Corrections to the spectrum of Hydrogen atom

We have seen that energy levels in the hydrogen atom are highly degenerate for $\nu > 1$. This makes some of them prone to small perturbations which lift the degeneracy. In this Chapter we explore such perturbations to make the picture of the hydrogen atom more realistic. Some of the considerations will be rather generic and can be used for other atoms/system as well, i.e. the hydrogen atom system is used solely for making a specific example.

Spin-orbit interaction
Formally, spin-orbit interaction is an immediate consequence of the relativistic Dirac equation. Since we do not study it here, I will present hand-waving arguments explaining its origin. We recall from E&M that, as seen in a moving frame, the components of the electric and magnetic fields which are parallel to $\mathbf{v}$ do not change while (keeping only the leading order corrections in the Lorentz transformation)

$$
\mathbf{E}' \approx \mathbf{E} - \mathbf{B} \times \mathbf{v}, \quad \mathbf{B}' \approx \mathbf{B} + \frac{1}{c} \mathbf{E} \times \mathbf{v}.
$$

Then, in particular, since in the rest frame of the electron, the proton is seen to be moving with velocity $\mathbf{v}$, we have

$$
\mathbf{B} \approx \frac{1}{c} \mathbf{E} \times \mathbf{v} = \frac{1}{c} \left( -\nabla \frac{Ze}{r} \right) \times \mathbf{v} = \frac{Ze}{mc^2} \mathbf{r} \times \mathbf{p} = \frac{Ze}{mc^2} \mathbf{L}.
$$

This generates coupling between the electron magnetic moment and magnetic field

$$
H_{SL} = -\mu \cdot \mathbf{B} = \frac{g \mu_B Ze}{mc^2} \mathbf{S} \cdot \mathbf{L}.
$$

This calculation is rather an idea hinting at the origin of the spin-orbit coupling done in the rest frame of an electron. The proper relativistic calculation done by Thomas in the rest frame of the proton changes this result by exactly a factor of $1/2$. The correct answer is

$$
H_{SL} = g \frac{Ze^2}{4m^2c^2r^3} \mathbf{S} \cdot \mathbf{L}.
$$

Let us see now how this term in the Hamiltonian changes the energy spectrum of the hydrogen atom $(Z = 1)$. First, an estimate of what to expect. If we consider $s = 1/2$, $l = 1$ and $r$ with $10^{-8}$ cm $\approx 2a_B$, we get

$$
E_{SL} \sim \frac{\alpha^2}{a_B} \frac{\hbar^2}{m a_B^2} \frac{1}{64m c^2} \sim 27 \text{ eV} \quad \frac{27 \text{ eV}}{64 \times 5 \times 10^5 \text{ eV}} \approx 2 \times 10^{-5} \text{ eV},
$$

i.e. a value some six orders of magnitude smaller than the typical energy splitting between hydrogen levels. This immediately suggests that we can resort to the first-order perturbation theory unless we face degenerate or near-degenerate levels. In general, one can use the basis of $|a\rangle = |\nu,l,m\rangle \otimes |s,\sigma\rangle$ functions and construct the $(H_{SL})_{ab}$ matrix

$$
(H_{SL})_{ab} = g \frac{Ze^2}{4m^2c^2} \left| \langle \nu', l', m' | \mathbf{S} \cdot \mathbf{L} | \nu, l, m \rangle \right|^2.
$$
There are no matrix elements for the fully symmetric $s$-state because they have no angular momentum, i.e. $L\psi_{n,0,0} = 0$. Thus $\Delta E_{SL} = 0$ for $1s$, $2s$, $3s$, etc. states. However, in the $2p$ subset of states we do have non-zero matrix elements. Since these states are degenerate we have to proceed with the full matrix. At this point there are two routes one can take, either continue working with the $|\nu, l, m\rangle \otimes |s, \sigma\rangle$ basis or switch to the $|\nu,j,m_j\rangle$ basis. In the former case we compute matrix elements for $S \cdot L = S_z L_z + (S_+ L_+ + S_- L_-)/2$, which is relatively easy, and then diagonalize the $6 \times 6$ Hamiltonian matrix acting in this $(2l+1)(2s+1) = 6$-fold degenerate subspace of levels (this is not too hard since the matrix breaks into blocks with the largest block being only $2 \times 2$). In the latter case we solve the problem immediately because $S \cdot L$ is diagonal in the $|\nu,j,m_j\rangle$ basis (Homework Problem 46.)

