

External fields: the Zeeman and Stark effects

So far only internal magnetic fields in the atoms were discussed.

In this chapter we discuss the role of external magnetic and electric fields.

Effects of magnetic fields on optical spectra:

- splitting.

Weak fields – normal and anomalous Zeeman effects.

Strong fields - Paschen Back effect,

Cont.

- Normal Zeeman effect-can be explained by classical theory – without spin.
- Anomalous Zeeman effect – due to spin – pure quantum mechanical effect.

The normal Zeeman effect

- Appears only in spinless atoms.
- Recall: The total atomic spin:

$$S = \sum_{i=1}^N s_i$$

- Odd # of electrons – S will be different from 0.
- 2 valence electrons can be parallel or antiparallel. $S = 1/2 \oplus 1/2$ Can be 0 or 1.
- Ground state of the second Coloumn (Be, Mg, Ca) has a ground state with $S=0$.

The dipole is due to orbital angular momentum only.

- The proportionality constant – the gyromagnetic ratio. $\mu_B/\hbar = e/2m_e$

$$\mu = -\frac{\mu_B}{\hbar} L$$

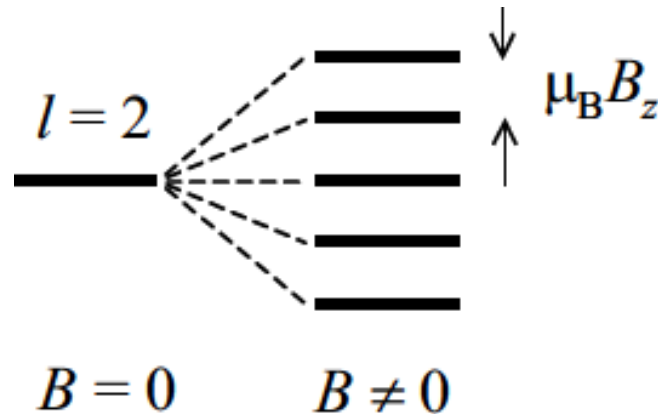
- Interaction energy with the magnetic field:

$$\Delta E = -\mu \cdot B$$

- Traditionally Z is the direction of the field.
- The interaction energy is: $\Delta E = -\mu_z B_z = \mu_B B_z m_l$
 - removing the degeneracy of m_l which is called the magnetic quantum number.

The splitting of an m_l state

- With $l=2$:



- We have seen selection rules of $\Delta m_l = 0$ or ± 1 and get the frequencies:

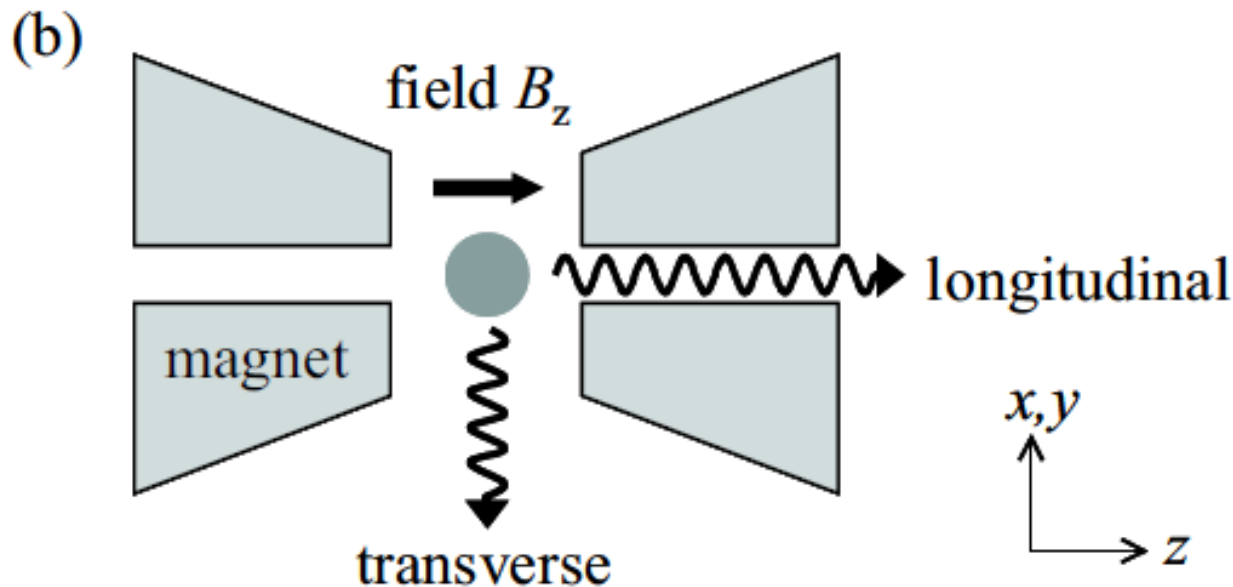
$$h\nu = h\nu_0 + \mu_B B_z \quad \Delta m_l = -1$$

$$h\nu = h\nu_0 \quad \Delta m_l = 0,$$

$$h\nu = h\nu_0 - \mu_B B_z \quad \Delta m_l = +1$$

Optical polarization:

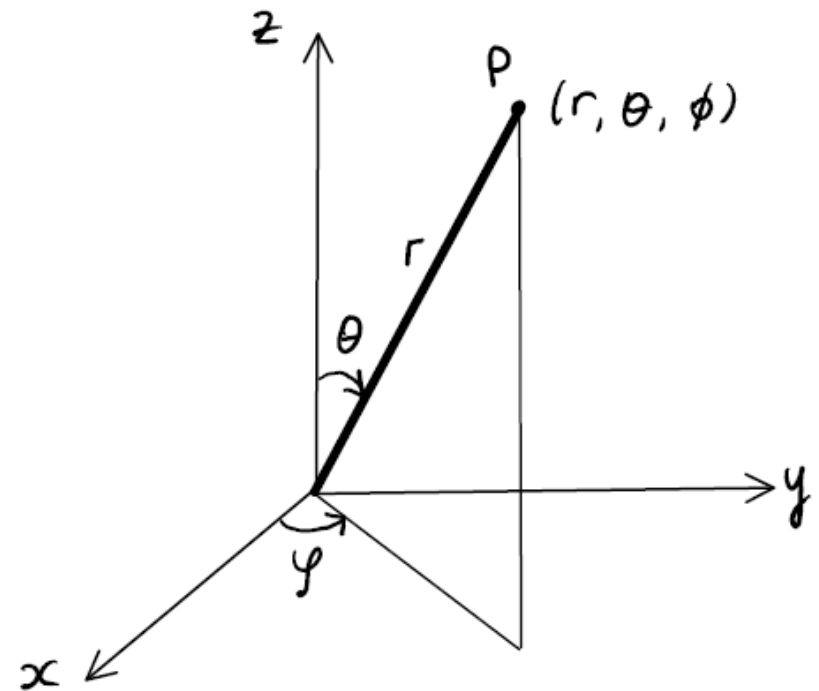
- **Recall:** we have the selection rules:
 $\Delta m_l = 0$ or ± 1
- This depends on the orientation of the direction of propagation with respect to the magnetic field.



Recall:

- The spherical harmonics:

l	m	$Y_{l,m}(\theta, \phi)$
0	0	$\sqrt{\frac{1}{4\pi}}$
1	0	$\sqrt{\frac{3}{4\pi}} \cos \theta$
1	± 1	$\mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi}$
2	0	$\sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$
2	± 1	$\mp \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{\pm i\phi}$
2	± 2	$\sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{\pm 2i\phi}$



Cont.

Recall (for x): $M_{12} \propto \int \psi_1 x \psi_2 d^3r$

Thus ψ_1 and ψ_2 must have a different parity.

