The atom in electric field

- The electric field in the direction of the Oz axis
- The interaction with the electric field

$$H_E = \mathcal{E} \sum_i z_i$$

- We assume, it is stronger than the spin-orbit interaction (valid for E>10^5 V/m

- For the hydrogen atom – the energy levels are degenerate (except the ground state)
- For the ground state the first-order perturbation correction is

$$E_E = \mathcal{E} \langle 1s | z | 1s \rangle$$

- Because z is an uneven function, this integral is 0

- **More general reasoning:**

$$z = r\cos\theta = \frac{2}{\sqrt{3}} Y_{10}(\theta)$$

- **The orbital part of the integral:**

$$\int d\hat{\mathbf{r}} Y_{00}^{*}(\hat{\mathbf{r}}) Y_{10}(\hat{\mathbf{r}}) Y_{00}(\hat{\mathbf{r}}) = 0.$$

- **Because**

$$\int Y_{l_a m_a}^{*}(\hat{\mathbf{r}}) Y_{l_b m_b}(\hat{\mathbf{r}}) Y_{l_c m_c}(\hat{\mathbf{r}}) d\hat{\mathbf{r}} = \sqrt{\frac{(2l_b+1)(2l_c+1)}{4\pi(2l_a+1)}} C_{l_b 0 l_c 0}^{l_a 0} C_{l_b m_b l_c m_c}^{l_a m_a}$$

- **The first-order perturbation correction for the ground state is 0, there is no linear Stark effect**

- The excited states are n^2-fold degenerate in respect with l and m_l
- We apply the perturbation method for n=2

$$\begin{vmatrix} H_{ss}-E_E & H_{sp0} & H_{sp+1} & H_{sp-1} \\ H_{p0s} & H_{p0p0}-E_E & H_{p0p+1} & H_{p0p-1} \\ H_{p+1s} & H_{p+1p0} & H_{p+1p+1}-E_E & H_{p+1p-1} \\ H_{p-1s} & H_{p-1p0} & H_{p-1p+1} & H_{p-1p-1}-E_E \end{vmatrix} = 0$$

- Here

$$\begin{aligned} H_{ss} &= \langle 2s|H_E|2s\rangle \\ H_{spm_l} &= \langle 2s|H_E|2p_{m_l}\rangle \\ H_{pm_lpm_l'} &= \langle 2p_{m_l}|H_E|2p_{m_l'}\rangle . \end{aligned}$$

- All matrix elements are zero, except that between 2s and $2p_0$

$$
\begin{aligned}
H_{sp0} &= \langle 2s|H_E|2p_0\rangle = \langle 2p_0|H_E|2s\rangle \\
&= \mathcal{E}\frac{2}{\sqrt{3}}\int d\hat{\mathbf{r}}Y_{00}^*(\hat{\mathbf{r}})Y_{10}(\hat{\mathbf{r}})Y_{10}(\hat{\mathbf{r}})\int_0^\infty drr^3R_{2s}(r)R_{2p}(r) \\
&= -\frac{3}{Z}\mathcal{E}, \qquad (
\end{aligned}
$$

- **The equation becomes**

$$
\begin{vmatrix}
-E_E & H_{sp0} & 0 & 0 \\
H_{sp0} & -E_E & 0 & 0 \\
0 & 0 & -E_E & 0 \\
0 & 0 & 0 & -E_E
\end{vmatrix} = 0
$$

