

Lecture notes 15

Time-independent perturbation theory

Introduction

As discussed in Lecture notes 14, relatively few problems in quantum mechanics are exactly solvable. **Time-independent perturbation theory** is used when one wishes to find energy eigenstates and the corresponding energy *levels* for a system for which the Hamiltonian H is not very different from the Hamiltonian H_0 of an exactly solvable system, that is to say when¹

$$H = H_0 + V, \quad (\text{T15.1})$$

where the perturbation term V is in some sense small (or weak) compared to H_0 . Starting from the exact solutions corresponding to H_0 , one can then in a systematic way find successively better approximations to the energy eigenstates and the corresponding energy levels. As stated, one needs to know the exact solutions of the eigenvalue equation

$$H_0 |n\rangle = E_n^0 |n\rangle, \quad (\text{T15.2})$$

for the unperturbed system, that is [with $\langle \mathbf{r} | n \rangle \equiv \psi_n^0(\mathbf{r})$] the solutions of the Schrödinger equation

$$H_0 \psi_n^0(\mathbf{r}) = E_n^0 \psi_n^0(\mathbf{r}).$$

As mentioned, the method will work best when the perturbing term V is weak compared to H_0 .

Of course, it is not always possible to divide the Hamiltonian into $H = H_0 + V$, where V is small *and* the system described by H_0 is exactly solvable. One must then use other methods than perturbation theory. One such method, that can be applied to one-dimensional problems, is the WKB method, which will not be treated here.² Another possibility is Rayleigh–Ritz’ variational method.

15.1 Qualitative discussion

As an example, let us consider the hydrogen atom. Here we know (from Lecture notes 5) the exact eigenfunctions $\psi_{nlm}(\mathbf{r}) = R_{nl}(r) Y_{lm}(\theta, \phi)$ of the Hamiltonian

$$H_0 = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r}.$$

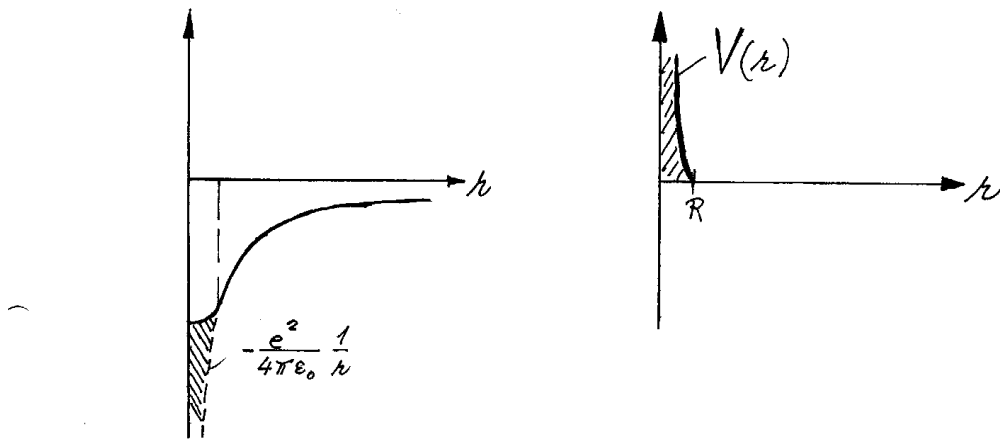
¹For the sake of simplicity, we do not use “hats” over the operators in this chapter. Thus H really means \hat{H} , etc.

²The **Wentzel–Kramers–Brillouin** method (1926) is described in section 8.4 in Bransden & Joachain.

However, this Hamiltonian does not give an exact description of the interaction between the electron and the proton. The most important correction terms which must be added to H_0 are due to relativistic corrections, and lead e.g. to the **fine-structure splitting** of the hydrogen energy levels. You can find descriptions of these corrections in section 8.2 in Bransden & Joachain.

We shall here consider another correction, which is due to the fact that the proton is not a point particle but has **finite size**. The proton consists of two u-quarks of charge $2e/3$ and one d-quark of charge $-e/3$. The quantum state of this system is such that the proton charge is *distributed* inside a radius R of the order of 1 femtometer.³ Let us assume that this charge distribution is spherically symmetric. This isn't necessarily realistic, but gives us a simple model. (The corrections due to the finite size are anyhow so small that they are not of practical importance.)

Inside the proton "radius" R the potential will not have Coulomb form as in the expression for H_0 , but rather behave like the solid line in the figure on the left.



Figur 1: The solid line on the left indicates how the potential behaves inside the proton radius.

This means that we have to add to H_0 a positive perturbation term $V = V(r)$, shown in the figure on the right. This perturbation term is repulsive, because the attraction between the electron and the proton is not as strong as assumed in H_0 when the electron is inside the radius R . Even though the perturbation term is very large numerically in this region, we may still regard the perturbation $V(r)$ to be weak. The reason is that the proton radius $R \sim 1$ fm is much smaller than the Bohr radius $a_B \approx 0.5 \cdot 10^5$ fm, which means that it is very improbable (or very "seldom") that the electron is in this region and "feels" the perturbation (or the lack of the full Coulomb attraction implied by H_0). Based on these semi-classical considerations, we must expect that the perturbed energies (that is, the energies of the eigenstates of $H = H_0 + V(r)$) lie only slightly higher than the unperturbed energies (slightly smaller binding energies.)

We shall soon see that perturbation theory supports this argumentation: To lowest order, it turns out that the energy corrections are given by the expectation values of the perturbation term V , calculated using the unperturbed eigenfunctions:

$$\Delta E_{nlm} = \langle \psi_{nlm}^0 | V | \psi_{nlm}^0 \rangle \equiv \int \psi_{nlm}^{0*}(\mathbf{r}) V(r) \psi_{nlm}^0(\mathbf{r}) d^3r.$$

³ 1 fm=1 fermi=1 femtometer= 10^{-15} m is a suitable unit of length when dealing with nucleons and nuclei.

These corrections are small, because the probabilities of finding the electron in the region where the perturbation term $V(r)$ is large, $\int_0^R |\psi_{nlm}^0|^2 d^3r$, are very small.

From Lecture notes 5, we know that this probability is largest for the $1s$ -state, and decreases with increasing principal quantum number (n). Furthermore, it will decrease with increasing l , because of the centrifugal barrier (cf Lecture notes 5). Therefore the energy correction due to the finite size of the proton will be largest for the ground state, somewhat smaller for the $2s$ -state ($n = 2, l = 0$) and even smaller than that for $2p$ ($n = 2, l = 1$).