- **The orbital quantum number l:** Parity of spherical harmonics: $(-1)^l$.
- Δl has to be odd. Actually the rule is: $\Delta l = \pm 1$.
Can be observed performing the matrix element calculation. **Recall:** Angular momentum of photon can be $\pm \hbar$ (light with circular polarization).
- Thus absorption and emission of photons can be only if $\Delta l = \pm 1$

The magnetic quantum # m :

- **Recall:** The dipole moment of the transition:

$$M_{12} \propto \int_{r=0}^{\infty} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \Psi_{n',l',m'}^* r \Psi_{n,l,m} r^2 \sin \theta \, dr d\theta d\phi$$

- Consider the Φ part alone:

- $$M_{12} \propto \int_0^{2\pi} e^{-im'\phi} r e^{im\phi} d\phi$$

- **Recall:**

- For z polarized light: $z = r \cos \theta$. $m' = m$

$$M_{12} \propto \int_0^{2\pi} e^{-im'\phi} z e^{im\phi} d\phi \propto \int_0^{2\pi} e^{-im'\phi} \cdot 1 \cdot e^{im\phi} d\phi,$$

The other dipole moments:

Light polarized in the x and y directions:

$$M_{12} \propto \int_0^{2\pi} e^{-im'\phi} x e^{im\phi} d\phi \propto \int_0^{2\pi} e^{-im'\phi} \cdot e^{\pm i\phi} \cdot e^{im\phi} d\phi$$

Recall $x = r \sin \theta \cos \phi = r \sin \theta \frac{1}{2} (e^{+i\phi} + e^{-i\phi})$,

M_{12} will not be 0 if: $m' - m = \pm 1$.

Similar for y

The electric and magnetic fields are perpendicular to the direction of polarization

- In the longitudinal case, the electric or magnetic fields are perpendicular and only circularly polarized transitions, σ^+ and σ^- are available. $\Delta m_l = \pm 1$

In the transverse case, there are electric and magnetic fields also in the z direction and all three lines are available.

The anomalous Zeeman effect

- Observed in atoms with non zero spin. – atoms with odd # of electrons.
- In the LS coupling we observe a total angular momentum J .

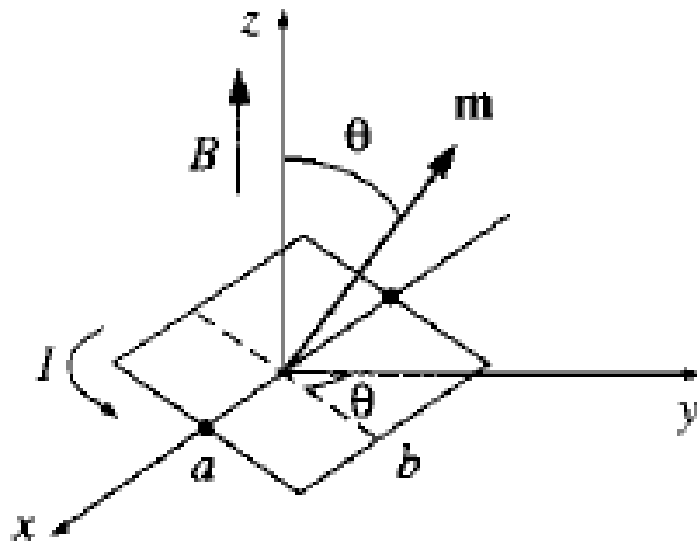
$$J = L + S$$

- **Recall:** Vectorial definition of torque: $\tau = r \times F$
 - Parallel to the axis of rotation. and
- $\Sigma \tau = dl/dt$.
- One can write: $dl/dt = r \times F$.

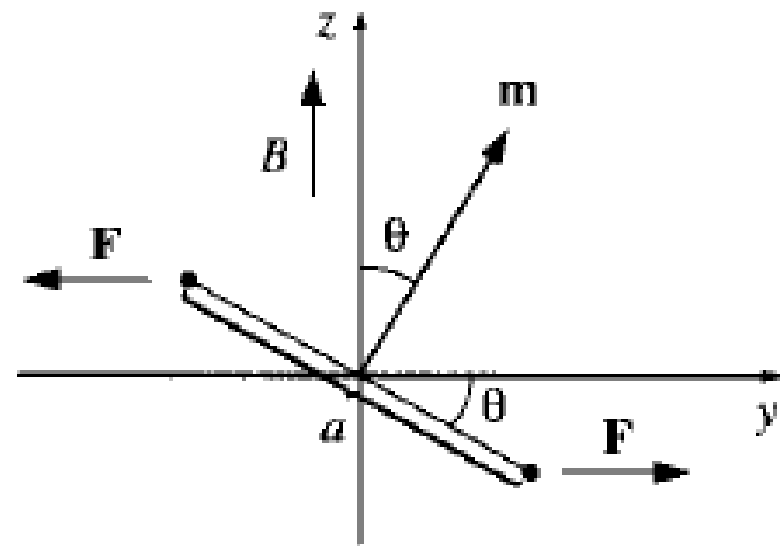
The change in angular momentum – perpendicular to both F and r .

Force on static magnetic dipole:

- Tends to align the magnetic dipole with the field.



(a)



(b)

The Larmor precession.

- When the moment is due to angular momentum – we observe a different scenario:

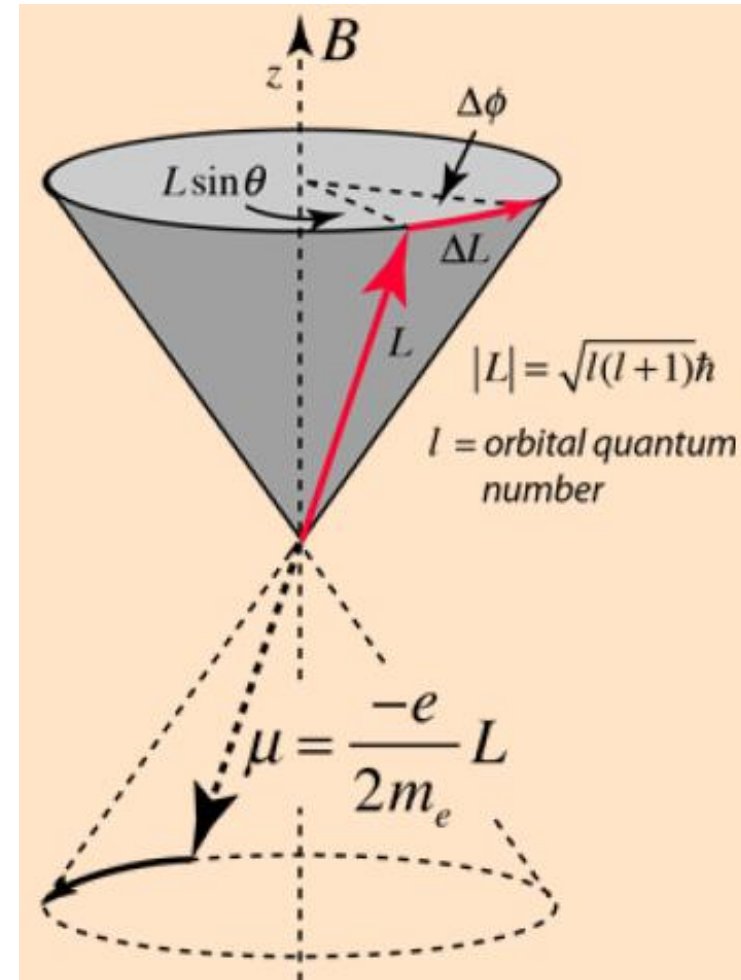
Per definition:

$$\tau = \frac{\Delta L}{\Delta t} = \frac{L \sin \theta \Delta \phi}{\Delta t}$$

$$= |\mu B \sin \theta| = \frac{e}{2m_e} LB \sin \theta$$

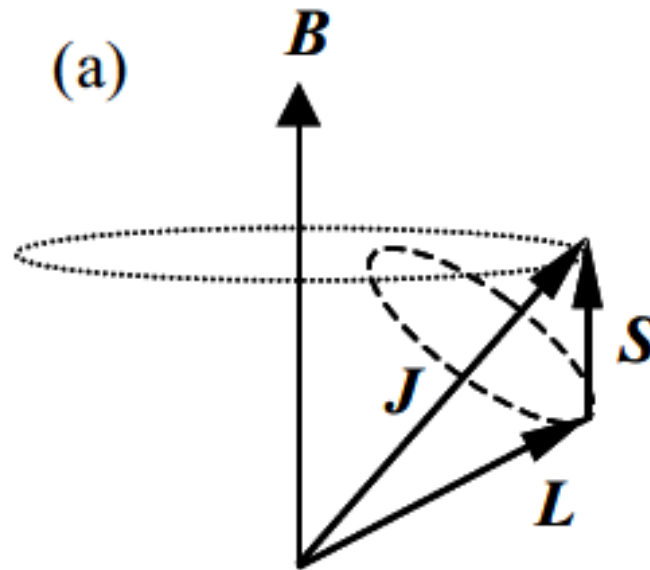
The Larmor frequency:

$$\omega_{Larmor} = \frac{d\phi}{dt} = \frac{e}{2m_e} B$$



The total angular momentum J precesses around the field.

