

Chapter 9: Time-Independent Perturbation Theory

→ Only very few quantum mechanical problems can be solved exactly. For most problems one has to rely on approximations.

There are many approximation methods. One that is frequently used concerns the case of a Hamilton operator for which the energy eigenvalue problem cannot be solved exactly, but which is "very close" to a Hamilton operator for which the solutions are known.

The method is called time-independent perturbation theory.

9.1. Perturbative Series

→ Assume a Hamilton operator H , which has the form

$$H = H_0 + \lambda H_1$$

and that the energy eigenvalues E_n^0 and the corresponding eigenstates $|n^0\rangle$ are known:

$$H_0 |n^0\rangle = E_n^0 |n^0\rangle , \quad \sum |n^0\rangle \langle n^0| = 1$$

For simplicity we assume that the energy spectrum is discrete, but most of the manipulations also apply in the continuous case.

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What we are looking for are solutions of the eigenvalue problem

$$H|u\rangle = E_n|u\rangle$$

and we assume that the eigenvalues and eigenstates can be written as a Taylor series in powers of λ (called: "perturbative series in λ ")

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots$$

$$|u\rangle = |u^0\rangle + \lambda |u^1\rangle + \lambda^2 |u^2\rangle + \dots$$

Comments:

(1) The perturbative series is in general not convergent. However, it may be still practically useful as long as $E_n \rightarrow E_n^0$ and $|u\rangle \rightarrow |u^0\rangle$ for $\lambda \rightarrow 0$.

This means that the exact solutions merge into the unperturbed ($\lambda=0$) solutions in the limit $\lambda \rightarrow 0$. Such perturbative series are called asymptotic series.

Most perturbative series in quantum physics are asymptotic.

(2) There are cases where the solutions for $\lambda \neq 0$ are fundamentally different from the cases $\lambda=0$ (e.g. $H_0 = \vec{p}^2/2m$ vs. $H = H_0 - e^2/|x|$ for the bound states). In such cases time-independent perturbation theory is of no use.

(3) The parameter λ does not necessarily have to be small. It is the effect of λH_0 that has to be small such that perturbation theory is useful.

9.1.1. Non-Degenerate Perturbation Theory

→ We assume a non-degenerate energy spectrum: $E_n^0 \neq E_m^0$ for $|u^0\rangle \neq |u^m\rangle$

→ We start from the combined eigenvalue equation

$$(H_0 + \lambda H_1)(|u^0\rangle + \lambda |u^1\rangle + \lambda^2 |u^2\rangle + \dots) = (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots)(|u^0\rangle + \lambda |u^1\rangle + \lambda^2 |u^2\rangle + \dots)$$

and compare coefficients:

$$\lambda^0 : H_0|u^0\rangle = E_n^0|u^0\rangle \quad \leftarrow \text{unperturbed problem: nothing new}$$

$$\lambda^1 : H_0|u^1\rangle + H_1|u^0\rangle = E_n^0|u^1\rangle + E_n^1|u^0\rangle$$

$$\lambda^2 : H_0|u^2\rangle + H_1|u^1\rangle = E_n^0|u^2\rangle + E_n^1|u^1\rangle + E_n^2|u^0\rangle$$

⋮

⋮

$$\lambda^m : H_0|u^m\rangle + H_1|u^{m-1}\rangle = E_n^0|u^m\rangle + E_n^1|u^{m-1}\rangle + \dots + E_n^m|u^0\rangle$$

It is convenient for the following manipulations to impose the normalization

$$\langle u^0 | u \rangle = 1$$

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This normalization is not mandatory, but entails that :

(a) The eigenstates $|u\rangle$ that come out of the calculations are (in general) not anymore normalized : $\langle u | u \rangle = 1 + O(\lambda) \neq 1$.

