75(13): Expectation Value for 1s Orbital of H.

The expectation value is:

$$\langle [r^2, \hat{p}_r^2] \rangle = 2\hbar^2 + 4i\hbar \langle r\hat{p}_r \rangle \quad -(1)$$

where:

$$\langle r\hat{p}_r \rangle = \int \phi^* r \hat{p} \phi \, d\tau = -i\hbar \int \phi^* r \frac{\partial \phi}{\partial r} d\tau \quad -(2)$$

where:

$$\phi^* = \frac{1}{(\pi a^3)^{1/2}} e^{-r/a} \quad -(3)$$

$$\frac{\partial \phi}{\partial r} = -\frac{1}{a} \cdot \frac{1}{(\pi a^3)^{1/2}} e^{-r/a} \quad -(4)$$

So

$$\langle r\hat{p}_r \rangle = \frac{i\hbar}{\pi a^4} \int r e^{-2r/a} d\tau$$

$$= \frac{i\hbar}{\pi a^4} \int_0^\infty r^3 e^{-2r/a} \int_0^{2\pi} \int_0^{\pi} \sin\theta \, d\theta \, d\phi \, dr \quad -(5)$$

$$= \frac{4i\hbar}{a^4} \int_0^\infty r^3 e^{-2r/a} dr \quad -(6)$$

Now use:

$$\int x^n e^{ax} dx = \frac{x^n}{a} e^{ax} - \frac{n}{a} \int x^{n-1} e^{ax} dx \quad -(7)$$

and

$$\int x^2 e^{-\alpha x} dx = e^{-\alpha x} \left( -\frac{x^2}{\alpha} - \frac{2x}{\alpha^2} - \frac{2}{\alpha^3} \right) \quad -(8)$$

So

$$\int x^3 e^{-\alpha x} dx = e^{-\alpha x} \left( -\frac{x^3}{\alpha} - \frac{3x^2}{\alpha^2} - \frac{6x}{\alpha^3} - \frac{6}{\alpha^4} \right) \quad -(9)$$

2)

So:

$$\int_0^\infty r^3 e^{-\alpha r} dr = \frac{6}{\alpha^4}, \quad \alpha = \frac{2}{a} \quad -(10)$$

i.e.

$$\int_0^\infty r^3 e^{-\alpha r} dr = \frac{3}{8} a^4 \quad -(11)$$

Therefore:

$$\langle r \hat{p}_r \rangle = \frac{4 i \hbar}{a^4} \cdot \frac{3}{8} a^4 = \frac{3 i \hbar}{2} \quad -(12)$$

It follows from eq. (1) that:

$$\boxed{\langle [r^2, \hat{p}_r^2] \rangle = -4\hbar^2} \quad -(13)$$

Therefore for the 1s orbital of H the expectation value is negative. In contrast, the expectation value for the harmonic oscillator is always zero. The conclusion is that $[r^2, \hat{p}_r^2]$ cannot be interpreted according to the Heisenberg uncertainty principle because it is sometimes zero and sometimes non-zero.

Expectation values such as these can be used to build up a new description of the H atom. Another example is:

$$\phi_{2p_z}(\underline{r}) = \frac{1}{4}\left(\frac{1}{2\pi a^3}\right)^{1/2} \rho \cos\theta \exp\left(-\frac{\rho}{2}\right), \quad -(14)$$

$$\rho = \frac{r}{a}$$

3)

So:

$$\psi^*\psi = \frac{1}{32\pi a^3}\frac{r^2}{a^2}\cos^2\theta \exp\left(-\frac{r}{a}\right) \quad -(15)$$

First check the normalization:

$$\int \psi^*\psi \, d\tau = \frac{1}{32\pi a^5}\int_0^\infty r^4 e^{-r/a}\int_0^{2\pi}\int_0^{\pi}\cos^2\theta\sin\theta \, d\theta \, d\phi \, dr \quad -(16)$$

where

$$\int_0^{\pi}\cos^2\theta\sin\theta \, d\theta = -\frac{1}{3}\cos^3\theta\Big|_0^{\pi} \quad -(17)$$

$$= \frac{2}{3},$$

so

$$\int_0^{2\pi}\int_0^{\pi}\cos^2\theta\sin\theta \, d\theta \, d\phi = \frac{8\pi}{3} \quad -(18)$$

and

$$\int \psi^*\psi \, d\tau = \frac{1}{24a^5}\int_0^\infty r^4 e^{-r/a} dr \quad -(19)$$