Thus the perturbation in principle removes some of the degeneracy of this system. However, the three $2p$ -states, and more generally the $2l + 1$ states for a given l (and n), will still be degenerate. This is because the perturbation $V(r)$ (and hence the total potential) in this example is spherically symmetric. (The l -degeneracy is broken because we no longer have a pure $1/r$ potential; cf the discussion in Lecture notes 5). This example illustrates the fact that the symmetry properties of both the unperturbed and the perturbed systems determine to what extent the degeneracy is broken by the perturbation.

15.2 Perturbation theory for non-degenerate levels

We shall now formulate the perturbation method for energy levels which are not degenerate (like e.g. the ground state of the hydrogen atom). (The necessary modifications for degenerate levels will be discussed in section 4 below.)

It is convenient to study the solutions for a system described by the Hamiltonian

$$H = H_0 + \lambda V, \quad (\text{T15.3})$$

where we have multiplied the perturbation term V by a real parameter λ , which we can think of as a variable parameter. Both the energy levels and the corresponding eigenfunctions then become functions of λ .

Let us imagine that λ is lowered gradually from 1 to 0, corresponding to the perturbation gradually being “turned off”. The energy $E_n(\lambda)$ of state number n must then just as gradually approach the unperturbed energy E_n^0 of state n .⁴ In the Rayleigh-Schrödinger perturbation theory we assume that the energy $E_n(\lambda)$ can be expanded in a power series in λ . The first term must then be E_n^0 :

$$E_n = E_n(\lambda) = E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \quad (\text{T15.4})$$

Whether this expansion at all converges depends on the nature of the perturbation. Provided that it does, the series converges faster the weaker the perturbation λV is, and when it is sufficiently weak, the correction terms $\lambda E_n^{(1)}$, $\lambda^2 E_n^{(2)}$ etc will be small and the expansion converges fast.

Furthermore, we assume that also the λ -dependence of the perturbed eigenfunctions can be expressed in terms of powers of λ :

$$\psi_n = \psi_n^0 + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots$$

⁴In the present section it is practical to let the index n enumerate *states*. Later, in section 4 below, we shall let n enumerate the *energy levels*. We must then use an additional index to enumerate the states within a given level.

Here, ψ_n^0 is the eigenfunction of state number n in the limit $\lambda \rightarrow 0$, while the functions $\lambda\psi_n^{(1)}$, $\lambda^2\psi_n^{(2)}$ etc are the corrections to this state for $\lambda V \neq 0$. The eigenfunction ψ_n corresponds to a state vector which we may call $|\psi_n\rangle$;

$$|\psi_n\rangle = |\psi_n^0\rangle + \lambda |\psi_n^{(1)}\rangle + \dots \quad (\text{T15.5})$$

Thus $|\psi_n\rangle$ is the perturbed state which corresponds to the unperturbed $|n\rangle$, while $\lambda|\psi_n^{(1)}\rangle$ is the first-order correction, etc.

Substitution into the eigenvalue equation

The various terms of the state vector (T15.5) and of the energy (T15.4) are all determined by the eigenvalue equation

$$[H(\lambda) - E_n(\lambda)] |\psi_n(\lambda)\rangle = 0. \quad (\text{T15.6})$$

Inserting (T15.4) and (T15.5) we get:

$$\begin{aligned} [H_0 - E_n^0 + \lambda(V - E_n^{(1)}) - \lambda^2 E_n^{(2)} - \dots] \\ \times \{|\psi_n^0\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \dots\} = 0. \end{aligned} \quad (\text{T15.7})$$

This equation must be satisfied for all λ , and must therefore hold order by order in λ . To zeroth, first and second order in λ we then find:

$$(H_0 - E_n^0)|\psi_n^0\rangle = 0, \quad (\text{T15.8})$$

$$(H_0 - E_n^0)|\psi_n^{(1)}\rangle + (V - E_n^{(1)})|\psi_n^0\rangle = 0, \quad (\text{T15.9})$$

$$(H_0 - E_n^0)|\psi_n^{(2)}\rangle + (V - E_n^{(1)})|\psi_n^{(1)}\rangle - E_n^{(2)}|\psi_n^0\rangle = 0, \quad (\text{T15.10})$$

and so on.

State vector to zeroth order. Normalization and phase choice

"The zeroth-order equation" (T15.8) shows that the first-order term in the expansion of the state vector, $|\psi_n^0\rangle$, satisfies the same eigenvalue equation (T15.2) as the unperturbed eigenvector $|n\rangle$. Because the non-degenerate energy level E_n^0 has only one eigenvector, $|n\rangle$, it follows that

$$|\psi_n^0\rangle = c|n\rangle \quad (\text{for a non-degenerate level}), \quad (\text{T15.11})$$

where c is a constant. We shall now see that this constant can be set equal to 1.

Proof: We start by noting that the eigenvalue equation (T15.6) determines the perturbed state $|\psi_n\rangle$ to within a complex constant factor. Thus we are free to choose the normalization and the phase of this state as follows:

(a) We choose to give $|\psi_n\rangle$ the *same phase* as the unperturbed vector $|n\rangle$, so that the scalar product between these two vectors (or, if you like, the component of $|\psi_n\rangle$ in the $|n\rangle$ -direction) becomes real and positive:

$$\langle n|\psi_n\rangle = c\langle n|n\rangle + \lambda\langle n|\psi_n^{(1)}\rangle + \lambda^2\langle n|\psi_n^{(2)}\rangle + \dots \quad \text{real and positive.}$$

This equation must (like (T15.7)) be satisfied order by order. With orthonormalized unperturbed eigenvectors, so that $\langle n|n\rangle = 1$, we then see that it follows from the above phase choice alone that

$$c \text{ is real and positive,} \quad (\text{T15.12})$$

$$\langle n|\psi_n^{(1)}\rangle, \langle n|\psi_n^{(2)}\rangle \quad \text{etc are real.} \quad (\text{T15.13})$$

(b) Next, we choose to *normalize* $|\psi_n\rangle$ to 1. Using the relation $\langle b|a\rangle = \langle a|b\rangle^*$ together with (T15.12) and (T15.13) we can write the normalization condition on the form

$$\begin{aligned} 1 = \langle \psi_n | \psi_n \rangle &= [c\langle n | + \lambda\langle \psi_n^{(1)} | + \dots][c|n\rangle + \lambda|\psi_n^{(1)}\rangle + \dots] \\ &= c^2 + \lambda [c\langle n | \psi_n^{(1)} \rangle + c\langle \psi_n^{(1)} | n \rangle] \\ &\quad + \lambda^2 [c\langle n | \psi_n^{(2)} \rangle + c\langle \psi_n^{(2)} | n \rangle + \langle \psi_n^{(1)} | \psi_n^{(1)} \rangle] \\ &\quad + \lambda^3 [\dots] + \dots \\ &= c^2 + \lambda [2c\langle n | \psi_n^{(1)} \rangle] \\ &\quad + \lambda^2 [2c\langle n | \psi_n^{(2)} \rangle + \langle \psi_n^{(1)} | \psi_n^{(1)} \rangle] + \dots \end{aligned}$$

