and a transmitted beam to the right (amplitude given by F).
- $A = 0$: incident beam from right (G) splits into reflected beam back to right (F) and transmitted beam to left (B).

In the first scenario (the second is symmetrical), we get reflection and transmission coefficients

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

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

where $\beta = \frac{m\alpha}{\hbar^2 k} = \frac{\alpha}{\hbar} \sqrt{\frac{m}{2E}}$. Note that $E \rightarrow \infty$ means $\beta \rightarrow 0$ and thus $T \rightarrow 1$: higher energy means greater transmission.

We can get normalizable states by taking wave packets of the eigenstates, so the reflection and transmission coefficients could also be interpreted as probabilities of the transmission or reflection of single particles with energy *approximately* E .

2.6 The finite square well

The potential studied in this section is

$$V(x) = \begin{cases} -V_0 & a \leq x \leq a \\ 0 & \text{elsewhere} \end{cases}$$

for some constant a . In each of the regions $x < -a$, $-a < x < a$, and $x > a$, the potential V is flat, so the solutions (as we're used to by now) are a combination of two sinusoids or exponentials.

For bound states $-V_0 < E < 0$ (having energy less than the minimum of V , as Griffiths remarks, is impossible), eigenstates must decay exponentially as $x \rightarrow \infty$ for $|x| > a$ and oscillate sinusoidally inside V_0 .

Furthermore (this is the logic by which Griffiths intends you to solve problem 2.1(c)), suppose ψ is any wavefunction, and write $\psi_-(x) = \psi(-x)$. If V and ψ are even, then $\psi''_-(x) = \psi''(x)$ and $V(x)\psi''_-(x) = V(x)\psi''(x)$; if V is even and ψ is odd, then $\psi''_-(x) = -\psi''(x)$ and $V(x)\psi_-(x) = -V(x)\psi(x)$. In either case, if ψ solves $-\frac{\hbar^2}{2m}\psi''(x) +$

$V(x)\psi(x) = E\psi(x)$, then so does ψ_- with the same eigenvalue (the two sides of the eigenvalue equation keeping the same value if ψ is even and flipping sign if ψ is odd). So any eigenstate ψ can be split into the sum of an even part $\psi(x) + \psi(-x)$ and an odd part $\psi(x) - \psi(-x)$ with necessarily the same eigenvalue, so if we have separate bases of odd and even eigenstates, putting them together gives a basis of all eigenstates.

The general form of an even eigenstate is

$$\psi(x) = \begin{cases} Fe^{-\kappa|x|} & |x| > a \\ D \cos(\ell x) & |x| < a \end{cases}$$

where $\kappa = \frac{\sqrt{-2mE}}{\hbar}$ (as in bound states of the delta potential) and $\ell = \frac{\sqrt{2m(E + V_0)}}{\hbar}$ (like the constant k in the free particle, only with potential energy measured relative to a baseline of $-V_0$ rather than zero).

The general form for an odd eigenstate, on the other hand, would look like

$$\psi(x) = \begin{cases} -Fe^{\kappa x} & x < -a \\ D \sin(\ell x) & -a < x < a \\ Fe^{-\kappa x} & x > a \end{cases}$$

As V doesn't have Dirac terms, so ψ and ψ' are continuous at $x = \pm a$. These conditions yield the transcendental equation (Griffiths gives the full derivation)

$$\tan z = \sqrt{(z_0/z)^2 - 1}$$

where $z = \ell a = a \frac{\sqrt{2m(E + V_0)}}{\hbar}$ and $z_0 = \frac{a}{\hbar} \sqrt{2mV_0}$.

Griffiths shows a graphical solution on p. 218. The number of solutions is z_0/π rounded up, with the n th solution (counting from zero) having the form $\pi n + f(n)$ where $f(n)$ decreases monotonically from $\pi/2$ to 0. As the well becomes wider and deeper, approaching an infinite square well ($z_0 \rightarrow \infty$), the number of bound states increases; a small well, though, will have only one even bound state.

