



UNIVERSITY OF  
CAMBRIDGE

NST Part II Physics  
Michaelmas Term 2022  
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# ADVANCED QUANTUM PHYSICS

## Handout 8

- 
- ▶ Zeeman effect
  - ▶ Stark effect
  - ▶ Molecules:  $\text{H}_2^+$  and  $\text{H}_2$

# The Zeeman Effect

- When an  $N$ -electron atom is placed in an external magnetic field  $\mathbf{B}$ , the contribution of the  $i$ 'th electron to the Hamiltonian is (with  $g_e \approx 2.002$ )

$$\hat{H}_B^{(i)} = \frac{e}{2m_e} (\hat{\mathbf{L}}_i + g_e \hat{\mathbf{S}}_i) \cdot \mathbf{B} + \frac{e^2}{8m_e} [B^2 r_i^2 - (\mathbf{B} \cdot \mathbf{r}_i)^2]$$

- Neglecting the quadratic  $B^2$  terms (see slide 3.28), and summing over all atomic electrons, the overall interaction with the magnetic field is

$$\hat{H}_B = \frac{e}{2m_e} (\hat{\mathbf{L}} + g_e \hat{\mathbf{S}}) \cdot \mathbf{B}$$

where  $\mathbf{L}$  and  $\mathbf{S}$  are the total electron orbital and spin angular momenta :

$$\hat{\mathbf{L}} = \sum_{i=1}^N \hat{\mathbf{L}}_i ; \quad \hat{\mathbf{S}} = \sum_{i=1}^N \hat{\mathbf{S}}_i$$

## The Zeeman effect (2)

- The contribution  $H_B$  is the sum of two magnetic dipole interactions :

$$\hat{H}_B = -\hat{\mu}_L \cdot \mathbf{B} - \hat{\mu}_S \cdot \mathbf{B} \quad \left\{ \begin{array}{l} \hat{\mu}_L = -\frac{\mu_B}{\hbar} g_L \hat{\mathbf{L}} ; \quad g_L = 1 \\ \hat{\mu}_S = -\frac{\mu_B}{\hbar} g_S \hat{\mathbf{S}} ; \quad g_S = g_e \approx 2 \end{array} \right.$$

- Taking the  $z$  axis to be along the  $\mathbf{B}$  field direction,  $\mathbf{B} = (0, 0, B_z)$ , this is

$$\hat{H}_B = (g_L \hat{L}_z + g_S \hat{S}_z) \frac{\mu_B B_z}{\hbar} \quad (8.3.1)$$

- The resulting energy correction (the *Zeeman effect*) is of order

$$\mu_B B_z \sim 5.8 \times 10^{-5} (B/T) \text{ eV}$$

This is small relative to typical atomic binding energies, so first-order perturbation theory should be reliable

Atomic energy levels have degeneracy  $g = 2J + 1$

→ we need to use *degenerate* perturbation theory

## The Zeeman effect (3)

- For a general field strength  $B$ , first-order perturbation theory involves an explicit matrix diagonalization, whatever the choice of basis for the unperturbed states
  - algebraically involved, or can only be carried out numerically
- However for sufficiently large or sufficiently small field strengths, the first-order energy corrections can be obtained analytically :

**Strong field :**  $\mu_B B \gg (\Delta E)_{\text{FS}}$

→ use the *uncoupled* basis  $|L, m_L, S, m_S\rangle$

**Weak field :**  $\mu_B B \ll (\Delta E)_{\text{FS}}$

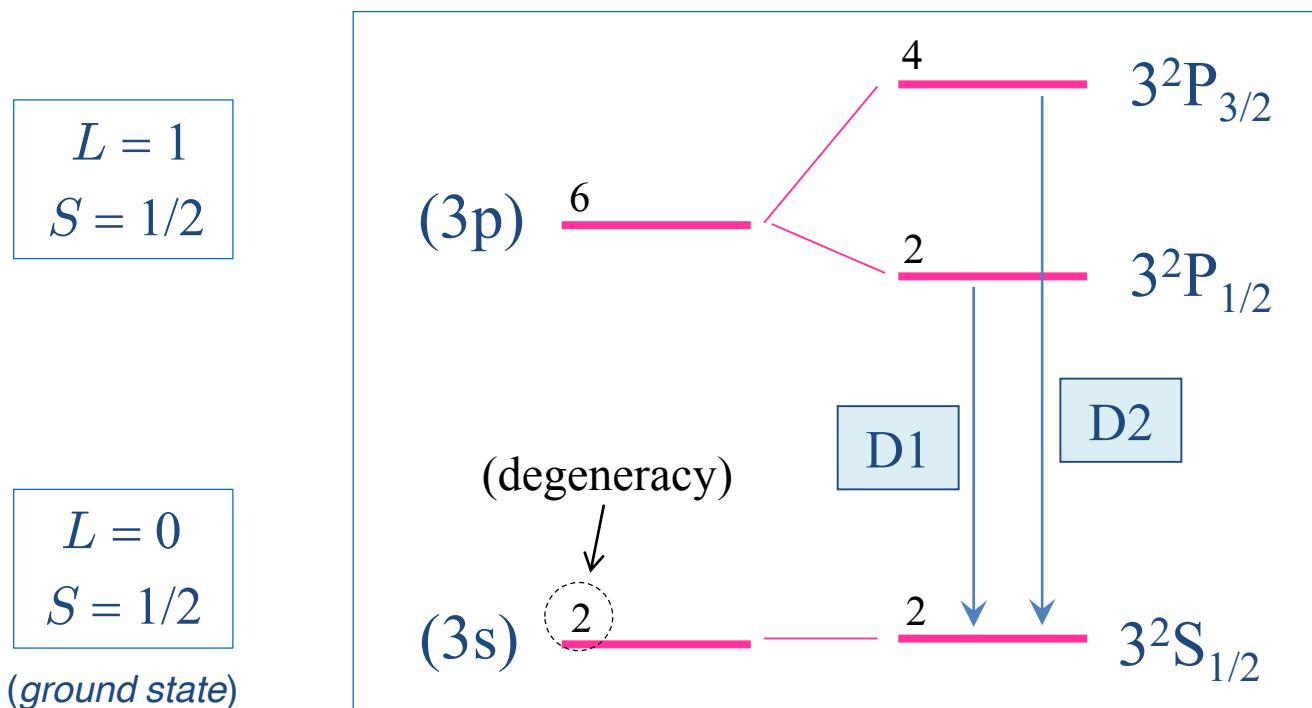
→ use the *coupled* basis  $|J, m_J, L, S\rangle$

where  $(\Delta E)_{\text{FS}}$  represents a typical fine structure splitting at zero field

## The Zeeman effect (4)

- We consider first the strong-field limit; then the weak-field limit; then we join them both together

As our primary example throughout, we consider the Zeeman effect for the (yellow) “D-line” doublet of sodium :



- Initially we consider fine structure only; later we reconsider the analysis with nuclear spin and hyperfine structure “switched on”

# The Strong-Field Zeeman Effect

- Suppose the  $\mathbf{B}$  field is strong enough that the resulting energy shifts are much larger than those due to fine (and hyperfine) structure :

$$\mu_B B \gg \langle \hat{H}_2 \rangle \sim \langle \xi(r) \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \rangle$$

Then the spin-orbit contribution  $H_2$  to the atomic structure can be neglected, leaving the unperturbed Hamiltonian as  $H_0 + H_1$  :

$$\hat{H} = (\hat{H}_0 + \hat{H}_1) + \hat{H}_B$$

- Neglecting fine structure, states of different  $J$  are degenerate in energy

e.g. for sodium (previous slide), the  $^2\text{P}_{1/2}$  and  $^2\text{P}_{3/2}$  levels become degenerate

(the D1/D2 doublet becomes a singlet)

$$L = 1, \quad S = 1/2$$

D1/D2

Each level is degenerate w.r.t.  $m_L$  and  $m_S$

The degeneracy is  $g = (2L + 1)(2S + 1)$

$$L = 0, \quad S = 1/2$$

## The strong field Zeeman effect (2)

- Each level is characterised by fixed values of  $L$  and  $S$   
Within each level, the matrix representation of  $H_B$  is diagonal in the uncoupled basis  $|L, m_L, S, m_S\rangle$ :

$$\hat{H}_B \propto (g_L \hat{L}_z + g_S \hat{S}_z)$$

$$(g_L \hat{L}_z + g_S \hat{S}_z) |\alpha L S m_L m_S\rangle = (g_L m_L + g_S m_S) \hbar |\alpha L S m_L m_S\rangle$$

$$\langle \alpha L S m'_L m'_S | (g_L \hat{L}_z + g_S \hat{S}_z) | \alpha L S m_L m_S \rangle = (g_L m_L + g_S m_S) \hbar \delta_{m'_L m_L} \delta_{m'_S m_S}$$

[  $H_B$  would not be diagonal in the coupled basis  $|J, m_J, L, S\rangle$  ]

- Thus no explicit matrix diagonalization is needed; the first-order energy corrections are given by the diagonal elements (expectation values)

$$(\Delta E)_B = \frac{\mu_B B_z}{\hbar} \langle \alpha L S m_L m_S | (g_L \hat{L}_z + g_S \hat{S}_z) | \alpha L S m_L m_S \rangle$$

$$\Rightarrow (\Delta E)_B = (g_L m_L + g_S m_S) \mu_B B_z \quad (8.7.1)$$

## The strong field Zeeman effect (3)

- In the approximation  $g_L = 1$  and  $g_e = 2$  (and hence  $g_S = 2$ ), the energy corrections become

$$(\Delta E)_B = (m_L + 2m_S)\mu_B B_z$$

Thus, in a strong magnetic field  $B$ , the original level splits into several equally spaced levels, with energy separation given by

$$\Delta E = \begin{cases} 2\mu_B B & (L = 0) \\ \mu_B B & (L > 0) \end{cases} \quad \begin{array}{l} \rightarrow 2S + 1 \text{ levels} \\ \rightarrow 2(L+2S) + 1 \text{ levels} \end{array}$$

- The magnetic field therefore lifts the original degeneracy with respect to the quantum numbers  $m_L$  and  $m_S$
- For example, for the sodium D-line transition  $(3p) \rightarrow (3s)$  :
  - the  $3p$ ,  $3s$  levels split into **5**, **2** equally spaced levels
  - the D-line splits into **3** spectral components, with spacing  $\mu_B B_z$

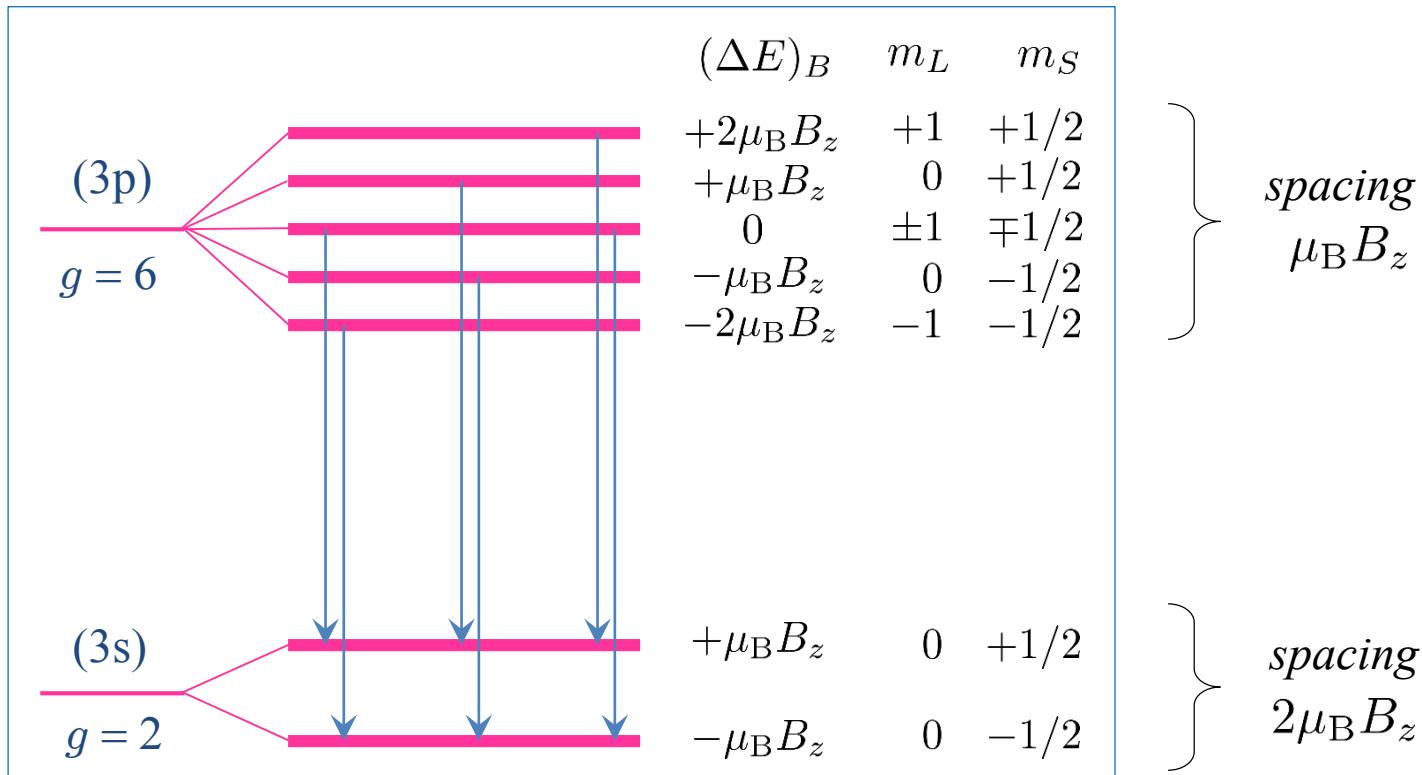
## Strong field Zeeman : sodium (3p) $\rightarrow$ (3s)