(b) Comparing coefficients one obtains due to $\langle u^0 | u^0 \rangle = 1$ the useful relations :

$$\lambda \langle u^0 | u^1 \rangle + \lambda^2 \langle u^0 | u^2 \rangle + \dots = 0 \quad \Rightarrow \quad \langle u^0 | u^m \rangle = 0, \quad m = 1, 2, 3, \dots$$

→ First order energy correction:

We multiply the $O(\lambda)$ equality from left by $\langle u^0 | : \langle u^0 | H_0 | u^1 \rangle + \langle u^0 | H_1 | u^0 \rangle - E_u^0 \langle u^0 | u^1 \rangle + E_u'$

$$\hookrightarrow E_u' = \langle u^0 | H_1 | u^0 \rangle$$

$$= E_u^0 \langle u^0 | u^1 \rangle$$

→ First order eigenstate correction:

The unperturbed eigenstates form a CONS

$$\hookrightarrow |u'\rangle = \sum_{m \neq n} c_m |u^m\rangle, \quad c_m = \langle u^0 | u^1 \rangle \quad (m \neq n)$$

We multiply the $O(\lambda)$ equality from left by $\langle u^0 |$:

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$$\xrightarrow{\text{E}_n^0 \text{ } c_m} \langle u^0 | H_0 | u^1 \rangle + \langle u^0 | H_1 | u^0 \rangle = E_n^0 \langle u^0 | u^1 \rangle + E_n^1 \langle u^0 | u^0 \rangle$$

$$\Leftrightarrow c_m (E_n^0 - E_m^0) = \langle u^0 | H_1 | u^0 \rangle \Leftrightarrow c_m = \frac{\langle u^0 | H_1 | u^0 \rangle}{E_n^0 - E_m^0}$$

$$\begin{aligned} \xrightarrow{\text{I}} |u^1\rangle &= \sum_{m \neq n} \frac{\langle u^0 | H_1 | u^0 \rangle}{E_n^0 - E_m^0} |u^0\rangle \\ &= \sum_{m \neq n} \frac{|u^0\rangle \langle u^0|}{E_n^0 - E_m^0} H_1 |u^0\rangle \end{aligned}$$

We see that the formulae (incl. $E_n^1 = \langle u^0 | H_1 | u^0 \rangle$) are only valid for non-degenerate energy eigenvalues ($E_n^0 \neq E_m^0$ for $n \neq m$).

Second order energy correction:

We multiply the $O(x^2)$ equality from left by $\langle u^0 |$ and use the solution for $|u^1\rangle$:

$$\langle u^0 | H_0 | u^2 \rangle + \langle u^0 | H_1 | u^1 \rangle = E_n^0 \langle u^0 | u^2 \rangle + E_n^1 \langle u^0 | u^1 \rangle + E_n^2$$

$$\begin{aligned} \xrightarrow{\text{I}} E_n^2 &= \langle u^0 | H_0 | u^1 \rangle = \sum_{m \neq n} \frac{|\langle u^0 | H_1 | u^0 \rangle|^2}{E_n^0 - E_m^0} \\ &= \sum_{m \neq n} \langle u^0 | H_1 \frac{|u^0\rangle \langle u^0|}{E_n^0 - E_m^0} H_1 |u^0\rangle \end{aligned}$$

$$= \frac{1}{E_n - E_m} \langle u^0 | H_1 | u^0 \rangle$$

9.1.2 Perturbation Theory for Degenerate States

→ We now assume that the energy eigenvalues E_1^0, \dots, E_r^0 are degenerate:

$$E_1^0 = E_2^0 = \dots = E_r^0$$

We only consider the 1st order energy correction.

→ The expressions for the $O(\lambda^0)$ equalities remain unchanged, but we spot a problem already for the $O(\lambda^1)$ equality when multiplying it with $\langle u^0 |$ from the left for $n \in \{1, \dots, r\}$:

$$\langle u^0 | H_0 | u^1 \rangle + \langle u^0 | H_1 | u^0 \rangle = E_n^0 \langle u^0 | u^1 \rangle + E_n^1 \langle u^0 | u^0 \rangle$$

$$\Leftrightarrow \underbrace{(E_n^0 - E_n^1) \langle u^0 | u^1 \rangle}_{A} + \underbrace{\langle u^0 | H_1 | u^0 \rangle}_{B} = E_n^1 \delta_{nn}$$

In the non-degenerate case (9.1.1) A was non-zero for $m \neq n$, so because H_1 in general is non-diagonal in the CONS $\{|u^0\rangle\}$ (i.e. $\langle u^0 | H_1 | u^0 \rangle \neq 0$ for $m \neq n$), the A-term can compensate for B ≠ 0, so the equality A+B=0 can hold.