For scattering states with $E > 0$, eigenstates oscillate sinusoidally with period $\frac{\sqrt{2mE}}{\hbar}$ outside the well and with period $\frac{\sqrt{2m(E + V_0)}}{\hbar}$ inside it. The general solution is a piecewise composite of three functions with two coefficients each (left, inside, and right of the well) with four boundary conditions (continuity of wavefunction and derivative at $x = \pm a$).

Transmission coefficients can be analyzed just as with the delta potential: the results are that (a) transmission generally increases as energy increases, but (b) transmission coefficients oscillate, and for energies corresponding to bound states of the infinite square well of the same size, transmission is perfect.

Chapter 3

Formalism

Little in this chapter should be new if you have previous experience with the abstract approach to linear algebra. The main points that may bear reiteration are:

1. Observable quantities are represented by Hermetian operators. A state with a definite value of some observable quantity is an eigenvalue of that operator. Expectation values for any particular state are weighted averages of the eigenvalues with real weights, so if all the eigenvalues are real, then any expectation value must also be real.
2. A *complete* basis for a Hilbert space is one such that every element of the space can be written as an *infinite* sum of multiples of the basis elements. (In Hilbert spaces, unlike in generic vector spaces, we do have a notion of infinite sums).
It's an axiom of QM that if an operator represents an observable quantity, then its eigenfunctions are complete.
3. An eigenvalue is *degenerate* if the corresponding eigenspace has dimension 2 or greater.
4. There are some operators that have continuous spectra (sets of eigenvalues) and eigenstates that aren't actually normalizable. Griffiths gives the example of the momentum operator $-i\hbar \frac{d}{dx}$ with eigenstates $\exp \frac{ipx}{\hbar}$. Non-normalizability means that we don't have inner products in the usual sense, but we can get what Griffiths calls "Dirac orthonormality": if we abuse Fourier analysis to get the formula

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(ikx) dk$$

then we have eigenstates $f_p(x) = \frac{\exp(ipx/\hbar)}{\sqrt{2\pi\hbar}}$ such that

$$\int_{-\infty}^{\infty} f_{p'}(x)^* f_p(x) = \delta(p - p').$$

Much of what Griffiths calls the "generalized statistical interpretation" is covered in the introduction in Section 0.6. The important takeaways that aren't are:

1. To get the probability that a particle's position will be measured in a certain region, integrate the squared absolute value of the wavefunction over that region.

2. To get the probability that a particle's momentum will be measured in a certain range, compute the Fourier transform

$$\Phi(p, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{-ipt} \Psi(x, t)$$

and then integrate $|\Phi^2|$ over the range of momenta.

Chapter 4

Quantum mechanics in three dimensions

4.1 The Schrödinger equation in three dimensions

Three-dimensional operators Griffiths introduces the new notation

$$\nabla = \frac{\partial}{\partial x} \hat{i} + \frac{\partial}{\partial y} \hat{j} + \frac{\partial}{\partial z} \hat{k}$$
$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

For the same reasons as their one-dimensional counterparts, ∇ is skew-Hermitian and ∇^2 is Hermitian. (Also important: the output of ∇ is a *vector* and the output of ∇^2 is a *number*. The notation is standard, but a bit confusing: ∇^2 is not just ∇ composed with itself.) We also have the canonical substitutions

1. Vector momentum: $-i\hbar\nabla$
2. Kinetic energy: $\frac{\hbar^2}{2m}\nabla^2$.

The commutation relations generalize: $[x, p_x] = i\hbar$ (and likewise for the other dimensions), and $[x, p_y] = 0$ (and likewise for position in one dimension and momentum component in another). Intuitively, this should be clear: if you multiply a wavefunction by x , then you can just treat the x as a constant for the sake of differentiating by y to compute p_y .

