

Sommerfeld model

Sommerfeld in 1916 derived the following energy eigenvalues for hydrogen. These eigenvalues explain fine structure lines in the hydrogen spectrum.

$$E = mc^2 \left[1 + \left(\frac{\alpha}{n - k + \sqrt{k^2 - \alpha^2}} \right)^2 \right]^{-1/2}$$

Parameters n and k are the quantum numbers

$$\begin{aligned} n &= 1, 2, 3, \dots \\ k &= 1, 2, \dots, n \end{aligned}$$

Expand E as a Taylor series in α .

$$E = mc^2 \left[1 - \frac{\alpha^2}{2n^2} - \frac{\alpha^4}{2kn^3} + \frac{3\alpha^4}{8n^4} + \mathcal{O}(\alpha^6) \right] \quad (1)$$

The leading term is electron rest-mass energy which can be discarded as unobservable in atomic spectra. $\mathcal{O}(\alpha^6)$ is also discarded to obtain the approximation

$$E = mc^2 \left[-\frac{\alpha^2}{2n^2} - \frac{\alpha^4}{2kn^3} + \frac{3\alpha^4}{8n^4} \right]$$

Typically this is written as

$$E = -\frac{\alpha^2 mc^2}{2n^2} \left[1 + \frac{\alpha^2}{n} \left(\frac{1}{k} - \frac{3}{4n} \right) \right] \quad (2)$$

By the substitution

$$\alpha^2 = \frac{e^4}{(4\pi\epsilon_0\hbar c)^2}$$

we also have

$$E = -\frac{e^4}{(4\pi\epsilon_0\hbar)^2} \frac{m}{2n^2} \left[1 + \frac{\alpha^2}{n} \left(\frac{1}{k} - \frac{3}{4n} \right) \right]$$

Eigenmath script