$L = 1, S = 1/2$

$3^2P_{1/2, 3/2}$

$L = 0, S = 1/2$

$3^2S_{1/2}$



3 equally spaced transition energies :

$$\begin{array}{c} \uparrow \\ E_0 - \mu_B B_z \end{array} \quad \begin{array}{c} \uparrow \\ E_0 \end{array} \quad \begin{array}{c} \uparrow \\ E_0 + \mu_B B_z \end{array}$$

(where  $E_0$  is the zero-field transition energy)

- The electric dipole (E1) selection rule  $\Delta m_S = 0$  forbids 6 of the  $6 \times 2 = 12$  possible (3p)  $\rightarrow$  (3s) transitions

# The Weak-Field Zeeman Effect

- Now consider the opposite extreme, where the energy corrections from the magnetic field are much smaller than those due to fine structure

$$\mu_B B \ll \langle \hat{H}_2 \rangle \sim \langle \xi(r) \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \rangle$$

Then we can no longer neglect  $H_2$  in the unperturbed Hamiltonian :

$$\hat{H} = (\hat{H}_0 + \hat{H}_1 + \hat{H}_2) + \hat{H}_B$$

- In this weak-field limit, each fine-structure level (i.e. each term  $^{2S+1}\text{L}_J$ , with definite values of  $L$ ,  $S$  and  $J$ ) must be considered separately

Each unperturbed fine-structure level has degeneracy  $g = 2J + 1$   
(due to the degeneracy with respect to  $m_J$ )

- Within each level, the matrix representation of  $H_B$  is diagonal in the coupled basis of states

$$|\alpha J m_J L S\rangle$$

[ but  $H_B$  is not diagonal in the uncoupled basis  $|L, m_L, S, m_S\rangle$  ]

## The weak field Zeeman effect (2)

- Take  $H_B$  as in equation (8.3.1) :

$$\hat{H}_B = (g_L \hat{L}_z + g_S \hat{S}_z) \frac{\mu_B B_z}{\hbar}$$

The projection formula (slide 5.70) shows that the  $z$  component of a vector operator is diagonal with respect to  $m_J$  :

$$\langle \alpha J m'_J LS | \hat{V}_z | \alpha J m_J LS \rangle = \langle \alpha J m_J LS | \hat{V}_z | \alpha J m_J LS \rangle \delta_{m'_J, m_J}$$

Hence, within each fine-structure level, the matrix representation of  $H_B$  is also diagonal with respect to  $m_J$  :

$$\langle \alpha J m'_J LS | \hat{H}_B | \alpha J m_J LS \rangle = \langle \alpha J m_J LS | \hat{H}_B | \alpha J m_J LS \rangle \delta_{m'_J, m_J}$$

→ no explicit matrix diagonalization is needed (in the coupled basis)

- The first-order energy corrections are given by the diagonal matrix elements (the expectation values) :

$$(\Delta E)_B = \frac{\mu_B B_z}{\hbar} \langle \alpha J m_J LS | (g_L \hat{L}_z + g_S \hat{S}_z) | \alpha J m_J LS \rangle$$

## The weak field Zeeman effect (3)

- From slide 5.74, this is

$$(\Delta E)_B = \frac{\mu_B B_z}{\hbar} g_J \langle J m_J L S | \hat{J}_z | J m_J L S \rangle = \frac{\mu_B B_z}{\hbar} g_J m_J \hbar$$

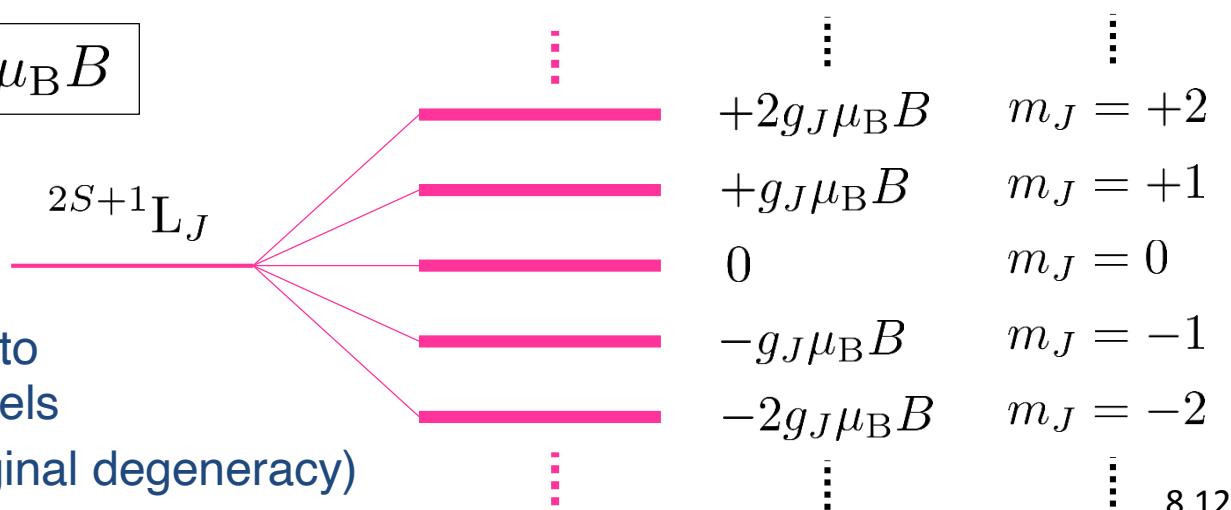
where the Landé  $g$ -factor,  $g_J$ , is given by

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

- The first-order energy shifts in a weak field  $B$  are therefore

$$(\Delta E)_B = m_J g_J \mu_B B$$

The original level splits into  
 $2J+1$  equally spaced levels  
(completely lifting the original degeneracy)



## The weak field Zeeman effect (4)

- Thus, in the weak-field limit, the magnetic contribution becomes *effectively*

$$\hat{H}_B = -\hat{\mu}_J \cdot \mathbf{B} ; \quad \hat{\mu}_J = -\frac{\mu_B}{\hbar} g_J \hat{\mathbf{J}}$$

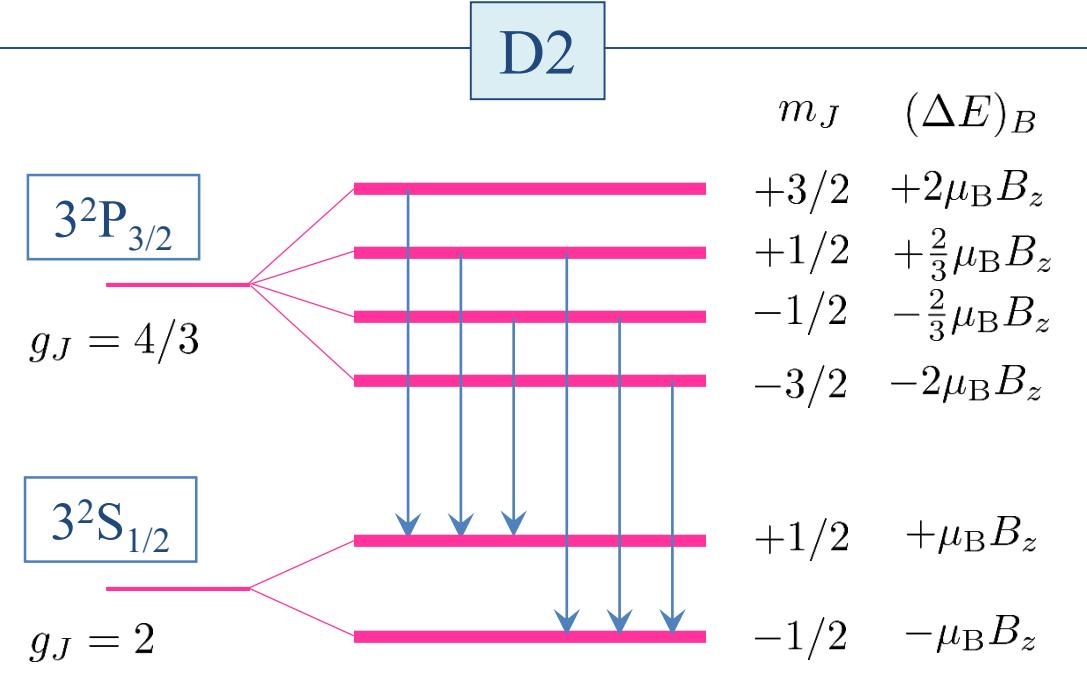
The  $L$  and  $S$  dipoles have combined (“coupled”) to give a single  $J$  dipole

- In the approximation  $g_L = 1$ ,  $g_e = 2$ , the Landé  $g$ -factor simplifies as

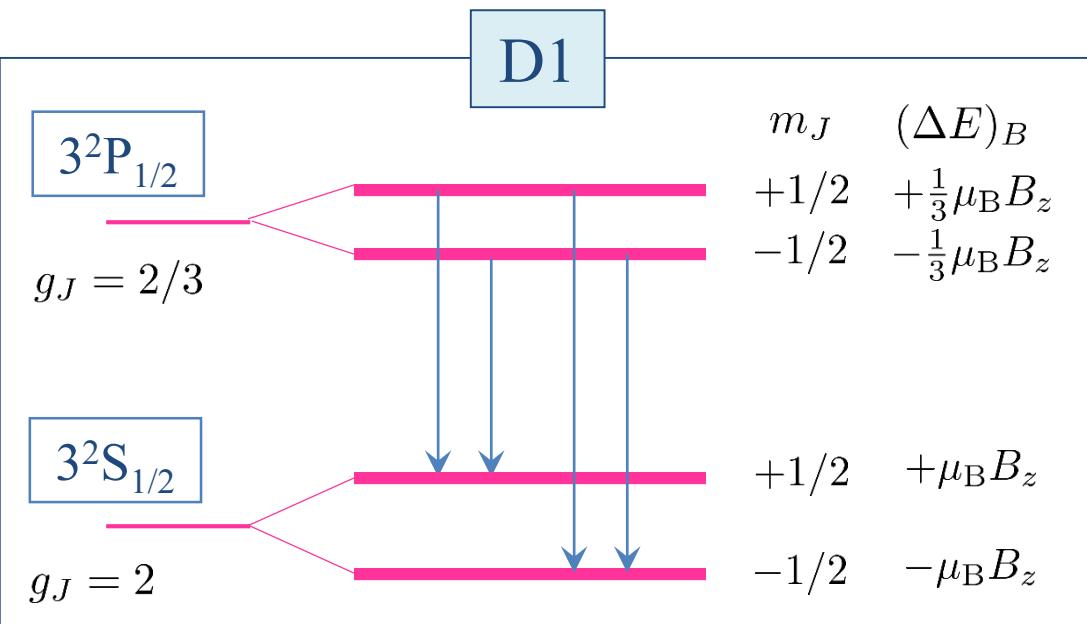
$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

- For the upper and lower levels of the sodium D-lines, for example, the  $g$ -factors are :

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



$m_J$	$\Delta E$
$+\frac{3}{2} \rightarrow +\frac{1}{2}$	$+\mu_B B_z$
$+\frac{1}{2} \rightarrow +\frac{1}{2}$	$-\frac{1}{3}\mu_B B_z$
$-\frac{1}{2} \rightarrow +\frac{1}{2}$	$-\frac{5}{3}\mu_B B_z$
$+\frac{1}{2} \rightarrow -\frac{1}{2}$	$+\frac{5}{3}\mu_B B_z$
$-\frac{1}{2} \rightarrow -\frac{1}{2}$	$+\frac{1}{3}\mu_B B_z$
$-\frac{3}{2} \rightarrow -\frac{1}{2}$	$-\mu_B B_z$



**E1 transitions**

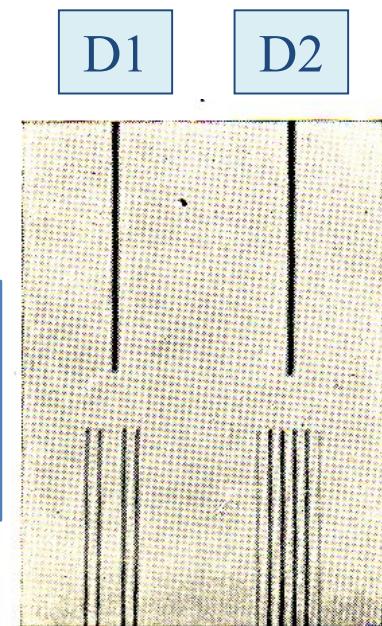
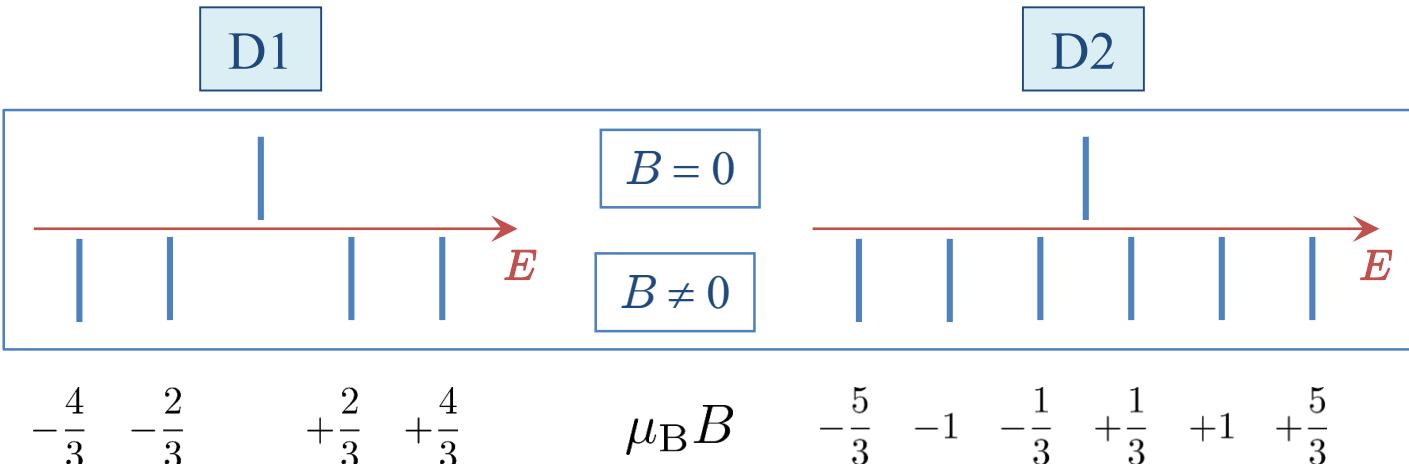
$m_J$	$\Delta E$
$+\frac{1}{2} \rightarrow +\frac{1}{2}$	$-\frac{2}{3}\mu_B B_z$
$-\frac{1}{2} \rightarrow +\frac{1}{2}$	$-\frac{4}{3}\mu_B B_z$
$+\frac{1}{2} \rightarrow -\frac{1}{2}$	$+\frac{4}{3}\mu_B B_z$
$-\frac{1}{2} \rightarrow -\frac{1}{2}$	$+\frac{2}{3}\mu_B B_z$