Polar coordinates Griffiths' version of polar coordinates is the convention in physics: r is distance from origin, θ is angle from z -axis in the range $[0, \pi]$, and ϕ is the counterclockwise angle from the x -axis to a vector's projection into the xy -plane. In pure mathematics, the convention is to have θ and ϕ the other way around.

Finally, recall (as Griffiths notes on p. 138) that the volume element in spherical coordinates is $r^2 \sin \theta dr d\theta d\phi$.

Spherical harmonics It's easy to get lost in Griffiths' discussion of spherical harmonics, and even he glosses over many details. You also won't have to work much with the formulas for the spherical harmonics.

The upshot of Griffiths' discussion of is that if V is a function purely of distance from the origin, then the associated eigenstates Φ can be written using separation of variables as

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

The possible angular functions Y , meanwhile, can be indexed as Y_ℓ^m for integers $\ell \geq 0$ and $-\ell \leq m \leq \ell$. These are called spherical harmonics, and they all have the form

$$Y_\ell^m(\theta, \psi) = (\text{normalization constant}) \times (\text{polynomial in } \cos \theta) \times (\sin \theta \text{ if } m \text{ is odd}) \times e^{im\phi}$$

The polynomials in question are *associated Legendre functions* and are derived from the Legendre polynomials.

This result holds for any V that depends only on r , it affects only the radial part R of eigenstates, not the spherical harmonics. Note also that since ϕ only enters into Y in the factor $e^{im\phi}$, which has absolute value 1 and doesn't affect the amplitude (and hence, energy) at any point. So the energy of the resulting wavefunction is independent of m . (Griffiths makes this point with regard to several individual systems, but it is true in general.)

The equation for the radial part R gives a more convenient equation for $u(r) = rR(r)$ (Griffiths' eq. 4.37, which he calls the *radial equation*):

$$-\frac{\hbar^2}{2m} \frac{d^2u}{dr^2} + \left[V + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] u = Eu.$$

The second term in square brackets is called the *centrifugal term*. Normalization of u is just $\int_0^\infty |u|^2 dr = 1$. Valid wavefunctions have to have $\lim_{r \rightarrow 0} u(r) = 0$ (otherwise $R(r) = u(r)/r$ has a pole).

The infinite spherical well A quick recapitulation and summary of Griffiths' argument. The potential in question is

$$V(r) = \begin{cases} 0 & r \leq a \\ \infty & r > a \end{cases}$$

so we need to solve the radial equation

$$-\frac{\hbar^2}{2m} \frac{d^2u}{dr^2} + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} u = Eu$$

or, defining $k = \frac{\sqrt{2mE}}{\hbar}$,

$$\frac{d^2u}{dr^2} = \left[\frac{l(l+1)}{r^2} - k^2 \right] u$$

with boundary conditions $u(0) = u(a) = 0$.

For $\ell = 1$, this is just the one-dimensional infinite square well with sides 0 and a , with solutions

$$u(r) = A \sin(kr) + B \cos(kr)$$

where $u(0) = 0$ forces $B = 0$ and $u(a) = 0$ forces $k = \frac{\pi}{a}n$ for integer n .

For $l \geq 1$, the solutions to this equation, ignoring boundary conditions, are in terms of the spherical Bessel function j_l and Neumann function n_l :

$$u(r) = Arj_l(kr) + Brn_l(kr).$$

The Neumann functions have poles at the origin, so $B = 0$; and k has to be chosen so that ka equals a zero of j_l . (Zeros of Bessel functions, unfortunately, generally have no closed forms.)

4.2 The hydrogen atom

Again, a short synopsis of Griffiths' method on pp. 146–149 might be useful for review, or for just keeping your bearings.