Since also this relation must hold order by order, we can conclude that $c = 1$, while all the square brackets must be equal to zero. With the choices (a) and (b) above, the zeroth-order term $|\psi_n^0\rangle$ in (T15.5) is thus identical to the unperturbed state vector $|n\rangle$, while

$$\langle n | \psi_n^{(1)} \rangle = 0, \quad (\text{T15.14})$$

$$\langle n | \psi_n^{(2)} \rangle = -\frac{1}{2} \langle \psi_n^{(1)} | \psi_n^{(1)} \rangle, \quad \text{etc.} \quad (\text{T15.15})$$

Note that the first of these equations tells us that the component in the $|n\rangle$ -direction of $|\psi_n^{(1)}\rangle$ is equal to zero; $|\psi_n^{(1)}\rangle$ is orthogonal to the unperturbed vector. (The same is the case when we rotate an ordinary vector.)

The energy to first order

The other components of the first-order term $|\psi_n^{(1)}\rangle$, and the first-order correction $E_n^{(1)}$ to the energy, can be found using the first-order equation (T15.9). By projecting this equation onto the unperturbed vector number m , that is, by multiplying from the left by $\langle m|$, we find:

$$\langle m | H_0 - E_n^0 | \psi_n^{(1)} \rangle + \langle m | V - E_n^{(1)} | n \rangle = 0.$$

Using the relation

$$\langle m | H_0 = \langle \psi_m^0 | H_0 = \langle m | E_m^0, \quad (\text{T15.16})$$

which follows by taking the adjoint of (T15.8), we then have

$$(E_m^0 - E_n^0) \langle m | \psi_n^{(1)} \rangle + \langle m | V | n \rangle - E_n^{(1)} \delta_{mn} = 0. \quad (\text{T15.17})$$

For $m = n$ this gives

$$E_n^{(1)} = \langle n | V | n \rangle : \quad (\text{T15.18})$$

*To first (lowest) order the energy correction
is equal to the expectation value of the perturbation,
taken in the unperturbed state.*

This is the most central formula in time-independent perturbation theory, as we mentioned already in the introductory discussion. Note that we need only the unperturbed energy eigenstates $|n\rangle$ when calculating $E_n^{(1)}$.

First-order correction to the state vector

The first-order correction to the state vector (and hence to the wavefunction) is of course in itself an important correction. In addition, this correction must be known if one wants to calculate the second-order correction to the energy. By choosing $m \neq n$ in (T15.17) we find the components of $|\psi_n^{(1)}\rangle$ in all directions $|m\rangle \neq |n\rangle$:

$$\langle m|\psi_n^{(1)}\rangle = \frac{\langle m|V|n\rangle}{E_n^0 - E_m^0}; \quad m \neq n. \quad (\text{T15.19})$$

Because $\langle n|\psi_n^{(1)}\rangle = 0$, we can then conclude that the first-order correction to the state vector is

$$\lambda|\psi_n^{(1)}\rangle = \lambda \sum_m |m\rangle \langle m|\psi_n^{(1)}\rangle = \sum_{m \neq n} \frac{\langle m|\lambda V|n\rangle}{E_n^0 - E_m^0} |m\rangle, \quad (\text{T15.20})$$

so that the perturbed vector for state number n is

$$|\psi_n\rangle = |n\rangle + \sum_{m \neq n} \frac{\langle m|\lambda V|n\rangle}{E_n^0 - E_m^0} |m\rangle + O(\lambda^2), \quad (\text{T15.21})$$

to first order.

Comments:

(i) We note that the first-order term in general may contain contributions along all the unperturbed vectors $|m\rangle \neq |n\rangle$. Using the unperturbed states as a basis, we may then state that the perturbation causes a “rotation” of state number n , “mixing in” contributions along $|m\rangle \neq |n\rangle$. The degree of this “mixing” or “coupling” to state number m is determined by the matrix element $\langle m|\lambda V|n\rangle$ and the energy difference $E_n^{(0)} - E_m^{(0)}$, or more precisely by the ratio between these two quantities, as is evident in (T15.21). This is what determines the size of the correction $|\psi_n^{(1)}\rangle$.

(ii) In the above derivation, all the levels were supposed to be non-degenerate. Another possibility is that level number n is non-degenerate, while the other levels may be degenerate. The formulae above are then valid provided that the sum over m is taken to be a sum over states (that is, a double sum: over levels, and for each level over states).

(iii) In practice, many of the matrix elements $\langle m|V|n\rangle$ may be equal to zero, so that the sum within each level is restricted, some times to only one contribution. (We shall later see examples of this.)

The energy to second order. Summary

By projecting (T15.10) onto $|n\rangle$ we find:

$$\langle n|H_0 - E_n^0|\psi_n^{(2)}\rangle + \langle n|V|\psi_n^{(1)}\rangle - E_n^{(1)}\langle n|\psi_n^{(1)}\rangle - E_n^{(2)}\langle n|n\rangle = 0.$$

Equations (T15.16), (T15.14) and (T15.20) then give

$$\begin{aligned} E_n^{(2)} = \langle n|V|\psi_n^{(1)}\rangle &= \sum_{m \neq n} \frac{\langle m|V|n\rangle \langle n|V|m\rangle}{E_n^0 - E_m^0} \\ &= \sum_{m \neq n} \frac{|\langle m|V|n\rangle|^2}{E_n^0 - E_m^0}. \end{aligned}$$

We could continue in this manner, but choose to stop here, summing up as follows:

The solution of the eigenvalue problem⁵

$$(H_0 + \lambda V) |\psi_n\rangle = E_n |\psi_n\rangle \quad (\text{T15.22})$$

is

$$|\psi_n\rangle = |n\rangle + \sum_{m \neq n} \frac{\langle m|\lambda V|n\rangle}{E_n^0 - E_m^0} |m\rangle + O(\lambda^2), \quad (\text{T15.23})$$

$$E_n = E_n^0 + \langle n|\lambda V|n\rangle + \sum_{m \neq n} \frac{|\langle m|\lambda V|n\rangle|^2}{E_n^0 - E_m^0} + O(\lambda^3). \quad (\text{T15.24})$$

