Errors in the Quantum Mechanical calculation of the fine structure spectrum of the hydrogen atom

Jorma Jormakka
Vantaa, Finland
jorma.o.jormakka@gmail.com

Abstract: The article explains why the Quantum Mechanical derivation of the fine structure spectrum is incorrect. The main error is that in this derivation the substitution of the momentum to partial derivatives of space coordinates is not the same as in the non-relativistic case and therefore the energy levels that are obtained are not energy levels for the relativistic Hamiltonian, they are energy levels for the non-relativistic Hamiltonian and different. If the error is corrected, the fine structure spectrum formula is not obtained correctly. There are also two other errors in the Quantum Mechanical derivation.

Keywords: Fine structure spectrum, Quantum Mechanics, Dirac's equation, apparent mass.

1. Fine structure spectrum of the hydrogen atom in old quantum theory

Sommerfeld found the fine structure constant α and derived the fine structure spectrum of the hydrogen atom as the formula

$$E_{n,k} = -\frac{hcR_\infty}{n^2}\left(1+\frac{\alpha^2}{n^2}\left(\frac{n}{k}-\frac{3}{4}\right)\right). \tag{1}$$

In this formula α is the fine structure constant

$$\alpha = \frac{e^2}{4\pi\varepsilon_0 c\hbar}. \tag{2}$$

Sommerfeld defined α as

$$\alpha = \frac{v}{c} \tag{3}$$

where v is the speed of an electron on the lowest energy orbit in Bohr's atomic model. In Bohr's atomic model one electron moves around a proton with a constant speed v in a circular orbit. The centrifugal force and the Coulomb force are set to equal:

$$F_C = \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r^2} = \frac{m_e v^2}{r} = F_{centr.fug.} \tag{4}$$

Bohr's quantization rule is $m_e v r = n\hbar$, thus

$$v = \frac{e^2}{4\pi\varepsilon_0}\frac{1}{m_e v r} = \frac{e^2}{4\pi\varepsilon_0 m_e n\hbar} \tag{5}$$

and

$$r = \frac{n\hbar}{m_e v} = \frac{4\pi\varepsilon_0 n\hbar}{e^2}\frac{n\hbar}{m_e} = n^2 4\pi\varepsilon_0\frac{\hbar}{m_e e^2} = n^2 a_0 \tag{6}$$

where

$$a_0 = 4\pi\varepsilon_0 \frac{\hbar^2}{m_e e^2} \tag{7}$$

is the Bohr radius. The energy levels are obtained from the nonrelativistic kinetic energy as

$$E_n = -\frac{1}{2}m_e v^2 = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{2a_0}\frac{1}{n^2} \tag{8}$$

$$= -\frac{e^2}{4\pi\varepsilon_0 c\hbar}\frac{1}{4\pi a_0}ch\frac{1}{n^2} = -\frac{\alpha}{4\pi a_0}ch\frac{1}{n^2} = -\frac{hcR_\infty}{n^2} \tag{9}$$

where the Rydberg constant is

$$R_\infty = \frac{\alpha}{4\pi a_0}. \tag{10}$$

In Quantum Mechanics the fine structure spectrum formula expressed with Rydberg's constant for the hydrogen atom ($Z = 1$) is

$$E_{n,j} = -\frac{hcR_\infty}{n^2}\left(1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right)\right). \tag{11}$$

Comparing this formula to Sommerfeld's formula we see only one difference: Sommerfeld has a quantum number k, the azimuthal quantum number, and the Quantum Mechanics formula has $j = l + m_s$ and $m_s = \pm 1/2$. Sommerfeld's k is not quite the same as l in Quantum Mechanics. An electron on the lowest orbit has the angular momentum $L = m_e v a_0 = \hbar$ by Bohr's quantization rule. In Quantum Mechanics $l = 0$ on the lowest orbit and therefore $L = 0$. However, on the lowest orbit m_s can only be $m_s = 1/2$ and $j + 1/2 = l + m_s + 1/2 = l + 1 = 1$. This corresponds to $k = 1$ on the lowest orbit in Sommerfeld's fine structure spectrum. Sommerfeld's formula does not include $m_s = -\frac{1}{2}$ states, but otherwise the formula is the same.

Sommerfeld's derivation is now considered obsoleted, however, the present derivation is incorrect. I will use lectures in an open MIT course [1] to show three errors.