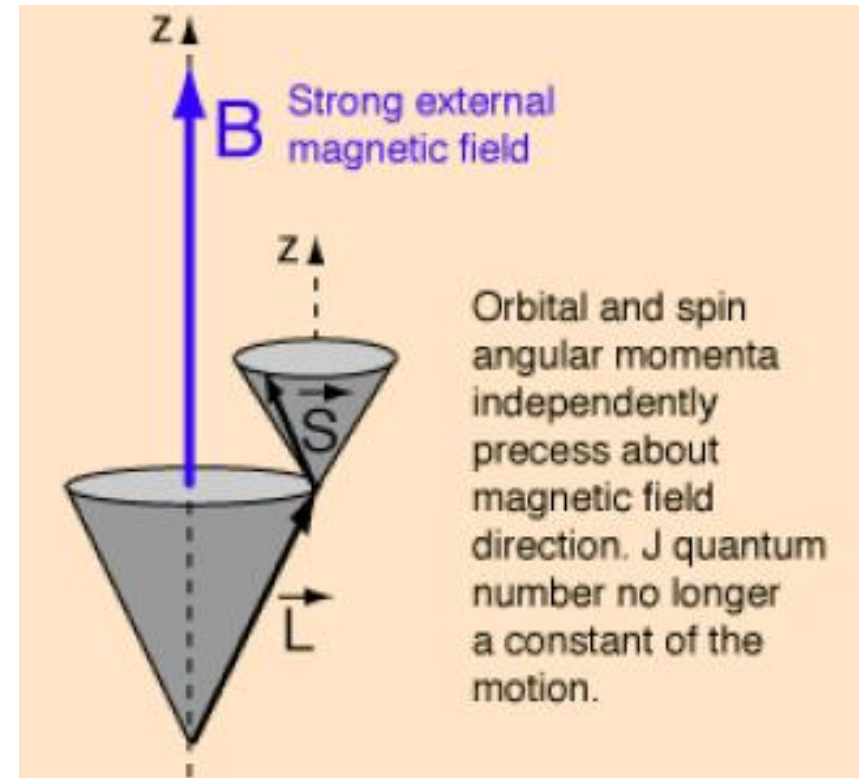
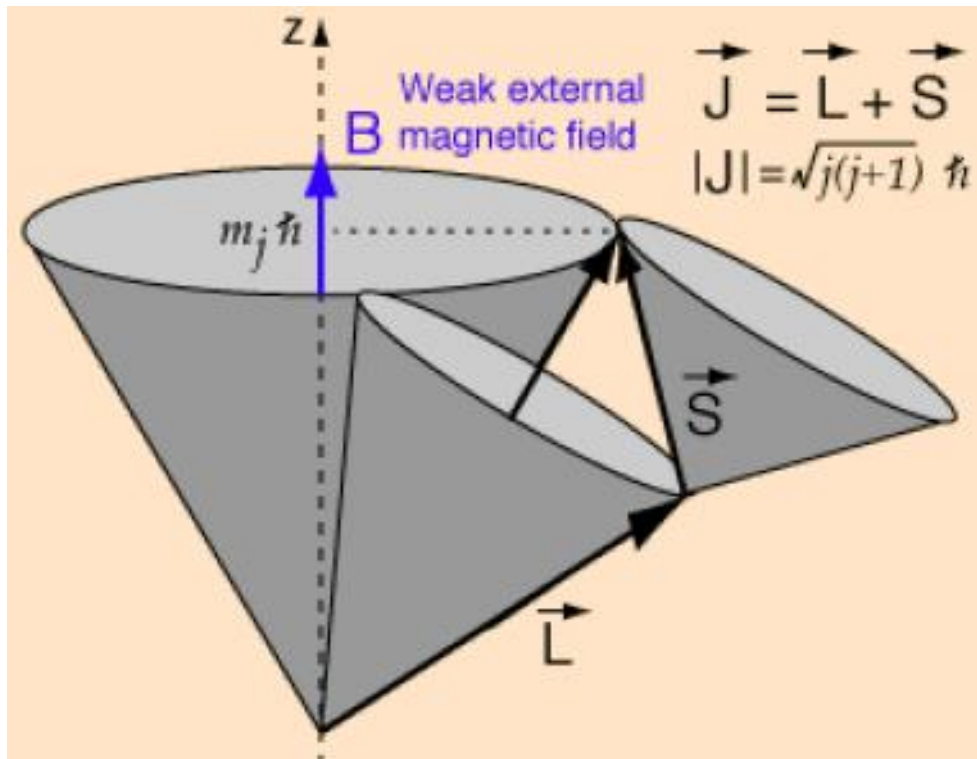
- L and S precesses much faster around J due to spin orbit coupling.



- Paschen – back effect- when the field interaction approaches SO coupling.

The Paschen Back effect:

- The coupling to create the J quantum # is not effective.



Interaction with the magnetic field:

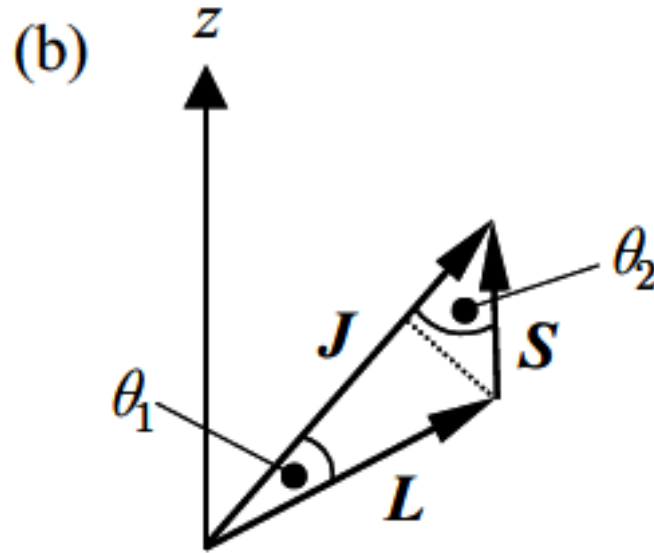
- A sum of the interaction of the spin and the orbital angular momentum.

$$\begin{aligned}\Delta E &= -\mu_z B_z = -(\mu_z^{\text{spin}} + \mu_z^{\text{orbital}}) B_z \\ &= \langle g_s \mathbf{S}_z + \mathbf{L}_z \rangle \frac{\mu_B}{\hbar} B_z\end{aligned}$$

- $\langle \rangle$ refers to the expectation value.
- In the case of a precessing atomic magnet: only the J angular momentum is relevant($\mathbf{J}_z = M_J \hbar$).
- Necessary procedure: projection of S and L on J and then projection of J on B .

