

Week 3

PHY 304 Quantum Mechanics-II

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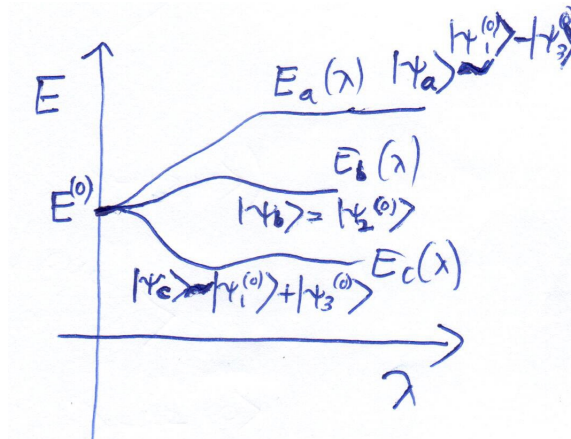
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7.2 Degenerate perturbation theory

There were various indications earlier that perturbation theory runs into complications if the unperturbed spectrum includes degeneracies $E_n^{(0)} = E_\ell^{(0)}$ for $n \neq \ell$. Expressions (7.21) and (7.23) then contain possibly diverging or indeterminate terms, and the validity condition (7.35) might not be possible to fulfill.

In the first order correction for the energy (7.12) the problem with degeneracy is less obvious, but there is one as well: Recall from (3.4.1), that in case of a D-fold degenerate eigenvalue $E_d^{(0)} = E^{(0)}$ for D different indices d , already the eigenvectors belonging to that eigenvalue are not uniquely defined. If we found $\hat{H}^{(0)}|\psi_d^{(0)}\rangle = E^{(0)}|\psi_d^{(0)}\rangle$, for $d = 1, \dots, D$, we could use the orthonormal set $\{|\psi_d^{(0)}\rangle\}$, or instead change the set of eigenvectors to any other orthonormal set $\{|\tilde{\psi}_d^{(0)}\rangle\}$ within the subspace spanned by the first set.

Now, usually the perturbation $\lambda\hat{H}'$ lifts the degeneracy, such that for $\lambda > 0$ eigenvectors $|\psi_n\rangle$ for different eigenvalues are clearly defined.



left: Then even for $\lambda = 0$ we can find a unique eigenvector through the limit $\lim_{\lambda \rightarrow 0} |\psi_n\rangle$, as sketched in the example to the left.

Unfortunately, unless we have found the perturbed solution, we don't know what to use as unperturbed eigenstates $|\psi_d^{(0)}\rangle$ at $\lambda = 0$, so we wouldn't know what to insert into the first order formula (7.12).

Hence let us leave the unperturbed eigenstate(s) belonging to $E^{(0)}$ unspecified for now, as in

$$|\psi^{(0)}\rangle = \sum_d c_d |\psi_d^{(0)}\rangle \quad (7.36)$$

with some complex coefficients c_d . We then insert this into Eq. (7.9), which is valid just as before (we have suppressed the eigenstate index n as in the above).

$$\hat{H}^{(0)}|\psi^{(1)}\rangle + \hat{H}'|\psi^{(0)}\rangle = E^{(0)}|\psi^{(1)}\rangle + E^{(1)}|\psi^{(0)}\rangle, \quad (7.37)$$

$$\hat{H}^{(0)}|\psi^{(1)}\rangle + \hat{H}' \sum_d c_d |\psi_d^{(0)}\rangle = E^{(0)}|\psi^{(1)}\rangle + E^{(1)} \sum_d c_d |\psi_d^{(0)}\rangle. \quad (7.38)$$

Now we take the scalar product with $\langle \psi_{d'}^{(0)} |$

$$\underbrace{\langle \psi_{d'}^{(0)} | \hat{H}^{(0)} | \psi^{(1)} \rangle}_{=E^{(0)}\langle \psi_{d'}^{(0)} |} + \langle \psi_{d'}^{(0)} | \hat{H}' \sum_d c_d |\psi_d^{(0)}\rangle = E^{(0)}\langle \psi_{d'}^{(0)} | \psi^{(1)} \rangle + E^{(1)} \sum_d c_d \underbrace{\langle \psi_{d'}^{(0)} | \psi_d^{(0)} \rangle}_{=\delta_{dd'}}. \quad (7.39)$$

The first terms on the LHS and RHS cancel as they did before, and we can rewrite the remainder using matrix elements $H'_{d'd} = \langle \psi_{d'}^{(0)} | \hat{H}' | \psi_d^{(0)} \rangle$ of the perturbation in the degenerate subspace:

$$\sum_d H'_{d'd} c_d = E^{(1)} c_{d'}. \quad (7.40)$$

With the coefficient vector $\mathbf{c} = [c_1 \cdots c_D]^T$ similar to (3.30) we finally have:

First order correction to the energy (degenerate)

$$\underline{\underline{H'}} \cdot \mathbf{c} = E^{(1)} \mathbf{c}. \quad (7.41)$$

where $\underline{\underline{H'}}$ is the matrix form of the Hamiltonian in the degenerate subspace.

