Chem 3502/4502 **Physical Chemistry II (Quantum Mechanics)** 3 Credits

Spring Semester 2006

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Lecture 6, January 30, 2006

Solved Homework

We are given that $A\Psi = a\Psi$ and $A^*\Psi = a\Psi$ where a is a real number. As both $A\Psi$ and $A^*\Psi$ are equal to the same thing, they must be equal to one another, i.e., $A\Psi = A^*\Psi$. If we multiply each on the left and integrate, we have

$$\int_{-\infty}^{\infty} \Psi^* \left(A\Psi\right) dr = \int_{-\infty}^{\infty} \Psi^* \left(A^*\Psi\right) dr$$

which is the *first* equality that we are tasked to prove. If we take the complex conjugate of both sides we have

$$\left[\int_{-\infty}^{\infty} \Psi^* \left(A\Psi\right) dr\right]^* = \left[\int_{-\infty}^{\infty} \Psi^* \left(A^*\Psi\right) dr\right]^*$$

which is the *last* equality that we are asked to prove. To prove the central equality, let us simply evaluate the relevant integrals, thus

$$\begin{aligned} \int_{-\infty}^{\infty} \Psi^* \left(A^*\Psi\right) dr &= \int_{-\infty}^{\infty} \Psi^* \left(a\Psi\right) dr \\ &= a\int_{-\infty}^{\infty} \Psi^* \Psi dr \\ &= a|\Psi|^2 \end{aligned}$$

and

$$\begin{aligned} \left[\int_{-\infty}^{\infty} \Psi^* \left(A\Psi\right) dr\right]^* &= \left[\int_{-\infty}^{\infty} \Psi^* \left(a\Psi\right) dr\right]^* \\ &= \left[a\int_{-\infty}^{\infty} \Psi^* \Psi dr\right]^* \\ &= \left[a|\Psi|^2\right]^* \end{aligned}$$

but a is a real number, and the square modulus of a wave function is also a real number, so it must be true that

$$\left[a|\Psi|^2\right]^* = a|\Psi|^2$$

Q.E.D.

Stationary States

Recall that the general solution to the time-dependent Schrödinger equation is the superposition-of-states wave packet defined by

$$\Psi(x,y,z,t) = \sum_{n=1}^{\infty} c_n \psi_n(x,y,z) e^{-iE_n t/\hbar} \tag{6-1}$$

Let us consider what is required for the probability density at any position in space *not* to be varying with time. That is, the system is "stationary" or in a "stationary state". The probability density at a particular position is

$$\begin{aligned}
\Psi^*(x,y,z,t)\Psi(x,y,z,t) &= \sum_{m=1}^{\infty} c_m^* \psi_m^*(x,y,z) e^{iE_m t/\hbar} \sum_{n=1}^{\infty} c_n \psi_n(x,y,z) e^{-iE_n t/\hbar} \\
&= \sum_{m,n=1}^{\infty} c_m^* c_n \psi_m^*(x,y,z) \psi_n(x,y,z) e^{iE_m t/\hbar} e^{-iE_n t/\hbar} \\
&= \sum_{i=1}^{\infty} |c_i|^2 \psi_i^*(x,y,z) \psi_i(x,y,z) \\
&\quad + \sum_{m \neq n}^{\infty} c_m^* c_n \psi_m^*(x,y,z) \psi_n(x,y,z) e^{i(E_m - E_n)t/\hbar}
\end{aligned} \tag{6-2}$$

Notice that we are not integrating over all space here, we are only asking about a particular position, so the various terms in the second sum of the bottom equality are *not* necessarily zero. It is these terms that include a time dependence, so for a system to have a stationary probability density, we must find a way to make every term in the second sum equal to zero. There is only one way to do this (unless all states are degenerate): every value of $\{c\}$ must be zero except for a single one. That is

$$\Psi(x,y,z,t) = c_j \psi_j(x,y,z) e^{-iE_j t/\hbar} \tag{6-3}$$

Since both the time-dependent and time-independent wave functions are normalized over all space, note that

$$\begin{aligned}
\langle \Psi(x,y,z,t) | \Psi(x,y,z,t) \rangle &= \langle c_j \psi_j(x,y,z) e^{-iE_j t/\hbar} | c_j \psi_j(x,y,z) e^{-iE_j t/\hbar} \rangle \\
&= c_j^* e^{iE_j t/\hbar} c_j e^{-iE_j t/\hbar} \langle \psi_j(x,y,z) | \psi_j(x,y,z) \rangle \\
&= |c_j|^2
\end{aligned} \tag{6-4}$$

Thus, the square modulus of c_j must be one (since Ψ is normalized).