Now use:

$$\int x^4 e^{-\alpha x} dx = e^{-\alpha x}\left(-\frac{x^4}{\alpha} - \frac{4x^3}{\alpha^2} - \frac{12x^2}{\alpha^3} - \frac{24x}{\alpha^4} - \frac{24}{\alpha^5}\right) \quad -(20)$$

to find that:

$$\int_0^\infty r^4 e^{-r/a} dr = 24a^5 \quad -(21)$$

so:

$$\int \psi^*\psi \, d\tau = 1 \quad -(22)$$

Q.E.D.

7) The relevant expectation value to compute is:

$$\langle r\hat{p}_r \rangle = -i\hbar \int \phi^* r \frac{\partial \phi}{\partial r} d\tau \quad -(23)$$

where: $$\phi^* = \left(\frac{1}{32\pi a^5}\right)^{1/2} r\cos\theta \exp\left(-\frac{r}{2a}\right) \quad -(24)$$

and $$\frac{\partial \phi}{\partial r} = \left(\frac{1}{32\pi a^5}\right)^{1/2} \cos\theta \left(1 - \frac{r}{2a}\right) \exp\left(-\frac{r}{2a}\right) \quad -(25)$$

so:

$$\langle r\hat{p}_r \rangle = -\frac{i\hbar}{32\pi a^5} \int r^2 \cos^2\theta \left(1 - \frac{r}{2a}\right) e^{-r/a} d\tau \quad -(26)$$

$$= \frac{-i\hbar}{32\pi a^5} \int_0^\infty r^4 \left(1 - \frac{r}{2a}\right) e^{-r/a} \int_0^{2\pi} \int_0^{\pi} \cos^2\theta \sin\theta \, d\theta \, d\phi \, dr$$

$$= -\frac{i\hbar}{24a^5}\left(\int_0^\infty r^4 e^{-r/a} dr - \int_0^\infty \frac{r^5}{2a} e^{-r/a} dr\right)$$

Therefore:

$$\langle r\hat{p}_r \rangle = -i\hbar + \frac{i\hbar}{48a^6} \int_0^\infty r^5 e^{-r/a} dr. \quad -(27)$$

Use $$\int_0^\infty r^5 e^{-r/a} dr = \left[ e^{-\alpha r}\left(-\frac{x^5}{\alpha} - \frac{5x^4}{\alpha^2} - \frac{20x^3}{\alpha^3} - \frac{60x^4}{\alpha^4} - \frac{120x^5}{\alpha^5} - \frac{120}{\alpha^6}\right), \right] \quad -(28)$$

$$\alpha = \frac{1}{a}$$

5)

So
$$\langle r\hat{p}_r\rangle = -i\hbar + \frac{120}{48} i\hbar \quad -(29)$$

$$\boxed{\langle r\hat{p}_r\rangle = \frac{11}{4} i\hbar}$$

It follows from eq. (1) that:
$$\langle [r^2, \hat{p}_r^2]\rangle = 2\hbar^2 - 11\hbar^2 = -9\hbar^2 \quad -(30).$$

Results

| Orbital | $\langle r\hat{p}_r\rangle$ | $\langle [r^2, \hat{p}_r^2]\rangle$ |
|---|---|---|
| 1s | $\frac{3}{2} i\hbar$ | $-4\hbar^2$ |
| $2p_z$ | $\frac{11}{4} i\hbar$ | $-9\hbar^2$ |

Computer Algebra

It seems that the expectation values increase with orbital. In order to check these hand calculations and to construct a table of expectation values, the use of computer algebra is necessary. The general wave function is :

$$\psi = A(\theta)B(\phi)C(r) \quad -(31)$$

where:

$$A(\theta) = \left\{\frac{(2\ell+1)(\ell-|m_\ell|)!}{2(\ell+|m_\ell|)!}\right\} P_\ell^{|m_\ell|}(\cos\theta)$$

$$B(\phi) = \left(\frac{1}{2\pi}\right)^{1/2} \exp(i m_\ell \phi)$$

$$C_{n\ell}(r) = -\left(\frac{1}{na}\right)\left\{\frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}\right\} \rho^\ell \times L_{n+\ell}^{2\ell+1}(\rho) \exp(-\rho/2)$$

$\rho = \left(\frac{2}{na}\right) r$, $a$ = Bohr radius.