- In words, we find the first order corrections $E^{(1)}$ of the D -fold degenerate eigenvalue $E^{(0)}$ by diagonalising the $D \times D$ matrix form of the perturbation Hamiltonian $\underline{\underline{H'}}$ in the degenerate subspace. The eigenvectors \mathbf{c} provide the relevant first order states via (7.36).

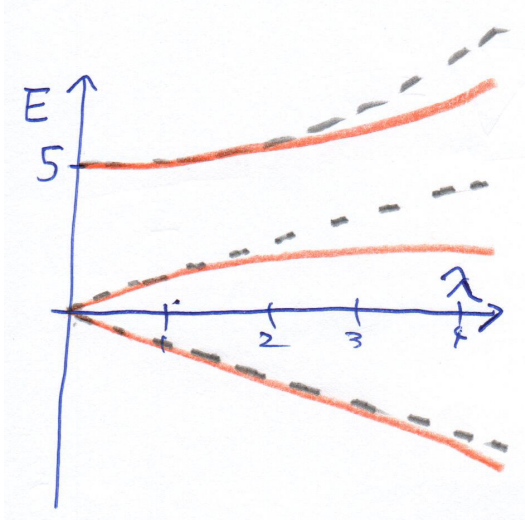
Example 57, Perturbed three level system with degeneracy: Let us make example 56 slightly more complex, going to three levels, two of which are degenerate in the absence of the perturbation. Using $E^{(0)} \neq E_3^{(0)}$, we write

$$\hat{H}^{(0)} = \begin{bmatrix} E^{(0)} & 0 & 0 \\ 0 & E^{(0)} & 0 \\ 0 & 0 & E_3^{(0)} \end{bmatrix}, \quad \hat{H}' = \lambda \begin{bmatrix} 0 & \kappa & | & 0 \\ \kappa & 0 & | & \kappa \\ \hline 0 & \kappa & | & 0 \end{bmatrix}. \quad (7.42)$$

To find the perturbation of $E^{(0)}$ Eq. (7.41) instructs us to diagonalize \hat{H}' in the degenerate subspace, i.e. the part in between dashed lines above:

$$\underline{\underline{H'}} = \lambda \begin{bmatrix} 0 & \kappa \\ \kappa & 0 \end{bmatrix}. \quad (7.43)$$

Example continued: which has eigenvalues $E^{(1)} = \pm\lambda\kappa$, with eigenvectors $\mathbf{c} = [1\pm 1]^T/\sqrt{2}$. For the perturbation of $E_3^{(0)}$ we can use the non-degenerate result, (7.12), which gives $E_3^{(1)} = 0$ (exercise), thus we move to second order (7.23), which gives $E_3^{(2)} = |\lambda\kappa|^2/(E_3^{(0)} - E_1^{(0)})$ (exercise).



left: For small λ , energies from perturbation theory (black dashed) agree well with the exact eigenvalues of $\hat{H}^{(0)} + \hat{H}'$ which can easily be found numerically (brown solid). For the figure we set $\kappa = 1$, $E^{(0)} = 0$ and $E^{(3)} = 5$ (in some arbitrary units).

Note, that accidentally using the non-degenerate result (7.12) for the perturbation of one of the degenerate eigenenergies $E_0^{(0)}$ gives $E_0^{(1)} = 0$ and hence the wrong scaling of the perturbation with $(\lambda\kappa)^2$ (as lowest remaining possible power of κ) instead of linear in κ . Using (7.23) would not work at all, since it blows up.

- See Griffith for one other extensive example with a 2D harmonic oscillator.
- While the above example is designed to stress the point that using non-degenerate perturbation theory in cases with degeneracy can give wrong results, there are also cases where one can get away with it. These are those where the perturbation Hamiltonian \hat{H}' happens to be diagonal in the unperturbed basis $|\psi^{(0)}\rangle$, in particular the part used to describe the degenerate subspace. This implies that in (7.21) and (7.23) we have $\langle \psi_\ell^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle = 0$ for all index pairs n, ℓ for which $E_n^{(0)} - E_\ell^{(0)} = 0$, and thus there is the possibility that the sum remains finite.

7.3 Example applications: Atomic finestructure and external fields

In the present section we will take a closer (“zoomed”) look at the spectrum of the Hydrogen atom. For the purpose of the present course the main objective is to practice the perturbation methods and revise some of QM-I weeks 9,10,11. However all this lays also the basis for the later development of atomic physics, which you will see in PHY402 next year, to where I defer most of the implications of what we calculate here.

7.3.1 Finestructure

In section 4.6 we have neglected a couple of effects (three for now) which provide small corrections to the energies in a Hydrogen atom. These can be calculated using perturbation theory.

