

Polarizability of the hydrogen atom

In order to calculate the polarizability of the hydrogen atom we need the transition moments for the allowed transitions. In the presence of a Z-polarized applied electric field we have the induced dipole moment

$$\langle \Psi_0 | qZ | \Psi_0 \rangle = -2q^2 E_0 \sum_n \left(\frac{\langle n, l, m | Z | 1, 0, 0 \rangle^2}{E_1 - E_n} \right)$$

Since $\mu = \alpha E_0$ we have for the polarizability

$$\alpha = -2q^2 \sum_n \left(\frac{\langle n, l, m | Z | 1, 0, 0 \rangle^2}{E_1 - E_n} \right)$$

obtained from Cohen-Tannoudji (page 1280). It appears from the selection rules that $\Delta n = \text{any value}$, $\Delta l = \pm 1$, and $\Delta m = 0$.

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We have the following matrix elements:

$$\langle 2,1,0|Z|1,0,0\rangle = \int_0^\infty \frac{1}{\sqrt{32\pi}} \left(\frac{r}{a_0^{5/2}}\right) e^{-r/2a_0} r \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0} r^2 dr \int_0^\pi \cos^2 \theta \sin \theta d\theta \int_0^{2\pi} d\phi$$

making the substitution $x = \cos\theta$, and collecting constants we have

$$\langle 2,1,0|Z|1,0,0\rangle = \frac{2\pi}{\sqrt{32\pi}} \left(\frac{1}{a_0^4}\right) \int_0^\infty e^{-3r/2a_0} r^4 dr \int_{-1}^1 x^2 dx$$

Let $u = 3r/2a_0$, then $r = (2a_0/3)u$ and $dr = (2a_0/3)du$ so

$$\langle 2,1,0|Z|1,0,0\rangle = \frac{64}{243\sqrt{32}} a_0 \int_0^\infty e^{-u} u^4 du \int_{-1}^1 x^2 dx$$

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Evaluating the integrals we obtain

$$\langle 2, 1, 0 | Z | 1, 0, 0 \rangle = \frac{64}{243\sqrt{32}} a_0 4! \frac{2}{3} = 0.744 a_0$$

The energy levels are given by

$$E_n = -\frac{\hbar^2}{2\mu a_0^2 n^2}$$

The energy difference in the denominator is

$$E_1 - E_n = \frac{\hbar^2}{2\mu a_0^2} \left(\frac{1}{n^2} - 1 \right)$$

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The polarizability can be expressed

$$\alpha = \frac{2\mu q^2 a_0^2}{\hbar^2} \sum_n \left(\frac{\langle n, l, m | Z | 1, 0, 0 \rangle^2}{1 - \frac{1}{n}} \right)$$

Thus, for example for the 210 state we have

$$\alpha_{210} = \frac{2\mu q^2 a_0^4}{\hbar^2} \frac{0.744^2}{1 - \frac{1}{4}} = (3.8 \text{ \AA}^3) 0.738 = 2.80 \text{ \AA}^3$$

The constant in front of the polarizability expression is:

$$\frac{2\mu q^2 a_0^4}{\hbar^2} = \frac{2(9.109 \times 10^{-31} \text{ kg})(1.62 \times 10^{-19} \text{ C})^2 (5.29 \times 10^{-11} \text{ m})^4}{(1.054 \times 10^{-34} \text{ Js})^2}$$

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The units work out as follows:

$$\frac{2\mu q^2 a_0^4}{\hbar^2} = 3.37 \times 10^{-41} \text{ C}^2 \text{ m}^2 / \text{J}$$

$$\begin{aligned} \frac{2\mu q^2 a_0^4}{\epsilon_0 \hbar^2} &= \frac{3.37 \times 10^{-41} \text{ C}^2 \text{ m}^2 / \text{J}}{8.854 \times 10^{-12} \text{ C}^2 \text{ m}^{-1} / \text{J}} \\ &= 3.80 \times 10^{-30} \text{ m}^3 = 3.80 \text{ \AA}^3 \end{aligned}$$