## Weak-field Zeeman effect : sodium 'D' lines

- For D2, the selection rule  $\Delta m_J = 0, \pm 1$  forbids two of the  $4 \times 2 = 8$  possible transitions :  
 $(+\frac{3}{2} \not\rightarrow -\frac{1}{2}), \quad (-\frac{3}{2} \not\rightarrow +\frac{1}{2})$

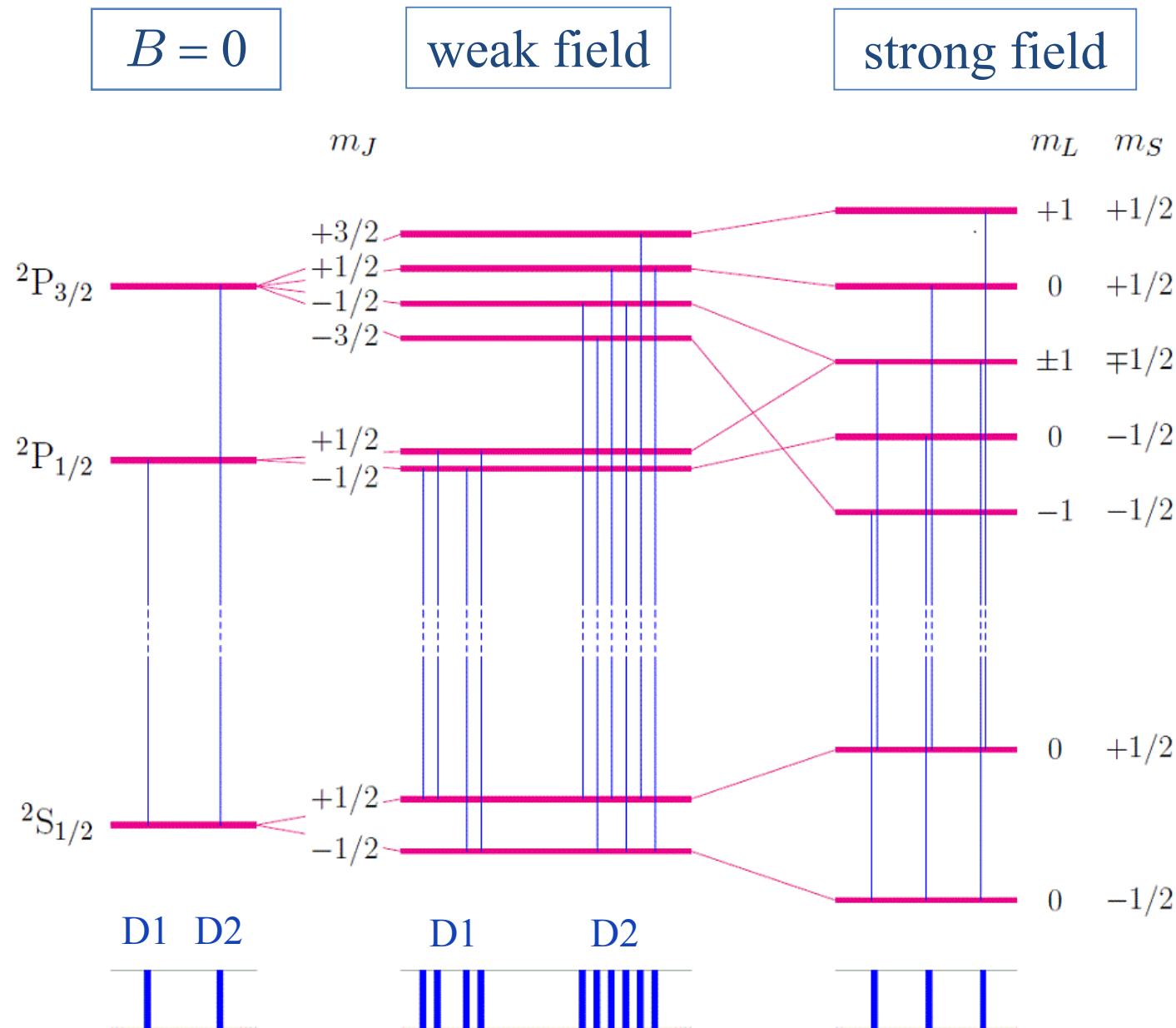
For D1, there are no restrictions

- the D2 line splits into 6 equally spaced lines
- the D1 line splits into 4 variably spaced lines



- The Zeeman effect is a powerful way of determining the  $J, L, S$  quantum numbers of the levels involved in a spectral line

# Zeeman effect : summary for weak and strong fields



# Zeeman Effect for general field strength

- In an external magnetic field  $\mathbf{B}$ , an atom is no longer an isolated system
  - ⇒ the total angular momentum  $\mathbf{J} = \mathbf{L} + \mathbf{S}$  of the atom is no longer expected to be conserved
  - ⇒ the operator  $\mathbf{J}$  is not expected to commute with the Hamiltonian  $H$
- The components  $J_x$  and  $J_y$  are easily seen not to commute with  $H_B$ :

$$[\hat{H}_B, \hat{J}_x] = \frac{\mu_B B_z}{\hbar} (g_L [\hat{L}_z, \hat{J}_x] + g_S [\hat{S}_z, \hat{J}_x]) = i\mu_B B_z (g_L \hat{L}_y + g_S \hat{S}_y) \neq 0$$

However, because

$$[\hat{L}_z, \hat{J}_z] = [\hat{S}_z, \hat{J}_z] = 0$$

the  $z$  component  $J_z$  does commute with  $H_B$ , and hence also with the total Hamiltonian :

$$\boxed{[\hat{H}_B, \hat{J}_z] = 0 , \quad [\hat{H}, \hat{J}_z] = 0} \quad (8.17.1)$$

- This reflects the fact that the system still has rotational (cylindrical) symmetry about the  $\mathbf{B}$  field direction (the  $z$  axis)

## Zeeman effect : general field strength (2)

- The relations (8.17.1) imply that, in the presence of a magnetic field (of any strength),  $m_J$  is still a good quantum number even though  $J$  is not
  - the quantum number  $m_J$  can be used to track the energy eigenstates as they evolve with varying magnetic field strength :  
$$(\text{weak-field state } m_J) \leftrightarrow (\text{strong-field state with } m_L + m_S = m_J)$$
  
(as indicated schematically by the weak  $\leftrightarrow$  strong links on slide 8.16)
- A quantitative analysis requires that the perturbations due to the **B**-field and due to fine structure must be treated together, in a common basis :

$$\hat{H}' = \hat{H}_{\text{FS}} + (g_L \hat{L}_z + g_S \hat{S}_z) \frac{\mu_B B_z}{\hbar}$$

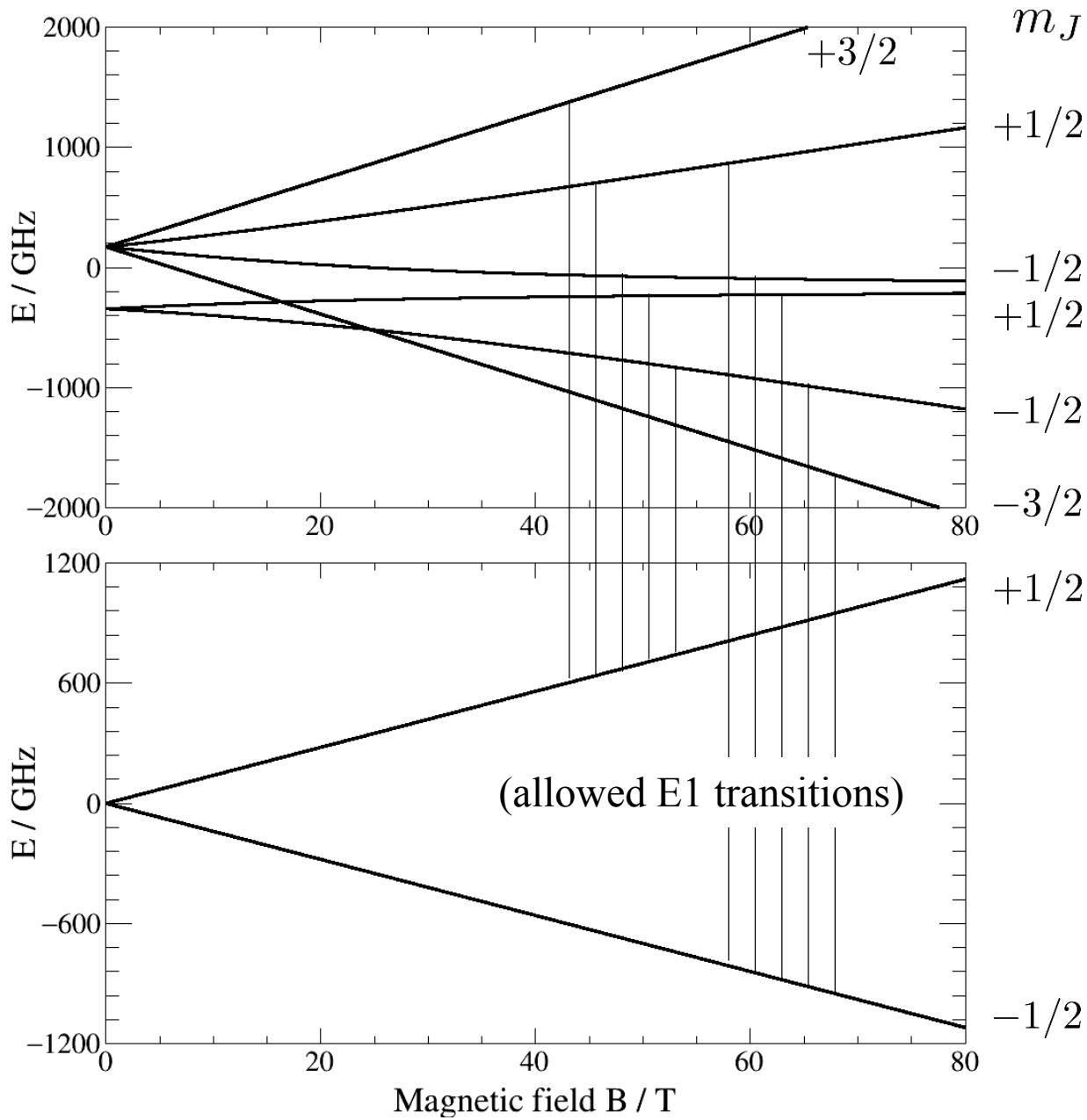
- In general, this can only be done numerically

For example, for the (3p) level of sodium :

the  $3P_{1/2}$  and  $3P_{3/2}$  levels must be considered together, taking their zero-field fine structure splitting into account

→ involves the diagonalisation of a  $6 \times 6$  matrix

## Zeeman effect : sodium 3S and 3P energy levels



## Zeeman effect : sodium D-line transition energies

- The selection rule  $\Delta m_J = 0, \pm 1$  forbids two of the  $6 \times 2 = 12$  possible  $3P \rightarrow 3S$  transitions :  
$$\left( +\frac{3}{2} \not\rightarrow -\frac{1}{2} \right), \quad \left( -\frac{3}{2} \not\rightarrow +\frac{1}{2} \right)$$