15.3 Example: Perturbed harmonic oscillator

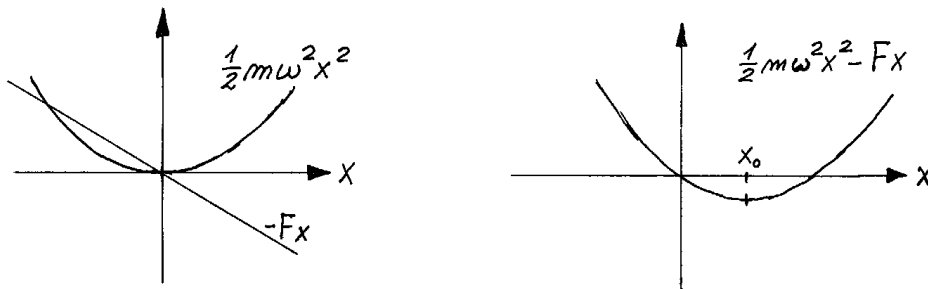
A harmonic oscillator, with $H_0 = \frac{p_x^2}{2m} + \frac{1}{2}m\omega^2 x^2$, is perturbed by a force F in the positive x -direction, corresponding to the perturbing term $-Fx$. (Here λ has been set equal to 1, and we may instead think of F as a variable parameter.)

Exact solutions: In this case, we know the exact solutions, which follow from a slight rewriting of the Hamiltonian:

$$\begin{aligned} H = H_0 - Fx &= \frac{p_x^2}{2m} + \frac{1}{2}m\omega^2 \left(x^2 - \frac{2F}{m\omega^2} x + \frac{F^2}{m^2\omega^4} \right) - \frac{F^2}{2m\omega^2} \\ &\equiv \frac{p_x^2}{2m} + \frac{1}{2}m\omega^2 (x - x_0)^2 - \frac{F^2}{2m\omega^2}. \end{aligned}$$

As we see, the perturbed Hamiltonian describes a harmonic oscillator with equilibrium position at the point $x_0 \equiv \frac{F}{m\omega^2}$ and energy levels

$$E_n(F) = \hbar\omega \left(n + \frac{1}{2} \right) - \frac{F^2}{2m\omega^2} \equiv E_n^0 - \frac{F^2}{2m\omega^2}. \quad (\text{T15.25})$$



The force F shifts the equilibrium position to the right and the energy levels downwards.

⁵The parameter λ in these formulae may be set equal to 1,

Note that the lowering of the energy levels is of the order of F^2 . The eigenfunctions are the well-known oscillator solutions, shifted according to the new equilibrium position $x_0 = F/m\omega^2$:

$$\psi_n(x) = \psi_n^0(x - x_0). \quad (\text{T15.26})$$

Solving this problem using perturbation theory

Attacking this problem with non-degenerate perturbation theory, we find to lowest order

$$E_n^{(1)} = \langle n | -Fx | n \rangle = -F \langle n | x | n \rangle = -F \int_{-\infty}^{\infty} \psi_n^{0*}(x) x \psi_n^0(x) dx = 0, \quad (\text{T15.27})$$

because the integrand is antisymmetric. To first order in F the energy correction thus is equal to zero. This is not surprising, because the exact correction is of order F^2 , as we have just seen in (T15.25). The last step in (T15.27) is an example of a selection rule: The matrix element $\langle n | x | n \rangle$ is always equal to zero when the wavefunction $\psi_n^0(x) \equiv \langle x | n \rangle$ is an eigenstate of the parity operator, being either symmetric or antisymmetric with respect to space inversion.

It should also be noted that (T15.27) follows from the relations

$$x = \sqrt{\frac{\hbar}{2m\omega}} (a + a^\dagger); \quad a | n \rangle = \sqrt{n} | n - 1 \rangle; \quad a^\dagger | n \rangle = \sqrt{n + 1} | n + 1 \rangle, \quad (\text{T15.28})$$

which give

$$\langle k | x | n \rangle = \sqrt{\frac{\hbar}{2m\omega}} (\sqrt{n} \delta_{k,n-1} + \sqrt{n+1} \delta_{k,n+1}). \quad (\text{T15.29})$$

This last formula can also be used to calculate the energy correction to second order:

$$\begin{aligned} E_n^{(2)} &= \sum_{k \neq n} \frac{|\langle k | -Fx | n \rangle|^2}{E_n^0 - E_k^0} = F^2 \frac{\hbar}{2m\omega} \left(\frac{n}{E_n^0 - E_{n-1}^0} + \frac{n+1}{E_n^0 - E_{n+1}^0} \right) \\ &= -F^2 \frac{1}{2m\omega^2}. \end{aligned}$$

This is seen to be identical to the exact correction in (T15.25), and that was to be expected because the latter goes as F^2 . For the same reason, all higher-order corrections to the energies must be equal to zero in this case. (This has to do with the selection rule (T15.29).) Note also that (T15.29) limits the above sum over k to only two terms, for the “neighbouring” values $k = n - 1$ and $k = n + 1$.

Let us also calculate the state vector to first order:

$$\begin{aligned} |\psi_n\rangle &\approx |n\rangle + \sum_{k \neq n} \frac{\langle k | -Fx | n \rangle}{E_n^0 - E_k^0} |k\rangle \\ &= |n\rangle - F \sqrt{\frac{\hbar}{2m\omega}} \left(\frac{\sqrt{n}}{\hbar\omega} |n-1\rangle + \frac{\sqrt{n+1}}{-\hbar\omega} |n+1\rangle \right) \\ &= |n\rangle - F \sqrt{\frac{\hbar}{2m\omega}} \frac{1}{\hbar\omega} (a - a^\dagger) |n\rangle \\ &= \left(1 - i \frac{F}{m\omega^2 \hbar} p_x \right) |n\rangle = (1 - ip_x x_0 / \hbar) |n\rangle. \end{aligned} \quad (\text{T15.30})$$

(In the third step, we have used the relations (T15.28). In the next step we have used that $p_x = -i\sqrt{m\omega\hbar/2} (a - a^\dagger)$. Thus to first order the eigenfunction is

$$\psi_n(x) = \langle x | \psi_n \rangle = \langle x | 1 - ip_x x_0 / \hbar | n \rangle = \left(1 - x_0 \frac{d}{dx} \right) \psi_n^0(x).$$

(Here we have used the relation (T10.63) in Lecture notes 10: $\langle x | p_x = \frac{\hbar}{i} \frac{\partial}{\partial x} \langle x |$). This result agrees with the first two terms in the Taylor expansion around the point x of the exact result (T15.26):

$$\begin{aligned} \psi_n(x) &= \psi_n^0(x - x_0) = \\ &= \psi_n^0(x) - x_0 \frac{d}{dx} \psi_n^0(x) + \frac{(-x_0)^2}{2!} \frac{d^2}{dx^2} \psi_n^0(x) + \dots \\ &= \sum_{k=0}^{\infty} \frac{(-x_0 \frac{d}{dx})^k}{k!} \psi_n^0(x) \equiv e^{-x_0 \frac{d}{dx}} \psi_n^0(x). \end{aligned} \tag{T15.31}$$

