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Week 3

PHY 402 Atomic and Molecular Physics
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2.2 Interaction of one electron atoms with static electric and magnetic fields

Useful for: Probing, trapping, and controlling atoms

Probing fields

2.2.1 The Stark effect: (Electric fields)

Hamiltonian for electron in both electric field of core and external field:

$$\hat{H} = \overbrace{-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_\circ r}}^{\hat{H}_\circ} + \overbrace{e\mathbf{E}\cdot\mathbf{r}}^{\hat{H}'}. \tag{2.44}$$

- Let us assume $\mathbf{E} = E_\circ \hat{\mathbf{k}}$ (along z-axis) and constant across atom.
- Hamiltonian (2.44) assumes **E**-field strong enough for fine-structure to be negligible.
- TISE Eq. (1.7) can still be fully solved analytically without perturbation theory, exploiting the cylindrical symmetry around the direction of **E** and using parabolic coordinates. *see BJ book.*
- Here, we use the approach of perturbation theory, splitting the Hamiltonian into $\hat{H}_\circ + \hat{H}'$.

Linear Stark effect:

First order energy shift of a state $|nlm\rangle$ from Eq. (1.50)

$$\Delta E = e\mathbf{E}\cdot\langle\phi_{nlm}|\,\mathbf{r}\,|\phi_{nlm}\rangle = 0 \qquad \forall\, nlm. \tag{2.45}$$

- You derived this in assignment 1. The simplest way to show it, is by remembering the symmetry of spherical harmonics under a parity operation: $Y_{lm}(\mathbf{r}) = (-1)^l Y_{lm}(-\mathbf{r})$, thus they are either symmetric or anti-symmetric. Then

$$\begin{aligned} e\mathbf{E}\cdot\langle\phi_{nlm}|\,\mathbf{r}\,|\phi_{nlm}\rangle &= e\mathbf{E}\cdot\int d^3\mathbf{r}\,|R_{nl}(\mathbf{r})|^2|Y_{lm}(\mathbf{r})|^2\mathbf{r} \\ &\overset{\tilde{\mathbf{r}}=-\mathbf{r}}{=} e\mathbf{E}\cdot\int d^3\tilde{\mathbf{r}}\,|R_{nl}(-\tilde{\mathbf{r}})|^2|Y_{lm}(-\tilde{\mathbf{r}})|^2(-\tilde{\mathbf{r}}) \\ &= e\mathbf{E}\cdot\int d^3\tilde{\mathbf{r}}\,|R_{nl}(\tilde{\mathbf{r}})|^2|(-1)^l Y_{lm}(\tilde{\mathbf{r}})|^2(-\tilde{\mathbf{r}}) \\ &\overset{\text{rename }\tilde{\mathbf{r}}\to\mathbf{r}}{=} -e\mathbf{E}\cdot\langle\phi_{nlm}|\,\mathbf{r}\,|\phi_{nlm}\rangle. \end{aligned} \tag{2.46}$$

  The only way for this to be true is if the integral vanishes.

- Caution: We cannot apply Eq. (1.50) if states are degenerate. So the result that the first order shift $\Delta E = 0$ is valid for $|100\rangle$ only.

- For other state we need to think again, using Eq. (1.52) for degenerate perturbation theory.

So fix $n = n_\circ$ and write $\langle\phi_{n_\circ lm}|e\mathbf{E}\cdot\mathbf{r}\,|\phi_{n_\circ l'm'}\rangle \to \underline{\underline{H}}'$ as a matrix.
e.g. for $n_\circ = 2$, Eq. (1.52) becomes

$$\begin{pmatrix} 0 & 0 & H'_{00} & 0 \\ 0 & 0 & 0 & 0 \\ H'_{00} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} C_{200} \\ C_{21-1} \\ C_{210} \\ C_{211} \end{pmatrix} = E^{(1)}_{n=2} \begin{pmatrix} C_{200} \\ C_{21-1} \\ C_{210} \\ C_{211} \end{pmatrix}. \tag{2.47}$$

(see also later chapter-3, dipole selection rules)

- We can use (2.46) to quickly eliminate all diagonal entries, but have to look now at non-diagonal matrix-elements:

