Atomic Dipoles

a) Both the 1s and 2s states are parity even, whereas the dipole is parity odd, so:

$$\boxed{\langle 2s | e\hat{z} | 1s \rangle = 0} \qquad (1)$$

$$\text{even} \times \text{odd} \times \text{even} = \text{odd}. \quad \int \text{odd} = 0$$

b) In atomic units

$$\psi_{2p_z} = \frac{1}{4\sqrt{2\pi}} r e^{-r/2} \cos\theta$$

$$\psi_{2p\pm} = \pm \frac{1}{8\sqrt{\pi}} r e^{-r/2} \sin\theta \, e^{\pm i\phi}$$

Now since neither ψ_{1s} or $ez = er\cos\theta$ have any ϕ dependance, we must have

$$\boxed{\langle 2p\pm | \hat{z} | 1s \rangle = 0} \quad \left(\begin{matrix}\text{atomic} \\ \text{units}\end{matrix} \; e=1\right) \qquad (2)$$

because

$$\int_0^{2\pi} d\phi \, e^{\pm i\phi} = \mp i \left[e^{\pm i 2\pi} - e^{\pm i 0} \right]$$

$$= \mp i \left[1 - 1 \right] = 0$$

So we are left with

$$\langle 2p_z | \hat{z} | 1s \rangle =$$

$$\frac{1}{\sqrt{\pi}} \frac{1}{4\sqrt{2\pi}} \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \int_0^{\infty} dr \, r^2 \, r e^{-r/2} \cos\theta \, (r\cos\theta) e^{-r}$$

$$= \frac{1}{\cancel{4}\sqrt{2}\,\cancel{\pi}}\,\cancel{2\pi}\int_0^{\pi} d\theta\,\cos^2\theta\sin\theta \int_0^{\infty} dr\, r^4 e^{-\frac{3}{2}r}$$

2

$u = \cos\theta$
$du = -\sin\theta$

$z = \frac{3}{2}r$
$dz = \frac{3}{2}dr$

$$= \frac{1}{2\sqrt{2}}\int_{-1}^{1} du\,u^2 \quad \left(\frac{2}{3}\right)^5 \underbrace{\int_0^{\infty} dz\, z^4 e^{-z}}_{\Gamma(5)=4!}$$

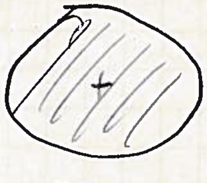
$$= \frac{1}{2\sqrt{2}}\left(\frac{2}{3}\right)\left(\frac{3}{3}\right)^5 4!$$

$$= \boxed{0.745 \ \text{a.u.}}$$ (3)

Since we are already in atomic units and the atomic unit of dipole is ea_0, the dipole is

$$\boxed{\langle 2p_z | e\hat{z} | 1s\rangle = 0.745\, ea_0}$$ (4)

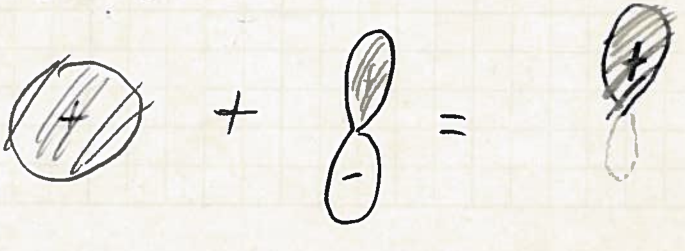
c) Drawing the orbitals

$|1s\rangle =$ 

$|2p_z\rangle =$ 

(5)

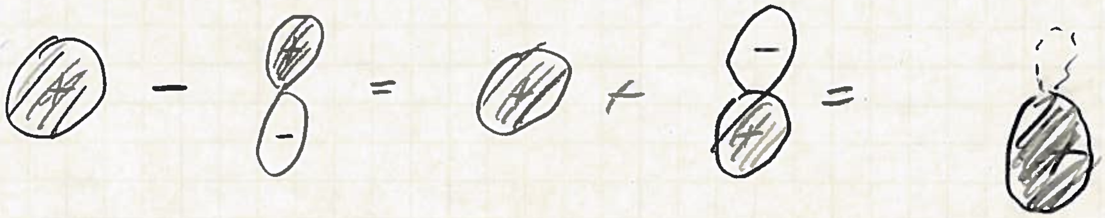
so now the phase difference between them will oscillate at frequency $\omega = (E_2 - E_1)/\hbar$, so adding the two at $\omega t = 0$, we get



Top lobe adds bottom lobes destructively interfere.

(6)

But a half cycle later $\omega t = \pi$, we have



since the charge density is $\propto |\psi|^2$, the charge density is oscillating along the z-axis and the atom is behaving like a small broadcast antenna, radiating EM waves.

A deeper question is why an atom in only $|2p_z\rangle$ will decay to $|1s\rangle$ by radiating, as there no superposition here at $t=0$, and thus no radiation in this picture.

Understanding "Spontaneous Emission" requires quantization of the electromagnetic field.