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# Quantum Mechanics II
# Solution Sheet 3

FS 09
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**Exercise 3.1 Degenerate Perturbation Theory III: The Stark Effect**

a) The energy levels of the free hydrogen atom are determined by the electric field of the proton in which the electron moves. The Coulomb field of the proton for average atomic distances, i.e. the Bohr radius $a_0$, is given by

$$|\mathbf{E}_{nucl}| \sim \frac{e}{a_0^2} \sim 5 \cdot 10^9 \,\mathrm{V/cm} \,. \tag{1}$$

Hence, external fields much smaller than $10^9\,\mathrm{V/cm}$, a property that holds for typical strong electric fields accessible in laboratories, can be thought of weakly perturbing the free hydrogen levels.

b) In the basis

$$\big\{\, |2,0,0\rangle, |2,1,+1\rangle, |2,1,0\rangle, |2,1,-1\rangle \big\} \,, \tag{2}$$

the restriction of the perturbation $\delta H$ to the degenerate $n = 2$ subspace is a $4 \times 4$ matrix. In order to determine the first order perturbative corrections, we have to calculate matrix elements of the form

$$eF_0 \langle 2,l,m|\, \hat{\mathbf{z}}\, |2,k,n\rangle \,, \quad (l,k = 0,1 \,;\; m,n = 0,\pm 1) \,, \tag{3}$$

where we have denoted the absolute value of the electric field with $F_0$.

First we note that the operator $\hat{\mathbf{z}}$ is of odd parity. The eigenstates of free hydrogen atom are also states of well defined parity. Therefore, the action of $\hat{\mathbf{z}}$ on a certain state $|2,l,m\rangle$ of parity $\pm 1$, leads to a state of parity $\mp 1$. Because scalar products of states with different parity eigenvalues identically vanish, most of the matrix elements of the form (3) vanish. The states $|2,l,m\rangle$ have parity $(-1)^l$ and therefore, those matrix elements where bra and ket have different parity are

$$eF_0 \langle 2,1,m|\, \hat{\mathbf{z}}\, |2,0,0\rangle \,, \tag{4}$$

together with the hermitian conjugates. Consequently, in the basis (2), the diagonal elements of the perturbation matrix must vanish, which illustrates that if a perturbation leads to a finite first order energy correction, is necessarily mixes the degenerate eigenstates (2).

The perturbation, which is proportional to $\hat{\mathbf{z}}$, obviously commutes with the $z$-component of the angular momentum operator, and therefore cannot mix the eigenstates of (2) which belong to different $z$-projections of the angular momentum:

$$eF_0 \langle 2,1,m \neq 0|\, \hat{\mathbf{z}}\, |2,0,0\rangle \equiv 0 \,, \tag{5}$$

In summary, the only matrix elements that are not constrained to vanish by symmetry are

$$eF_0 \langle 2,1,0|\, \hat{\mathbf{z}}\, |2,0,0\rangle =: M \quad \text{and} \quad eF_0 \langle 2,0,0|\, \hat{\mathbf{z}}\, |2,1,0\rangle =: M^* \,. \tag{6}$$

These matrix elements (denoted by $M$ respectively $M^*$) can be explicitly written as

$$M = eF_0 \int dr\, r^2 \int d\Omega \left( \frac{1}{\sqrt{8a_0^3}} \frac{r}{\sqrt{3}a_0}\, e^{-\frac{r}{2a_0}}\, Y_{1,0}(\theta,\phi) \right)^* z \\ \times \left( \frac{1}{\sqrt{8\pi a_0^3}} \left(1 - \frac{r}{2a_0}\right) e^{-\frac{r}{2a_0}} \right) . \tag{7}$$