The effective atomic dipole is:

- Taking into account the relative orientation:



$$\mu = - \left\langle |\mathbf{L}| \cos \theta_1 \frac{J}{|\mathbf{J}|} + 2|\mathbf{S}| \cos \theta_2 \frac{J}{|\mathbf{J}|} \right\rangle \frac{\mu_B}{\hbar},$$

- The value of 2 is due to $g_e=2$.

Using the scalar product definition:

- We get: $L \cdot J = |L| |J| \cos \theta_1$
 $S \cdot J = |S| |J| \cos \theta_2$

a new definition of the effective atomic dipole:

$$\mu = - \left\langle \frac{L \cdot J}{|J|^2} + 2 \frac{S \cdot J}{|J|^2} \right\rangle \frac{\mu_B}{\hbar} J$$

Recall – the definition of J: $S = J - L$

We get:

$$S \cdot S = (J - L) \cdot (J - L) = J \cdot J + L \cdot L - 2L \cdot J$$

And therefore:

$$\left\langle \frac{L \cdot J}{|J|^2} \right\rangle = \frac{[J(J+1) + L(L+1) - S(S+1)]\hbar^2 / 2}{J(J+1)\hbar^2}$$

Cont:

$$= \frac{[J(J + 1) + L(L + 1) - S(S + 1)]}{2J(J + 1)}$$

Similarly: $S \cdot J = (J \cdot J + S \cdot S - L \cdot L)/2$

And so:

$$\begin{aligned} \left\langle \frac{S \cdot J}{|J|^2} \right\rangle &= \frac{[J(J + 1) + S(S + 1) - L(L + 1)]\hbar^2 / 2}{J(J + 1)\hbar^2} \\ &= \frac{[J(J + 1) + S(S + 1) - L(L + 1)]}{2J(J + 1)}. \end{aligned}$$

Thus the effective magnetic dipole:

$$\mu = - \left(\frac{[J(J+1) + L(L+1) - S(S+1)]}{2J(J+1)} + 2 \frac{[J(J+1) + S(S+1) - L(L+1)]}{2J(J+1)} \right) \frac{\mu_B}{\hbar} \mathbf{J}$$

Which can be written as:

$$\mu = -g_J \frac{\mu_B}{\hbar} \mathbf{J}$$

• Where $g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$

is the Lande g factor.

and $\mu_z = -g_J \mu_B M_J$

$$\Delta E = -\mu_z B_z = g_J \mu_B B_z M_J$$

In the levels of the Na d lines:

Level	J	L	S	g_J
${}^2P_{3/2}$	$3/2$	1	$1/2$	$4/3$
${}^2P_{1/2}$	$1/2$	1	$1/2$	$2/3$
${}^2S_{1/2}$	$1/2$	0	$1/2$	2

In the normal Zeeman effect – $g = 1$.

When $L=0$ (spin only) $g=2$.

Recall: optical spectrum obeys the selection rules:

$$\Delta J = 0, \pm 1;$$

$$\Delta M_J = 0, \pm 1$$

Cont.

- Additional selection rules:

$$\Delta l = \pm 1 \text{ and } \Delta S = 0$$

$\Delta J = 0$ is forbidden if $J=0$ in both states.

$$\Delta M_J = 0 \text{ forbidden for } \Delta J = 0$$

transitions

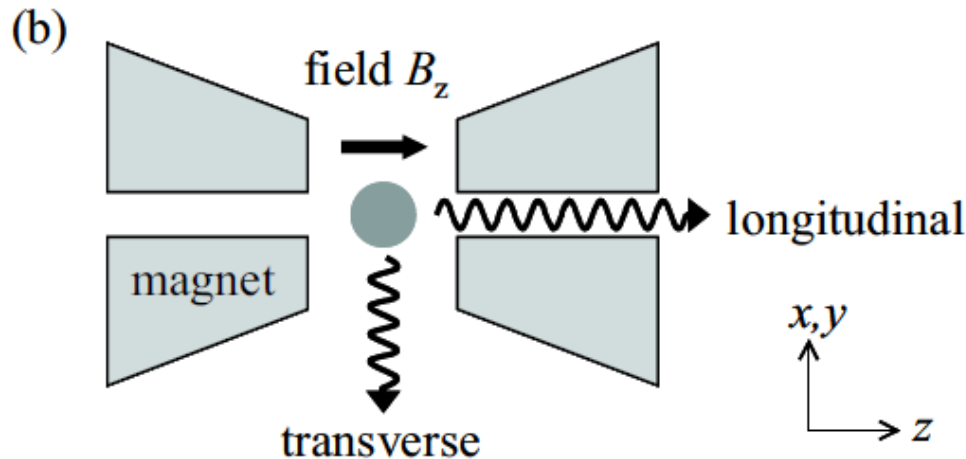
We observe the transition energy shift:

$$h\Delta\nu = (h\nu - h\nu_0),$$

$$= (g_J^{\text{upper}} M_J^{\text{upper}} - g_J^{\text{lower}} M_J^{\text{lower}}) \mu_B B_z,$$

$h\nu_0$ is the transition energy at $B_z = 0$

Recall: In a similar way to the normal Zeeman effect:



Longitudinal observation: $\Delta M_J = 0$

is absent. And $\Delta M_J = \pm 1$ transitions are σ^\pm circularly polarized.

Transverse observation: $\Delta M_J = 0$ transitions

Linear polarization in the z direction $\Delta M_J = \pm 1$

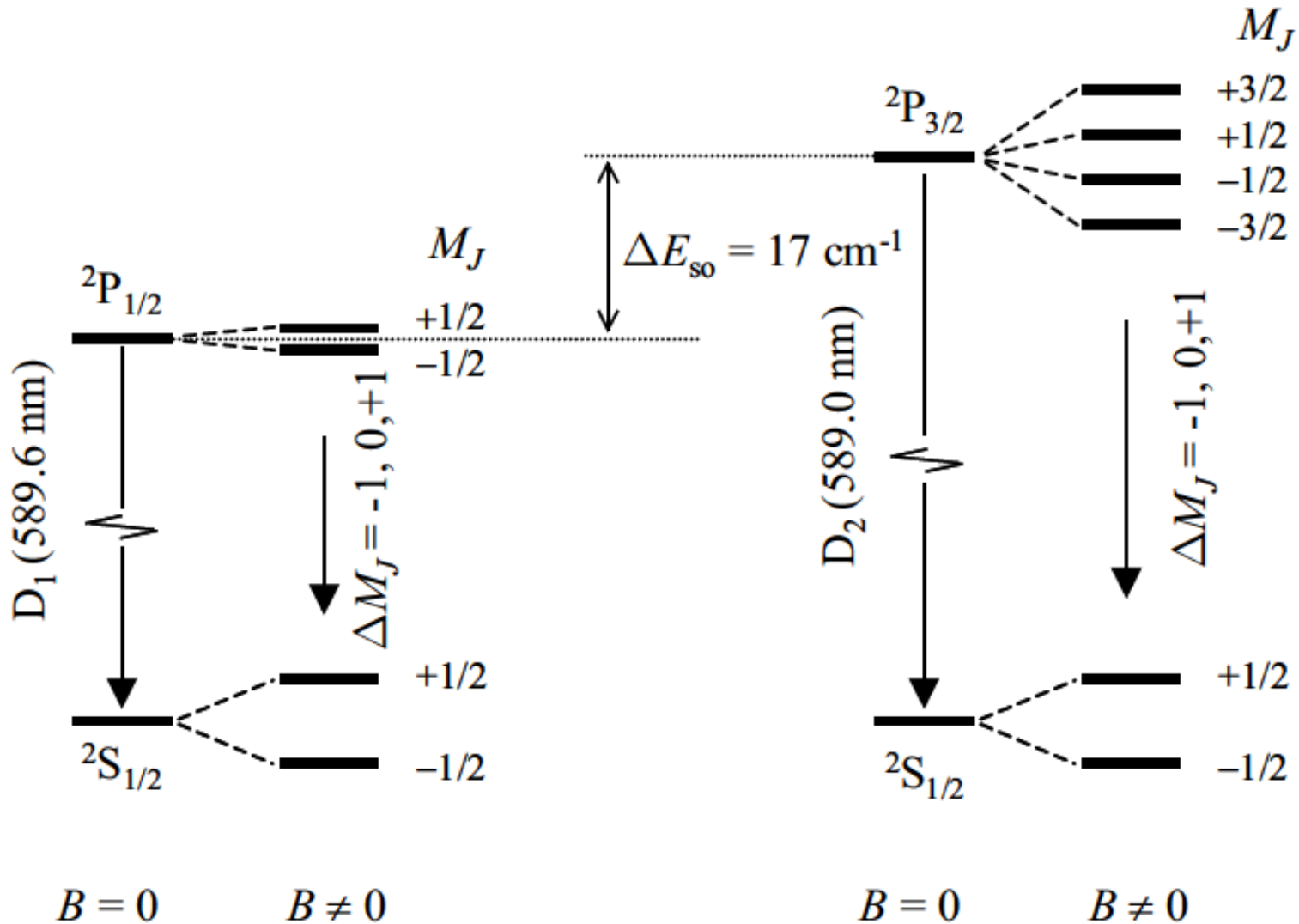
- Linear polarization along x, y directions.