- The solutions are

$$E_E(\pm 1) = 0$$ for $m_l = +1$ and -1

$$E_E(0)_{1,2} = \pm H_{sp0} = \mp \frac{3}{Z}\mathcal{E}$$ for $m_l = 0$

The wavefunctions are

$$\psi_1 = \frac{1}{\sqrt{2}}(2s - 2p_0)$$

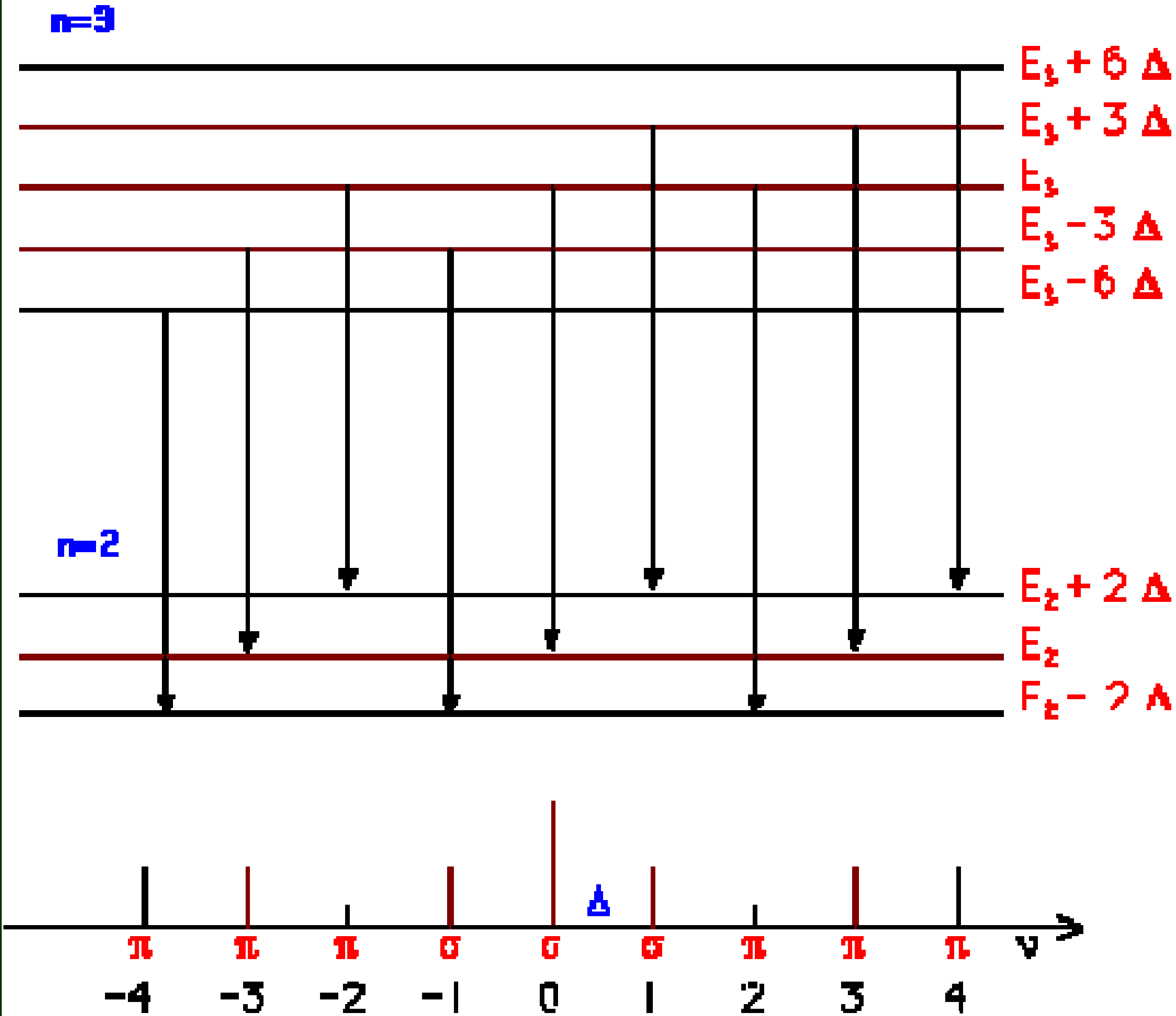
