Chapter 8

Perturbation Theory, Zeeman Effect, Stark Effect

Unfortunately, apart from a few simple examples, the Schrödinger equation is generally not exactly solvable and we therefore have to rely upon approximative methods to deal with more realistic situations. Such methods include *perturbation theory*, the *variational method* and the *WKB*[1]*-approximation*. In our Scriptum we, however, just cope with perturbation theory in its simplest version. It is a systematic procedure for obtaining approximate solutions to the unperturbed problem which is assumed to be known exactly.

8.1 Time–Independent Perturbation Theory

The method of perturbation theory is that we deform slightly – perturb – a known Hamiltonian H_0 by a new Hamiltonian H_{I}, some potential responsible for an interaction of the system, and try to solve the Schrödinger equation approximately since, in general, we will be unable to solve it exactly. Thus we start with a Hamiltonian of the following form

$$H \;=\; H_0 \,+\, \lambda\, H_{\mathrm{I}} \quad \text{where} \quad \lambda \,\in\, [0,1]\,, \tag{8.1}$$

where the Hamiltonian H_0 is perturbed by a smaller term, the interaction H_{I} with λ small. The unperturbed Hamiltonian is assumed to be solved and has well-known eigenfunctions and eigenvalues, i.e.

$$H_0 \,\big|\, n^0 \,\big\rangle \;=\; E_{\mathrm{n}}^{(0)} \,\big|\, n^0 \,\big\rangle \;\;, \tag{8.2}$$

where the eigenfunctions are chosen to be normalized

$$\big\langle\, m^0 \,\big|\, n^0 \,\big\rangle \;=\; \delta_{\mathrm{mn}}\,. \tag{8.3}$$

The superscript " ^{0} " denotes the eigenfunctions and eigenvalues of the unperturbed system H_0 , and we furthermore require the unperturbed eigenvalues to be non-degenerate

$$E_{\mathrm{m}}^{(0)} \;\neq\; E_{\mathrm{n}}^{(0)}\,, \tag{8.4}$$

[1], named after Wentzel, Kramers and Brillouin.

otherwise we would use a different method leading to the so-called *degenerate perturbation theory*. What we are now going to investigate are the eigenvalues E_n and eigenfunctions $|\, n \,\rangle$ of the total Hamiltonian H

$$H \,|\, n \,\rangle \;=\; E_\mathrm{n} \,|\, n \,\rangle \;. \tag{8.5}$$

The basic idea of perturbation theory then is to expand the eigenvalues and eigenfunctions in a power series, without taking care of the corresponding convergence properties. In many cases, considering just the first few terms of the power series gives us reasonable results, even if the whole power series can be shown to be divergent.

Let us therefore start with a power series in the parameter λ, which is a good approximation for small λ

$$E_\mathrm{n} \;=\; E_\mathrm{n}^{(0)} \,+\, \lambda\, E_\mathrm{n}^{(1)} \,+\, \lambda^2\, E_\mathrm{n}^{(2)} \,+\, \cdots \tag{8.6}$$

$$|\, n \,\rangle \;=\; \left|\, n^0 \,\right\rangle \,+\, \lambda \left|\, n^1 \,\right\rangle \,+\, \lambda^2 \left|\, n^2 \,\right\rangle \,+\, \cdots \;, \tag{8.7}$$

where we have coefficient functions of lambda, the unperturbed term, first and second order perturbative corrections and so on. Inserting these expansions into the Schrödinger equation (8.5) together with Hamiltonian (8.1), we get

$$\begin{aligned} &(H_0 \,+\, \lambda\, H_\mathrm{I})\, (|\, n^0 \,\rangle \,+\, \lambda \,|\, n^1 \,\rangle \,+\, \lambda^2 \,|\, n^2 \,\rangle \,+\, \cdots) \;= \\ =\; &\left(E_\mathrm{n}^{(0)} \,+\, \lambda\, E_\mathrm{n}^{(1)} \,+\, \lambda^2\, E_\mathrm{n}^{(2)} \,+\, \cdots\right) (|\, n^0 \,\rangle \,+\, \lambda \,|\, n^1 \,\rangle \,+\, \lambda^2 \,|\, n^2 \,\rangle \,+\, \cdots) \;. \end{aligned} \tag{8.8}$$