With $z = r\cos\theta$ we can further simplify the matrix element (7) by separating the integration in radial and spherical parts:

$$\begin{aligned} M =& eF_0 \int dr\, r^2 \left( \frac{1}{\sqrt{8a_0^3}} \frac{r}{\sqrt{3}a_0} e^{-\frac{r}{2a_0}}\, r\, \frac{1}{\sqrt{8\pi a_0^3}} \left(1 - \frac{r}{2a_0}\right) e^{-\frac{r}{2a_0}} \right) \\ & \times \int d\theta d\phi\, \sin\theta \Big( Y_{1,0}(\theta,\phi) \cos\theta \Big) \\ =& eF_0 \underbrace{\frac{1}{\sqrt{8a_0^3}} \frac{1}{\sqrt{3}a_0} \frac{1}{\sqrt{8\pi a_0^3}}}_{\frac{1}{8a_0^4\sqrt{3\pi}}} \\ & \times \underbrace{\int_0^\infty dr\, r^4\, e^{-\frac{r}{a_0}} \left(1 - \frac{r}{2a_0}\right)}_{-36a_0^5} \\ & \times \underbrace{\int_0^{2\pi} d\phi \int_0^\pi d\theta \left( \sin\theta \sqrt{\frac{3}{4\pi}} \cos\theta\, \cos\theta \right)}_{2\sqrt{\frac{\pi}{3}}} \end{aligned} \tag{8}$$

Finally, we find a compact expression for $M$:

$$M \equiv M^* = -3\, e\, a_0\, F_0 \tag{9}$$

Now, that we know the matrix elements of the perturbation $\delta H$ in degenerate $n = 2$ subspace represented in the basis (2),

$$\begin{pmatrix} 0 & 0 & M & 0 \\ 0 & 0 & 0 & 0 \\ M & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} , \tag{10}$$

we can apply the formalism of degenerate perturbation theory.

The perturbation mixes the states $|2,1,0\rangle$ and $|2,0,0\rangle$. The other states are in first order not affected by the perturbation. We do not want to consider second order and thus only concentrate on the subspace of the two mixed states. The problem reduces to degenerate perturbation theory as considered in exercise 2.1. We first have to find a new basis in which the perturbation is diagonal:

$$|\text{Stark high}\rangle = \frac{1}{\sqrt{2}} \left( |2,1,0\rangle - |2,0,0\rangle \right) \tag{11}$$

$$|\text{Stark low}\rangle = \frac{1}{\sqrt{2}} \left( |2,1,0\rangle + |2,0,0\rangle \right) \tag{12}$$

Then we can proceed with the formula of degenerate perturbation theory that gives the corrections in energy as expectation values of the perturbation. The expectation value of $\delta H$ for the two states (11,12) are

$$\langle \text{Stark high}|\, \delta H\, |\text{Stark high}\rangle = -M\ , \tag{13}$$
$$\langle \text{Stark low}|\, \delta H\, |\text{Stark low}\rangle = +M\ , \tag{14}$$

where $M$ is a negative energy.

In summary, we observe a partial splitting of the degenerate $n = 2$ level of the hydrogen atom in presence of a strong electric field.

In the following table, we sketch the first order Stark effect:

| **State** | | **Energy correction to first order** |
|---|---|---|
| $\|2,1,+1\rangle$ | $\longrightarrow$ | $0$ |
| $\|2,1,-1\rangle$ | $\longrightarrow$ | $0$ |
| $\|\text{Stark high}\rangle$ | $\longrightarrow$ | $3\,e\,a_0\,F_0$ |
| $\|\text{Stark low}\rangle$ | $\longrightarrow$ | $-3\,e\,a_0\,F_0$ |

**Exercise 3.2 Time-Dependent Perturbation of a Two-Level System**

The system is completely determined by the initial setup boundary condition

$$c_1(0) = 1\ , \quad c_2(0) = 0\ , \tag{15}$$

and the first order coupled system of differential equations

$$i\hbar\, \dot{c}_k(t) = \sum_{n=1}^{2} V_{kn}(t)\, e^{i\omega_{kn}t}\, c_n(t)\ , \quad (k = 1, 2)\ . \tag{16}$$

a) We want to show that $|c_1(t)|^2 + |c_2(t)|^2 = 1$ holds for all times. First note that this equality is trivial for $t = 0$, i.e. $c_1(0) = 1$ and $c_2(0) = 0$. Therefore, it remains to be shown that

$$\frac{d}{dt}\left(|c_1(t)|^2 + |c_2(t)|^2\right) = 0\ . \tag{17}$$

Equation (16) determines the time dependence of the coefficients $c_i(t)$ as follows:

$$\dot{c}_1(t) = \frac{\gamma}{i\hbar} e^{i(\omega-\omega_{21})t}\, c_2(t) \tag{18}$$
$$\dot{c}_2(t) = \frac{\gamma}{i\hbar} e^{-i(\omega-\omega_{21})t}\, c_1(t) \tag{19}$$

We find

$$\begin{aligned}
\frac{d}{dt}\left(|c_1(t)|^2 + |c_2(t)|^2\right) &= c_1^*(t)\dot{c}_1(t) + \dot{c}_1^*(t)c_1(t) + c_2^*(t)\dot{c}_2(t) + \dot{c}_2^*(t)c_1(t) \\
&= c_1^*(t)\frac{\gamma}{i\hbar} e^{i(\omega-\omega_{21})t}\, c_2(t) + \frac{\gamma}{-i\hbar} e^{-i(\omega-\omega_{21})t}\, c_2^*(t)c_1(t) \\
&\quad + c_2^*(t)\frac{\gamma}{i\hbar} e^{-i(\omega-\omega_{21})t}\, c_1(t) + \frac{\gamma}{-i\hbar} e^{i(\omega-\omega_{21})t}\, c_1(t)^* c_2(t) \\
&= 0\ .
\end{aligned} \tag{20}$$

b) From part a) we know that, $|c_2(t)|^2 = 1 - |c_1(t)|^2$. Hence, we solve only for $c_1(t)$. We start with taking another time derivative of the differential equation (16).

$$i\hbar\ddot{c}_1(t) = \gamma e^{i(\omega-\omega_{21})t}\left(i(\omega-\omega_{21})c_2(t) + \dot{c}_2(t)\right) \tag{21}$$

Now we can eliminate $c_2$ and $\dot{c}_2$ from equation (21) by use of (16).

$$\ddot{c}_1(t) - i(\omega-\omega_{21})\dot{c}_1(t) + \frac{\gamma^2}{\hbar^2}c_1(t) = 0 \tag{22}$$

This differential equation of second order is solved by the following ansatz:

$$c_1(t) \longmapsto e^{i\Omega t} \tag{23}$$

With this we find for $\Omega$:

$$\begin{aligned} &\Omega^2 - \Omega(\omega-\omega_{21}) - \frac{\gamma^2}{\hbar^2} = 0 \\ \Rightarrow \quad &\Omega_\pm = \frac{\omega-\omega_{21}}{2} \pm \sqrt{\left(\frac{\omega-\omega_{21}}{2}\right)^2 + \frac{\gamma^2}{\hbar^2}} \end{aligned} \tag{24}$$

The general solution for $c_1(t)$ is then given by a linear superposition of the two special solutions with $\Omega_\pm$:

$$c_1(t) = \alpha\, e^{i\Omega_+ t} + \beta\, e^{i\Omega_- t} \tag{25}$$

Making use of the boundary condition (15), we can determine $\alpha$ and $\beta$ as

$$c_1(0) = 1 \quad \Rightarrow \quad \alpha + \beta = 1 \tag{26}$$

$$c_2(0) = 0 \quad \Rightarrow \quad \dot{c}_1(0) = 0 \tag{27}$$

$$\Rightarrow \quad 0 = \alpha\Omega_+ + \beta\Omega_- = \frac{\omega-\omega_{21}}{2} + (\alpha-\beta)\sqrt{\left(\frac{\omega-\omega_{21}}{2}\right)^2 + \frac{\gamma^2}{\hbar^2}} \tag{28}$$

$$\Rightarrow \quad \alpha = \frac{1}{2}\left(1 - \frac{\frac{\omega-\omega_{21}}{2}}{\sqrt{\left(\frac{\omega-\omega_{21}}{2}\right)^2 + \frac{\gamma^2}{\hbar^2}}}\right) \tag{29}$$

$$\Rightarrow \quad \beta = \frac{1}{2}\left(1 + \frac{\frac{\omega-\omega_{21}}{2}}{\sqrt{\left(\frac{\omega-\omega_{21}}{2}\right)^2 + \frac{\gamma^2}{\hbar^2}}}\right) \tag{30}$$

To simplify notation, we can introduce

$$\overline{\Omega} = \frac{\omega-\omega_{21}}{2}\,, \tag{31}$$

$$\delta = \sqrt{\overline{\Omega}^2 + \frac{\gamma^2}{\hbar^2}}\,. \tag{32}$$

With this, we end up with

$$\begin{aligned} c_1(t) &= e^{i\overline{\Omega}t}\left\{\frac{1}{2}\left(e^{i\delta t} + e^{-i\delta t}\right) - \frac{\overline{\Omega}}{\delta}\frac{1}{2}\left(e^{i\delta t} - e^{-i\delta t}\right)\right\} \\ &= e^{i\overline{\Omega}t}\left\{\cos(\delta t) - i\frac{\overline{\Omega}}{\delta}\sin(\delta t)\right\}\,. \end{aligned} \tag{33}$$

The modulus is then given by

$$\begin{aligned} |c_1(t)|^2 &= \cos^2(\delta t) + \frac{\overline{\Omega}}{\delta}\sin^2(\delta t) \\ &= 1 - \frac{\delta^2 - \overline{\Omega}^2}{\delta^2}\sin^2(\delta t)\ , \end{aligned} \tag{34}$$

and with part a)

$$|c_2(t)|^2 = \frac{\delta^2 - \overline{\Omega}^2}{\delta^2}\sin^2(\delta t)\ . \tag{35}$$

We find that the system, although at $t = 0$ completely in state $|1\rangle$, harmonically oscillates between the two states with an oscillation amplitude that is determined by the coefficients $\omega, \omega_{21}$ and $\gamma$. In the case of $\omega = \omega_{21}$, i.e. $\overline{\Omega} = 0$, at the times $t = k\,\frac{\hbar\pi}{2\gamma}$, $k \in \mathbb{N}$, the state $|1\rangle$ is completely depleted and the system is entirely in state $|2\rangle$.

c) In case of the discrete two-level system we consider in this exercise, the population coefficients of the states $|1\rangle$ and $|2\rangle$ are given by the expansion

$$c_k(t) = c_k^{(0)} + c_k^{(1)}(t) + c_k^{(2)}(t) + \dots\ , \quad (k = 1, 2)\ . \tag{36}$$

The zeroth order contribution is given by $c_k^{(0)} = \delta_{ki}$, if the system is set up at $t = 0$ in state $|i\rangle$. In this part of the exercise we derive the first order contribution $c_k^{(1)}(t)$, given by the equation

$$c_k^{(1)}(t) = \frac{-i}{\hbar}\int_0^t dt'\, e^{i\omega_{ki}t'} V_{ki}(t')\ , \tag{37}$$

where $|\psi(t = 0)\rangle = |i\rangle$ is used.