Example: The sodium D lines

- Corresponds to: $3p \rightarrow 3s$ transition. If $B=0$, The SO coupling splits the upper $3p$ 2P term into the $^2P_{3/2}$ and $^2P_{1/2}$ separate by 17cm^{-1} .
- The lower $^2S_{1/2}$ has no SO coupling.
- The Lande g -factors for these terms:

Level	J	L	S	g_J
$^2P_{3/2}$	$3/2$	1	$1/2$	$4/3$
$^2P_{1/2}$	$1/2$	1	$1/2$	$2/3$
$^2S_{1/2}$	$1/2$	0	$1/2$	2

Splitting in the presence of a magnetic field:



- The ${}^2P_{3/2}$ level splits into four M_J states.
- the two $J = 1/2$ levels each split into two states. In each level, different Lande g factor. applying the $\Delta M_J = 0, \pm 1$ selection rule, four allowed transitions for the D_1 line and six for the D_2 .

M_J^{upper}	M_J^{lower}	ΔM_J	Transition energy shift	
			D_1 line	D_2 line
$+\frac{3}{2}$	$+\frac{1}{2}$	-1		+1
$+\frac{1}{2}$	$+\frac{1}{2}$	0	$-\frac{2}{3}$	$-\frac{1}{3}$
$+\frac{1}{2}$	$-\frac{1}{2}$	-1	$+\frac{4}{3}$	$+\frac{5}{3}$
$-\frac{1}{2}$	$+\frac{1}{2}$	+1	$-\frac{4}{3}$	$-\frac{5}{3}$
$-\frac{1}{2}$	$-\frac{1}{2}$	0	$+\frac{2}{3}$	$+\frac{1}{3}$
$-\frac{3}{2}$	$-\frac{1}{2}$	+1		-1

The Paschen-Back effect

- Observed in strong magnetic fields – stronger than the SO coupling.

$$\mu_B B_z \gg \Delta E_{so}$$

- Precession around the field – stronger than the SO coupling. The external magnetic field should be larger than the internal.
- A comparison: In H atom ($n=1$) field was found to be 12T.
- In heavier atoms:

$$|\Delta E_{so}| = \left(\frac{Z^4}{n^5} \right) \frac{\mu_0 \alpha c e^2 \hbar}{8\pi m_e a_0^2} \equiv \alpha^2 \frac{Z^2}{n^3} |E_n|$$

12T is a very large field

- Observed only with a powerful superconducting magnets.
- For Na D lines we get a larger field, observed only with hybride magnets.

$$B_z = \frac{\Delta E_{so}}{\mu_B} = \frac{17 \text{ cm}^{-1}}{9.27 \times 10^{-24} \text{ JT}^{-1}} = 36 \text{ T}$$

In Li SO coupling only 0,3 cm⁻¹ Paschen Back effect observed at fields > 0.6T.

L and S precess around the field separately, with a different frequency

- J is no longer a good quantum # and is not a constant of the motion.
- The interaction energy is:

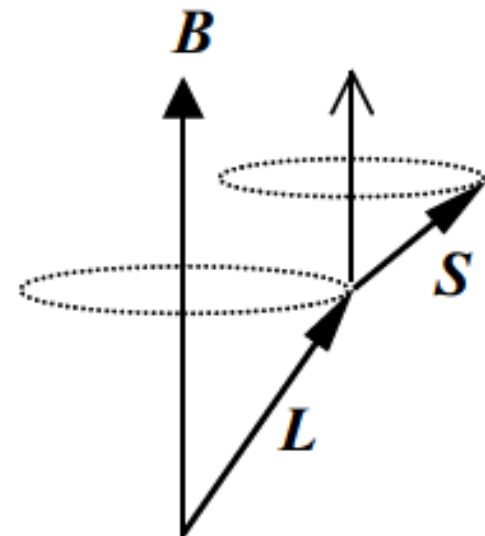
$$\Delta E = -\mu_z B_z = -(\mu_z^{\text{orbital}} + \mu_z^{\text{spin}}) B_z = (M_L + g_s M_S) \mu_B B_z$$

- The shifts of the spectral lines:

$$\Delta(h\nu) = (\Delta M_L + g_s \Delta M_S) \mu_B B_z .$$

An optical transition does not affect the spin:

$$\Delta(h\nu) = \mu_B B_z \Delta M_L$$

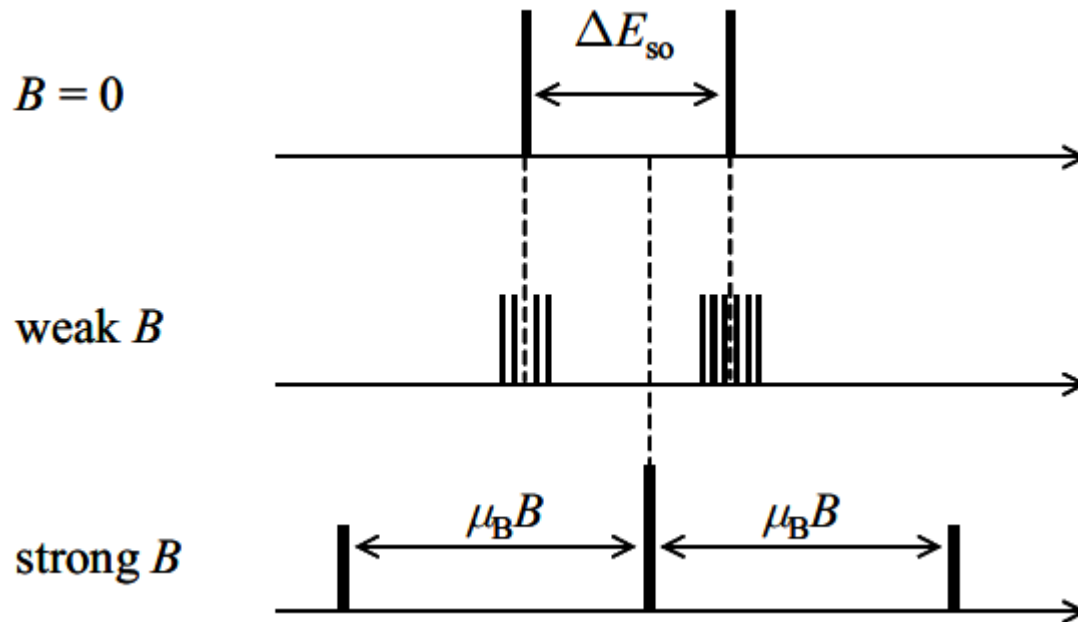


Cont.

- We revert to the normal Zeeman effect:

$$\Delta M_L = 0 \text{ or } \pm 1$$

- The gradual development of the spectrum when the field is increased (p- \rightarrow s transition in alkali atoms).