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In the degenerate case we arrive at a problem when $m, n \in \{1, \dots, r\}$, because $A=0$:

$$\hookrightarrow E_n^* \delta_{mn} = \langle u^0 | H_n | u^0 \rangle$$

Since in general H_n is non-diagonal ($\langle u^0 | H_n | u^0 \rangle \neq 0$ for $m \neq n$) there can be a contradiction for $n \neq m$.

→ The issue is resolved by the fact that for the subspace of \mathcal{H} that is spanned by the eigenstates to the energy eigenvalue $E_1^0 = \dots = E_r^0$, $\{|1^0\rangle, \dots, |r^0\rangle\}$, we can as well adopt an alternative CONS $\{|1'^0\rangle, \dots, |r'^0\rangle\}$.

These two CONS are related by a unitary matrix U_{nm} : (sum convention)

$$|u'^0\rangle = U_{nm}|u^0\rangle \quad \text{and} \quad |u^0\rangle = (U^*)_{nm}|u'^0\rangle$$

In the primed basis we can now derive the equation

$$E_{n'}^* \delta_{nn'} = \langle u^0 | H_n | u^0 \rangle = (U^*)_{m'm} \langle u^0 | H_n | u^0 \rangle U_{mm'}.$$

So the primed basis $\{|1'^0\rangle, \dots, |r'^0\rangle\}$ is the one in which H_n is diagonalized

$$\langle u^0 | H_n | u^0 \rangle = \begin{pmatrix} E_1^* & & \\ & E_2^* & 0 \\ 0 & \ddots & \ddots \end{pmatrix}$$

← Is possible because H_n is Hermitian on any subspace. (Does not have to be closed!)

$$\langle u^{(0)} | H_1 | u^{(0)} \rangle = \begin{pmatrix} E_1 & & & \\ & E_2 & & 0 \\ & & \ddots & \\ 0 & & & E_r & \min \end{pmatrix}$$

← Is possible because H_1 is Hermitian on any subspace. (Does not have to be closed!)

and is the proper one to be adopted to determine the perturbative series

The diagonal entries E_1^1, \dots, E_r^1 are the 1st order energy corrections.

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9.2. Relativistic Corrections to the Hydrogen Atom

- One can use time-independent perturbation theory to determine the 1st order relativistic corrections to the energy levels of the hydrogen atom.

9.2.1 $O(\alpha^4)$ Relativistic Corrections

- There are 3 sources of relativistic corrections which give $O(\alpha^4)$ relativistic corrections to the $O(\alpha^2)$ energy levels $E_n^0 = -\frac{1}{2n^2} \frac{e^2}{4\pi\epsilon_0 c^2} \alpha^2$ obtained in the non-relativistic approximation.

(a) Relativistic kinetic energy

↳ Expression for the relativistic total energy of a free particle with rest mass m and momentum \vec{p} :

$$E = \sqrt{\vec{p}^2 c^2 + m^2 c^4} \stackrel{\vec{p}^2 c^2 \ll m^2 c^4}{=} mc^2 + \frac{\vec{p}^2}{2m} - \frac{1}{8} \frac{(\vec{p}^2)^2}{m^3 c^2} + \dots$$

\uparrow rest mass term \uparrow \uparrow ↴
non-relativistic kinetic energy correction

term

Correction

non-relativistic
kinetic energy

↳ Hamilton operator for the relativistic kinetic energy correction:

$$H_1 = -\frac{1}{8} \frac{(\vec{p}_r)^2}{m^3 c^2}$$

(b) Spin-Orbit-Coupling

↳ From the relativistic Dirac equation one can derive the spin-orbit-coupling correction

$$H_2 = \frac{1}{2m^2 c^2} \vec{S} \cdot \vec{L} + \frac{1}{r} \frac{d}{dr} V(r), \quad V(r) = -\frac{e^2}{r}$$

The spin-orbit coupling is coming from the effect that the electron sees a magnetic field caused by the proton that circulates around the electron (seen from the electron rest frame).

Heuristic derivation:

$$\text{Electric field by proton: } \vec{E} = -\vec{\nabla} V(r) = -\frac{\vec{x}}{r} \frac{d}{dr} V(r)$$

$$\text{B-field seen by electron due to circulating proton: } \vec{B} = -\vec{v} \times \vec{E}/c$$

Energy of the magnetic moment due to the electron spin:

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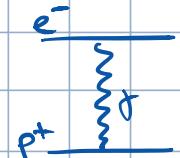
$$-\frac{e}{mc} \vec{S} \cdot \vec{B} = -\frac{e}{mc^2} \vec{S} \cdot (\vec{v} \times \vec{x}) \frac{1}{r} \frac{d}{dr} V(r) = \frac{1}{m^2 c^2} \vec{S} \cdot \vec{L} \frac{1}{r} \frac{d}{dr} V(r)$$

The correct relativistic calculation that accounts for the fact that the electron rest frame is not an inertial frame gives H_1 shown above.