(i) *Relativistic correction:* The calculations in section 4.6 were fully non-relativistic, i.e. we used a kinetic energy $\hat{T} = \frac{p^2}{2m_e}$ not

$$\hat{T} = \sqrt{p^2 c^2 + m_e^2 c^4} - m_e c^2 = m_e c^2 \left(\sqrt{1 + \left(\frac{p}{m_e c} \right)^2} - 1 \right) \quad (7.44)$$

which is the relativistic expression for the kinetic energy. For a very rough estimate as to how justified this was, we can calculate e.g. a velocity scale for the electron from $\Delta v = \Delta p / m_e = \hbar / (2a_0 m_e) \approx 10^6$ m/s, where we used the HUP (1.46) and a position uncertainty $\Delta x \sim a_0$. This is about $3 \times 10^{-3}c$. Much slower than the speed of light, but not so slow that relativistic corrections might not have a minor quantitative impact.

One could now go to a fully relativistic description of the electron, using the Dirac equation (see later QM-II-week 12), but based on Δv above that might be overkill. Instead we just Taylor expand the squareroot in (7.44) to reach

$$\hat{T} = \frac{p^2}{2m_e} - \underbrace{\frac{p^4}{8m_e^3 c^2}}_{=\hat{H}'_1} + \dots \quad (7.45)$$

The first term was taken care of earlier. The second term is declared our perturbation, and treated using perturbation theory. We know that all the unperturbed Hydrogen states with $n > 1$ are degenerate, since energies (4.90) do not depend on ℓ and m . However this is a case where we can still use the simpler non-degenerate perturbation theory, since $[\hat{H}'_1, \hat{L}]$. See discussion after example 57.

According to (7.12), we should evaluate

$$E^{(1)} = -\frac{1}{8m_e^3 c^2} \langle \hat{p}^4 \rangle, \quad (7.46)$$

where the expectation value is to be taken in the Hydrogen state ϕ_{nlm} for which we want to know the energy correction. In principle we could write the momentum operator through derivatives and evaluate this directly. The integral becomes slight less messy by using the trick:

$$\langle \hat{p}^4 \rangle = \langle \phi_{nlm} | \hat{p}^4 | \phi_{nlm} \rangle = \langle \hat{p}^2 \phi_{nlm} | \hat{p}^2 \phi_{nlm} \rangle \quad (7.47)$$

and then rewriting the TISE (1.62) we have $\hat{p}^2 \phi_{nlm} = 2m_e(E_n - V)\phi_{nlm}$ and thus

$$E^{(1)} = -\frac{1}{m_e c^2} \left[E_n^2 + 2E_n \frac{e^2}{4\pi\epsilon_0} \left\langle \frac{1}{r} \right\rangle + \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \left\langle \frac{1}{r^2} \right\rangle \right]. \quad (7.48)$$

Both expectation values are still 3D integrations, that come out as $\langle \frac{1}{r} \rangle = 1/(n^2 a_0)$ and $\langle \frac{1}{r^2} \rangle = 1/[(\ell + 1/2)n^3 a_0^2]$ (assignment 3). We can insert these results into (7.48) and simplify to find

$$E^{(1)} = -\frac{E_n^2}{2m_e c^2} \left[\frac{4n}{\ell + \frac{1}{2}} - 3 \right]. \quad (7.49)$$

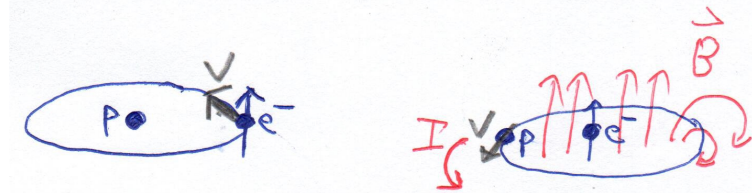
We do not yet interpret (7.49) since there is two more contributions to the finestructure to be calculated, but we already see that this is a small correction to earlier Hydrogen energies, by a factor of roughly $E_n/(m_e c^2) \approx 2 \times 10^{-5}$.

(ii) *Spin orbit coupling*: In our earlier treatment of the Hydrogen atom, we did not consider the spin of the electron, let us rectify that. First we write Hydrogen states containing the spin $|nlms\rangle$, such that their position space representation is:

$$\langle \mathbf{r} | nlms \rangle = \phi_{nlm}(\mathbf{r})\chi_s \quad (7.50)$$

with $\phi_{nlm}(\mathbf{r})$ as before in Eq. (4.91) and χ as spinor, see Eq. (4.107).

It turns out the leading effect of the electron spin on atomic energies is through the interaction between the magnetic moment associated with the spin, see section 4.7.1, with the magnetic field created by the orbital motion of particles.



left: To understand why the latter exists, see figure on the left, showing a classical picture of the orbit of the electron.