Now, for any operator that does not depend on time, notice that for a stationary state we have

$$\begin{aligned}\langle\Psi(x,y,z,t)|A|\Psi(x,y,z,t)\rangle &= \left\langle \psi_j(x,y,z)e^{-iE_jt/\hbar}|A|\psi_j(x,y,z)e^{-iE_jt/\hbar}\right\rangle \\ &= e^{iE_jt/\hbar}e^{-iE_jt/\hbar}\langle\psi_j(x,y,z)|A|\psi_j(x,y,z)\rangle \\ &= \langle\psi_j(x,y,z)|A|\psi_j(x,y,z)\rangle\end{aligned} \tag{6-5}$$

That is, for a stationary state we can work exclusively with the time-*independent* spatial wave functions.

Operators

In lecture 3 we discussed a few operators, but let us make a list here of many which will prove useful as we go on. The table on the next page provides names, symbols, and operations for the most common operators in both 1 and 3 dimensions. Note that momentum in a single dimension is still a vector quantity, but since there is only one dimension it is often denoted as the scalar "component" times the vector basis for the dimension (e.g., the **i** vector of Cartesian space). Thus the parenthetical notations for this quantity, indicating optional representations. Note also that "del" is a vector quantity, while "del-squared" is a scalar. I can't seem to convince my Equation Editor to make del boldface, but it should be, to indicate its vector status.

Expectation Values

Operators that Commute with the Hamiltonian. Recall that if two Hermitian operators commute (and remember that all quantum mechanical operators are Hermitian) then they share a common set of eigenfunctions. Thus, if the system is in a stationary state, the single eigenfunction of the Hamiltonian describing the system according to eq. 6-3 will also be an eigenfunction of any operator that commutes with the Hamiltonian. In that case, the expectation value will simply be

$$\begin{aligned}\langle\psi_j(x,y,z)|A|\psi_j(x,y,z)\rangle &= \langle\psi_j(x,y,z)|a_j\psi_j(x,y,z)\rangle \\ &= a_j\langle\psi_j(x,y,z)|\psi_j(x,y,z)\rangle \\ &= a_j\end{aligned} \tag{6-6}$$

where a_j is the eigenvalue for eigenfunction ψ_j. Note that there is no variation in this eigenvalue—it will be returned by every measurement for any system characterized by ψ_j.

Table of Observables and Corresponding Operators

Observable	No. of Dimensions	Operator Symbol	Operator
Position	1 (scalar)	x	multiply by x
	3 (vector)	$\mathbf{r}$	multiply by $\mathbf{r}$
Momentum	1	$\mathbf{p}$ (or p_x)	$-i\hbar(\mathbf{i})\frac{d}{dx}$
(always vector)	3	$\mathbf{p}$	$-i\hbar\left(\mathbf{i}\frac{\partial}{\partial x}+\mathbf{j}\frac{\partial}{\partial y}+\mathbf{k}\frac{\partial}{\partial z}\right)$ or $-i\hbar\nabla$
Kinetic Energy	1	T	$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$
(always scalar)	3	T	$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$ or $-\frac{\hbar^2}{2m}\nabla^2$
Potential Energy	1	$V(x)$	multiply by $V(x)$
(always scalar, position dependent)	3	$V(x,y,z)$	multiply by $V(x,y,z)$
Total Energy, E	1	H	$T+V$
(always scalar)	3	H	$T+V$
Angular Momentum			
x component	(part of 3)	L_x	$-i\hbar\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)$
y component	(part of 3)	L_y	$-i\hbar\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)$
z component	(part of 3)	L_z	$-i\hbar\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)$
scalar square	3	L^2	$L_x^2+L_y^2+L_z^2$