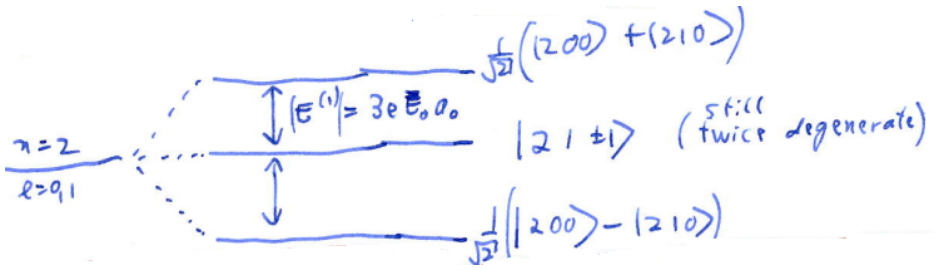
$$\begin{aligned} &e\mathbf{E}\cdot\langle\phi_{n_0lm}|\,\mathbf{r}\,|\phi_{n_0l'm'}\rangle = eE_0\langle\phi_{n_0lm}|r\cos\theta\,|\phi_{n_0l'm'}\rangle \\ &= eE_0\tilde{\mathcal{N}}\int_0^\infty r^2 R_{n_0l}(r) r R_{n_0l'}(r)\underbrace{\int_0^\pi d\theta\sin[\theta]P_l^m(\cos[\theta])P_{l'}^{m'}(\cos[\theta])}_{\sim\delta_{l(l'\pm1)}}\underbrace{\int_0^{2\pi}d\varphi e^{i(m'-m)\varphi}}_{\sim\delta_{mm'}}, \end{aligned} \tag{2.48}$$

  where $\mathcal{N}$ is just the collection of all normalisation factors from (1.36)-(1.37).

- We now see $eE_o\langle\phi_{n_olm}|rcos\theta|\phi_{n_ol'm'}\rangle \sim \delta_{ll'\pm1}\delta_{mm'}$. (obtained by explicit integration or realizing that $\hat{H}'$ is odd under parity, and $[\hat{H}', \hat{L}_z] = 0$)

- The only non-zero matrix element is thus $H'_{00} = eE_\circ\langle\phi_{200}|rcos\theta|\phi_{210}\rangle = -3ea_\circ E_\circ$. (*do this explicitly as an exercise, like for assignment 1*)

Linear Stark effect: After diagonalisation, we obtain the following picture



(2.49)

- Note that the energy shift $|E^{(1)}|$ cam about in first order PT and is $\sim E_0$, hence there in fact is a first order (linear) energy shift for degenerate states. *Note: This is an example where the invalid application of degenerate PT clearly gives the wrong result.*

Non-linear Stark effect: For non-degenerate states (in Hydrogen only $|100\rangle$), we have to go to second order perturbation theory to get a non-vanishing Stark effect

$$\Delta E^{(2)}_{100} = \sum_{n\neq 1,l,m} \frac{|\langle \phi_{nlm}| eE_0 z |100\rangle|^2}{E_{100} - E_{nlm}}. \tag{2.50}$$

- Technically $|\phi_{nlm}\rangle$ includes continuum (unbound states), let's ignore these for now.
- As in Eq. (2.47), all matrix elements $|\langle \phi_{n10}| eE_0 z |100\rangle|^2$ will be non-zero. Also $E_{100} - E_{n10} < 0$ for all n.

We then deduce $\Delta E^{(2)}_{100} < 0$ and $\sim (eE_0)^2 \implies$ quadratic stark effect.

Interpretation of both variants of the Stark effect: Non-degenerate states do not possess any permanent dipole moment (*see assignment-1*). However, the external field can induce one $\sim E$, which then in turn interacts with the field $\sim E^2$. In contrast, out of degenerate states you can form superpositions (that are also energy eigenstates), which do have a non-vanishing dipole moment, such as $|\Psi\rangle = (|ns0\rangle + |np0\rangle)/\sqrt{2}$, for which you did this in assignment 1. That's why we get a first order shift here.