Taking the position of the proton as fixed at the origin, the electrostatic potential energy of the electron is

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

where e is elementary charge and ϵ_0 is permittivity of free space. We want bound states with $E < 0$. Defining constants $\kappa = \frac{\sqrt{-2mE}}{\hbar}$ (with units (distance)⁻¹, essentially giving a characteristic distance scale for the electron's distribution) and $\rho_0 = \frac{me^2}{2\pi\epsilon_0\hbar^2k}$ (a dimensionless function of E and fundamental physical constants), as well as a new dimensionless distance variable $\rho = \kappa r$, makes the equation

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2} \right] u.$$

The general procedure is this:

1. Check the asymptotic behavior for the differential equation at $\rho \rightarrow 0$ (which should give a polynomial) and $\rho \rightarrow \infty$ (which should give a decaying exponential).
2. Assume that the the general solution is the $\rho \rightarrow 0$ asymptotic f , times the $\rho \rightarrow \infty$ asymptotic g (which should get smaller faster than f gets larger at $\rho \rightarrow \infty$), times some power series for a function h .
3. Plug a generic form $u(\rho) = f(\rho)g(\rho)(c_0 + c_1\rho + c_2\rho^2 + \dots)$ into the differential equation to get a recursive expression for the coefficients c_n . Call the function represented by the power series h .
4. Check the asymptotic growth of the coefficients of the power series to get an asymptotic estimate for h , assuming every coefficient is nonzero. If in general $\lim_{\rho \rightarrow \infty} f(\rho)g(\rho)h(\rho) \neq 0$, then the only differential equations that give a physically acceptable solution are the ones in which the constants guarantee that all the coefficients turn to zero at some point.

In this case, the requirements in point 4 force $\rho = 2n$ for n an integer, which gives the energy (the Bohr formula)

$$E_n = - \left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2}$$

where n is a positive integer. These energies, unlike the general case for radial potential, do not depend on l (which takes integer values in the range $[0, n]$).

4.3 Angular momentum

The angular momentum operators are L_x, L_y, L_z for components along each axis, and $L^2 = L_x^2 + L_y^2 + L_z^2$. Note that angular momentum has units mass \times distance² \times time⁻¹, the same as the units of \hbar .

The most important facts about angular momentum operators, with a brief sketch of the derivation:

1. The formula $L_x = yp_z - zp_y$, just as in classical mechanics (and the other formulas obtainable by cycling $x \rightarrow y \rightarrow z \rightarrow x$). These are sums of commuting Hermitian operators such as y and p_z , so they are also Hermitian.
2. The commutator $[L_x, L_y] = i\hbar L_z$ (and other formulas obtainable by cycling x, y, z). You can get this result by substituting $L_x = yp_z - zp_y$ and $L_y = zp_x - xp_z$, then expanding the commutator bracket by linearity in each argument and eliminating commutators of position along one axis with momentum along another.
3. The commutator $[L^2, L_x] = [L^2, L_y] = [L^2, L_z] = 0$. You can get this by substituting $L^2 = L_x^2 + L_y^2 + L_z^2$, expanding the commutator bracket, eliminating some of the resulting brackets by noting that any operator commutes with its square, and simplifying the remainder with the formula $[A^2, B] = A^2B - BA^2 = A(AB - BA) + (AB - BA)A = A[A, B] + [A, B]A$.
4. The ladder operators $L_{\pm} = L_x \pm iL_y$ map common eigenstates of L^2 and L_z to each other, incrementing or decrementing the eigenvalue of L_z by \hbar while preserving the eigenvalue of L^2 . The effects of ladder operators on the eigenvalues can be worked out like this:
 - (a) Get the commutators $[L_z, L_{\pm}] = \pm\hbar L_{\pm}$ and $[L^2, L_{\pm}] = 0$ by expanding the commutator bracket into $[L_z, L_x] \pm i[L_z, L_y]$ (and likewise for L^2).
 - (b) L^2 commutes with L_{\pm} , so if f is an eigenstate of L^2 with eigenvalue λ , then $L^2(L_{\pm}f) = L_{\pm}(L^2f) = \lambda L_{\pm}f$, so $L_{\pm}f$ is also an eigenstate with eigenvalue λ .
 - (c) The commutator $[L_z, L_{\pm}] = \pm\hbar L_{\pm}$ means that $L_z L_{\pm} = L_{\pm}(L_z \pm \hbar)$, so if f is an eigenstate of L_z with eigenvalue μ , then $L_z L_{\pm}f = L_{\pm}(L_z \pm \hbar)f = (\mu \pm \hbar)L_{\pm}f$, so $L_{\pm}f$ is an eigenstate of L_z with eigenvalue $\pm\mu$. (We could have $L_{\pm}f = 0$: remember that the zero state is an eigenstate of every operator and has every eigenvalue.)

