HW7

PHYS4210: Quantum Mechanics

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Problem 1. (5.4)

a) Equation (5.17) is

$$\psi_\pm(\mathbf{r}_1,\mathbf{r}_2) = A[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) \pm \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)] \tag{1.1}$$

By inspection, it's probably going to be $1/\sqrt{2}$. But, of course, let's check. Imposing the normalization condition,

$$\int |\psi_\pm(\mathbf{r}_1,\mathbf{r}_2)|^2 \, \mathrm{d}^3\mathbf{r}_1 \mathrm{d}^3\mathbf{r}_2 = 1 \tag{1.2}$$

The square of the wavefunction is

$$|\psi_\pm(\mathbf{r}_1,\mathbf{r}_2)|^2 = |A|^2 \left[\psi_a^*(\mathbf{r}_1)\psi_b^*(\mathbf{r}_2) \pm \psi_b^*(\mathbf{r}_1)\psi_a^*(\mathbf{r}_2)\right] \times \left[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) \pm \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)\right]. \tag{1.3}$$

Now, when we do the multiplication, the cross terms will look like $\psi_b^*(\mathbf{r}_1)\psi_a(\mathbf{r}_2)$, which, since ψ_a and ψ_b are orthogonal, will integrate to zero when we normalize. Therefore, the square of the wavefuntion is *effectively*

$$|\psi_\pm(\mathbf{r}_1,\mathbf{r}_2)|^2 = |A|^2 \left[|\psi_a(\mathbf{r}_1)|^2|\psi_b(\mathbf{r}_2)|^2 + |\psi_b(\mathbf{r}_1)|^2|\psi_a(\mathbf{r}_2)|^2\right] \tag{1.4}$$

Doing the integration:

$$\int |\psi_\pm(\mathbf{r}_1,\mathbf{r}_2)|^2 \, \mathrm{d}^3\mathbf{r}_1 \mathrm{d}^3\mathbf{r}_2 = |A|^2 \Bigg[\left(\int \mathrm{d}^3\mathbf{r}_1 \, |\psi_a(\mathbf{r}_1)|^2\right)\left(\int \mathrm{d}^3\mathbf{r}_2 \, |\psi_b(\mathbf{r}_2)|^2\right) + \left(\int \mathrm{d}^3\mathbf{r}_1 \, |\psi_b(\mathbf{r}_1)|^2\right)\left(\int \mathrm{d}^3\mathbf{r}_2 \, |\psi_a(\mathbf{r}_2)|^2\right) \Bigg] \tag{1.5}$$

$$\int |\psi_\pm(\mathbf{r}_1,\mathbf{r}_2)|^2 \, \mathrm{d}^3\mathbf{r}_1 \mathrm{d}^3\mathbf{r}_2 = 2|A|^2. \tag{1.6}$$

So, $A = 1/\sqrt{2}$, as expected.

b) If the two wavefunctions are the same, then

$$\psi_\pm(\mathbf{r}_1,\mathbf{r}_2) = 2\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2), \tag{1.7}$$

meaning

$$\int |\psi_\pm(\mathbf{r}_1,\mathbf{r}_2)|^2 \, \mathrm{d}^3\mathbf{r}_1 \mathrm{d}^3\mathbf{r}_2 = 4|A|^2 \left(\int |\psi_a(\mathbf{r}_1)|^2 \, \mathrm{d}^3\mathbf{r}_1 \times \int |\psi_b(\mathbf{r}_2)|^2 \, \mathrm{d}^3\mathbf{r}_2 \right) = 4|A|^2 = 1, \tag{1.8}$$

so this time, $A = 1/2$.

Problem 2. (5.6)

We will need the expectation values which we already solved for in a previous HW:

$$\langle x \rangle = \frac{a}{2} \tag{2.1}$$
$$\langle x^2 \rangle = a^2 \left(\frac{1}{3} - \frac{1}{2(n\pi)^2} \right) \tag{2.2}$$

a) For the case of distinguishable particles, we can use Equation (5.23):

$$\begin{aligned} \left\langle (x_1 - x_2)^2 \right\rangle_d &= \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2 \langle x \rangle_a \langle x \rangle_b && (2.3) \\ &= a^2 \left[\frac{2}{3} - \frac{1}{2} \left(\frac{1}{(n\pi)^2} + \frac{1}{(\ell\pi)^2} \right) \right] && (2.4) \\ &\boxed{= a^2 \left[\frac{1}{6} - \frac{1}{2\pi^2} \left(\frac{1}{n^2} + \frac{1}{\ell^2} \right) \right].} && (2.5) \end{aligned}$$

b) In the case of identical bosons, we need a term $-2|\langle x \rangle_{ab}|^2$ where

$$\langle x \rangle_{ab} = \int x \psi_a^*(x) \psi_b(x) \, \mathrm{d}x. \tag{2.6}$$

