Chem221a : Midterm Solutions

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Problem 1

(a) The wavefunction tunnels into the classically forbidden zone on either side. Wavefunctions alternate even/odd from the bottom, start with no nodes, and add one node with each wavefunction.

Figure 1: Invisible solution to 1a (to be made visible later)

(b) The trick to this one is to cut the picture above in half. Putting an infinite wall at the origin, and just looking at the right side of the potential, gives us the modified potential.

We know that the wavefunction must go to zero at the infinite wall, so any solution to the general problem with $\psi(0) \neq 0$ is not a solution to this problem. However, any solution with $\psi(0) = 0$ *is* a solution for the modified potential. So the odd wavefunctions (and their associated energies) from part (a) are also solutions to part (b). This means that the modified potential will only have two bound states. As always, the lowest energy wavefunction has no nodes, and the first excited state has one node.

Figure 2: Invisible solution to 1b (to be made visible later)

Problem 2

If the initial state of the electron is $|\psi(t=0)\rangle = |S_x;+\rangle$, then we can represent it in the $|\pm\rangle$ basis as:

$$|\psi(t=0)\rangle \doteq \begin{pmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix} \tag{1}$$

We're going to be calculating the time evolution of this state, which we have expressed in terms of our $|\pm\rangle$ states:

$$|\psi(t)\rangle = e^{-iHt/\hbar} |\psi(0)\rangle \tag{2}$$

$$= \sum_{j\in\{+,-\}} e^{-i\omega S_z t/\hbar} |j\rangle \langle j|\psi(0)\rangle \tag{3}$$

The above expression is completely general, but just to remind you what it means, our initial state gives

$$\langle + | \psi(0) \rangle = 1/\sqrt{2} \tag{4}$$
$$\langle - | \psi(0) \rangle = 1/\sqrt{2} \tag{5}$$

We choose the $|\pm\rangle$ basis because that will give us a simple formula for the time evolution (and because we know representations of all the spin operators in that basis). Since the Hamiltonian is only a function of S_z, the eigenkets of S_z will also be eigenkets of the Hamiltonian. Specifically, $S_z |\pm\rangle = \pm\frac{\hbar}{2} |\pm\rangle$. So:

$$|\psi(t)\rangle = e^{-i\omega S_z t/\hbar} |+\rangle \langle + | \psi(0)\rangle + e^{-i\omega S_z t/\hbar} |-\rangle \langle - | \psi(0)\rangle \tag{6}$$
$$= e^{-i\omega(\hbar/2)t/\hbar} |+\rangle \left(\frac{1}{\sqrt{2}}\right) + e^{-i\omega(-\hbar/2)t/\hbar} |-\rangle \left(\frac{1}{\sqrt{2}}\right) \tag{7}$$

Representing this as a vector in the $|\pm\rangle$ basis:

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{-i\omega t/2} \\ e^{i\omega t/2} \end{pmatrix} \tag{8}$$

With that, we can move on to calculating expectation values.

(a) $\langle S_x \rangle_t$

As always, the expectation value is taking by sandwiching the relevant operator between the states in question. Here, we use our time-dependent states, remembering that the bra is represented as the complex conjugate-transpose of the ket representation:

$$\langle S_x \rangle_t = \langle \psi(t) | S_x | \psi(t) \rangle \tag{9}$$
$$= \left(\frac{1}{\sqrt{2}} \begin{pmatrix} e^{i\omega t/2} & e^{-i\omega t/2} \end{pmatrix}\right) \left(\frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\right) \left(\frac{1}{\sqrt{2}} \begin{pmatrix} e^{-i\omega t/2} \\ e^{i\omega t/2} \end{pmatrix}\right) \tag{10}$$
$$= \frac{\hbar}{2} \left(\frac{1}{2} \left(e^{i\omega t} + e^{-i\omega t}\right)\right) \tag{11}$$
$$= \frac{\hbar}{2} \cos(\omega t) \tag{12}$$

Some of you may be wondering why this doesn't have the expectation value of the $|S_x; +\rangle$ eigenstate. The reason is that the Hamiltonian isn't a function of S_x. An eigenstate is only time-independent if it is an energy eigenstate (this is a common confusion). Of course, at time $t = 0$ this expression gives us what we would expect.[1]

[1] No pun intended.