We move to the *rest-frame* of the electron, where the proton moves with velocity $-\mathbf{v}$ (where \mathbf{v} is the electron velocity in the lab-frame). The electron then "sees" a positively charged proton orbiting itself and hence a magnetic field:

$$\mathbf{B} = -\frac{e\mu_0}{4\pi} \frac{\mathbf{v} \times \mathbf{r}}{r^3} \quad \left(\text{from } \mathbf{B} = \frac{\mu_0}{4\pi} \frac{q\mathbf{v} \times \hat{\mathbf{r}}}{r^2}, \text{ see electro-magnetism lectures} \right) \quad (7.51)$$

Now we use the

Hamiltonian for a magnetic moment in a magnetic field

$$\hat{H}_{mag} = -\hat{\boldsymbol{\mu}} \cdot \mathbf{B} \quad \text{Energy of spin in magnetic field} \quad (7.52)$$

$$\hat{\boldsymbol{\mu}} = -g_s \mu_b \hat{\mathbf{S}} / \hbar \quad \text{Electron magnetic moment} \quad (7.53)$$

$$\hat{H}_{mag} = +g_s \frac{\mu_b}{\hbar} \mathbf{B} \cdot \hat{\mathbf{S}} \quad \hat{\boldsymbol{\mu}} \sim -\hat{\mathbf{S}} \text{ since } \mathbf{q} < \mathbf{0} \quad (7.54)$$

$$g_s \simeq 2 \quad \text{Gyromagnetic factor} \quad (7.55)$$

$$\mu_B = \frac{e\hbar}{2m_e} \quad \text{Bohr Magneton } e>0 \text{ here} \quad (7.56)$$

and then get:

$$\hat{H}_{mag} = g_s \underbrace{\frac{\mu_b}{\hbar}}_{=\frac{e}{2m_e}} \underbrace{\left(-\frac{\mu_0 e}{4\pi m_e} \frac{\mathbf{p} \times \mathbf{r}}{r^3} \right)}_{=\mathbf{B}} \cdot \hat{\mathbf{S}} \quad (7.57)$$

$$\underbrace{\mathbf{L}=\mathbf{r} \times \mathbf{p}}_{=\mathbf{L}} \frac{g_s \mu_0 \epsilon_0}{2m_e^2} \underbrace{\frac{e^2}{4\pi \epsilon_0 r^3}}_{=\frac{1}{r} \frac{dV(r)}{dr}} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = 2\hat{H}'_2. \quad (7.58)$$

It turns out the actual perturbation, \hat{H}'_2 , is a factor of two smaller, due to the e^- rest frame not being inertial, see Shankar.

This time we can not directly use non-degenerate perturbation theory to handle \hat{H}'_2 , since \hat{H}'_2 is not evidently diagonal in the basis of unperturbed Hydrogen states $|nlms\rangle$. First, we shall define the

Total angular momentum of the electron

$$\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}, \quad (7.59)$$

- We use the addition of two angular momenta presented in section 4.8, if you haven't yet, please revise that now.

From this we know that after that definition, we can use new eigenstates of the total angular momentum of the electron $|\phi_{n,\ell,s,j,m_j}\rangle$, such that

$$\hat{\mathbf{J}}^2|\phi\rangle = \hbar^2 j(j+1)|\phi\rangle, \quad (7.60)$$

$$\hat{J}_z|\phi\rangle = \hbar m_j|\phi\rangle. \quad (7.61)$$

The range of the total angular momentum according to Eq. (4.126) is $j = |\ell - s|, \dots, \ell + s$, where ℓ is the orbital angular momentum quantum number and $s = 1/2$ the spin angular momentum quantum number of the electron. Thus

$$j = \frac{1}{2} \quad (\ell = 0, s = \frac{1}{2}), \quad (7.62)$$

$$j = \ell \pm \frac{1}{2} \quad (\ell > 0, s = \frac{1}{2}). \quad (7.63)$$

One case we can handle quickly first is $\ell = 0$. In that case $(\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}) = 0$, since the angular momentum is zero. (*Technically we only know $\hat{\mathbf{L}}^2|\ell = 0\rangle = 0$ and $\hat{L}_z|\ell = 0\rangle = 0$ (since $m = 0$). Show $\langle \hat{L}_x \rangle = \langle \hat{L}_y \rangle = 0$ as an exercise*). Now, for looking at $\ell > 0$, the point of introducing the total angular momentum, was that we can now write

$$\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \frac{1}{2} (\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2). \quad (7.64)$$

Hence we see that $[\hat{H}'_2, \hat{\mathbf{J}}] = 0$ (simple exercise), so if we use states $|\phi_{n,\ell,s,j,m_j}\rangle$ as unperturbed basis $|\psi^{(0)}\rangle$ for perturbation theory, we can again use non-degenerate perturbation theory. Then

$$E^{(1)} = \langle \phi_{nljm_j} | \hat{H}'_2 | \phi_{nljm_j} \rangle \quad (7.65)$$

$$= \frac{\hbar^2}{2} \langle \xi(r) \rangle \left[j(j+1) - l(l+1) - \frac{3}{4} \right]. \quad (7.66)$$

The factor $\frac{\hbar^2}{2}$ comes from $\frac{\mathbf{J}^2}{2}$ etc., and we used the short hand $\hat{H}'_2 = \xi(r) \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$ such that

$$\langle \xi(r) \rangle = \int d^3r \phi_{nljm_j}^*(\mathbf{r}) \xi(\mathbf{r}) \phi_{nljm_j}(\mathbf{r}). \quad (7.67)$$