for the higher energy level, and

$$\psi_2 = \frac{1}{\sqrt{2}}(2s + 2p_0)$$

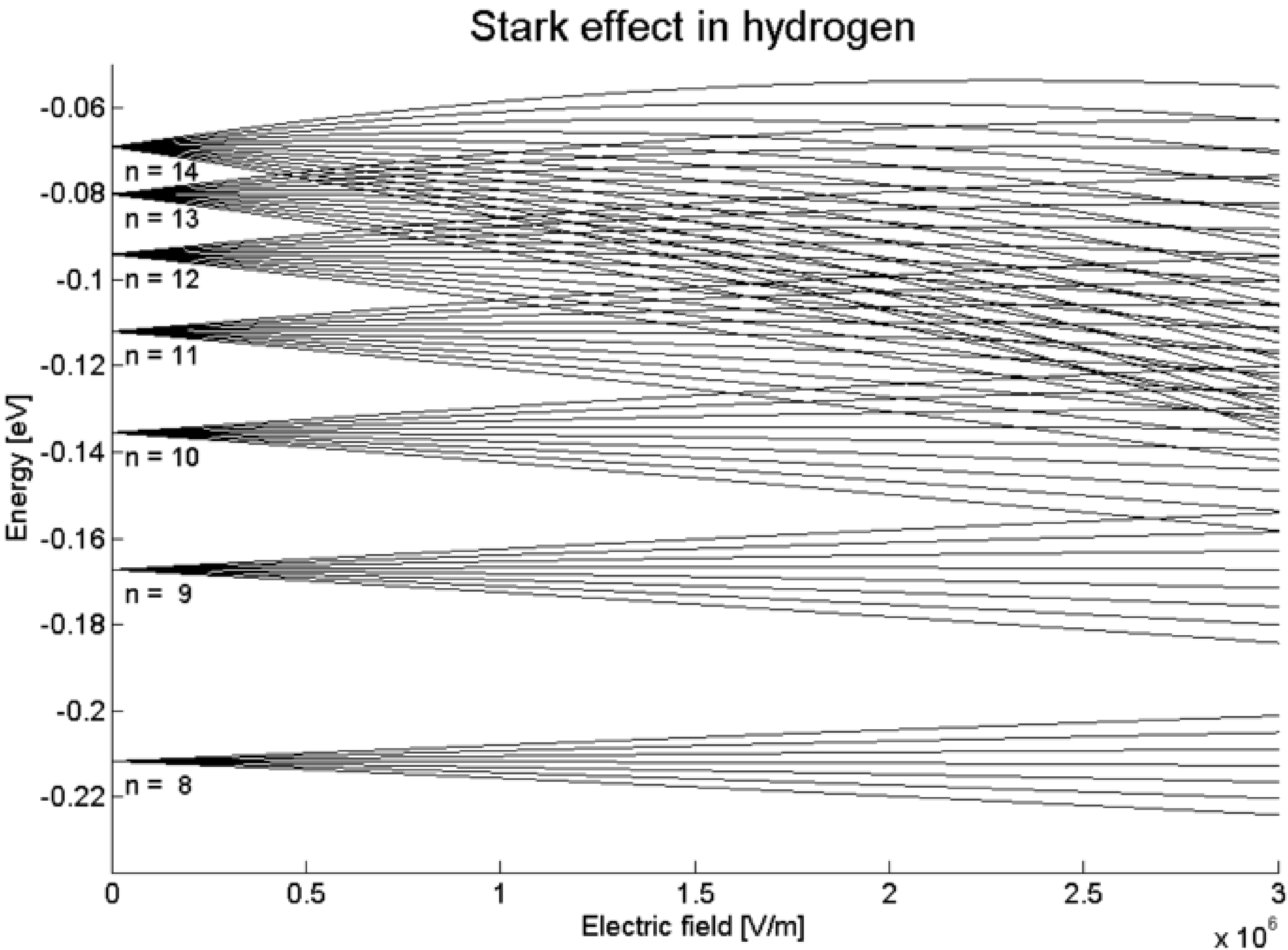
for the lower energy level.

- For n=2 we have the linear Stark effect (proportional with E), because this degenerate level has not a specific parity