Equating coefficients we obtain the following relations:

$$\lambda^0 : \qquad H_0 \,|\, n^0 \,\rangle \;=\; E_\mathrm{n}^{(0)} \,|\, n^0 \,\rangle \tag{8.9}$$

$$\lambda^1 : \qquad H_0 \,|\, n^1 \,\rangle \,+\, H_\mathrm{I} \,|\, n^0 \,\rangle \;=\; E_\mathrm{n}^{(0)} \,|\, n^1 \,\rangle \,+\, E_\mathrm{n}^{(1)} \,|\, n^0 \,\rangle \tag{8.10}$$

$$\lambda^2 : \quad H_0 \,|\, n^2 \,\rangle \,+\, H_\mathrm{I} \,|\, n^1 \,\rangle \;=\; E_\mathrm{n}^{(0)} \,|\, n^2 \,\rangle \,+\, E_\mathrm{n}^{(1)} \,|\, n^1 \,\rangle \,+\, E_\mathrm{n}^{(2)} \,|\, n^0 \,\rangle \;. \tag{8.11}$$

Additionally, it is convenient to normalize the following transition amplitude for the perturbed energy eigenstate $|\, n \,\rangle$

$$\left\langle\, n^0 \,|\, n \,\right\rangle \;=\; 1 \tag{8.12}$$

$$\Rightarrow \quad \lambda \left\langle\, n^0 \,\middle|\, n^1 \,\right\rangle \,+\, \lambda^2 \left\langle\, n^0 \,\middle|\, n^2 \,\right\rangle \,+\, \cdots \;=\; 0 \tag{8.13}$$

$$\Rightarrow \quad \left\langle\, n^0 \,\middle|\, n^1 \,\right\rangle \;=\; \left\langle\, n^0 \,\middle|\, n^2 \,\right\rangle \;=\; \cdots \;=\; 0 \;. \tag{8.14}$$

8.1.1 First Order Corrections

To derive the first order corrections we multiply the first order coefficient equation (Eq. 8.10) with $\langle\, n^0 \,|$ from the left and let the hermitian, unperturbed Hamiltonian $H_0^\dagger = H_0$ act to the left on $\langle\, n^0 \,|$

$$E_\mathrm{n}^{(0)} \underbrace{\left\langle\, n^0 \,\middle|\, n^1 \,\right\rangle}_{0} \,+\, \left\langle\, n^0 \,\middle|\, H_\mathrm{I} \,\middle|\, n^0 \,\right\rangle \;=\; E_\mathrm{n}^{(0)} \underbrace{\left\langle\, n^0 \,\middle|\, n^1 \,\right\rangle}_{0} \,+\, E_\mathrm{n}^{(1)} \underbrace{\left\langle\, n^0 \,\middle|\, n^0 \,\right\rangle}_{1} \;. \tag{8.15}$$

This leads us directly to the following fundamental result, which is already a sufficient correction for many cases to reproduce physical observations:

Theorem 8.1 *The perturbative energy corrections of first order are given by the expectation value of the perturbing Hamiltonian in the unperturbed states*

$$E_{\mathrm{n}}^{(1)} = \left\langle n^0 \middle| H_{\mathrm{I}} \middle| n^0 \right\rangle$$

Although we now have the energy correction we are interested in, we are curious as to how the state itself is perturbed. We therefore expand the first order expansion state $|\, n^1 \,\rangle$ into a complete orthonormal system $\{|\, n^0 \,\rangle\}$

$$\left| n^1 \right\rangle = \sum_{m \neq n} \left| m^0 \right\rangle \left\langle m^0 \middle| n^1 \right\rangle \,, \tag{8.16}$$

where all the terms for $m = n$ vanish due to our choice of normalization (Eq. 8.14). We are then interested in the expansion coefficient $\langle\, m^0 \,|\, n^1 \,\rangle$, which we calculate by using again Eq. (8.10). This time, however, we multiply the equation with $\langle\, m^0 \,|$

$$E_{\mathrm{m}}^{(0)} \left\langle m^0 \middle| n^1 \right\rangle + \left\langle m^0 \middle| H_{\mathrm{I}} \middle| n^0 \right\rangle = E_{\mathrm{n}}^{(0)} \left\langle m^0 \middle| n^1 \right\rangle + E_{\mathrm{n}}^{(1)} \left\langle m^0 \middle| n^0 \right\rangle \,. \tag{8.17}$$