2.2.2 The Zeeman effect (Magnetic fields)

Hamiltonian for electron in electric field of core and external magnetic field:

$$\hat{H} = \overbrace{\frac{1}{2m}\big(\mathbf{p} + e\mathbf{A}\big)^2 - \frac{Ze^2}{4\pi\epsilon_{\circ} r}}^{\text{see electro-dynamics}} + \overbrace{\frac{g_s\mu_B}{\hbar}\mathbf{B}\cdot\mathbf{S} + \zeta(r)\mathbf{L}\cdot\mathbf{S}}^{\text{added a in section 2.1.1}} \ . \tag{2.51}$$

- For interaction of e^- spin $\hat{S}$ with field, see Eq. (2.8).

Classical vector potential:

$$\mathbf{A} = \frac{1}{2}\big(\mathbf{B}\times\mathbf{r}\big) \text{ for a constant B-field.} \tag{2.52}$$

Insert $\mathbf{A}$, $\mathbf{p}$ and lots of vector calculus (see book)

$$\hat{H} = \overbrace{-\frac{\hbar^2}{2m}\nabla^2}^{\hat{H}_a} \overbrace{- \frac{Ze^2}{4\pi\epsilon_{\circ} r}}^{\hat{H}_b} \overbrace{+ \zeta(r)\mathbf{L}\cdot\mathbf{S}}^{\hat{H}_c} \overbrace{+ \frac{\mu_B}{\hbar}\big(\mathbf{L}+2\mathbf{S}\big)\mathbf{B}}^{\hat{H}_d} \overbrace{+ \frac{e^2}{8m}\big(\mathbf{B}\times\mathbf{r}\big)^2}^{\hat{H}_e} . \tag{2.53}$$

For $\hat{H}_c$ and $\hat{H}_d$, see Eq. (2.5) and Eq. (2.8) respectively.

Let $\mathbf{B} = B_o\hat{\mathbf{k}}$ (along z-axis).
Now analyze Eq. (2.53) with perturbation theory depending on relative importance of terms $a-e$, which depends on the state to be perturbed $|\phi_{nlm}\rangle$ and the magnetic field strength $|\mathbf{B}|$.

<u>Linear Zeeman effect</u>: (strong B-field)

- Energy due to magnetic field is large compared to fine-structure.

First neglect $\hat{H}_c$ and $\hat{H}_e$. Then, $\hat{H}_{\circ} = \hat{H}_a + \hat{H}_b + \hat{H}_d$.

The first two just constitute the usual Hydrogen Hamiltonian Eq. (1.28) and the last part

$$\hat{H}_d = \frac{\mu_B}{\hbar}B_0\big(\hat{L}_z + 2\hat{S}_z\big)$$

can be expressed in terms of angular momentum z-components (and thus commutes with $\hat{\mathbf{L}}^2$, $\hat{S}_z$, $\hat{\mathbf{S}}^2$, $\hat{S}_z$. So, $|\phi_{nlm_l}\rangle\otimes|sm_s\rangle$ of Eq. (1.35) are already eigenfunctions of $\hat{H}$ in Eq. (2.53), solving

$$\hat{H}_{\circ}|\phi_{nlm_lsm_s}\rangle = E_{nm_lm_s}|\phi_{nlm_lsm_s}\rangle.$$

to obtain

Zeeman-shifted energies

$$E_{nm_l m_s} = \overbrace{E_n}^{\text{see Eq. (1.43)}} + \mu_B B_0(m_l + 2m_s), \quad m_s = \pm\frac{1}{2}. \tag{2.54}$$

Interpretation: **L** and **S** decouple in B-field and align to it separately.

Paschen-Back effect: (medium B-field)

We now add spin-orbit coupling $\hat{H}' = \hat{H}_c = \zeta(r)\mathbf{L}\cdot\mathbf{S}$ as a perturbation.

- This is for slightly lower fields.

Can use non-degenerate perturbation theory Eq.(1.26) (see book for subtle reasons) to find

$$\Delta E = \langle\phi_{nlm_l sm_s}|\hat{H}'|\phi_{nlm_l sm_s}\rangle \tag{2.55}$$
$$= \langle\phi_{nlm_l sm_s}|\zeta(r)(\hat{L}_x\hat{S}_x + \hat{L}_y\hat{S}_y + \hat{L}_z\hat{S}_z)|\phi_{nlm_l sm_s}\rangle. \tag{2.56}$$