If the spherical harmonics are denoted by:

$Y_{\ell m_\ell}(\theta, \phi) = f(\theta, \phi)$ then:

1) For $\ell = 0$, $m_\ell = 0$, $Y = \frac{1}{(4\pi)^{1/2}}$

2) For $\ell = 1$, $m_\ell = 0$, $Y = \frac{1}{2}\left(\frac{3}{\pi}\right)^{1/2} \cos\theta$

3) For $\ell = 1$, $m_\ell = \pm 1$, $Y = \mp \frac{1}{2}\left(\frac{3}{2\pi}\right)^{1/2} \sin\theta \exp(\pm i\phi)$

4) For $\ell = 2$, $m_\ell = 0$, $Y = \frac{1}{4}\left(\frac{5}{\pi}\right)^{\frac{1}{2}} (3\cos^2\theta - 1)$

5) For $\ell = 2$, $m_\ell = \pm 1$, $Y = \mp \frac{1}{2}\left(\frac{15}{2\pi}\right)^{1/2} \cos\theta \sin\theta \exp(\pm i\phi)$

7)

6) For $\ell = 2$, $m_\ell = \pm 2$, $Y = \frac{1}{4}\left(\frac{15}{2\pi}\right)^{1/2} \sin^2\theta \exp(\pm 2i\phi)$

7) For $\ell = 3$, $m_\ell = 0$, $Y = \frac{1}{4}\left(\frac{7}{\pi}\right)^{1/2}(2 - 5\sin^2\theta)\cos\theta$.

8) For $\ell = 3$, $m_\ell = \pm 1$, $Y = \mp\frac{1}{8}\left(\frac{21}{\pi}\right)^{1/2}(5\cos^2\theta - 1)\sin\theta \exp(\pm i\phi)$

9) For $\ell = 3$, $m_\ell = \pm 2$, $Y = \frac{1}{4}\left(\frac{105}{2\pi}\right)^{1/2}\cos\theta \sin^2\theta \exp(\pm 2i\phi)$

10) For $\ell = 3$, $m_\ell = \pm 3$, $Y = \mp\left(\frac{35}{\pi}\right)^{1/2} \sin^3\theta \exp(\pm 3i\phi)$

If the radial functions are denoted by $R_{n\ell}(r)$,:

1) For $n = 1$ $\ell = 0$ (1s) $R_{n\ell}(r) = 2\left(\frac{1}{a}\right)^{3/2}\exp\left(-\frac{\rho}{2}\right)$

2) For $n = 2$, $\ell = 0$ (2s), $R_{n\ell} = \frac{1}{2\sqrt{2}}(1/a)^{3/2}(2-\rho)\exp(-\rho/2)$

3) For $n = 2$, $\ell = 1$ (2p), $R_{n\ell} = \frac{1}{2\sqrt{6}}\left(\frac{1}{a}\right)^{3/2}\rho\exp(-\rho/2)$

4) For $n = 3$, $\ell = 0$ (3s), $R_{n\ell} = \frac{1}{9\sqrt{3}}\left(\frac{1}{a}\right)^{3/2}(6 - 6\rho + \rho^2)\exp\left(\frac{-\rho}{2}\right)$

5) For $n=3$, $\ell = 1$ (3p), $R_{n\ell} = \frac{1}{9\sqrt{6}}(4-\rho)\rho\exp(-\rho/2)\left(\frac{1}{a}\right)^{3/2}$

6) For $n=3$, $\ell = 2$ (3d), $R_{n\ell} = \frac{1}{9\sqrt{30}}\left(\frac{1}{a}\right)^{3/2}\rho^2\exp\left(-\frac{\rho}{2}\right)$

where $\rho = \frac{2}{na}r$.