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

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Answers to Homework Set 2

From lecture 5: Consider a pair of degenerate, normalized eigenfunctions, ϕ_1 and ϕ_2, of a Hermitian operator A with common eigenvalue a. Show that two new functions defined as $u_1 = \phi_1$ and $u_2 = \phi_2 + S\phi_1$ are orthogonal, provided that S is properly chosen (i.e., determine what value of S is required to enforce orthogonality). Show that u_1 and u_2 remain degenerate with common eigenvalue a.

We are told that ϕ_1 and ϕ_2 are degenerate eigenfunctions of A with eigenvalue a. The question is how to pick a value S such that the two functions

$$u_1 = \phi_1 \quad \text{and} \quad u_2 = \phi_2 - S\phi_1$$

will be orthogonal to one another and still be eigenfunctions of A with eigenvalue a.

To begin, we simply proceed from the definition of orthogonality (and practice our newfound mastery of Dirac notation

$$\begin{aligned}
0 &= \langle u_1 | u_2 \rangle \\
&= \langle \phi_1 | \phi_2 - S\phi_1 \rangle \\
&= \langle \phi_1 | \phi_2 \rangle - \langle \phi_1 | S\phi_1 \rangle \\
&= \langle \phi_1 | \phi_2 \rangle - S\langle \phi_1 | \phi_1 \rangle \\
&= \langle \phi_1 | \phi_2 \rangle - S|\phi_1|^2 \\
&= \langle \phi_1 | \phi_2 \rangle - S
\end{aligned}$$

Where the last line follows from the normalization of ϕ_1.

From rearranging, we have

$$S = \langle \phi_1 | \phi_2 \rangle$$

This integral (S) is called the "overlap integral" between functions ϕ_1 and ϕ_2. Notice that it is zero if the functions are already orthogonal, and it is the square modulus of ϕ_1 if the functions are identical (equal to one when the functions are normalized). Thus, S, ranges from 0 to 1 depending on how much the two functions "overlap" and hence its name.

This choice of S guarantees orthogonality, but we need to verify that u_1 and u_2 are eigenfunctions of A with eigenvalues a. Of course, by definition of u_1 this is a given, since it is unchanged from ϕ_1, but what about u_2?

The expectation value of A for u_2 is

$$
\begin{aligned}
\langle A(u_2)\rangle &= \frac{\langle u_2|A|u_2\rangle}{|u_2|^2} \\
&= \frac{\langle \phi_2 - \langle\phi_1|\phi_2\rangle\phi_1|A|\phi_2 - \langle\phi_1|\phi_2\rangle\phi_1\rangle}{|\phi_2 - \langle\phi_1|\phi_2\rangle\phi_1|^2} \\
&= \frac{\langle \phi_2 - \langle\phi_1|\phi_2\rangle\phi_1|a\phi_2 - \langle\phi_1|\phi_2\rangle a\phi_1\rangle}{|\phi_2 - \langle\phi_1|\phi_2\rangle\phi_1|^2} \\
&= a\frac{|\phi_2 - \langle\phi_1|\phi_2\rangle\phi_1|^2}{|\phi_2 - \langle\phi_1|\phi_2\rangle\phi_1|^2} \\
&= a
\end{aligned}
$$

QED.

For those eager for more details, this technique for orthogonalizing functions is called Gram-Schmidt orthogonalization. It is easily generalized to multiple functions (first you make all other functions orthogonal to the first, now you hold the new second one fixed and make all remaining functions orthogonal to it, etc.). The second term in the definition of u_2 is sometimes called an "orthogonality tail", since it is a little piece of ϕ_1 tacked onto ϕ_2 in order to orthogonalize it.

From lecture 6: 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 $n = 5$ stationary state? Note that since the eigenfunctions in this case are not normalized, the expectation value for a given operator A is 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?

(a) Recalling the definitions of the two operators,

$$\begin{aligned} H &= T \\ &= -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \end{aligned} \qquad \text{and} \qquad \mathbf{p} = -i\hbar(\mathbf{i})\frac{d}{dx}$$

the only mathematical operations that we really need to perform are to take the first and second derivatives of the trial functions, thus

$$\frac{d}{dx}\left[\sin(jx) + i\cos(jx)\right] = j\left[\cos(jx) - i\sin(jx)\right]$$

and

$$\frac{d^2}{dx^2}\left[\sin(jx) + i\cos(jx)\right] = -j^2\left[\sin(jx) + i\cos(jx)\right]$$

