First order corrections to the energy levels of a one-electron atom

As we have seen above the predictions of the Schrodinger equation for the ionization and transition energies in H are very close to the experimental values. Accordingly the effect of the additional terms in the Pauli Hamiltonian will be estimated using perturbation theory. Taking the unperturbed Hamiltonian as $\hat{H}^0_{Schrodinger}$ with eigenfunctions $R_{n\ell}(r)\Phi_{jm_j\ell}(\theta,\phi,\alpha,\beta)$ where $\Phi_{jm_j\ell}(\theta,\phi,\alpha,\beta)$ was defined above in the spin-orbit discussion. We first evaluate the correction due to the mass velocity term. Since the unperturbed functions are eigenfunctions of $\hat{H}^0_{Schrodinger}$ it's convenient to express the mass velocity term in terms of $\hat{H}^0_{Schrodinger}$ by recognizing that

$$\frac{\hat{p}^2}{2m} = \hat{H}^0_{Schrodinger} + \frac{Ze^2}{4\pi\varepsilon_0 r}$$

and so

$$\hat{H}_{mv} = -\frac{\hat{p}^4}{8m^3c^2} = -\frac{1}{2mc^2}\left(\hat{H}^0_{Schrodinger} + \frac{Ze^2}{4\pi\varepsilon_0 r}\right)^2$$

and so

$$\left\langle R_{n0}\alpha Y_0^0 \middle| \hat{H}_{mv} \middle| R_{n0}\alpha Y_0^0 \right\rangle = -\frac{1}{2mc^2}\left(E_{ns}^2 + E_{ns}\frac{2Ze^2}{4\pi e_0}\left\langle\frac{1}{r}\right\rangle_{ns} + \left(\frac{Ze^2}{4\pi e_0}\right)^2\left\langle\frac{1}{r^2}\right\rangle_{ns}\right)\langle\alpha|\alpha\rangle$$

Since $\left\langle\frac{1}{r}\right\rangle_{ns} = \frac{Z}{n^2a_0}$ and $\left\langle\frac{1}{r^2}\right\rangle_{ns} = \frac{2Z^2}{n^3a_0^2}$

We have

$$\left\langle R_{n0}\alpha Y_0^0 \middle| \hat{H}_{mv} \middle| R_{n0}\alpha Y_0^0 \right\rangle = -\frac{R_\infty^2 Z^4}{2mc^2n^4}(-3+8n)$$

This correction is often written in terms of the fine structure constant α, defined as $\alpha^2 = \frac{2R_\infty}{mc^2}$, and so

$$\left\langle R_{n0}\alpha Y_0^0 \middle| \hat{H}_{mv} \middle| R_{n0}\alpha Y_0^0 \right\rangle = \left\langle R_{n0}\beta Y_0^0 \middle| \hat{H}_{mv} \middle| R_{n0}\beta Y_0^0 \right\rangle = -\frac{Z^4R_\infty\alpha^2}{4n^4}(-3+8n)$$

Note that in what follows the fine structure constant α and the spin α will be distinguished by context. Let's now consider the Darwin term. A required matrix element is

$$\left\langle R_{n0}\alpha Y_0^0 \middle| \hat{H}_D \middle| R_{n0}\alpha Y_0^0 \right\rangle = \frac{\pi\hbar^2}{2m^2c^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\left\langle R_{n0}Y_0^0 \middle| \delta(\vec{r}) \middle| R_{n0}Y_0^0 \right\rangle \left\langle \alpha \middle| \alpha \right\rangle$$

where $\left\langle \alpha \middle| \alpha \right\rangle = 1$ and

$$\left\langle R_{n0}Y_0^0 \middle| \delta(\vec{r}) \middle| R_{n0}Y_0^0 \right\rangle = \frac{1}{4\pi}\int_0^\infty R_{n0}^2(r)\delta(r)\,dr = \frac{Z^3}{\pi a_0^3 n^3}$$

