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Chapter 5

Quantum Mechanics and Atomic Physics

Quantum mechanics no doubt seemed somewhat bizarre when you were first introduced to it. Nice classical particles which followed deterministic trajectories were replaced by mysterious wavefunctions and particles which no longer had properties until you measured them – and let’s not even mention the long philosophical blathering that accompany explanations of the Copenhagen Interpretation, nonlocal hidden variables, and the like. The good news is that *none of this is relevant* for the GRE, so we won’t waste your time with it. This will be a lightning review of how to *compute* things in quantum mechanics: you can leave the deep thought to a situation where you don’t have less than two minutes per question.

While quantum mechanics itself is rather underrepresented on the GRE (only 12% of questions, according to ETS), the atomic physics section (10%) is really quantum mechanics in disguise, which is why we include it in the same chapter as quantum mechanics. Throw in a couple questions from the Miscellaneous and Optics/Waves categories, and quantum phenomena really make up about a full 25% of the test, so it pays to know this material in detail.

5.1 Formalism (a.k.a. how to calculate)

5.1.1 Wavefunctions and operators

The state of a quantum system, whether a single particle or a collection of 10^{23} particles, is described by a single *complex-valued* function of position and time called the *wavefunction*, usually denoted $\Psi(x, t)$. If there are multiple particles in the system, Ψ is a function of all the coordinates x_1, x_2, \dots of the various particles as well as time. It’s likely that the only time you’ll be concerned with multiple-particle wavefunctions on the GRE is when dealing with Bose or Fermi statistics, which we’ll get to later, so for now we assume that our quantum system is just a single particle. Given the wavefunction, the rules for calculating quantities of interest in one-dimensional quantum mechanics are the following:

1. The probability that the particle with wavefunction $\Psi(x, t)$ will be found between positions x and $x + dx$ is $|\Psi(x, t)|^2 dx$.

2. Observables A are represented by Hermitian operators \hat{A} which act on Ψ . The expectation value of an observable A in the state Ψ is

$$\langle A \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{A} \Psi dx. \quad (5.1)$$

3. A measurement of an observable A at a time t_0 on a state Ψ will always return one of the eigenvalues of \hat{A} . To find the probability that a particular eigenvalue λ_n is observed, expand $\Psi(x, t_0) = \sum_k c_k f_k(x)$ in a basis of orthonormal eigenfunctions $f_k(x)$ for \hat{A} with eigenvalues λ_k . The desired probability is $|c_n|^2$. After measurement, the wavefunction of the particle at time t_0 is now $f_n(x)$.

Let's now examine each of these rules in detail.

1. Position measurements. Notice that the quantity that appears is the *complex modulus* $|\Psi(x, t)|^2$, not $\Psi(x, t)$ itself. This is comforting because probabilities had better be non-negative real numbers. In fact, the probability of finding the particle *somewhere* had better be exactly 1:

$$\int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx = 1. \quad (5.2)$$

This extremely important consistency condition means that the wavefunction must be *normalized*. The fact that we can actually *do* this normalization means that Ψ can't do anything funny at $x = \pm\infty$ – it has to vanish fast enough for the integral to converge. Always keep normalization in the back of your mind when calculating probabilities on the GRE – if the problem doesn't explicitly state that the wavefunction is normalized, you should normalize it *before* computing anything else. By the way, for a particle living in more than one dimension, this rule generalizes appropriately: the probability of finding a particle in a small box with opposite corners (x, y, z) and $(x+dx, y+dy, z+dz)$ is $|\Psi(x, y, z, t)|^2 dx dy dz$, and the probability of finding a particle in a spherical shell at radius r with thickness dr is¹ $|\Psi(r, \theta, \phi, t)|^2 (4\pi r^2 dr)$. Dimensional analysis can also help you with normalization: since $|\Psi|^2$ must be integrated over space to give a probability, which is dimensionless, the wavefunction has dimensions of $(\text{length})^{-d/2}$ in d spatial dimensions.

An aside about normalization: note that we could multiply Ψ by some phase factor, $e^{i\theta}$, which would not change the normalization, since $e^{i\theta}$ and $e^{-i\theta}$ cancel out in $|\Psi|^2$. The interpretation is that Ψ and $e^{i\theta}\Psi$ represent the *same state*. However, *relative* phases between two wavefunctions are physical: if we have a wavefunction like $\Psi = \psi_1 + e^{i\alpha}\psi_2$, we can multiply Ψ by a phase (which preserves the relative phase $e^{i\alpha}$ between ψ_1 and ψ_2) but we are *not* allowed to multiply ψ_1 and ψ_2 individually by their own phase factors. Only the total wavefunction is defined up to a phase.

¹Note, however, that it is conventional to normalize the radial and angular parts of a three-dimensional wavefunction *separately*: see Section 5.4.1.

2. Observables. First, some definitions. An *operator* is just a rule instructing us to *do* something to a function $f(x)$. For example, the operator x says “multiply a function by x ,” and the operator $5d/dx$ says “differentiate a function with respect to x and multiply by 5.” The rule is that operators are read from right to left, such that the piece closest to the function acts first. This is important when derivatives are involved: the operator $x d/dx$ means “differentiate with respect to x , *then* multiply by x ,” not the other way around! To distinguish an operator from an ordinary function, we put a hat on it, like \hat{O} .

Sometimes, acting on a function $f(x)$ with an operator \hat{O} may return the *same* function, multiplied by a constant c . Here are some examples:

- $3 \cdot f(x) = 3f(x)$ for any function $f(x)$. In other words, the operator “3” acting on any $f(x)$ just returns $f(x)$ multiplied by the constant 3.
- $\frac{d}{dx} e^{\lambda x} = \lambda e^{\lambda x}$. The operator d/dx , acting on a certain function $f(x) = e^{\lambda x}$, returns $\lambda f(x)$.

In this case, we say that $f(x)$ is an *eigenfunction* of the operator \hat{O} with *eigenvalue* c . So in the examples above, all functions whatsoever are eigenfunctions of the operator $\hat{O} = 3$ with eigenvalue 3, but only functions of the form $e^{\lambda x}$ are eigenfunctions of $\hat{O} = d/dx$ with eigenvalue λ . Note that this is *not* always the case: $\frac{d}{dx} \sin x = \cos x$, so $\sin x$ is *not* an eigenfunction of d/dx . Indeed, eigenfunctions are special (and extremely useful) because they reduce the potentially complicated action of an operator to something very simple, namely multiplication by a constant.

A *Hermitian* operator \hat{A} is one such that

$$\int_{-\infty}^{\infty} f(x)^* (\hat{A}g(x)) dx = \int_{-\infty}^{\infty} (\hat{A}f(x))^* g(x) dx \quad (5.3)$$

for any $f(x)$ and $g(x)$. Here are some useful facts (definitely worth memorizing!) about Hermitian operators:

- All their eigenvalues are real.
- Eigenfunctions corresponding to different eigenvalues are orthogonal: if $f(x)$ and $g(x)$ are eigenfunctions with different eigenvalues, then $\int_{-\infty}^{\infty} f(x)^* g(x) dx = 0$.

Now, in classical mechanics, *all* observables can be built out of the two quantities x and p , position and momentum. For example, kinetic energy is $E = p^2/2m$, the potential energy of a harmonic oscillator is $\frac{1}{2}kx^2$, angular momentum in three dimensions is $\mathbf{r} \times \mathbf{p}$, and so on. In quantum mechanics, these observables are represented by the operators:

$$\hat{x} = x, \quad \hat{p} = -i\hbar \frac{\partial}{\partial x}. \quad (5.4)$$

It's easy to see that \hat{x} , so defined, is Hermitian according to (5.3): you should check for yourself that \hat{p} is Hermitian, using integration by parts (notice the very important factor of $-i$ which makes this work). Any operators which are the quantum analogues of classical observables (like angular momentum, potential energy, and so on) can be built out of these two operators. For the purposes of the GRE, the *only* operators which can't be built out of x and p are the spin operators – we'll treat those in great detail in the following sections. We will often refer to “observables” and “operators” interchangeably, sometimes sloppily with the same notation for both (omitting the hat), but remember that “observable” refers to a physical quantity to be measured, while “operator” refers to its mathematical representation in the formalism of quantum mechanics.

3. **Measurements.** The radical departure of quantum mechanics from classical mechanics arises from the first sentence of point 3 – a measurement of A will *always* return an eigenvalue λ_n , and if the eigenvalues are discrete rather than continuous, the measurement of A is *quantized*. To go further, we use the previously mentioned facts about Hermitian operators: since the eigenfunctions are orthogonal, we can build an orthonormal *basis* from them, and express any normalized wavefunction $\Psi(x, t)$ as a linear combination of these basis functions $f_n(x)$. The coefficient c_n is then given by

$$c_n = \int_{-\infty}^{\infty} f_n(x)^* \Psi(x, t) dx \quad (5.5)$$

Taking the complex modulus squared of this number then gives the probability of getting eigenvalue λ_n when measuring A on the state Ψ at time t . Once this happens, the state of the system is *no longer* Ψ : it is simply $f_n(x)$. Thus a subsequent measurement of A immediately following the first measurement is *guaranteed* to return the value λ_n , and no other.

Expectation values are very easy to compute once you have the decomposition of Ψ in an orthonormal basis: if $\Psi(x, t_0) = \sum_k c_k f_k(x)$, then

$$\langle A \rangle = \sum_k \lambda_k |c_k|^2. \quad (5.6)$$

When using this formula, make sure your eigenfunction expansion matches the observable whose expectation value you are trying to compute! Notice that expectation values are *averages*, so are not required to be equal to one of the eigenvalues, just as the average of a set of integers need not be an integer.

5.1.2 Dirac notation

All this talk about eigenvalues and eigenvectors, basis decompositions and normalization should remind you of linear algebra. This is no accident – the formalism of quantum mechanics is best expressed in this language, and Dirac notation provides an extremely convenient and intuitive way to do this. You may find it unfamiliar to think of functions (the

wavefunction in particular) as elements of a vector space. This is actually not so bad, and we'll give the "dictionary" now.

Dirac notation represents a vector as a *ket*, like this: $|a\rangle$. Here, a is just a label – we could have written $|1\rangle$, or $|\text{Bob}\rangle$. To each ket $|a\rangle$ is associated another object, the *bra* $\langle a|$, which allows us to take inner products:

$$\text{Inner product of } |a\rangle \text{ and } |b\rangle \equiv \langle b|a\rangle. \quad (5.7)$$

The inner product is a complex number, and in this notation is also called the *bracket* of $|a\rangle$ and $|b\rangle$, hence the names *bra(c)ket* for these objects. The vector space that the kets live in is called *Hilbert space*, which is just a fancy name for a vector space where we are allowed to take the inner products of vectors. We will always work with complex vector spaces, so we define the inner product to behave as follows under complex conjugation:

$$\langle a|b\rangle := \langle b|a\rangle^*. \quad (5.8)$$

The reason for this is that $\langle a|a\rangle = \langle a|a\rangle^*$, so the norm of a vector is a real number.

To show the action of an operator \hat{A} on a vector $|b\rangle$, we make the following convenient definition:

$$\hat{A}|b\rangle \equiv |\hat{A}b\rangle.$$

Note that this is *just notation*, since as we have previously stated, the text that goes inside the ket is just a label. The power of this notation comes when we now take the bracket with another vector:

$$\langle a|\hat{A}b\rangle := \langle \hat{A}^\dagger a|b\rangle \quad (5.9)$$

This *defines* \hat{A}^\dagger , the Hermitian conjugate of \hat{A} . Most importantly, this means that in a bracket $\langle a|\hat{A}b\rangle$, we can let an observable act *either* "on the left" on ket $|b\rangle$, or let its Hermitian conjugate \hat{A}^\dagger act "on the right" on bra $\langle a|$. We have defined \hat{A}^\dagger so we get the same answer either way.

If \hat{A} is Hermitian – in other words, if $\hat{A}^\dagger = \hat{A}$ – then both sides of (5.9) contain the same operator \hat{A} , so we might as well define another convenient notation:

$$\hat{A} \text{ Hermitian} \implies \langle a|\hat{A}b\rangle = \langle \hat{A}a|b\rangle \equiv \langle a|\hat{A}|b\rangle.$$

Note the similarity with (5.3). These two conditions are in fact *identical* provided we make the following definitions:

$$\langle x|f\rangle := f(x) \quad (5.10)$$

$$\langle f|g\rangle := \int_{-\infty}^{\infty} f(x)^* g(x) dx. \quad (5.11)$$

The second of these just says that the inner product on *function space* is given by f^*g . The first is a little more subtle: it says that a function f should really be thought of not as a vector itself, but as a collection of coefficients $f(x)$, one for each point x . In other words, $|f\rangle$

is the abstract vector, and $\langle x|f\rangle$ represents the decomposition of f along the basis vectors $|x\rangle$.

If the last two sentences didn't make total sense to you, don't worry. This part of Dirac notation is not really relevant for the GRE: we only include it so that if you see a statement like "Let $|1\rangle$ be the ground state of the harmonic oscillator," you'll understand that $|1\rangle$ plays the role of $|f\rangle$, and you won't find yourself wondering what happened to the wavefunction $f(x)$. Indeed, we'll see below that many quantum mechanics problems can be solved totally within the confines of Dirac notation, without ever having to resort to the wavefunction.

One final comment about Dirac notation: if we are working in a finite-dimensional vector space, for example when talking about spin-1/2, then kets are just column vectors, operators are just matrices, and we have the following simple dictionary:

$$\begin{aligned}\langle b | &:= (b^T)^* \\ A^\dagger &:= (A^T)^*\end{aligned}$$

where the superscript T denotes the transpose (of either a vector or a matrix).

5.1.3 Schrodinger equation

In all of the previous description, we assumed we were *given* the wavefunction. But how do we find it in the first place? The answer is given by the Schrodinger equation:

$$i\hbar \frac{\partial}{\partial t} \Psi(x, t) = \hat{H} \Psi(x, t). \quad (5.12)$$

Here, we have introduced time-dependence in the wavefunction, and the operator \hat{H} appearing on the right-hand side is the Hamiltonian operator, which represents the total energy. *Almost always,*

$$\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}(x) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \hat{V}(x), \quad (5.13)$$

where $V(x)$ is the potential energy. The two exceptions are the presence of an external magnetic field, which modifies the first (kinetic) term, and when the potential V also depends on time. Both of these cases require a different kind of analysis, which is more advanced than what you'll need on the GRE.

There is a useful way to read (5.12). We could view the left-hand side as an operator in its own right, and define $\hat{E} := i\hbar \partial/\partial t$ to be the total energy operator. Then, by rule 3 above, a measurement of the energy will always return an eigenvalue of \hat{E} , which by the Schrodinger equation, is also an eigenvalue of \hat{H} . Therefore, *to find the possible energies of the system, we must find all the eigenvalues of \hat{H}* . Suppose we have done this, and we have a system in the state $\psi_n(x)$ with eigenvalue E_n . Then the Schrodinger equation reads

$$i\hbar \frac{\partial}{\partial t} \Psi(x, t) = E_n \Psi(x, t), \quad (5.14)$$

where E_n on the right-hand side is *just a number*, not an operator. Now we can solve this equation:

$$\Psi(x, t) = e^{-iE_nt/\hbar} \psi_n(x).$$

The most general wavefunction $\Psi(x, t)$ will just be a linear combination of all the eigenfunctions of \hat{H} , with appropriate time dependence $e^{-iE_nt/\hbar}$ tacked on.

This line of reasoning leads to a recipe for finding the time evolution of a quantum-mechanical system with Hamiltonian \hat{H} :

1. Solve the eigenvalue equation $\hat{H}\psi(x) = E\psi(x)$ to find a set of *time-independent* eigenfunctions $\psi_n(x)$ (also called *stationary states*) with eigenvalues E_n .
2. Given the wavefunction at time $t = 0$, $\Psi(x, 0)$, decompose it along the basis of eigenfunctions $\psi_n(x)$: $\Psi(x, 0) = \sum_n c_n \psi_n(x)$.
3. The full time-dependent wavefunction is $\Psi(x, t) = \sum_n c_n e^{-iE_nt/\hbar} \psi_n(x)$.

On the GRE, you will *never* have to complete all these steps from scratch. Almost always, you will be given a well-known Hamiltonian, for which the eigenfunctions are either given to you or which you are supposed to remember yourself. You will then be asked about time dependence, or to compute expectation values of various observables in these states. You may also be asked conceptual questions about this procedure: for example, you should check that if $\Psi(x, 0) = \psi_n(x)$ (that is, at $t = 0$ the system is in a stationary state of energy E_n), then the probability of getting energy E_n at some other time t is always exactly 1.

Here is a useful list (worth memorizing) of general properties of the time-independent energy eigenfunctions $\psi_n(x)$, valid for any Hamiltonian you will encounter on the GRE:

- ψ_n for different values of n are orthogonal, since they correspond to different energy eigenvalues.
- ψ is always continuous. Its derivative $d\psi/dx$ is also always continuous, *except* at a boundary where the potential $V(x)$ is infinite. This exception will be treated in various contexts in Section 5.3.
- ψ can be taken to be purely real, without loss of generality.² Note this is *not* true for the full time-dependent wavefunction, since we must attach the complex exponential factors. However, it does lead to an extremely convenient computational shortcut: if a particle is in a stationary state ψ_n which is taken to be real, the expectation value of its momentum *must vanish*. The proof is as follows:

$$\langle p \rangle = \int \psi(x) e^{+iE_nt/\hbar} \left(-i\hbar \frac{\partial}{\partial x} \right) \psi(x) e^{-iE_nt/\hbar} dx = -i\hbar \times (\text{something real}),$$

²This is not to say that ψ *must* be real, only that we *can* choose a real basis of energy eigenfunctions. For example, $e^{\pm ipx/\hbar}$ are eigenfunctions of the free particle Hamiltonian, but so are the real linear combinations $\sin(px/\hbar)$ and $\cos(px/\hbar)$. Of course, these latter two are not momentum eigenstates, but that's an added requirement we're not concerned with here.

because the exponential factors $e^{\pm iE_n t/\hbar}$ cancel with each other. But expectation values must be real for such real wavefunctions, hence $\langle p \rangle = 0$. Caution: this does *not* apply to a superposition of stationary states, for example $\Psi(x, t) = \psi_1 e^{-iE_1 t/\hbar} + \psi_2 e^{-iE_2 t/\hbar}$, because the exponential factors will not cancel completely and $\Psi^* \Psi$ will contain a real term $\cos((E_2 - E_1)t/\hbar)$.