\[
\left\langle 2p, j', m'_j \, \left| \frac{S \cdot L}{r^3} \right| 2p, j, m_j \right\rangle = \delta_{j,j'}\delta_{m_j,m'_j} \left\langle 2p \, | r^{-3} \rangle \, 2p \right\rangle \frac{j(j+1)-s(s+1)-l(l+1)}{2}.
\]

Averaging over the radial coordinate gives

\[
\left\langle 2p \, | r^{-3} \rangle \, 2p \right\rangle = \int_0^\infty \frac{r^2}{r^3} |R_{2,1}(r)|^2 = \frac{1}{24a_B^3} \int_0^\infty \rho d\rho e^{-\rho} = \frac{1}{24a_B^3},
\]

and we arrive at the final answer (for electron we can use $g \approx 2$)

\[
E^{(1)}_{2p,j,m_j} = \frac{e^2\hbar^2}{4m^2c^2} \frac{1}{24a_B^3} j(j+1) - s(s+1) - l(l+1) = \frac{e^2\hbar^2}{96m^2c^2a_B^3} [j(j+1) - 11/4].
\]

Thus the set of 6 degenerate levels is split into two groups, one group of 4 levels corresponds to the total momentum $j = 3/2$ and has its energy shifted relative to the 'zeroth order' answer upwards by

\[
E^{(1)}_{2p,3/2} = \frac{e^2\hbar^2}{96m^2c^2a_B^3},
\]

the other 2-fold degenerate group corresponds to $j = 1/2$ with

\[
E^{(1)}_{2p,1/2} = -\frac{e^2\hbar^2}{48m^2c^2a_B^3}.
\]

Thus some of the degeneracies are removed as shown in the figure.

**Problem 55. Spin-orbit coupling**

Find first-order energy shifts due to spin-orbit coupling and classify quantum numbers of eigenenergy states corresponding to the ten $3d$ states of the hydrogen atom.
The general formula for energy corrections to \( \nu, j = l \pm 1/2 \) levels is (below \( l > 0 \))

\[
E^{(1)}_{\nu,j=t\pm1/2} = \frac{e^2 \hbar^2}{4m^2 c^2} \left( \int_0^\infty \frac{dr}{r} |R_{\nu,l}(r)|^2 \right) \left\{ \begin{array}{c} l \\ -l \end{array} \right\}.
\]

Look here for wavefunctions: [http://quantummechanics.ucsd.edu/ph130a/130_notes/node233.html](http://quantummechanics.ucsd.edu/ph130a/130_notes/node233.html)

**Hyperfine interaction.**

So far in our discussion of the hydrogen atom we treated the proton was playing an idle role. Now we recall that it is a spin-1/2 particle with nonzero magnetic moment

\[
\mu_p = \frac{e_p}{2m_p c} \mathbf{I} \quad \text{with} \quad g_p \approx 5.58,
\]

where \( \mathbf{I} \) is the nuclear spin operator and the \( e/2m_p c \) unit used to gauge nuclear magnetic moments is the nuclear Bohr magneton. The point here is that magnetic moments generate magnetic field around them and other magnetic moments couple to it

\[
\mathbf{B} = \nabla \times \mathbf{A} = -\nabla \times \frac{g_p e}{2mc} \mathbf{I} \times \nabla \frac{1}{r} = -\frac{g_p e}{2m_p c} \left[ \mathbf{I} \nabla^2 \frac{1}{r} - \nabla \left( \mathbf{I} \cdot \nabla \frac{1}{r} \right) \right].
\]