For this we need another integration from assignment 3 which is

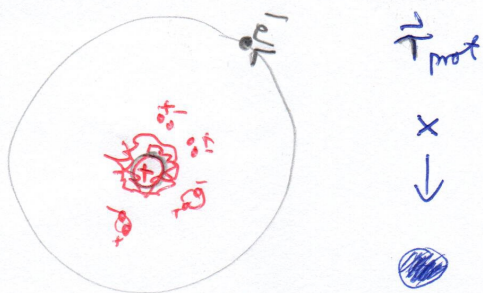
$$\langle \frac{1}{r^3} \rangle = \frac{1}{\ell(\ell + \frac{1}{2})(\ell + 1)n^3 a_0^3}, \quad (7.68)$$

which also makes sense only for $\ell > 0$. Then altogether

$$E_{SOC}^{(1)} = \frac{E_n^2}{m_e c^2} \frac{j(j+1) - l(l+1) - \frac{3}{4}}{\ell(\ell + \frac{1}{2})(\ell + 1)}, \quad (7.69)$$

where we have re-shuffled all the constants, using the unperturbed Hydrogen energies E_n from (4.90). The expression makes it clear that the spin-orbit correction $E_{SOC}^{(1)}$ is smaller than E_n by the ratio $E_n/m_e c^2$ of electronic energy to electron rest-mass energy.

(iii) *Darwin term*: There is one last correction to take care of: A further consequence of relativistic QM is the existence of anti-particles (e.g. positrons, e^+). These can then be part of vacuum fluctuations (see QED/quantum field theory), and interact with the proton/nucleus.



left: This gives rise to tiny random kicks in the proton that effectively smear its position out and make it blurry (cartoon on the right) (*Some call this “Zitterbewegung”, which is German for “shaky movement”*).

It turns out this can be described by a perturbation Hamiltonian $\hat{H}'_3 = -\frac{\pi\hbar^2}{2m^2c^2} \frac{Ze^2}{4\pi\epsilon_0} \delta(\mathbf{r})$. Thanks to the delta-function, the energy corrections is very easy to evaluate as

$$\Delta E_3 = \langle \phi_{nljm_j} | \hat{H}'_3 | \phi_{nljm_j} \rangle = \frac{\pi\hbar^2}{2m_e^2c^2} \frac{Ze^2}{4\pi\epsilon_0} |\phi_{nljm_j}(0)|^2 = E_n \frac{\alpha^2}{n} \delta_{\ell,0} \quad (7.70)$$

From Eq. (4.92) we see that this shifts only the $\ell = 0$ states, since $|\phi_{nlm}(0)|^2 = 0$ for $\ell > 0$. *Confusing subtlety:* If we try to use the result (7.69) at $\ell = 0$ even though the in-between step (7.68) is not valid there, we have to insert $j = 1/2$ in the numerator. After cancellations the result is actually finite, and incidentally the same as (7.70). However the approach taken here seems safer overall.

Combination into finestructure correction: Altogether, we have used the

Fine-structure Hamiltonian

$$\hat{H}'_{FS} = \hat{H}'_1 + \hat{H}'_2 + \hat{H}'_3. \quad (7.71)$$

$$\hat{H}'_1 = -\frac{p^4}{8m^3c^2} \quad \text{relativistic correction to kinetic energy} \quad (7.72)$$

$$\hat{H}'_2 = \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV}{dr} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \quad \text{spin-orbit coupling} \quad (7.73)$$

$$\hat{H}'_3 = -\frac{\pi\hbar^2}{2m^2c^2} \frac{e^2}{4\pi\epsilon_0} \delta(\mathbf{r}) \quad \text{Darwin term} \quad (7.74)$$

to find the

Fine structure of the Hydrogen energies

$$E_{n_j} = E_n \left[1 + \frac{\alpha^2}{n^2} \left(\frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right) \right] \quad (7.75)$$

with E_n from Eq. (4.90) and $\alpha = \frac{e^2}{(4\pi\epsilon_0)\hbar c} \simeq \frac{1}{137}$ the finestructure constant.

- For this we have added (7.49), (7.69), (7.70) and simplified
- An important change is that the degeneracy of energy in j is lifted by finestructure corrections.
- Note $E_n < 0$, the sign of shift depends on n, j but is mostly towards lower energies. See Griffith for some drawings and diagrams.
- Some of the Hamiltonians used for fine structure are not rigorously found here, but motivated somewhat ad-hoc. All these arise in a treatment of the Dirac equation, which is the special relativistic quantum wave equation, when taking the limit of small velocities. In particular this takes care of “confusing subtlety” above.

7.3.2 External electric fields, Stark effect

Further good applications of perturbation theory are atoms placed in external fields. You can calculate that the electric field created by the proton at a distance of $r = a_0$ is $\mathcal{E} = 5 \times 10^9 \text{ V/cm}$. Compared to that, many fields that we would prepare in the lab are indeed a small perturbation.