- The ground state ψ_0 , corresponding to the lowest energy E_0 , has no *nodes*: a node is a point at which the wavefunction vanishes (excluding the case where the wavefunction vanishes at a boundary, as in the infinite square well). Recalling the probabilistic interpretation, this means that there are no points where the particle is guaranteed not to be found. Each successive energy eigenstate has one more node than the previous one: ψ_1 has one node, ψ_2 has two nodes, and so on. So even if you know nothing about a given Hamiltonian, you can say something about its energy eigenfunctions just by looking at their graphs. Indeed, a classic GRE problem gives you sketches of possible wavefunctions for an unspecified Hamiltonian and asks you questions about them.
- If the potential $V(x)$ is *even* (that is, if $V(x) = V(-x)$), then $\psi(x)$ can be taken to have definite parity. This means that $\psi(x)$ is either even, $\psi(x) = \psi(-x)$, or odd, $\psi(x) = -\psi(-x)$. Furthermore, the parity of ψ_n alternates as we change n : The ground state ψ_0 is even, the first excited state ψ_1 is odd, and so on.
- For ψ to be normalizable, we must have $E > V_{min}$, where V_{min} is the global minimum of $V(x)$. The intuition, borrowed from classical mechanics, is that if the particle has less energy than the minimum of V , its kinetic energy must be negative, which is impossible. As we have emphasized, this classical reasoning does not hold strictly true in quantum mechanics, but it is a good mnemonic.

5.1.4 Commutators and the uncertainty principle

If you remember only one thing about operators in quantum mechanics, remember this:

Operators don't commute (in general).

That is, applying \hat{A} , followed by \hat{B} , is in general not the same thing as applying \hat{B} followed by \hat{A} . If you know a little linear algebra, this follows in the finite-dimensional case from the fact that matrices don't commute in general. It's even true in the infinite-dimensional case, though. Consider the two operators \hat{x} and \hat{p} , defined in (5.4). Let them act on a test function $f(x)$:

$$\begin{aligned} (\hat{x} \circ \hat{p})f(x) &= x \left(-i\hbar \frac{d}{dx} f(x) \right) = -i\hbar(x f'(x)) \\ (\hat{p} \circ \hat{x})f(x) &= -i\hbar \frac{d}{dx} (x f(x)) = -i\hbar(f(x) + x f'(x)) \\ \implies (\hat{x} \circ \hat{p} - \hat{p} \circ \hat{x})f(x) &= i\hbar f(x). \end{aligned}$$

Since the last line is true regardless of the function $f(x)$, we can drop f and write a relation only involving the operators:

$$[\hat{x}, \hat{p}] = i\hbar. \quad (5.15)$$

This is perhaps the most important equation in quantum mechanics. The symbol $[,]$ stands for the *commutator* of two operators: compose them in one order, then subtract the result of composing them in the other order. It can be quite easy to get confused when computing commutators of operators like this, since just writing down $\hat{p} \circ \hat{x} = -i\hbar \frac{d}{dx}x$ might lead us to assume that only x is supposed to be differentiated, and we would lose the second term that we got from the product rule by acting on a test function $f(x)$ above. So, *when computing commutators where the operators involve derivatives, always act on a test function*. One other important thing to note is that the commutator, in general, is *itself an operator*: in this case it's a particularly simple operator, given by multiplication by the constant $i\hbar$.

Here are two useful identities for computing commutators of products of operators:

- $[AB, C] = A[B, C] + [A, C]B$
- $[A, BC] = [A, B]C + B[A, C]$

Both are fairly easy to remember, since they resemble product rules for derivatives. But to rederive them in a pinch, just write out the commutators as if they were matrix multiplication: $[A, B] = AB - BA$ and so forth. You can be even more economical and note that one rule follows from the other by changing the order of the commutator using $[A, B] = -[B, A]$, and relabeling.

Commutators are intimately tied up with the uncertainty principle, for the following reason. The commutator measures the difference between the results of applying two operators in different orders, which according to the rules given above, represents the difference between outcomes of measurements of two observables applied in different orders. If the commutator vanishes, it means that we can measure the two observables in either order, and we're guaranteed to get the same answer. A nonzero commutator $[\hat{A}, \hat{B}]$, however, means that in general, if we measure B and put the system in an eigenstate of \hat{B} , a follow-up measurement of observable A will destroy this state and put the system back in a linear combination of eigenstates of \hat{B} . In other words, there is a fundamental uncertainty in measurements of A versus measurements of B .

This is made precise by the following statement:

$$\sigma_A^2 \sigma_B^2 \geq \left(\frac{1}{2i} \langle [\hat{A}, \hat{B}] \rangle \right)^2. \quad (5.16)$$

Here, σ_A^2 is the statistical *variance* of a measurement of A , defined as

$$\sigma_A^2 := \langle A^2 \rangle - \langle A \rangle^2, \quad (5.17)$$

and similarly for σ_B^2 . Note that what appears on the right-hand side of (5.16) is the *expectation value* of the commutator $[\hat{A}, \hat{B}]$: this means that the uncertainty *bound* (the right-hand

side) depends in general on what state the system is in. Of course, the actual uncertainty (the left-hand side) also depends on the state of the system. In particular, if we can find a state such that the inequality becomes an equality, we call such a state a *minimal-uncertainty state* for the two observables A and B . And once again, if the commutator vanishes identically, so does the uncertainty bound: we can find states for which both uncertainties are zero.

The case you are undoubtedly familiar with is $A = x$, $B = p$, in which case the RHS becomes $(i\hbar/2i)^2 = \hbar^2/4$. Taking the square root of both sides gives the familiar relation

$$\sigma_x \sigma_p \geq \frac{\hbar}{2}. \quad (5.18)$$

Notice that because the commutator $[\hat{x}, \hat{p}]$ is just a number, its expectation value is independent of the state, and the minimum uncertainty is always the same, $\hbar/2$.

It is a very important fact (derived in all basic quantum mechanics books) that *the position-space wavefunction of a minimum-uncertainty state is a Gaussian*. Indeed, because it's a minimum-uncertainty state, its momentum-space wavefunction is *also* a Gaussian. Even if we're not dealing with a minimum-uncertainty state, most systems do not conspire to exceed the uncertainty bound by huge amounts, so the following “folklore” statement,

$$\Delta x \Delta p \approx \hbar, \quad (5.19)$$

holds quite generally. Note the missing factor of 2, and the replacement of the precisely-defined σ_x and σ_p by the rather vague $\Delta x \Delta p$; this is because this statement is *only intended to give an order-of-magnitude estimate*. Nevertheless, it is quite useful, as you will see in the problems.

A similar “folklore” statements holds for energy and time,

$$\Delta E \Delta t \approx \hbar. \quad (5.20)$$

The standard application of (5.20) is to decay processes: Δt represents the lifetime (mean lifetime, or half-life, or whatever, since this is just an order-of-magnitude estimate) of the unstable state, and ΔE represents the uncertainty in energy of the decay process. For example, when an unstable particle with an extremely short lifetime decays at rest, its decay products can have widely varying total energy because of the large value of ΔE . Equally well, when a short-lived atomic excited state decays by emitting a photon, the energy of the photon is not precisely determined, but has a spread ΔE . In both of these contexts, ΔE is known as the *width* (either of the excited state, or of the emission line).

Finally, one very important remark regarding energy and commutators:

If an operator $\hat{\mathcal{O}}$ commutes with the Hamiltonian, it is conserved.

In other words, we can simultaneously diagonalize $\hat{\mathcal{O}}$ and the Hamiltonian, and label states of the system by eigenvalues of $\hat{\mathcal{O}}$ and energies at a given time. The above statement guarantees that at any subsequent time, these labels don't change.

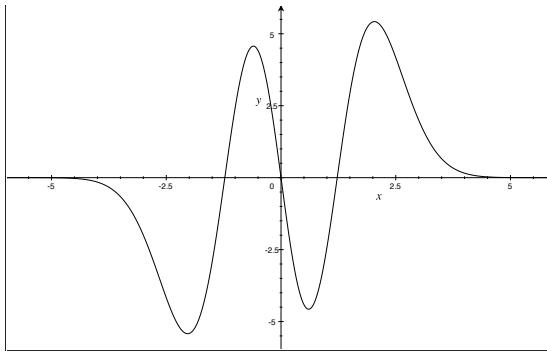
5.1.5 Problems

1. A particle has the wavefunction $\Psi(x) = A(1 - x^2)$ for $|x| \leq 1$, and $\Psi(x) = 0$ elsewhere. What is the probability the particle will be found in the region $x < 0$?
 - (A) 0
 - (B) 1/4
 - (C) 1/2
 - (D) 3/4
 - (E) 1

2. A particle has normalized wavefunction $\Psi(x) = Ae^{-x^2/2\ell^2}$. What is the value of $(\hat{x}\hat{p} + \hat{p}\hat{x})\Psi(x)$?
 - (A) $i\hbar Ae^{-x^2/2\ell^2}$
 - (B) $i\hbar A(x/\ell)^2 e^{-x^2/2\ell^2}$
 - (C) $i\hbar A((x/\ell)^2 - 1)e^{-x^2/2\ell^2}$
 - (D) $i\hbar A(2(x/\ell)^2 - 1)e^{-x^2/2\ell^2}$
 - (E) 0

3. Let ψ_1 and ψ_2 be energy eigenstates of a time-independent Hamiltonian with energies E_1 and E_2 . At time $t = 0$, a system is in state $\frac{1}{\sqrt{2}}(\psi_1 - \psi_2)$. At time t , what is the probability that a measurement of the energy of the system will return E_1 ?
 - (A) 0
 - (B) $1/\sqrt{2}$
 - (C) 1/2
 - (D) $\cos[(E_2 - E_1)/\hbar]$
 - (E) $\cos[(E_2 + E_1)/\hbar]$

4. Let $|a\rangle$ and $|b\rangle$ denote momentum eigenstates with eigenvalues a and b respectively, where $a \neq b$. What is $\langle a|\hat{p}|b\rangle$?
 - (A) a
 - (B) b
 - (C) $|ab|$
 - (D) $|ab|^{1/2}$
 - (E) 0



5. The wavefunction shown in the diagram above represents one of the excited states of the harmonic oscillator. What is the energy of the state?
- $\hbar\omega/2$
 - $3\hbar\omega/2$
 - $5\hbar\omega/2$
 - $7\hbar\omega/2$
 - $9\hbar\omega/2$
6. Which of the following is a Hermitian operator?
- $\begin{pmatrix} 1 & 0 \\ -1 & 0 \end{pmatrix}$
 - $\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$
 - $\begin{pmatrix} 1 & 2 \\ 2 & 1 \end{pmatrix}$
- I only
 - II only
 - III only
 - I and III
 - II and III
7. A particle is in the state $|\psi\rangle = A(2|1\rangle + 3|2\rangle + |5\rangle)$, where $|n\rangle$ denotes the normalized eigenstate of an observable \mathcal{O} with eigenvalue n , and A is a normalization constant. What is the expectation value of \mathcal{O} in the state $|\psi\rangle$?
- 13/14

- (B) 1
 (C) $13/\sqrt{14}$
 (D) $27/14$
 (E) 27
8. Let $|s\rangle$ and $|t\rangle$ denote orthonormal states. Let $|\Psi_1\rangle = |s\rangle + 2i|t\rangle$ and $|\Psi_2\rangle = 2|s\rangle + x|t\rangle$. What must the value of x be so that $|\Psi_1\rangle$ and $|\Psi_2\rangle$ are orthogonal?
 (A) i
 (B) $-i$
 (C) 1
 (D) -1
 (E) $i/\sqrt{5}$
9. Which of the following is equal to the commutator $[\hat{x}^2, \hat{p}^2]$?
 (A) 0
 (B) $i\hbar$
 (C) $-\hbar^2$
 (D) $4i\hbar\hat{x}\hat{p}$
 (E) $2i\hbar(\hat{x}\hat{p} + \hat{p}\hat{x})$
10. An unstable particle with a lifetime of 1.0×10^{-23} s and a mass of $500 \text{ MeV}/c^2$ is measured in a new experiment to have a mass of $450 \text{ MeV}/c^2$. The mass resolution of the experiment is $10 \text{ MeV}/c^2$. The difference between the observed mass and the expected mass is most likely due to
 (A) violation of conservation of energy
 (B) the uncertainty principle
 (C) experimental error
 (D) time dilation
 (E) the Mossbauer effect
11. The nitrogen molecule consists of two nitrogen atoms joined by a covalent bond with length approximately 100 pm. What is the approximate kinetic energy of one of the covalently bonded electrons?
 (A) 4 meV
 (B) 4 eV
 (C) 4 keV
 (D) 4 MeV
 (E) 4 GeV

5.2 Harmonic oscillator

5.2.1 One dimension

The Hamiltonian for the quantum harmonic oscillator in one dimension is

$$H = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2. \quad (5.21)$$

In this form, it's totally useless – we only include it to remind you that if a problem says “A system has Hamiltonian given by equation (5.21),” it's just talking about a harmonic oscillator. It may be written in terms of the spring constant $k = m\omega^2$ instead of the angular frequency ω , but no matter: if the potential is quadratic, you have a harmonic oscillator on your hands. Just remember to match the form given above by relating ω to the coefficient of the quadratic.

A clever change of variables brings it to the following, much more useful, form:

$$H = \hbar\omega \left(a^\dagger a + \frac{1}{2} \right). \quad (5.22)$$

How we arrived at the form (5.22) is irrelevant for GRE purposes – what's important is that there exists an operator a (called a *lowering operator* or *annihilation operator*), and its Hermitian conjugate a^\dagger (called a *raising operator* or *creation operator*), which are linear combinations of \hat{x} and \hat{p} such that H can be transformed as above. It's worth memorizing the commutation relation of a and a^\dagger , since it's very simple:

$$[a, a^\dagger] = 1. \quad (5.23)$$

The reason (5.22) is useful is that we can read off the eigenstates of H right away. Suppose there exists a state called³ $|0\rangle$ which is killed by a : $a|0\rangle = 0$. Then

$$H|0\rangle = \frac{\hbar\omega}{2}|0\rangle,$$

and $|0\rangle$ is an eigenstate of H with eigenvalue $\hbar\omega/2$. Indeed, one can prove that this is the lowest-energy eigenstate of H , so another fact worth memorizing is *the ground state of the harmonic oscillator has energy $\hbar\omega/2$* . Using the commutation relation (5.23) and the Hamiltonian (5.22), one can also prove that acting with a^\dagger on $|0\rangle$ produces yet another energy eigenstate, with energy $3\hbar\omega/2$. (Exercise: check this yourself.) We can continue this process indefinitely, so we have derived the spectrum of the harmonic oscillator:

$$H|n\rangle = \hbar\omega \left(n + \frac{1}{2} \right) |n\rangle, \quad n = 0, 1, 2, \dots \quad (5.24)$$

³Remember, this is *not* the zero vector! The 0 inside the ket is just a label. However, the action of a on $|0\rangle$ *does* give the zero vector.

As usual, the states $|n\rangle$ are orthogonal, because they are eigenvectors of H with different eigenvalues. They are also assumed to be normalized. However, $a^\dagger|n\rangle$ is *not* automatically normalized to $|n+1\rangle$ – the normalization factor will be provided to you on the test if you need it, but it's important to keep in mind that when calculating expectation values, $|n\rangle$ is normalized while $a^\dagger|n\rangle$ and $a|n\rangle$ are not. For convenience, we'll give you the normalization factors,

$$a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle; \quad a|n\rangle = \sqrt{n}|n-1\rangle,$$

but remember, you need *not* memorize these.

A standard question about the harmonic oscillator asks you to calculate the expectation value of some observable written in terms of a and a^\dagger . We'll walk you through this calculation once because it is both an excellent example of the use of Dirac notation, but also an illustration of how to calculate expectation values by using only orthonormality and commutation relations.

What is the expectation value of $(a + a^\dagger)^2$ in the state $|3\rangle$? We want to calculate

$$\langle 3|(a + a^\dagger)^2|3\rangle = \langle 3|a^2 + aa^\dagger + a^\dagger a + (a^\dagger)^2|3\rangle.$$

Notice that because a and a^\dagger don't commute, the order matters when expanding out the square, so we can't just combine the two middle terms. Now comes the clever part. Examining the first term, a^2 will act on the $|3\rangle$ on the right to give something proportional to $|1\rangle$; but $|3\rangle$ and $|1\rangle$ are orthogonal, so this term vanishes. Equally well, a^2 can act on the $\langle 3|$ on the left to give something proportional to $\langle 5|$ (remembering (5.9), a acts like its Hermitian conjugate a^\dagger when acting on a bra). But $|5\rangle$ and $|3\rangle$ are also orthogonal, so this term still vanishes. An identical argument holds for the $(a^\dagger)^2$ term.

Thus the only two terms which contribute are the two middle terms, which each raise once and lower once, bringing us back to state $|3\rangle$ which has nonzero inner product with itself. Using the normalization relations,

$$aa^\dagger|3\rangle = \sqrt{4}(a|4\rangle) = \sqrt{4}\sqrt{4}|3\rangle = 4|3\rangle,$$

and similarly,

$$a^\dagger a|3\rangle = \sqrt{3}(a^\dagger|2\rangle) = \sqrt{3}\sqrt{3}|3\rangle = 3|3\rangle.$$

Let's check that this makes sense using the commutation relation:

$$[a, a^\dagger] = 1 \implies aa^\dagger - a^\dagger a = 1,$$

and indeed, subtracting $a^\dagger a|3\rangle$ from $aa^\dagger|3\rangle$ gives just $|3\rangle$. So instead of calculating both terms separately, we could have combined them using the commutation relation – either method is fine.