Taking derivatives in this expression is tricky. To understand the final answer we use the Fourier representation

\[
\frac{1}{r} = \int \frac{dq}{(2\pi)^3} e^{i\mathbf{q} \cdot \mathbf{r}} 4\pi \frac{q^2}{q^2},
\]

and observe that

\[
\nabla^2 \frac{1}{r} = -4\pi \int \frac{dq}{(2\pi)^3} e^{i\mathbf{q} \cdot \mathbf{r}} \frac{q^2}{q^2} = -4\pi \delta(\mathbf{r}).
\]

To deal with the other derivatives we notice that

\[
\nabla_i \nabla_j \frac{1}{r} = -4\pi \int \frac{dq}{(2\pi)^3} e^{i\mathbf{q} \cdot \mathbf{r}} \frac{q_i q_j}{q^2} = -4\pi \int \frac{dq}{(2\pi)^3} e^{i\mathbf{q} \cdot \mathbf{r}} \frac{q_i q_j - \delta_{i,j} q^2/3}{q^2} - \delta_{i,j} \frac{4\pi}{3} \delta(\mathbf{r}).
\]

where the last \( \delta \)-functional term is obtained after we ‘regularize’ the angular behavior of the integral for \( r \to 0 \) using \( q_i q_j \to (q_i q_j - q^2 \delta_{i,j}/3) + q^2 \delta_{i,j}/3 \) to produce zero under angle averaging for the first term. Only after this tricky manipulation we go back and calculate \( \nabla_i \nabla_j \frac{1}{r} = (3r_i r_j - r^2 \delta_{i,j})/r^5 \) for non-zero \( r \). Thus

\[
\nabla_i \nabla_j \frac{1}{r} = \frac{3r_i r_j - r^2 \delta_{i,j}}{r^5} - \delta_{i,j} \frac{4\pi}{3} \delta(\mathbf{r}),
\]

and

\[
\mathbf{B} = \frac{g_p e}{2m_p c} \left[ \mathbf{I} \frac{8\pi}{3} \delta(\mathbf{r}) + \frac{3\mathbf{r} (\mathbf{I} \cdot \mathbf{r}) - (\mathbf{S} \cdot \mathbf{I}) r^2}{r^5} \right].
\]

With this we find for the interaction between the electron and proton spins

\[
H_{HF} = -\mu_e \mathbf{B} = \frac{g_e g_p e^2}{4m_e m_p c^2} \left[ \mathbf{S} \cdot \mathbf{I} \frac{8\pi}{3} \delta(\mathbf{r}) + \frac{3(\mathbf{S} \cdot \mathbf{r})(\mathbf{I} \cdot \mathbf{r}) - (\mathbf{S} \cdot \mathbf{I}) r^2}{r^5} \right].
\]

Since the average of the second term in brackets over spherically symmetric spatial states is zero only the first term contributes to the energy shifts of \( s \)-states

\[
E^{(1)}_{\nu,s,j} = \frac{g_e g_p e^2}{6m_e m_p c^2} |R_{\nu,0}(0)|^2 \langle j | \mathbf{S} \cdot \mathbf{I} | j \rangle = \frac{g_e g_p e^2}{6m_e m_p c^2} |R_{\nu,0}(0)|^2 \left\{ \begin{array}{c} 1/4 \quad \text{for} \quad j = 1 \\ -3/4 \quad \text{for} \quad j = 0 \end{array} \right\},
\]

3
where $j$ is the total spin value. The magnitude of the splitting between the $J = 1$ triplet and $J = 0$ singlet is very small. For the $1s$ state we obtain

$$\Delta E = E_{1s,j=1}^{(1)} - E_{1s,j=0}^{(1)} = \frac{2g_e g_p e^2}{3m_e m_p c^2 a_B} \sim 10^{-5} \text{eV}.$$ 

This energy splitting corresponds to the 21 cm wavelength of light which is sought by astronomers.

