

## 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

$$(0.1) \quad \Psi(\mathbf{r}, 0) = \frac{1}{\sqrt{2}} (\psi_{211} + \psi_{21-1})$$

We've already worked out the two stationary states:

$$(0.2) \quad \psi_{211} = -\frac{1}{8\sqrt{\pi}} \frac{r}{a^{5/2}} e^{-r/2a} \sin \theta e^{i\phi}$$

$$(0.3) \quad \psi_{21-1} = \frac{1}{8\sqrt{\pi}} \frac{r}{a^{5/2}} e^{-r/2a} \sin \theta e^{-i\phi}$$

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

$$(0.4) \quad \Psi(\mathbf{r}, t) = \frac{1}{\sqrt{2}} e^{-iE_2t/\hbar} (\psi_{211} + \psi_{21-1})$$

$$(0.5) \quad = \frac{1}{\sqrt{2}} e^{-iE_2t/\hbar} \frac{1}{8\sqrt{\pi}} \frac{r e^{-r/2a}}{a^{5/2}} \sin \theta (-2i \sin \phi)$$

$$(0.6) \quad = -\frac{ri}{4\sqrt{2\pi}a^5} e^{-r/2a} e^{-iE_2t/\hbar} \sin \theta \sin \phi$$

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)

$$(0.7) \quad V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$

We do the integral

$$(0.8) \quad \langle V \rangle = \int \Psi^* V \Psi d^3 \mathbf{r}$$

$$(0.9) \quad = \frac{-e^2}{128\pi^2 a^5 \epsilon_0} \int_0^{2\pi} \int_0^\pi \int_0^\infty r^3 e^{-r/a} \sin^3 \theta \sin^2 \phi dr d\theta d\phi$$

$$(0.10) \quad = -\frac{e^2}{16\pi a \epsilon_0}$$

$$(0.11) \quad = -1.09 \times 10^{-18} \text{ Joules}$$

$$(0.12) \quad = -6.81 \text{ eV}$$

using the values (in MKS units):

$$(0.13) \quad e = 1.6 \times 10^{-19} \text{ Coulombs}$$

$$(0.14) \quad \frac{1}{4\pi\epsilon_0} = 8.99 \times 10^9 \text{ Nm}^2/\text{C}^2$$

$$(0.15) \quad a = 0.529 \times 10^{-10} \text{ m}$$

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  $\Psi$ .