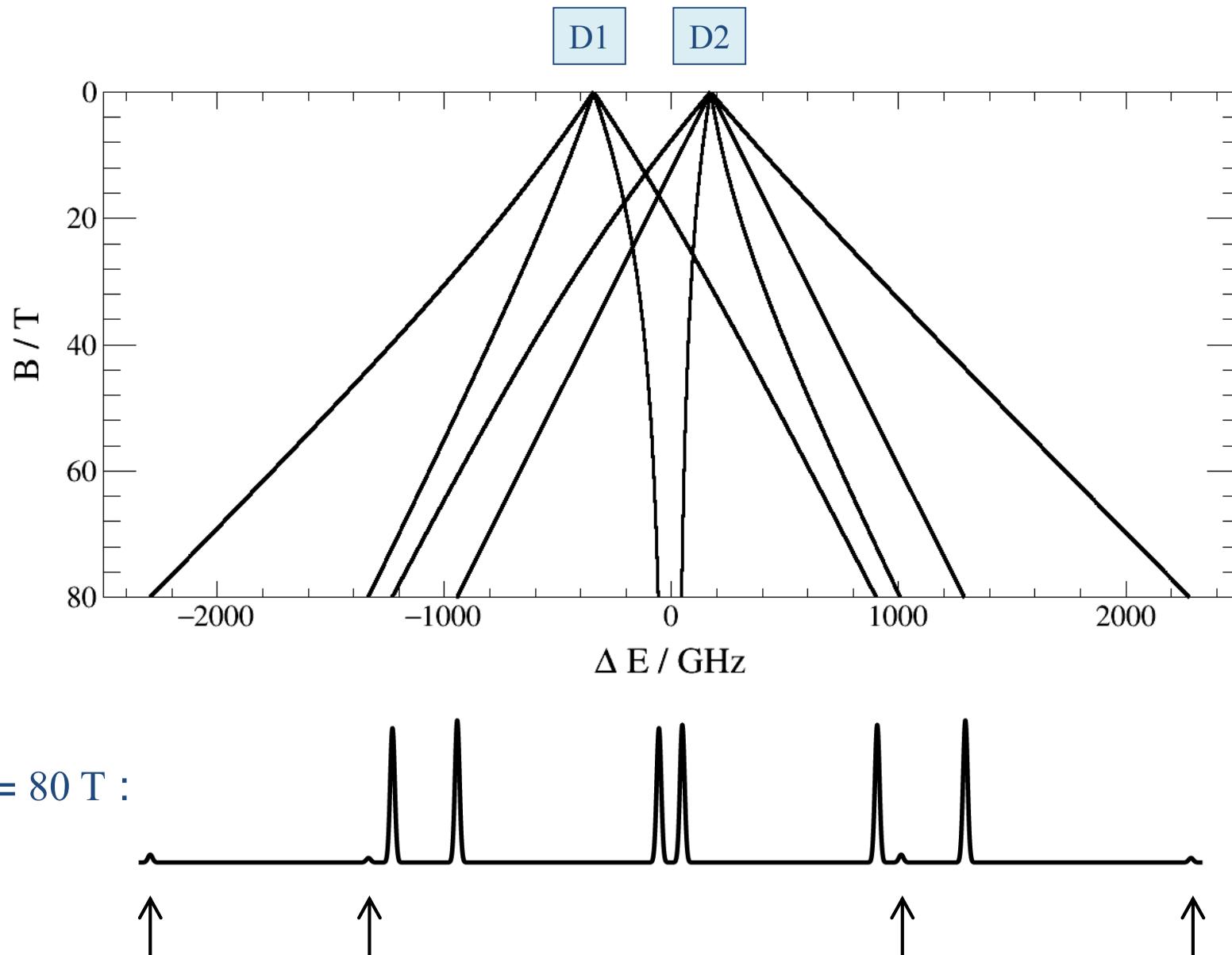
The 10 remaining allowed E1 transitions all have different energies

- the D1/D2 doublet transition splits into **10** separate spectral lines (see plot on next slide)

- At low field, the results agree with the weak-field analysis of slide 8.15  
But for a *strong* field, the analysis of slide 8.9 predicted a splitting into only **3** spectral lines, not 10
- The explanation is that, at high field, the *intensity* of 4 of the 10 lines becomes negligibly small (see bottom of next slide) ;  
→ the 6 high intensity lines form **3** equally spaced doublets

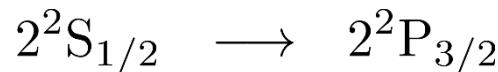
The strong field limit of slide 8.9 is never truly reached; a remnant of the original fine structure splitting is always present as a doublet structure

## Zeeman effect : sodium D-line transition energies



## Zeeman effect : hydrogen $n = 2$

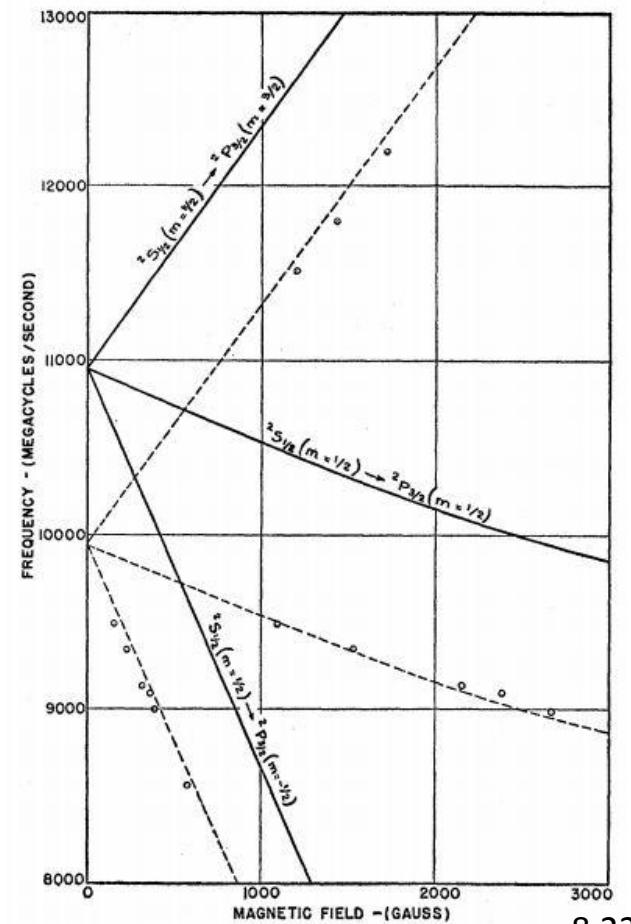
- The  $n = 2$  level of hydrogen is similar to sodium, with the added complication that the  $2S_{1/2}$  level lies close to the  $2P_{1/2}$  and  $2P_{3/2}$  levels :
  - the  $2S_{1/2}$ ,  $2P_{1/2}$  and  $2P_{3/2}$  levels must be considered simultaneously
  - must now diagonalise an  $8 \times 8$  matrix
- The Lamb shift discovery plot on slide 4.43 shows measurements of various  $2^2S_{1/2} \rightarrow 2^2P_{3/2}$  transition energies in a magnetic field



$$m_J = +\frac{1}{2} \longrightarrow m_J = +\frac{3}{2}$$

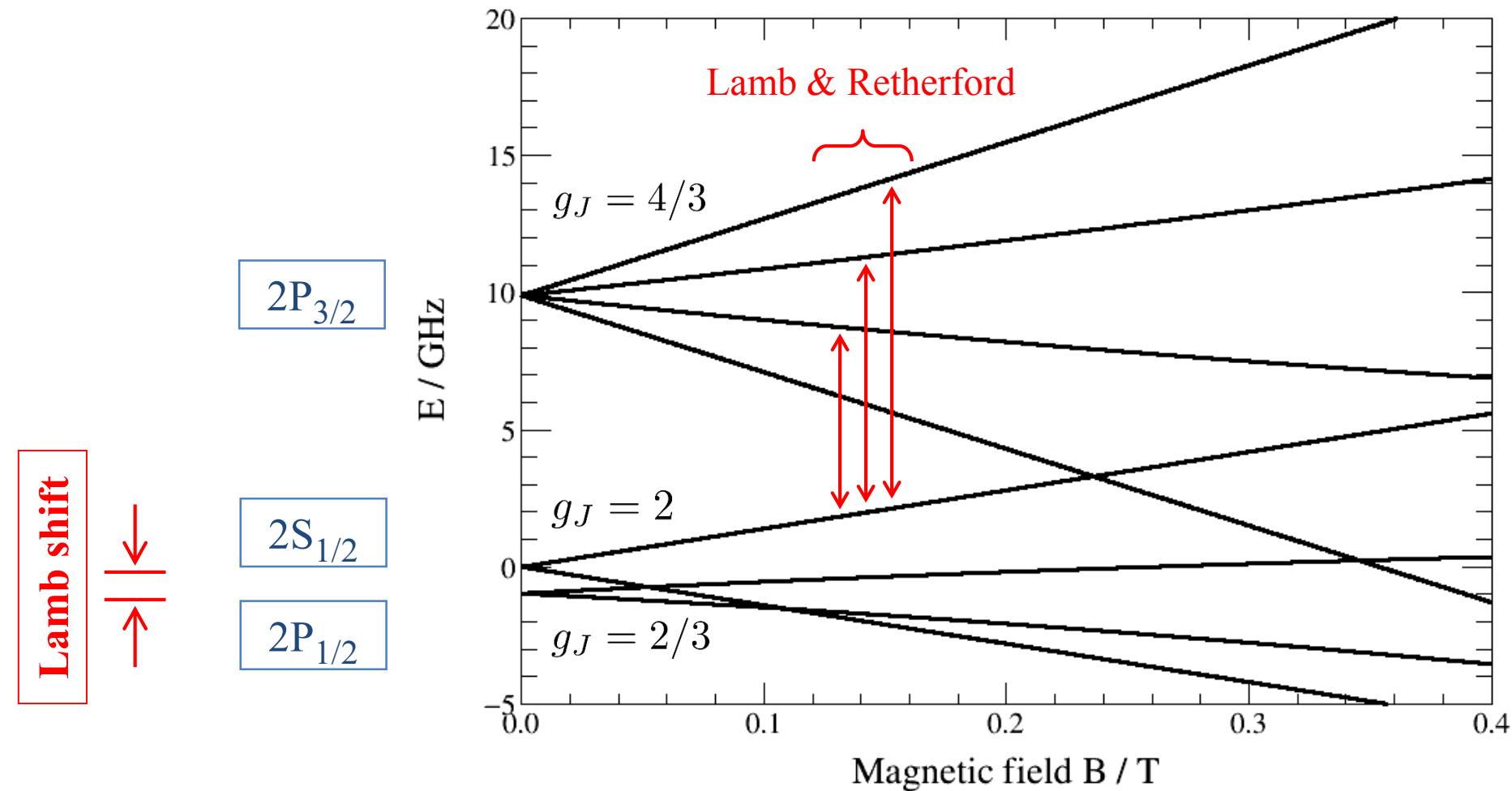
$$m_J = +\frac{1}{2} \longrightarrow m_J = +\frac{1}{2}$$

$$m_J = +\frac{1}{2} \longrightarrow m_J = -\frac{1}{2}$$



## Zeeman effect : hydrogen $n = 2$

- The energy corrections for the  $n = 2$  level of hydrogen evolve as



- Note that the axis scales are very different to those used for sodium

## Zeeman Effect for Hyperfine Levels

- Now consider a magnetic field  $\mathbf{B}$  which is small enough that the resulting energy shifts are comparable to those due to *hyperfine* structure :

$$\mu_B B \lesssim (\Delta E)_{\text{HFS}}$$

We can no longer neglect the hyperfine contribution in the unperturbed Hamiltonian :

$$\hat{H} = (\hat{H}_0 + \hat{H}_1 + \hat{H}_2 + \hat{H}_{\text{HF}}) + \hat{H}_B$$

We must include the perturbation due to the nuclear magnetic moment  $\mu_I$  :

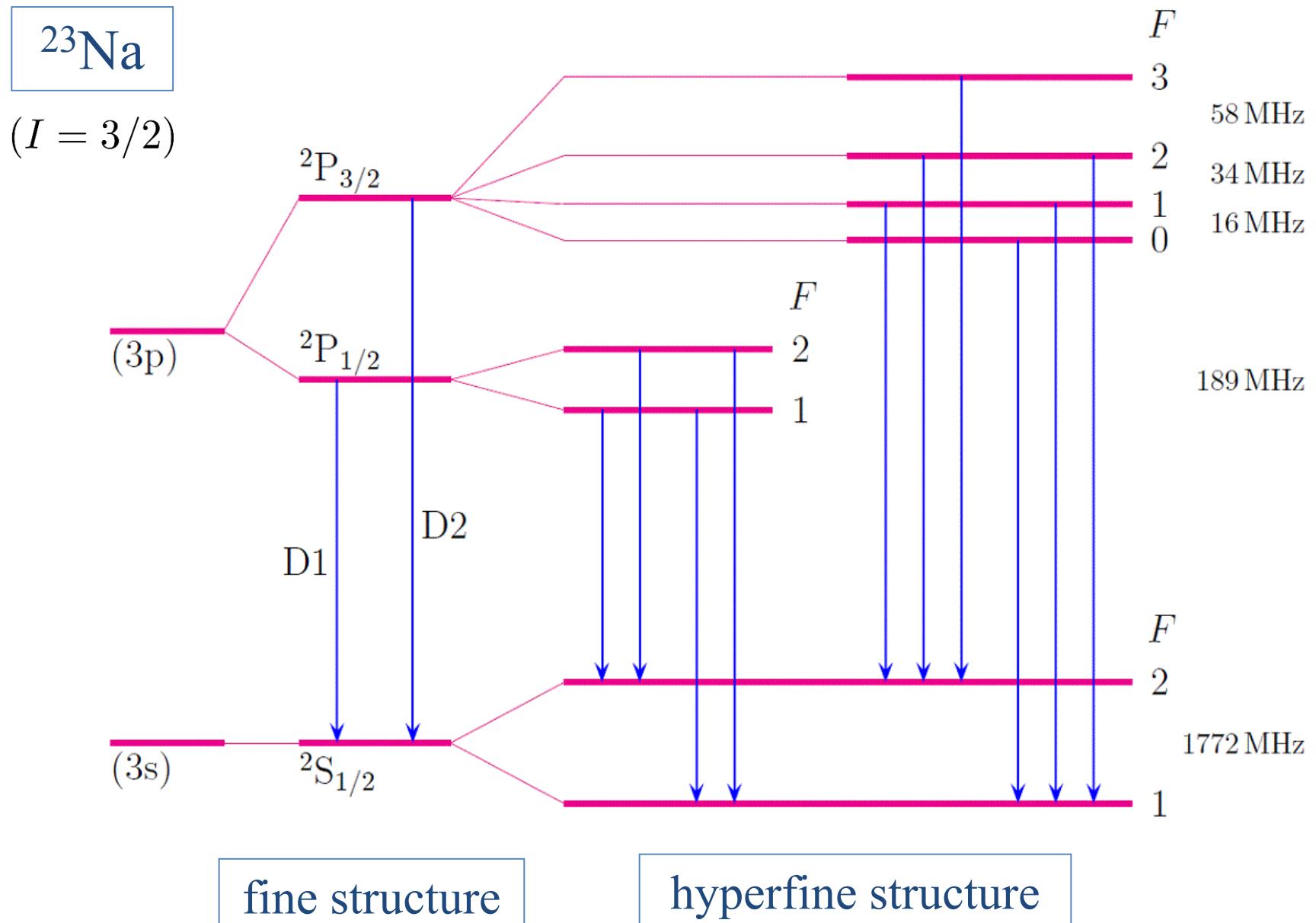
$$\hat{H}_B = -\hat{\mu}_L \cdot \mathbf{B} - \hat{\mu}_S \cdot \mathbf{B} - \hat{\mu}_I \cdot \mathbf{B} \quad (8.24.1)$$