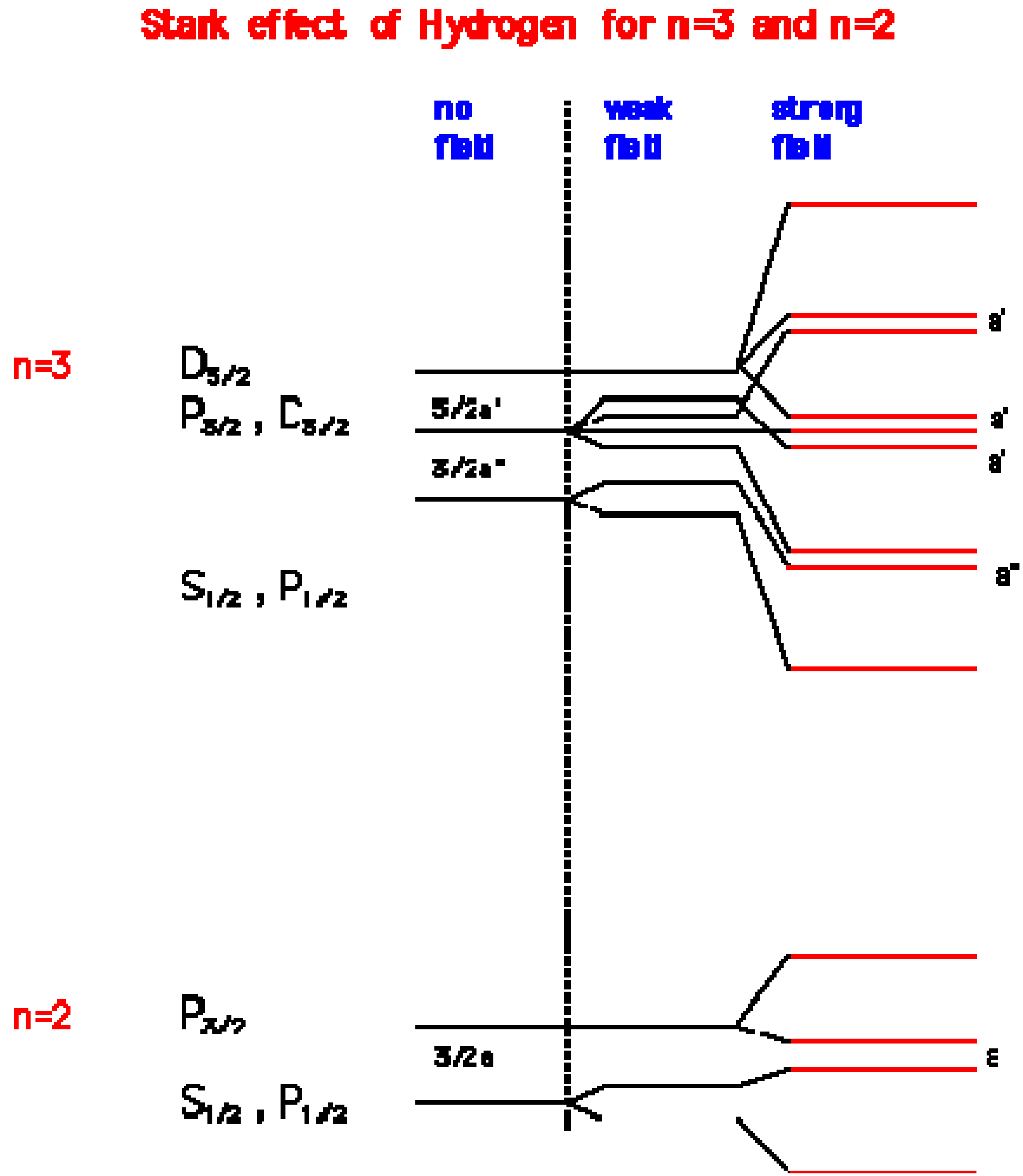
Energy term diagram for the linear Stark effect



Higher energy levels



Taking into account the spin-orbit splitting



- **For the ground state we calculate the second-order perturbation correction**

$$E_E^{(2)} = \sum_{n\neq 1,l,m} \frac{|\langle \psi_{nlm}|H_E|1s\rangle|^2}{E_1 - E_n}$$
$$= \mathcal{E}^2 \sum_{n\neq 1,l,m} \frac{|\langle \psi_{nlm}|z|1s\rangle|^2}{E_1 - E_n},$$

- **Replacing En by E2 we obtain the upper limit (in absolute value) of the correction**

$$E_E^{(2)} > \mathcal{E}^2 \frac{1}{E_1 - E_2} \sum_{n\neq 1,l,m} |\langle \psi_{nlm}|z|1s\rangle|^2$$

- **Taking into account that** $\langle 1s|z|1s\rangle = 0$

$$
\begin{aligned}
\sum_{n\neq 1,l,m} |\langle \psi_{nlm}|z|1s\rangle|^2 &= \sum_{n,l,m} |\langle \psi_{nlm}|z|1s\rangle|^2 \\
&= \sum_{n,l,m} \langle 1s|z|\psi_{nlm}\rangle\langle \psi_{nlm}|z|1s\rangle \\
&= \langle 1s|z^2|1s\rangle,
\end{aligned}
$$