Going back to our original expectation value,

$$\langle 3|a^2 + aa^\dagger + a^\dagger a + (a^\dagger)^2|3\rangle = (4 + 3)\langle 3|3\rangle = 7,$$

since by assumption $|3\rangle$ is normalized. That's all there is to it.

We'll finish this lightning review of the harmonic oscillator with some bits of trivia.

- The ground state of the harmonic oscillator happens to be a minimum-uncertainty state, so its position-space wavefunction is a Gaussian. You probably won't need it, but you can get an estimate of its width from dimensional analysis: the parameters of the harmonic oscillator Hamiltonian are \hbar , m , and ω , and the only combination of these with the dimensions of length is $\sqrt{\hbar/m\omega}$.
- The position-space wavefunctions are related to so-called *Hermite polynomials*.
- All energy eigenstates of the harmonic oscillator obey the virial theorem, which states for the harmonic oscillator

$$\langle T \rangle = \langle V \rangle = \frac{E_n}{2}. \quad (5.25)$$

In general, this theorem does *not* apply to superpositions of energy eigenstates, but in certain particular cases it does – see the problems for an example.

5.2.2 Three dimensions

The generalization of the harmonic oscillator Hamiltonian to three dimensions is simple: it's just three identical copies of the one-dimensional version. The quadratic potential is the reason this works: $r^2 = x^2 + y^2 + z^2$, so a potential which is quadratic in r , the 3-dimensional distance to the origin, is the sum of quadratic potentials in the three rectangular coordinates x , y , and z . This is *very special* to the harmonic oscillator, but also very convenient. It means that the energy eigenfunctions are products of the energy eigenfunctions for the coordinates x , y , and z , and the energies are sums of the individual energies:

$$\psi_N(x, y, z) = \psi_{n_1}(x)\psi_{n_2}(y)\psi_{n_3}(z); \quad E_N = \left(N + \frac{3}{2}\right)\hbar\omega \text{ with } N = n_1 + n_2 + n_3. \quad (5.26)$$

In particular, this means while the ground state is non-degenerate (all the n_i must be 0 for N to be 0), the first excited state is 3-fold degenerate, because the three permutations

$$(n_1, n_2, n_3) = (1, 0, 0), (0, 1, 0), (0, 0, 1)$$

all give the same energy. (Of course, the same general arguments would hold if we had a system confined to two dimensions, though the details change - be careful!)

5.2.3 Problems

1. What is the expectation value of the operator $a^\dagger a + aa^\dagger$ in the ground state of the harmonic oscillator?
 - (A) 0
 - (B) 1
 - (C) $\sqrt{2}$

- (D) 2
 (E) $\hbar\omega$
2. A particle of mass m in a harmonic oscillator potential with angular frequency ω is in the state $\frac{1}{\sqrt{2}}(|1\rangle + |4\rangle)$. What is $\langle p^2 \rangle$ for this particle?
- (A) $3\hbar\omega/2$
 (B) $9\hbar\omega/2$
 (C) $6\sqrt{2}m\hbar\omega/2$
 (D) $3m\hbar\omega$
 (E) $6m\hbar\omega$
3. Which of the following is NOT true of the spectrum of the one-dimensional quantum harmonic oscillator?
- (A) The ground state energy is equal to the classical ground state energy.
 (B) There are an infinite number of bound states.
 (C) The energy levels are equally spaced relative to the ground state.
 (D) The ground state saturates the uncertainty principle bound.
 (E) The spectrum is nondegenerate.
4. A charged particle confined to two dimensions and subject to an external magnetic field can be modeled by a two-dimensional harmonic oscillator potential, $V(x, y) = \frac{1}{2}m\omega^2(x^2 + y^2)$. What is the degeneracy of the state with energy $3\hbar\omega$?
- (A) 1
 (B) 2
 (C) 3
 (D) 4
 (E) There is no state with this energy.

5.3 Other standard Hamiltonians

There are four other classic one-dimensional quantum mechanical Hamiltonians which it pays to be familiar with. Most of the technical information in this section (energies and eigenfunctions) will likely be given to you on the test, so you need not memorize it, but being intimately familiar with it means much less time spent puzzling over a complicated-looking formula. What *is* important to memorize is the methodology for approaching each particular Hamiltonian, as this can be very difficult to derive from scratch and very easily lead to lots of wasted time. These four Hamiltonians all admit *bound states*, which we'll

study first; the last two also admit *scattering states*, whose analysis is a little different, so we treat it separately.

Keep in mind as we proceed that the essential difference between bound and scattering states is that bound states have discrete energy eigenvalues, whose values are determined by enforcing boundary conditions on the wavefunction. In the case where $V(x)$ goes to zero as x goes to $\pm\infty$, bound states are the ones with $E < 0$, and scattering states have $E > 0$. Along the same lines, if the potential goes to infinity at $x = \pm\infty$, as in the infinite square well or the harmonic oscillator, *every* state is bound.

As a guide to your studying, the following four Hamiltonians are listed in order of decreasing priority. Only the square well is listed explicitly on the official ETS list of topics, and the free particle is important in its own right, as a basis for many other solutions of the Schrodinger equation. However, you may not see the delta-function well or the finite square well on your exam, so don't work too hard on them. Scattering is a bit of a wild card: you will probably see *something* related to scattering, but it will likely be a conceptual rather than a computational question.

5.3.1 Infinite square well

This Hamiltonian is particularly simple:

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x), \quad V(x) = \begin{cases} 0, & 0 \leq x \leq a \\ \infty, & \text{otherwise} \end{cases}$$

The eigenfunctions are found by requiring the wavefunction to vanish at $x = 0$ and $x = a$, the endpoints of the well. An important subtlety arises here: usually we require the wavefunction *and* its derivatives to be continuous, but for the infinite square well, this is impossible. In general, when the potential is *infinite* at a boundary, the derivative of the wavefunction will *not* be continuous there – we'll see another example of this below, with the delta-function potential. The best we can do is to make the wavefunction continuous by vanishing at the endpoints, and let the derivative be what it is. Solving the differential equation $H\psi = E\psi$ gives the normalized wavefunctions and energy eigenvalues

$$\psi_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right), \quad E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}.$$

Unlike the harmonic oscillator, we start counting from $n = 1$, since $n = 0$ would give a wavefunction which is identically zero, hence not normalizable. So once again, the ground state has nonzero energy $E_1 = \pi^2\hbar^2/2ma^2$. We can almost derive the formula for the energies just by pure dimensional analysis: the parameters of the Hamiltonian are \hbar , m , and a , and the only combination with the units of energy is \hbar^2/ma^2 . We can't get the factors of π or 2 correct from this argument, but it does tell us that if we double the mass, we halve the ground state energy, and if the well expands by a factor of 2, then each energy changes by a factor of 1/4. This kind of reasoning *is* important on the GRE, so you should get familiar with it.

By the way, the infinite square well in three dimensions, defined by

$$V(x, y, z) = \begin{cases} 0, & 0 \leq x, y, z \leq a \\ \infty, & \text{otherwise} \end{cases}$$

behaves the same way as the three-dimensional harmonic oscillator: the wavefunctions are just products of the 1-dimensional versions, and the energies just add. Note that this is *not* the same as the infinite *spherical* well, which would have $V(x, y, z) = 0$ for $r < a$, where $r = \sqrt{x^2 + y^2 + z^2}$. This is an entirely different beast, which we will cover in Section 5.4 on 3-dimensional quantum mechanics.

5.3.2 Free particle

By definition, a free particle isn't acted upon by any forces, so there is no potential and the Hamiltonian is simply

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}.$$

Solving this system reduces to finding the eigenfunctions of d^2/dx^2 , which are easily checked to be exponentials, $e^{\pm ikx}$ and $e^{\pm \kappa x}$. If we adopt the convention that k and κ must both be real, then only the oscillating exponentials $e^{\pm ikx}$ are eigenfunctions with positive energy:

$$\psi(x) = e^{\pm ikx}, \quad E = \frac{\hbar^2 k^2}{2m}. \quad (5.27)$$

We gave this equation a number because it *is* worth memorizing. The energy shouldn't take too much work to memorize: remembering the de Broglie formula,

$$p = \hbar k, \quad (5.28)$$

(5.27) just says the energy is equal to $p^2/2m$, just as for a classical particle. But there are no boundary conditions anywhere to be found, so nothing restricts the value of k : the free particle can have *any momentum at all*. The form of the eigenfunctions is no more difficult: they represent *waves* (hence the name wavefunction) with constant modulus throughout all of space. This last statement implies that the energy eigenfunctions for the free particle are *not normalizable*.

From here, most books launch into a long story about Fourier transforms, wave packets, and such, but we just list a few salient points:

- We can construct a normalizable wavefunction by forming a continuous superposition of wavefunctions $\psi(x)$ with different values of k . The more values of k we throw in, the more possible values of momentum we could measure for the particle. It's not important for the GRE to know how to do this superposition, just to know it can be done in principle. The resulting wave function is called a *wave packet*. In fact, by a clever choice of coefficients, we can construct a *minimum-uncertainty wave packet*, which will of course be a Gaussian in x .

- The non-normalizability of the energy eigenstates (which are, incidentally, momentum eigenstates as well) just says there is no such thing as a particle with a perfectly defined value of momentum. This makes sense in the context of the uncertainty principle: the uncertainty in position would have to be infinite.
- The same story will hold for positive-energy solutions of an arbitrary Hamiltonian, wherever the potential is zero: these are called *scattering states*. The eigenfunctions will be oscillating exponentials, and while we could form wave packets to make the whole thing normalizable, this is rarely necessary in practice. Scattering problems require their own tricks of the trade and will be treated below.
- The formula for the energy can be read as a *dispersion relation* for a free quantum particle. Einstein's relation

$$E = \hbar\omega \quad (5.29)$$

implies that $\omega(k) = \hbar k^2 / 2m$, so $\omega(k)$ is quadratic in k . This should be contrasted with the case of a classical wave, which has $\omega = ck$ where c is the wave velocity.

5.3.3 Delta-function

Recall that a delta-function $\delta(x)$ is zero everywhere except at $x = 0$, where the delta-function is infinite. So if we let $V(x) = -A\delta(x)$ (a delta-function potential well), the Hamiltonian we end up with,

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} - A\delta(x),$$

is the same as the free-particle Hamiltonian, *except* at the single point $x = 0$. The fact that the potential is infinite there shouldn't scare you: we've already dealt with an infinite potential in the infinite square well above. It just means we have to be careful about the boundary conditions for $d\psi/dx$.

Exploiting the similarity with the free particle, the wavefunction will be an exponential to the left and to the right. Whether we get an oscillatory exponential $e^{\pm ikx}$ or a growing/decaying exponential $e^{\pm \kappa x}$ depends on whether we want to consider positive or negative energy solutions; in other words, scattering states or bound states. Here we consider bound states. The wavefunctions ψ_- on the left of the delta-function and ψ_+ on the right must decay at $x = \pm\infty$, so we must have $\psi_- \propto e^{\kappa x}$ and $\psi_+ \propto e^{-\kappa x}$. (It's the same value of κ for both because both pieces must be energy eigenfunctions with the same eigenvalue.) Now the crucial part: κ is determined by the boundary conditions enforced by the delta-function. To find these boundary conditions, we use the trick of integrating the Schrodinger equation $H\psi = E\psi$ on an infinitesimal interval $(-\epsilon, \epsilon)$ about $x = 0$:

$$\int_{-\epsilon}^{\epsilon} \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) \right) dx - A \int_{-\epsilon}^{\epsilon} \delta(x) \psi(x) dx = E \int_{-\epsilon}^{\epsilon} \psi(x) dx$$

Now take $\epsilon \rightarrow 0$. The term on the RHS vanishes, because ψ is continuous and we're integrating it over an interval whose size goes to zero. The LHS is more interesting:

$$\int_{-\epsilon}^{\epsilon} \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) \right) dx - A \int_{-\epsilon}^{\epsilon} \delta(x) \psi(x) dx = -\frac{\hbar^2}{2m} \left(\frac{d\psi}{dx} \right) \Big|_{-\epsilon}^{\epsilon} - A\psi(0),$$

where we have used the fact that the delta-function integrates to 1 over any interval containing zero. The first term measures the discontinuity in $d\psi/dx$ about $x = 0$, so we can solve for κ in terms of A and $\psi(0)$. Rather than do this, though, we will once again point out that κ is essentially determined by dimensional analysis. This time our dimensional parameters are \hbar and m , as usual, and the constant A , which has *dimensions of energy × length*. This follows from the fact that $\delta(x)$ has dimensions of 1/length, since it integrates to a pure number. The only combination of these units with dimensions of 1/length is mA/\hbar^2 , and indeed this is correct even up to numerical factors:

$$\psi(x) = \frac{\sqrt{mA}}{\hbar} e^{-mA|x|/\hbar^2}, \quad E = -\frac{mA^2}{2\hbar^2}.$$

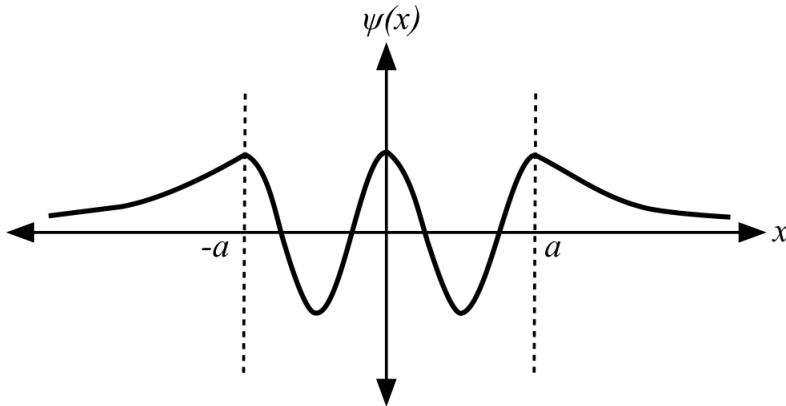
We could also get E (up to the factor of 1/2) from an identical dimensional analysis argument. As usual, it's useless to memorize the wavefunction and the energy; what matters is the method. An upshot of this analysis is *the delta-function potential admits only one bound state*, with energy and wavefunction given above.

5.3.4 Finite square well

The finite square well is similar to the infinite square well, except the potential well has finite depth. For what follows it will be convenient to center the well at $x = 0$, so the Hamiltonian is as follows:

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x), \quad V(x) = \begin{cases} -V_0, & -a \leq x \leq a \\ 0, & \text{otherwise} \end{cases}$$

We'll consider bound states, which have $E < 0$. We will exploit the fact that $V(x)$ is even, so ψ can be chosen to have definite parity; this means we only have to find the wavefunction for $x < 0$, and the rest of it will be determined by $\psi(x) = \psi(-x)$ or $\psi(x) = -\psi(-x)$. Outside the well, where $V = 0$, the solutions are as for the free particle: the normalizable one is $e^{\kappa x}$. Inside the well, we are solving the differential equation $-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi - V_0 \psi = E \psi$, and by moving V_0 to the right-hand side we get the same equation as for the free particle. However, since the minimum of the potential is $-V_0$, we must have $E > -V_0$, and $E + V_0 > 0$. So instead of being decaying exponentials, the solutions should be oscillating sines and cosines. The wavefunction then looks as follows:



This is essentially all you need to know about the finite square well. The constants k and κ , and from them the energies, are determined by solving a transcendental equation arising from the boundary conditions, and this is way beyond the level of stuff you're expected to do in two minutes on the GRE. One final piece of trivia: since the potential is even, the ground state is even. As the well gets shallower and shallower, the excited states disappear one by one, until all that is left is a single bound state, which is even.

5.3.5 Scattering states: reflection and transmission

The delta-function and the finite square well potentials share the feature that they are both *localized*: the potential is zero for $x \ll 0$, becomes nonzero in some small region, and is then zero again for $x \gg 0$. This is the setup for a scattering problem, where something (the *incident wave*) comes in from the left, interacts with the potential, and then separates into two parts: the *reflected wave*, which travels back to the left, and the *transmitted wave*, which goes through the potential and travels to the right. Following the convention that e^{ikx} with $k > 0$ represents a plane wave traveling to the right, the wavefunction for a particle incident from the left on a generic potential localized to $|x| < a$ can be written as:

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx}, & x \leq -a \\ \text{something,} & -a \leq x \leq a \\ Ce^{ikx}, & x \geq a \end{cases}$$

Here, A is the amplitude of the incident wave, B is the amplitude of the reflected wave, and C is the amplitude of the transmitted wave. Determining the ratios of these amplitudes as a function of k is well beyond what you're expected to know for the GRE, but the following qualitative knowledge is important:

- The behavior of the wavefunction in the region $|x| < a$ depends on the energy and the height of the potential. For example, in a square *well*, the wavefunction is sinusoidal, but in a square *barrier* of height $+V_0$, if $0 < E < V_0$, the wavefunction will decay exponentially inside the barrier. This is the phenomenon of *tunneling*: a classical

particle wouldn't have enough energy to get over the barrier, but a quantum particle can.

- The delta-function potential has the curious property that the reflection and transmission probabilities are the *same* for a delta-function well ($V(x) = -A\delta(x)$) and a delta-function barrier ($V(x) = A\delta(x)$).
- The probabilities of reflection and transmission go like the square of the wavefunction:

$$R = \frac{|B|^2}{|A|^2}, \quad T = \frac{|C|^2}{|A|^2}.$$

Conservation of probability requires $R + T = 1$.

One simple scattering problem whose exact solution *did* appear on a recent test is that of a step potential,

$$V(x) = \begin{cases} 0, & x \leq 0 \\ V_0, & x \geq 0 \end{cases}$$

Rather than derive the solution here, we'll illustrate how this setup might appear on the test in the problems.