(b) $\langle S_y \rangle_t$

$$\begin{aligned}
\langle S_y \rangle_t &= \langle \psi(t)|S_y|\psi(t)\rangle && (13)\\
&= \frac{\hbar}{4}\begin{pmatrix} e^{i\omega t/2} & e^{-i\omega t/2}\end{pmatrix}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} e^{-i\omega t/2} \\ e^{i\omega t/2}\end{pmatrix} && (14)\\
&= \frac{\hbar}{4} i \left(-e^{i\omega t} + e^{-i\omega t}\right) && (15)\\
&= \frac{\hbar}{2}\frac{1}{2i}\left(e^{i\omega t} - e^{-i\omega t}\right) && (16)\\
&= \frac{\hbar}{2}\sin(\omega t) && (17)
\end{aligned}$$

(c) $\langle S_z \rangle_t$

$$\begin{aligned}
\langle S_z \rangle_t &= \langle \psi(t)|S_z|\psi(t)\rangle && (18)\\
&= \frac{\hbar}{4}\begin{pmatrix} e^{i\omega t/2} & e^{-i\omega t/2}\end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} e^{-i\omega t/2} \\ e^{i\omega t/2}\end{pmatrix} && (19)\\
&= \frac{\hbar}{4}(1-1) && (20)\\
&= 0 && (21)
\end{aligned}$$

This zero means that the spin is precessing in the $z = 0$ plane. This sort of thing is really important to those of you who do NMR (or who will have Alex Pines on your qual committee!)

Problem 3

As some of you may have noticed, this problem is based on Sakurai, Chapter 2, #5, although it has been broken down to make it a little easier. So let's do it, part by part:

(a) We just need to calculate the commutator $[H, x]$. There are several ways of doing this, but they all start with the same process:

$$\begin{aligned}
[H, x] &= \left[\frac{p^2}{2m} + V(x), x\right] && (22)\\
&= \left[\frac{p^2}{2m}, x\right] + [V(x), x] && (23)\\
&= \left[\frac{p^2}{2m}, x\right] && (24)\\
&= \frac{1}{2m}\left[p^2, x\right] && (25)
\end{aligned}$$

since an (analytic) function of any operator commutes with that operator and $[\lambda A, B] = \lambda[A, B]$.

(i) The easiest method is probably to use a trick that Prof. Neumark mentioned briefly on 5 October: if both A and B commute with their commutator, $[A, B]$, then $[A, f(B)] =$

$[A,B]f'(B)$. This means that $[f(B),A] = [B,A]f'(B)$. For us, $A \mapsto x$ and $f(B) \mapsto p^2$. So

$$\begin{aligned} \frac{1}{2m}\left[p^2,x\right] &= \frac{1}{2m}[p,x](2p) && (26)\\ &= \frac{\hbar}{i}\frac{p}{m} && (27) \end{aligned}$$

(ii) Another way to solve this would be to use our rule about $[AB,C]$ (since $p^2 = pp$):

$$\begin{aligned} \frac{1}{2m}\left[p^2,x\right] &= \frac{1}{2m}\left(p[p,x]+[p,x]p\right) && (28)\\ &= \frac{1}{2m}\left(-2i\hbar p\right) && (29)\\ &= \frac{\hbar}{i}\frac{p}{m} && (30) \end{aligned}$$