Now we have to look at the

Hamiltonian for an electron in an electric field (of the proton and an external one):

$$\hat{H} = \overbrace{-\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}}^{\hat{H}_0} + \overbrace{e\mathbf{E} \cdot \mathbf{r}}^{\hat{H}'}. \quad (7.76)$$

- Let us assume $\mathbf{E} = \mathcal{E}\hat{\mathbf{e}}_z$ (along z-axis) and constant across atom.
- The Hamiltonian (7.76) assumes the \mathbf{E} -field is strong enough for fine-structure to be negligible.
- For our application of perturbation theory, we split the Hamiltonian into \hat{H}_0 and \hat{H}' as indicated. Clearly the unperturbed states $|\phi_{nlm}^{(0)}\rangle$ are just the Hydrogen states found in section 4.6 (Eq. (4.91)).

Linear Stark effect: Let us first look at any shifts of first order in \mathcal{E} . For non-degenerate states (for Hydrogen only the $n = 1$ state), we can use Eq. (7.12): In fact for all nlm

$$E^{(1)} = e\mathbf{E} \cdot \langle \phi_{nlm} | \mathbf{r} | \phi_{nlm} \rangle = 0. \quad (7.77)$$

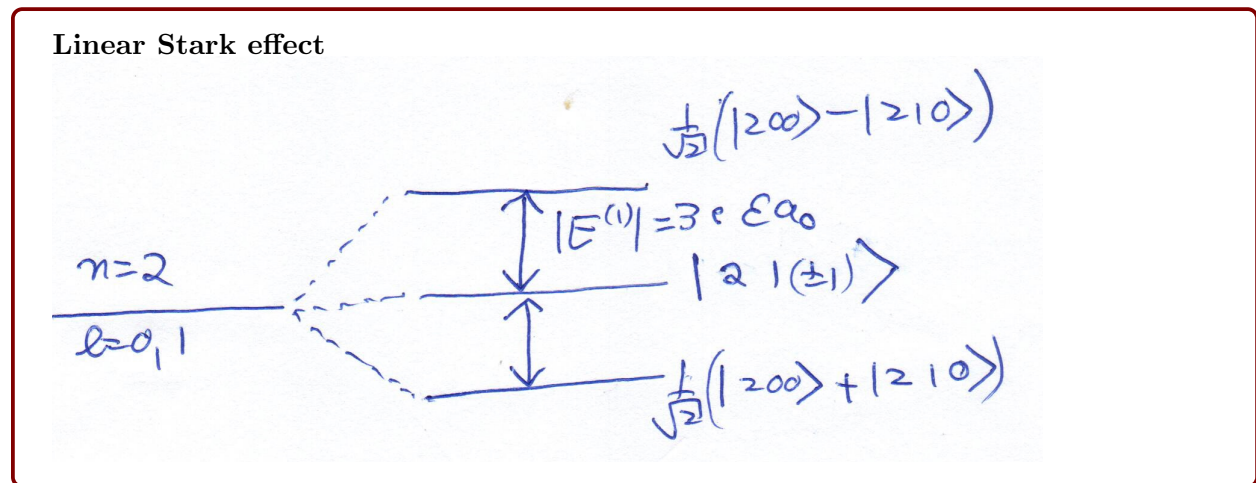
- Proof: See example 50. Physically this means that the unperturbed Hydrogen state does not have a mean electric dipole and hence no mean energy in an external electric field.

However all $n > 1$ states are degenerate, so we have to use degenerate perturbation theory. Let us take $n = 2$ as the simplest example, for which there are four degenerate states $|\phi_{200}\rangle$, $|\phi_{21(-1)}\rangle$, $|\phi_{210}\rangle$ and $|\phi_{211}\rangle$. To use (7.41), we have to set up the Hamiltonian matrix in the degenerate subspace, with the above ordering of basis states Eq. (7.41) becomes

$$\begin{pmatrix} 0 & 0 & \kappa & 0 \\ 0 & 0 & 0 & 0 \\ \kappa & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} c_{200} \\ c_{21-1} \\ c_{210} \\ c_{211} \end{pmatrix} = E^{(1)} \begin{pmatrix} c_{200} \\ c_{21-1} \\ c_{210} \\ c_{211} \end{pmatrix}. \quad (7.78)$$

with $\kappa = e\mathcal{E}\langle 210|z|200\rangle = e\mathcal{E}\langle 210|r\cos\theta|200\rangle = -3ea_0\mathcal{E}$ the only nonzero matrix element of \underline{H}' . We had already seen that all diagonal entries are zero in (7.77). We can also see directly that $\langle 2\ell m|r\cos\theta|2\ell' m'\rangle$ must be proportional to $\delta_{m,m'}$, since the operator in the matrix element does not contain the azimuthal angle φ .