- The hyperfine case lies within the weak-field regime for fine structure  
Therefore the  $L$  and  $S$  contributions above combine as on slide 8.13 to form a single dipole,  $J$  :

$$\hat{H}_B = -\hat{\mu}_J \cdot \mathbf{B} - \hat{\mu}_I \cdot \mathbf{B}$$

$$\hat{\mu}_J = -\frac{\mu_B}{\hbar} g_J \hat{\mathbf{J}} ; \quad \hat{\mu}_I = -\frac{\mu_B}{\hbar} g_I \hat{\mathbf{I}}$$

# The Zeeman effect : sodium-23 at zero-field



## Zeeman effect for hyperfine levels (2)

- Taking the  $z$  axis to be along the **B** field direction,  $\mathbf{B} = (0, 0, B_z)$ , the Hamiltonian for the hyperfine case is then

$$\hat{H}_B = (g_J \hat{J}_z + g_I \hat{I}_z) \frac{\mu_B B_z}{\hbar}$$

- The analysis of the hyperfine case is essentially a carbon copy of the fine structure analysis, with the replacements

$$(\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}) \quad \longrightarrow \quad (\hat{\mathbf{F}} = \hat{\mathbf{J}} + \hat{\mathbf{I}})$$

We again consider the weak-field and strong-field limits, and then link them both together

- In the hyperfine case, as a result of rotational symmetry about the **B** field direction, the operator  $F_z$  commutes with the total Hamiltonian

$$[\hat{H}_B, \hat{F}_z] = 0, \quad [\hat{H}, \hat{F}_z] = 0$$

Hence the quantum number  $m_F$  remains a good quantum number which labels each eigenstate as it evolves with varying field strength  $B$

## Zeeman effect : hyperfine weak field

- First consider the hyperfine *weak-field* limit, such that the energy corrections due to the  $\mathbf{B}$  field are much less than the hyperfine separation,

$$\mu_B B \ll \langle \hat{\mathbf{L}} \cdot \hat{\mathbf{I}} \rangle$$

In this case, the  $\mathbf{J}$  and  $\mathbf{I}$  dipoles couple to give a single  $\mathbf{F}$  dipole :

$$\hat{H}_B = -\hat{\boldsymbol{\mu}}_F \cdot \mathbf{B} ; \quad \hat{\boldsymbol{\mu}}_F = -\frac{\mu_B}{\hbar} g_F \hat{\mathbf{F}}$$

where the Landé  $g$ -factor,  $g_F$ , depends on  $F$ ,  $I$  and  $J$  via the hyperfine equivalent of the expression on slide 8.12 :

$$g_F = g_J \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)} + g_I \frac{F(F+1) + I(I+1) - J(J+1)}{2F(F+1)}$$

- The energy corrections due to  $\mathbf{B}$  are proportional to  $m_F$  :

$$(\Delta E)_B = m_F g_F \mu_B B$$

Each hyperfine level  $F$  splits into  $2F+1$  equally spaced levels

## Zeeman effect : hyperfine weak field (2)

- Since nuclear magnetic dipole moments are small,  $|g_I| \ll 1$ , we can usually neglect the  $g_I$  contribution and take

$$g_F \approx g_J \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)}$$

$$|g_I| \ll |g_J|$$

- For the sodium D-line levels for example, the table on slide 8.13 can be extended to include the hyperfine  $g$ -factors :

$$(g_L = 1, g_S = 2)$$

term	$L$	$S$	$J$	$F$	$g_J$	$g_F$
${}^2P_{3/2}$	1	1/2	3/2	3	4/3	2/3
				2		2/3
				1		2/3
				0		0
$F = I \otimes J$	1	1/2	1/2	2	2/3	1/6
				1		-1/6
$I = 3/2$	0	1/2	1/2	2	2	1/2
				1		-1/2
${}^2P_{1/2}$	1	1/2	1/2	2	2/3	1/6
				1		-1/6
${}^2S_{1/2}$	0	1/2	1/2	2	2	1/2
				1		-1/2

## Zeeman effect : hyperfine strong field

- In the *strong-field* hyperfine regime, states of different  $F$  within a given term  $^{2S+1}\text{L}_J$  effectively become degenerate

The energy corrections are given by the hyperfine equivalent of equation (8.7.1) :

$$(\Delta E)_B = (g_I m_I + g_J m_J) \mu_B B_z$$

The dominant contribution comes from the second term :

$$(\Delta E)_B \approx g_J m_J \mu_B B_z \quad (|g_I| \ll |g_J|)$$

In this approximation, at high field, we obtain  $(2J + 1)$  equally spaced levels

- The subdominant contribution  $(\Delta E)_B \propto g_I m_I$  in principle splits each of these  $(2J + 1)$  levels into  $(2I + 1)$  very closely spaced levels

In practice, this  $g_I m_I$  substructure is much too small to be easily seen

$(2I + 1)$  substructure is seen at high-field (see plots below), but this is essentially just an evolved relic of the weak-field behaviour

## Zeeman effect : hyperfine general field

- For a general field strength  $B$ , the hyperfine and  $\mathbf{B}$  field perturbations must be treated together :

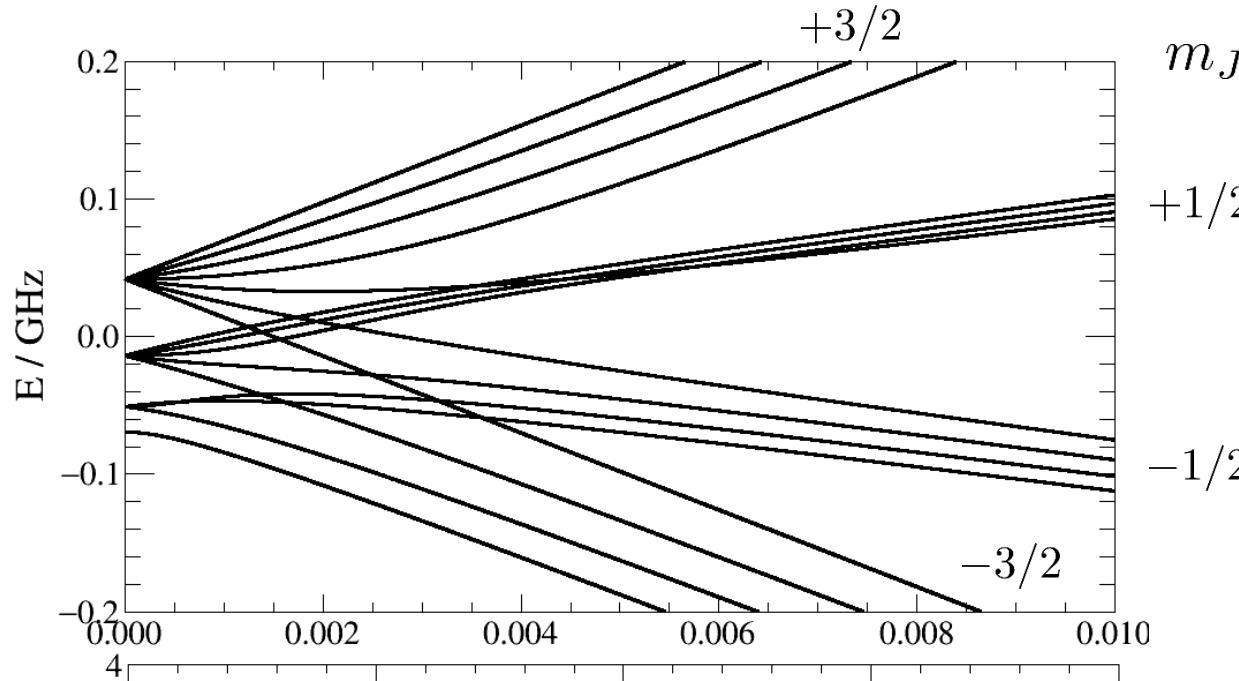
$$\hat{H} = \hat{H}_{\text{HF}} + (g_I \hat{I}_z + g_J \hat{J}_z) \frac{\mu_{\text{B}} B_z}{\hbar}$$

- we have to diagonalise a square matrix of dimension  $(2I + 1)(2J + 1)$ , which in general can only be done numerically
- For example, consider the sodium D2 line :
  - the upper level,  ${}^2\text{P}_{3/2}$ , requires diagonalization of a  $16 \times 16$  matrix
  - the lower level,  ${}^2\text{S}_{1/2}$ , requires diagonalization of an  $8 \times 8$  matrix
- The electric dipole (E1) selection rule  $\Delta m_F = 0, \pm 1$  forbids 60 of the  $16 \times 8 = 128$  possible transitions
  - the D2 line splits into **68** separate lines, of varying intensity

# Zeeman effect : sodium D2 hyperfine levels

$3^2P_{3/2}$

$F = 3$   
 $F = 2$   
 $F = 1$   
 $F = 0$



$m_J$

$I = 3/2$

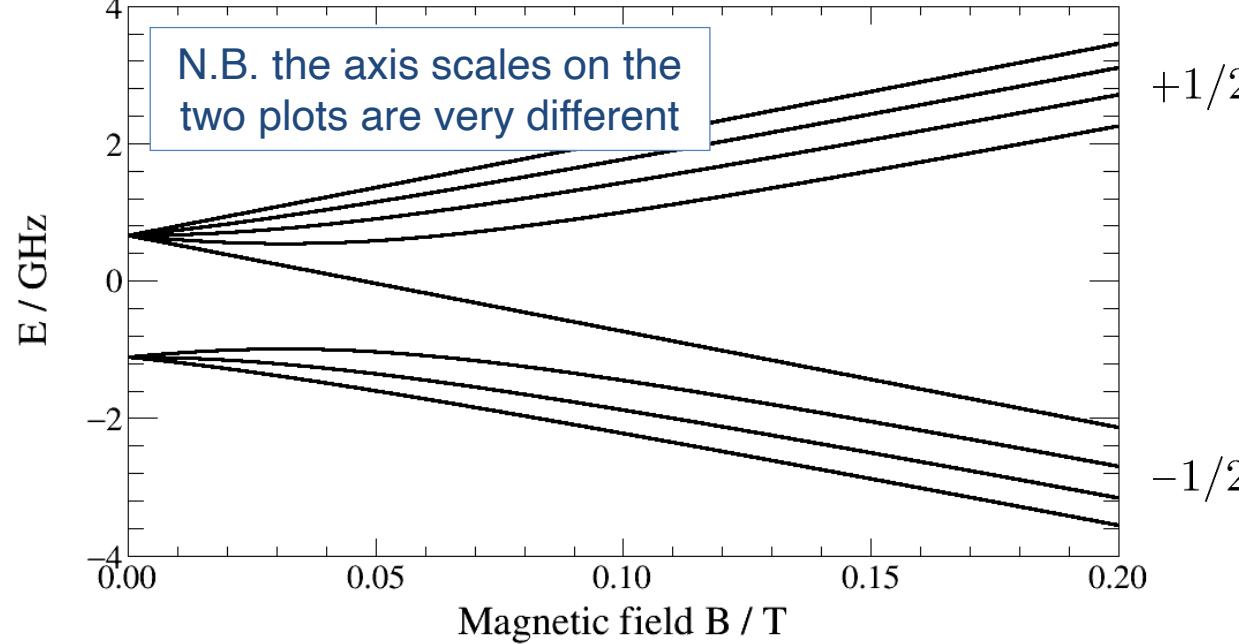
+1/2

At high field :

$2J + 1 = 4$   
 primary levels  
 with  
 $2I + 1 = 4$   
 substructure

$3^2S_{1/2}$

$F = 2$   
 $F = 1$



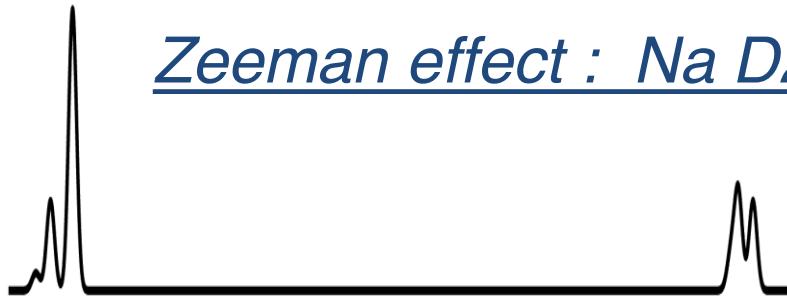
+1/2

At high field :