Use

Raising and lowering operators (*BJ book 2.185*)

$$\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y \implies \hat{L}_x = (\hat{L}_+ + \hat{L}_-)/2, \quad \hat{L}_y = -i(\hat{L}_+ - \hat{L}_-)/2 \tag{2.57}$$

$$\hat{L}_\pm|lm\rangle = \hbar[l(l+1) - m(m\pm1)^{1/2}]|l(m\pm1)\rangle$$

to see that the first two terms in Eq. (2.56) vanish and thus

$$\Delta E = \langle\phi_{nlm_l sm_s}|\zeta(r)\underbrace{\hat{L}_z\hat{S}_z}_{=\hbar^2 m_l m_s}|\phi_{nlm_l sm_s}\rangle = \lambda_{nl}\, m_l m_s \tag{2.58}$$

with $\lambda_{nl} = \hbar^2\int_0^\infty dr\, r^2[R_{nl}(r)]^2\zeta(r) = -\frac{\alpha^2 Z^2}{n}\frac{E_n}{[l(l+\frac{1}{2})(l+1)]}$; $l \neq 0$.

- Now shift dependent on l (unlike Eq. (2.54)).

Anomalous Zeeman effect: (weak B-field, most common case)

- The name "anomalous" is historical.
- We now consider

$$\hat{H}_\circ = \hat{H}_a + \hat{H}_b + \hat{H}_c \text{ with } \hat{H}' = \hat{H}_d \text{ (still neglect } \hat{H}_e)$$

Eigenstates of $\hat{H}_\circ$ are the same as for fine-structure (section 2.1.1). Can expand total angular momentum states in terms of orbital angular momentum and spin states as section 1.2.2.

$$|j,l,s,m_j\rangle = \sum_{m_l,m_s} \underbrace{\langle l,s,m_l,m_s|j,l,m_j\rangle}_{\equiv C^{l,s;m_l,m_s}_{j,m_j}} |l,s,m_l,m_s\rangle,$$

where $C^{l,s;m_l,m_s}_{j,m_j}$ are **Clebsch-Gordan coefficients** (cgc), see section 1.2.2.

Using the coupled j basis as for fine-structure, let us first evaluate the easy part:

$$\begin{aligned}\Delta E &= \langle \phi_{njlm_j}| \frac{\mu_B}{\hbar}(\hat{J}_z + \hat{S}_z) B_\circ |\phi_{njlm_j}\rangle \\ &= \mu_B m_j B_\circ + \frac{\mu_B B_\circ}{\hbar}\langle \phi_{njlm_j}|\hat{S}_z|\phi_{njlm_j}\rangle. \end{aligned} \tag{2.59}$$

Now we need some cgc, but we only look at $s = \frac{1}{2}$, so $j = l \pm \frac{1}{2}$. Then

$$\begin{aligned}\left|\left(j = l + \frac{1}{2}\right), l, s, m_j\right\rangle = &\sqrt{\frac{l + m_j + 1/2}{2l+1}}\left|l, s, m_l = m_j - \frac{1}{2}, m_s = \frac{1}{2}\right\rangle \\ &+ \sqrt{\frac{l - m_j + 1/2}{2l+1}}\left|l, s, m_l = m_j + \frac{1}{2}, m_s = \frac{-1}{2}\right\rangle \end{aligned} \tag{2.60}$$

and

$$\begin{aligned}\left|\left(j = l - \frac{1}{2}\right), l, s, m_j\right\rangle = &-\sqrt{\frac{l - m_j + 1/2}{2l+1}}\left|l, s, m_l = m_j - \frac{1}{2}, m_s = \frac{1}{2}\right\rangle \\ &+ \sqrt{\frac{l + m_j + 1/2}{2l+1}}\left|l, s, m_l = m_j + \frac{1}{2}, m_s = \frac{-1}{2}\right\rangle. \end{aligned} \tag{2.61}$$

We now use these two expressions in Eq. (2.59) and simplify to get

Anomalous Zeeman shift

$$\Delta E = g_s \mu_B m_j B_\circ, \tag{2.62}$$

with Landé g-factor

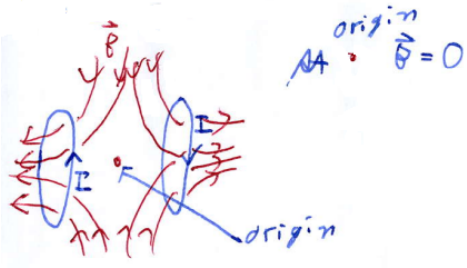
$$g = 1 + \frac{j(j+1) + s(s+2) - l(l+1)}{2j(j+1)}.$$

So the number of split energy levels is now given by the number of different values for m_j.