(See footnote).⁶

15.4 Perturbation theory for degenerate levels

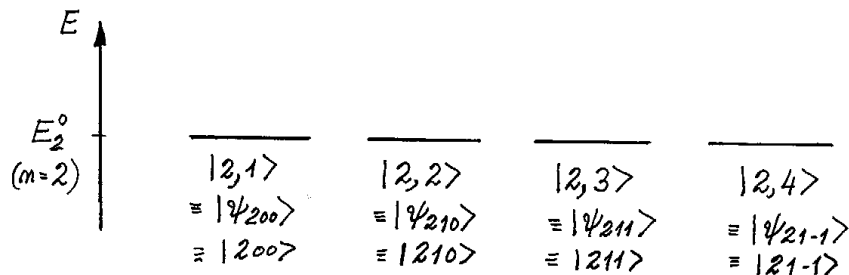
Let us consider an unperturbed system for which level number n , with energy E_n^0 , is degenerate, with $g(n)$ known, orthonormalized states;

$$\begin{aligned} H_0 |n, r\rangle &= E_n^0 |n, r\rangle; & r &= 1, \dots, g; \\ \langle n, s | n, r \rangle &= \delta_{sr}. \end{aligned}$$

As a concrete example we can consider the first excited level of the hydrogen atom, with $n = 2$ and $g = 4$. Here, we can let the indices $r = 1, \dots, 4$ correspond to the quantum number combinations

$$(l, m) = (0, 0), (1, 0), (1, 1) \text{ og } (1, -1),$$

meaning that the unperturbed state $|\psi_{200}\rangle$ is labeled as $|2, 1\rangle \equiv |n = 2, r = 1\rangle$ etc.



The unperturbed states $|n, r\rangle$ for level 2 of the hydrogen atom.

⁶Here we realize that the exact result for the state vector is

$$|\psi_n\rangle = e^{-ip_x x_0 / \hbar} |n\rangle. \tag{T15.32}$$

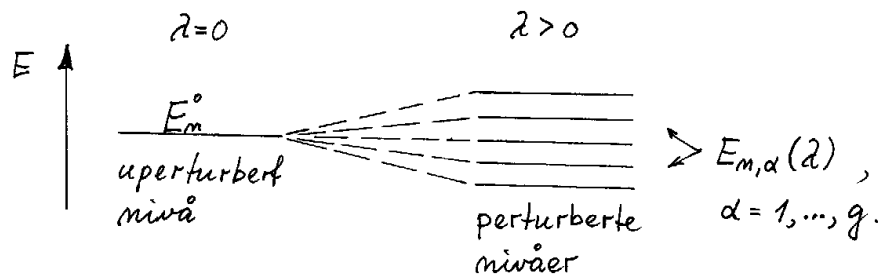
The operator on the right, which is equal to $e^{-x_0 d/dx}$ in the position representation, thus has the property that it “moves” the state a distance x_0 . This operator therefore is a **translation operator**.

When such a system is perturbed by a term λV , we get — instead of the $g(= 4)$ states $|n, r\rangle$ — $g(= 4)$ *new* (perturbed) states, which we may call $|\psi_{n\alpha}\rangle$, where the index α goes from 1 to $g(= 4)$. As in section 15.2 we assume that these states can be expanded in a power series in λ :

$$|\psi_{n\alpha}\rangle = |\psi_{n\alpha}^0\rangle + \lambda|\psi_{n\alpha}^{(1)}\rangle + \lambda^2|\psi_{n\alpha}^{(2)}\rangle + \dots \quad (\text{T15.33})$$

The perturbation will often remove the degeneracy or part of it. The energies of the g perturbed states will therefore in principle depend on α :

$$E_{n\alpha}(\lambda) = E_n^0 + \lambda E_{n\alpha}^{(1)} + \lambda^2 E_{n\alpha}^{(2)} + \dots \quad (\text{T15.34})$$



The perturbation may cause a splitting of the degenerate level, or break the degeneracy, as we say.

The g eigenstates $|\psi_{n\alpha}\rangle$ and the corresponding eigenvalue $E_{n\alpha}$ for the perturbed system are of course determined by the eigenvalue equation $H|\psi_{n\alpha}\rangle = E_{n\alpha}|\psi_{n\alpha}\rangle$. We now insert the expansions (T15.33) and (T15.34) into this equation, and get:

$$[H_0 - E_n^0 + \lambda(V - E_{n\alpha}^{(1)}) - \lambda^2 E_{n\alpha}^{(2)} - \dots] \times \{|\psi_{n\alpha}^0\rangle + \lambda|\psi_{n\alpha}^{(1)}\rangle + \lambda^2|\psi_{n\alpha}^{(2)}\rangle + \dots\} = 0. \quad (\text{T15.35})$$

This equation — which again must be satisfied order by order in λ — determines the correction terms $E_{n\alpha}^{(1)}$ etc to the energy and the correction terms $|\psi_{n\alpha}^{(1)}\rangle$ etc to the state vectors, and — last but not least — the **zeroth-order terms** $|\psi_{n\alpha}^0\rangle$ in (T15.33). Finding the latter is the most important task, because for small λ they are indeed the dominant contributions to the perturbed states $|\psi_{n\alpha}\rangle$; cf the expansion (T15.33). From this expansion we also note that $|\psi_{n\alpha}^0\rangle$ is the state that the *perturbed* state $|\psi_{n\alpha}\rangle$ approaches when λ goes towards zero. Therefore the g states $|\psi_{n\alpha}^0\rangle$ may be called “**limit states**”. To find these, we first note that (T15.35) gives to zero order in λ

$$(H_0 - E_n^0)|\psi_{n\alpha}^0\rangle = 0, \quad (\text{T15.36})$$

and by taking the adjoint (for later use à la (T15.16))

$$\langle\psi_{n\alpha}^0| H_0 = \langle\psi_{n\alpha}^0| E_n^0; \quad (\alpha = 1, \dots, g). \quad (\text{T15.37})$$

Equation (T15.36) shows that each of the “limit states” satisfies the same unperturbed eigenvalue equation as the g unperturbed eigenstates $|n, r\rangle$ ($r = 1, \dots, g$). This (which

should not come as a surprise) only tells that each of the limit states must be a linear combination of the unperturbed set:

$$\begin{aligned} |\psi_{n\alpha}^0\rangle &= \sum_{r=1}^g c_r |n, r\rangle = \sum_{r=1}^g \langle n, r | \psi_{n\alpha}^0 \rangle |n, r\rangle \\ &\equiv \sum_{r=1}^g U_{r\alpha} |n, r\rangle, \quad (\alpha = 1, \dots, g). \end{aligned} \quad (\text{T15.38})$$

Thus the problem still is not solved; for each α it remains to find the coefficients $U_{r,\alpha}$ ($r = 1, \dots, g$), which decide how the limit state $|\psi_{n\alpha}^0\rangle$ looks.