Electric fields:

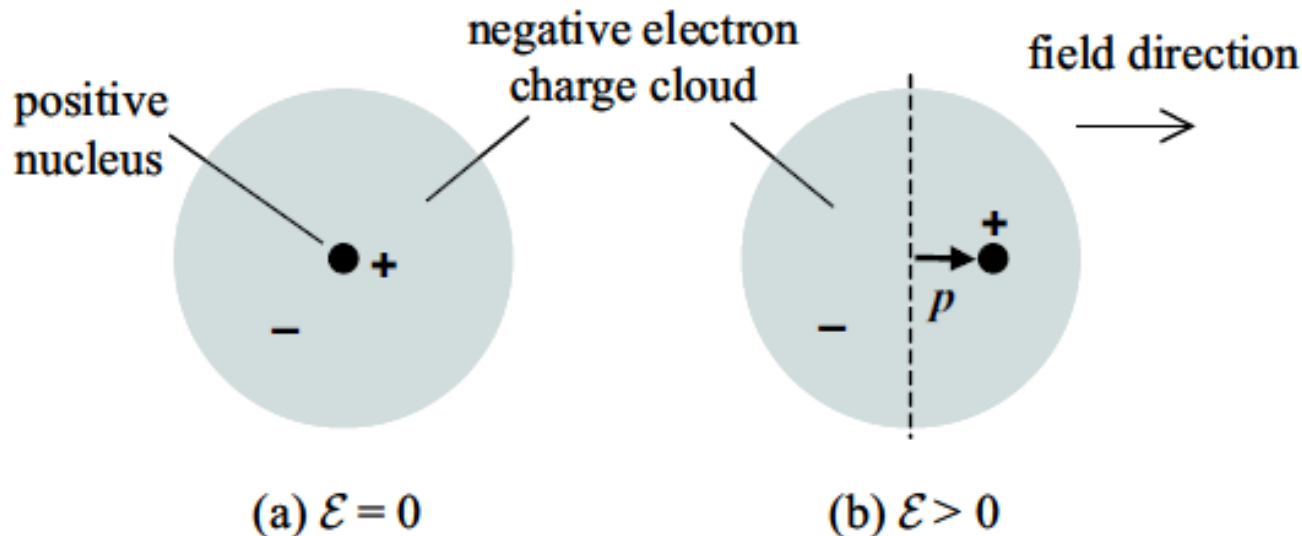
- Shifting and splitting with electric fields – Stark effect.
- More difficult to observe than the Zeeman effect.
- More common – quadratic Stark effect. Less – linear Stark effect.
- In solid state physics – strong Stark effect – quantum – confined Stark effect.

The quadratic Stark effect:

- Most atoms – red shift (to lower energies)
– proportional to the square of the electric field.
- The energy of an atom in an electric field:

$$E = -p \cdot \mathcal{E}$$

- p - the atomic electric dipole.



An atomic electric dipole is formed by the electric field.

- The electrons and the nucleus are moved in opposite directions.
- A dipole is formed. The proportionality constant – the electrical polarizability.

$$p = \alpha \mathcal{E}$$

- The energy shift as a result of the field:

$$\Delta E = - \int_0^{\mathcal{E}} p \cdot d\mathcal{E}' = - \int_0^{\mathcal{E}} \alpha \mathcal{E}' d\mathcal{E}' = -\frac{1}{2} \alpha \mathcal{E}^2 ;$$

- A quadratic red shift.

Perturbation theory:

- Time independent case:
- Starting point – unperturbed Schrodinger equation:

$$H_0 |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle, \quad n = 1, 2, 3, \dots$$

- We add a small perturbation:

$$H = H_0 + \lambda V \quad (H_0 + \lambda V) |n\rangle = E_n |n\rangle.$$

- Mclaurin Series expansion:

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

$$|n\rangle = |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \dots$$

Cont.

- Where the terms are:

$$E_n^{(k)} = \frac{1}{k!} \frac{d^k E_n}{d\lambda^k} \Big|_{\lambda=0} \quad |n^{(k)}\rangle = \frac{1}{k!} \frac{d^k |n\rangle}{d\lambda^k} \Big|_{\lambda=0}$$

- Substitution in the Schrodinger eqn. :

$$(H_0 + \lambda V) (|n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \dots) = (E_n^{(0)} + \lambda E_n^{(1)} + \dots) (|n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \dots)$$

- First order eqn:

$$H_0 |n^{(1)}\rangle + V |n^{(0)}\rangle = E_n^{(0)} |n^{(1)}\rangle + E_n^{(1)} |n^{(0)}\rangle$$

- Where the energy shift is:

$$E_n^{(1)} = \langle n^{(0)} | V |n^{(0)}\rangle$$

Second order correction:

- Due to orthogonality of unperturbed wave functions:

$$E_n(\lambda) = E_n^{(0)} + \lambda \langle n^{(0)} | V | n^{(0)} \rangle + \lambda^2 \sum_{k \neq n} \frac{|\langle k^{(0)} | V | n^{(0)} \rangle|^2}{E_n^{(0)} - E_k^{(0)}}$$

A perturbative approach:

- An electric field in the z direction:

$$H' = - \sum_i (-er_i) \cdot \mathcal{E} = e\mathcal{E} \sum_i z_i$$

- r_i the relative displacement of the electron w.r to the nucleus.
- Only valence electrons are considered. The movement of internal electrons is negligible because of the strong interaction with the nucleus.
- For simplicity - a single valence electron is considered – alkali atom.

The perturbation is:

- A single term: $H' = e\mathcal{E}z$.

- First order energy shift:

$$\Delta E = \langle \psi | H' | \psi \rangle = e\mathcal{E} \langle \psi | z | \psi \rangle$$

- Where: $\langle \psi | z | \psi \rangle = \iiint_{\text{all space}} \psi^* z \psi \, d^3r$

- Parity consideration:

- $\psi^* \psi = |\psi|^2$ is necessarily even. Z is odd.

$$\langle \psi | z | \psi \rangle = \iiint_{\text{all space}} (\text{even function}) \times (\text{odd function}) \, d^3r = 0$$

- First order shift is 0. Shift is quadratic.

Second order perturbation:

- The shift is:
$$\Delta E_i = \sum_{j \neq i} \frac{|\langle \psi_i | H' | \psi_j \rangle|^2}{E_i - E_j}$$

- The stark shift is:
$$\Delta E_i = e^2 \mathcal{E}^2 \sum_{j \neq i} \frac{|\langle \psi_i | z | \psi_j \rangle|^2}{E_i - E_j}$$

Looking for example on the sodium atom, there is a single valence electron in 3s state. the summation is running over excited states (3p, 3d, 4s 4p...) requiring different parities in the i and j state.

- The parity is equal to: $(-1)^l$. Largest contribution from the excited state 3p (a smaller one from the excited f states)

Calculation of shift magnitude:

- The denominator in the eqn. for ΔE_i is always negative – red shift.
- A crude approximation: The expectation value of z smaller than the radius of Na atom (0.18nm).
- The energy difference: $E_{3p} - E_{3s} = 2.1 \text{ eV}$.
- Thus we can estimate ΔE_i :

$$\Delta E_{3s} \lesssim -\frac{e^2 a^2}{E_{3p} - E_{3s}} \mathcal{E}^2$$

For an electric field of $2.5 \cdot 10^{-7} \text{V/m}$:

- We get a shift of $-1 \cdot 10^{-5} \text{ eV}$ (-0.08 cm^{-1}).
- Which is quite close to the experimental value: $-0.6 \cdot 10^{-5} \text{ eV}$ (-0.05 cm^{-1}).
- Till when the S.O perturbation theory valid? It breaks when:

$$e\mathcal{E} |\langle \psi_{3s} | z | \psi_{3p} \rangle| \sim (E_{3p} - E_{3s})$$

By estimating again $|\langle \psi_{3s} | z | \psi_{3p} \rangle| = a$

- We get $\mathcal{E} \sim 10^{10} \text{ V/m}$,
- Which is an extremely large field. In most cases, the S.O. perturbation is a valid approximation.