In our case then

$$\langle x \rangle_{n\ell} = \frac{2}{a} \int_0^a \int x \sin\left(\frac{n\pi x}{a} \right) \sin\left(\frac{\ell\pi x}{a} \right) \, \mathrm{d}x. \tag{2.7}$$

I'll just use Mathematica:

$$|\langle x \rangle_{n\ell}|^2 = \frac{16a^2 n^2 \ell^2 ((-1)^{n+\ell} - 1)^2}{\pi^4 (n^2 - \ell^2)^4}. \tag{2.8}$$

So,

$$\boxed{\langle (x_1 - x_2)^2 \rangle = a^2 \left[\frac{1}{6} - \frac{1}{2\pi^2} \left(\frac{1}{n^2} + \frac{1}{\ell^2} \right) \right] - \frac{32a^2 n^2 \ell^2 ((-1)^{n+\ell} - 1)^2}{\pi^4 (n^2 - \ell^2)^4}.} \tag{2.9}$$

c) For identical fermions, the last term just picks up a minus:

$$\boxed{\langle (x_1 - x_2)^2 \rangle = a^2 \left[\frac{1}{6} - \frac{1}{2\pi^2} \left(\frac{1}{n^2} + \frac{1}{\ell^2} \right) \right] - \frac{32a^2 n^2 \ell^2 ((-1)^{n+\ell} - 1)^2}{\pi^4 (n^2 - \ell^2)^4}.} \tag{2.10}$$

Problem 3. (5.17)

a) This part is super straightforward, so I am guessing that the "Explain your answers for each element" is for the second part. We fill up the first s orbital, then the s orbital in the next energy level, then since the next energy level admits another value of l, we get a p orbital. That's it.

$$\begin{aligned}
\text{H: } & (1s) \\
\text{He: } & (1s)^2 \\
\text{Li: } & (1s)^2(2s) \\
\text{Be: } & (1s)^2(2s)^2 \\
\text{B: } & (1s)^2(2s)^2(2p) \\
\text{C: } & (1s)^2(2s)^2(2p)^2 \\
\text{N: } & (1s)^2(2s)^2(2p)^3 \\
\text{O: } & (1s)^2(2s)^2(2p)^4 \\
\text{F: } & (1s)^2(2s)^2(2p)^5 \\
\text{Ne: } & (1s)^2(2s)^2(2p)^6
\end{aligned}$$

b) The first four atoms in their ground states have $\ell = 0$, meaning the letter will be S for all of them. For hydrogren, the single electron can only have spin $s = 1/2$, so $2S + 1 = 2$. Therefore the grand total $J = 1/2$, so Hydrogen has ${}^2S_{1/2}$.

Helium fills the $1s$ orbital, so they now occupy a singlet configuration with spin 0: thus Helium has ${}^1S_0$.

Lithium has a new electron in the $2s$ orbital. There is still no orbital angular momentum and the spin of a single filled s orbital is zero so really this is the same as Hydrogen: ${}^2S_{1/2}$.

In a similar vein, Beryllium will be the same as Helium: ${}^1S_0$.

Boron fills both $(1s)$ and $(2s)$ orbitals. Again, these have 0 angular momentum, so all we really care about is the electron in the $(2p)$ orbital. It is a single electron, so it has spin $1/2$, and with orbital angular momentum $\ell = 1$, the total angular momentum is either $3/2$ or $1/2$. The letter is now P since $\ell = 0$. So the two possibilities for Boron are: ${}^2P_{3/2}$ and ${}^2P_{1/2}$.

For carbon, the two electrons can have total spin 1 or 0, and the total orbital angular momentum can now be 2, 1, or 0, so it's a bit more complicated. For $L = 0$, it is simple, but when $L = 1$, S can be 0 or 1. In the latter, we therefore have $J = 2, 1, 0$. Similarly, when $L = 2$ and $S = 1$, we will have $J = 3, 2, 1$. So: ${}^1S_0$, ${}^3S_1$, ${}^1P_1$, ${}^3P_2$, ${}^3P_1$, ${}^3P_0$, ${}^1D_2$, ${}^3D_3$, ${}^3D_2$, ${}^3D_1$.

Lastly, for nitrogen, $L = 3, 2, 1$ or 0, and $S = 3/2$ or $1/2$. Following a similar process as before we get: ${}^2S_{1/2}$, ${}^4S_{3/2}$, ${}^2P_{3/2}$, ${}^2P_{1/2}$, ${}^4P_{5/2}$, ${}^4P_{3/2}$, ${}^4P_{1/2}$, ${}^2D_{5/2}$, ${}^2D_{3/2}$, ${}^4D_{7/2}$, ${}^4D_{5/2}$, ${}^4D_{3/2}$, ${}^4D_{1/2}$, ${}^2F_{7/2}$, ${}^2F_{5/2}$, ${}^4F_{9/2}$, ${}^4F_{7/2}$, ${}^4F_{5/2}$, ${}^4F_{3/2}$.