2. Fine structure spectrum of the hydrogen atom in Quantum Mechanics

The Quantum Mechanical calculation is as follows. The nonrelativistic Hamiltonian is

$$H^{(0)} = \frac{\hat{\boldsymbol{p}_0}^2}{2m_e} + V \qquad V = -\frac{1}{4\pi\varepsilon}\frac{e^2}{r}. \tag{12}$$

The momentum that is turned into an operator is $\boldsymbol{p}_0 = m_e\boldsymbol{v}$, not $\boldsymbol{p} = \gamma m_e \boldsymbol{v}$. The mass should be the reduced mass of an electron and a proton, but as the mass of a proton is so much larger, the mass can be taken as the mass m_e of an electron in the accuracy of the calculation.

This is the only case where the Schrödinger equation has been analytically solved, therefore the energy levels have been calculated, they are as in Bohr's atomic model

$$E_n^{(0)} = -\frac{hcR_\infty}{n^2}. \tag{13}$$

These energy levels correspond to the nonrelativistic momentum $\boldsymbol{p}_0 = m_e\boldsymbol{v}$. If we change the momentum to $\boldsymbol{p} = \gamma m_e \boldsymbol{v}$, the energy levels must be multiplied by γ. This is because the Schrödinger equation does not act on v, it only has a partial derivative of the components of $\boldsymbol{x}$. Therefore the Lorentz factor γ is a constant in the Schrödinger equation and the mass m_e is simply replaced by γm_e. The result is that a_0 changes to $a_0\gamma^{-1}$ and E_n changes to $E_n\gamma$.

This nonrelativistic Hamiltonian is upgraded to

$$H^{(1)} = \frac{\hat{\boldsymbol{p}}^2}{2m_e} + V + H_{rel} + H_{SO} + H_{Darwin} \tag{14}$$

where the first-order relativistic correction is

$$H_{rel} = -\frac{\hat{\boldsymbol{p}}^4}{8m_e^3c^2}. \tag{15}$$

Notice that here we have $\boldsymbol{p} = \gamma m_e \boldsymbol{v}$, more about this in section 3.

The spin-orbit coupling is

$$H_{SO} = -\frac{1}{2m_e^2c^2}\frac{1}{r}\frac{dV}{dr}\boldsymbol{S}\cdot\boldsymbol{L} \tag{16}$$

and the Darwin term is

$$H_{Darwin} = -\frac{\hbar^2}{8m_e^2c^2}\nabla^2 V. \tag{17}$$

The relativistic correction term is evaluated as

$$< \psi|\hat{\boldsymbol{p}}^4|\psi > = < \psi\hat{\boldsymbol{p}}^2|\hat{\boldsymbol{p}}^2\psi > \tag{18}$$

$$\frac{\hat{\boldsymbol{p}}^2}{2m_e}\psi + V\psi = E_n^{(0)}\psi \qquad \hat{\boldsymbol{p}}^2\psi = 2m_e(E_n^{(0)} - V)\psi \tag{19}$$

$$< \psi\hat{\boldsymbol{p}}^2|\hat{\boldsymbol{p}}^2\psi > = (2m_e)^2 < \psi|(E_n^{(0)} - V)^2|\psi > \tag{20}$$

$$E_{rel} = -\frac{1}{8m_e^3c^2}(2m)^2\left((E_n^{(0)})^2 - 2E_n^{(0)} < V > + < V^2 >\right). \tag{21}$$

Then [1] inserts

$$< V > = 2E_n \tag{22}$$

using the virial theorem.

Lecture [1] states that

$$< r^2 >= \frac{1}{n^3 a_0^3 (l+\frac{1}{2})}. \tag{23}$$

A small comment is needed. Lecture [1] sets $4\pi\varepsilon_0$ to one, and possibly some other constants are also set to one. Consequently the Coulomb potential between the electron and the proton is given as

$$V = -\frac{e^2}{r}. \tag{24}$$

This will not affect the analysis and in this section we can use the formulas directly as they are in [1], but one must remember that some constants are set to one in the equations that follow in this section. In the next section(s) we will return to showing all constants.