The set of eigenvalues of the matrix in (7.78) is $E^{(1)} = \{+3ea_0\mathcal{E}, -3ea_0\mathcal{E}, 0, 0\}$ with eigenvectors $\mathbf{c} = \{[1, 0, -1, 0]/\sqrt{2}^T, [1, 0, 1, 0]/\sqrt{2}^T, [0, 1, 0, 0]^T, [0, 0, 0, 1]^T\}$. We thus reach the picture of the



- Thus, for all excited Hydrogen states there is an energy shift $E^{(1)}$ to first order PT proportional to the electric field strength \mathcal{E} , this is called linear Stark effect. The reason is, that you can form a state as a linear combination of the degenerate e.g. $n = 2$ states that do have a dipole, namely $|\phi_{200}\rangle \pm |\phi_{210}\rangle$. You had seen in Assignment 1 Q1, how superpositions such as these shift the electron cloud up or down on the z-axis, relative to the proton, thus creating a net dipole.

For $n = 1$, we have to go to second order since the first order effect was zero. There we find the

Non-linear Stark effect: For non-degenerate states (in Hydrogen only $|100\rangle$), we have to go to second order perturbation theory to get a non-vanishing Stark effect

$$\Delta E_{100}^{(2)} = \sum_{n \neq 1, l, m} \frac{|\langle \phi_{nlm} | e\mathcal{E}z | 100 \rangle|^2}{E_{100} - E_{nlm}}. \quad (7.79)$$

- As in Eq. (7.78), all matrix elements $|\langle \phi_{n10} | e\mathcal{E}z | 100 \rangle|^2$ will be non-zero, and $E_{100} - E_{n10} < 0$ for all n . Thus $\Delta E_{100}^{(2)} < 0$ and $\sim (e\mathcal{E})^2 \implies$ quadratic Stark effect.
- For the quadratic Stark effect, the external field can induce an electric dipole, which is then $\sim \mathcal{E}$, and in turn interacts with the field, providing a net scaling $\sim \mathcal{E}^2$.

7.3.3 External magnetic fields, Zeeman effect

Finally, let us consider a uniform external magnetic field $\mathbf{B} = B\mathbf{e}_z$ along the z -direction. This is described by the

Hamiltonian for Hydrogen in an external magnetic field:

$$\hat{H} = \overbrace{\frac{1}{2m}(\mathbf{p} + e\mathbf{A})^2 - \frac{e^2}{4\pi\epsilon_0 r}}^{\text{see electro-dynamics}} + \overbrace{\frac{g_s\mu_B}{\hbar}\mathbf{B} \cdot \mathbf{S}}^{\text{see Eq. (7.54)}} + \overbrace{\zeta(r)\mathbf{L} \cdot \mathbf{S}}^{\text{see Eq. (7.73)}}, \quad (7.80)$$

with vector potential

$$\mathbf{A} = \frac{1}{2}(\mathbf{B} \times \mathbf{r}) \text{ for a constant B-field.} \quad (7.81)$$

- We can rewrite (7.80) as

$$\hat{H} = \overbrace{-\frac{\hbar^2}{2m}\nabla^2}^{\hat{H}_a} - \overbrace{\frac{e^2}{4\pi\epsilon_0 r}}^{\hat{H}_b} + \overbrace{\zeta(r)\mathbf{L} \cdot \mathbf{S}}^{\hat{H}_c} + \overbrace{\frac{\mu_B}{\hbar}(\mathbf{L} + 2\mathbf{S})\mathbf{B}}^{\hat{H}_d} + \overbrace{\frac{e^2}{8m}(\mathbf{B} \times \mathbf{r})^2}^{\hat{H}_e}, \quad (7.82)$$

using a lot of vector calculus.

We now analyze Eq. (7.80) with perturbation theory depending on relative importance of terms $a - d$, which depends on the state to be perturbed $|\phi_{nlm}\rangle$ and the magnetic field strength B . We neglect \hat{H}_e , since it will only become relevant at extremely strong magnetic fields.

Linear Zeeman effect: (strong B -field) Let us first assume the energy due to the magnetic field is large compared to the fine-structure energy. Then in a first step we neglect \hat{H}_c and take our unperturbed Hamiltonian to be $\hat{H}_0 = \hat{H}_a + \hat{H}_b + \hat{H}_d$.

For this we actually already know the eigenfunctions, since the first two terms just constitute the usual Hydrogen Hamiltonian and for magnetic field in the z -direction, the last part

$$\hat{H}_d = \frac{\mu_B}{\hbar} B_0 (\hat{L}_z + 2\hat{S}_z)$$

can be expressed in terms of angular momentum z -components (and thus commutes with \hat{L}^2 , \hat{S}_z , \hat{S}^2 , \hat{S}_z . Thus, $|\phi_{nlm_l}\rangle \otimes |sm_s\rangle$ already fulfil

$$\hat{H}_0 |\phi_{nlm_l m_s}\rangle = E_{nlm_l m_s} |\phi_{nlm_l m_s}\rangle.$$

with

Zeeman-shifted energies

$$E_{nlm_l m_s} = \underbrace{\text{see Eq. (4.90)}}_{E_n} + \mu_B B_0 (m_l + 2m_s), \quad m_s = \pm \frac{1}{2}. \quad (7.83)$$

We could as a next step add \hat{H}_c in (7.82) as a perturbation, which gives the energy spectrum for medium B -fields (Paschen-Back effect, see Assignment 3).