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**Problem 56. Positronium in magnetic field**

The spin-dependent part of the Hamiltonian of positronium atom (electron plus positron) in the $1s$ state in a magnetic field $B$ along $z$-direction is to a good approximation given by

$$H = AS_1 \cdot S_2 + 2\mu_B B(S_{1z} - S_{2z}),$$

where $A$ is the hyperfine constant. The electron is labeled as particle 1 and the positron as particle 2. Using total spin $S^2 = (S_1 + S_2)^2$ and its projection $S_z = S_{1z} + S_{2z}$ representation, obtain the energy eigenvalues and spin eigenstates.

---

**Coupling to external fields.**

Often, perturbation theory is used in the context of coupling to external fields because if one is to probe the system gently then external fields have to be weak. Here we explore (in notes and in the homework) how the system responds to the electric and magnetic fields. The classical non-relativistic Hamiltonian for an article in the electro-magnetic field is

$$H = \frac{p^2}{2m} + \frac{[p - eA(r)]^2}{2m} + e\phi(r),$$

where $A(r)$ and $\phi(r)$ are the vector and scalar potentials. To check for correctness, start with the rules of Hamiltonian dynamics and see if you get the right equations of motion

$$\dot{r} = \frac{\partial H}{\partial p} = \frac{1}{m} (p - eA), \quad \dot{p} = -\frac{\partial H}{\partial r} = -e\nabla \phi + \frac{1}{m} (p - eA_i \nabla (eA_i)).$$

The first equation reads

$$p = m\dot{r} + eA \quad \rightarrow \quad \dot{p} = m\dot{r} + e \frac{d}{dt} A(r(t)) = m\dot{r} + e \left[ \frac{\partial A}{\partial t} + (\dot{r} \cdot \nabla) A \right].$$

Now we simply substitute $\dot{p}$ from the second equation to get

$$-e\nabla \phi + e\dot{r}_i \nabla A_i = m\ddot{r} + e \left[ \frac{\partial A}{\partial t} + (\dot{r} \cdot \nabla) A \right],$$

i.e.

$$m\ddot{r} = -e \left( \nabla \phi + \frac{\partial A}{\partial t} \right) + e (\dot{r}_i \nabla A_i - (\dot{r} \cdot \nabla) A) = eE + e\dot{r} \times (\nabla \times A) = e(E + \dot{r} \times B),$$

as expected (Coulomb + Lorentz forces).
For a static electric field we can write (taking external field $E_0$ along $z$-axis)

$$H_{\text{pert}} = -eE_0 z.$$ 

The first-order shift is

$$E^{(1)} = -eE_0 \langle \psi | z | \psi \rangle.$$ 

Since $|\psi|^2$ is even under reflection (for odd or even $\psi$) and $z = r \sqrt{4\pi/3} Y_{1,0}$ changes sign, we immediately conclude that the first order correction is zero. For the ground state $\psi_{100}$ we will have then to do the second order perturbation theory, the so-called second-order Stark effect (Problem 43.). However, for degenerate subsets of levels we have to be more careful and calculate the Hamiltonian matrix. So, consider four $\nu = 2$ levels (ignore spin in this setup) and evaluate $\langle \nu = 2, l', m' | z | \nu = 2, l, m \rangle$. To simplify notations, let us label

$$e_1 = \psi_{2,0,0}, \quad e_2 = \psi_{2,1,0}, \quad e_3 = \psi_{2,1,-1}, \quad e_4 = \psi_{2,1,1},$$

and look at $\langle e_i | z | e_j \rangle = \langle e_j | z | e_i \rangle^*$. We need to find 10 matrix elements (at and above the diagonal) to complete the matrix, but as mentioned above four of them are zero, $z_{ii} = 0$. Next we notice that $L_z = -ih(\partial/\partial \varphi)$ commutes with $z = r \cos(\theta)$, and thus $z$ operator can not change the quantum number $m$. This means that 5 of the remaining 6 matrix elements zero and the only matrix element to calculate is actually

$$z_{12} = \langle \psi_{2,0,0} | z | \psi_{2,1,0} \rangle = \int r^3 dr R_{2,0}^*(r)R_{2,1}(r) \int d\Omega Y_{1,0}^* Y_{1,0} = \sqrt{\frac{1}{3}} \int r^3 dr R_{2,0}^*(r)R_{2,1}(r).$$