Inserting $< r^{-1} >$ and $< r^{-2} >$ gives

$$E_{rel} =< nlm|H_{rel}|nlm >= -\frac{(E_n^{(0)})^2}{2m_e c^2}\left(\frac{4n}{l+\frac{1}{2}} - 3\right). \tag{25}$$

The spin-orbit coupling term is evaluated by inserting

$$\mathbf{S}\cdot\mathbf{L} = \frac{1}{2}\hbar(j(j+1) - l(l+1) - s(s+1)) \tag{26}$$

$$= \frac{1}{2}\hbar\left(j(j+1) - l(l+1) - \frac{3}{4}\right) \tag{27}$$

and using what [1] states is a know result (for the hydrogen atom $Z = 1$)

$$< \frac{1}{r^3} >= \frac{Z^3}{n^3 a_0^3}\frac{1}{l(l+\frac{1}{2})(l+1)}. \tag{28}$$

Lecture [1] explains why using a different basis does not matter for the calculated energy. Inserting these equations gives

$$E_{SO} =< njm_j|H_{SO}|njm_j >= \frac{(E_n^{(0)})^2}{m_e c^2} n \frac{\left(j(j+1) - l(l+1) - \frac{3}{4}\right)}{l(l+\frac{1}{2})(l+1)}. \tag{29}$$

Then

$$E_{rel} + E_{SO} = \frac{(E_n^{(0)})^2}{m_e c^2} n \frac{\left(j(j+1) - 3l(l+1) - \frac{3}{4}\right)}{l(l+\frac{1}{2})(l+1)}. \tag{30}$$

Rather amaxingly, this expression gives the same value for both possible values of j, $j = l \pm \frac{1}{2}$. We can insert $l = j + \frac{1}{2}$ and eliminate l. The expression simplifies to

$$E_{rel} + E_{SO} = \frac{(E_n^{(0)})^2}{m_e c^2}\left(3 - \frac{2n}{j+\frac{1}{2}}\right). \tag{31}$$

Adding the term $E_n^{(0)}$

$$E_{n,j,fine-spectrum} = E_n^{(0)} + E_{rel} + E_{SO} \tag{32}$$

and simplifying gives the fine structure spectrum equation (11).

The Darwin term is evaluated in [1], but it is not needed in (32) because it is cancelled by E_{SO} in the calculation in [1].

3. Three errors in this derivation

The first error is in the relativistic approximation. For convenience we rotate the coordinate system so that $\boldsymbol{p}$ is in the direction of the x-axis, then $\boldsymbol{p}^2 = p_x^2$, a scalar. We will write $p = \gamma m_0 v$ and $p_0 = m_0 v$.

The relativistic kinetic energy can be decomposed into a series in the following ways

$$\sqrt{p^2c^2 + m_0^2c^4} - m_0c^2 = \frac{p^2}{2m_0} - \frac{1}{8}\frac{p^4}{m_0^3c^2} + \cdots \tag{33}$$

and

$$\sqrt{p^2c^2 + m_0^2c^4} - m_0c^2 = \frac{p_0^2}{2m_0} + \frac{3}{8}\frac{p_0^4}{m_0^3c^2} + \cdots . \tag{34}$$

In the non-relativistic $H^{(0)}$ we make the substitition $p_0 \to -i\hbar\frac{\partial}{\partial x}$, then the operator is

$$H^{(0)} = -\frac{\hbar^2}{2m_0}\frac{\partial^2}{\partial x^2} + V(x) \tag{35}$$

and we get the energy levels $E_n^{(0)}$ that agree with the energy levels from Bohr's atomic model.

If we make the substitution $p \to -i\hbar\frac{\partial}{\partial x}$ in (33) and only take the first term and $V(x)$, we do get a Hamiltonian that has an identical form as $H^{(0)}$

$$H^{(0')} = -\frac{\hbar^2}{2m_0}\frac{\partial^2}{\partial x^2} + V(x) \tag{36}$$

and it gives the same energy levels as $H^{(0)}$, but is this correct? Let us consider the following case. Let the semi-classical Hamiltonian be

$$H = \frac{1}{2}f(v)^2 m_0 v^2 + V(x) \tag{37}$$

where $f(v)$ is any function. We choose to call with the name momentum the expression $p = f(v)m_0 v$ and write the Hamiltonian as

$$H = \frac{p^2}{2m_0} + V(x). \tag{38}$$

Then we apply the substitution $p \to -i\hbar\frac{\partial}{\partial x}$ and get again a form that is identical with $H^{(0)}$

$$H = -\frac{\hbar^2}{2m_0}\frac{\partial^2}{\partial x^2} + V(x). \tag{39}$$

It gives the same energy levels as $H^{(0)}$. Is this correct? Certainly the semi-classical Hamiltonian (37) does not have these energy levels for every $f(v)$. The problem is that there must be a connection from p to $-i\hbar\frac{\partial}{\partial x}$ that makes the semi-classical Hamiltonian and the quantized Hamiltonian to give the same energy levels. The semi-cassical Hamiltonian is Bohr's atomic model. We cannot use any other substitution than $p_0 \to -i\hbar\frac{\partial}{\partial x}$ if we want to keep this connection with the physical reality. If we make the substitution $p \to -i\hbar\frac{\partial}{\partial x}$ in (33), then the energy levels that we get are not energy levels to (33). They are energy levels to the original non-relativistic Hamiltonian.