We take a great leap forward by multiplying the first-order part of (T15.35),

$$(H_0 - E_n^0) |\psi_{n\alpha}^{(1)}\rangle + (V - E_{n\alpha}^{(1)}) |\psi_{n\alpha}^0\rangle = 0, \quad (\text{T15.39})$$

from the left by $\langle \psi_{n\beta}^0 |$ — the dual (or adjoint) of one of the g unknown "limit states". Using the orthonormality of the latter together with (T15.37) we then find that

$$\langle \psi_{n\beta}^0 | \lambda V | \psi_{n\alpha}^0 \rangle = \lambda E_{n\alpha}^{(1)} \delta_{\beta\alpha}. \quad (\text{T15.40})$$

This important formula shows that

$$\begin{aligned} &\text{A property of the linear combinations we are seeking is that} \\ &\text{the matrix } V_{\beta\alpha} \equiv \langle \psi_{n\beta}^0 | V | \psi_{n\alpha}^0 \rangle \text{ is diagonal,} \quad \text{and:} \end{aligned} \quad (\text{T15.41})$$

The diagonal elements are the energy corrections to first order.

Dagonalization and "limit states"

In order to solve the diagonalization problem, we multiply (T15.39) from the left by one of the unperturbed bra vectors, $\langle n, s |$:

$$\begin{aligned} \langle n, s | (V - E_{n\alpha}^{(1)}) \sum_{r=1}^g U_{r\alpha} |n, r\rangle &= 0, \quad \text{or} \\ \sum_r (V_{sr} - E_{n\alpha}^{(1)} \delta_{rs}) U_{r\alpha} &= 0. \end{aligned} \quad (\text{T15.42})$$

Here the matrix elements

$$V_{sr} \equiv \langle n, s | V | n, r \rangle \quad (\text{T15.43})$$

are known; they can be calculated using the unperturbed vectors $|n, r\rangle$.

The set of equations (T15.42) (for $\alpha = 1, \dots, g$) for the unknown coefficients $U_{r\alpha}$ may also be written on matrix form:

$$\begin{pmatrix} V_{11} - E^{(1)} & V_{12} & \cdots & V_{1g} \\ V_{21} & V_{22} - E^{(1)} & \cdots & \cdot \\ \vdots & & & \vdots \\ V_{g1} & \cdots & & V_{gg} - E^{(1)} \end{pmatrix} \begin{pmatrix} U_{1\alpha} \\ U_{2\alpha} \\ \vdots \\ U_{g\alpha} \end{pmatrix} = 0. \quad (\text{T15.44})$$

This set of equations has solutions (for $E^{(1)}$) when the system determinant is equal to zero, that is, when

$$\det \begin{pmatrix} V_{11} - E^{(1)} & \cdots \\ \vdots & \end{pmatrix} = 0, \quad (\text{T15.45})$$

which gives an equation of degree g for the energy correction $E^{(1)}$. The g solutions of this equation are the energy corrections $E_{n\alpha}^{(1)}$, $\alpha = 1, \dots, g$ which we are seeking.

Here we can stop if we are content with finding these energy corrections. If we also want to find the corrections $|\psi_{n\alpha}^{(1)}\rangle$ and $E_{n\alpha}^{(2)}$, then the equation system (T15.44) must be solved consecutively for the g $E^{(1)}$ -values, so that we find $U_{r\alpha}$ and hence the limit vectors

$$|\psi_{n\alpha}^0\rangle = \sum_{r=1}^g U_{r\alpha} |n, r\rangle, \quad (\alpha = 1, \dots, g).$$

Using these vectors, we can calculate $|\psi_{n\alpha}^{(1)}\rangle$ and $E_{n\alpha}^{(2)}$ following the same procedure as in section 2 above.

It is important to understand that the cumbersome diagonalization procedure in many cases can be avoided, if one chooses the unperturbed set of states $|n, r\rangle$ in such a way that $V_{sr} \equiv \langle n, s|V|n, r\rangle$ becomes diagonal already from the outset, that is, in such a way that the perturbation does not “couple” the g states of level number n . Examples showing how this can be done are given in sections 5 and 6 below.

15.5 Hydrogen atom. Spherically symmetric perturbation $\lambda V(r)$

A spherically symmetric perturbation $\lambda V(r)$ of the hydrogen atom, like that discussed qualitatively in section 1, is diagonalized by the “ordinary” unperturbed set $|nlm\rangle$, which corresponds to the unperturbed wavefunctions ψ_{nlm} . This follows because

$$\langle kl'm'|\lambda V(r)|nlm\rangle = \delta_{ll'}\delta_{mm'} \int_0^\infty R_{kl} \lambda V(r) R_{nl} r^2 dr, \quad (\text{T15.46})$$

showing that there is no coupling between states with different l and/or m . According to (T15.40) the energy corrections to lowest order then are

$$\lambda E_{nl}^{(1)} = \int_0^\infty R_{nl}^2 \lambda V(r) r^2 dr. \quad (\text{T15.47})$$

Here we see that the m -degeneracy is kept (because the perturbation does not change the spherical symmetry), while the l -degeneracy is removed (broken), because the perturbation $\lambda V(r)$ removes the pure $1/r$ -form of the Coulomb potential (cf the discussion in section 1). In this case, both H_0 and $H = H_0 + \lambda V(r)$ commute with the angular-momentum operators \mathbf{L}^2 and L_z . We can then search for perturbed eigenstates with well-defined quantum numbers l and m . Let us call these states $|\psi_{nlm}\rangle$. The expansion of such a state in the unperturbed basis $|nlm\rangle$ can only contain vectors $|klm\rangle$ with the chosen values of l and m , that is, one such vector per energy level. Then it should be obvious that we can in this case use the formulae of the non-degenerate case:

$$|\psi_{nlm}\rangle = |nlm\rangle + \sum_{k \neq n} \frac{\langle klm|\lambda V(r)|nlm\rangle}{E_n^0 - E_k^0} |klm\rangle + \dots, \quad (\text{T15.48})$$

$$E_{nl} = E_n^0 + \langle nlm | \lambda V(r) | nlm \rangle + \sum_{k \neq n} \dots \quad (\text{T15.49})$$

Here, the first-order term in the energy is written out more explicitly in (T15.47).