5.3.6 Problems

1. A particle of mass m is in the ground state of an infinite square well of width L . A second particle of mass $2m$ is in the ground state of another infinite square well, with width L' . What is L'/L such that the two particles have identical energies?
 - $1/2$
 - $1/\sqrt{2}$
 - 1
 - $\sqrt{2}$
 - 2
2. Which of the following is true of the wavefunction of a particle in an energy eigenstate of the infinite square well?
 - I. It vanishes at the boundaries of the well.
 - II. It is discontinuous at the boundaries of the well.
 - III. Its derivative is discontinuous at the boundaries of the well.
 - I only
 - II only
 - I and II

- (D) I and III
 (E) II and III
3. A free particle of mass m is in a momentum eigenstate $|p\rangle$. What is the uncertainty on a measurement of its energy?
- (A) zero
 (B) infinity
 (C) $p^2/2m$
 (D) p
 (E) Cannot be determined from the information given
4. A free particle has the wavefunction $\sin(kx)$. The particle has
- I. A definite value of position
 - II. A definite value of momentum
 - III. A definite value of energy
- (A) I only
 (B) II only
 (C) III only
 (D) I and II
 (E) II and III
5. A particle of mass m and energy E is incident on a finite square barrier $V(x) = V_0$ for $0 < x < a$, where $E > V_0$. At $x = a/2$, what is the particle's de Broglie wavelength?
- (A) $\frac{h}{\sqrt{2m(E - V_0)}}$
 (B) $\frac{\hbar}{\sqrt{2m(E - V_0)}}$
 (C) $\frac{h}{\sqrt{2m(V_0 - E)}}$
 (D) $\frac{m\hbar}{\sqrt{E - V_0}}$
 (E) $\frac{2\pi mh}{E - V_0}$

6. A particle of mass m and energy E is incident from the left on a step potential,

$$V(x) = \begin{cases} 0, & x \leq 0 \\ V_0, & x \geq 0, \end{cases}$$

where $E > V_0$. The wavefunction in the region $x \leq 0$ is $Ae^{ik_L x} + Be^{-ik_L x}$, and the wavefunction in the region $x > 0$ is $Ce^{ik_R x}$. Which of the following gives the transmission probability for the particle to be found in the region $x > 0$?

- (A) 0
- (B) 1
- (C) $\frac{k_L}{k_R}$
- (D) $\left(\frac{k_L - k_R}{k_L + k_R}\right)^2$
- (E) $\frac{4k_L k_R}{(k_L + k_R)^2}$

5.4 Three dimensions

The generalization from one dimension to three dimensions is really quite simple. In three dimensions, the momentum operator is a vector: $\hat{\mathbf{p}} = -i\hbar\nabla$. In Cartesian components, $\hat{p}_x = -i\hbar\partial/\partial x$, $\hat{p}_y = -i\hbar\partial/\partial y$, $\hat{p}_z = -i\hbar\partial/\partial z$. The position operator generalizes similarly: $\hat{x} = x$, $\hat{y} = y$, and $\hat{z} = z$. So a general Hamiltonian in three dimensions is

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \quad (5.30)$$

where ∇^2 is the three-dimensional Laplacian, $\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$. The final ingredient is the extension of the canonical commutation relations, and all there is to remember is that *different coordinates commute with each other*. So we have

$$[\hat{x}, \hat{p}_x] = i\hbar, \quad [\hat{y}, \hat{p}_y] = i\hbar, \quad [\hat{z}, \hat{p}_z] = i\hbar, \quad (5.31)$$

but

$$[\hat{x}, \hat{y}] = 0, \quad [\hat{x}, \hat{p}_y] = 0, \quad [\hat{x}, \hat{p}_z] = 0, \dots \quad (5.32)$$

So we can feel free to form observables such as $\hat{x}\hat{y}^2\hat{p}_z$ without worrying about ambiguities coming from nonzero commutators.

5.4.1 Radial equation and effective potential

Suppose the potential depends only on the distance from the origin: $V = V(r)$. Then, just as in classical mechanics, we can separate out the angular and radial parts of the problem (Section 1.6). In classical mechanics, we used conservation of angular momentum to reduce the dynamics to a one-dimensional problem involving an effective potential. A very similar thing happens in quantum mechanics, but the technical details are different: we will use the technique of *separation of variables* to obtain a radial equation involving an effective potential, and an angular equation whose solutions will be treated in Section 5.4.2.

For a central potential $V = V(r)$, it is most convenient to work in spherical coordinates. From the general equation (5.30), this will involve the Laplacian in spherical coordinates. No doubt you've seen the exact form of this object before: it's quite complicated and totally unnecessary to memorize, but what's important is that it can be separated into a radial piece and an angular piece,

$$\nabla^2 = \nabla_r^2 + \frac{1}{r^2} \nabla_{\theta,\phi}^2.$$

If we then assume that the wavefunction is a product of a radial part and an angular part, $\psi(\mathbf{r}) = R(r)Y(\theta, \phi)$, we can use the usual technique of separation of variables to get separate equations for R and Y . For completeness, the radial equation is

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

where $u(r) = rR(r)$ and $l(l+1)$ is a separation constant related to the eigenvalue of Y under the operator $\nabla_{\theta,\phi}^2$. So just as in classical mechanics, we get an effective potential, equal to the original potential plus a piece which depends on angular momentum (as will be seen below). Note that because of this effective potential term, the infinite spherical well has rather different eigenfunctions for $l \neq 0$ than the infinite square well in three dimensions.

Because we've separated the wavefunction into a radial and an angular piece, it is conventional to normalize each piece separately:

$$\int_0^\infty |R(r)|^2 r^2 dr = 1, \quad \int_0^{2\pi} \int_0^\pi |Y(\theta, \phi)|^2 \sin \theta d\theta d\phi = 1 \quad (5.33)$$

Notice how the spherical volume element $dV = r^2 \sin \theta dr d\theta d\phi$ gets split up between the two normalization integrals.

5.4.2 Angular momentum and spherical harmonics

The story of how angular momentum relates to symmetries in quantum mechanics is a subtle and beautiful one, which for better or for worse has no place on the GRE. This section will simply be a review of the relevant rules for dealing with systems involving angular momentum.

Just as angular momentum was defined in classical mechanics as $\mathbf{L} = \mathbf{r} \times \mathbf{p}$, the quantum operator for orbital angular momentum $\hat{\mathbf{L}}$ is defined similarly: $\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$. In components,

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y \quad (5.34)$$

$$\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z \quad (5.35)$$

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x. \quad (5.36)$$

By using the commutation relations for $\hat{\mathbf{r}}$ and $\hat{\mathbf{p}}$, we get the following commutation relations for $\hat{\mathbf{L}}$:

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z, \text{ and cyclic permutations of } x, y, z. \quad (5.37)$$

You *may* be given these relations on the GRE (one recent test gave them, another did not), so it's a good idea to be safe and memorize them anyway.

Another useful operator is the dot product of $\hat{\mathbf{L}}$ with itself, known as the *total (orbital) angular momentum* \hat{L}^2 :

$$\hat{L}^2 := \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \quad (5.38)$$

Most importantly, \hat{L}^2 commutes with all the other \hat{L}_i (exercise: check this!). So we can find simultaneous eigenfunctions of \hat{L}^2 and one of the \hat{L}_i , conventionally chosen to be \hat{L}_z . In spherical coordinates, these operators take a familiar form:

$$\hat{L}^2 = -\hbar^2\nabla_{\theta,\phi}^2$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$

where $\nabla_{\theta,\phi}^2$ is the angular part of the Laplacian introduced in Section 5.4.1.

The simultaneous eigenfunctions of these two operators are the *spherical harmonics*, $Y_l^m(\theta, \phi)$ where θ and ϕ are the usual angles in a spherical coordinate system. Despite the complicated notation, they are just certain functions of θ and ϕ , whose explicit forms you will probably never need for the GRE. Their eigenvalues, labeled by the orbital quantum number l and the azimuthal quantum number m , are important and are given as follows:

$$\hat{L}_z Y_l^m = m\hbar Y_l^m \quad (5.39)$$

$$\hat{L}^2 Y_l^m = l(l+1)\hbar^2 Y_l^m \quad (5.40)$$

Here, m and l are integers, with $l \geq 0$. However, l and m are not totally independent: given a value of l , the corresponding allowed values of m are

$$m = l, l-1, l-2, \dots, -l. \quad (5.41)$$

These restrictions are intuitively obvious: l is the quantum-mechanical analogue of the length of the angular momentum vector, which must be nonnegative, and m is one component of that vector, which can't exceed the total length of the vector. Note that these intuitive reasons are *not* strictly true, since quantum operators behave nothing like classical vectors, but they are useful mnemonics for remembering the correct relations.

Some important facts about (normalized) spherical harmonics:

- They are orthonormal:

$$\int_0^{2\pi} \int_0^\pi (Y_l^m(\theta, \phi))^* Y_{l'}^{m'}(\theta, \phi) \sin \theta d\theta d\phi = \delta_{ll'} \delta_{mm'}, \quad (5.42)$$

which follows from the fact that they are eigenfunctions for the Hermitian operators \hat{L}_z and \hat{L}^2 with different eigenvalues.

- The ϕ dependence of Y_l^m is always of the form $e^{im\phi}$. The θ dependence is more complicated, being contained in the so-called Legendre polynomials, which will always be given to you on the test should you need them.
- Y_0^0 is simply a constant, with no θ or ϕ dependence – again there’s no need to memorize its value (although it’s easy to work out), since you will always be given the functional form on the test should you need it.
- If the angular part of a particle’s wavefunction is exactly equal to one of the spherical harmonics Y_l^m , the particle has a *definite value* of total angular momentum l and z -component of angular momentum m . More generally, the spherical harmonics are a *complete* set of functions, which means that the angular part of any wavefunction on the sphere can be expressed as a linear combination of them. So to answer the question “what is the probability a system will be found with total angular momentum l and z -component of angular momentum m ,” we must decompose the wavefunction into spherical harmonics and compute the probability from the coefficients as discussed in Section 5.1. This just requires a lot of ugly integrals, so on the GRE, you will most likely be given the decomposition into spherical harmonics, or will be asked a question about a system with definite values of l and m .

5.4.3 The hydrogen atom

The hydrogen atom receives so much attention in quantum mechanics texts because it is one of the very few exactly solvable problems which accurately represents a realistic system. Some of this attention is also for historical reasons: the birth of quantum mechanics began with the Bohr formula for the hydrogen energy levels, which despite being derived using an lucky combination of classical mechanics and blind intuition, turned out to be correct. Since it is treated in such great detail, it’s also a favorite on the GRE.

The potential energy for the hydrogen atom is the Coulomb potential for an electron of charge $-e$ and a proton of charge $+e$, so the Hamiltonian is

$$H = -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}. \quad (5.43)$$

Note the μ in the denominator of the kinetic term, rather than m_e : this is because, just as in classical mechanics, we must use the *reduced mass* $\mu = m_1 m_2 / (m_1 + m_2)$ to reduce the two-body problem of electron and proton to an equivalent one-body problem. In the case

of hydrogen, μ is very close to m_e because the proton is so much heavier than the electron. Nevertheless, the reduced mass is what shows up in all the formulas for the energies and the wavefunctions, and by writing μ we can use (5.43) as a model for all hydrogen-*like* systems (for example, positronium, with a positron replacing the proton), except with different values of the reduced mass. This applies to all the formulas in this section.

From here, it is simply several pages of algebra to derive the energies and the wavefunctions from the radial equation. This is done in all quantum mechanics texts, so instead we will get the answer by dimensional analysis. The dimensionful parameters in this problem are μ , \hbar , and the combination $e^2/4\pi\epsilon_0$ which has units of energy \times length. As usual, there is only one way we can combine these to get a length, which is so special that it gets its own name, the *Bohr radius*:

$$a = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2}. \quad (5.44)$$

(Sometimes this is denoted a_0 rather than a .) Because of the factor of μ , there is a different “Bohr radius” for each hydrogen-like atom. A favorite GRE question asks how the Bohr radius of positronium differs from that of hydrogen: because $\mu = m_e/2$ for positronium and $\mu \approx m_e$ for hydrogen, the Bohr radius of positronium is double that of hydrogen. You could play the same game with muonium, where a muon (essentially a heavy electron) replaces the electron, or with any number of other fundamental particles.

Because of the electrostatic attraction between the electron and the proton, intuition suggests that the wavefunction of the electron should be sharply peaked near the origin. Since the only length in the problem is a , a reasonable guess for the (un-normalized) ground state wavefunction is

$$\psi_1(r) \propto e^{-r/a}, \quad (5.45)$$

and indeed, this is correct. As for the ground state energy, it has the same form as for the infinite square well of width a (the other standard Hamiltonian with a given length scale), but the numerical factors are different:

$$-E_1 = \frac{\hbar^2}{2\mu a^2} = \frac{\mu e^4}{2(4\pi\epsilon_0)^2\hbar^2} = 13.6 \text{ eV for hydrogen.} \quad (5.46)$$

(The minus sign is there because all energies are measured relative to $V(\infty) = 0$.) The importance of memorizing this single number, 13.6 eV, cannot be overemphasized. Not only does it tell you that the energy scale of atomic processes is of the order of 1 eV, it can be used to derive approximate ionization energies for hydrogen-like atoms, and its numerical value is often a GRE question in and of itself. In fact, both expressions for E_1 are worth memorizing; luckily, this is probably the most complicated formula you’ll have to memorize for the test. Again, the numerical factors are not important but the dependence on μ is: the second formula, containing all explicit factors of μ , shows that the ground state energy is proportional to the reduced mass. So in positronium, halving the reduced mass compared to hydrogen gives a binding energy which is half that of hydrogen. Another trap to beware of is the e^4 in the second formula for E_1 : this does *not* mean that a helium ion (an electron orbiting a nucleus of charge $2e$) has ground state energy $2^4 \times E_1$. Rather, $e^4 = (e^2)^2$ is the

square of the e^2 appearing in the Coulomb potential, which is the product of the electron charge and the nuclear charge. For a nucleus of charge $2e$, the Coulomb potential is stronger by a factor of 2, so E_1 is greater by a factor of only $2^2 = 4$.

The last thing to remember is that the energies decrease like $1/n^2$:

$$-E_n = \frac{\hbar^2}{2\mu a^2} \frac{1}{n^2}, \quad n = 1, 2, 3, \dots, \quad (5.47)$$

which gives the famous Rydberg formula for the frequency of light emitted in hydrogen transitions,

$$f \propto \frac{1}{n_f^2} - \frac{1}{n_i^2}.$$

You might have noticed that the formula for E_n doesn't depend on the angular quantum numbers l and m : this is a special property of the Coulomb potential, and this degeneracy will go away when we include various small effects which we have neglected. As this is more properly an atomic physics topic, we will treat it in Section 5.7 at the end of this chapter.

We finish with some important trivia about the hydrogen atom:

- The energies don't depend on l or m , but of course the wavefunctions do, with the angular dependence carried in the spherical harmonics. The radial part of the wavefunction is determined by so-called *Laguerre polynomials*, which depend on l but not m .
- The wavefunction is *zero* at the origin for states with $l \neq 0$. However, this does *not* mean that states with zero angular momentum can be found at the origin, because the probability density $|\Psi(r)|^2 dV$ contains the volume factor $dV = r^2 \sin \theta dr d\theta d\phi$ in spherical coordinates, which kills any wavefunction at $r = 0$. It just means that states with zero angular momentum have *the highest probability* of being found near the origin. In particular, the state $n = 1$ has the highest probability of all the states of being found near $r = 0$.
- If we include the speed of light c as a dimensionful parameter, we can form a *dimensionless* constant called the *fine-structure constant*,

$$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \approx 1/137. \quad (5.48)$$

Note that this does not involve the mass μ : it just characterizes the general quantum-mechanical strength of electromagnetic interactions. Perturbations to the hydrogen atom are usually expressed in terms of powers of α , and the reason they can be treated as perturbations is the fortunate situation $\alpha \ll 1$.

5.4.4 Problems

1. A free particle in three dimensions has the normalized radial wavefunction

$$\psi(r) = \begin{cases} 0, & 0 \leq r \leq a \\ \sqrt{3a^3}/r^3, & r > a. \end{cases}$$

What is the expectation value of r in this state?

- (A) a
- (B) $3a/2$
- (C) $a\sqrt{3}$
- (D) $3a$
- (E) ∞

2. A spin-zero particle has angular wavefunction

$$\frac{1}{\sqrt{2}}(Y_3^2(\theta, \phi) + Y_2^1(\theta, \phi)),$$

where $Y_l^m(\theta, \phi)$ are the normalized spherical harmonics. What is the expectation value of the total spin L^2 ?

- (A) $2\hbar^2$
- (B) $5\hbar^2/2$
- (C) $3\hbar^2$
- (D) $9\hbar^2$
- (E) $18\hbar^2$

3. Let $\hat{\mathbf{J}}$ be a quantum-mechanical angular momentum operator. What is the value of the commutator $[[\hat{J}_x, \hat{J}_y], [\hat{J}_y, \hat{J}_z]]$?