$2J + 1 = 2$   
 primary levels  
 with  
 $2I + 1 = 4$   
 substructure

N.B. the axis scales on the  
 two plots are very different

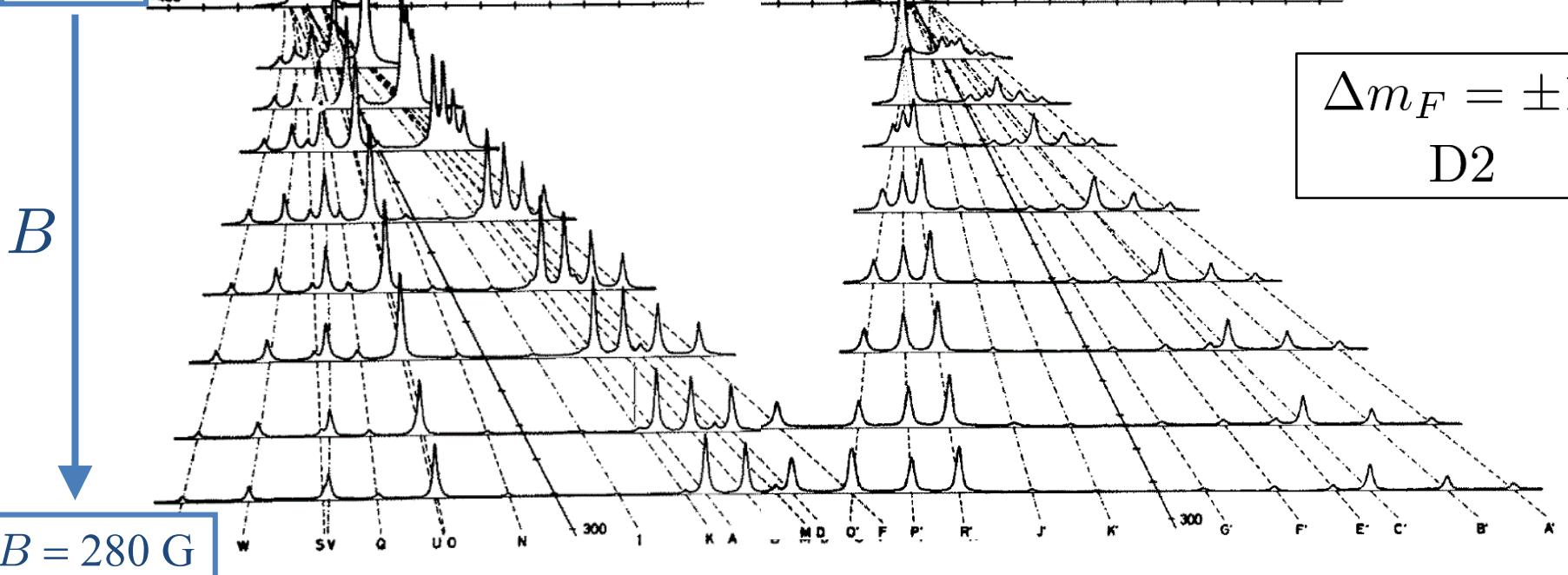
## Zeeman effect : Na D2 hyperfine



$B = 0$  prediction

[L. Windholz + M. Musso, Z. Phys. D 8 \(1988\) 239](#)

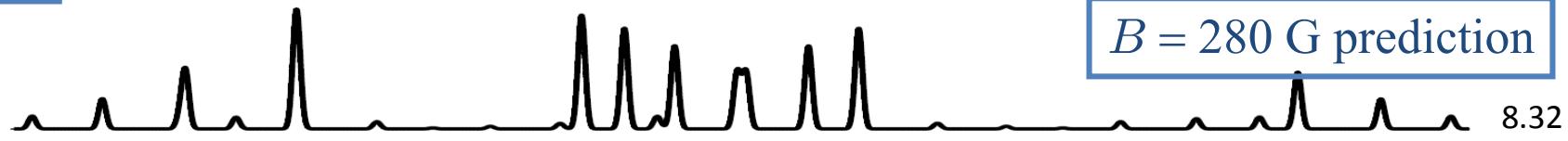
$B = 0$



$\Delta m_F = \pm 1$   
D2

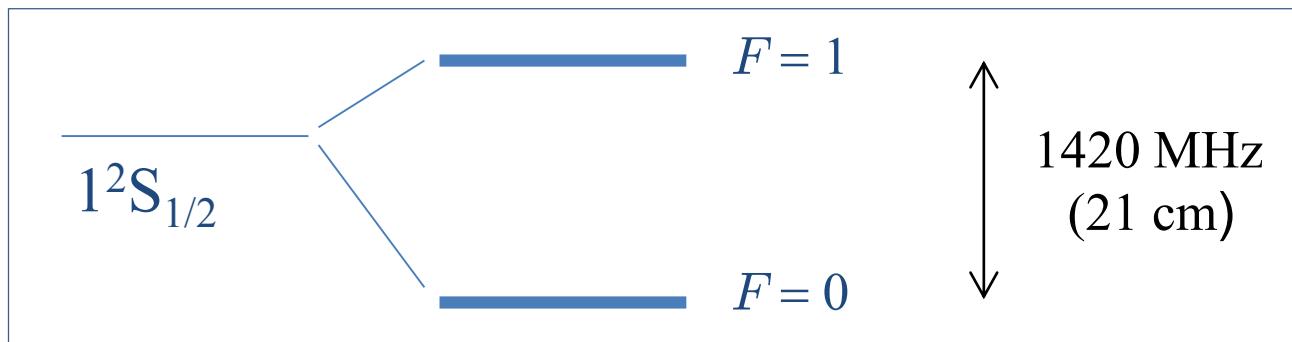
$B = 280$  G

$B = 280$  G prediction



## Zeeman hyperfine : hydrogen ground state

- An important example of the Zeeman effect for hyperfine levels is the ground state of the hydrogen atom :



Forms the basis of the *hydrogen maser*, used in atomic clocks for example

- This case requires the diagonalisation of only a  $4 \times 4$  matrix containing a  $2 \times 2$  submatrix
  - can be solved analytically (known as the *Breit-Rabi formula*)

Modelling the atomic hyperfine Hamiltonian  $H_{\text{HF}}$  as  $A\mathbf{I} \cdot \mathbf{J}$ ,

$$\hat{H} = A\hat{\mathbf{I}} \cdot \hat{\mathbf{J}} + (g_I\hat{I}_z + g_J\hat{J}_z)\frac{\mu_B B_z}{\hbar}$$

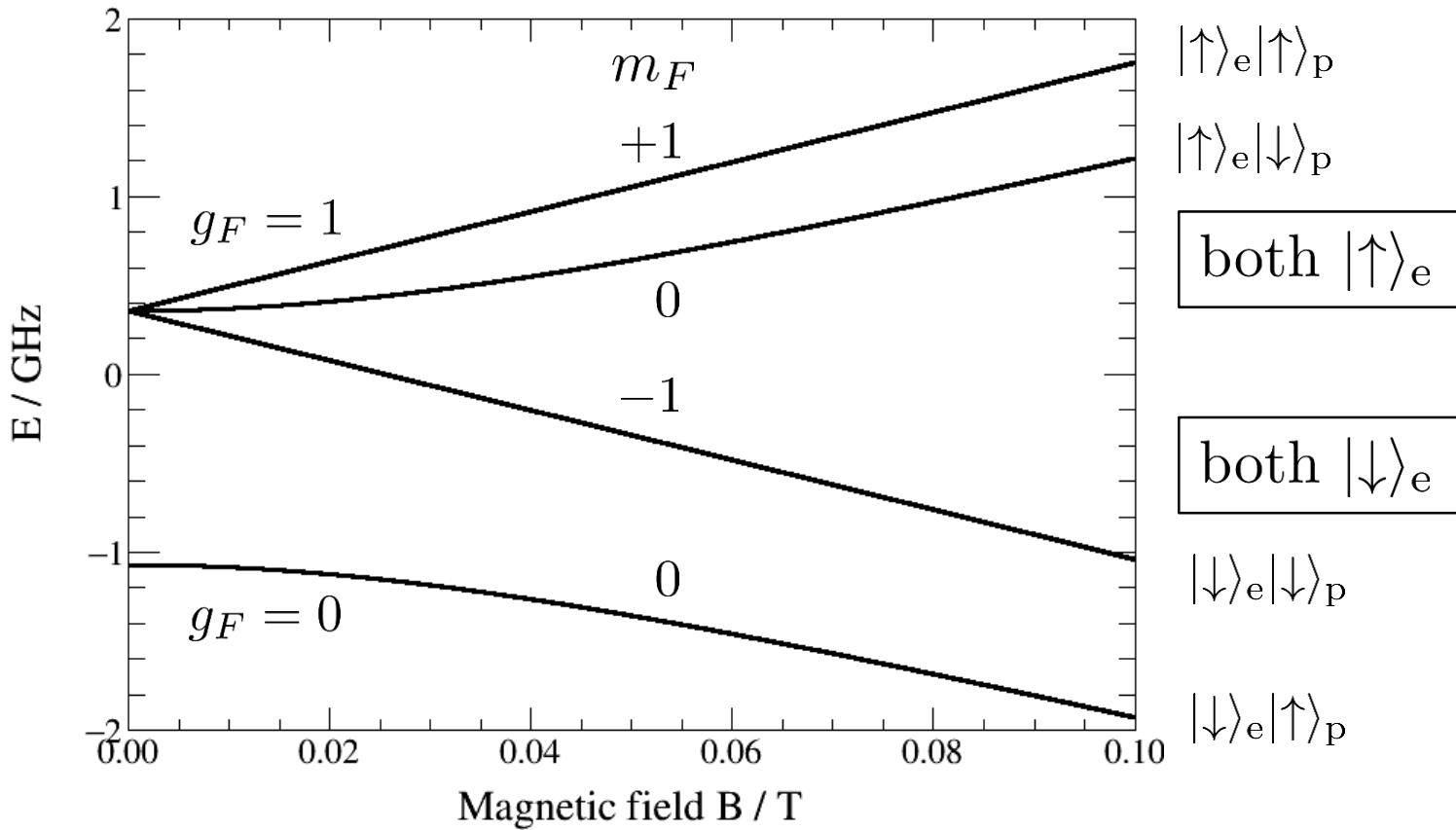
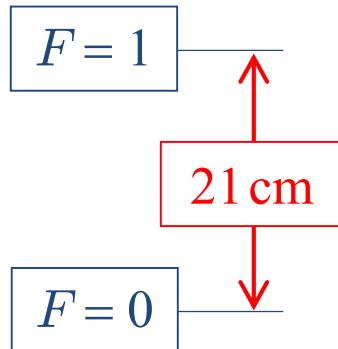
this is exactly the calculation carried out in Q18 on the Examples Sheet

## Zeeman hyperfine : hydrogen ground state

-- The H atom ground state quantum numbers and  $g$ -factors are :

$$I = 1/2$$

term	$L$	$S$	$J$	$F$	$g_L$	$g_S$	$g_J$	$g_F$
$^2S_{1/2}$	0	1/2	1/2	1	1	2	2	1
				0				0



## Zeeman hyperfine : hydrogen ground state

- In the limit  $B \rightarrow 0$ , the first-order energy correction for the two states with  $m_F = 0$  vanishes
  - the magnetic field has no effect (zero slope)

The transition between the two  $m_F = 0$  states is very insensitive to the value of  $B$ , and is used as the basis of the hydrogen maser atomic clock

- Hydrogen atoms in their ground state will typically (in thermal equilibrium for example) be an equal mix of each hyperfine state

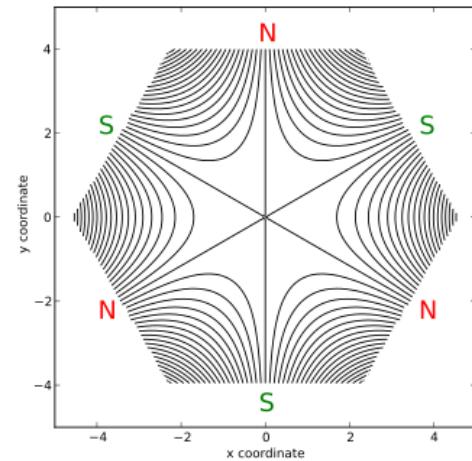
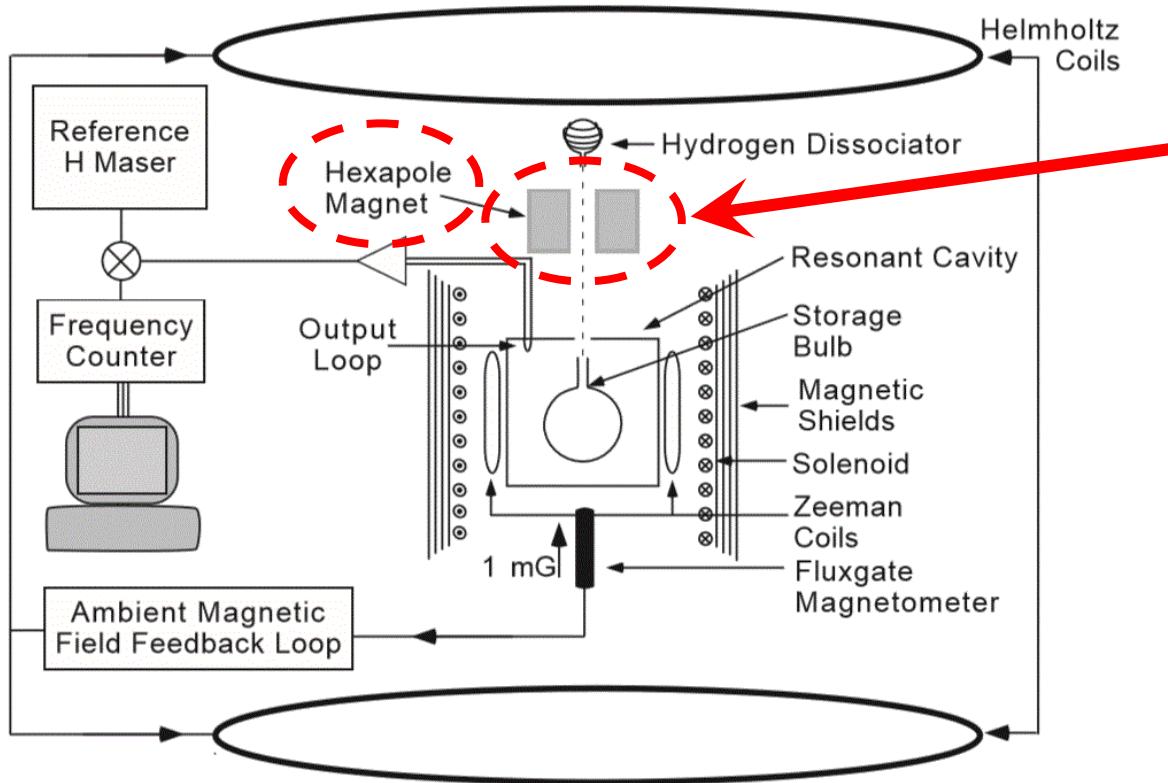
$$|F, m_F\rangle = |11\rangle, |10\rangle, |1, -1\rangle, |00\rangle$$