Operators that Do Not *Commute with the Hamiltonian.* An operator A that does *not* commute with the Hamiltonian has its own set of eigenfunctions, let's call them $\{\phi\}$. As these eigenfunctions form a complete set and depend on exactly the same variables as the Hamiltonian's eigenfunctions (that is, the spatial coordinates of all electrons and nuclei) we may actually express stationary state ψ_j as a linear combination of the ϕ's. That is

$$\psi_j(x,y,z) = \sum_{n=1}^{\infty} c_n \phi_n(x,y,z) \tag{6-7}$$

so, if we consider the expectation value of A we have

$$\begin{aligned}
\langle \psi_j | A | \psi_j \rangle &= \left\langle \sum_{m=1}^{\infty} c_m \phi_m | A | \sum_{n=1}^{\infty} c_n \phi_n \right\rangle \\
&= \left\langle \sum_{m=1}^{\infty} c_m \phi_m \middle| \sum_{n=1}^{\infty} a_n c_n \phi_n \right\rangle \\
&= \sum_{m,n=1}^{\infty} c_m^* c_n a_n \langle \phi_m | \phi_n \rangle \\
&= \sum_{m,n=1}^{\infty} c_m^* c_n a_n \delta_{mn} \\
&= \sum_{i=1}^{\infty} |c_i|^2 a_i
\end{aligned} \tag{6-8}$$

The way to interpret eq. 6-8 is that any sampling will collapse the system into an eigenstate of the operator (but it will no longer be a stationary state, since wave functions ϕ are not eigenfunctions of the Hamiltonian) and return one of the eigenvalues of operator A. However, *which* eigenvalue is obtained is probability dependent. In particular, the probability for each state is the square modulus of the coefficient for that state in the expansion of eq. 6-7. Thus, over multiple measurements on otherwise identical systems in stationary state ψ_j, $\langle A \rangle$ will reflect a probability-weighted distribution of different results—a very different situation from the case for operators commuting with the Hamiltonian.

To determine the values c_n is actually rather straightforward. If we left multiply each side of eq. 6-7 by the complex conjugate of any one ϕ_i and integrate we have

$$\begin{aligned}
\langle \phi_i | \psi_j \rangle &= \left\langle \phi_i \middle| \sum_{n=1}^{\infty} c_n \phi_n \right\rangle \\
&= \sum_{n=1}^{\infty} c_n \langle \phi_i | \phi_n \rangle \\
&= \sum_{n=1}^{\infty} c_n \delta_{in} \\
&= c_i
\end{aligned} \tag{6-9}$$

Thus, each c_i is simply the projection of ψ_j onto ϕ_i. The more the two overlap (this is an overlap type integral) the greater the probability that the sampled eigenfunction will be ϕ_i.

The Uncertainty Principle

One of the deepest consequences of quantum mechanics is the uncertainty principle, first described by Heisenberg (a brilliant theoretical physicist, but alas, also a Nazi who ran Germany's nuclear bomb project during WWII—Bohr and Heisenberg were close friends and collaborators until the war, at which point their differences in political philosophies came to the fore; this is the subject of the popular theatrical work *Copenhagen*). In a nutshell, it says the following: When two operators fail to commute, any attempt to simultaneously measure the properties to which they correspond will be *intrinsically incapable* of providing simultaneous accuracy for both quantities beyond a certain level. Moreover, as the accuracy of one measurement becomes increasingly great, the accuracy of the other will become increasingly less good. Mathematically, we say

$$\sigma_A^2 \sigma_B^2 \geq -\frac{1}{4}\langle [A,B] \rangle^2 \tag{6-10}$$

where A and B are two operators with commutator $[A,B]$ and σ^2 is the "variance" in the measurement of a quantity, defined as

$$\sigma_A^2 = \left\langle \left(A - \langle A \rangle \right)^2 \right\rangle \tag{6-11}$$

That is, it measures the square of the difference between any single measurement, and the average of all measurements, averaged *itself* over the same large number of measurements (this is completely analogous to the statistical quantity having the same name). The standard deviation is the square root of the variance, and one also sees the uncertainty principle written as

$$\sigma_A \sigma_B \geq \left| \frac{i}{2}\langle [A,B] \rangle \right| \tag{6-12}$$

where the absolute value sign on the right ensures that the order of the operators doesn't matter (remember that the commutator changes sign when order is reversed).