Note that the unperturbed set in this case is *complete* only if one includes also the continuum states $|Elm\rangle$, with $E > 0$, in addition to the bound states $|nlm\rangle$. The sum over k in the formulae above must therefore in this case be interpreted as a sum over bound states together with an integral over the continuous part of the spectrum ($0 < E < \infty$).

15.6 Hydrogen atom in external magnetic field

We take the magnetic field to point in the z -direction. One of the perturbation terms then is due to the coupling between the magnetic field and the magnetic moment corresponding to the orbital angular momentum:

$$\lambda V = -\boldsymbol{\mu} \cdot \mathbf{B} = B \frac{e}{2m_e} L_z.$$

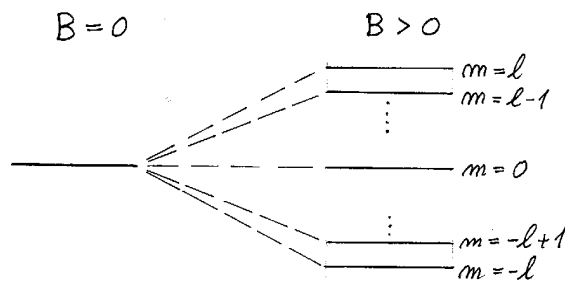
(In this example we neglect the magnetic moment associated with the spin of the electron, for simplicity.) Since $L_z |nlm\rangle = \hbar m |nlm\rangle$, we again get matrix elements which are diagonal with respect to l and m :

$$\langle nl'm' | \lambda V | nlm \rangle = \frac{Be}{2m_e} \langle nl'm' | L_z | nlm \rangle = m \frac{Be\hbar}{2m_e} \delta_{l'l} \delta_{m'm}. \quad (\text{T15.50})$$

Thus the energy corrections are to first order

$$\lambda E_{nlm}^{(1)} = m \frac{Be\hbar}{2m_e}, \quad m = 0, \pm 1, \dots, \pm l.$$

(See the figure.)



Neglecting the spin, we find that the level is split in $2l + 1$ lines.

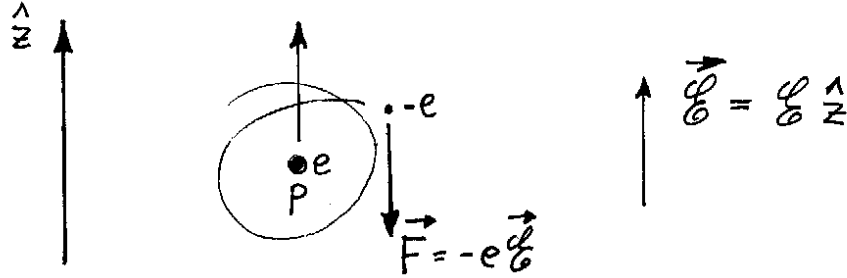
This is the Zeeman splitting for the $2l + 1$ states for a given l (and n). Note that also in this case the perturbation term λV does not “couple” states with different l and/or m . Therefore, we may again use the non-degenerate formalism for higher-order calculations.

What if the magnetic field points instead in the x -direction? In that case, the unperturbed states $|\psi_{nlm}^0\rangle$ will *not* diagonalize the perturbation term $\lambda V = \frac{Be}{2m_e} L_x$, (because these states are eigenstates of L_z , but not of L_x). In this case, the perturbation is diagonalized by the unperturbed eigenstates of H_0, \mathbf{L}^2 and L_x . In the limit $B \rightarrow 0$, the perturbed eigenstates

will in this case approach “limit states” which are certain linear combinations of the set $|nlm\rangle$.

The point we wish to exemplify here is that the symmetry properties of H_0 and of the perturbation term in many cases makes it easy to choose the correct basis set $|\psi_{n\alpha}^0\rangle$ from the beginning.

15.7 Hydrogen atom in electric field. Stark effect



With an electric field in the z -direction, the external force on the electron corresponds to a perturbation term $\lambda V = e\mathcal{E}z$, and a Hamiltonian $H = H_0 + e\mathcal{E}z$. This perturbation removes almost all of the symmetries of the unperturbed system. The only symmetry left is the rotational one with respect to the z -axis.

The Hamiltonian $H = H_0 + e\mathcal{E}z$ commutes with $L_z = xp_y - yp_x$, but not with \mathbf{L}^2 . We can therefore attempt to find perturbed states which are simultaneous eigenstates of H and L_z , with well-defined energy and magnetic quantum number m . Thus the latter is still a so-called “good” quantum number.

We shall consider the first excited level, where we have for $\mathcal{E} = 0$ four unperturbed states $|nlm\rangle$, with energy $E_2^0 = -\frac{1}{2}\alpha^2 m_e c^2 / 4$, for $(nlm) = (200)$, (210) , (211) and $(2, 1, -1)$. For $m = 1$ it is easy: Here we have only one unperturbed state, $|211\rangle$. This must therefore be the “limit state” corresponding to a perturbed state $|\psi_{n=2, m=1}\rangle$. For $n = 2$ and $m = 1$ (and likewise for $m = -1$) we can therefore use the formulae in section 2 [see comment (ii) of that section]:

$$|\psi_{n=2, m=\pm 1}\rangle = |21, \pm 1\rangle + e\mathcal{E} \sum_{k \neq 2} \sum_{l=0}^{k-1} \frac{\langle kl, \pm 1 | z | 21, \pm 1 \rangle}{E_2^0 - E_k^0} |kl, \pm 1\rangle, \quad (\text{T15.51})$$

$$\begin{aligned} E_{n=2, m=\pm 1} &= E_2^0 + e\mathcal{E} \langle 21, \pm 1 | z | 21, \pm 1 \rangle + O(\mathcal{E}^2) \\ &= E_2^0 + O(\mathcal{E}^2). \end{aligned} \quad (\text{T15.52})$$

Here the first-order term in the energy expression vanishes, because the expectation value of z is zero for all parity eigenstates. (ψ_{nlm} has parity $(-1)^l$ and z has parity -1 , cf the discussion in section 3.) Thus the energy correction is of the order of \mathcal{E}^2 and therefore very small (*quadratic Stark effect*), when the “limit state” has a definite parity as in this case.

For the hydrogen atom, this is the case for the ground state and for the maximal and minimal values of m for each principal quantum number n (that is, for $m = \pm(n-1)$).

The Stark effect will also be quadratic for *all* states in *heavier* atoms, because for these there is no l -degeneracy; there is only one state $|nlm\rangle$ with given m for each level E_{nl}^0 .