with those in hand we may note

$$\begin{aligned} H\psi_j &= \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\left[\sin(jx) + i\cos(jx)\right] \\ &= \left[-\frac{\hbar^2}{2m}\left(-j^2\right)\right]\left[\sin(jx) + i\cos(jx)\right] \\ &= \left(\frac{\hbar^2 j^2}{2m}\right)\psi_j \end{aligned}$$

and

$$\begin{aligned} \mathbf{p}\psi_j &= \left[-i\hbar(\mathbf{i})\frac{d}{dx}\right]\left[\sin(jx) + i\cos(jx)\right] \\ &= \left[-i\hbar(\mathbf{i})(j)\right]\left[\cos(jx) - i\sin(jx)\right] \\ &= \left[-\hbar(\mathbf{i})(j)\right]\left[i\cos(jx) + \sin(jx)\right] \\ &= \left[-(\hbar j)(\mathbf{i})\right]\psi_j \end{aligned}$$

which illustrates the eigenfunction/eigenvalue relationships between the functions and the operators.

(b) To evaluate the expectation values we must multiply the above equations on the left by the complex conjugate of ψ_5 and integrate over all x. However, since we have just shown that ψ_5 is an eigenfunction, we may replace the operators in the integrals with their respective eigenvalues, move them in front of the integrals, and we will be left having to evaluate only $< \psi_5 \mid \psi_5 >$. Actually, that is not so easy in this case. However, as noted above for these unnormalized wave functions, we will simply divide by that quantity as well in computation of the expectation values, so the only thing to survive will be the eigenvalues. Of course, this is as it must be—we're using eigenfunctions of the operators as our wave functions. The expectation value of an eigenfunction is just the eigenvalue, by definition. Thus, for $n = 5$, we will have expectation values

$$\langle H \rangle_{j=5} = \frac{25\hbar^2}{2m} \qquad \text{and} \qquad \langle \mathbf{p} \rangle_{n=5} = -5\hbar(\mathbf{i})$$

(c) The relationship between the expectation values is fairly trivial. Recall that T (the first part of the Hamiltonian) is $|\mathbf{p}|^2 / 2m$ and indeed we see that momentum can be either positive or negative depending on the sign of j in the eigenfunction, but the kinetic energy is always positive as it depends on j^2.

From lecture 7: For the particle in a box of length L, what is the probability of finding the particle in the intervals $0.45L$ to $0.55L$ for the following levels: (a) $n = 1$; (b) $n = 2$; (c) $n = 7{,}503$; (d) The Bohr correspondence principle states that quantum mechanics should reduce to classical mechanics for very large quantum numbers. Is your final answer consistent with classical mechanics? Explain the direction of deviations from the classical answer, if any, for cases (a), (b), and (c).

We will proceed by solving the probabilities generally, and then evaluate those probabilities for the particular cases of $n = 1$, 2, etc.. For the probability over the indicated interval, we need to evaluate the square modulus of the wave function integrated from $0.45L$ to $0.55L$

$$\begin{aligned}
P_1 &= \frac{2}{L}\int_{0.45L}^{0.55L}\left[\sin\left(\frac{n\pi x}{L}\right)\right]^* \sin\left(\frac{n\pi x}{L}\right)dx \\
&= \frac{1}{L}\int_{0.45L}^{0.55L}\left[1-\cos\left(\frac{2n\pi x}{L}\right)\right]dx \\
&= \frac{1}{L}\left[\int_{0.45L}^{0.55L}dx - \int_{0.45L}^{0.55L}\cos\left(\frac{2n\pi x}{L}\right)dx\right] \\
&= \frac{1}{L}\left[0.55L-0.45L-\frac{L}{2n\pi}\sin(1.1n\pi)+\frac{L}{2n\pi}\sin(0.9n\pi)\right] \\
&= 0.1-\frac{1}{2n\pi}\left[\sin(1.1n\pi)-\sin(0.9n\pi)\right]
\end{aligned}$$

If we evaluate this for $n = 1$, 2, 7,503, and infinity (a very large quantum number) the probabilities are 0.19836316, 0.00645107, 0.10003432, and 0.1, respectively.

Case (a) deviates to higher probability because the chosen interval spans the center of the box, and the ground-state wave function has its extra amplitude in the center of the box. Case (b) deviates to lower probability because its only node is smack in the middle of the chosen interval. Case (c) is very, very close to the classical answer because it is such a high quantum number (note that the classical answer is equal probability everywhere, so if I pick *any* interval that is 10% of the box, the probability of finding the particle there is 0.1 -- as is shown by the choice of n being infinity).