Problem 4. (6.1c)

Parity only affects the angular part like $\hat{\Pi}\, Y_\ell^m(\theta, \phi) = Y_\ell^m(\pi - \theta, \phi + \pi)$. Recall,

$$Y_\ell^m(\theta, \phi) = \sqrt{\frac{(2\ell + 1)}{4\pi} \frac{(\ell - m)!}{(\ell + m)!}} e^{im\phi} P_\ell^m(\cos\theta). \tag{4.1}$$

The coefficient obviously doesn't change. The exponential turns into:

$$e^{im(\phi+\pi)} = e^{im\pi} e^{im\phi} = (-1)^m e^{im\phi}. \tag{4.2}$$

For the associated Legendre polynomials, we are taking $\cos\theta \to \cos(\pi - \theta) = -\cos\theta$ and $\sin\theta \to \sin(\pi - \theta) = \sin\theta$. Using the definition of the associated Legendre functions and the ℓth Legendre function, we can see that taking $x \to -x$ results in a factor of -1 only if the quantity $\ell + m$ is odd, because we only see x^2, but the derivatives will pick up a minus. Therefore, we can have a general factor of $(-1)^{\ell+m}$, which, combining with the $(-1)^m$ from before:

$$(-1)^m(-1)^{\ell+m} = (-1)^{2m}(-1)^{\ell}. \tag{4.3}$$

-1 raised to any even number is always 1, so all we have leftover is $(-1)^{\ell}$. Therefore:

$$\boxed{\hat{\Pi}\,\psi_{n\ell m}(r,\theta,\phi) = (-1)^{\ell}\psi_{n\ell m}(r,\theta,\phi).} \tag{4.4}$$

Problem 5. (6.8)

We did this one in class!

a) First,

$$\left\langle f \,\middle|\, \hat{\Pi} \,\middle|\, g \right\rangle = \int_{-\infty}^{\infty} f^*(x)g(-x)\,\mathrm{d}x. \tag{5.1}$$

Taking $x \to -x$:

$$= \int_{\infty}^{-\infty} f^*(-x)g(x)\,(-\mathrm{d}x) = \int_{-\infty}^{\infty} f^*(-x)g(x)\,\mathrm{d}x = \left\langle f \,\middle|\, \hat{\Pi}^\dagger \,\middle|\, g \right\rangle, \tag{5.2}$$

so $\boxed{\hat{\Pi}^\dagger = \hat{\Pi}.}$

b) As a unitary operator, we have that

$$\hat{\Pi}^\dagger\hat{\Pi}\,\psi = |\lambda|^2\psi = \psi, \tag{5.3}$$

where the second expression follows from applying the operators to the wavefunction and getting the eigenvalues and the third follows from the unitarity of the parity operator rendering $\hat{\Pi}^\dagger\hat{\Pi} = 1$. Now, since the parity operator is also Hermitian, it means that its eigenvalues must also be real, so it must be that $\lambda^2 = 1$, meaning $\lambda = 1$ or -1.

Problem 6. (6.10)

a) For $\hat{x}$:

$$\begin{aligned}
\left\langle f \,\middle|\, \hat{\Pi}^\dagger\hat{x}\hat{\Pi} \,\middle|\, g \right\rangle &= \int_{-\infty}^{\infty} f^*(-x)xg(-x)\,\mathrm{d}x && (6.1)\\
&= \int_{\infty}^{-\infty} f^*(x)(-x)g(x)\,(-\mathrm{d}x) && (6.2)\\
&= \int_{-\infty}^{\infty} f^*(x)(-x)g(x)\,\mathrm{d}x = \langle f \,|\, (-\hat{x}) \,|\, g\rangle, && (6.3)
\end{aligned}$$

so $\boxed{\hat{x}' = -\hat{x}.}$

b) For $\hat{p}$, we have

$$\left\langle f \,\middle|\, \hat{\Pi}^\dagger\hat{p}\hat{\Pi} \,\middle|\, g \right\rangle = \int_{-\infty}^{\infty} f^*(-x)(-i\hbar)\frac{\mathrm{d}g(x)}{\mathrm{d}x}\,\mathrm{d}x. \tag{6.4}$$