(iii) We can also put this into one of the representations (we'll try position representation, even though momentum representation would be easier):

$$\begin{aligned} [p^2,x]\psi(x) &= \left[\frac{-\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2},x\right]\psi(x) && (31)\\ &= \frac{-\hbar^2}{2m}\left[\frac{\mathrm{d}^2}{\mathrm{d}x^2},x\right]\psi(x) && (32)\\ &= \frac{-\hbar^2}{2m}\left(\frac{\mathrm{d}^2}{\mathrm{d}x^2}\left(x\psi(x)\right) - x\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi(x)\right) && (33)\\ &= \frac{-\hbar^2}{2m}\left(\frac{\mathrm{d}}{\mathrm{d}x}\left(x\psi'(x)+\psi(x)\right) - x\psi''(x)\right) && (34)\\ &= \frac{-\hbar^2}{2m}\left(\psi'(x)+x\psi''(x)+\psi'(x)-x\psi''(x)\right) && (35)\\ &= \frac{-\hbar^2}{m}\frac{\mathrm{d}}{\mathrm{d}x}\psi(x) && (36)\\ &= \frac{\hbar}{i}\frac{p}{m}\psi(x) && (37) \end{aligned}$$

Therefore

$$[H,x] = \frac{\hbar}{i}\frac{p}{m} \qquad (38)$$

As a quick aside, let's think about what this means. Classically, p/m is the velocity, which is also the time derivative of x. So the commutator of the Hamilonian with x is proportional to the time derivative of x.... The intrepid among you should look up the Heisenberg equation of motion.

(b) Now we'll plug in our result from above to solve this part:

$$[[H,x],x] = \left[\frac{\hbar}{i}\frac{p}{m}, x\right] \tag{39}$$

$$= \frac{\hbar}{im}[p,x] \tag{40}$$

$$= \frac{-\hbar^2}{m} \tag{41}$$

(c) Finally, let's find this one. The easiest way to do it is to start with the result from the previous part (multiplied by $-1/2$):

$$\frac{\hbar^2}{2m} = \frac{1}{2}[x,[H,x]] \tag{42}$$

$$= \frac{1}{2}[x, Hx - xH] \tag{43}$$

$$= \frac{1}{2}\left(xHx - x^2H - Hx^2 + xHx\right) \tag{44}$$

Now we sandwich this with a bra and ket of $|n\rangle$ on either side.

$$\left\langle n\middle|\frac{\hbar^2}{2m}\middle|n\right\rangle = \frac{1}{2}\left\langle n\middle|2xHx - x^2H - Hx^2\middle|n\right\rangle \tag{45}$$

$$\frac{\hbar^2}{2m} = \frac{1}{2}\left(2\langle n|xHx|n\rangle - \left\langle n\middle|x^2H\middle|n\right\rangle - \left\langle n\middle|Hx^2\middle|n\right\rangle\right) \tag{46}$$

Next we'll use the fact that $H|n\rangle = E_n|n\rangle$, and that H is Hermitian:

$$\frac{\hbar^2}{2m} = \frac{1}{2}\left(2\langle n|xHx|n\rangle - 2E_n\left\langle n\middle|x^2\middle|n\right\rangle\right) \tag{47}$$

$$= \langle n|xHx|n\rangle - E_n\left\langle n\middle|x^2\middle|n\right\rangle \tag{48}$$

$$= \sum_{n'}\langle n|xH|n'\rangle\langle n'|x|n\rangle - \sum_{n''}E_n\langle n|x|n''\rangle\langle n''|x|n\rangle \tag{49}$$

$$= \sum_{n'}E_{n'}\langle n|x|n'\rangle\langle n'|x|n\rangle - \sum_{n''}E_n\langle n|x|n''\rangle\langle n''|x|n\rangle \tag{50}$$

$$= \sum_{n'}E_{n'}\left|\langle n|x|n'\rangle\right|^2 - \sum_{n''}E_n\left|\langle n|x|n''\rangle\right|^2 \tag{51}$$

Since we're *adding* these two summations together, we can match like terms, and therefore we can combine the sums under one index.

$$\frac{\hbar^2}{2m} = \sum_{n'}E_{n'}\left|\langle n|x|n'\rangle\right|^2 - E_n\left|\langle n|x|n'\rangle\right|^2 \tag{52}$$

$$= \sum_{n'}(E_{n'} - E_n)\left|\langle n|x|n'\rangle\right|^2 \quad \square \tag{53}$$

Many of you tried to solve this by simplifying the expression with the sum instead of creating it from the commutator. That's okay; so did I when I first tried it. It can be done, although I can't take credit for all the ideas.