Though the last term on the right side of Eq. (8.17) would be nonzero if $m = n$, the state expansion excludes this case in the summation and therefore we can ignore this term, which allows us to express the expansion coefficient as

$$\left\langle m^0 \middle| n^1 \right\rangle = \frac{\langle\, m^0 \,|\, H_{\mathrm{I}} \,|\, n^0 \,\rangle}{E_{\mathrm{n}}^{(0)} - E_{\mathrm{m}}^{(0)}} \,, \tag{8.18}$$

where the matrix element $\langle\, m^0 \,|\, H_{\mathrm{I}} \,|\, n^0 \,\rangle$ has to be calculated.

So the important result for the first order state correction is:

Theorem 8.2 *The perturbative state corrections of first order are given by the superposition of all unperturbed states with energies different from the considered state*

$$\left| n^1 \right\rangle = \sum_{m \neq n} \frac{\left\langle m^0 \middle| H_{\mathrm{I}} \middle| n^0 \right\rangle}{E_{\mathrm{n}}^{(0)} - E_{\mathrm{m}}^{(0)}} \left| m^0 \right\rangle$$

Remark: Due to the energy denominator the adjacent energy levels contribute in this approximation stronger to the corrections of the state (assuming nearly constant matrix elements) than the more remote ones, what is intuitively expected.

8.1.2 Second Order Corrections

To find the corrections of second order, we start similar as in the last subsection, by this time multiplying Eq. (8.11) by $\langle\, n^0 \,|$

$$E_{\mathrm{n}}^{(0)} \underbrace{\left\langle\, n^0 \,\middle|\, n^2 \,\right\rangle}_{0} + \left\langle\, n^0 \,\middle|\, H_{\mathrm{I}} \,\middle|\, n^1 \,\right\rangle = E_{\mathrm{n}}^{(0)} \underbrace{\left\langle\, n^0 \,\middle|\, n^2 \,\right\rangle}_{0} + E_{\mathrm{n}}^{(1)} \underbrace{\left\langle\, n^0 \,\middle|\, n^1 \,\right\rangle}_{0} + E_{\mathrm{n}}^{(2)} \underbrace{\left\langle\, n^0 \,\middle|\, n^0 \,\right\rangle}_{1} \,. \tag{8.19}$$

Further inserting our result of Section 8.1.1 (Theorem 8.2), we get

$$E_{\mathrm{n}}^{(2)} = \sum_{m \neq n} \left\langle\, n^0 \,\middle|\, H_{\mathrm{I}} \,\middle|\, m^0 \,\right\rangle \frac{\langle\, m^0 \,|\, H_{\mathrm{I}} \,|\, n^0 \,\rangle}{E_{\mathrm{n}}^{(0)} - E_{\mathrm{m}}^{(0)}} \,, \tag{8.20}$$

then we immediately find the result for the second order energy correction as:

Theorem 8.3 *The perturbative energy corrections of second order are determined by all unperturbed states with energy different from the considered state*

$$E_{\mathrm{n}}^{(2)} = \sum_{m \neq n} \frac{\left|\left\langle\, m^0 \,\middle|\, H_{\mathrm{I}} \,\middle|\, n^0 \,\right\rangle\right|^2}{E_{\mathrm{n}}^{(0)} - E_{\mathrm{m}}^{(0)}}$$

Remark I: Again, the adjacent energy levels contribute to the majority of the correction if the matrix elements are assumed to be of approximately the same order.

Remark II: For the ground state the energy correction of second order is always negative, i.e. $E_1^{(2)} < 0$, since $E_1^{(0)} < E_{\mathrm{m}}^{(0)}$.

8.2 Zeeman Effect

The energy levels of particles carrying a magnetic dipole moment, e.g. the H-atom, in an exterior (homogeneous) magnetic field are further split up, i.e., the degeneracy of the energy eigenvalues is removed.