- (A) 0
- (B) $i\hbar\hat{J}_x$
- (C) $-i\hbar\hat{J}_x$
- (D) $i\hbar^3\hat{J}_y$
- (E) $-i\hbar^3\hat{J}_y$

4. The radiation emitted by the first excited state of hydrogen as it drops to the ground state is called the Lyman alpha line, and has wavelength 122 nm. An excited hydrogen atom is observed radiating light at wavelength 488 nm. This most likely results from the transition

- (A) $n = 2$ to $n = 1$
 (B) $n = 3$ to $n = 1$
 (C) $n = 3$ to $n = 2$
 (D) $n = 4$ to $n = 1$
 (E) $n = 4$ to $n = 2$
5. It is theoretically possible for an electron and a neutron to form a bound state where the binding force is due to *gravity*, rather than electrostatic attraction. Let G_N denote Newton's constant and m_e and m_n denote the mass of the electron and neutron, respectively. Under the approximation $m_e \ll m_n$, which of the following gives the "Bohr radius" of the gravitationally bound electron?
- (A) $\frac{\hbar^2}{G_N m_e^2 m_n}$
 (B) $\frac{\hbar^2}{G_N m_e m_n}$
 (C) $\frac{\hbar^2}{G_N m_e m_n^2}$
 (D) $\frac{\hbar^2 G_N}{m_e m_n}$
 (E) $\frac{\hbar^2 G_N m_e}{m_n^2}$
6. Positronium is a bound state of an electron and a positron. What is the energy of the photon emitted in transitions of positronium from the first excited state to the ground state?
- (A) 1.7 eV
 (B) 5.1 eV
 (C) 6.8 eV
 (D) 13.6 eV
 (E) 20.4 eV
7. A new hydrogen-like atom is discovered where the particle orbiting the proton has mass $2m_e$ and charge $2e$, where m_e and e are the charge and mass of the electron, respectively. What is the binding energy of this atom, in terms of the binding energy E of ordinary hydrogen?
- (A) $E/2$
 (B) E

- (C) $2E$
- (D) $4E$
- (E) $8E$

5.5 Spin

It is an observational fact that all quantum particles carry an “intrinsic” quantum number known as *spin*, whose operators \hat{S}_x , \hat{S}_y , and \hat{S}_z obey the same commutation relations as the angular momentum operators. In contrast to total orbital angular momentum, whose value depends on what state the particle is in, a particle’s total spin is a characteristic of the particle itself and never changes. Spin is usually denoted s , where s plays the same role as l in the nomenclature of angular momentum: for example, a particle with $s = 1/2$ has \hat{S}^2 (the dot product of $\hat{\mathbf{S}}$ with itself) eigenvalue of $s(s+1)\hbar^2 = \frac{3}{4}\hbar^2$ always and forever, and we say the particle has *spin-1/2*.

In contrast to the orbital angular momentum l , which must be an integer, s can be *either an integer or half-integer*. Other than that, all the same rules still apply: the z -component of spin, denoted m_s , can still range from $-s$ to s in integer steps, and can change depending on what state the particle is in. But since s is always fixed, there are always the same number of possible m_s for a given particle, and the Hilbert space has dimension $2s+1$. For spin-1/2, we have only two states: spin-up, with $m_s = +1/2$, denoted by $|\uparrow\rangle$, and spin-down, with $m_s = -1/2$, denoted by $|\downarrow\rangle$. There is no such convenient notation for spin $s = 1$ and higher, but for the purposes of the GRE, pretty much all you have to know is spin-1/2.

5.5.1 Spin-1/2

Because the Hilbert space is finite-dimensional, the spin operators, instead of being differential operators, are just matrices. The only ones you have to be familiar with are those for spin-1/2, known as the Pauli matrices: $\hat{S}_x = \frac{\hbar}{2}\sigma_x$, $\hat{S}_y = \frac{\hbar}{2}\sigma_y$, and $\hat{S}_z = \frac{\hbar}{2}\sigma_z$, where

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

Notice that the σ ’s are Hermitian matrices, so the corresponding operators are Hermitian, as observables should be. As with the angular momentum commutation relations, it’s not necessary to memorize these matrices because they will be given to you on the test if you need them, but it pays to be intimately familiar with them. Since σ_z is diagonal, the vectors corresponding to $|\uparrow\rangle$ and $|\downarrow\rangle$ are particularly simple: $|\uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $|\downarrow\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$. You can check that these have the correct eigenvalues under \hat{S}_z , namely $+\hbar/2$ and $-\hbar/2$, respectively. In the case of spin-1/2, it’s particularly simple to verify that \hat{S}^2 commutes with all the other spin operators, since \hat{S}^2 turns out to be proportional to the identity matrix.

With a finite-dimensional Hilbert space, we have to slightly modify our rules for computing things like expectation values. Luckily, we have already taken care of most of this

in Section 5.1.2. Instead of integrating to compute an inner product, we just take a dot product, and the action of Hermitian observables is by matrix multiplication. For example, the expectation value of \hat{S}_x in the state $|\uparrow\rangle$ is computed as follows:

$$\langle \uparrow | \hat{S}_x | \uparrow \rangle = \frac{\hbar}{2} \left[(1 \ 0) \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \right] = \frac{\hbar}{2} \left[(1 \ 0) \begin{pmatrix} 0 \\ 1 \end{pmatrix} \right] = 0.$$

Another common question asks you the probability of measuring a particular value of \hat{S}_z for a given state. If the normalized wavefunction is $\Psi = \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$ (in this context, normalized means $|\alpha|^2 + |\beta|^2 = 1$), then the probability of measuring $\hat{S}_z = +\hbar/2$ is $|\alpha|^2$, and the probability of measuring $-\hbar/2$ is $|\beta|^2$. To see why this is true, write the wavefunction in Dirac notation,

$$\Psi = \alpha \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \beta \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \alpha |\uparrow\rangle + \beta |\downarrow\rangle,$$

which is just the expansion of a vector in its basis components. Now we can just apply the usual rules of quantum mechanics.

To avoid doing repeated calculations, it's extremely useful to remember the eigenvectors of \hat{S}_x and \hat{S}_y . Instead of doing the usual steps of finding the characteristic equation of the matrix, finding the eigenvalues, and then solving for the eigenvectors, we can take a convenient shortcut. The possible values of m_s are $\pm\hbar/2$ no matter what basis we happen to be working in, since that's what it means for a particle to have spin-1/2. We chose the \hat{S}_z basis because it was conventional, but it had no physical meaning. Thus, the eigenvalues of \hat{S}_x and \hat{S}_y must *also* be $\pm\hbar/2$, and thus the eigenvalues of the Pauli matrices σ_i are all ± 1 . Now, we can figure out the eigenvectors almost just by staring at the matrices:

$$|\uparrow\rangle_x = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \quad |\downarrow\rangle_x = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \quad (5.49)$$

$$|\uparrow\rangle_y = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \end{pmatrix}, \quad |\downarrow\rangle_y = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \end{pmatrix} \quad (5.50)$$

In the ket notation, we would say $|\uparrow\rangle_y = \frac{1}{\sqrt{2}} (|\uparrow\rangle + i|\downarrow\rangle)$, and so on. These are simple enough to memorize (just remember an extra factor of i for the y vectors), but by remembering what the eigenvalues are, it's at most a 1-minute derivation if you forget. In any problem where you'll need this information, finding the eigenvectors is 90% of the work, so this would be a minute well spent.

One final detail, which you will likely not have to know for the GRE but will be important for what follows here: there is a spin analogue to the raising and lowering operators of the harmonic oscillator. The linear combinations

$$\hat{S}_+ := \hat{S}_x + i\hat{S}_y, \quad \hat{S}_- := \hat{S}_x - i\hat{S}_y \quad (5.51)$$

are called the spin raising and lowering operators. You can show they deserve their names by acting on $|\uparrow\rangle$ and $|\downarrow\rangle$ with them. You should find

$$\hat{S}_+ |\uparrow\rangle = 0, \quad \hat{S}_- |\uparrow\rangle = \hbar |\downarrow\rangle. \quad (5.52)$$

and

$$\hat{S}_+ |\downarrow\rangle = \hbar |\uparrow\rangle, \quad \hat{S}_- |\downarrow\rangle = 0. \quad (5.53)$$

The spin raising operator \hat{S}_+ turns a down spin into an up spin, but kills the up spin vector. Likewise, the lowering operator \hat{S}_- turns an up spin into a down spin, and kills the down spin.

These relations generalize to higher spin: what the lowering operator does, in general, is preserve the total spin s but reduce the value of m_s by one unit of \hbar . When acting on the lowest possible m_s , it annihilates that state. The raising operator does just the opposite. Beware, though: just like their harmonic oscillator counterparts, the states created by raising and lowering operators are not automatically normalized!

5.5.2 Spin and the wavefunction

The next step is to detail how spin fits into the more general picture of a particle's wavefunction. The simplest way to think about it is that the total wavefunction is always (a linear combination of) a *product* of a spatial wavefunction and a spin wavefunction. For systems of identical particles, the symmetry properties of both pieces of the wavefunction can have important effects, as we will see in much more detail in Section 5.5.4 below, so keeping track of both pieces is crucial. For example, a spin-1/2 particle in the ground state of the infinite square well and $m_s = +1/2$ would have the total wavefunction

$$\Psi(x, t) = \left[\sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right) \otimes \begin{pmatrix} 1 \\ 0 \end{pmatrix} \right] e^{-iE_1 t/\hbar}$$

The funny symbol \otimes stands for a tensor product, and is there to remind you that the spin part and spatial part are separate entities which never get mixed. The usual position and momentum operators act on the spatial part, but don't touch the spin part; likewise, the spin operators act on the spin part but leave the spatial part alone. In practice, this means that *spin operators always commute with spatial operators*: in particular, $[\hat{\mathbf{L}}, \hat{\mathbf{S}}] = 0$. Going back to our example,

$$\begin{aligned} \hat{p} \Psi(x, t) &= \left[-i\hbar \frac{\pi}{a} \sqrt{\frac{2}{a}} \cos\left(\frac{\pi x}{a}\right) \otimes \begin{pmatrix} 1 \\ 0 \end{pmatrix} \right] e^{-iE_1 t/\hbar} \\ \hat{S}_y \Psi(x, t) &= \left[\frac{\hbar}{2} \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right) \otimes \begin{pmatrix} 0 \\ i \end{pmatrix} \right] e^{-iE_1 t/\hbar} \end{aligned}$$

Notice that we can pull the constants which multiply either piece out to the front of the whole wavefunction: that's all the tensor product means. It's just a way of writing a product of two completely independent pieces where constants can be absorbed into either one. This means the we are free to normalize each piece separately, which is always done in practice. Finally, note that if a particle has spin-0, the spin part of its wavefunction just doesn't exist: the system is completely described by just a spatial wavefunction.

One important caveat to the preceding discussion is that the Hamiltonian *can* contain both spatial operators and spin operators. Indeed, this is exactly what happens when a quantum system is exposed to a magnetic field: a particle's spin makes it act like a magnetic dipole, and there is a corresponding term in the Hamiltonian representing the energy of a magnetic dipole in an external field. While it's true that the spatial and spin parts never get mixed up with each other, it's important to remember that the Hamiltonian can act on both pieces, and thus both pieces can contribute to the total energy of the system.

5.5.3 Adding spins

Suppose we have a particle of spin s and a particle of spin s' . The system of the two particles taken together also has a total spin, but it's *not* simply $s + s'$. In fact, that's just one of many possibilities. The possible spin states of the system are

$$\text{Spin } s \text{ and spin } s' : s_{\text{tot}} = s + s', s + s' - 1, s + s' - 2, \dots, |s - s'|. \quad (5.54)$$

In other words, we can get any spin between $|s - s'|$ and $s + s'$ in integer steps. Thankfully, m_s values *do* add,

$$m_{\text{tot}} = m_s + m'_{s'}, \quad (5.55)$$

which restricts the possibilities for s_{tot} . For instance, if you have a spin-1 particle with $m_s = +1$ and a spin-1/2 particle with $m_s = +1/2$, then $m_{\text{tot}} = +3/2$, and the system must be in the state with $s_{\text{tot}} = 3/2$. On the other hand, if the spin-1/2 particle had $m_s = -1/2$, then $m_{\text{tot}} = +1/2$ and *either* $s_{\text{tot}} = 3/2$ or $s_{\text{tot}} = 1/2$ are allowed. In fact, the system can be described as a linear combination of states with different values of s_{tot} .

The more common situation, though, is when we know the total spin and m_s value of the system, but *not* of the individual particles. The all-important application is to two spin-1/2 particles, so let's walk through that case in detail. The possible spins are $1/2 + 1/2 = 1$, or $1/2 - 1/2 = 0$. As described above, if both of the particles have their maximum value of m_s , then our job is easy: the system is in the state $s = 1, m_s = 1$. We denote this as follows:

$$s = 1, m = 1 : |\uparrow\rangle|\uparrow\rangle$$

Now, the *total* spin operator is $\hat{\mathbf{S}} = \hat{\mathbf{S}}^{(1)} + \hat{\mathbf{S}}^{(2)}$, where the superscripts 1 and 2 refer to particles 1 and 2. As with spin-1/2, we can form the total raising and lowering operators by just adding together the contributions for particles 1 and 2, with the understanding that the 1 operators only act on the first spin, and the 2 operators only act on the second. Using the relations (5.53), we can act on the state $|\uparrow\rangle|\uparrow\rangle$ with the lowering operator:

$$\hat{S}_- = (\hat{S}_-^{(1)} + \hat{S}_-^{(2)}) |\uparrow\rangle|\uparrow\rangle = \hbar(|\downarrow\rangle|\uparrow\rangle + |\uparrow\rangle|\downarrow\rangle).$$

By the rules for the action of the lowering operator, this must (after normalization) represent a state with $s = 1$ but one less unit of m_s :

$$s = 1, m = 0 : \frac{1}{\sqrt{2}} (|\downarrow\rangle|\uparrow\rangle + |\uparrow\rangle|\downarrow\rangle).$$

Finally, acting once more with the lowering operator, we obtain the state with $m = -1$:

$$s = 1, m = -1 : |\downarrow\rangle|\downarrow\rangle$$

This is precisely as expected, since we could have written down this state from the beginning: it has the minimum possible values of m_s for both particles, so it must have the largest of the available s values.

There is one state remaining, since we started with a Hilbert space of dimension 4 (2 states for particle 1 times 2 states for particle 2), and we only have three states so far. We know this state must have $s = 0$, and hence $m = 0$. Since m values add, it must be a linear combination of $|\uparrow\rangle|\downarrow\rangle$ and $|\downarrow\rangle|\uparrow\rangle$, and since it has a different eigenvalue for \hat{S}_z from the $s = 1, m = 0$ state, it must be orthogonal to that state. This uniquely fixes the remaining state to be

$$s = 0, m = 0 : \frac{1}{\sqrt{2}} (|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle). \quad (5.56)$$

This state is given its own name, the *singlet*, and it shows up everywhere. It's the unique combination of two spin-1/2 states with total spin zero, and it's also the only combination antisymmetric under the interchange of particles 1 and 2. The other three states, with $s = 1$, are called the *triplet* states, and they are symmetric under the interchange of 1 and 2.

Note that the way to add more than two spins is to add them in groups of two. For example, consider a system of three spin-1/2 particles. Adding the first two spins gives possible values of $s = 1$ and $s = 0$, and now adding the third spin gives possible values $s = 3/2, 1/2, 1/2$. Note the duplication of $s = 1/2$: one copy came from adding spin-1/2 to spin 1, and the second copy came from adding spin-1/2 to spin-0. Finally, this formalism applies not only to spins, but to any operators obeying the angular momentum commutation relations, most notably orbital angular momentum as discussed in Section 5.4.2. Perhaps the most important example of addition of angular momenta is in forming the total angular momentum of a system, $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$, where as usual $\hat{\mathbf{L}}$ is the orbital angular momentum operator and $\hat{\mathbf{S}}$ is the spin operator. For a given spin s and orbital angular momentum l , the possible eigenvalues for \hat{J}^2 and \hat{J}_z are then given by (5.54) and (5.55) with $s' = l$. You'll see several examples of this in the problems, both in this section and in Section 5.7.

5.5.4 Bosons and fermions

Particles with integer versus half-integer spin behave so radically differently that they are given their own names: integer spin particles are *bosons*, and half-integer spin particles are *fermions*. The reason for their difference in behavior only arises when we consider collections of these particles:

Under the interchange of two identical particles, boson wavefunctions are symmetric, and fermion wavefunctions are antisymmetric.

Note the caveat “identical!” This only applies to systems of three electrons, or five photons, not an electron and a proton: while the electron and proton are indeed both fermions, they

are not identical, so exchanging these particles need not transform the wavefunction in this manner. This means, for example, that if we have a collection of three identical bosons with coordinates x_1 , x_2 , and x_3 , the wavefunction of the system $\Psi(x_1, x_2, x_3)$ will obey

$$\Psi(x_1, x_2, x_3) = \Psi(x_1, x_3, x_2) = \Psi(x_2, x_1, x_3) = \dots$$

In other words, the wavefunction remains the same under any permutation of particles 1, 2, and 3: it is *totally symmetric*.

Fermions, on the other hand, pick up a minus sign under the interchange of particles: the wavefunction is *totally antisymmetric*. For a system of two identical fermions at x_1 and x_2 , the wavefunction $\Phi(x_1, x_2)$ satisfies

$$\Phi(x_1, x_2) = -\Phi(x_2, x_1)$$

For more than two particles, two consecutive swaps result in an overall plus sign, so one has to keep track of the so-called sign of the permutation, but this is more than you'll need for the exam. Remember that overall phase factors don't change the quantum state, so the interchange of fermions doesn't change the state of the system: this is a reflection of the fact that identical quantum particles are indistinguishable even in principle. However, the minus sign can result in interesting interference effects. More importantly, it restricts the possible states of multi-fermion systems, which is encapsulated in the Pauli exclusion principle:

No two identical fermions can occupy the same quantum state.

This follows from the antisymmetry of the wavefunction: if two fermions were in the same state $\psi(x)$, then the only way to make an antisymmetric combination out of $\psi(x_1)\psi(x_2)$ would be $\psi(x_1)\psi(x_2) - \psi(x_2)\psi(x_1) = 0$, and the whole wavefunction just vanishes.

The whole story becomes a little trickier when we include spin. Remember, the spin and spatial parts of the wavefunctions are independent, so for the *total* wavefunction to have a certain symmetry property, the symmetries of the spin part and the spatial part must combine in the correct way. Usually, this means both the spin and spatial parts have definite symmetry or antisymmetry.⁴ For a concrete example, consider the electrons in a helium atom. The two-electron wavefunction $\Psi(\mathbf{r}_1, \mathbf{r}_2) = \psi(\mathbf{r}_1, \mathbf{r}_2)\chi(\mathbf{s}_1, \mathbf{s}_2)$ must be antisymmetric overall, so we can either have a symmetric ψ and an antisymmetric χ , or an antisymmetric ψ and a symmetric χ . You'll finish this analysis in the problems below.

To conclude, we list two important facts relating spin and symmetry.