5. The possible eigenvalues of L_z for states that are also eigenstates of L^2 are $-l, -l+1, \dots, l-1, l$ where $l(l+1)$ is the eigenvalue of L^2 . In particular, $2l$ has to be an integer.

Slight rearrangement of Griffiths' argument: You can't raise or lower a state to the point that $L_z^2 > L^2$, so the only eigenvalues of L_z for physically allowable states have to be an integer multiple of \hbar away from the eigenvalue of some nonzero state f such that $L_+f = 0$ (and ditto for $L_-f = 0$).

Suppose f is an eigenstate of L^2 with eigenvalue $l(l+1)\hbar^2 > 0$ and of L_z with eigenvalue $m\hbar$, and $L_+f = 0$ but $f \neq 0$. Then $L_-L_+f = 0$. From the definitions $L_{\pm} = L_x \pm iL_y$ and the commutator $[L_x, L_y] = \hbar L_z$, you can get the formula $L_-L_+ = L^2 - L_z^2 - \hbar L_z$.

So $L_-L_+f = [l(l+1) - m(m+1)]\hbar^2 f = 0$, so if $f \neq 0$ then either $m = -l - 1$ (which would give L_z^2 a larger eigenvalue than L^2 , which is unphysical) or $m = l$. Similarly, the smallest allowable eigenvalue of L_z is $m = -l$.

Every allowable value of m has to be an integer distance away from both l and $-l$, so $2l$ has to be an integer.

6. L_+f is not necessarily normalized; knowing the normalization coefficient will be important for the spin-1/2 particles. To work out the normalization coefficient (this is Griffiths' problem 4.18), we can note that L_x and L_y are Hermitian (because they're sums of compositions of commuting Hermitian operators for position and momentum), so $L_+ = L_x + iL_y$ and $L_- = L_x - iL_y$ are each other's adjoints. This means that $\langle f, L_-L_+f \rangle = \langle L_+f, L_+f \rangle$, and you can compute $\langle f, L_-L_+f \rangle$ from the equation $L_-L_+ = L^2 - L_z^2 - \hbar L_z$ and assuming that f is an eigenstate of both L^2 and L_z .
7. There's no wavefunction corresponding to half-integer l , but the same commutators and ladder operators apply to the spin of a single particle, a property that doesn't depend on its location in space.

It may also help seeing Griffiths' derivation of the eigenstates of L^2 outlined so that the actual equations on pp. 167–169 are easier to follow. The method is:

1. Start with the classical formula $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ and make the canonical substitution $\mathbf{p} = -i\hbar\nabla$ to get an equation for \mathbf{L} in spherical coordinates.
2. Write $\hat{\theta}, \hat{\phi}$ in terms of $\hat{\mathbf{i}}, \hat{\mathbf{j}}, \hat{\mathbf{k}}$ to get an expression for \mathbf{L} with Cartesian vector components multiplied by coefficients written in spherical variables. These coefficients are spherical expressions for L_x, L_y, L_z .
3. Compute $L^2 = L_x^2 + L_y^2 + L_z^2$; there is a shortcut from using $L_+L_- = L^2 - L_z^2 + \hbar L_z$ to avoid computing L_x^2 and L_y^2 directly.
4. Recognize that the eigenstate equation $L^2 f = \hbar^2 l(l+1)f$ has identical form to the equation for the angular component of the energy eigenstates of an arbitrary radial potential (and this equation is only solvable when l is an integer).