To amplify on key points, if A and B commute, it is possible to have no variance in the measurement of either property. This will happen when the wave function is simultaneously an eigenfunction of both operators (possible, since they commute) in which case every measurement will give a and b and the variance will be zero. But, if A and B do not commute, there is a limit to how low the product of the two variances can be. Indeed, if the variance in one is brought to zero, by having the wave function be an eigenfunction of that operator, then it must be *infinite* for the other operator, which is to say you cannot know *anything* about that property! To be crystal clear, this uncertainty

has nothing to do with your abilities as a scientist to carry out a measurement accurately. Instead, it is a fundamental property of the quantum mechanical universe that you simply cannot state with any certainty the simultaneous values of two properties whose operators do not commute. Indeed, *the very concept that they have simultaneous values is fallacious.*

Equation 6-10 is so important that it is worth proving. We begin with a proof of the so-called Schwartz inequality. It is a given that

$$\langle f + \lambda g | f + \lambda g \rangle \geq 0 \tag{6-13}$$

for any pair of functions f and g and some arbitrary complex number λ. We can expand this to

$$\langle f | f \rangle + \lambda^* \langle g | f \rangle + \lambda \langle f | g \rangle + |\lambda|^2 \langle g | g \rangle \geq 0 \tag{6-14}$$

This must be true for *any* choice of λ, so let us choose

$$\lambda = -\frac{\langle g | f \rangle}{\langle g | g \rangle} = -\frac{\langle f | g \rangle^*}{\langle g | g \rangle} \tag{6-15}$$

When we plug one of these values in for λ (noting that $< g \mid g >^* = < g \mid g >$ since the square modulus is always a non-negative real number and, as implied also in 6-15, $< f \mid g > = < g \mid f >^*$) we have

$$\langle f | f \rangle - \frac{\langle f | g \rangle}{\langle g | g \rangle} \langle g | f \rangle - \frac{\langle g | f \rangle}{\langle g | g \rangle} \langle f | g \rangle + \frac{\langle f | g \rangle \langle g | f \rangle}{\left(\langle g | g \rangle \right)^2} \langle g | g \rangle \geq 0 \tag{6-16}$$

If we collect like terms and multiply through by $< g \mid g >$, we have

$$\langle f | f \rangle \langle g | g \rangle - \langle f | g \rangle \langle g | f \rangle \geq 0 \tag{6-17}$$

or

$$\langle f | f \rangle \langle g | g \rangle \geq \langle f | g \rangle \langle g | f \rangle \tag{6-18}$$

Note that $< f \mid g >< g \mid f >$ is just a different way of writing $| < f \mid g > |^2$. Given that, we may go a bit further with the Schwartz inequality. We may state

$$\langle f | g \rangle \langle g | f \rangle \geq \frac{1}{4} \left(\langle f | g \rangle + \langle g | f \rangle \right)^2 \tag{6-19}$$

To prove this, it is easiest simply to recall that $< f \mid g >$ is simply a number. Let us say that it is the arbitrary complex number $c = a + bi$ where a and b are real constants. In that case, $< g \mid f >$ is $c^* = a - bi$. If we insert these values into eq. 6-19 we have

$$(a + bi)(a - bi) \geq \frac{1}{4}\left[(a + bi) + (a - bi)\right]^2 \tag{6-20}$$

which reduces to

$$a^2 + b^2 \geq a^2 \tag{6-21}$$

which does indeed always hold true for a and b real numbers. Note that the equality holds when $b = 0$, that is, when the integrals are real numbers, and not complex numbers. By combining eq. 6-18 and 6-19, we have

$$\langle f | f \rangle \langle g | g \rangle \geq \frac{1}{4}\left(\langle f | g \rangle + \langle g | f \rangle\right)^2 \tag{6-22}$$

So, all that is left is to connect eq. 6-22 to eq. 6-12. We do this by choosing for f and g in eq. 6-22 the following

$$f = \left(A - \langle A \rangle\right)\Psi \quad \text{and} \quad g = i\left(B - \langle B \rangle\right)\Psi \tag{6-23}$$

In that case, we have

$$\begin{aligned} &\left\langle \left(A - \langle A \rangle\right)\Psi \middle| \left(A - \langle A \rangle\right)\Psi \right\rangle \left\langle i\left(B - \langle B \rangle\right)\Psi \middle| i\left(B - \langle B \rangle\right)\Psi \right\rangle \\ &\geq \frac{1}{4}\left[\left\langle \left(A - \langle A \rangle\right)\Psi \middle| i\left(B - \langle B \rangle\right)\Psi \right\rangle + \left\langle i\left(B - \langle B \rangle\right)\Psi \middle| \left(A - \langle A \rangle\right)\Psi \right\rangle\right]^2 \end{aligned} \tag{6-24}$$

