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
$$\langle A\rangle = \int_{-\infty}^{\infty} \Psi^* \hat{A}\Psi\,dx. \tag{5.1}$$

3. A measurement of an observable A at a time t_0 on a state Ψ will always return one of the eigenvalues λ_n of $\hat{A}$. To find the probability that this happens, 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:
$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2\,dx = 1 \tag{5.2}$$
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 is $|\Psi(r,\theta,\phi,t)|^2(4\pi r^2\,dr)$. 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, be very careful when dealing with sums: if we have a wavefunction like $\Psi = \Psi_1 + e^{i\alpha}\Psi_2$, multiplying Ψ by a phase preserves the relative phase $e^{i\alpha}$ between Ψ_1 and Ψ_2. In other words, 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.