The Hamiltonian of the electron in the H-atom therefore has an additional term, the ***Zeeman term*** H_{Z}, perturbing the already known term $H_{\mathrm{Coul.}}$ which contains the Coulomb potential (Eq. 6.95). We thus have the total Hamiltonian

$$H = H_{\mathrm{Coul.}} + H_{\mathrm{Z}} \,, \tag{8.21}$$

where the Zeeman term is the scalar product of the magnetic dipole moment $\vec{\mu}$ and the exterior magnetic field $\vec{B}$, see Eq. (7.4)

$$H_{\mathrm{Z}} = -\,\vec{\mu}\,\vec{B} = -\,\frac{q}{2\,m\,c}\left(\vec{L} + g\,\vec{S}\right)\vec{B} \,. \tag{8.22}$$

We now assume without loss of generality that the magnetic field is oriented along the z-direction, where it has the strength $B^{\text{ext.}}$, and insert the electron mass m_{e}, charge $e = -|e|$ and g-factor $g_{\text{e}} = 2$

$$H_{\text{Z}} = \frac{|e|}{2\, m_{\text{e}}\, c}\, (\, L_{\text{z}} + 2\, S_{\text{z}}\,)\; B^{\text{ext.}} \; . \tag{8.23}$$

We further assume that the magnetic field is sufficiently strong, such that the orbital angular momentum $\vec{L}$ and the spin $\vec{S}$ decouple and the unperturbed states are product states of the form

$$|\, n,\, l,\, m_l \rangle\; |\!\uparrow\rangle \quad \text{and} \quad |\, n,\, l,\, m_l \rangle\; |\!\downarrow\rangle \; , \tag{8.24}$$

which is called the *Paschen–Back Effect*. The (first order) energy corrections $\Delta\, E$ to the pure Coulomb energy are then given by Theorem 8.1, where we immediately see that

$$\Delta\, E^{(1)}_{\text{n},\, l,\, \text{m}_l,\, \text{m}_s} = \frac{|e|\, \hbar}{2\, m_{\text{e}}\, c}\, (\, m_l + \underbrace{2\, m_s}_{\pm 1}\,)\, B^{\text{ext.}} \; . \tag{8.25}$$

Thus every, until now degenerate, l-level is split up by the energy correction term, depending on the spin orientation. When recalling the energy levels of the Coulomb potential (Eq. 6.104)

$$E^{\text{Coul.}}_{\text{n},\, l} = -\, \frac{E_{\text{I}}}{n^2} = -\, \frac{13,6\, eV}{n^2} \, , \tag{8.26}$$

and Bohr's magneton μ_{B}

$$\mu_{\text{B}} = \frac{|e|\, \hbar}{2\, m_{\text{e}}\, c} = 5,788 \times 10^{-5}\, eV \,/\, \text{Tesla} \, , \tag{8.27}$$

we see that the Zeeman energy term is a small correction with respect to the Coulomb energy, even for very strong magnetic fields ($B^{\text{ext.}} \approx$ Tesla).

8.3 Stark Effect

The Stark effect is the electric analogue to the Zeeman effect, i.e., a particle carrying an electric dipole moment, like the H-atom, will get a splitting of its energy levels when subjected to an exterior electric field. The Hamiltonian of the H-atom thus has (another) additional term, the ***Stark term*** H_{Stark}, which is perturbing the Coulomb Hamiltonian

$$H_{\text{Stark}} = -\, \vec{\mathcal{E}}\, \vec{\mu}_{\text{el}} = -\, \underbrace{q}_{-|e|}\, \vec{\mathcal{E}}\, \vec{x} = |e|\, \mathcal{E}\, z \; , \tag{8.28}$$

where $\vec{\mathcal{E}}$ denotes the external electric field which, without loss of generality, we choose along the z-direction, and $\vec{\mu}_{\text{el}}$ is the electrical dipole moment. For the simple case of an electron of charge $-|e|$ placed at a distance $\vec{x}$ of the oppositely charged proton, resting at the origin, the electric dipole moment reduces to $\vec{\mu}_{\text{el}} = -|e|\vec{x}$.