Now we consider the stark shift of 3p state.

- 3p has an odd parity. – non zero contribution from even parity levels – ns and nd:

$$\Delta E_{3p} = e^2 \mathcal{E}^2 \left(\frac{|\langle \psi_{3p} | z | \psi_{3s} \rangle|^2}{E_{3p} - E_{3s}} + \frac{|\langle \psi_{3p} | z | \psi_{3d} \rangle|^2}{E_{3p} - E_{3d}} + \frac{|\langle \psi_{3p} | z | \psi_{4s} \rangle|^2}{E_{3p} - E_{4s}} + \dots \right)$$

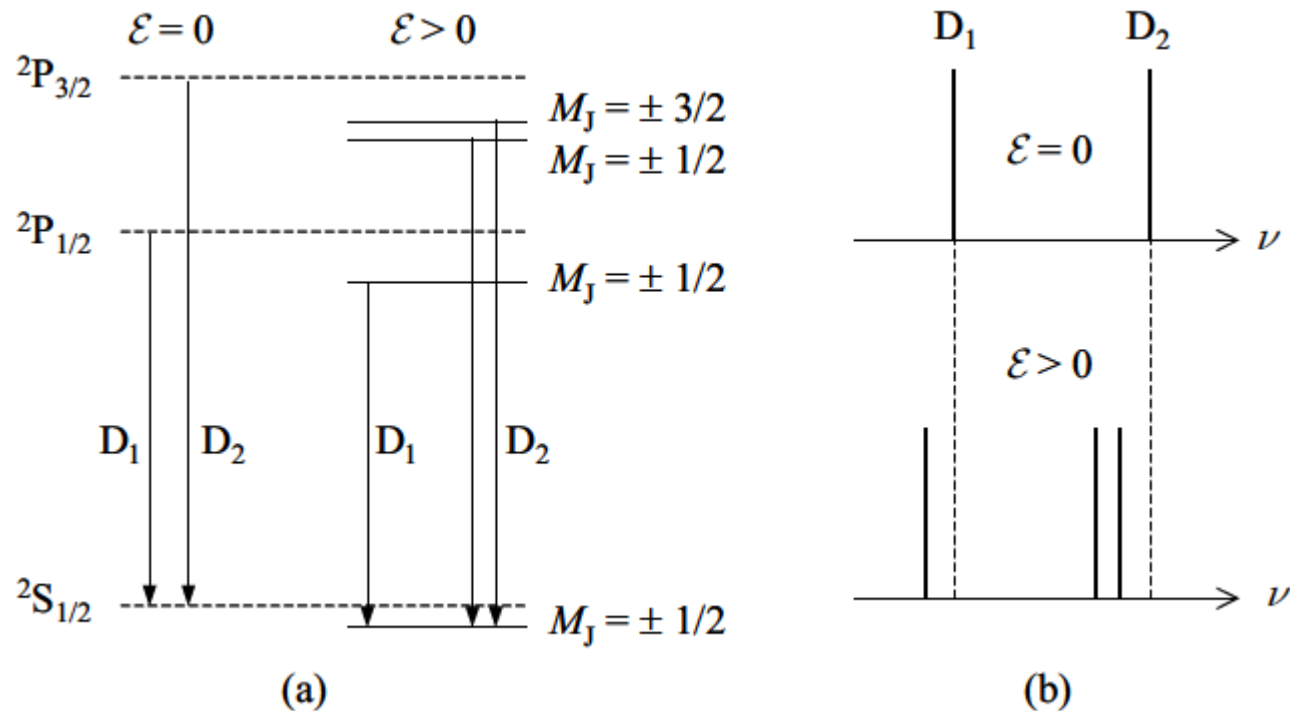
- The first term – positive ($E_{3p} - E_{3s}$ is positive). Since the energy difference of the excited states tends to get smaller at higher states, also in this case the shift is expected to be negative.

In the case of Na 3p state:

- largest contribution comes from the 3d state which lies 1.51 eV above the 3p state,
- the 4s state is closer (relative energy +1.09 eV). – *the s state has a smaller matrix element.*

Recall - In the Zeeman effect, the magnetic field remove the degeneracy between all M_J states.

- In the Zeeman effect, the energy shift is proportional to M_J .
- This is not the case with the Stark effect.



The stark effect of the Na D lines (in the previous slide):

- All states are shifted to lower energy, with those of the same M_J values being shifted equally for a given level.
- The two M_J states in the P levels are shifted to the same extent.
- Thus the D_1 (${}^2P_{1/2} \rightarrow {}^2S_{1/2}$) line does not split

The electric field can cause the appearance of forbidden transitions

- If it is getting close to the field of the nuclei.
- We get mixing for example between the 3S and 3p states,
- Forbidden transitions (such as s-> s, p->p d->s) where the levels have the same parity, begin to appear.
- The intensity of these forbidden
- transitions increases in proportion to ϵ^2 .

The linear Stark effect:

- Recall – degenerate perturbation theory:

In case when the energies of the perturbed wavefunctions – are close, the perturbative terms diverge.

A different approach can be adopted:

We have n nearly degenerate wave functions ϕ_n

Any linear combination of these states, is also an eigenstate.

The Hamiltonian within the space of these eigenstates is:

Cont.

- $$\sum_{i \in \mathcal{N}} \langle \phi^{(j)} | H_0 + H_1 | \phi^{(i)} \rangle \alpha_i = E \alpha_j.$$

- We have to diagonalize the Hamiltonian:

$$\begin{pmatrix} H_{11} & H_{12} & \dots & H_{1n} \\ H_{21} & H_{22} & \dots & H_{2n} \\ \dots & \dots & \dots & \dots \\ H_{n1} & H_{n2} & \dots & H_{nn} \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \dots \\ \alpha_n \end{pmatrix} = E \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \dots \\ \alpha_n \end{pmatrix}$$

- The eigenstates are linear combinations of the ϕ_n s with the corresponding eigenvalues.

The linear stark effect can be solved only by nearly degenerate perturbation theory

- In a hydrogen atom, unlike the others, the l state, in a given n are degenerate – states with opposite parities are degenerate – and the second order perturbation terms – diverge.
- In the case of $1s$, the transition can be to a higher level with opposite parity - and indeed a small red shift is observed.
- As a result of the degeneracy in the $n=2$ states we can apply nearly degenerate perturbation theory.

We have a 4-fold basis

- :
$$\psi_{n=2} = \sum_{i=1}^4 c_i \psi_i$$

- The basis is characterized by: (n,l,m).

$$\begin{aligned} \psi_1 &\equiv \psi_{2,0,0}; & \psi_2 &\equiv \psi_{2,1,-1} \\ \psi_3 &\equiv \psi_{2,1,0}; & \psi_4 &\equiv \psi_{2,1,+1} \end{aligned}$$

- The first order shift:

$$\Delta E = e\mathcal{E} \sum_{i,j} c_i c_j \langle \psi_i | z | \psi_j \rangle$$

For a non zero shift, the wave functions have to be with opposite parity.

- The non zero element is:

$$\gamma = e\mathcal{E} \langle \phi_{200} | z | \phi_{210} \rangle$$

- The matrix to be diagonalized is:

$$\begin{array}{l} \phi_{200} \\ \phi_{211} \\ \phi_{210} \\ \phi_{21-1} \end{array} \begin{pmatrix} 0 & 0 & \gamma & 0 \\ 0 & 0 & 0 & 0 \\ \gamma & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \end{pmatrix} = E^{(1)} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \end{pmatrix}$$

- Recall: the radial probability density to be found between r and $r+dr$:

Cont.