At this point we have to use the exact radial wavefunctions

$$R_{2,0} = \frac{2 - r/a_B}{2 \sqrt{2a_B^3}} e^{-r/2a_B}, \quad R_{2,1} = \frac{r/a_B}{2 \sqrt{6a_B^3}} e^{-r/2a_B},$$

to take the last integral. We finally get

$$(H_{\text{pert}})_{12} = -eE_0 \frac{1}{24a_B^3} \int_0^\infty dr r^3 \frac{r}{a_B} \left( 2 - \frac{r}{a_B} \right) e^{-r/a_B} = -eE_0a_B \frac{1}{24} [2 + 4! - 5!] = 3eE_0a_B.$$

Let us summarize:

$$(H_{\text{pert}})_{ij} = \begin{pmatrix} 0 & 3eE_0a_B & 0 \ 3eE_0a_B & 0 & 0 \ 0 & 0 & 0 \end{pmatrix}.$$ 

Clearly the $\psi_{2,1,1}$ and $\psi_{2,1,-1}$ state are not affected by the perturbation (to leading order) while levels $\psi_{2,1,0}$ and $\psi_{2,0,0}$ are now mixed similarly to the symmetric two level system

$$\tilde{e}_1 = \frac{e_1 - e_2}{\sqrt{2}}, \quad E_1 = E_{\nu=2} - 3eE_0a_B,$$

$$\tilde{e}_2 = \frac{e_1 + e_2}{\sqrt{2}}, \quad E_2 = E_{\nu=2} + 3eE_0a_B.$$

This result can be understood as follows. Formally, in the original basis none of the states was having a non-zero average electric dipole moment, i.e. $\langle e_i | -ez | e_i \rangle = 0$. However, for degenerate
levels one is free to choose a different rotated basis \( \hat{e}_1, \hat{e}_2, e_3, e_4 \). Now the first two states possess a non-zero electric dipole moment \( d \) along the \( z \) direction

\[
d_1 = \langle \hat{e}_1 | ez | \hat{e}_1 \rangle = \frac{e}{2} ( -2 ) \langle e_1 | z | e_2 \rangle = 3e \alpha_B , \quad d_2 = \langle \hat{e}_2 | ez | \hat{e}_2 \rangle = -3e \alpha_B ,
\]

and in the rotated basis we have simple answers for the diagonal first-order energy shifts \( E_1^{(1)} = -d_1 E_0 = -3e \alpha_B a_B \) and \( E_2^{(1)} = -d_2 E_0 = 3e \alpha_B a_B \). Thus, depending on the basis choice in the degenerate subspace, we can say that the 'bare' hydrogen states are having a non-zero dipole moment.

Consider now an atom in a uniform magnetic field oriented along the \( z \) direction. For this setup

\[
A = \frac{1}{2} B_0 \times r , \quad \text{because} \quad \nabla \times A = \frac{1}{2} [ B_0 ( \nabla \cdot r ) - ( B_0 \cdot \nabla ) r ] = B_0 ,
\]

and the coupling is obtained from

\[
H_B = \frac{1}{2m} \left( p - \frac{q}{2c} B_0 \times r \right) ^2 = \frac{p^2}{2m} - \frac{q}{2mc} B_0 \cdot r \times p + \frac{q^2}{8mc^2} B_0 ^2 ( x^2 + y^2 ) .
\]

We have used here the fact that \( p \) commutes with \( B \times r \). Thus

\[
H_{\text{pert}} = -\frac{q}{2mc} B_0 L_z + \frac{q^2}{8mc^2} B_0 ^2 ( x^2 + y^2 ) .
\]

In this discussion I will concentrate on the linear in \( B_0 \) effects and neglect the second term; it is important though for diamagnetic susceptibility of atoms with net zero angular momentum and spin since it gives a non-zero contribution \( \Delta E = -\chi B_0 ^2 / 2 = -(e^2 B_0 ^2 / 8mc^2) (x^2 + y^2) \).