(c) Darwin - Correction

↳ Comes from a relativistic correction to the photon exchange that causes the Coulomb potential:

$$H_3 = \frac{\pi \hbar^2 e^2}{2m^2 c^2} \delta^{(2)}(\vec{x})$$



9.2.2. Calculation of the $O(\lambda^4)$ Corrections to the Bound State Energies

→ We use the 1st order energy correction formulae from Ch. 9.2.1 to calculate the $O(\lambda^4)$ corrections to the bound state energy spectrum of the hydrogen.

We are having a case where the energy eigenvalues of the unperturbed problem (with the Hamilton operator $H_0 = \frac{\vec{p}^2}{2mc^2} - \frac{e^2}{r}$) are degenerate. So we need to check each time whether the matrix elements of H_i ($i=1,2,3$) in the basis of the states $\langle \vec{x} | u_l m \rangle = R_{lm}(r) Y_{lm}(\theta, \phi)$ (see Ch. 7.5) are diagonal!

whether the matrix elements of H_i ($i=1,2,3$) in the basis of the states $\langle \vec{x} | u l m \rangle = R_{lm}(r) Y_{lm}(\theta, \phi)$ (see Ch. 7.5) are diagonal!

(a) Relativistic kinetic energy correction

$$\text{We use } H_0 = \frac{\vec{p}^2}{2m_e} - \frac{e^2}{r} \iff \frac{\vec{p}^2}{2m_e} = H_0 + \frac{e^2}{r}$$

$$\hookrightarrow H_1 = -\frac{1}{8} \frac{(\vec{p}^2)^2}{m_e^3 c^2} = -\frac{1}{2m_e^2} \left(H_0 + \frac{e^2}{r} \right)^2, \quad r = |\vec{x}|$$

Check of diagonality of $\langle u l m | H_1 | u l' m' \rangle$:

\hookrightarrow (We know that H_1 is invariant under rotations: $\Rightarrow [H_1, \vec{L}^2] = 0, [H_1, L_z] = 0$

$$\begin{aligned} \Rightarrow \text{tr}_m \langle u l m | H_1 | u l' m' \rangle &= \langle u l m | L_z H_1 | u l' m' \rangle = \langle u l m | H_1 L_z | u l' m' \rangle \\ &= \text{tr}_{m'} \langle u l m | H_1 | u l' m' \rangle \quad \Rightarrow \langle u l m | H_1 | u l' m' \rangle = 0 \text{ for } m \neq m' \end{aligned}$$

$$\begin{aligned} h^2 l(l+1) \langle u l m | H_1 | u l' m' \rangle &= \langle u l m | L^2 H_1 | u l' m' \rangle = \langle u l m | H_1 L^2 | u l' m' \rangle \\ &= h^2 l'(l'+1) \langle u l m | H_1 | u l' m' \rangle \quad \Rightarrow \langle u l m | H_1 | u l' m' \rangle = 0 \text{ for } l \neq l' \end{aligned}$$

\hookrightarrow The matrix elements $\langle u l m | H_1 | u l' m' \rangle$ are already diagonal. There is no need to change basis.

First order energy correction due to H_n :

$$(\Delta E_{\text{new}})_{H_n} = \langle u_l m_l | H_n | u_l m_l \rangle$$

$$= -\frac{1}{2m_ec^2} \left(E_n^2 + 2E_n c^2 \left\langle \frac{1}{r} \right\rangle_{\text{ne}} + c^4 \left\langle \frac{1}{r^2} \right\rangle_{\text{ne}} \right) \quad c^2 = \alpha \hbar c$$

$$\text{where } \left\langle \frac{1}{r^n} \right\rangle_{\text{ne}} = \int dr r^2 d\Omega |Y_{l,m_l}(r, \theta, \phi)|^2 \frac{1}{r^n} = \int_0^\infty dr r^{2-n} |R_{l,n}(r)|^2$$