4.4 Spin

Formalism and most important operators

1. A particle with spin s is always an eigenstate of the overall squared spin operator S^2 , with eigenvalue $s(s+1)\hbar^2$. It has $2s+1$ possible values $-\hbar s, -\hbar(s+1), \dots, \hbar(s-1), \hbar s$ of the spin S_z along the z -axis. For spin-1/2 particles such as electrons, this means two spins: 1/2 and $-1/2$.

Griffiths uses the notation $|s m\rangle$ to refer to a spin- s particle with angular momentum $\hbar m$ in the z -direction.

2. The states $|s(-s)\rangle, |s(-s+1)\rangle, \dots, |s s\rangle$ form a basis for the total particle state space, which has dimension $2s+1$ and can be represented by the space of column vectors with $2s+1$ entries.
3. The commutation relations $[S_x, S_y] = i\hbar S_z$ etc. are still valid (Griffiths suggests we just take this as a postulate), as are the raising and lowering operators $S_{\pm} = S_x \pm iS_y$ which increment or decrement the z -component of the spin.

For spin-1/2 particles, the state space is two-dimensional, and Griffiths represents the basis elements $|\frac{1}{2} \frac{1}{2}\rangle$ and $|\frac{1}{2}(-\frac{1}{2})\rangle$ respectively as $\chi_+ = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$ and $\chi_- = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$.

Operators on this space can all be represented as 2×2 matrices, and expressions for the basic spin operators relative to the standard basis $\{\chi_+, \chi_-\}$ can be worked out algebraically (Griffiths does this on p. 174, but it's worth repeating his method for completeness):

1. Every state is an eigenstate of S^2 with eigenvalue $3\hbar^2/4$, so $S^2 = \frac{3}{4}\hbar^2 \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$.
2. χ_+ and χ_- are eigenstates of S_z with eigenvalues $\hbar/2$ and $-\hbar/2$, so $S_z = \frac{\hbar}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$.
3. $S_+\chi_- = \hbar\chi_+$ and $S_+\hbar = 0$ (this is a special case of working out the normalization coefficients for ladder operators, which is Griffiths' problem 4.19 and for which we outlined a method in the previous section), so $S_+ = \hbar \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}$. Similarly, $S_- = \hbar \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}$.
4. The system $S_+ = S_x + iS_y, S_- = S_x - iS_y$ is equivalent to $S_x = \frac{1}{2}(S_+ + S_-)$, $S_y = \frac{1}{2i}(S_+ - S_-)$, from which we get

$$S_x = \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

$$S_y = \frac{\hbar}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$$

The Pauli spin matrices $\sigma_x, \sigma_y, \sigma_z$ are just the matrices S_x, S_y, S_z with the factor $\hbar/2$ removed; note that they all have characteristic polynomial $x^2 - 1$ and thus

eigenvalues ± 1 (that is, S_x, S_y, S_z all have eigenvalues $\pm \frac{\hbar}{2}$). Griffiths provides the eigenvectors of σ_x but leaves the problem of finding eigenvectors of σ_y to 4.19.

Note also that the *squares* of the Pauli matrices are $\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$: that is, every state is an eigenstate of $S_x, S_y,$ and $S_z,$ with eigenvalue $\frac{\hbar^2}{4}$.

Probability of spin measurements. The upshot of Griffiths' discussion of spin measurements is that if you can express some state with the column vector $\begin{bmatrix} a \\ b \end{bmatrix}$ relative to a basis in which $\begin{bmatrix} 1 \\ 0 \end{bmatrix}$ is spin-up along some axis and $\begin{bmatrix} 0 \\ 1 \end{bmatrix}$ is spin-down along the same axis, then the probability of a spin-up measurement is $|a|^2$ and the probability of a spin-down measurement is $|b|^2$, where normalization is $|a|^2 + |b|^2 = 1$.