The error made in using $E^{(0)}$ that is calculated from $\boldsymbol{p}_0$ when the momentum actually is $\boldsymbol{p}$ is four times larger than the relativistic correction, therefore this error is too large to be ignored. The consequence is that the step where l is eliminated fails. If this error is corrected, the result is not the correct fine structure spectrum formula.

The second error is in the calculation of H_{SO}. It is a logical consequence: the calculation is wrong because there is the first error in the calculation, yet the result is the correct fine structure formula. This means that there must be a second error that compensates for the first error and it must be in the calculation of H_{SO} (or the whole approach of Quantum Mechanics fails). Checking the calculations in [1] shows that there are no calculation errors. Therefore the natural place where the error can be is the claims that $< \frac{1}{r^2} >$ and $< \frac{1}{r^3} >$ have the stated values. Lecture [1] does not derive these expressions and directly integrating them from the wavefunction for the hydrogen atom is very difficult. But we can compare the given expresions for $< r^{-1} >$, $< r^{-2} >$ and $< r^{-3} >$ and notice that the given expressions do not seem to have a similarity that one would expect if each of them is integrated with the same wavefunctions.

The third error is in the way the Darwin term is eliminated. The Darwin term is calculated and it gives a non-zero contribution to S-states. Lecture [1] eliminates this Darwin term contribution with the argument that if l is taken as a continuous variable in E_{SO}, then the limit of E_{SO} when $l \to 0$ from above exactly equals the negative of the Darwin term and cancels it. This argument is invalid. The quantum number l is discrete and it cannot be considered as a continuous variable. At $l = 0$ the spin-orbit coupling term vanishes and it cannot cancel the Darwin term.

The first error is fatal to this calculation, there is a confusion between the relativistic momentum and the non-relativistic momentum. Certainly this error must have been noticed, but it was ignored. Probably articles in the Internet that state that the fine structure spectrum is derived from the non-relativistic Dirac equation refer to this error and try to make it sound unimportant. But the Dirac equation is relativistic and in order to get $H^{(0]}$ as the first term in the Hamiltonian, it is necessary to develop the series as in (34). The error does not go away.

The error also does not go away by noticing that the relativistic kinetic energy formula is incorrect. It is indeed incorrect, it conflicts with Bertozzi's measurements, see [2] and [3] and the figure below from [3]:

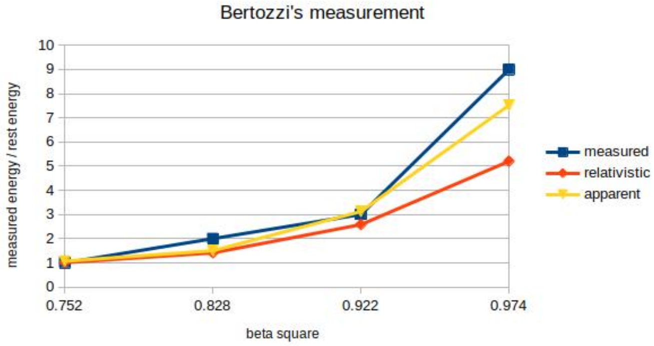

Figure 1. The figure plots E_k/m_ec^2 (measured), $0.5\gamma^{1.5}m_ev^2$ (kinetic energy of the apparent mass) and $\gamma - 1$ (relativistic kinetic energy) as an function of $v^2/c^2 = \beta^2$. The y-axis gives the ratio of energy and the rest energy of an electron.

This figure shows that $T = \sqrt{p^2c^2 + m_0^2c^4} - m_0c^2 = (\gamma - 1)m_0c^2$ is too small and the correct energy is about $(1/2)\gamma^{1.5}m_ov^2$.

However, this does not affect the error in the Quantum Mechanical calculation: the more correct kinetic energy formula $(1/2)\gamma^{1.5}m_ov^2$ gives exactly the same first order approximations (33) and (34) as T.

3. References

[1] Zweibach, B., Chapter 2 of lecture notes to Quantum Physics III, Spring 2018. Open lecture course in MIT, available in ocw.mit.edu/courses/8-06-quantum-physics-iii-spring-2018.

[2] Jormakka, J., "Calculation of the longitudinal mass from Bertozzi's experiment", ResearchGate, 2025

[3] Jormakka, J., "Apparent momentum in Compton scattering, ResearchGate", 2025.