We start with that sum, use the eigenvalues to get the Hamiltonian back out, and get rid of the sum over states:

$$\begin{aligned}
\sum_{n'}(E_{n'} - E_n)\left|\langle n|x|n'\rangle\right|^2 &= \sum_{n'}(E_{n'} - E_n)\langle n|x|n'\rangle\langle n'|x|n\rangle && (54)\\
&= \sum_{n'}\left(\langle n|xE_{n'}|n'\rangle\langle n'|x|n\rangle - \langle n|E_n x|n'\rangle\langle n'|x|n\rangle\right) && (55)\\
&= \sum_{n'}\left(\langle n|xH|n'\rangle\langle n'|x|n\rangle - \langle n|Hx|n'\rangle\langle n'|x|n\rangle\right) && (56)\\
&= \langle n|xHx|n\rangle - \left\langle n\middle|Hx^2\middle|n\right\rangle && (57)\\
&= \langle n|[x, Hx]|n\rangle && (58)
\end{aligned}$$

However, this was not the only place we could put our E_n in order to get the Hamiltonian back. We have also obtained the expression

$$\sum_{n'}(E_{n'} - E_n)\left|\langle n|x|n'\rangle\right|^2 = \langle n|xHx|n\rangle - \left\langle n\middle|x^2H\middle|n\right\rangle \tag{59}$$

Setting these two equal to each other gives us

$$\left\langle n\middle|x^2H\middle|n\right\rangle = \left\langle n\middle|Hx^2\middle|n\right\rangle \tag{60}$$

Note that this means that the expectation values are equal for any given energy eigenstate. That's not the same as saying that the operators are equal. In general, H does *not* commute with x^2.

However, now we can find a value for that using our previous result:

$$\begin{aligned}
&= \langle n|[x, [H, x]]|n\rangle && (61)\\
&= 2\langle n|xHx|n\rangle - \left\langle n\middle|x^2H\middle|n\right\rangle - \left\langle n\middle|Hx^2\middle|n\right\rangle && (62)
\end{aligned}$$

Using equation (60), this becomes

$$\begin{aligned}
\frac{\hbar^2}{m} &= 2\langle n|xHx|n\rangle - 2\left\langle n\middle|Hx^2\middle|n\right\rangle && (63)\\
&= 2\langle n|[x, Hx]|n\rangle && (64)\\
\frac{\hbar^2}{2m} &= \langle n|[x, Hx]|n\rangle && (65)
\end{aligned}$$

Comparing this with equation (58), we see that

$$\sum_{n'}(E_{n'} - E_n)\left|\langle n|x|n'\rangle\right|^2 = \frac{\hbar^2}{2m} \tag{66}$$

As one last interesting comment, we learn something interesting if we use the result from part (a) in equation (57). We'll assume that you've shown the result of this problem:

$$\frac{\hbar^2}{2m} = \langle n|xHx - Hxx|n\rangle \tag{67}$$

$$= \langle n|[x, H]x|n\rangle \tag{68}$$

$$= \left\langle n\middle|-\frac{\hbar}{im}px\middle|n\right\rangle \tag{69}$$

$$= -\frac{\hbar}{im}\langle n|px|n\rangle \tag{70}$$

$$-\frac{i\hbar}{2} = \langle n|px|n\rangle \tag{71}$$

So $\langle n|px|n\rangle$ is purely imaginary. This means that its complex conjugate is also purely imaginary: $\langle n|px|n\rangle^* = \langle n|xp|n\rangle$. Defining $ib = \langle n|px|n\rangle$, this gives us two interesting expressions:

$$\langle n|\{x, p\}|n\rangle = 0 \tag{72}$$

$$\langle n|[x, p]|n\rangle = -2ib \tag{73}$$

However, we know the canonical commutator $[x, p] = i\hbar$, so this wraps around full circle to show us that $ib = \langle n|px|n\rangle = -i\hbar/2$.

The fact that the expectation value of the anticommutator is zero can be shown from the continuity equation.