$$\text{One finds: } \left\langle \frac{1}{r} \right\rangle_{\text{ne}} = \frac{1}{a n^2}, \quad \left\langle \frac{1}{r^2} \right\rangle_{\text{ne}} = \frac{1}{a^2 n^3 (l+\frac{1}{2})}, \quad E_n = -\frac{m_e c^2 \alpha^2}{2 n^2}, \quad a = \frac{\alpha}{m_e c \alpha}$$

$$\Rightarrow (\Delta E_{\text{new}})_{H_n} = -\frac{m_e c^2 \alpha^2}{2 n^2} \frac{\alpha^2}{n^2} \left(\frac{n}{l+\frac{1}{2}} - \frac{3}{4} \right)$$

Note: The spin of the electron does not play any role because H_n is diagonal with respect to the S_z eigenstates $| \pm \frac{1}{2} \rangle$ and because $(\Delta E_{\text{new}})_{H_n}$ is independent of which spin state the electron has:

$$(\Delta E_{\text{new}})_{H_n} = \langle u_l m_l \sigma | H_n | u_l m_l \sigma \rangle = \langle u_l m_l | H_n | u_l m_l \rangle$$

(b) Spin-Orbit Coupling Correction

The spin-orbit coupling correction Hamilton operator: $H_2 = \frac{1}{2m_e^2 c^2} \vec{S} \cdot \vec{L} \frac{e^2}{r^3}$

We now have to take into account the spin of the electron and check whether H_2

The Spin-Orbit Coupling Correction hamilton operator : $H_2 = 2m_e^2c^2 \vec{S} \cdot \vec{L} / r^3$

We now have to take into account the spin of the electron and check whether H_2 is diagonal with respect to the unperturbed states $|lmlm\rangle = |lml\rangle \otimes |\sigma\rangle$.

We consider the total angular momentum operator $\vec{J} = \vec{L} + \vec{S}$.

Because we have

$$\vec{S} \cdot \vec{L} = \frac{1}{2} (\vec{J}^2 - \vec{L}^2 - \vec{S}^2)$$

We know from Ch. 8 that the states $|lmlm\rangle$ do not diagonalize $\vec{S} \cdot \vec{L}$ because they are not eigenstates of \vec{J}^2 . So we switch basis to the states (see Ch. 8.3).

we drop the \vec{S}^2 quantum number

$$|nljm;ls\rangle = |n, l \pm \frac{1}{2}, m_j; l, \pm\rangle = \downarrow \pm |n, l, m_j, \pm, \uparrow\rangle + \downarrow \pm |n, l, m_j, \pm, \downarrow\rangle$$

$$\text{eigenstates of } H_0, \vec{J}^2, J_z, \vec{L}, \vec{S}^2 \quad \text{eigenstates of } H_0, \vec{L}^2, \vec{S}^2, L_z, S_z$$

$$\begin{aligned} \Rightarrow \vec{S} \cdot \vec{L} |n, l \pm \frac{1}{2}, m_j; l\rangle &= \frac{\hbar^2}{2} \left(\begin{array}{c} (l \pm \frac{1}{2})(l \pm \frac{3}{2}) - l(l+1) - \frac{3}{4} \\ (l \mp \frac{1}{2})(l \pm \frac{1}{2}) - l(l+1) - \frac{3}{4} \end{array} \right) |n, l \pm \frac{1}{2}, m_j; l\rangle \\ &= \frac{\hbar^2}{2} \left(\begin{array}{c} l \\ -(l+1) \end{array} \right) |n, l \pm \frac{1}{2}, m_j; l\rangle \end{aligned}$$

We see: For $l=0$ (s-wave) states only the $j=l \pm \frac{1}{2} = \frac{1}{2}$ states exist and the spin-orbit coupling 1st order energy correction is zero.