If H atoms are passed through a Stern-Gerlach apparatus, we could in principle see four emerging beams, one for each hyperfine state

In practice, the experimental resolution is usually insufficient, and only two emerging beams are seen

## Zeeman hyperfine : the hydrogen maser

- In the hydrogen maser, a hexapole magnet is typically used, to focus the states  $|11\rangle$ ,  $|10\rangle$ , and defocus the states  $|1,-1\rangle$ ,  $|00\rangle$



$(B = 0$  along the beam axis)

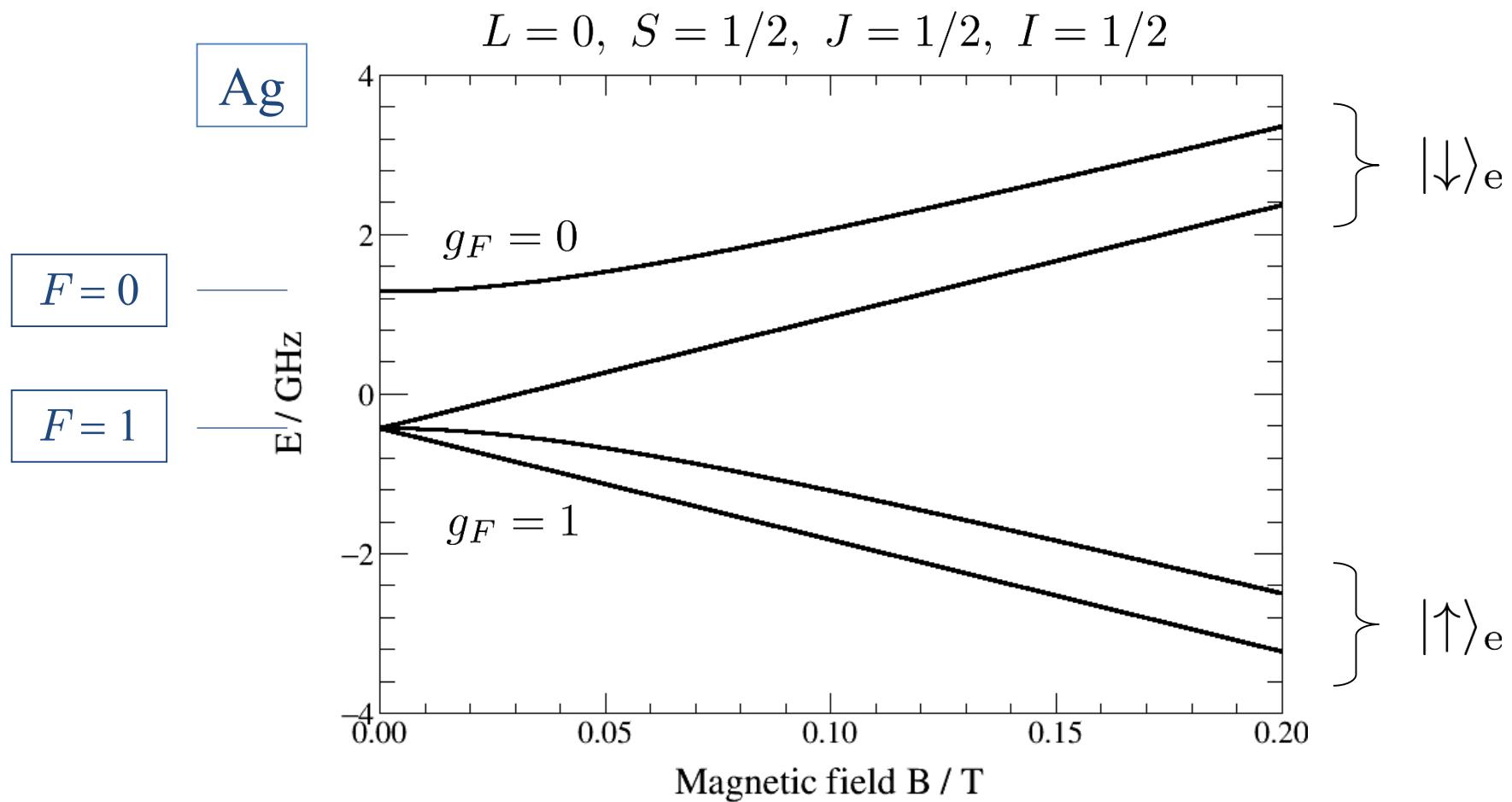
[D. F. Phillips et al., Phys. Rev. D 63 \(2001\) 111101](#)

This gives the *population inversion* required for amplification (see lasers)

- Provides a highly stable oscillator : better than  $10^{-15}$  over several hours

## Zeeman hyperfine : Stern-Gerlach revisited

- The original Stern-Gerlach expt (slide 3.77) used a beam of *silver* atoms  
The ground state of silver has the same quantum numbers as hydrogen, though for silver, the hyperfine level  $F = 1$  lies below  $F = 0$  :



## Zeeman hyperfine : Stern-Gerlach revisited (2)

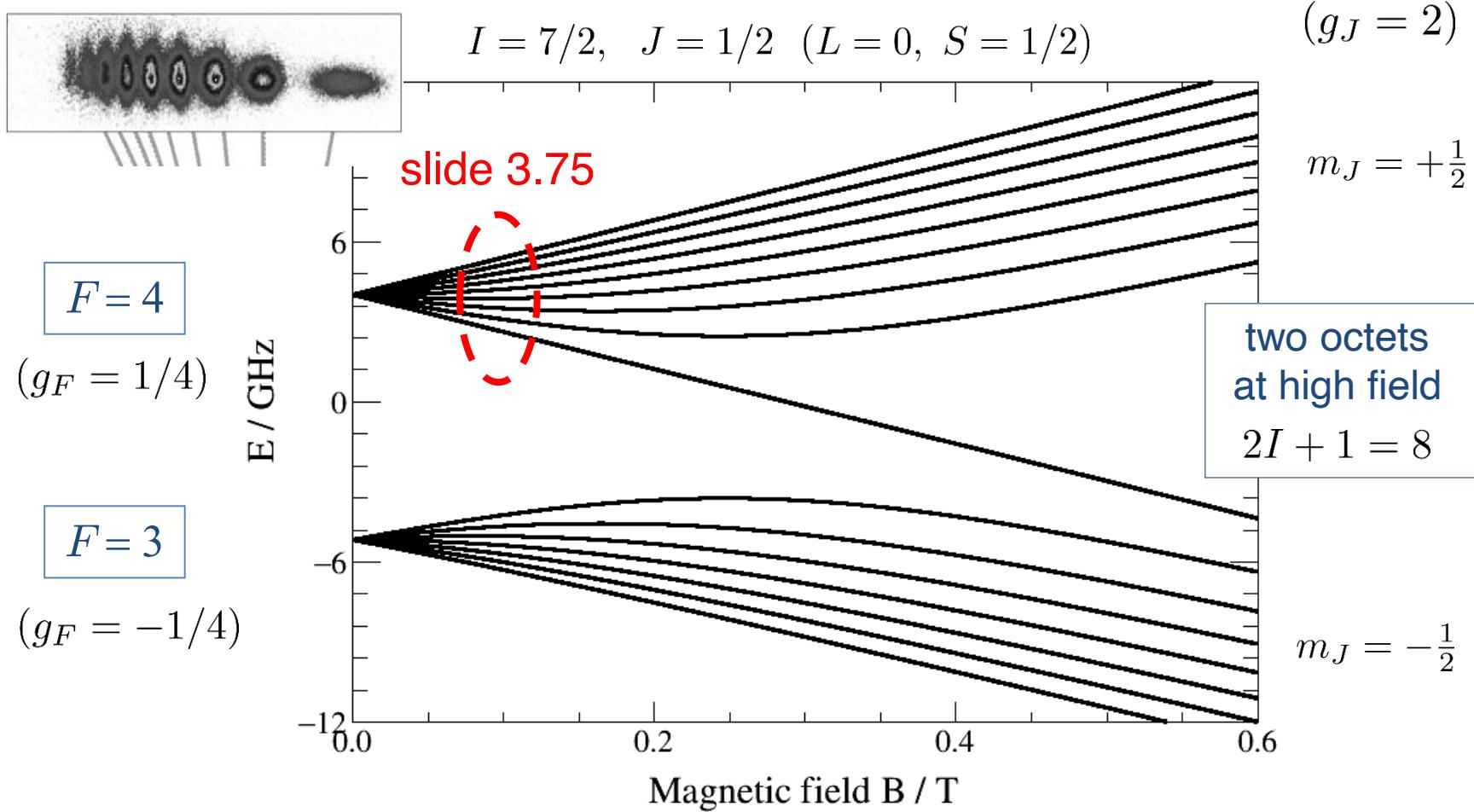
- Stern and Gerlach saw two emerging beams, not four, because they were using a relatively high field ( $B \sim 0.1$  T), and had limited resolution
- A qualitative overview of the Stern-Gerlach experiment is :
  - the ground state of silver ( $Z = 47$ ) is  $(1s)^2(2s)^2\dots(4d)^{10}(5s)$
  - the 46 core electrons combine together to give no net spin or orbital angular momentum, and no net spin or orbital magnetic moment
  - the valence (5s) electron, with  $\ell = 0$ , has no orbital magnetic moment, just a spin magnetic moment; we effectively have just  $\mathbf{F} = \mathbf{I} + \mathbf{S}$
  - the magnetic moment of the nucleus is negligible in comparison to that of the valence electron
  - at high field, the nuclear and electron spins “decouple”, and the electron magnetic moment interaction overwhelmingly dominates :

$$\hat{H}_B \approx -(\hat{\boldsymbol{\mu}}_S)_{e(5s)} \cdot \mathbf{B}$$

- the two emerging beams thus correspond to the “spin-up” and “spin-down” states of the single valence electron

## Zeeman hyperfine example : Cs-133

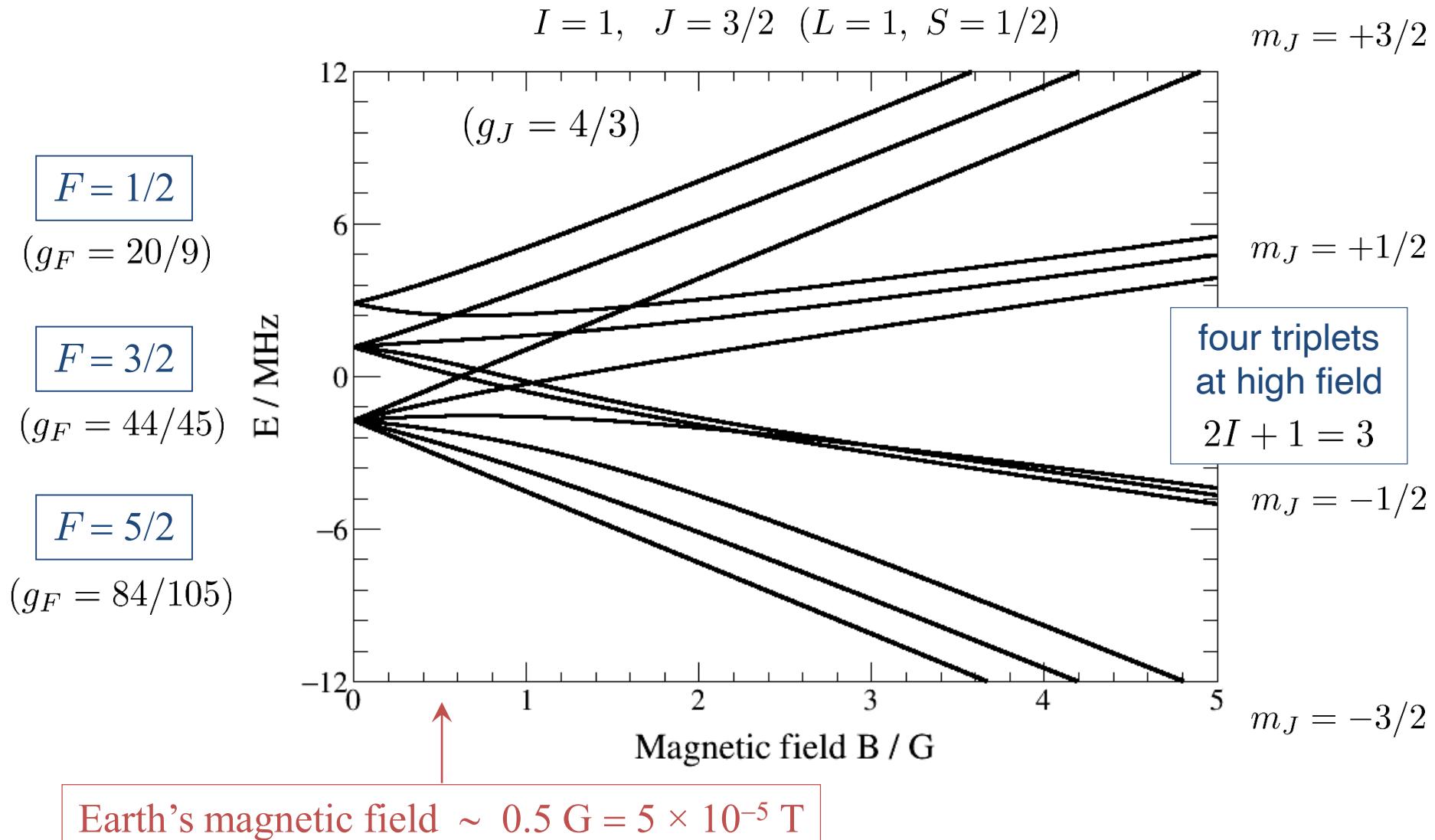
- The ground state of caesium is similar to silver and hydrogen, but the caesium nucleus has spin  $I = 7/2$  (diagonalise a  $16 \times 16$  matrix) :



