1)

Complete Functional Differentiation of the 2p Orbitals

The problem is to find $1/r_{vac}$ from:

$$\boxed{\nabla^2 \phi = -\left(\frac{4\pi c}{\hbar}\right)\frac{1}{r_{vac}}\phi} \quad -(1)$$

where:

$$\nabla^2 \phi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \phi}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial \phi}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 \phi}{\partial \phi^2} \quad -(2)$$

and

$$\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta \, d\theta = 4\pi \quad -(3)$$

$2p_z$ Orbital

$$\phi(2p_z) = \frac{1}{2}\left(\frac{3}{\pi}\right)^{1/2}\cos\theta \left(\frac{1}{a}\right)^{3/2}\left(\frac{1}{2\sqrt{6}}\right)\frac{r}{a}\exp\left(-\frac{r}{2a}\right) \quad -(4)$$

$2p_y$ Orbital

$$\phi(2p_y) = -\frac{1}{2}\left(\frac{3}{\pi}\right)^{1/2}\sin\theta\, e^{i\phi}\left(\frac{1}{a}\right)^{3/2}\left(\frac{1}{2\sqrt{6}}\right)\frac{r}{a}\exp\left(-\frac{r}{2a}\right) \quad -(5)$$

$2p_x$ Orbital

$$\phi(2p_x) = \frac{1}{2}\left(\frac{3}{\pi}\right)^{1/2}\sin\theta\, e^{-i\phi}\left(\frac{1}{a}\right)^{3/2}\left(\frac{1}{2\sqrt{6}}\right)\frac{r}{a}\exp\left(-\frac{r}{2a}\right) \quad -(6)$$

Volume element:

$$d\tau = r^2 dr \sin\theta \, d\theta \, d\phi \quad -(7)$$

Probability of finding the electron in a spherical shell of thickness dr and radius r is found by integrating in the range:

$$0 \leq \theta \leq \pi, \quad 0 \leq \phi \leq 2\pi \quad -(8)$$

2) The probability is:

$$\underline{P} = \int_0^{\pi}\int_0^{2\pi} |\psi(r,\theta,\phi)|^2 \sin\theta \, r^2 \, dr \, d\phi \, d\theta \quad \text{— (9)}$$

<u>Method.</u>

Use computer algebra to solve eq (1) for each orbital, and find r(vac) (r, θ, ϕ) for each. Then

$$\langle r(\text{vac})\rangle = \int_0^{\pi}\int_0^{2\pi} r(\text{vac}) \, d\phi \sin\theta \, d\theta, \quad \text{— (10)}$$

for each orbital. The average over three orbitals is:

$$\langle\langle r(\text{vac})\rangle\rangle_{2p} = \frac{1}{3}\left(\langle r(\text{vac})_x\rangle + \langle r(\text{vac})_y\rangle + \langle r(\text{vac})_z\rangle\right) \quad \text{— (11)}$$

The Lamb shift is proportional to:

$$\frac{1}{\langle r(\text{vac})_{2s}\rangle} - \frac{1}{\langle\langle r(\text{vac})\rangle\rangle_{2p}} . \quad \text{— (12)}$$

Thus $\langle r(\text{vac})\rangle = 4\pi \, r(\text{vac})$ — (13)

This procedure integrates out ~~the~~ θ and ϕ, i.e. averages over them. Alternatively we could use:

$$\langle \psi^2(2p_z)\rangle^{1/2} = \left(\int_0^{\pi} \sin\theta \, \psi^2_{2p_z} \, d\theta\right)^{1/2} \quad \text{— (14)}$$

etc.

3) If the average $\langle r(vac) \rangle$ vanishes, then it would be possible to use:

$$\langle r^2(vac) \rangle^{1/2} = \left(\int_0^{\pi} \int_0^{2\pi} r^2(vac)\, d\phi \sin\theta\, d\theta \right)^{1/2} \quad — (15)$$

Notes

1) In general, $r(vac)$ is a function of r, θ and ϕ for each orbital.

2) For the 2s orbital, $r(vac)$ is a function of only r. In this case:

$$\langle r(vac)_{2s} \rangle = \int_0^{\pi} \int_0^{2\pi} r(vac)_{2s}\, d\phi \sin\theta\, d\theta \quad — (16)$$

$$= 4\pi\, r(vac)_{2s},$$

and: $$\langle r^2(vac)_{2s} \rangle^{1/2} = \langle r(vac)_{2s} \rangle. \quad — (17)$$

3) The type of averaging is important, e.g.

$$\langle \phi(2p_z) \rangle = \frac{1}{2} \left(\frac{3}{\pi} \right)^{1/2} \left(\frac{1}{a} \right)^{3/2} \left(\frac{1}{2\sqrt{6}} \right) \frac{r}{a} \exp\left(-\frac{r}{2a} \right) \int_0^{\pi} \sin\theta \cos\theta\, d\theta \quad — (18)$$

$$= 0$$

so this type of averaging cannot be used.