But let us now concentrate on the hydrogen atom, for which we shall see that also a *linear* Stark effect occurs. We stay at the first excited level, where for $m = 0$ there are *two* unperturbed states, $|200\rangle$ and $|210\rangle$, with the same energy E_2^0 . These two states have opposite parities. A linear combination of them will then not have a definite parity, and will therefore have $\langle z \rangle \neq 0$. If we subject this atom to a weak \mathcal{E} -field, it is then clear that the atom can be in a state with $\langle z \rangle \neq 0$, so that the energy correction $\mathcal{E}^{(1)} \propto \mathcal{E} \langle z \rangle$ becomes linear in \mathcal{E} , if it chooses to be in a state which is a linear combination of $|200\rangle$ and $|210\rangle$. We shall see that this is precisely what comes out of the perturbation formalism: The two *perturbed* states for $m = 0$ have "limit states" which make $\langle z \rangle$ as large (respectively as small (< 0) as possible for a linear combination of $|200\rangle$ and $|210\rangle$.

Let us see how this comes about. We seek to find two perturbed states with $m = 0$,

$$\begin{aligned} |\psi_{n=2,m=0,\alpha}\rangle &\equiv |\psi_{20\alpha}\rangle \\ &= |\psi_{20\alpha}^0\rangle + \mathcal{E}|\psi_{20\alpha}^{(1)}\rangle + \dots, \end{aligned} \quad (\text{T15.53})$$

where the two "limit states" are linear combinations of $|200\rangle$ and $|210\rangle$:

$$|\psi_{20\alpha}^0\rangle = \sum_{l=0}^1 U_{l\alpha} |2l0\rangle. \quad (\text{T15.54})$$

We shall let the two indices $\alpha = +$ and $\alpha = -$ denote the two states.

The first step is to calculate the matrix elements of the perturbation term $\lambda V = e\mathcal{E}z$ in the unperturbed basis (cf lign. (T15.40)). With $z = r \cos \theta$ we find

$$\begin{aligned} V_{l'l} &= e\mathcal{E} \langle 2l'0 | z | 2l0 \rangle \\ &= e\mathcal{E} \int_0^\infty R_{2l'} r R_{2l} r^2 dr \int Y_{l'0}^* \cos \theta Y_{l0} d\Omega. \end{aligned} \quad (\text{T15.55})$$

Here, we have already seen that the diagonal elements disappear (parity argument). The two non-diagonal elements V_{10} and V_{01} (which are equal because V is Hermitian) can be calculated using the formulae

$$\begin{aligned} Y_{00} &= \frac{1}{\sqrt{4\pi}}; & R_{20} &= (8a_B^3)^{-\frac{1}{2}} \left(2 - \frac{r}{a_B}\right) e^{-r/2a_B}, \\ Y_{10} &= \sqrt{\frac{3}{4\pi}} \cos \theta; & R_{21} &= (24a_B^3)^{-\frac{1}{2}} \frac{r}{a_B} e^{-r/2a_B}. \end{aligned}$$

We find

$$\begin{aligned} V_{01} = V_{10} &= e\mathcal{E} \frac{a_B}{32\pi} \int_0^\infty d\left(\frac{r}{a_B}\right) \left[2\left(\frac{r}{a_B}\right)^4 - \left(\frac{r}{a_B}\right)^5\right] e^{-r/a_B} \\ &\times \int_0^{2\pi} d\phi \int_{-1}^1 d(\cos \theta) \cos^2 \theta = -3e\mathcal{E}a_B, \end{aligned}$$

since the first integral is $2 \cdot 4! - 5!$ and the second one is $2\pi \cdot 2/3$. Thus, in the unperturbed basis (the l -basis) the V -matrix has the form

$$V_{ll} = \begin{pmatrix} 0 & -3e\mathcal{E}a_B \\ -3e\mathcal{E}a_B & 0 \end{pmatrix}.$$

Inserting into (T15.45), we can then at once determine the energy corrections to first order: The equation

$$0 = \det \begin{pmatrix} -E^{(1)} & -3e\mathcal{E}a_B \\ -3e\mathcal{E}a_B & -E^{(1)} \end{pmatrix} = [E^{(1)}]^2 - (3e\mathcal{E}a_B)^2$$

gives the two solutions $E_{\pm}^{(1)} = \pm 3e\mathcal{E}a_B$, that is,

$$E_{n=2,m=0,\alpha=\pm} = E_2^0 \pm 3e\mathcal{E}a_B + O(\mathcal{E}^2), \quad (\text{T15.56})$$

and hence a linear Stark effect, as predicted above. (Even this linear splitting is rather small, except for extremely high field strengths.)

Let us go on and determine the coefficients $U_{l\alpha}$, to check that the “limit states” (T15.54) come out as predicted. We must then solve (T15.44), first for $\alpha = +$: Inserting $E_+^{(1)}$ we get

$$-3e\mathcal{E}a_B \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} U_{0+} \\ U_{1+} \end{pmatrix} = 0, \quad \text{that is,}$$

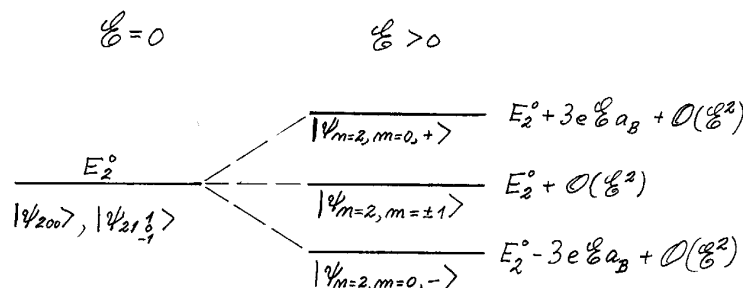
$$U_{0+} = -U_{1+} = 1/\sqrt{2}.$$

For $\alpha = -$ we similarly find that $U_{0+} = U_{1+}$. The “limit states” we are seeking thus are

$$|\psi_{20\pm}^0\rangle \equiv \lim_{\mathcal{E} \rightarrow 0} |\psi_{n=2,m=0,\alpha=\pm}\rangle = \frac{1}{\sqrt{2}} (|200\rangle \mp |210\rangle). \quad (\text{T15.57})$$

It is easy to verify that these are the linear combinations which maximize (respectively minimize) the expectation value of z . (It turns out that $\langle z \rangle = \pm 3a_B$.)

The Stark effect for the first excited level of the hydrogen atom thus becomes as illustrated in the figure:



It can also be verified that due to the rotational symmetry with respect to the z -axis, the two states with $m = 1$ and $m = -1$ have exactly the same energy. This is because the relevant matrix elements are independent of the sign of m . This, then, is what is left of the degeneracy for $n = 2$.