Since magnetic field also couples to the electron spin we have for linear in \( B_0 \) terms

\[
H_{\text{pert}} = \mu_B B_0 ( L_z + g_e S_z ) .
\]

Strictly speaking, this perturbation has to be considered along with the spin-orbit coupling

\[
H_{SL} = \frac{g_e \mu_B ^2}{r^3} S \cdot L ,
\]

because it can be easily comparable in strength for realistic experimental parameters.

Let us start from the case when spin-orbit coupling is strong and an external field is weak, i.e. we are dealing with the case when an appropriate basis set is defined by the \( \{ j, l, s, m_j \} \) quantum numbers with \( s = 1/2 \). To simplify the calculation we write

\[
\Delta E^{(1)} = \mu_B B_0 \langle j, l, s, m_j | L_z + 2S_z | j, l, s, m_j \rangle = \mu_B B_0 ( m_j + \langle j, l, s, m_j | S_z | j, l, s, m_j \rangle) .
\]

To complete the calculation all we have to do is to use states from SLalbegra.pdf notes adopted for the \( s = 1/2 \) case:

\[
| j = l + 1/2, m = \pm(l + 1/2) \rangle = | m = \pm l, s = \pm 1/2 \rangle
\]

\[
| j = l + 1/2, l - 1/2 \rangle = \sqrt{\frac{2l}{2l + 1}} | l - 1, 1/2 \rangle + \sqrt{\frac{1}{2l + 1}} | l, -1/2 \rangle ,
\]

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\[ |j = l - 1/2, l - 1/2 \rangle = \sqrt{ \frac{1}{2l + 1} } |l - 1, 1/2 \rangle - \sqrt{ \frac{2l}{2l + 1} } |l, -1/2 \rangle , \]

e etc.

\[ |j = l + 1/2, m_j \rangle = \sqrt{ \frac{l + 1/2 + m_j}{2l + 1} } |m_j - 1/2, 1/2 \rangle + \sqrt{ \frac{l + 1/2 - m_j}{2l + 1} } |m_j + 1/2, -1/2 \rangle , \]

\[ |j = l - 1/2, m_j \rangle = \sqrt{ \frac{l + 1/2 - m_j}{2l + 1} } |m_j - 1/2, 1/2 \rangle - \sqrt{ \frac{l + 1/2 + m_j}{2l + 1} } |m_j + 1/2, -1/2 \rangle , \]

We have to do it because \( S_z \) operator has non-diagonal matrix elements in the total momentum basis. So,

\[ \langle j = l \pm 1/2, m_j | S_z | j = l + 1/2, m_j \rangle = \frac{1}{2} l + 1/2 \pm m_j \quad \text{for} \quad j = l \pm 1/2 . \] (2)

This result is identical to what one would get for the magnetic moment with \( g \) factor

\[ g_j = 1 \pm \frac{1}{2l + 1} = 1 + \frac{j(j + 1) + s(s + 1) - l(l + 1)}{2j(j + 1)} , \] (3)

which is called the Lande factor.

This is an important result that composite moments are indistinguishable in their behavior from ordinary angular momenta and spins, except that their \( g \) factors may be significantly different from 1 and 2. In the Appendix I show that (3) is the correct formula for arbitrary \( L, S \) and \( J \). The energy splitting \( \sim g \mu_B B_0 m_j \) is called the Zeeman effect.