Slightly more abstractly (though Griffiths doesn't mention this): if you have some state $|+\mathbf{w}\rangle$ that has deterministic spin up along the axis w , and you can write it is $|+\mathbf{w}\rangle = a|+\mathbf{z}\rangle + b|-\mathbf{z}\rangle$, where $|+\mathbf{z}\rangle$ and $|-\mathbf{z}\rangle$ are what Griffiths calls $|\frac{1}{2} \frac{1}{2}\rangle$ and $|\frac{1}{2}(-\frac{1}{2})\rangle$. Then you can use $|+\mathbf{z}\rangle$ and $|-\mathbf{z}\rangle$ to define an orthogonal sesquilinear inner product, and the probability that any other state $|\psi\rangle = c|+\mathbf{z}\rangle + d|-\mathbf{z}\rangle$ will be found in state $|+\mathbf{a}\rangle$ for a spin measurement along a is

$$|\langle +\mathbf{w}|\psi\rangle|^2 = |(a^* \langle +\mathbf{z}| + b^* \langle -\mathbf{z}|)(c|+\mathbf{z}\rangle + d|-\mathbf{z}\rangle)|^2 = |a^*c + b^*d|^2$$

because $\langle +\mathbf{z}|+\mathbf{z}\rangle = \langle -\mathbf{z}|-\mathbf{z}\rangle = 1$ and $\langle +\mathbf{z}|-\mathbf{z}\rangle = \langle -\mathbf{z}|+\mathbf{z}\rangle = 0$.

Remark on the Stern–Gerlach device. Griffiths makes a slightly obscure remark on p. 183 that the state in which a spin-1/2 particle with initial state $a\chi_+ + b\chi_-$ emerges from the Stern–Gerlach device, namely

$$(ae^{i\gamma TB_0/2}\chi_0) e^{i(\omega\gamma T/2)z} + (be^{-i\gamma TB_0/2}\chi_0) e^{-i(\omega\gamma T/2)z}$$

has terms with momentum in the z -direction. To see this, remember that e^{ikz} is an eigenstate of the momentum operator p_z with eigenvalue (i.e. momentum) k , or simply note that if you apply the momentum operator $p_z = -i\hbar \frac{\partial}{\partial z}$ to this state, the large terms in parentheses can be treated as constants with respect to the differential, which just extracts $\pm \frac{\alpha\gamma T}{2}$ from each of the z -dependent exponential terms.

Two-particle states. A few bits of formalism implicit in Griffiths' discussion that it may help to see spelled out:

1. If the configuration space for one particle is the vector space V , then the configuration space for two particles (for now ignoring considerations for if the particles are identical: those are covered in Chapter 5) is the *tensor product* $V \otimes V$, the set of ordered pairs of a configuration for the first particle and a configuration for the second.

2. The operator $S^{(1)}$ acts on an ordered pair of configurations $(\mathbf{v}_1, \mathbf{v}_2)$ as $S^{(1)}(\mathbf{v}_1, \mathbf{v}_2) = (S\mathbf{v}_1, \mathbf{v}_2)$. It's easy to prove that this is linear as an operator on V^2 if S is linear as an operator on V .

The formatting of the Clebsch–Gordan coefficient table is a bit hard to understand, and Griffiths doesn't explain it well.

1. The large labels such as $1/2 \times 1/2$ denote the spins s_1, s_2 of each of the two particles.
2. Each large label introduces a sequence of tables moving down and to the left. Each entry in the tables has two headers for its row and two headers for its column. The column headers denote the *total* state's values of spin s and z -component of spin m , and each separate table has the same value of m . Note that $|s_1 - s_2| \leq s \leq s_1 + s_2$ and $|m| \leq s$.
3. The row headers denote the z -components m_1, m_2 of each individual particle, with $m_1 + m_2 = m$.

Chapter 5

Identical particles