

## HYDROGEN ATOM - MIXED INITIAL STATE AND MEAN POTENTIAL ENERGY

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References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 4.15.

We've looked at the stationary states of the hydrogen atom, but suppose an atom starts off in a mixture of two states, as in

$$\Psi(\mathbf{r}, 0) = \frac{1}{\sqrt{2}} (\psi_{211} + \psi_{21-1}) \quad (1)$$

We've already worked out the two stationary states:

$$\psi_{211} = -\frac{1}{8\sqrt{\pi}} \frac{r}{a^{5/2}} e^{-r/2a} \sin\theta e^{i\phi} \quad (2)$$

$$\psi_{21-1} = \frac{1}{8\sqrt{\pi}} \frac{r}{a^{5/2}} e^{-r/2a} \sin\theta e^{-i\phi} \quad (3)$$

Since both states have the same value of  $n$ , they both have the same energy, so the time-dependent wave function is

$$\Psi(\mathbf{r}, t) = \frac{1}{\sqrt{2}} e^{-iE_2t/\hbar} (\psi_{211} + \psi_{21-1}) \quad (4)$$

$$= \frac{1}{\sqrt{2}} e^{-iE_2t/\hbar} \frac{1}{8\sqrt{\pi}} \frac{r e^{-r/2a}}{a^{5/2}} \sin\theta (-2i \sin\phi) \quad (5)$$

$$= -\frac{ri}{4\sqrt{2\pi}a^5} e^{-r/2a} e^{-iE_2t/\hbar} \sin\theta \sin\phi \quad (6)$$

where we have used  $e^{i\phi} - e^{-i\phi} = 2i \sin\phi$ .

We can now calculate  $\langle V \rangle$ , the average of the potential. The potential function is (from Coulomb's law)

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r} \quad (7)$$

We do the integral

$$\langle V \rangle = \int \Psi^* V \Psi d^3 \mathbf{r} \quad (8)$$

$$= \frac{-e^2}{128\pi^2 a^5 \epsilon_0} \int_0^{2\pi} \int_0^\pi \int_0^\infty r^3 e^{-r/a} \sin^3 \theta \sin^2 \phi dr d\theta d\phi \quad (9)$$

$$= -\frac{e^2}{16\pi a \epsilon_0} \quad (10)$$

$$= -1.09 \times 10^{-18} \text{ Joules} \quad (11)$$

$$= -6.81 \text{ eV} \quad (12)$$

using the values (in MKS units):

$$e = 1.6 \times 10^{-19} \text{ Coulombs} \quad (13)$$

$$\frac{1}{4\pi\epsilon_0} = 8.99 \times 10^9 \text{ Nm}^2/\text{C}^2 \quad (14)$$

$$a = 0.529 \times 10^{-10} \text{ m} \quad (15)$$

The value in eV is given by the conversion  $1 \text{ eV} = 1.6 \times 10^{-19} \text{ Joules}$ . The average potential is independent of time, since the time appears only in the complex exponential which cancels out when we take the square modulus of  $\Psi$ .