- When adding n identical spin-1/2 particles, the states with the highest value of l (namely $l = n/2$) are *always* symmetric. We saw this above for the case of two spin-1/2 particles: the triplet states were all symmetric. Continuing on, adding three spin-1/2 particles gives possible values $l = 3/2$ and $l = 1/2$, and all four states with $l = 3/2$ are symmetric under interchange of spins. On the other hand, the $l = 1/2$ states have mixed symmetry, neither symmetric nor antisymmetric.

⁴These are the only possibilities for a two-particle state. For three or more particles, there can be states of mixed symmetry, which can combine to give an overall symmetric or antisymmetric total wavefunction, but you won't have to worry about these on the GRE.

- All of the symmetry arguments apply to *subsystems* of identical particles. For example, there are six fermions in the ${}^4\text{He}$ atom: two protons, two neutrons, and two electrons. We are free to consider the symmetry or antisymmetry of just the identical electrons, as we did above, while ignoring the fermions in the nucleus. However, the total spin of the system will of course have to include contributions from all the fermions.

5.5.5 Problems

1. A spin-1/2 particle has the spin wavefunction $\chi = A \binom{1+i}{2}$ where A is a normalization constant. What is the expectation value of \hat{S}_z ?
 - $-\hbar/6$
 - $-\hbar/3$
 - $-\hbar/2$
 - $\hbar/2$
 - $\hbar/3$
2. A spin-1/2 particle is initially measured to have $S_z = \hbar/2$. A subsequent measurement of S_x returns $-\hbar/2$. If a third measurement is made, this time of S_z again, what is the probability the measurement returns $\hbar/2$?
 - 0
 - 1/4
 - 1/2
 - 3/4
 - 1
3. A meson is a bound state of a quark and an antiquark, both with spin 1/2. Which of the following is a possible value of *total* angular momentum j for a meson with orbital angular momentum $l = 2$?
 - $j = 0$
 - $j = 1$
 - $j = 2$
 - $j = 3$
 - I and II
 - I and III
 - II and IV

- (D) I, II, and III
 (E) II, III, and IV
4. A deuterium atom, consisting of a proton and neutron in the nucleus with a single orbital electron, is measured to have total angular momentum $j = 3/2$ and $m_j = 1/2$ in the ground state. Let $|\uparrow\rangle_p$ and $|\uparrow\rangle_n$ denote spin-up protons and neutrons, respectively, and $|\downarrow\rangle_p$ and $|\downarrow\rangle_n$ denote spin-down protons and neutrons. Assuming the nucleus has no orbital angular momentum, the spin state of the nucleus could be
- I. $\frac{1}{\sqrt{2}}(|\uparrow\rangle_p |\downarrow\rangle_n - |\downarrow\rangle_p |\uparrow\rangle_n)$
 - II. $|\uparrow\rangle_p |\uparrow\rangle_n$
 - III. $\frac{1}{\sqrt{2}}(|\uparrow\rangle_p |\downarrow\rangle_n + |\downarrow\rangle_p |\uparrow\rangle_n)$
 - IV. $|\downarrow\rangle_p |\downarrow\rangle_n$
- (A) I only
 (B) I and III
 (C) II and IV
 (D) II and III
 (E) III and IV
5. In the ground state of helium, which of the following gives the total spin quantum numbers of the two electrons?
- (A) $s = 0, m_s = 0$
 (B) $s = 1, m_s = 1$
 (C) $s = 1, m_s = 0$
 (D) $s = 1, m_s = -1$
 (E) $s = 1/2, m_s = 1/2$
6. Two spin-1/2 electrons are placed in a one-dimensional harmonic oscillator potential of angular frequency ω . If a measurement of S_z of the system returns \hbar , which of the following is the smallest possible energy of the system?
- (A) $\hbar\omega/2$
 (B) $\hbar\omega$
 (C) $3\hbar\omega/2$
 (D) $2\hbar\omega$
 (E) $5\hbar\omega/2$

5.6 Approximation methods

Exactly solvable quantum mechanics problems are few and far between. The hydrogen atom is pretty much the only example of a realistic system with a closed-form solution, and as soon as we include relativistic and spin-related corrections, we lose the exact solution. To this end, numerous approximation schemes have been developed. By *far* the most important, both on the GRE and in the everyday life of a physicist, is perturbation theory, discussed below. The variational principle and the adiabatic theorem are both important, but the variational principle is too involved to actually apply on a GRE-type question, and the adiabatic theorem is more of a heuristic which applies to only certain types of problems. So we'll discuss perturbation theory in great detail, but spend only a short paragraph on the other two methods.

5.6.1 Time-independent perturbation theory: first and second order

Suppose the Hamiltonian H of a quantum system can be written as

$$H = H_0 + \lambda H',$$

where λ is a dimensionless number which is small compared to 1. Suppose further that we *know* the exact energies E_n^0 and corresponding eigenfunctions ψ_n^0 of H_0 , and that H' is independent of time. Then perturbation theory gives us a recipe for computing corrections to these energies and eigenfunctions, as a power series in the strength of the perturbation λ . To start, the first-order energy shift to the n th level is

$$E_n = E_n^0 + \lambda \langle \psi_n^0 | H' | \psi_n^0 \rangle. \quad (5.57)$$

In other words, the first-order correction to the n th energy E_n^0 is proportional to λ and the *expectation value of H' in the unperturbed state*. So we don't need to solve the Schrodinger equation anew in order to find these first-order shifts: all we have to do is compute an expectation value for some given observable, H' , which is usually pretty easy.

If the first-order shift happens to vanish, then we must go to second order in λ to find a nonzero correction. The formula is considerably more complicated, but we present it here for completeness:

$$E_n = E_n^0 + \lambda^2 \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0}. \quad (5.58)$$

Rather than memorize this formula, just remember its important features:

- It still only involves brackets of H' with the unperturbed states, except instead of being expectation values, they are *off-diagonal matrix elements* $H'_{mn} = \langle \psi_m^0 | H' | \psi_n^0 \rangle$.
- The numerator is always non-negative, so the sign of the denominator is important: it tends to push neighboring energies away from each other. In other words, if E_m^0 is only a

little smaller than E_n^0 , the denominator will be small and positive, so E_n will be pushed even farther away from E_m^0 . This is known as the *no level-crossing* phenomenon. In fact, remembering that levels don't cross is an excellent way to remember the sign of the denominator in the first place.

- If there is degeneracy in H_0 , that is if $E_n^0 = E_m^0$ for some m , we're screwed because the denominator goes to zero.

This last observation is the basis of degenerate perturbation theory. Before discussing this, we should mention that there is a similar formula to (5.58) for the first-order correction to the wavefunctions, but it's never been asked for on the GRE and so is probably not worth learning.

If H_0 is degenerate, then there are multiple linearly independent eigenfunctions corresponding to the same energy eigenvalue. We are free to apply the first-order formula as long as we choose the basis of eigenfunctions appropriately. The solution, which you should be able to quote in your sleep, is

Diagonalize the perturbation in the subspace of degenerate states.

This sounds scary but it's really not. For example, say some state of H_0 was twofold degenerate, with eigenstates ψ_a and ψ_b . Then in the degenerate subspace, the perturbation is a 2×2 matrix:

$$H'_{\text{degen}} = \begin{pmatrix} H'_{aa} & H'_{ab} \\ H'_{ba} & H'_{bb} \end{pmatrix} \equiv \begin{pmatrix} \langle \psi_a | H' | \psi_a \rangle & \langle \psi_a | H' | \psi_b \rangle \\ \langle \psi_b | H' | \psi_a \rangle & \langle \psi_b | H' | \psi_b \rangle \end{pmatrix}.$$

Now diagonalize this matrix, and the eigenvalues are your first-order shifts. Clean and simple. In fact, you're not even required to find the eigenvectors first: the eigenvalues give you all the information about the energy that you need. Also, if it happens that a state has some large degeneracy, but most of the matrix elements vanish, you can simply exclude those states with vanishing matrix elements from consideration until you get down to a matrix which doesn't have any rows or columns which are identically zero. We'll see some examples of this in Section 5.7.4.

Incidentally, the problem of the denominator vanishing is taken care of by excluding the degenerate states from the sum (5.58). But again, this is too advanced for the GRE: all you really need to know about second-order perturbation theory is that it only matters if the first-order shift vanishes. Because it's so important, we'll repeat the mantra of degenerate perturbation theory again: *diagonalize the perturbation*. This will be extremely useful when we have all sorts of competing perturbations H' , of different strengths, as we'll see Section 5.7.4.

5.6.2 Variational principle

The variational principle is a method for approximating the ground state energy of a system for which the Hamiltonian is known. It is based on the simple observation that *for any normalized wavefunction, the expectation value of the energy is greater than the ground state*

energy E_0 .⁵ Roughly, this is because a normalized wavefunction that is not the ground state wavefunction will contain admixtures of other excited state wavefunctions, which push the expectation value of the energy above E_0 . This leads to a method of calculating the ground state energy by picking a trial wavefunction with an adjustable parameter (say, a Gaussian of variable width), then calculating $\langle E \rangle$ and minimizing it with respect to this parameter. You won't have to do this on the GRE, but it's worth knowing how the procedure works since you may be asked questions about it.

5.6.3 Adiabatic theorem

Suppose a particle is in the n th eigenstate of a Hamiltonian H . The adiabatic theorem states that if we slowly change H to H' , then at the end of the process the particle will end up in the corresponding eigenstate of H' . For the purposes of the GRE, that's all you need to know: whenever you see "slowly" on a quantum mechanics problem, you should immediately think of the adiabatic theorem. The standard applications take a one-dimensional Hamiltonian, like the infinite square well or the harmonic oscillator, and "slowly" change one of the parameters: for example, letting the well expand slowly to some other width, or slowly changing the spring constant of the harmonic oscillator. Then the final energy is determined by the corresponding eigenstate of the Hamiltonian with the new parameters. This is really simple in practice, and is best illustrated through an example problem – see below.

5.6.4 Problems

- A harmonic oscillator Hamiltonian of angular frequency ω is perturbed by a potential of the form $V = K(a - a^\dagger)^2$, where K is a constant and the operators a and a^\dagger satisfy $a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle$ and $a|n\rangle = \sqrt{n}|n-1\rangle$. What is the energy shift of the state with unperturbed energy $3\hbar\omega/2$, to first order in perturbation theory?
 - $-3K$
 - $-K$
 - 0
 - K
 - $2K$
- A particle in the ground state of an infinite square well between $x = 0$ and $x = a$ is subject to a perturbation $\Delta H = Vx$, where V is a constant. What is the first-order shift in the energy?
 - $\frac{V\sqrt{2a^3}}{\pi}$
 - $-Va/2$

⁵Of course, it's equal to E_0 if you happened to pick the ground state wavefunction itself.

- (C) 0
- (D) $Va/2$
- (E) $2Va/\pi$

3. A particle of mass m is subject to an infinite square well potential of size a , and is found to have energy E . The well is now expanded *slowly* to size $2a$. What is E'/E , where E' is the expectation value of the energy of the particle after the expansion has finished?

- (A) 0
- (B) 1
- (C) $1/\sqrt{2}$
- (D) $1/2$
- (E) $1/4$

5.7 Atomic physics topics

5.7.1 Bohr model

Why you would need to remember an obviously incorrect formulation of quantum mechanics is beyond us, but questions on the Bohr model of the hydrogen atom have appeared on recent GRE exams, so here is a brief review.

- The electron moves in *classical* circular orbits around the nucleus, called energy shells or energy levels, with *quantized* values of angular momentum: $L = n\hbar$ with $n = 1, 2, \dots$.
- Electrons in a given shell do not radiate as they move around the nucleus – this accounts for the stability of the atom. This was a big problem in early 20th century physics, since classically, the electron would radiate at all times during its orbit (since it's moving in a circle, it's accelerating) and spiral into the proton, collapsing the atom.
- The energy of transitions between energy shells can be shown to match the Rydberg formula given in Section 5.4.3.

If asked about the Bohr model, you will likely either get a simple calculation question about angular momentum quantization, or a conceptual question about why the Bohr model rescued the stability of the atom.

5.7.2 Perturbations to hydrogenic atoms

The hydrogen atom as described in Section 5.4.3 is a great approximation, but it's not the whole story. There are several important corrections to the spectrum of hydrogen, all of which give interesting observable effects. In the discussion below (and in Section 5.7.4), keep in mind that because L^2 , S^2 , and $J^2 = (\mathbf{L} + \mathbf{S})^2$ commute with everything, states of hydrogen can always be labeled by any combination of s , l , and j . However, in the presence of some of these perturbations, the corresponding m -values may *not* be conserved.

- **Fine structure.** These corrections are order α^2 smaller than the Bohr energies, and arise from two very different physical phenomena: replacing the electron kinetic energy term in the Hamiltonian with the correct relativistic form, and the spin-orbit coupling between the electron's orbital angular momentum and its spin, of the form $\mathbf{L} \cdot \mathbf{S}$. Note that this is *not* the interaction of the electron's orbit with the *nuclear* spin: nuclear spin only gets into the game when we discuss hyperfine structure below. Actually calculating the energy shifts requires way more math than you'll have time for on the GRE, but the upshot is that the hydrogen energy levels acquire a dependence on the *total* spin j : since \mathbf{J} commutes with $\mathbf{L} \cdot \mathbf{S}$ (exercise: check this), m_j is also conserved. The energies are still degenerate in m_j , but the degeneracy in l is broken: states with different values of l can have different energies.
- **Lamb shift.** This effect is smaller than fine structure by an *additional* factor of α , and splits the $2s$ and the $2p$ level with $j = 1/2$, which are degenerate even including fine structure since they both have the same j . The physical mechanism comes from quantum electrodynamics, far beyond the scope of the GRE, but the Lamb shift could appear as a trivia-type question.
- **Spin-spin coupling.** This correction is a magnetic dipole-dipole interaction between the spins of the electron and the proton. The energy corrections are of the same order in α as fine-structure, but are further suppressed by the ratio m_e/m_p because the gyromagnetic ratio of point particles depends on their masses. The result is that the ground state of hydrogen is split depending on whether the two spins are in the singlet or triplet state; the triplet has the higher energy (roughly because the spins are aligned, and magnetic dipoles want to be anti-aligned), and the wavelength of the emitted photon in a transition between these two states is about 21 cm, with energy about 5×10^{-6} eV.

It's extremely unlikely that you'll have to calculate anything relating to these perturbations, but their relative strengths and the physical mechanisms responsible for them is certainly fair game for the GRE. In passing, we will mention one calculational trick that is

useful when dealing with fine structure:

$$\begin{aligned} J^2 &= (\mathbf{L} + \mathbf{S})^2 \\ &= L^2 + 2\mathbf{L} \cdot \mathbf{S} + S^2 \\ \implies \mathbf{L} \cdot \mathbf{S} &= \frac{1}{2} (J^2 - L^2 - S^2) \end{aligned} \quad (5.59)$$

For a system with definite values of j , l , and s , this lets you calculate the eigenvalues of the spin-orbit operator $\mathbf{L} \cdot \mathbf{S}$ immediately.

5.7.3 Shell model and electronic notation

Let's go back to high school chemistry. There, you learned that an atom has various energy shells, numbered 1, 2, You also learned that each electron could occupy one of many orbitals, labeled s , p , d , f , This is just saying that atomic electrons lie in hydrogenic states ψ_{nlm} : the energy shells are labeled by n , and the orbitals are labeled by l (s is $l = 0$, p is $l = 1$, d is $l = 2$, and f is $l = 3$). This naming scheme is stupid but unfortunately must be memorized. For a given n , there are n^2 possible combinations of l and m , but since an electron has spin-1/2, it can be either spin-up or spin-down in any of these states. This gives a total of $2n^2$ possible orbitals in each energy shell. Since m can take any value from $-l$ to l , there are $2(2l + 1)$ possible states in each orbital. The counting for the first few goes as follows:

$1s$	2 states
$2s$	2 states
$2p$	6 states
$3s$	2 states
$3p$	6 states
$3d$	10 states

Electronic notation represents the electron configuration of an atom by putting the number of electrons in each orbital as an exponent next to the orbital name. For example, hydrogen is $1s^1$, helium is $1s^2$, and the noble gas neon is $1s^2 2s^2 2p^6$. The detailed description of how the shells get filled is more chemistry than physics, but a few points to remember:

- The shells fill in order, preferring smaller values of l , up through argon with atomic number 18 where the rules break down due to complicated interactions among the electrons and the nucleus. So continuing after helium, lithium has $1s^2 2s^1$, beryllium has $1s^2 2s^2$, boron has $1s^2 2s^2 2p^1$, and so on.
- Noble gases are chemically inert because they have totally filled energy shells. This means that there are the maximum possible number of electrons in each orbital.

- Alkali metals have one “extra” electron compared to the noble gases: for example, sodium has $3s^1$ in addition to the $1s^2 2s^2 2p^6$ of neon. Their chemical tendency is to shed this extra electron to form ions. Similarly, halogens have one fewer electron, like fluorine ($1s^2 2s^2 2p^5$), and want to gain an electron. This accounts for salts like NaF, where sodium transfers an electron to fluorine in an ionic bond.

5.7.4 Stark and Zeeman effects

Placing an atom in external electric or magnetic fields tends to split degenerate energy levels into closely-spaced multiplets. The splitting by an electric field is called the Stark effect, and the splitting by a magnetic field is called the Zeeman effect. Calculating the energy shifts usually involves the whole machinery of degenerate perturbation theory, so you’re unlikely to have to do a full-blown calculation on the GRE, but there are some important facts and conceptual statements about each that you should be aware of.

Stark effect:

- The change in the Hamiltonian from the potential energy of a charge $-e$ in a uniform electric field \mathbf{E} is

$$\Delta H = e\mathbf{E} \cdot \mathbf{r}. \quad (5.60)$$

If $|\mathbf{E}|$ is small, this can be treated as a perturbation, at least for small r .

- There is *no change* in the ground state energy of a hydrogenic atom, to first order in $|\mathbf{E}|$.
- The first states to show a first-order shift are the $n = 2$ states. The states with $m = \pm 1$ are unperturbed, but the $2s$ state and the $2p$ state with $m = 0$ are split. The magnitude of the splitting is likely unimportant for the GRE, but we can get pretty close just by dimensional analysis. Dimensional analysis tells us the energy splitting must be of the form $\Delta E = ke|\mathbf{E}|d$, where k is a constant and d is some length. The only length scale of the hydrogen atom is the Bohr radius, so we can take $d = a_0$ and all that is left undetermined is some number k .