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For $l \geq 1$ states the 1st order energy correction due to the spin-orbit-coupling is:

$$(\Delta E_{n,j=l\pm\frac{1}{2},m_j=\pm\frac{1}{2}})_{H_2} = \frac{1}{2m_e^2 c^2} \frac{\hbar^2}{2} \binom{l}{-(l+1)} e^2 \left\langle \frac{1}{r^3} \right\rangle_{ne}$$

We have $\left\langle \frac{1}{r^3} \right\rangle_{ne} = \frac{1}{a^3 n^3 l(l+\frac{1}{2})(l+\frac{1}{2})} = \frac{m_e^3 c^5 \alpha^3}{\hbar^3 n^3 l(l+\frac{1}{2})(l+\frac{1}{2})}$ which gives

$$(\Delta E_{n,j=l\pm\frac{1}{2},m_j=\pm\frac{1}{2}})_{H_2} = \frac{m_e c^2 \lambda^4}{4m_e^3 l(l+\frac{1}{2})(l+\frac{1}{2})} \binom{l}{-(l+1)}$$

(c) Darwin Term Correction

The Darwin term Hamilton operator is already diagonal for the $|nlm\rangle$ states since it only depends on $\delta^{(1)}(\vec{x})$. We thus obtain:

$$\begin{aligned} (\Delta E_{new})_{H_2} &= \langle nlm | H_2 | nlm \rangle = \frac{\pi \hbar^2 e^2}{2m_e^2 c^2} \langle nlm | \delta^{(1)}(\vec{x}) | nlm \rangle \\ &= \frac{\pi \hbar^2 e^2}{2m_e^2 c^2} |\Psi_{nlm}(r=0)|^2 \end{aligned}$$

We recall that $\Psi_{nlm}(r, \theta, \phi) = R_{nlm}(r) Y_{lm}(\theta, \phi) \rightarrow$ Only $l=0$ (s-wave) states contribute!

$$\hookrightarrow R_{nlm}(r=0) = - \left[\frac{(n-1)! (2/n)^n}{2n(n!)^2} \right]^{1/2} L_n'(0) \delta_{l0}, \quad L_n'(0) = - \frac{(n!)^2}{(n-1)!}$$

$$= \left[\frac{(2/n)^n n!}{2n(n-1)!} \right]^{1/2} \delta_{l0} = \frac{2}{(n-1)^{3/2}} \delta_{l0}$$

$$a = \frac{\hbar}{m_e e N}$$

$$\hookrightarrow K_{\text{Lc}}(r=0) = - \left[\frac{1}{2n(n!)^3} \right] L_n(0) \delta_{2,0}, \quad L_n(0) = - \frac{1}{(n-1)!}$$

$$= \left[\frac{(2n\alpha)^n n!}{2n(n-1)!} \right]^{1/2} \delta_{2,0} = \frac{2}{(n\alpha)^{3/2}} \delta_{2,0}$$

$$\Psi_{n(l=0)m}(\vec{x}=0) = \frac{1}{(4\pi)^{1/2}} \frac{2}{(n\alpha)^{3/2}} = \frac{1}{(\pi n^3 \alpha^3)^{1/2}} = \left(\frac{m_e^3 c^5 \alpha^5}{\hbar^3 \pi^3 n^3} \right)^{1/2}$$

$$\alpha = \frac{\hbar}{m_e c \kappa}$$

So we obtain

$$(\Delta E_{\text{new}})_{H_3} = \frac{m_e c^2 \alpha^4}{2n^3} \delta_{2,0}$$

Sum of all corrections

$$\underline{l=0, j=\frac{1}{2}} : \quad (\Delta E_{\text{new}})_{H_1} + (\Delta E_{\text{new}})_{H_3} = \frac{m_e c^2 \alpha^2}{2} \frac{\alpha^2}{n^4} \left(\frac{3}{4} - n \right)$$

$$\underline{l \geq 1, j=l+\frac{1}{2}} : \quad (\Delta E_{\text{new}})_{H_1} + (\Delta E_{n,j=l+1/2,m,l})_{H_2} = \frac{m_e c^2 \alpha^2}{2} \frac{\alpha^2}{n^4} \left(\frac{3}{4} - \frac{n}{l+1} \right)$$

$$\underline{l \geq 1, j=l-\frac{1}{2}} : \quad (\Delta E_{\text{new}})_{H_1} + (\Delta E_{n,j=l-1/2,m,l})_{H_2} = \frac{m_e c^2 \alpha^2}{2} \frac{\alpha^2}{n^4} \left(\frac{3}{4} - \frac{n}{l} \right)$$

We see that the result can be written as:

$$(\Delta E_{n,j=l \pm \frac{1}{2},m,l}) = \frac{m_e c^2 \alpha^2}{2} \frac{\alpha^2}{n^4} \left[\frac{3}{4} - \frac{n}{j \pm \frac{1}{2}} \right]$$

These $O(\alpha^4)$ corrections to the bound state energy levels are called "fine structure corrections".