- Even stronger fields than for Eq. (2.54) $\implies$ Treat $\hat{H}_e$, even neglect $\hat{H}_b$ (**Landau levels**).
- Even weaker fields than for Eq. (2.62) $\implies$ Consider hyperfine-structure (**Breit-Rabi equation**).

Example-(1) for section section 2.2: Magnetic trapping

Consider double anti-Helmholtz coil (quadrupole trap) with current I.



This is designed to have a local minimum of the magnetic field strength $|\mathbf{B}(\mathbf{x})|$ at the origin Assume a single atom is in $m_j = \frac{1}{2}$. According to Eq. (2.62) its energy is

$$\Delta E = g_s \mu_B m_j |\mathbf{B}(\mathbf{x})| \tag{2.63}$$

This energy shift increases everywhere from origin $\implies$ atom can be trapped at origin.

Q: Can one magnetically trap $m_j < 0$ states?
Caution: Typical magnetic traps have so weak fields that we need to look at the Zeeman effect of hyperfine-structure, roughly similar to Eq. (2.62) with $m_j \to m_F$.

Example-(2) for section section 2.2: (*see online code "zeeman_effect_of_finestructure.m"*
From strong to weak fields: The energy shifts in Eq. (2.54) and Eq. (2.62), valid for different regimes of magnetic field strengths, depend on different quantum numbers. How does the transitions happen for intermediate magnetic fields?

Let us consider hydrogen $|2p\rangle$, with spin we have $2p_{\frac{1}{2}}$, $p_{\frac{3}{2}}$.
Use coupled basis $A = \left\{|2p_{\frac{3}{2}}, m_j = \frac{3}{2}\rangle, |\frac{3}{2}, \frac{1}{2}\rangle, |\frac{3}{2}, -\frac{1}{2}\rangle, |\frac{3}{2}, -\frac{3}{2}\rangle, |2p_{\frac{1}{2}}, m_j = \frac{1}{2}\rangle, |\frac{1}{2}, -\frac{1}{2}\rangle\right\}$.

In matrix form

$$\hat{H}_{FS\,(Fine-Structure)} = \begin{pmatrix} E_{3/2} & 0 & 0 & 0 & 0 & 0 \\ 0 & E_{3/2} & 0 & 0 & 0 & 0 \\ 0 & 0 & E_{3/2} & 0 & 0 & 0 \\ 0 & 0 & 0 & E_{3/2} & 0 & 0 \\ 0 & 0 & 0 & 0 & E_{1/2} & 0 \\ 0 & 0 & 0 & 0 & 0 & E_{1/2} \end{pmatrix}_{Basis-A}$$

The energy terms on the diagonal follow from Eq. (2.25).

Example-(2) contd.: The effect of the magnetic field is easier to capture in the uncoupled basis $B = \{|2p_1, m_l = \frac{1}{2}\rangle, |0, \frac{1}{2}\rangle, |-1, \frac{1}{2}\rangle, |1, -\frac{1}{2}\rangle, |0, -\frac{1}{2}\rangle, |-1, -\frac{1}{2}\rangle\}$, using part d of Hamiltonian Eq. (2.53), which gives

$$\hat{H}_d = \frac{\mu_B B_o}{\hbar} \begin{pmatrix} \hbar\left(1 + 2 \cdot \frac{1}{2}\right) & 0 & 0 & 0 & 0 & 0 \\ 0 & \hbar & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \hbar & 0 \\ 0 & 0 & 0 & 0 & 0 & 2\hbar \end{pmatrix}_{Basis-B} .$$

Here the energy terms on the diagonal follow from Eq. (2.53), part d.

To write it all into one matrix we perform a basis transform on the latter part, thus Now,

$$\hat{H}_{tot} = \hat{H}_{fs} + \hat{U}^\dagger \hat{H}_d \hat{U},$$

where $\hat{U}$ is the unitary matrix converting from A to B.

Eigenvalues of $\hat{H}_{tot}$, from numerical diagonalisation as a function of magnetic field strength: