Time-Independent Perturbation Theory

➢ <u>Review: The Non-Degenerated Case</u>

- Perturbation theory is a very powerful tool used to solve problems in theoretical physics. It is used to find approximative solutions in cases where an exact solution is not possible.

- Assume that we know the exact solution of the original problem

$$\hat{H}_0|n\rangle = \epsilon_n|n\rangle.$$

- Let's assume the new Hamiltonian operator is given by

$$\hat{H} = \hat{H}_0 + \hat{V}.$$

perturbing potential!

- This means we are looking for the solution of

$$\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle.$$

- We assume that the perturbing potential $\hat{V}$ is small.

Time-Independent Perturbation Theory

➢ <u>Review: The Non-Degenerated Case</u>

- We often approximate

$$E_n \approx \epsilon_n + \langle n|\hat{V}|n\rangle + \sum_{m\neq n} \frac{\left|\langle n|\hat{V}|m\rangle\right|^2}{\epsilon_n - \epsilon_m}$$

Second-order perturbation theory!

$$|\psi_n\rangle \approx |n\rangle + \sum_{m\neq n} \frac{\langle m|\hat{V}|n\rangle}{\epsilon_n - \epsilon_m}|m\rangle.$$

First-order perturbation theory!

- This means we go up to second-order in the energy and up to first order in the states.

- Note: everything we have done so far is only valid if

$$\epsilon_n \neq \epsilon_m \qquad \text{for} \qquad n \neq m.$$

Time-Independent Perturbation Theory

- <u>Degenerate Perturbation Theory</u>
  - Assume that $N \geq 2$ states have the same (unperturbed) ϵ so that

$$\hat{H}_0 \big|\alpha\big\rangle = \epsilon \big|\alpha\big\rangle, \qquad \alpha = 1, 2, \ldots, N.$$

  - The $\big|\alpha\big\rangle$ are the <u>degenerate states</u> and ϵ the corresponding energies.
  - In the following we are only interested in <u>first-order</u> corrections.
  - What we have used before is

$$\big|\psi_n\big\rangle = \big|n\big\rangle + \big|\psi_n^{(1)}\big\rangle = \big|n\big\rangle + \lambda \sum_{m \neq n} a_{nm}^{(1)} \big|m\big\rangle$$

and

$$E_n = \epsilon_n + \lambda E_n^{(1)}.$$

  - Furthermore

this does not work anymore!

$$a_{nm}^{(1)} = \frac{\langle m | \hat{V} | n \rangle}{\epsilon_n - \epsilon_m} \quad \text{for} \quad n \neq m.$$

Time-Independent Perturbation Theory

- <u>Degenerate Perturbation Theory</u>

  - Let's do the following

$$|\psi\rangle = \underbrace{\sum_{\alpha=1}^{N} c_\alpha |\alpha\rangle}_{\text{all states with same energy contribute}} + \underbrace{\lambda \sum_{\alpha=1}^{N} a_\alpha^{(1)} |\alpha\rangle + \lambda \sum_{m\neq\alpha} a_m^{(1)} |m\rangle}_{\text{as before, but we split the sum}}.$$

This notation means sum over all non-degenerate states

  - For energy we use

$$E = \epsilon + \lambda E^{(1)}.$$

  - Schrödinger's equation is

$$(\hat{H}_0 + \lambda \hat{V})|\psi\rangle = E|\psi\rangle.$$

  - Therein we now use our two expansions and keep terms in lowest and first order in λ.

Time-Independent Perturbation Theory

➢ <u>Degenerate Perturbation Theory</u>

- We find

$$\left(\hat{H}_0 + \lambda\hat{V}\right)\left[\sum_{\alpha=1}^{N} c_\alpha|\alpha\rangle + \lambda\sum_{\alpha=1}^{N} a_\alpha^{(1)}|\alpha\rangle + \lambda\sum_{m\neq\alpha} a_m^{(1)}|m\rangle\right]$$

$$= \quad \left(\epsilon + \lambda E^{(1)}\right)\left[\sum_{\alpha=1}^{N} c_\alpha|\alpha\rangle + \lambda\sum_{\alpha=1}^{N} a_\alpha^{(1)}|\alpha\rangle + \lambda\sum_{m\neq\alpha} a_m^{(1)}|m\rangle\right].$$

- Up to first order this becomes

use eigenvalue equation

$$\cancel{\sum_{\alpha=1}^{N} c_\alpha\hat{H}_0|\alpha\rangle} + \lambda\sum_{\alpha=1}^{N} c_\alpha\hat{V}|\alpha\rangle + \lambda\cancel{\sum_{\alpha=1}^{N} a_\alpha^{(1)}\hat{H}_0|\alpha\rangle} + \lambda\sum_{m\neq\alpha} a_m^{(1)}\hat{H}_0|m\rangle$$

$$= \quad \epsilon\cancel{\sum_{\alpha=1}^{N} c_\alpha|\alpha\rangle} + \lambda\epsilon\sum_{m\neq\alpha} a_m^{(1)}|m\rangle + \lambda\epsilon\cancel{\sum_{\alpha=1}^{N} a_\alpha^{(1)}|\alpha\rangle} + \lambda E^{(1)}\sum_{\alpha=1}^{N} c_\alpha|\alpha\rangle.$$

Time-Independent Perturbation Theory

➢ Degenerate Perturbation Theory

- After using the eigenvalue equation and cancelling the λ, we find

$$\sum_{\alpha=1}^{N} c_\alpha \hat{V}\big|\alpha\big\rangle + \sum_{m\neq\alpha} a_m^{(1)}\epsilon_m\big|m\big\rangle = \epsilon \sum_{m\neq\alpha} a_m^{(1)}\big|m\big\rangle + E^{(1)}\sum_{\alpha=1}^{N} c_\alpha\big|\alpha\big\rangle.$$

- We now multiply this from the left with one of the degenerate states, namely $\big\langle\beta\big|$.

- Note, we have

$$\big\langle\beta\big|m\big\rangle = 0 \qquad \text{if} \qquad m\neq\beta.$$

- We get

$$\sum_{\alpha=1}^{N} c_\alpha \big\langle\beta\big|\hat{V}\big|\alpha\big\rangle = E^{(1)}\sum_{\alpha=1}^{N} c_\alpha \big\langle\beta\big|\alpha\big\rangle = E^{(1)}c_\beta.$$

Time-Independent Perturbation Theory

➢ <u>Degenerate Perturbation Theory</u>

- We found

$$\sum_{\alpha=1}^{N} c_\alpha \langle \beta | \hat{V} | \alpha \rangle = E^{(1)} \sum_{\alpha=1}^{N} c_\alpha \langle \beta | \alpha \rangle = E^{(1)} c_\beta .$$

- We can write this as the a matrix equation of the form

$$V c = E^{(1)} c.$$

matrix of the potential operator

- From this we obtain the eigenvectors *c* and eigenvalues $E^{(1)}$.

- We find the corrections

$$E_\gamma \approx \epsilon + E_\gamma^{(1)} \qquad \text{and} \qquad |\psi_\gamma\rangle \approx \sum_{\alpha=1}^{N} c_\alpha^{(\gamma)} |\alpha\rangle .$$

eigenvalue with number γ

α-component of eigenvector with number γ

Time-Independent Perturbation Theory

- A Simple Example
  - We consider a case where the quantum system has only two unperturbed states so that

    $$\hat{H}_0|1\rangle = \epsilon_1|1\rangle \qquad \text{and} \qquad \hat{H}_0|2\rangle = \epsilon_2|2\rangle.$$

  - We now add a perturbing potential so that the new Hamiltonian is

    $$\hat{H} = \hat{H}_0 + \hat{V}.$$

  - The corresponding Schrödinger equation can be written as

    $$\left(\hat{H}_0 + \hat{V}\right)|\psi_n\rangle = E_n|\psi_n\rangle.$$

  - In the following we only determine the (perturbed) energy eigenvalues E_n and don't care about the states.
  - The perturbed states can be expanded via

    $$|\psi_n\rangle = \alpha|1\rangle + \beta|2\rangle.$$

Time-Independent Perturbation Theory

➢ <u>A Simple Example</u>

- Therewith, Schrödinger's equation can be written as

$$(\hat{H}_0 + \hat{V})(\alpha|1\rangle + \beta|2\rangle) = E_n(\alpha|1\rangle + \beta|2\rangle).$$

- Multiplying this from the left by $\langle 1|$ yields

$$\alpha\epsilon_1 + \alpha\langle 1|\hat{V}|1\rangle + \beta\langle 1|\hat{V}|2\rangle = E\alpha.$$

- Furthermore, we can multiply the equation above from the left with $\langle 2|$ to obtain

$$\beta\epsilon_2 + \alpha\langle 2|\hat{V}|1\rangle + \beta\langle 2|\hat{V}|2\rangle = E\beta.$$

- To continue we use the notation

$$V_{nm} = \langle n|\hat{V}|m\rangle.$$

matrix elements of the perturbing potential operator

Time-Independent Perturbation Theory

➢ <u>A Simple Example</u>

- Furthermore, our two equations can be written as the following matrix equation

$$\begin{pmatrix} \epsilon_1 - E + V_{11} & V_{12} \\ V_{12}^* & \epsilon_2 - E + V_{22} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = 0.$$

- Furthermore, we consider a potential so that $V_{11}=V_{22}=0$.
- Non-trivial solutions are obtained if the determinant of the above matrix is zero. Therefore, we find

$$\left(\epsilon_1 - E\right)\left(\epsilon_2 - E\right) - \left|V_{12}\right|^2 = 0.$$

- This can easily be written as

$$E^2 - E\left(\epsilon_1 + \epsilon_2\right) + \epsilon_1\epsilon_2 - \left|V_{12}\right|^2 = 0.$$

Time-Independent Perturbation Theory

➢ A Simple Example

- This quadratic equation has the solutions

$$\begin{aligned} E &= \frac{1}{2}(\epsilon_1+\epsilon_2) \pm \frac{1}{2}\sqrt{(\epsilon_1+\epsilon_2)^2 + 4|V_{12}|^2 - 4\epsilon_1\epsilon_2} \\ &= \frac{1}{2}(\epsilon_1+\epsilon_2) \pm \frac{1}{2}\sqrt{(\epsilon_1-\epsilon_2)^2 + 4|V_{12}|^2}. \end{aligned}$$

- Note, we looked at a very special case but our result for the energy is exact.
- In the following we look at the non-degenerated case meaning that we assume $\epsilon_1 \neq \epsilon_2$.
- In this case we can write

$$E = \frac{1}{2}(\epsilon_1+\epsilon_2) \pm \frac{1}{2}(\epsilon_1-\epsilon_2)\sqrt{1+\lambda} \quad \text{with} \quad \lambda = \frac{4|V_{12}|^2}{(\epsilon_1-\epsilon_2)^2}.$$

Time-Independent Perturbation Theory

➢ A Simple Example

- To continue we assume that λ is small and we Taylor-expand our result to find

$$\begin{aligned} E &= \frac{1}{2}(\epsilon_1+\epsilon_2) \pm \frac{1}{2}(\epsilon_1-\epsilon_2)\sqrt{1+\lambda} \\ &\approx \frac{1}{2}(\epsilon_1+\epsilon_2) \pm \frac{1}{2}(\epsilon_1-\epsilon_2)\left(1+\frac{1}{2}\lambda\right) \\ &= \frac{1}{2}(\epsilon_1+\epsilon_2) \pm \frac{1}{2}(\epsilon_1-\epsilon_2)\left(1+\frac{2|V_{12}|^2}{(\epsilon_1-\epsilon_2)^2}\right). \end{aligned}$$

- From this we can easily read off

$$E_1 = \epsilon_1 + \frac{|V_{12}|^2}{\epsilon_1-\epsilon_2} \qquad \text{and} \qquad E_2 = \epsilon_2 - \frac{|V_{12}|^2}{\epsilon_1-\epsilon_2}.$$

Time-Independent Perturbation Theory

- A Simple Example
  - We found

$$E_1 = \epsilon_1 + \frac{|V_{12}|^2}{\epsilon_1 - \epsilon_2} \qquad \text{and} \qquad E_2 = \epsilon_2 - \frac{|V_{12}|^2}{\epsilon_1 - \epsilon_2}.$$

  - Compare this with non-degenerated perturbation theory

$$E_n \approx \epsilon_n + \langle n|\hat{V}|n\rangle + \sum_{m\neq n} \frac{\left|\langle n|\hat{V}|m\rangle\right|^2}{\epsilon_n - \epsilon_m}.$$

  - We can easily see that the two results are the same.
  - What about the degenerate case where we have $\epsilon_1=\epsilon_2$?
  - We derived the exact result

$$E = \frac{1}{2}(\epsilon_1 + \epsilon_2) \pm \frac{1}{2}\sqrt{(\epsilon_1 - \epsilon_2)^2 + 4|V_{12}|^2}.$$

Time-Independent Perturbation Theory

- A Simple Example

  - For ϵ_1=ϵ_2, corresponding to the dengenerate case, our formula

    $$E = \frac{1}{2}\left(\epsilon_1 + \epsilon_2\right) \pm \frac{1}{2}\sqrt{\left(\epsilon_1 - \epsilon_2\right)^2 + 4\left|V_{12}\right|^2}$$

    simplifies to

    $$E = \epsilon \pm \left|V_{12}\right|.$$

  - For the degenerated case we derived in first order perturbation theory

    $$Vc = E^{(1)}c.$$

  - Note, here we have used the matrix V of the perturbing potential with respect to the unperturbed states.

  - $E^{(1)}$ corresponds to the first order energy corrections.

Time-Independent Perturbation Theory

- <u>A Simple Example</u>
  - We can write the matrix equation out and make the same assumptions concerning V as above.
  - We find

$$\begin{pmatrix} -E^{(1)} & V_{12} \\ V_{12}^{*} & -E^{(1)} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = 0.$$

  - Setting the determinant equal to zero gives us

$$E^{(1)} = \pm \left| V_{12} \right|.$$

  - Therefore, the corresponding (corrected) energy eigenvalues are

$$E = \epsilon \pm \left| V_{12} \right|$$

in agreement with the exact result derived above.

Time-Independent Perturbation Theory

- The Stark Effect
  - This is an application of perturbation theory.
  - The effect is named after physicist Johannes Stark who received the Nobel Prize of Physics in 1919.
  - Consider the effect of an external electric field on the energy levels of a hydrogen-like atom.
  - The unperturbed Hamiltonian operator is given by

$$\hat{H}_0 = -\frac{\hbar^2}{2\mu}\Delta - \frac{Ze^2}{4\pi\epsilon_0 r}.$$

Coulomb potential in *SI units*.

  - The perturbing potential is in our case

$$\hat{V} = eEz.$$

  - Here we assumed that the electric field is constant and points into the *z*-direction.

Time-Independent Perturbation Theory

- The Stark Effect
  - We start our investigations by considering the ground state and use first-order perturbation theory.
  - The unperturbed energy eigenvalues are

$$\epsilon_n = -\frac{1}{2}\mu c^2 \frac{Z^2\alpha^2}{n^2} \qquad \text{with} \qquad n = 1, 2, 3, \ldots .$$

  - Remember

$$n = n_r + \ell + 1 \quad \text{with} \quad n_r = 0, 1, 2, \ldots \quad \text{and} \quad \ell = 0, 1, 2, \ldots .$$

  - For $n=1$ (ground state) we have

$$n_r = 0 \qquad \text{and} \qquad \ell = 0.$$

  - This also means that $m=0$.

Time-Independent Perturbation Theory

- The Stark Effect
  - We conclude that we obtain the ground state for only one set of quantum numbers, namely

$$n = 1, \qquad \ell = 0, \qquad \text{and} \qquad m = 0.$$

  - Therefore, the ground state is not degenerate.
  - In the considered case we find in first-order perturbation theory

$$E_n^{(1)} = \langle n|\hat{V}|n\rangle = \langle 100|\hat{V}|100\rangle.$$

quantum numbers are *n*=1, *ℓ*=0, *m*=0.

  - In the following we evaluate this in position space

$$E_{100}^{(1)} = eE \int d^3r\, z \left|\Psi_{100}(\vec{r})\right|^2.$$

  - For central potential problems such as the Coulomb potential we had

$$\Psi_{n\ell m}(\vec{r}) = R_{n\ell}(r) Y_{\ell m}(\Theta, \Phi).$$

spherical harmonics

Time-Independent Perturbation Theory

➢ The Stark Effect

- In our case we only need

$$\Psi_{100}(\vec{r}) = R_{10}(r)Y_{00}(\Theta, \Phi) = \frac{1}{\sqrt{4\pi}} R_{10}(r).$$

- Using this in our integral yields

$$E_{100}^{(1)} = \frac{eE}{4\pi} \int d^3r \; zR_{10}^2(r) = \frac{eE}{4\pi} \int d^3r \; r\cos\Theta R_{10}^2(r).$$

- The Φ–integral gives 2π and the Θ-integral is

$$\int_{-1}^{+1} d\cos\Theta \;\; \cos\Theta = 0.$$

- Therefore we find

$$E_{100}^{(1)} = 0.$$

- There is no effect in first-order perturbation theory!

Time-Independent Perturbation Theory

➢ The Stark Effect

- To find an effect we need to perform second-order perturbation theory.
- The corresponding energy eigenvalues are now computed via

$$E_n^{(2)} = \sum_{m \neq n} \frac{\left|\langle n|\hat{V}|m\rangle\right|^2}{\epsilon_n - \epsilon_m}.$$

- Again we consider the effect on the ground state and, thus, we need

$$E_{100}^{(2)} = \sum_{m \neq n} \frac{\left|\langle 100|\hat{V}|m\rangle\right|^2}{\epsilon_{100} - \epsilon_m} = e^2 E^2 \sum_{m \neq n} \frac{\left|\langle 100|\hat{z}|m\rangle\right|^2}{\epsilon_1 - \epsilon_m}.$$

- This means we need to compute the matrix elements

$$\langle n\ell m|\hat{z}|100\rangle = \int d^3r \; \Psi_{100}(\vec{r}) z \Psi^*_{n\ell m}(\vec{r}).$$

Time-Independent Perturbation Theory

- The Stark Effect

  - We need to evaluate

$$\langle n\ell m|\hat{z}|100\rangle = \int d^3r\ \Psi_{100}(\vec{r})\, z\, \Psi^*_{n\ell m}(\vec{r}).$$

  - Therein we use

$$\Psi_{100}(\vec{r}) = R_{10}(r) Y_{00} = \frac{1}{\sqrt{4\pi}} R_{10}(r).$$

  - Furthermore, we employ

$$z = r\cos\Theta = \sqrt{\frac{4\pi}{3}}\, r Y_{10}.$$

  - Therewith our integral turns into

$$\langle n\ell m|\hat{z}|100\rangle = \frac{1}{\sqrt{3}} \int d^3r\ R_{10}(r) R_{n\ell}(r)\, r Y_{10}(\Theta,\Phi) Y^*_{\ell m}(\Theta,\Phi).$$

Time-Independent Perturbation Theory

- <u>The Stark Effect</u>
  - To simplify this we use the <u>orthogonality relation</u> for the spherical harmonics

$$\int d\Omega \, Y_{10}(\Theta,\Phi) Y^*_{\ell m}(\Theta,\Phi) = \delta_{\ell 1}\delta_{m0}.$$

  - Using this in our integral yields

We need only ℓ=1.

$$\langle n\ell m|\hat{z}|100\rangle = \frac{1}{\sqrt{3}}\delta_{\ell 1}\delta_{m0}\int_0^\infty dr\, r^3 R_{10}(r) R_{n\ell}(r).$$

  - Because of the two Kronecker deltas therein we find

$$E^{(2)}_{100} = \sum_{m\neq 1}\frac{\left|\langle 100|\hat{V}|m\rangle\right|^2}{\epsilon_1-\epsilon_m} = \sum_{n\neq 1}\frac{\left|\langle 100|\hat{V}|n10\rangle\right|^2}{\epsilon_1-\epsilon_n}.$$

Time-Independent Perturbation Theory

- <u>The Stark Effect</u>
  - We found

$$E_{100}^{(2)} = \sum_{m\neq 1} \frac{\left|\langle 100|\hat{V}|m\rangle\right|^2}{\epsilon_1 - \epsilon_m} = \sum_{n\neq 1} \frac{\left|\langle 100|\hat{V}|n10\rangle\right|^2}{\epsilon_1 - \epsilon_n}.$$

  - Therein we have

$$\langle n10|\hat{z}|100\rangle = \frac{1}{\sqrt{3}} \int_0^\infty dr\; r^3 R_{10}(r) R_{n1}(r).$$

Consider only contributions with *n*=2.

  - Furthermore, we use <u>another approximation</u>, namely

$$E_{100}^{(2)} = \sum_{n\neq 1} \frac{\left|\langle 100|\hat{V}|n10\rangle\right|^2}{\epsilon_1 - \epsilon_n} \approx \frac{\left|\langle 100|\hat{V}|210\rangle\right|^2}{\epsilon_1 - \epsilon_2}.$$

  - Note, this is an additional approximation usually **<u>not</u>** used in perturbation theory.

Time-Independent Perturbation Theory

➢ The Stark Effect

- We derived before

$$\langle n10|\hat{z}|100\rangle = \frac{1}{\sqrt{3}}\int_0^\infty dr\, r^3 R_{10}(r) R_{n1}(r).$$

- We now compute

$$\langle 210|\hat{z}|100\rangle = \frac{1}{\sqrt{3}}\int_0^\infty dr\, r^3 R_{10}(r) R_{21}(r).$$

- The two needed radial functions can be looked up:

$$R_{10}(r) = 2\left(\frac{Z}{a_B}\right)^{3/2} e^{-Zr/a_B},$$

$$R_{21}(r) = \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_B}\right)^{3/2} \frac{Zr}{a_B} e^{-Zr/(2a_B)}.$$

Time-Independent Perturbation Theory

- <u>The Stark Effect</u>
  - Therewith our integral becomes

$$\langle 210|\hat{z}|100\rangle = \frac{1}{3\sqrt{2}}\left(\frac{Z}{a_B}\right)^4 \int_0^\infty dr\, r^4 e^{-3Zr/(2a_B)}.$$

  - We need to evaluate an integral of the form

$$\begin{aligned}
\int_0^\infty dr\, r^n e^{-\alpha r} &= (-1)^n \frac{d^n}{d\alpha^n} \int_0^\infty dr\, e^{-\alpha r} \\
&= (-1)^n \frac{d^n}{d\alpha^n} \left[\frac{1}{-\alpha} e^{-\alpha r}\right]_0^\infty \\
&= (-1)^n \frac{d^n}{d\alpha^n} \alpha^{-1} \\
&= \frac{n!}{\alpha^{n+1}}.
\end{aligned}$$

Time-Independent Perturbation Theory

➢ <u>The Stark Effect</u>

- In our case we have $n=4$ and $\alpha=(3Z)/(2a_B)$.
- Therefore, we obtain

$$\int_0^\infty dr\, r^4 e^{-3Zr/(2a_B)} = 4!\left(\frac{3Z}{2a_B}\right)^{-5} = 24\left(\frac{2a_B}{3Z}\right)^5 .$$

- Using this in our formula for the matrix element yields

$$\langle 210|\hat{z}|100\rangle = \frac{1}{3\sqrt{2}}\left(\frac{Z}{a_B}\right)^4 \int_0^\infty dr\, r^4 e^{-3Zr/(2a_B)} = \frac{2^7}{3^5}\sqrt{2}\frac{a_B}{Z}.$$

- Therewith, the second-order energy corrections become

$$E_{100}^{(2)} \approx \frac{\left|\langle 210|\hat{V}|100\rangle\right|^2}{\epsilon_1 - \epsilon_2} = \frac{(eE)^2}{\epsilon_1 - \epsilon_2}\left(\frac{a_B}{Z}\right)^2 \frac{2^{15}}{3^{10}}.$$

Time-Independent Perturbation Theory

- The Stark Effect
  - We also need to consider the difference of the two unperturbed energy values.
  - We found for the unperturbed energies

$$\epsilon_n = -\frac{1}{2}\mu c^2 \frac{Z^2\alpha^2}{n^2} \qquad \text{with} \qquad n = 1, 2, 3, \ldots .$$

  - Using this for our case yields

$$\epsilon_1 - \epsilon_2 = -\frac{1}{2}\mu c^2 Z^2 \alpha^2 \left(1 - \frac{1}{4}\right) = -\frac{3}{8}\mu c^2 Z^2 \alpha^2 .$$

  - Therewith the <u>second-order energy corrections</u> become for *Z=1*

$$E_{100}^{(2)} \approx -\frac{8}{3}\frac{e^2 E^2 a_B^2}{\mu c^2 \alpha^2}\frac{2^{15}}{3^{10}} .$$

Time-Independent Perturbation Theory

- <u>The Stark Effect</u>

  - For the fine-structure constant we can use

$$\alpha = \frac{1}{4\pi\epsilon_0}\frac{e^2}{\hbar c} \qquad \text{and} \qquad \alpha = \frac{\hbar}{\mu c a_B}.$$

  - By multiplying these two formulas with each other we can easily derive (in *SI units*)

$$\alpha^2 = \frac{e^2}{4\pi\epsilon_0 c^2 a_B \mu}.$$

  - Using this in our formula to replace the fine-structure constant yields

$$E_{100}^{(2)} \approx -\frac{8}{3}\frac{e^2 E^2 a_B^2}{\mu c^2 \alpha^2}\frac{2^{15}}{3^{10}} = -\frac{2^{18}}{3^{11}} 4\pi\epsilon_0 E^2 a_B^3 \qquad \text{(SI units)}.$$

Time-Independent Perturbation Theory

- <u>The Stark Effect</u>
  - This can be written as

$$E_{100}^{(2)} \approx -1.48 \cdot 4\pi\epsilon_0 \cdot E^2 \cdot a_B^3.$$

  - This result was obtained by taking into account only the state $|210\rangle$.
  - Taking into account all bound states gives

$$E_{100}^{(2)} \approx -\frac{9}{4} \cdot 4\pi\epsilon_0 \cdot E^2 \cdot a_B^3.$$

  - In both cases we have

$$E_{100}^{(2)} \propto E^2.$$

  - Therefore, we call this the <u>quadratic Stark effect!</u>