9.2.3. Hydrogen Spectroscopy

→ For atoms the spectroscopical convention is used that energy levels with

spin s , orbital angular momentum L ,
total angular momentum j and
radial quantum number n

are named

$n^{2s+1} L_j$

For hydrogen we have $2s+1 = 2$.

$n=2, l=0,1$ Feinstruktur + Lamb-Verschiebg. + Hyperfeinstruktur

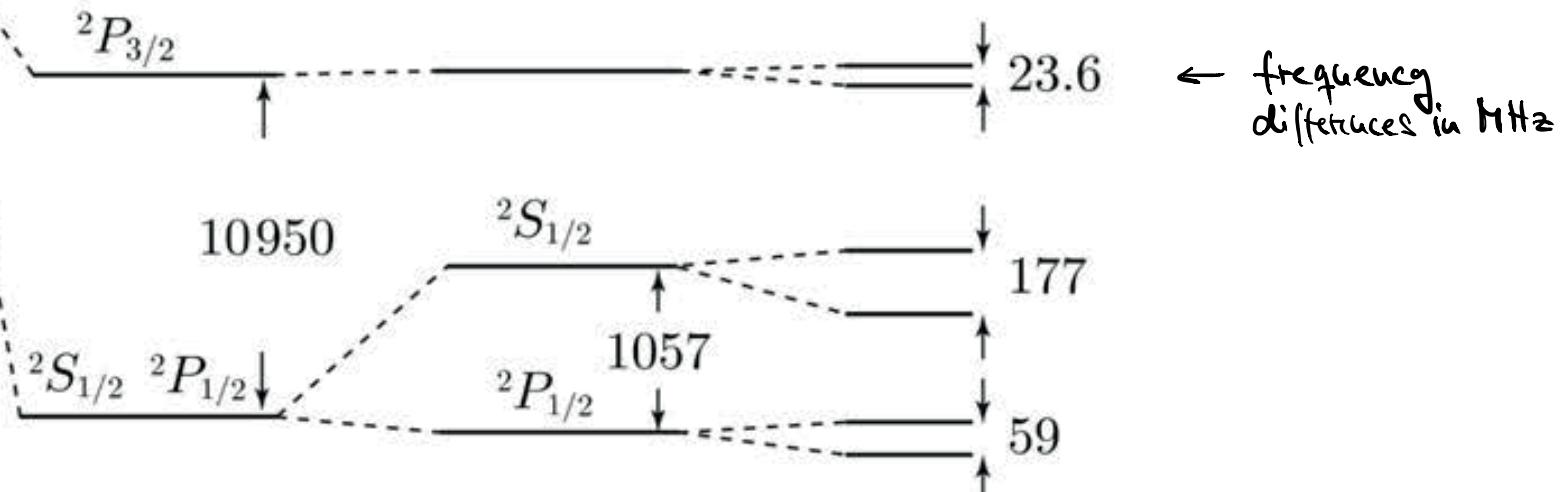
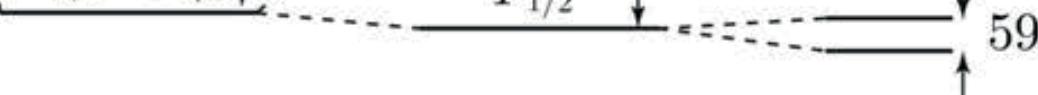


Abb. 12.1 Die Aufspaltung der Energieniveaus des Wasserstoffatoms in MHz auf


Abb. 12.1. Die Aufspaltung der Energieniveaus des Wasserstoffatoms in MHz auf Grund der relativistischen Korrekturen, der Lamb-Verschiebung und der Hyperfeinstruktur

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→ For the $n=2$ states (degeneracy: $2n^2 = 8$) one has

four $2^2P_{3/2}$ states
two $2^2S_{1/2}$ states
two $2^2P_{1/2}$ states } are still degenerate
at $O(\alpha^4)$

The $2^2S_{1/2}$ and $2^2P_{1/2}$ states are split by the "Lamb Shift" correction which is an $O(\alpha^5)$ correction that can be calculated with Quantum Electrodynamics (QED). The Lamb shift is an effect that arises from the effect that a photon (γ) participates in the $e^- - p^+$ bound state dynamics to form a $e^- - p^+ - \gamma$ three-body problem.