Now, noting that i in a bra comes out as $-i$ before the integral while i in a ket comes out as just i, and that for the Hermitian operators present in f and g we may use the turnover rule to move them from the bras to the kets, we have

$$\begin{aligned} &\left\langle \Psi \middle| \left(A - \langle A \rangle\right)^2 \middle| \Psi \right\rangle \left\langle \Psi \middle| \left(B - \langle B \rangle\right)^2 \middle| \Psi \right\rangle \\ &\geq \frac{1}{4}\left[i\left\langle \Psi \middle| \left(A - \langle A \rangle\right)\left(B - \langle B \rangle\right) \middle| \Psi \right\rangle - i\left\langle \Psi \middle| \left(B - \langle B \rangle\right)\left(A - \langle A \rangle\right) \middle| \Psi \right\rangle\right]^2 \\ &\geq -\frac{1}{4}\left[\left\langle \Psi | AB - A\langle B \rangle - \langle A \rangle B + \langle A \rangle \langle B \rangle | \Psi \right\rangle - \left\langle \Psi | BA - B\langle A \rangle - \langle B \rangle A + \langle B \rangle \langle A \rangle | \Psi \right\rangle\right]^2 \\ &\geq -\frac{1}{4}\left[\left\langle \Psi | AB - BA | \Psi \right\rangle\right]^2 \\ &\geq -\frac{1}{4}\left[\left\langle \Psi \middle| [A, B] \middle| \Psi \right\rangle\right]^2 \end{aligned} \tag{6-25}$$

which is the uncertainty principle, the desired result. Note that because <*A*> and <*B*> are simply numbers, we were able to cancel most integrals on the r.h.s. of 6-25 because the order of multiplication of an operator by a number does not matter. Only operator times operator is order sensitive, so the only terms that survive define the commutator.

The implications of the uncertainly principle are so profound that if you aren't awestruck by them, you just haven't grasped them yet... In that case, re-read the above until wonder overcomes you.

Homework

To be solved in class:

Given two Hermitian operators A and Z for which $[A,Z] = 0$ and a set of eigenfunctions ϕ common to both for which $A\phi_1 = a\phi_1$, $A\phi_2 = b\phi_2$, $A\phi_3 = b\phi_3$, and $A\phi_4 = c\phi_4$ ($a \neq b \neq c$), which of the following integrals *may* be nonzero and which *must* be zero?

(a) $< \phi_1 \mid \phi_4 >$ (e) $< \phi_1 \mid A \mid \phi_3 >$ (i) $< \phi_2 + \phi_3 \mid Z \mid \phi_2 - \phi_3 >$

(b) $< \phi_2 \mid \phi_4 >$ (f) $< \phi_2 \mid A \mid \phi_3 >$ (j) $< \phi_2 + \phi_3 \mid A \mid \phi_2 - \phi_3 >$

(c) $< \phi_2 \mid \phi_3 >$ (g) $< \phi_1 \mid Z \mid \phi_4 >$ (k) $< \phi_2 + \phi_3 \mid \phi_2 - \phi_3 >$

(d) $< \phi_3 \mid \phi_4 >$ (h) $< \phi_2 \mid Z \mid \phi_3 >$

To be turned in for possible grading Feb. 3:

The Hamiltonian operator for a particular one-dimensional system of mass m that is "free", in the sense that there is no potential energy dependent on the one-dimensional position coordinate x, is $H = T$ (i.e., $V = 0$).

(a) Show that the set of functions $\psi_j = \sin(jx) + i\cos(jx)$ where $j = \pm 1, 2, 3, \ldots$ are eigenfunctions of both H and of the one-dimensional momentum operator.

(b) What are the expectation values for H and $\mathbf{p}$ for the $j = 5$ stationary state? Note that since the eigenfunctions in this case are not normalized, the expectation value for a given operator A must be defined as

$$\langle A \rangle = \frac{\langle \psi | A | \psi \rangle}{\langle \psi | \psi \rangle}$$

(c) What is the relationship between these two expectation values?