- The matrix element:

$$\begin{aligned}\gamma &= e\mathcal{E} \int (2a_0)^{-3/2} 2 \left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0} Y_{00} z (2a_0)^{-3/2} \frac{1}{\sqrt{3}} \left(\frac{r}{a_0}\right) e^{-r/2a_0} Y_{10} d^3r \\ &= 2e\mathcal{E} (2a_0)^{-3} \frac{1}{\sqrt{3}} \int r^3 d^3r \left(1 - \frac{r}{2a_0}\right) \left(\frac{r}{a_0}\right) e^{-r/a_0} \int \frac{1}{\sqrt{4\pi}} \cos\theta Y_{10} d\Omega \\ &= 2eE(2)^{-3} \frac{1}{\sqrt{3}} \frac{1}{\sqrt{3}} \int_0^\infty \left(\frac{r^4}{a_0^4} - \frac{r^5}{2a_0^5}\right) e^{-r/a_0} dr \\ &= \frac{a_0 e\mathcal{E}}{12} \left[\int_0^\infty x^4 e^{-x} dx - \frac{1}{2} \int_0^\infty x^5 e^{-x} dx \right] \\ &= \frac{a_0 e\mathcal{E}}{12} \left[4 \cdot 3 \cdot 2 \cdot 1 - \frac{5 \cdot 4 \cdot 3 \cdot 2 \cdot 1}{2} \right] \\ &= \frac{a_0 e\mathcal{E}}{12} (-36) \\ &= -3e\mathcal{E}a_0 \quad \Rightarrow \quad E^{(1)} = \mp 3e\mathcal{E}a_0\end{aligned}$$

The field splits the degenerate energy $n=2$ level to three.

- Levels of: $-3ea_0\mathcal{E}$, 0 , and $+3ea_0\mathcal{E}$ compared to unperturbed level.

The magnitude is much stronger (by two orders of magnitude) ,

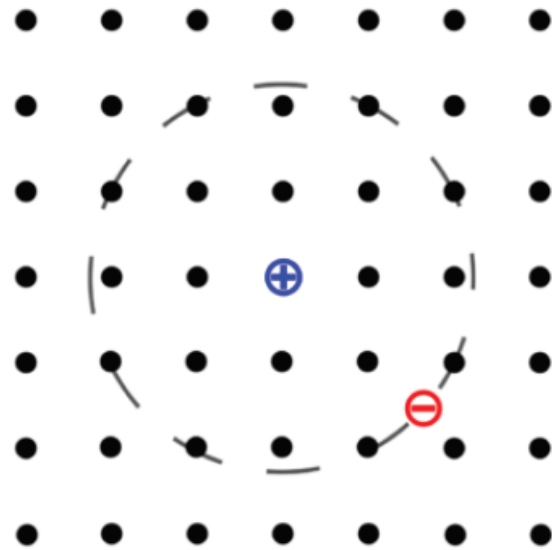
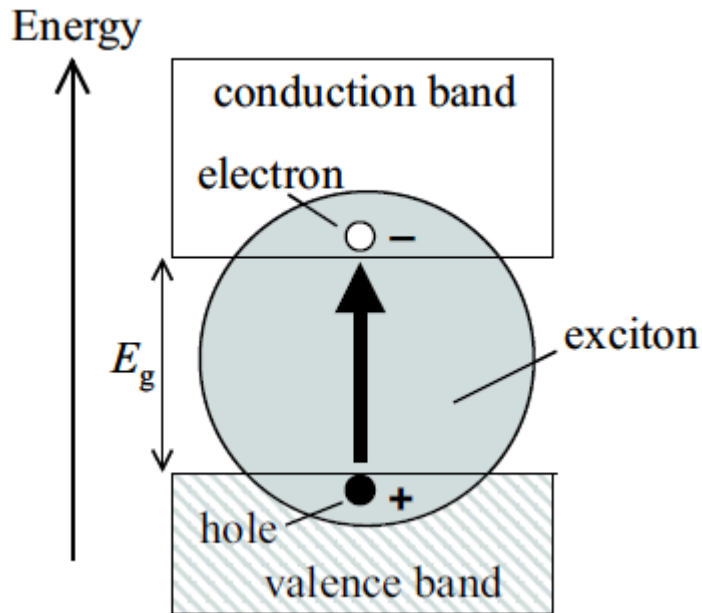
$$\text{at } \mathcal{E} = 2.5 \times 10^7 \text{ V/m.}$$

We get shifts of $\pm 4 \times 10^{-3} \text{ eV}$

In strong fields the quadratic stark effect is becoming linear, when the level involved are close in energy (He).

The quantum confined stark effect:

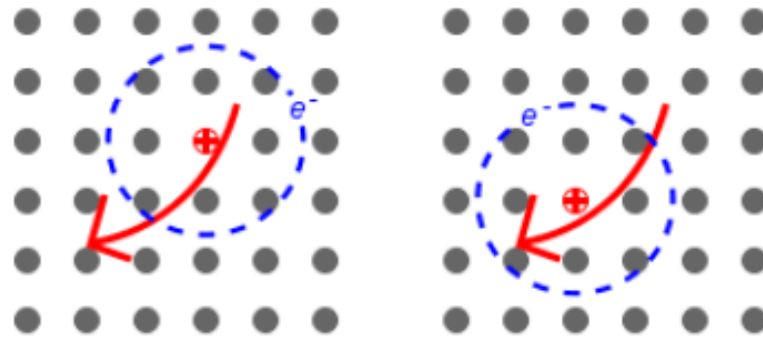
- Excitons – hydrogen like “atom” in a semiconductor. A bound state between an electron and a hole.



- Frenkel exciton an electron is bound to hole connected to a lattice site. Can be formed by photon excitation.

The Wannier Mott Exciton:

- Better Screening of Coulomb interaction and a small effective mass – The exciton is more mobile.



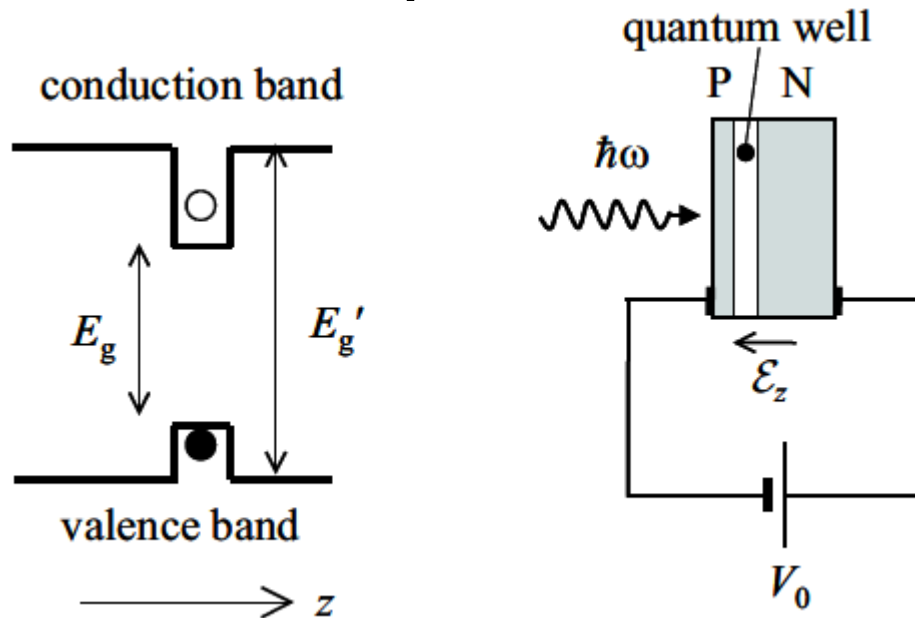
The result of a large dielectric constant -

$$\epsilon_r \sim 10$$

- A small effective mass $m \sim 0.1m_e$.
- Is – a binding energy of 0.01eV.

A 1s exciton should have a quadratic stark shift – but

- Because of the small interaction energy, the breaking of the bond often occurs – field ionization.
- This is different in quantum confined structure:



Electrooptical modulators.

- In the this well, the exciton is now trapped and the stark shift is observed.
- A reverse biased p-n junction can give a strong stark shift with the exciton stable