To calculate the energy corrections of first (Theorem 8.1) and second (Theorem 8.3) order , we need to consider expectation values or scalar products of the Stark term in the Coulomb states of the form $|\, n,\, l,\, m_l \,\rangle$. This is, however, more complicated than the situation we studied before. To make the problem more precise, let us calculate the following scalar product, where we already know from Eq. (6.5) that $L_{\rm z}$ and z commute

$$\langle\, n,\, l,\, m_l |\, \underbrace{[\, L_{\rm z}\,,\, z\,]}_{=0}\, |\, n',\, l',\, m_l' \,\rangle \;=\; (m_l \,-\, m_l')\, \langle\, n,\, l,\, m_l |\; z\; |\, n',\, l',\, m_l' \,\rangle \;=\; 0\,. \tag{8.29}$$

Since the commutator of $L_{\rm z}$ and z is zero we can conclude that the states $|\, n,\, l,\, m_l \,\rangle$ and $z\; |\, n',\, l',\, m_l' \,\rangle$ must be orthogonal for $m_l \neq m_l'$, and since we are only interested in nonzero matrix elements we choose

$$m_l \equiv m_l'\,. \tag{8.30}$$

At the same time, however, for the scalar product to be nonzero, we have to require that the azimuthal quantum numbers be unequal, i.e. $l \neq l'$. The reason for this is the parity of the z operator. We remember from Theorem 4.2 that a basis of states can be chosen for a symmetric potential, such as the Coulomb potential (Eq. (6.95)), that consists entirely of even and odd functions, which in this case are the Legendre polynomials $P_l(\cos\theta)$. These are polynomials of order l in $\cos\theta = \frac{z}{r}$ and thus alternately even and odd functions.

Therefore, if the functions $\psi_{\rm n,\, l,\, m_l}$ and $\psi_{\rm n',\, l',\, m_l}$ have the same azimuthal quantum number, i.e. parity, their product has parity $+1$. The z operator however changes its sign under a spatial inversion and the integration of the scalar product vanishes, because

$$\int\limits_{-a}^{+a} dx\; \underbrace{f(x)}_{\rm even}\, \underbrace{g(x)}_{\rm odd} \;\equiv\; 0\,. \tag{8.31}$$

We can then assume that

$$l' \;=\; l \,\pm\, 1\,, \tag{8.32}$$

which is a reasonable choice since the electric dipole interacts with the electric field by exchanging photons of spin 1, so the angular momentum of the electron must decrease or increase by 1. The Stark effect will therefore only occur for matrix elements of the form

$$\langle\, n,\, l,\, m_l |\; z\; |\, n',\, (l \,\pm\, 1),\, m_l \,\rangle \;\neq\; 0\,. \tag{8.33}$$

Let us now consider the energy correction for the ground state of the hydrogen atom, the first order correction is

$$E^{(1)}_{1,\,0,\,0} \;=\; |e|\, \mathcal{E}\; \langle\, 1,\, 0,\, 0 |\; z\; |\, 1,\, 0,\, 0 \,\rangle \;=\; 0\,. \tag{8.34}$$

It vanishes due to the requirement of Eq. (8.32) and we thus see that there is no linear Stark effect for the hydrogen ground state. The effect of second order is of the form

$$E^{(2)}_{1,\,0,\,0} \;=\; e^2\, \mathcal{E}^2 \sum_{n\,=\,2}^{\infty} \frac{|\, \langle\, n,\, 1,\, 0 |\; z\; |\, 1,\, 0,\, 0 \,\rangle\, |^2}{E^{(0)}_1 \;-\; E^{(0)}_n}\,, \tag{8.35}$$

where the unperturbed energy levels $E_n^{(0)}$ are given by Eq. (6.105). This expression can be calculated using perturbative methods, which leads to the result

$$E_{1,\,0,\,0}^{(2)} \;=\; -\,\frac{9}{4}\,\frac{\hbar^2}{m_{\mathrm{e}}\,e^2}\,\mathcal{E}^2 \;=\; -\,\frac{9}{4}\,r_{\mathrm{B}}\,\mathcal{E}^2\;, \tag{8.36}$$

where r_{B} is the Bohr radius (Eq. (6.97)).

The first excited state, in contrast to the ground state, is four-fold degenerate, i.e. there are 4 states $|\,2,\,0,\,0\,\rangle$, $|\,2,\,1,\,1\,\rangle$, $|\,2,\,1,\,0\,\rangle$ and $|\,2,\,1,\,-1\,\rangle$, that belong to the principal quantum number $n = 2$. In this case one has to consider degenerate perturbation theory, which leads to calculating the eigenvalues of a non-diagonal matrix.