- **Where we have used the closure relationship**

$$\sum_{n,l,m} |\psi_{nlm}\rangle\langle\psi_{nlm}| = 1$$

- **The matrix element can be calculated analytically**

$$\langle 1s|z^2|1s\rangle = \frac{1}{Z^2}$$

- With $E_1 = -Z^2/2$ and $E_2 = -Z^2/8$

we obtain

$$E_E^{(2)} > -\frac{8}{3}\frac{\mathcal{E}^2}{Z^4}$$

The exact solution leads to

$$E_E^{(2)} = -2,25\frac{\mathcal{E}^2}{Z^4}$$

This correction is the quadratic Stark effect

Multielectron atoms

- We introduce $$D_z = -\sum_i z_i$$

the z component of the electric dipole .

The $$H_E = \mathcal{E} \sum_i z_i$$ perturbation leads to

$$E_E^{(1)} = -\mathcal{E} \langle kLSJM_J | D_z | kLSJM_J \rangle$$

The unperturbed energy levels are not degenerated in respect with L,

the $|kLSJM_J\rangle$ states have a certain parity.

- Because the dipole operator has odd parity, all the matrix elements will be zero.

$$E_E^{(1)} = 0,$$

- For multielectron atoms there is not linear Stark effect
- The quadratic Stark effect (second-order perturbation correction):

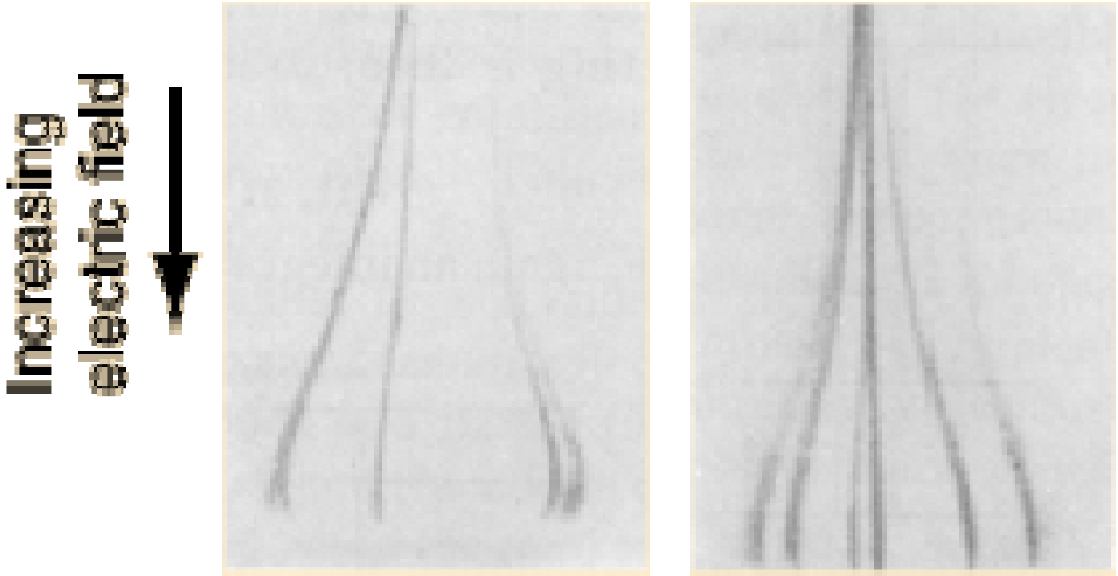
$$E_E^{(2)} = \mathcal{E}^2 \sum{}'_{k'L'S'J'M'_J} \frac{|\langle kLSJM_J|D_z|k'L'S'J'M'_J\rangle|^2}{E_{kLSJ} - E_{k'L'S'J'}}$$

- After some calculations one obtains

$$E_E^{(2)} = \mathcal{E}^2(a + bM_J^2)$$

- The degeneracy is only partly removed

Stark effect splitting of the helium transition at 438.8 nm.



Light polarized parallel to field

Light polarized perpendicular to electric field

Foster, J. S., J. Frank. Inst. 209, 585, (1930)

- **The multielectron atoms has no electric dipole momentum, and this is the reason why they show no linear Stark effect.**
- **The quadratic Stark effect may be interpreted as the induction of the dipole momentum by the external electric field, and the interaction of the induced momentum with this field.**
- **The hydrogen atom behaves, as if it would have electric dipole momentum.**