

FINE STRUCTURE OF HYDROGEN: SPIN-ORBIT COUPLING

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References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 6.16.

Another correction to the energy levels of hydrogen arises from spin-orbit coupling. Unlike the relativistic correction, spin-orbit coupling arises from the interaction of the magnetic moment due to the electron's spin and the magnetic field generated by its revolution around the nucleus. The derivation using non-relativistic electromagnetic theory isn't very satisfying since it's fundamentally incorrect, although by a series of fortuitous coincidences, it does give the right answer. We won't go into all the gory details here since Griffiths discusses some of the issues in his book in section 6.3.2; rather, we'll give a sketch of the argument.

In the reference frame of the electron, the proton appears to be rotating about it and, since its speed is very fast, it can be considered to be a steady current loop, which generates a magnetic field \mathbf{B} , given by the Biot-Savart law:

$$(1) \quad \mathbf{B} = \frac{\mu_0}{2r} I \hat{\mathbf{z}}$$

where I is the effective current generated by the proton, r is the radius of the orbit, and we're taking the axis of revolution to be the z axis.

The magnetic moment of the electron, as calculated from classical electrodynamics, is given in terms of the angular momentum \mathbf{S} (we've renamed some of the symbols in the electrodynamics formula to be consistent with Griffiths's QM book):

$$(2) \quad \boldsymbol{\mu} = -\frac{e}{2m} \mathbf{S}$$

where $-e$ is the electron charge.

The energy of a dipole in a magnetic field is:

$$(3) \quad U = -\boldsymbol{\mu} \cdot \mathbf{B}$$

so the correction to the hamiltonian is

$$(4) \quad H' = \left(\frac{e}{2m}\right) \left(\frac{\mu_0}{2r}I\right) \mathbf{S} \cdot \hat{\mathbf{z}}$$

The current I produced by the proton can be approximated by $I = ev/2\pi r$ where v is the linear speed of the proton in its apparent orbit about the electron. The orbital angular momentum of the electron is $L = mvr$, so $I = eL/2\pi mr^2$ so we get

$$(5) \quad \mathbf{B} = \frac{\mu_0 e}{4\pi m r^3} \mathbf{L}$$

and

$$(6) \quad H' = \frac{\mu_0 e^2}{8\pi m^2 r^3} \mathbf{S} \cdot \mathbf{L}$$

We can rewrite this using the relation $\mu_0 = 1/\epsilon_0 c^2$ (derived in electromagnetic theory) to get

$$(7) \quad H' = \frac{e^2}{8\pi \epsilon_0 m^2 c^2 r^3} \mathbf{S} \cdot \mathbf{L}$$

Since the perturbation depends on the interaction between the spin and orbital angular momentum operators, this is the spin-orbit coupling effect.

As I mentioned above, this derivation is seriously flawed because it ignores relativity but when relativistic effects are taken into consideration, they cancel each other, with the result that this equation actually turns out to be correct.

In order to apply degenerate perturbation theory to this correction to the hamiltonian, we'd like to find operators that commute with the original hamiltonian and with H' , and also have eigenvectors with distinct eigenvalues. Since the unperturbed hydrogen wave functions are derived from a spherically symmetric potential, their angular factors are the spherical harmonics, which are also the eigenfunctions of the orbital angular momentum operators L^2 and L_z meaning that this hamiltonian commutes with these operators, which in turn means that L^2 and L_z are conserved.

The introduction of H' , however, means that this is no longer true. We can see this by considering the commutation relations. The commutators for angular momentum are

$$(8) \quad [L_x, L_y] = i\hbar L_z$$

with cyclic permutations for the other two relations. The same commutators apply to spin with L replaced by S . Since L and S refer to different spaces, all components of L commute with all components of S .

First, we consider the commutator with \mathbf{L} :

$$(9) \quad [\mathbf{L} \cdot \mathbf{S}, \mathbf{L}] = i\hbar(-S_y L_z + S_z L_y) \hat{\mathbf{x}} + i\hbar(S_x L_z - S_z L_x) \hat{\mathbf{y}} + i\hbar(-S_x L_y + S_y L_x) \hat{\mathbf{z}}$$

$$(10) \quad = i\hbar \mathbf{L} \times \mathbf{S}$$

Thus H' does not commute with \mathbf{L} . By exactly the same argument

$$(11) \quad [\mathbf{L} \cdot \mathbf{S}, \mathbf{S}] = -\hbar \mathbf{S} \times \mathbf{L} = -[\mathbf{L} \cdot \mathbf{S}, \mathbf{L}]$$

so H' doesn't commute with \mathbf{S} either. However, for the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$, we get

$$(12) \quad [\mathbf{L} \cdot \mathbf{S}, \mathbf{J}] = [\mathbf{L} \cdot \mathbf{S}, \mathbf{L}] + [\mathbf{L} \cdot \mathbf{S}, \mathbf{S}] = 0$$

so the components of \mathbf{J} are conserved. Since $[\mathbf{L}, L^2] = [\mathbf{S}, S^2] = 0$, we get

$$(13) \quad [\mathbf{L} \cdot \mathbf{S}, L^2] = [\mathbf{L} \cdot \mathbf{S}, S^2] = 0$$

Finally, since $J^2 = L^2 + S^2 + 2\mathbf{L} \cdot \mathbf{S}$

$$(14) \quad [\mathbf{L} \cdot \mathbf{S}, J^2] = 0$$

Thus the conserved quantities are J_z , J^2 , L^2 and S^2 .

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