The above energy scheme breaks down when magnetic fields are strong enough (but not too strong to make \( e^2 B_0^2 (x^2 + y^2)/mc^2 \) terms important), i.e. comparable or larger than the spin-orbit splitting. In the limit when Zeeman energies are larger than the spin-orbit coupling we account for the the Zeeman effect in the energy spectrum

\[ E_{\nu,l,m,\sigma} = E_{\nu} + \mu_B B_0 (m + 2\sigma) \] (4)

and proceed with evaluating energy shifts induced by

\[ H_{SL} = \frac{g_s \mu_B^2}{r^3} \textbf{S} \cdot \textbf{L} . \]
We get
\[ E^{(1)}_{\nu,l,m,\sigma} = g_e \mu_B^2 \left( \int_0^\infty \frac{dr}{r} |R_{\nu,l}|^2 \right) \langle l, m, \sigma | S_z L_z + (S_+ L_- + S_- L_+) / 2 | l, m, \sigma \rangle = m\sigma \mu^2 \frac{B}{12a_B^2}. \]

The integral over \( dr \) is given for \( 2p \) state.

For the intermediate regime, one has to diagonalize the full matrix. E.g. for \( 2p \) states we have a \( 6 \times 6 \) matrix to deal with. Let us use the \( m, \sigma \) representation with energies (4). Non-diagonal matrix elements for the spin-orbit coupling in this basis are (diagonal were calculated above)

\[ \langle m', \sigma' | H_{SL} | m, \sigma \rangle = \frac{\mu_B^2}{24a_B^3} \langle m', \sigma' | S_+ L_- + S_- L_+ | m, \sigma \rangle = \frac{\sqrt{3} \mu_B^2}{24a_B^3} \text{ for } (m' = 0, \sigma' = 1/2, m = 1, \sigma = -1/2) \text{ and } (m' = -1, \sigma' = 1/2, m = 0, \sigma = -1/2) \]

(and their Hermitian conjugates).

Again, this matrix is block diagonal and we never have to solve anything more complex then \( 2 \times 2 \) blocks. If \( A = \mu_B B_0 \) and \( K = \mu_B^2 / (24a_B^3) \) then the matrix is shown to the left. It can be easily solved and checked to reproduce previous results in limiting cases of weak and strong fields. I will stop here because we already did this type of calculation several times. Other values of \( l \) are similar because \( S_+ L_- + S_- L_+ \) connect only two states with the same total \( S_z + L_z \) projection.

\[
\begin{pmatrix}
2A + B & 0 & 0 & 0 & 0 & 0 \\
0 & -B & \sqrt{2}B & 0 & 0 & 0 \\
0 & \sqrt{2}B & A & 0 & 0 & 0 \\
0 & 0 & 0 & -A & \sqrt{2}B & 0 \\
0 & 0 & 0 & \sqrt{2}B & -B & 0 \\
0 & 0 & 0 & 0 & 0 & -2A + B
\end{pmatrix}
\]

**Problem 57. Relativistic energy correction**

Show that the relativistic correction to the electron kinetic energy is given by \(-p^4/8m^3c^2\) and, using first-order perturbation theory, estimate the energy shift that this effect produces in the ground state of the hydrogen atom (in eV).
APPENDIX: Lande factors for arbitrary $L$ and $S$.

A shortcut to the final answer would be to state that the action of $g_lL + g_sS$ operator on the Hilbert space of levels with total momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ having a quantum number $j$ is equivalent to $g_j\mathbf{J}$. Then fixing the constant $g_j$ is simple: just multiply this operator by $\mathbf{J}$ to get

$$g_jj(j+1) = (L+S) \cdot (g_lL + g_sS) = g_l(l+1) + g_s(s+1) + (g_l + g_s)L \cdot S =$$

$$g_l(l+1) + g_s(s+1) + (g_l + g_s)\frac{j(j+1) - l(l+1) - s(s+1)}{2},$$

i.e.

$$g_j = g_l\frac{j(j+1) + l(l+1) - s(s+1)}{2j(j+1)} + g_s\frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}.$$  

This is the Lande factor for two momenta of any origin. Clearly, composite moments may have ‘strange’ $g$-factors even though their constituents have simple, e.g. integer $g$-factors. Proving rigorously that $g_lL + g_sS$ operator projected on the Hilbert space of fixed total momentum $j$ is indeed proportional to $\mathbf{J}$ requires more complex manipulations with the angular momentum algebra, and I will not go into further details here.