Zeeman effect:

- The Hamiltonian responsible for this effect is the interaction of *both* the electron’s orbital angular momentum and spin with a magnetic field \mathbf{B} :

$$\Delta H = \frac{e}{2m}(\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{B}. \quad (5.61)$$

The exact numerical factors are probably not important to memorize, but they have names: $e/2m$ is the electron’s classical *gyromagnetic ratio*, and the extra factor of 2 in front of the spin operator is because the quantum gyromagnetic ratio happens to be twice the classical value. The magnetic field picks out a preferred vector, so it is conventional to measure spins with respect to the direction of \mathbf{B} , which is equivalent to taking \mathbf{B} to point in the $\hat{\mathbf{z}}$ direction.

- The main pedagogical purpose of the Zeeman effect is to illustrate the concept of “good quantum numbers.” In play are three operators, \mathbf{L} , \mathbf{S} , and $\mathbf{J} = \mathbf{L} + \mathbf{S}$. Depending on the magnitude of \mathbf{B} , different combinations of these operators may be conserved (or approximately so), and hence different combinations of eigenvalues may label the energies.
- If $|\mathbf{B}|$ is small, the Zeeman Hamiltonian is a perturbation on top of fine structure, for which we have already seen that the energies are labeled by j , l , and m_j . The weak-field Zeeman effect splits the j states according to m_j , with the lowest energy for the most negative m_j : physically, the electron spin wants to be anti-aligned with the magnetic field, since this is energetically favorable.
- If $|\mathbf{B}|$ is large, we treat fine structure as a perturbation on top of the Zeeman Hamiltonian, the reverse of the weak-field case. Since we have taken \mathbf{B} to point in the $\hat{\mathbf{z}}$ direction, L_z and S_z *both* commute with the Zeeman Hamiltonian. This means that l , m_l , and m_s are now conserved before fine structure comes into the picture. The total spin j and m_j are *not* conserved, because the magnetic field provides an external torque. The energy of the Zeeman states depends on m_l and m_s in the same way as for the weak-field effect, and fine-structure causes these states to develop a dependence on l as well.

5.7.5 Selection rules

A rough characterization of atomic physics is the study of what happens when you poke atoms with light. That being said, the emission and absorption of electromagnetic radiation by atoms is really a topic for quantum field theory. Thankfully, it can be well-approximated by time-dependent perturbation theory in ordinary quantum mechanics, and many results summarized in a list of rules known as *selection rules* which are actually quite easy to remember. One caveat: the following rules apply only to the *electric dipole approximation*, which assumes that the wavelength of the electromagnetic radiation is large compared to the size of the atom, so that the spatial variation of the field is negligible and the atom feels a *constant* electric and magnetic field which oscillates sinusoidally in time. When we say that certain things can or can’t happen, we are working only in the context of this approximation. We emphatically do *not* mean that these processes can’t *ever* happen: in fact, any quantum process which is not forbidden by conservation laws (energy, momentum, charge, and so on) must occur with some nonzero probability.

The following selection rules refer to transitions between hydrogenic states ψ_{nlm} and $\psi_{n'l'm'}$. To a decent approximation, all atomic electrons are in one of these spatial wavefunctions, so we are considering excitation or de-excitation of a single atomic electron between two of these states. Of course, since we are dealing with quantum mechanics, the energy of the emitted or absorbed photon can only take certain discrete values, corresponding to the energy difference between the final and initial states.

- *No transitions occur unless $\Delta m = \pm 1$ or 0.* You can remember this by conservation of the z -component of angular momentum: the photon has spin 1, and hence must carry off $-\hbar$, 0, or \hbar units of angular momentum in the z -direction. If the incident electric field is oriented in the z -direction, we can be more precise: no transitions occur unless $\Delta m = 0$.
- *No transitions occur unless $\Delta l = \pm 1$.* Again, this sort of follows by the rules of addition of angular momentum, but the case $l = l'$ is conspicuously absent.

Note that the $2s \rightarrow 1s$ transition in hydrogen is technically forbidden by these rules, since this transition has $\Delta l = 0$. This transition does happen, but it gets around the rules because it occurs by *two-photon* emission. This also implies that if you shine light on the ground state of hydrogen, the first excited states you will populate are the $2p$ states, with $l = 1$.

5.7.6 Black-body radiation

One of the triumphs of early quantum mechanics was the derivation of the radiation spectrum of a *black-body*. This is an idealized object which absorbs all the radiation which hits it, while reflecting none of it, so that any radiation emitted from the black-body is a result of its overall temperature. Unlike in atomic transitions, this radiation is not all at one frequency: there is a whole spectrum. The word “black-body” is actually a bit misleading, because if this spectrum peaks in the visible region, the body will appear to be the color which corresponds to the peak frequency. This is in fact the case for the sun, which to a good approximation is a black-body whose spectrum peaks in the yellow part of the visible region. By using the dependence of the black-body spectrum on temperature, one can measure the temperature of an object by observing its color.

In equations, the *power spectrum*, which is the radiated power per unit area of the black-body per unit solid angle per unit frequency (what a mouthful!) as a function of frequency, is

$$I(\omega) \propto \frac{h\omega^3}{c^2} \frac{1}{e^{\hbar\omega/k_B T} - 1}. \quad (5.62)$$

You probably don't need to memorize this equation, but it is important for historical reasons: the classical formula contains only the first factor proportional to ω^3 , which would cause the power to grow without bound as the frequency of the radiation increased. This “ultraviolet catastrophe” was averted by Planck, who supplied the second factor and ushered in the era of quantum mechanics: you should recognize it as the Bose-Einstein factor (4.44) for identical photons, which are bosons. (The chemical potential for photons is $\mu = 0$, since there is no conservation law for photon number: they can be created or destroyed in physical processes.)

The two facts you *do* need to remember about black-body radiation are:

- Integrating (5.62) over everything but the area of the black-body, we obtain from the power spectrum the *Stefan-Boltzmann law*,

$$\frac{dP}{dA} \propto T^4, \quad (5.63)$$

where T is the temperature of the black-body. The exact prefactor isn't worth memorizing (for what it's worth, it's some dimensionful constant called the Stefan-Boltzmann constant), but the T^4 dependence is crucial.

- The location of the peak of the spectrum (5.62) is given by *Wien's displacement law*,

$$\lambda_{max} = (2.9 \times 10^{-3} \text{K} \cdot \text{m}) T^{-1} \quad (5.64)$$

The numerical prefactor *is* important this time: it's one of those constants which really should appear in the currently useless Table of Information at the top of your test, but it's not there. We strongly recommend that you memorize this number (approximate 2.9 to 3 if you like), since although the constant has shown up explicitly on recent tests, its appearance or non-appearance on past GRE tests is inconsistent. Notice that this formula is in terms of wavelength, not frequency: this is conventional. If you know the temperature of a black-body, you can use this formula to find the wavelength at which the power spectrum is at a maximum, or vice versa. (Try it yourself: plug in the wavelength of yellow light, and find the temperature of the sun.) Also note that the maximum wavelength is inversely proportional to temperature: as the body gets hotter, λ_{max} gets smaller, shifting toward the ultraviolet.

5.7.7 Problems

1. In the Bohr model of the hydrogen atom, let r_1 and r_2 be the radii of the $n = 1$ and $n = 2$ orbital shells, respectively. What is r_2/r_1 ?
 - $1/2$
 - $1/\sqrt{2}$
 - 1
 - 2
 - 4
2. The Bohr model is inconsistent with the modern picture of quantum mechanics because it predicts which of the following?
 - The electron will not lose energy as it orbits the nucleus.
 - The electron is confined to distinct energy shells.
 - Angular momentum of the atom is quantized.
 - The ground state has nonzero orbital angular momentum.
 - The energy levels go as $1/n^2$, where n is the principal quantum number.
3. An atom has electron configuration $1s^2 2s^2 2p^3$. A measurement of the total orbital angular momentum of the outermost electron in the ground state could return which of the following?

- (A) \hbar
(B) $\hbar\sqrt{2}$
(C) $2\hbar$
(D) $\hbar\sqrt{6}$
(E) $3\hbar$
4. An atom with the electron configuration $1s^22s^3$ is forbidden by which of the following?
- (A) Conservation of angular momentum
(B) Hund's Rule
(C) The Pauli exclusion principle
(D) The uncertainty principle
(E) None of the above
5. Which of the following is the most likely decay chain of the $3s$ state of hydrogen? Ignore all relativistic and fine-structure effects.
- (A) $3s \rightarrow 1s$
(B) $3s \rightarrow 2s \rightarrow 1s$
(C) $3s \rightarrow 2p \rightarrow 1s$
(D) $3s \rightarrow 2p \rightarrow 2s \rightarrow 1s$
(E) The $3s$ state is stable
6. Observations of the early universe show that it behaves as an almost perfect black-body, with associated radiation known as the cosmic microwave background (CMB). Given that the spectrum of the CMB peaks in the microwave region at a wavelength of 1.06 mm, which of the following is closest to the temperature of the CMB?
- (A) 0.03 K
(B) 0.3 K
(C) 3 K
(D) 30 K
(E) 300 K
7. A space heater whose heating elements are maintained at a constant temperature can heat a cold room from 15° C to 25° C in time t . If the temperature of the heating elements is doubled, how much time will it take to heat the room?
- (A) $t/16$
(B) $t/8$

- (C) $t/4$
- (D) $t/2$
- (E) t

5.8 Solutions

Formalism

1. C - We could calculate the normalization constant, and then do the integral $\int_{-\infty}^0 |\Psi(x)|^2 dx$ to find the probability. But it's much simpler to stare at the wavefunction and just write down the correct answer, $1/2$. The reason is that $\Psi(x)$ is symmetric with respect to $x = 0$, so the area under the curve of $|\Psi(x)|^2$ is equal for x positive and negative, independent of what A is. This is typical of the kind of shortcuts you might see on a GRE problem.

2. D - We just apply the definitions of the operators:

$$\begin{aligned}\hat{x}\hat{p}\Psi &= x \left(-i\hbar \frac{d}{dx} \right) \Psi = -i\hbar A(x(-x/\ell^2))e^{-x^2/2\ell^2} = i\hbar A(x/\ell)^2 e^{-x^2/2\ell^2} \\ \hat{p}\hat{x}\Psi &= -i\hbar A \frac{d}{dx} (xe^{-x^2/2\ell^2}) = -i\hbar A(1 - (x/\ell)^2)e^{-x^2/2\ell^2}\end{aligned}$$

Adding these gives $i\hbar A(2(x/\ell)^2 - 1)e^{-x^2/2\ell^2}$. As a check on the arithmetic, note that subtracting instead of adding gives $i\hbar\Psi(x)$, as it should from the canonical commutator $[\hat{x}, \hat{p}] = i\hbar$.

3. C - Let $\Psi(0) = \frac{1}{\sqrt{2}}(\psi_1 - \psi_2)$. The full time-dependent wavefunction is given by $\Psi(t) = \frac{1}{\sqrt{2}}(\psi_1 e^{-iE_1 t/\hbar} - \psi_2 e^{-iE_2 t/\hbar})$. However, note that the complex moduli of the coefficients multiplying ψ_1 and ψ_2 are the *same* as they were at $t = 0$, since the exponential factors have modulus 1 at any time t . So the probability of measuring E_1 is the same at time t as at time zero: namely, $(1/\sqrt{2})^2 = 1/2$. This is a general feature of time-independent potentials: even in superpositions of energy eigenstates, the energy eigenvalues and relative probabilities of energy measurements are *constant* in time. This is no longer true for time-dependent potentials, but luckily you won't have to worry about those on the GRE.
4. E - Since $|b\rangle$ is an eigenstate of \hat{p} , we have $\hat{p}|b\rangle = b|b\rangle$. But since \hat{p} is a Hermitian operator, eigenfunctions corresponding to different eigenvalues are orthogonal, and

$$\langle a|\hat{p}|b\rangle = b\langle a|b\rangle = 0.$$

We also could have proceeded by process of elimination. Since \hat{p} is Hermitian, we have $\langle a|\hat{p}|b\rangle = \langle b|\hat{p}|a\rangle$, so the answer must be symmetric in a and b , which eliminates choices

A and B. The answer must also have dimensions of momentum (the same units as a and b), which leaves D and E. It's hard to see how a square root might come out of a calculation like this, so E seems like the most reasonable choice.

5. D - Recall that the n th state of the harmonic oscillator has energy $(n + 1/2)\hbar\omega$. If you don't remember this, make sure you study Section 5.2! This wavefunction has three nodes, so it must represent the third excited state; since the harmonic oscillator starts counting with $n = 0$, this means it's the $n = 3$ state, with energy $7\hbar\omega/2$.
6. E - For a matrix to be a Hermitian operator, it must be equal to its Hermitian conjugate; in other words, transposing the matrix and complex-conjugating the entries must give back the original matrix. For matrices that consist of purely real entries, this just means the matrix must be symmetric: I fails but III passes. It turns out that II is also Hermitian, since transposing switches the i and $-i$, but conjugating switches them back. Incidentally, II is one of the Pauli matrices, and if you recognized this you could immediately determine that it is Hermitian – see Section 5.5.
7. D - The normalization constant is

$$A = \frac{1}{\sqrt{2^2 + 3^2 + 1^2}} = \frac{1}{\sqrt{14}}.$$

Thus the expectation value of \mathcal{O} is

$$\langle \mathcal{O} \rangle = \frac{2^2}{14}(1) + \frac{3^2}{14}(2) + \frac{1^2}{14}(5) = \frac{27}{14}$$

which is D. Note that there are no “cross-terms” from $\langle \psi | \mathcal{O} | \psi \rangle$ that we had to compute, such as $\langle 2 | \mathcal{O} | 3 \rangle$, because these are guaranteed to vanish by orthonormality; eigenstates corresponding to distinct eigenvalues of \mathcal{O} are orthogonal.

8. B - We want the inner product $\langle \Psi_1 | \Psi_2 \rangle$ to vanish. In taking the inner product, remember that we have to *complex-conjugate* the coefficients of $|\Psi_1\rangle$:

$$(1)(2) + (-2i)(x) = 0 \implies x = -i.$$

If we had forgotten to conjugate, we would have ended up with the trap answer A.

9. E - We'll do this problem in two ways: one by acting on a test function $f(x)$, and once by using commutator identities. Doing it the first way, we have

$$\hat{x}^2 \hat{p}^2 f(x) = (-i\hbar)^2 x^2 f''(x) = -\hbar^2 x^2 f''(x)$$

and

$$\begin{aligned} \hat{p}^2 \hat{x}^2 f(x) &= (-i\hbar)^2 \frac{d^2}{dx^2} (x^2 f(x)) \\ &= -\hbar^2 \frac{d}{dx} (2x f(x) + x^2 f'(x)) = -\hbar^2 (x^2 f''(x) + 4x f'(x) + 2f(x)) \end{aligned}$$

Subtracting these and replacing derivatives by the momentum operator, we find that

$$[\hat{x}^2, \hat{p}^2] = 4i\hbar\hat{x}\hat{p} + 2\hbar^2.$$

As this is not in the form of any of the answer choices, we recall that we can relate $\hat{x}\hat{p}$ to $\hat{p}\hat{x}$ by using the value of the canonical commutator: $[\hat{x}, \hat{p}] = i\hbar$ implies $\hat{p}\hat{x} = \hat{x}\hat{p} - i\hbar$. So, separating out the commutator into $2i\hbar\hat{x}\hat{p} + (2i\hbar\hat{x}\hat{p} + 2\hbar^2)$, we can rewrite the second term as

$$2i\hbar\hat{x}\hat{p} + 2\hbar^2 = (2i\hbar)(\hat{x}\hat{p} - i\hbar) = 2i\hbar\hat{p}\hat{x},$$

and we can rewrite the commutator as

$$[\hat{x}^2, \hat{p}^2] = 2i\hbar(\hat{x}\hat{p} + \hat{p}\hat{x}),$$

choice E. Doing the problem the second way, we use the commutator product identities, once on $\hat{x}^2 = \hat{x}\hat{x}$ and once on $\hat{p}^2 = \hat{p}\hat{p}$:

$$\begin{aligned} [\hat{x}^2, \hat{p}^2] &= \hat{x}[\hat{x}, \hat{p}^2] + [\hat{x}, \hat{p}^2]\hat{x} \\ &= \hat{x}([\hat{x}, \hat{p}]\hat{p} + \hat{p}[\hat{x}, \hat{p}]) + (([\hat{x}, \hat{p}]\hat{p} + \hat{p}[\hat{x}, \hat{p}])\hat{x}) \\ &= \hat{x}(i\hbar\hat{p} + i\hbar\hat{p}) + (i\hbar\hat{p} + i\hbar\hat{p})\hat{x} \\ &= 2i\hbar(\hat{x}\hat{p} + \hat{p}\hat{x}), \end{aligned}$$

which gives choice E again. This problem is much more involved than any you'd see on the GRE, but it does illustrate many of the effective methods for computing commutators which you *will* need to know.