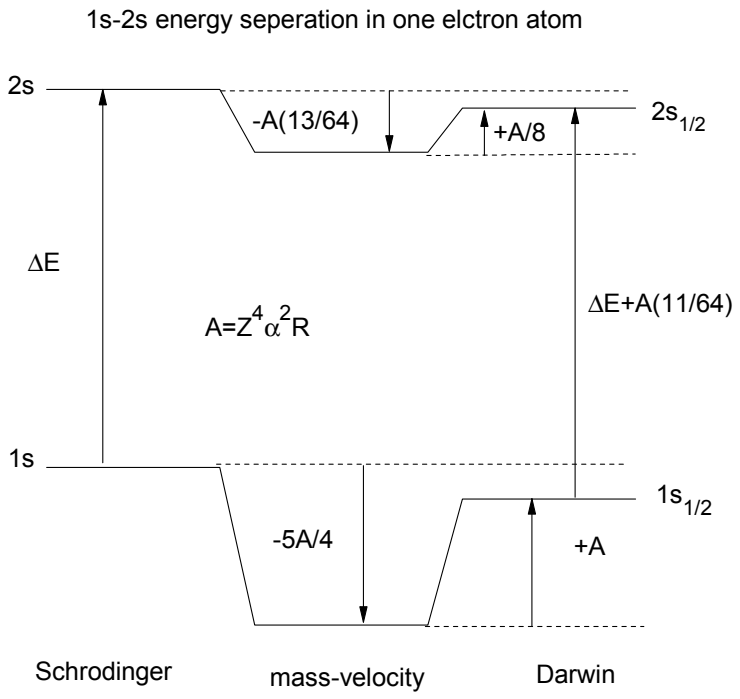
and so

$$\left\langle R_{n0}\alpha Y_0^0 \middle| \hat{H}_D \middle| R_{n0}\alpha Y_0^0 \right\rangle = \frac{\hbar^2 Z^4}{2m^2c^2a_0^2n^3}\left(\frac{e^2}{4\pi\varepsilon_0 a_0}\right) = \frac{\hbar^2 Z^4 R_\infty}{m^2c^2a_0^2n^3} = \frac{\hbar^2 Z^4\alpha^2}{2ma_0^2n^3} = \frac{Z^4\alpha^2 R_\infty}{n^3}.$$

The net shift in the energy of the *n*s level $E_{ns}^{(1)}$ is the sum of the mass velocity and Darwin terms

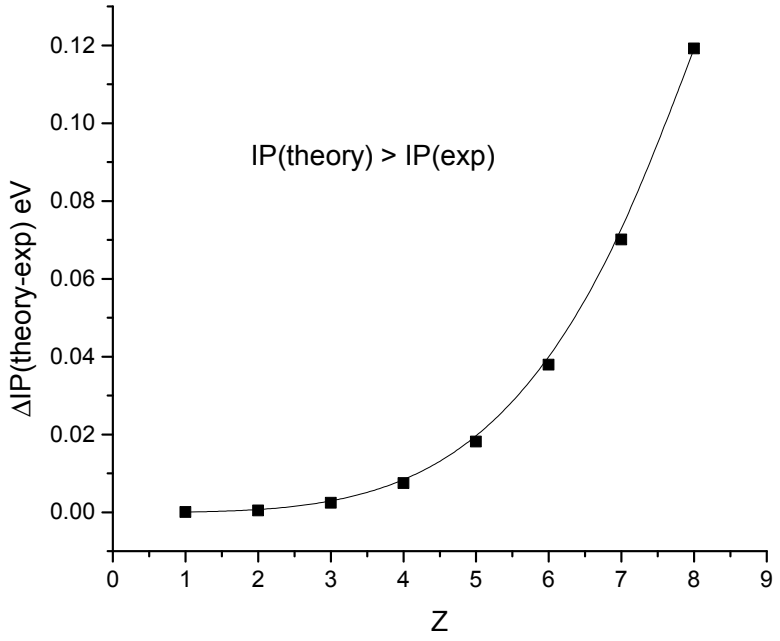
$$E_{ns}^{(1)} = -\frac{Z^4 R_\infty \alpha^2}{n^4}\left(n - \frac{3}{4}\right) = -\frac{Z^4}{n^4}\left(n - \frac{3}{4}\right)7.2455126\times10^{-4}\,eV$$

This correction is always negative, and decreases in importance as the principal quantum number n increases. The 1s energy level of H is lowered by 1.811x10^{-4} eV and the ionization energy relative to the Schrodinger theory will be increased by this amount. Recall that the Schrodinger ionization energy for H underestimated the observed IP by $\sim 1.4\times10^{-4}\,eV$ so with the first order relativistic correction the theoretical IP is $\sim 0.4\times10^{-4}\,eV$ larger than experiment. We compare the 1s-2s separation calculated with the Schrodinger theory with the corrections due to the mass-velocity and Darwin terms below.



Note that the mass-velocity perturbation lowers the energy while the Darwin term increases it. Both the 1s and 2s energies are lowered but the 1s more so and the net 1s-2s separation increases. A for H equals 5.8439 cm^{-1} so the net separation is increased by 1.0044 cm^{-1}.

Additionally since the 1s is lowered by $-A/4$ the ionization energy is increased and we plot the error in the ionization energy of the 1s orbital in the H-O sequence calculated with the Pauli correction below.



While the Pauli results improve the accuracy significantly relative to the Schrodinger equation they are not in perfect agreement with experiment.

When $\ell \neq 0$ each level is split into two with $j = \ell \pm 1/2$. Since the radial functions for $\ell \neq 0$ are zero at the origin the Darwin term doesn't contribute. Additionally the mass-velocity and spin-orbit perturbations are diagonal in the degenerate basis $R_{n\ell}(r)\Phi_{jm_j\ell 1/2}(\theta,\phi,\alpha,\beta)$ so non-degenerate perturbation theory is valid.