Because of the requirement of Eq. (8.30) we only consider elements with equal magnetic quantum number, which is only the case for the states $|\,2,\,0,\,0\,\rangle$ and $|\,2,\,1,\,0\,\rangle$. It leaves us a 2×2 matrix to diagonalize. The second requirement (Eq. (8.32)) rids us of the diagonal elements of the matrix. The remaining nonzero off-diagonal elements are

$$\langle\,2,\,1,\,0\,|\;z\;|\,2,\,0,\,0\,\rangle \;=\; \langle\,2,\,0,\,0\,|\;z\;|\,2,\,1,\,0\,\rangle\;. \tag{8.37}$$

The nonzero eigenvalues can thus be easily calculated and we conclude that the excited state has a linear Stark effect correction with the result

$$E_{2,\,l,\,\mathrm{m}_l}^{(1)} \;=\; \pm\,|e|\,r_{\mathrm{B}}\,\mathcal{E}\;. \tag{8.38}$$

Further splitting of the excited hydrogen energy levels can be seen in Fig. 8.1.

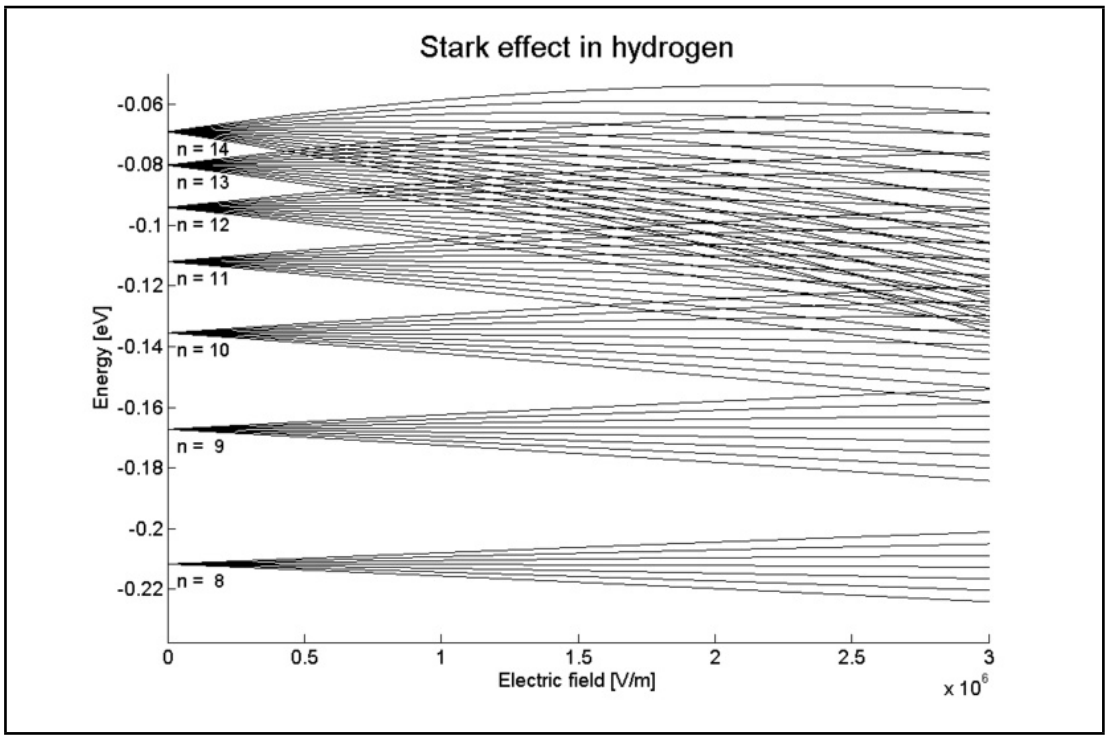

Figure 8.1: Stark Effect in Hydrogen: The until then degenerate excited energy levels are split up if an exterior electric field is applied. Figure from: http://en.wikipedia.org/wiki/Image:Stark_splitting.png