10. B - This is an application of the energy-time uncertainty principle, combined with a little special relativity which tells us a particle of mass m has rest energy mc^2 . From $\Delta E \Delta t \approx \hbar$, we plug in the lifetime of the particle for Δt and use the numerical value of \hbar (which would be given in the Table of Information at the top of the test, here we want units of $\text{eV} \cdot \text{s}$) to find $\Delta E \approx 66 \text{ MeV}$. In other words, a mass difference of greater than $66 \text{ MeV}/c^2$ from the central value of $500 \text{ MeV}/c^2$ represents one standard deviation, and is expected to happen about 32% of the time. Here the mass difference is only $50 \text{ MeV}/c^2$, so this may be expected to happen about 50% of the time. On the other hand, the mass difference is five times the expected experimental error, and a 5-sigma event happens much more rarely. So the difference is most likely due to the uncertainty principle, choice B.
11. B - This is a classic application of the “folklore” uncertainty principle (5.19):

$$(100 \text{ pm})(\Delta p) \approx \hbar \implies \Delta p \approx 2 \text{ keV}/c.$$

To do the arithmetic fast, we could use the fact that $hc = 1240 \text{ eV} \cdot \text{nm}$ (also given in the Table of Information on the most recently-released test) to get the momentum in natural units of eV/c . Now, find the energy by

$$E = \frac{p^2}{2m_e} \approx \frac{4 \text{ keV}^2/c^2}{1 \text{ MeV}/c^2} = 4 \text{ eV}.$$

This makes complete sense, since we know that chemical processes take place on the scale of eV, rather than MeV (the scale of nuclear physics) or GeV (the scale of particle accelerator physics). Using just this knowledge, we probably could have zeroed in on choice B right away, but it's nice to see it come out of the uncertainty principle.

Harmonic oscillator

1. B - We're looking for $\langle 0|a^\dagger a + aa^\dagger|0\rangle$. The first term is zero because $a|0\rangle = 0$ by definition. For the second term, we can use $[a, a^\dagger] = 1$ to find $aa^\dagger = a^\dagger a + 1$. The $a^\dagger a$ vanishes for the same reason as the first term, and the leftover piece is $\langle 0|0\rangle = 1$, which is the desired expectation value. We could also have done this problem using the normalizations given for the action of the raising and lowering operators, but this method is simpler because all you have to remember is the commutation relation for a and a^\dagger .
2. D - The key here is the virial theorem, supplemented by a bit of clever reasoning. Since $\langle T \rangle = E_n/2$ for any energy eigenstate, and $T = p^2/2m$, we have $\langle p^2 \rangle = mE_n$ for any energy eigenstate $|n\rangle$. Now, the virial theorem does not generally apply to superpositions of energy eigenstates, but in this particular case it does. The operator \hat{p} is a linear combination of a and a^\dagger , so \hat{p}^2 contains products of at most two of these operators, like $(a^\dagger)^2$ or $a^\dagger a$. Thus $\langle 1|\hat{p}^2|4\rangle = 0$, because applying a raising or lowering operator twice can never give a product of non-orthogonal states; we always get orthogonal combinations like $\langle 2|3\rangle$ or $\langle 1|2\rangle$. So *there are no cross-terms*, and the virial theorem still applies to each diagonal term in the expectation value. Denoting our state by $|\psi\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |4\rangle)$, we have

$$\langle \psi | \hat{p}^2 | \psi \rangle = \frac{1}{2}(\langle 1 | \hat{p}^2 | 1 \rangle + \langle 4 | \hat{p}^2 | 4 \rangle).$$

Using the virial theorem gives

$$\langle p^2 \rangle = \frac{1}{2}m(E_1 + E_4) = \frac{m}{2}(3\hbar\omega/2 + 9\hbar\omega/2) = 3m\hbar\omega,$$

choice D.

3. A - The classical ground state of the harmonic oscillator has zero energy, corresponding to a particle sitting at $x = 0$, where the potential vanishes, and having no kinetic energy. But the ground state of the quantum oscillator has energy $\hbar\omega/2$.
4. C - Let (n_x, n_y) label the levels of the independent x and y -coordinate oscillators. The total zero-point energy is $\hbar\omega/2 + \hbar\omega/2 = \hbar\omega$ in two dimensions, so the state with energy $3\hbar\omega$ has $n_x + n_y = 2$, which can occur in three ways: (2,0), (1,1), and (0,2). Thus this state has a degeneracy of 3.

Other standard Hamiltonians

1. B - The dependence of the infinite square well energies on m and L is $E \sim 1/mL^2$. For the energies to be equal, we need

$$mL^2 = (2m)L'^2 \implies \frac{L'}{L} = \frac{1}{\sqrt{2}}.$$

2. D - This is easiest to see from the explicit form of the wavefunction, $\sin(n\pi x/L)$. Even without the functional form, we can still eliminate B, C, and E because II is clearly false: the wavefunction is *always* continuous.
3. A - Since the particle is free, its Hamiltonian is just $\hat{p}^2/2m$, which *commutes* with the momentum operator \hat{p} . Thus if it has a precise value of momentum, it also has a precise value of energy, and the uncertainty is zero.
4. C - Clearly I is false because a definite value of position would mean the wavefunction must be a delta-function $\delta(x - x_0)$. In fact, this wavefunction represents a superposition of two momentum eigenstates, e^{+ikx} and e^{-ikx} , with equal but opposite values of momentum $p = \hbar k$. So II is false. However, the energy $\hbar^2 k^2 / 2m$ doesn't care about the sign of k , so the particle does have a definite value of energy. Only III is true, so C is correct.
5. A - at $x = a/2$ the particle is inside the barrier, and so has potential V_0 . The wavefunction is of the form e^{ikx} , so solving the time-independent Schrodinger equation,

$$\frac{\hbar^2 k^2}{2m} + V_0 = E \implies k = \frac{\sqrt{2m(E - V_0)}}{\hbar}.$$

The de Broglie wavelength is related to the wavenumber k by $\lambda = 2\pi/k$, so $\lambda = h/\sqrt{2m(E - V_0)}$, choice A. As usual, we could have made some progress by dimensional analysis and limiting cases: only choices A-C have units of length, and since the wavelength had better be real for no potential barrier ($V_0 = 0$), we narrow it down to A or B.

6. E - The incident wave has amplitude $|A|$, the reflected wave has amplitude $|B|$, and the transmitted wave has amplitude $|C|$, so the transmission probability is $|C|^2/|A|^2$ multiplied by an extra factor which takes into account the different speeds of the waves on the left and the right. Rather than solving for this quantity using conservation of probability, continuity of the wavefunction and its derivatives and so on, we can just use logic. Choices A and B are clearly false, for any finite nonzero value of V_0 . Furthermore, we should have the transmission probability going to 1 when $k_L = k_R$, since that corresponds to the step disappearing. This eliminates D. Furthermore, since probabilities are proportional to *squared* amplitudes, the only way a ratio like k_L/k_R would show up would be if solving the continuity conditions gave a \sqrt{k} factor: since

derivatives of the wavefunction will only give k and not \sqrt{k} , this seems rather unlikely. So E seems best, and indeed it is the correct answer. Notice that this kind of careful reasoning, while it may seem involved, took *much* less time than the corresponding calculations would have. In our opinion this is the best way to approach these kinds of quantum mechanics problems on the GRE.

Three dimensions

1. B - Applying the recipe (5.1) for computing expectation values, and remembering that the radial piece of the volume measure in 3 dimensions is $r^2 dr$, we have

$$\langle r \rangle = \int_a^\infty \frac{\sqrt{3a^3}}{r^3} r \frac{\sqrt{3a^3}}{r^3} (r^2 dr) = \int_a^\infty \frac{3a^3}{r^3} dr = \frac{3}{2}a,$$

choice B. Note that this has the correct units: the expectation value of an operator with units of length should also have units of length.

2. D - Since the spherical harmonics are eigenfunctions of \mathbf{L}^2 , Y_3^2 has eigenvalue $3(3+1)\hbar^2 = 12\hbar^2$ and Y_2^1 has eigenvalue $2(2+1)\hbar^2 = 6\hbar^2$. The squares of the coefficients in the given wavefunction are $1/2$ for both spherical harmonics, so the expectation value is $(1/2)6\hbar^2 + (1/2)12\hbar^2 = 9\hbar^2$, choice D.
3. E - Computing the commutators from the inside out, $[\hat{J}_x, \hat{J}_y] = i\hbar\hat{J}_z$ and $[\hat{J}_y, \hat{J}_z] = i\hbar\hat{J}_x$. What remains is

$$(i\hbar)^2 [\hat{J}_z, \hat{J}_x] = -\hbar^2 (i\hbar\hat{J}_y) = -i\hbar^3 \hat{J}_y,$$

choice E.

4. E - The given wavelength is exactly 4 times the wavelength of the Lyman alpha line, which comes from the $n = 2$ to $n = 1$ transition. Letting n_i and n_f be the initial and final states of the 488 nm transition, the Rydberg formula (inverted because we're dealing with wavelength rather than frequency) gives

$$4 = \frac{\frac{1}{1^2} - \frac{1}{2^2}}{\frac{1}{n_f^2} - \frac{1}{n_i^2}},$$

and this is solved just by doubling the n values for Lyman radiation: $n_i = 4$ and $n_f = 2$. This is choice E.

5. A - The gravitational potential is $G_N m_e m_n / r$, and the corresponding electric potential in the hydrogen atom is $e^2 / 4\pi\epsilon_0 r$, so we simply replace $e^2 / 4\pi\epsilon_0$ by $G_N m_e m_n$ in the formula for the Bohr radius. Since we're approximating $m_e \ll m_n$, we can use m_e instead of the reduced mass. This gives

$$a = \frac{\hbar^2}{m_e} \frac{1}{G_N m_e m_n} = \frac{\hbar^2}{G_N m_e^2 m_n},$$

which is A. We could also have made progress by dimensional analysis, since only A and C have the correct units. By the way, the reason we never see this bound state is that plugging in the numbers, $a = 1.2 \times 10^{29}$ m; for comparison, the radius of the observable universe is 4.7×10^{26} m!

6. B - As discussed in Section 5.4.3, for positronium the reduced mass is $m_e/2$. Thus the ground state energy, which is proportional to the reduced mass, is $E_1 = 6.8$ eV. By the Rydberg formula, the energy difference between the first excited state ($n = 2$) and the ground state $n = 1$ is

$$E_1 \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = (0.75)(6.8 \text{ eV}) = 5.1 \text{ eV},$$

choice B.

7. E - from (5.46), the ground state energy is proportional to the reduced mass and the square of the “electron” charge. This gives a total factor of $2(2^2) = 8$, choice E.

Spin

1. A - Finding the normalization constant first, $1 = |A|^2(|1+i|^2+2^2) = |A|^2(2+4) = 6|A|^2$, so $|A| = 1/\sqrt{6}$. Next compute the expectation value:

$$\langle \hat{S}_z \rangle = \frac{\hbar}{2} \frac{1}{6} (|1+i|^2(+1) + (2^2)(-1)) = \frac{\hbar}{12}(2-4) = -\frac{\hbar}{6},$$

choice A.

2. C - The first measurement is irrelevant. After the second measurement the particle is in the $-\hbar/2$ eigenstate of \hat{S}_x , which is $\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$. The components of $|\uparrow\rangle$ and $|\downarrow\rangle$ in this state have equal magnitude, so the probability of measuring either one is $1/2$, choice C.

3. E - Addition of spin angular momentum and orbital angular momentum add just like ordinary addition of spins. Here, the total spin s is either 0 or 1; adding $l = 2$ to the former gives only $j = 2$, and adding $l = 2$ to $s = 1$ gives $j = 3, 2$, or 1. Hence choice E.

4. D - The ground state has zero orbital angular momentum, so combined with the given information about the nucleus having no orbital angular momentum, we only have to worry about spins. To get $j = 3/2$ the nucleus must be in the triplet state, which rules out I. The z -component of spin of the electron can be either $1/2$ or $-1/2$, and so the nucleus could either have $m_j = 0$ (with $m_s = 1/2$ for the electron), or $m_j = 1$ (with $m_s = -1/2$ for the electron). So both II and III are viable options, choice D.

5. A - This is a classic problem and well worth remembering, so we'll reason through it carefully. Because the interaction of electron spins with the nucleus is an order of magnitude smaller than the Coulomb interaction between the electrons and the protons (see Section 5.7), the ground state is determined by the spatial wavefunction, and prefers both electrons to be in the same lowest-energy orbital, the $1s$ orbital. Since both electrons have the same spatial wavefunction, the spatial piece is symmetric, so the spin configuration which comes along for the ride must be antisymmetric. The possible spin configurations of two electrons are the singlet and the triplet, as discussed in Section 5.5.3. But only the singlet (choice A) is antisymmetric, so this must be the correct spin state. Helium is such a GRE favorite that it's best just to memorize the conclusion of this argument, rather than rederiving it each time: *the ground state of helium is the singlet state.*⁶ But really, you already knew this from high school chemistry, when you wrote the electron configuration of hydrogen as \uparrow , the configuration of helium as $\uparrow\downarrow$, and so on. While technically an imprecise shorthand, it's a good mnemonic nonetheless.
6. D - Total $S_z = \hbar$ means the electrons must be in the triplet state, which is symmetric. For a totally antisymmetric wavefunction, the spatial wavefunction must be antisymmetric. This knocks out the ground state, where both electrons are in the $n = 0$ state of the harmonic oscillator, since after antisymmetrization this vanishes identically. So the next available state is an antisymmetrized version having $n = 0$ and $n = 1$:

$$\psi_{spatial} = \frac{1}{\sqrt{2}}(|0\rangle_1|1\rangle_2 - |1\rangle_1|0\rangle_2).$$

This is an energy eigenstate with energy $\hbar\omega/2 + 3\hbar\omega/2$, choice D.

Approximation methods

1. A - The state with energy $3\hbar\omega/2$ is $|1\rangle$, so the shift we're looking for is $\langle 1|V|1\rangle$. Expanding out V isn't really that helpful. Instead, note that the only terms which survive in the expectation value contain exactly one a and exactly one a^\dagger , since otherwise we would have something of the form $\langle m|n\rangle$ which vanishes by orthogonality. There are two such terms: $-aa^\dagger$ and $-a^\dagger a$. (Remember to keep track of the order, since these operators don't commute!). We have

$$\begin{aligned}\langle 1|(-aa^\dagger)|1\rangle &= -(\sqrt{2})^2\langle 2|2\rangle = -2 \\ \langle 1|(-a^\dagger a)|1\rangle &= -(\sqrt{1})^2\langle 0|0\rangle = -1\end{aligned}$$

where in the first line we acted on $|1\rangle$ with a^\dagger and on $\langle 1|$ with a on the right, and similarly in the second line with the roles of a and a^\dagger reversed. Adding these up gives $\Delta E = K(-2 + 1) = -3K$, choice A.

⁶Note that there is an important subtlety in this discussion: the electron-electron repulsion in helium means that the ground states are *not* really the pure hydrogen orbitals. However, this line of reasoning does give the correct experimentally observed answer, which is all that matters. So feel free to regard this argument as a mnemonic for remembering the correct answer.

2. D - The ground state is $\psi(x) = \sqrt{2/a} \sin(\pi x/a)$, and the first-order shift is given by

$$\Delta E = \int \psi^*(x) \Delta H \psi(x) dx = V \frac{2}{a} \int_0^a x \sin^2(\pi x/a) dx.$$

This is likely more difficult than any integral you'll actually see on the GRE, but just in case, let's briefly review how to do it: use the half-angle identity to write

$$\sin^2(\pi x/a) = \frac{1}{2} (1 - \cos(2\pi x/a)).$$

Integrating the first term against x gives

$$V \frac{2}{a} \frac{1}{2} \int_0^a x dx = \frac{V}{2a} a^2 = \frac{Va}{2}.$$

Do the second integral $\int x \cos(2\pi x/a) dx$ by parts; the boundary term vanishes because $\sin(2\pi x/a)$ vanishes at both the endpoints, so the remaining integral is

$$-V \frac{2}{a} \frac{1}{2} \frac{a}{2\pi} \int_0^a \sin(2\pi x/a) dx = 0,$$

because $\cos(2\pi x/a)$ is equal to 1 at both endpoints. So the energy shift is simply $Va/2$, choice D.

3. E - After an energy measurement the particle is in some eigenstate of the infinite square well, say the n th state. Under a slow expansion of the well, the adiabatic theorem tells us the particle remains in the n th state of the infinite square well. Since the energies of the infinite square well are $\frac{n^2\pi^2\hbar^2}{2ma^2}$, the energy of the final configuration is 1/4 of the original energy, independent of n .

Atomic physics topics

1. E - We can eliminate A, B, and C right away since the $n = 2$ shell has more energy than $n = 1$, and hence must be farther away from the nucleus. The angular momentum for a circular orbit is $L = mvr$, and the orbital velocity can be determined from classical mechanics by setting the centripetal force equal to the Coulomb force:

$$\frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2} = \frac{mv^2}{r} \implies v \sim r^{-1/2}.$$

Thus $L \sim r^{1/2}$, and from $L_1 = \hbar$ and $L_2 = 2\hbar$, we get $r_2/r_1 = L_2^2/L_1^2 = 4$.

2. D - In the Bohr model, $L = n\hbar$, where $n > 0$, since otherwise the electron would be sitting right on top of the nucleus (its classical orbital radius would be zero). However, in the modern picture the ground state is ψ_{100} , which has orbital quantum number $l = 0$.

3. B - The outermost electron is in the p orbital, and so has $l = 1$. This means $L^2 = l(l+1)\hbar^2 = 2\hbar^2$, so $|\mathbf{L}| = \hbar\sqrt{2}$.
4. C - The $2s$ orbital has $l = 0$, and hence $m = 0$, so electrons in this orbital are distinguished only by the direction of their spin. There are only two independent spin states, so a third electron would have to be in the same state as one of the other two, violating the Pauli exclusion principle for fermions.
5. C - By the selection rules, $3s$ must decay to a state with $l = 1$, so the only option is the $2p$ state. From there, we again must have $\Delta l = \pm 1$, and so $1s$ is the only remaining possibility.
6. C - This is a straightforward application of Wien's Law. Solving for T , we get $T = (2.9 \times 10^{-3} \text{K} \cdot \text{m})/\lambda_{max}$, and approximating Wien's constant by 3 and the wavelength by 1 mm, we get $T \approx 3 \text{ K}$. (Even without any knowledge of Wien's constant, we could have eliminated choice E since the universe certainly isn't at room temperature.) By the way, questions on the CMB are fairly likely to appear on the GRE in some form, so it's worth remembering both the wavelength and the temperature if you can.
7. A - Treating the space heater as a black-body, the power (energy per unit time) is proportional to the fourth power of temperature. So doubling the temperature increases the power by a factor of 16, and for a constant desired energy, this means the time taken to deliver this energy will decrease by a factor of 16.