The mass-velocity contribution is calculated in the same way as with the ns states, the matrix element being

$$\left\langle R_{n\ell}\boldsymbol{\Phi}_{jm_j\ell s}\left|\hat{H}_{mv}\right|R_{n\ell}\boldsymbol{\Phi}_{jm_j\ell s}\right\rangle = -\frac{1}{2mc^2}\left(E_n^2 + E_n\frac{2Ze^2}{4\pi e_0}\left\langle\frac{1}{r}\right\rangle_{n\ell} + \left(\frac{Ze^2}{4\pi e_0}\right)^2\left\langle\frac{1}{r^2}\right\rangle_{n\ell}\right)\left\langle\boldsymbol{\Phi}_{jm_j\ell s}\middle|\boldsymbol{\Phi}_{jm_j\ell s}\right\rangle$$

Since

$$\left\langle\frac{1}{r}\right\rangle_{n\ell} = \frac{Z}{a_0 n^2} \text{ and } \left\langle\frac{1}{r^2}\right\rangle_{n\ell} = \frac{Z^2}{a_0^2 n^3(\ell+1/2)}$$

We have

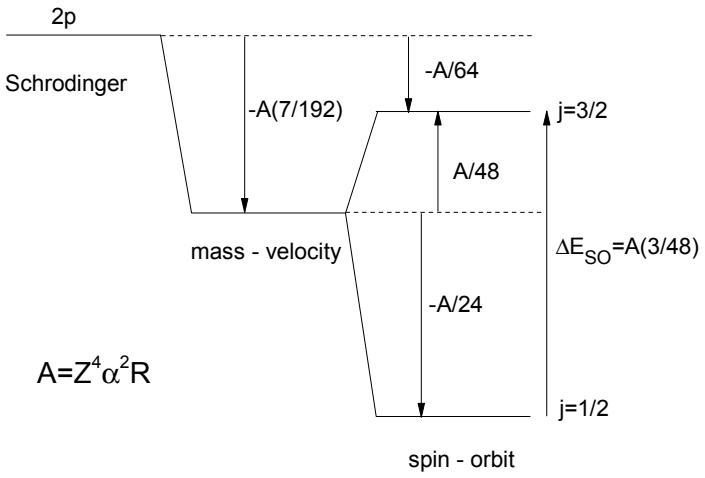
$$\left\langle R_{n\ell}\Phi_{jm_j\ell s}\left|\hat{H}_{mv}\right|R_{n\ell}\Phi_{jm_j\ell s}\right\rangle = -\frac{\alpha^2 Z^4}{4n^4}R_\infty\left(-3+\frac{4n}{\ell+1/2}\right)$$

The spin-orbit contribution was derived above and is

$$\left\langle R_{n\ell}\Phi_{jm_j\ell s}\left|\hat{H}_{SO}\right|R_{n\ell}\Phi_{jm_j\ell s}\right\rangle = \frac{Z^4\alpha^2 R_\infty}{2n^3}\left(\frac{j(j+1)-\ell(\ell+1)-3/4}{\ell(\ell+1/2)(\ell+1)}\right)$$

In the figure below we compare the splitting pattern for the Schrodinger 2p level resulting from the mass-velocity and spin orbit perturbations.

Pauli Hamiltonian corrections to the Schrodinger 2p energy levels in a one electron atom



Once again we see that the mass-velocity perturbation lowers the energy and in this case the spin orbit term both lowers (the j=1/2 level) and raises it (the j=3/2 level). Note that the $2p_{1/2}$ level is lower than the Schrodinger level by 5A/64, exactly the same as the $2s_{1/2}$ level. As noted previously the predicted ${}^2P_{1/2} - {}^2P_{3/2}$ spin orbit separation ΔE for other one-electron atoms is Z^4 times that of H and is quite accurate.

Combining the mass-velocity, Darwin and spin-orbit terms we can write the energy of a one-electron atom to first order in the relativistic corrections as

$$E(njm_j) = E_n\left(1+\left(\frac{\alpha Z}{n}\right)^2\left(\frac{n}{j+1/2}-\frac{3}{4}\right)\right).$$

Note that each j level is $2j+1$ degenerate and the factor that multiplies the Schrodinger energy, E_n is always positive so the Dirac energy to this order is always less than (more negative) than the Schrodinger energy. Since the eigenfunctions of the Pauli (and Dirac) Hamiltonians are eigenfunctions of $\hat{L}^2$ & $\hat{S}^2$ as well as $\hat{J}^2$ & $\hat{J}_Z$ we can label them using the term symbol ${}^{2S+1}L_j$ where one substitutes the letter equivalent for the orbital angular momentum L. All s states become ${}^2S_{1/2}$, all p states split into ${}^2P_{1/2}$ & ${}^2P_{3/2}$, all d states split into ${}^2D_{3/2}$ & ${}^2D_{5/2}$ and so on. In levels with the same principal quantum number *n*, since the energy is independent of ℓ, the ${}^2S_{1/2}$ and ${}^2P_{1/2}$ remain degenerate, the ${}^2P_{3/2}$ and ${}^2D_{3/2}$ remain degenerate, etc., consistent with the observed fine structure but of course without the Lamb shift.