Anomalous¹⁵ Zeeman effect: (weak B -field, most common case) For relatively weak magnetic fields, the fine-structure term \hat{H}_c will be larger than \hat{H}_d . We thus split the Hamiltonian according to

$$\hat{H}_0 = \hat{H}_a + \hat{H}_b + \hat{H}_c \text{ with } \hat{H}' = \hat{H}_d$$

Eigenstates of \hat{H}_0 are the same as we had found in the section for fine-structure, section 7.3.1, and are thus states with definite total angular momentum $|n, j, l, s, m_j\rangle$. To proceed further, we expand total angular momentum states in terms of orbital angular momentum and spin states as in Eq. (4.127).

$$|j, l, s, m_j\rangle = \sum_{\substack{m_l, m_s \\ m_l + m_s = m_j}} \underbrace{\langle l, s, m_l, m_s | j, l, m_j \rangle}_{\equiv C_{l, s; m_l, m_s}^{j, m_j}} |l, s, m_l, m_s\rangle,$$

where $C_{l, s; m_l, m_s}^{j, m_j}$ are Clebsch-Gordan coefficients (cgc).

Using the coupled j basis as for fine-structure, let us first evaluate the easy part:

$$\begin{aligned} \Delta E &= \langle \phi_{njl m_j} | \frac{\mu_B}{\hbar} (\hat{J}_z + \hat{S}_z) B_0 | \phi_{njl m_j} \rangle \\ &= \mu_B m_j B_0 + \frac{\mu_B B_0}{\hbar} \langle \phi_{njl m_j} | \hat{S}_z | \phi_{njl m_j} \rangle. \end{aligned} \quad (7.84)$$

Now we need some cgc, but we only look at $s = \frac{1}{2}$, so $j = l \pm \frac{1}{2}$. Then

$$\begin{aligned} \left| \left(j = l + \frac{1}{2} \right), l, s, m_j \right\rangle &= \sqrt{\frac{l + m_j + 1/2}{2l + 1}} \left| l, s, m_l = m_j - \frac{1}{2}, m_s = \frac{1}{2} \right\rangle \\ &+ \sqrt{\frac{l - m_j + 1/2}{2l + 1}} \left| l, s, m_l = m_j + \frac{1}{2}, m_s = \frac{-1}{2} \right\rangle \end{aligned} \quad (7.85)$$

¹⁵The name "anomalous" is historical

and

$$\begin{aligned} \left| \left(j = l - \frac{1}{2} \right), l, s, m_j \right\rangle &= -\sqrt{\frac{l - m_j + 1/2}{2l + 1}} \left| l, s, m_l = m_j - \frac{1}{2}, m_s = \frac{1}{2} \right\rangle \\ &+ \sqrt{\frac{l + m_j + 1/2}{2l + 1}} \left| l, s, m_l = m_j + \frac{1}{2}, m_s = \frac{-1}{2} \right\rangle. \end{aligned} \quad (7.86)$$

We now use these two expressions in Eq. (7.84) and simplify to get

Anomalous Zeeman shift

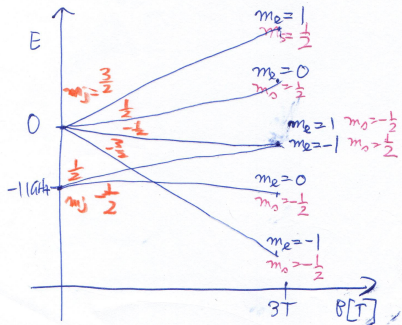
$$\Delta E = g\mu_B m_j B_0, \quad (7.87)$$

with Landé g -factor

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

So the number of split energy levels is now given by the number of different values for m_j .

Example 58, All fields Zeeman effect: The two cases above are for strong and weak fields and seemingly behave quite different.



left: It turns out for in between fields, the energy levels see a continuous transition between the two cases. For this one needs to diagonalise the full Hamiltonian, for example for $\ell = 1$ and $s = 1/2$ in a 6-dimensional Hilbertspace (e.g. $m_\ell = -1, 0, 1 \otimes m_s = -1/2, 1/2$). See more details in assignment 3.

7.3.4 Outlook on atomic physics

In PHY402 you will encounter at least two further “details” of atomic energy levels: The Lamb-shift, which is due to quantum-electro-dynamics (QED) and the hyperfine structure. Like the name of the latter suggests, these energy differences are again orders of magnitude smaller than the fine structure, and mostly have to do with the atomic nucleus.

Since we called everything starting from Fine structure small corrections, you might get the impression that this is unimportant details rarely needed. That impression is totally wrong since the adjective “small” is of course relative. The corrections are small compared to the basic electronic energies from QM-I week 10, but they can be huge compared to the energy resolution of modern lasers and energy scales relevant to modern quantum technology. For fields like quantum optics, quantum information, cold atomic physics, the effects previewed here and further developed in PHY402 are thus crucial for all experiments.