Considering the boundary conditions (15) together with $V_{11} = 0$, we immediately find

$$c_1^{(1)}(t) = 0\ . \tag{38}$$

For $c_2^{(1)}(t)$ we derive

$$\begin{aligned} c_2^{(1)}(t) =& -\frac{i}{\hbar}\int_0^t dt'\, V_{21}(t')e^{i\omega_{21}t'} \\ =& -i\frac{\gamma}{\hbar}\int_0^t dt'\, e^{-i(\omega-\omega_{21})t'} \\ =& \frac{\gamma}{\hbar(\omega-\omega_{21})}\left(e^{-i(\omega-\omega_{21})t} - 1\right) \\ =& -\frac{2i\gamma}{\hbar(\omega-\omega_{21})}\, e^{-i\frac{\omega-\omega_{21}}{2}t}\, \sin\left(\frac{\omega-\omega_{21}}{2}t\right) \end{aligned} \tag{39}$$

Hence, the modulus $|c_2(t)|^2$ is given to first order by

$$|c_2^{(0)} + c_2^{(1)}(t)|^2 = \frac{4\gamma^2}{\hbar^2(\omega-\omega_{21})^2}\sin^2\left(\frac{\omega-\omega_{21}}{2}t\right)\ . \tag{40}$$

d) Considering the system within first order perturbation theory corresponds to an expansion in powers of the perturbation which has the amplitude $\gamma$. In order to make perturbation theory reasonable, $\gamma$ is assumed to be much smaller than the energy difference of the two states. Because the leading order correction for $c_1(t)$ vanishes, we discuss only the comparison of the exact and perturbative solution for $c_2(t)$. It is trivial to note that the exact solution does not equal the perturbative approach which yields $c_1^{(0)} + c_1^{(1)}(t) \equiv 1$. Note that this result is not a contradiction to the result of part a), which corresponds to conservation of the probability or if one wants the conservation of particle number. The perturbative approach up to first order *in* $\gamma$ yields that $|c_2^{(0)} + c_2^{(1)}(t)|^2$ is proportional to $\gamma^2$. If one considers the equation $|c_1(t)|^2 + |c_2(t)|^2 = 1$ within perturbation theory, one must restrict the analysis to the order of perturbation theory applied, linear order in $\gamma$ in our case. Hence, $|c_1(t)|^2 + |c_2(t)|^2 = 1$, with $|c_1(t)|^2 = 1 + \mathcal{O}(\gamma^2)$ and $|c_2(t)|^2 = \mathcal{O}(\gamma^2)$, is fulfilled within a perturbative sense.

(i) We consider here the case $\gamma/\hbar \ll |\omega - \omega_{21}|/2$. In order to compare the perturbative approach with the exact solution, we consider the a first order expansion of the exact solution, which corresponds to a second order expansion of its modulus, with the result (40). Eq. (33), expanded to first order in $\gamma$ yields for $|c_2(t)|^2$ a value of

$$\frac{4\gamma^2}{\hbar^2(\omega - \omega_{21})^2} \sin^2\left(\frac{\omega - \omega_{21}}{2} t\right) . \tag{41}$$

This expression exactly equals the first order perturbative correction $|c_2^{(1)}(t)|^2$!

(ii) Now we assume $\omega$ to be very close to $\omega_{21}$, such that the difference is much smaller than $\gamma/\hbar$. If we then expand Eq. (35) in terms of $\overline{\Omega} = (\omega - \omega_{21})/2$, we find that the exact solution reduces to

$$|c_2(t)|^2 \approx \sin^2(\frac{\gamma t}{\hbar}) , \tag{42}$$

while the first order approximation yields in this limit

$$|c_2(t)|^2 \approx \frac{\gamma^2}{\hbar^2} t^2 . \tag{43}$$

For very short times, the perturbative approach yields reasonable results. But, as time goes on, the two approaches differ qualitatively. As the exact solution still shows oscillations in time, the perturbative approach only yields a quadratic growth of the population of state $|2\rangle$.

From the exact solution we know that for $\omega = \omega_{21}$ the system oscillates completely between the two states and even when set up entirely in state $|1\rangle$, after some time it will be found *exactly* in state $|2\rangle$. In this sense, the perturbation is not at all a *small* disturbance of the unperturbed system even for small $\gamma$. Here we have observed the appearance of a resonance. Resonances in general have to be considered very carefully, as we have found here, even for arbitrary weak coupling $\gamma$, the resonance invalidates the perturbative approach.