

Exact energy levels of a one-electron atom in the Dirac theory

As noted earlier the eigenvalues of the Dirac Hamiltonian are known exactly and are given by

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

where $E(n,j,Z)$ is the relativistic energy and m is the rest mass of the electron.

Unlike in the Schrodinger theory one cannot easily separate the center of mass in the Dirac theory so the energy is for an infinitely heavy nucleus. Since the relativistic energy and mc^2 are comparable the expression on the right is close to 1 making numerical evaluation of the non-relativistic energy difficult. It's the difference between two large numbers. Accordingly an expansion in powers of αZ is usually made. Curtis showed that if one defines $x = (\alpha Z / n)^2$ & $b = n / (j + 1/2)$ the Dirac energy becomes

$$\frac{E(n,j,Z)}{mc^2} = \left(1 + \frac{x}{\left(1 - \left(1 - \sqrt{1 - b^2 x} \right) / b \right)^2} \right)^{-1/2} = \sum_{P=0}^{\infty} x^P \sum_{Q=0}^{2P} b^Q C_{PQ}$$

where C_{PQ} are rational numbers independent of n, j or Z . Curtis gives a formula for C_{PQ} for arbitrary P & Q and tabulates values for $0 \leq P \leq 9$. The resulting expansion through $P = 4$ is

$$\begin{aligned} \frac{E(n,j,Z)}{mc^2} = & 1 - \frac{1}{2}x + \frac{1}{8}x^2(3 - 4b) + \frac{1}{16}x^3(-5 + 12b - 6b^2 - 2b^3) \\ & + \frac{1}{128}x^4(35 - 120b + 120b^2 - 8b^3 - 24b^4 - 8b^5) + \end{aligned}$$

Multiplying through by mc^2 we see that the first term is the relativistic energy of the electron and recognizing $\alpha^2 = 2R_\infty / mc^2$, $E_n = -\frac{R_\infty Z^2}{n^2}$ and therefore $xmc^2 = -2E_n$ we have

$$E(n,j,Z) = E_n \left(1 - x \left(\frac{3}{4} - b \right) - \frac{1}{8} x^2 (-5 + 12b - 6b^2 - 2b^3) - \frac{1}{64} x^3 (35 - 120b + 120b^2 - 8b^3 - 24b^4 - 8b^5) + \dots \right)$$

Notice that the first two terms are identical to the first order perturbation correction due to the Pauli Hamiltonian. Lets consider the importance of the various terms. For the 1s orbital $b = 1$ so the above becomes

$$E(1,1/2,Z) = E_{1s} \left(1 + \frac{x}{4} + \frac{x^2}{8} + \frac{5x^3}{64} + \dots \right)$$

with $x = (\alpha Z)^2$ and the Dirac 1s energy is always lower than the Schrodinger 1s so the Dirac ionization energy is always greater. The following table compares the Dirac, Schrodinger and experimental ionization energies (in Rydbergs) for selected one-electron atoms.

atom	Z	exp	Schrodinger	Dirac	Delta Schrodinger	Delta Dirac
H	1	0.999467	1.0	1.000013	0.000534	0.000547
B ⁺⁴	5	25.006151	25.0	25.008326	-0.006152	0.002175
Ne ⁺⁹	10	100.119792	100.0	100.13348	-0.119792	0.013692
P ⁺¹⁴	15	225.629193	225.0	225.67803	-0.629193	0.048837
Ca ⁺¹⁹	20	402.027412	400.0	402.15304	-2.027412	0.125630
Mn ⁺²⁴	25	630.026619	625.0	630.28867	-5.026619	0.262048
Zn ⁺²⁹	30	910.56948	900.0	911.04954	-10.56948	0.480065

The Dirac ionization energy is not only greater than the Schrodinger energy, it is also greater than experiment! Keep in mind that these energies are in Rydberg's and 1 Rydberg is 13.60569eV so the Schrodinger IP for Zn^{+29} is too low by 143.8eV and while the Dirac equation does much better it is still too high by 6.5eV.