When we do integration by parts, the term that we evaluate at the limits will go to zero like always so we have

$$
\begin{aligned}
\left\langle f \,\middle|\, \hat{\Pi}^{\dagger}\hat{p}\hat{\Pi} \,\middle|\, g \right\rangle &= -\int_{-\infty}^{\infty} (-i\hbar)\frac{\mathrm{d}f^*(-x)}{\mathrm{d}x} g(-x)\,\mathrm{d}x && (6.5)\\
&= -\int_{\infty}^{-\infty} (-i\hbar) - \frac{\mathrm{d}f^*(x)}{\mathrm{d}x} g(x)\,(-\mathrm{d}x) && (6.6)\\
&= -\int_{-\infty}^{\infty} i\hbar\frac{\mathrm{d}f^*(x)}{\mathrm{d}x} g(x)\,\mathrm{d}x && (6.7)\\
&= -\int_{-\infty}^{\infty} \left(-i\hbar\frac{\mathrm{d}f(x)}{\mathrm{d}x}\right)^* g(x)\,\mathrm{d}x = \langle f \,|\, (-\hat{p}) \,|\, g\rangle\,, && (6.8)
\end{aligned}
$$

so $\boxed{\hat{p}' = -\hat{p}.}$

Problem 7. (6.13)

a) For a single electron in the ground state of the hydrogren atom, there is perfect spherical symmetry, meaning that $\langle \mathbf{r} \rangle = 0$, so $\langle \mathbf{p}_e \rangle = q\,\langle \mathbf{r} \rangle = 0$.

b) For $n = 2$, we need to make use of Equation (6.26), and we can tell that there is possibility for two different values of ℓ and ℓ' such that $\ell + \ell'$ is not even. We need a single state/wavefunction, so we need a linear combination of two states with different ℓ values, say

$$|\psi\rangle = \frac{1}{\sqrt{2}}(|210\rangle + |200\rangle), \tag{7.1}$$

where

$$
\begin{aligned}
\psi_{200} &= \frac{1}{4\sqrt{a^3\pi}}\left(2 - \frac{r}{a}\right) e^{-r/2a}, \quad \text{and} && (7.2)\\
\psi_{210} &= \frac{1}{4\sqrt{a^3\pi}}\left(\frac{r}{a}\right) e^{-r/2a}\cos\theta. && (7.3)
\end{aligned}
$$

Thus,

$$\langle \psi \,|\, \hat{p}_e \,|\, \psi\rangle = \frac{1}{2}\left(\langle 200|\hat{p}_e|200\rangle + \langle 210|\hat{p}_e|210\rangle + \langle 210|\hat{p}_e|200\rangle + \langle 200|\hat{p}_e|210\rangle\right). \tag{7.4}$$

The first two terms in parentheses are zero since $\ell = \ell'$, so we are only left with

$$\langle \psi \,|\, \hat{p}_e \,|\, \psi\rangle = \frac{1}{2}\left(\langle 210|\hat{p}_e|200\rangle + \langle 200|\hat{p}_e|210\rangle\right). \tag{7.5}$$

For a generic complex number z, we have that $(z + z^*)/2 = \mathrm{Re}[z]$, and since the second term in parentheses is the complex conjugate of the first (because the position operator is Hermitian) then we can write this as

$$\langle \psi \,|\, \hat{p}_e \,|\, \psi\rangle = \mathrm{Re}[\langle 210|\hat{p}_e|200\rangle]. \tag{7.6}$$

Doing the actual calculation, $\mathbf{r}$ is a vector so: $\hat{\mathbf{r}} = \begin{pmatrix}\hat{x} & \hat{y} & \hat{z}\end{pmatrix} = \begin{pmatrix} r\sin\theta\cos\phi & r\sin\theta\sin\phi & r\cos\phi\end{pmatrix}$. The x component is

$$\langle \hat{p}_e \rangle_x = -e \cdot \mathrm{Re}\left[\int \psi_{210}^* (r \sin\theta \cos\phi) \psi_{200} \, \mathrm{d}^3\mathbf{r} \right] \hat{\imath} \tag{7.7}$$

The ϕ integration will be super easy, since neither wavefunctions contribute a ϕ component and $\mathrm{d}^3 r = r^2 \sin\theta \mathrm{d}r$ also doesn't contribute a ϕ component. Fortunately, however, we have that

$$\int_0^{2\pi} \cos\phi \, \mathrm{d}\phi = \int_0^{2\pi} \sin\phi \, \mathrm{d}\phi = 0, \tag{7.8}$$

so both the x and y components will be zero. The z component is (and since we know everything will be real now, we can drop the real specifier)

$$\langle 210 | \hat{p}_e | 200 \rangle_x = -\frac{e}{16 a^5 \pi} \int_0^{2\pi} \mathrm{d}\phi \int_0^{\pi} \cos^2\theta \sin\phi \, \mathrm{d}\theta \int_0^{\infty} r^4 (2a - r) e^{-r/a} \, \mathrm{d}r. \tag{7.9}$$

The ϕ integration is obviously 2π, Mathematica tells me the θ integral is $2/3$, and it also tells me the r integration is $-72/a^6$, so

$$\boxed{\langle \hat{p}_e \rangle = 6ea \, \hat{k}.} \tag{7.10}$$