- The nine S-G peaks seen on slide 3.75 correspond to  $F = 4$  in weak-field

## Zeeman hyperfine example : Li-6

-- The  $^2P_{3/2}$  excited state of  ${}^6\text{Li}$ , at hyperfine level (via a  $12 \times 12$  matrix) :



# Zeeman Effect : Summary

<b>FINE</b>	<b>HYPERFINE</b>
$\hat{\mu}_J = \hat{\mu}_L + \hat{\mu}_S$ $[\hat{H}, \hat{J}_z] = 0$ ( $m_J$ is a good q.n.)	$\hat{\mu}_F = \hat{\mu}_J + \hat{\mu}_I$ $[\hat{H}, \hat{F}_z] = 0$ ( $m_F$ is a good q.n.)
<b>WEAK FIELD</b>	
$(\Delta E)_B = m_J g_J \mu_B B$ ( $2J + 1$ ) equally spaced levels	$(\Delta E)_B = m_F g_F \mu_B B$ ( $2F + 1$ ) equally spaced levels
<b>STRONG FIELD</b>	
$(\Delta E)_B \approx (m_L + 2m_S) \mu_B B$ spacing $2\mu_B B$ ( $L = 0$ ) or $\mu_B B$ ( $L > 0$ )	$(\Delta E)_B \approx m_J g_J \mu_B B$ ( $2J + 1$ ) widely spaced multiplets, each with $(2I + 1)$ substructure

# The Stark Effect

- Consider the influence of an external electric field  $\mathbf{E}$  on a hydrogen atom :

$$\hat{H}_E = (-e)\phi(\mathbf{r}_e) + e\phi(\mathbf{r}_p) \quad (e > 0)$$

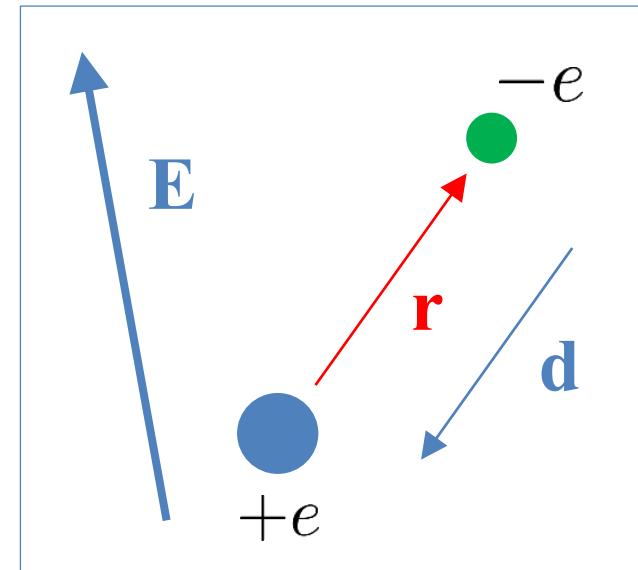
- Orienting the  $z$  axis along the  $\mathbf{E}$  field,

$$\mathbf{E} = (0, 0, \mathcal{E})$$

the electrostatic potential energies are

$$\phi(\mathbf{r}_e) = -\mathcal{E}z_e, \quad \phi(\mathbf{r}_p) = -\mathcal{E}z_p$$

$$\Rightarrow \hat{H}_E = e\mathcal{E}(z_e - z_p) = e\mathbf{E} \cdot (\hat{\mathbf{r}}_e - \hat{\mathbf{r}}_p)$$



- Hence, in general, the extra contribution to the Hamiltonian is

$$\hat{H}_E = -\mathbf{E} \cdot \hat{\mathbf{d}} ; \quad \hat{\mathbf{d}} = -e\hat{\mathbf{r}} \quad (\hat{\mathbf{r}} = \hat{\mathbf{r}}_e - \hat{\mathbf{r}}_p)$$

We expect this to *lower* the energy ( $\mathbf{d}$  tends to align itself along  $\mathbf{E}$ )

## The Stark effect (2)

- For  $\mathbf{E} = (0, 0, \mathcal{E})$ , and assuming an infinite mass proton, we have

$$\hat{H}_E = e\mathcal{E}z = e\mathcal{E}r \cos \theta$$

- Consider a level  $n^{2S+1}\text{L}_J$  of hydrogen, with eigenstates  $|n j m_j \ell s\rangle$

The level has degeneracy  $g = 2j + 1$ : the states are degenerate w.r.t.  $m_j$

Treating  $H_E$  as a perturbation, the first order energy correction involves the matrix elements

$$\langle n j m'_j \ell | z | n j m_j \ell \rangle ; \quad (m_j, m'_j = -\ell, -\ell + 1, \dots, +\ell)$$

- Since  $z$  is odd under spatial inversion, matrix elements of  $z$  vanish unless the states involved are of opposite parity (slide 5.49) :

$$\langle \alpha' \ell' | z | \alpha \ell \rangle = 0 \quad \text{if } (-1)^{\ell'} = (-1)^\ell$$

In particular, matrix elements involving a common value of  $\ell$  must vanish :

$$\langle n j m'_j \ell | z | n j m_j \ell \rangle = 0$$

## The Stark effect (2)

- Hence, in almost all circumstances (and not just for hydrogen) :
  - ⇒ the first-order perturbation theory energy correction vanishes
  - ⇒ we need to go to *second-order* perturbation theory
    - the quadratic Stark effect
- However, for large enough electric field strength, states of different  $\ell$  can effectively become degenerate
  - e.g. for the  $n = 2$  level of hydrogen :
    - the  $2p_{1/2}$  ( $\ell = 1$ ) and  $2s_{1/2}$  ( $\ell = 0$ ) levels are effectively degenerate
    - ⇒ the first-order energy correction becomes non-zero
      - the linear Stark effect
- We consider each of these in turn ...

# The Quadratic Stark Effect

- Consider the influence of an external electric field  $\mathbf{E}$  on the *ground state* of the hydrogen atom :

$$|n\ell m_\ell\rangle = |100\rangle$$

The first-order correction to the ground state energy vanishes, by parity :

$$(\Delta E)^{(1)} = \langle 100 | e\mathcal{E}z | 100 \rangle = 0$$

- Hence we need to go to *second-order* perturbation theory :

$$(\Delta E)^{(2)} = \sum_{n \geq 2, \ell, m} \frac{|\langle n\ell m | e\mathcal{E}z | 100 \rangle|^2}{E_1^{(0)} - E_n^{(0)}} \quad \left( E_n^{(0)} = -\frac{1}{n^2} R_\infty \right)$$

- The denominator above is always negative; hence, as expected, the energy correction due to the electric field must be negative :

$$(\Delta E)^{(2)} < 0$$

## The quadratic Stark effect (2)

- The infinite sum above can in fact be evaluated exactly (see Appendix A if interested) giving the second-order correction to the ground state energy as

$$(\Delta E)^{(2)} = -\frac{9}{4}(4\pi\epsilon_0)\mathcal{E}^2a_0^3$$

- The polarisability,  $\alpha$ , is defined (classically) by writing the interaction energy due to the electric field as

$$\Delta E = -\frac{1}{2}\mathbf{E} \cdot \mathbf{d} \equiv -\frac{1}{2}\alpha\epsilon_0\mathcal{E}^2$$

For the hydrogen atom ground state, the second-order perturbation theory prediction for the polarisability is therefore

$$\alpha = 18\pi a_0^3$$

- A reasonably good upper bound on  $\alpha$  can be obtained using a much simpler approximate analysis :

$$\alpha \leq \frac{64}{3}\pi a_0^3$$

[ EXAMPLES SHEET ]

# The Linear Stark Effect

- Now consider the  $n = 2$  states of the hydrogen atom :  
For a strong enough electric field, such that the energy corrections are much larger than the fine structure, the 2s and 2p states
$$|n\ell m\rangle = |200\rangle, |210\rangle, |211\rangle, |21, -1\rangle$$
are effectively all degenerate, with energy  $E_2^{(0)} = -\frac{1}{4}R_\infty$   
 $\Rightarrow$  we can now have a non-zero *first-order* energy correction
- First-order (degenerate) perturbation theory requires that we evaluate all matrix elements of the form
$$\langle 2\ell m | \hat{H}_E | 2\ell' m' \rangle ; \quad \hat{H}_E = e\mathcal{E}z = e\mathcal{E}r \cos \theta ; \quad \ell, \ell' = 0, 1$$
These matrix elements can be non-zero only if (see slide 5.58)
$$\Delta\ell = \pm 1 , \quad \Delta m_\ell = 0$$
Hence, for the  $n = 2$  level of hydrogen, only the matrix element  $\langle 200 | z | 210 \rangle$  can be non-zero

## Linear Stark effect (2)

- Using the  $|200\rangle$  and  $|210\rangle$  wavefunctions from slide 1.47 gives

$$\begin{aligned}\langle 200 | z | 210 \rangle &= \left( \frac{1}{32\pi a_0^3} \right) \int_0^\infty \int_{-1}^{+1} \int_0^{2\pi} e^{-r/2a_0} \left( 2 - \frac{r}{a_0} \right) \\ &\quad \times (r \cos \theta) e^{-r/2a_0} \frac{r}{a_0} \cos \theta r^2 dr d\theta d\phi\end{aligned}$$

- The right-hand side involves the  $r$ ,  $\theta$  integrals

$$\int_{-1}^{+1} \cos^2 \theta d\theta = \frac{2}{3}$$

$$\int_0^\infty \left( 2 - \frac{r}{a_0} \right) r^4 e^{-r/a_0} dr = -72a_0^5$$

$$\Rightarrow \langle 200 | z | 210 \rangle = -3a_0$$

- In summary, for  $n = 2$ , the non-zero matrix elements are

$$\boxed{\langle 200 | \hat{H}_E | 210 \rangle = \langle 210 | \hat{H}_E | 200 \rangle = -3e\mathcal{E}a_0}$$

## Linear Stark effect (3)

- In the basis of states

$$|n\ell m\rangle = |200\rangle, |210\rangle, |211\rangle, |21, -1\rangle$$

the perturbation  $H_E$  has the matrix representation

$$\hat{H}_E = \begin{pmatrix} 0 & -\Delta & 0 & 0 \\ -\Delta & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}; \quad \Delta \equiv 3e\mathcal{E}a_0$$

- The matrix  $\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$  has eigenvalues and eigenvectors given by

$$\lambda = \pm 1, \quad \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm 1 \end{pmatrix}$$

The zeroth-order eigenstates and first-order energy shifts are therefore

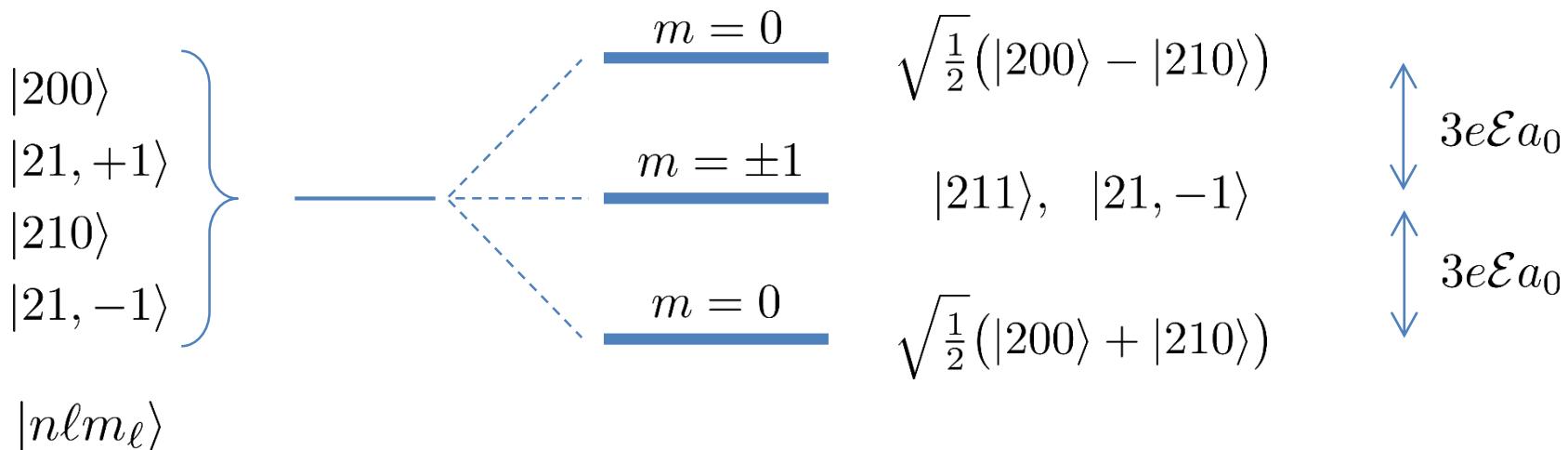
$$|\psi\rangle_{\pm} = \frac{1}{\sqrt{2}} (|200\rangle \pm |210\rangle)$$

$$(\Delta E)^{(1)} = \mp \Delta = \mp 3e\mathcal{E}a_0$$

The matrix representation of  $H_E$  is diagonal in the basis  $|\psi\rangle_+, |\psi\rangle_-$

## Linear Stark effect : hydrogen $n = 2$

- The states  $|211\rangle$  and  $|21,-1\rangle$  receive zero energy correction, so remain degenerate in energy
- In summary, for the  $n = 2$  level of hydrogen at high electric field, the first-order energy corrections and zeroth-order wavefunctions are :



To first order, the  $n = 2$  level splits into **3** equally spaced levels

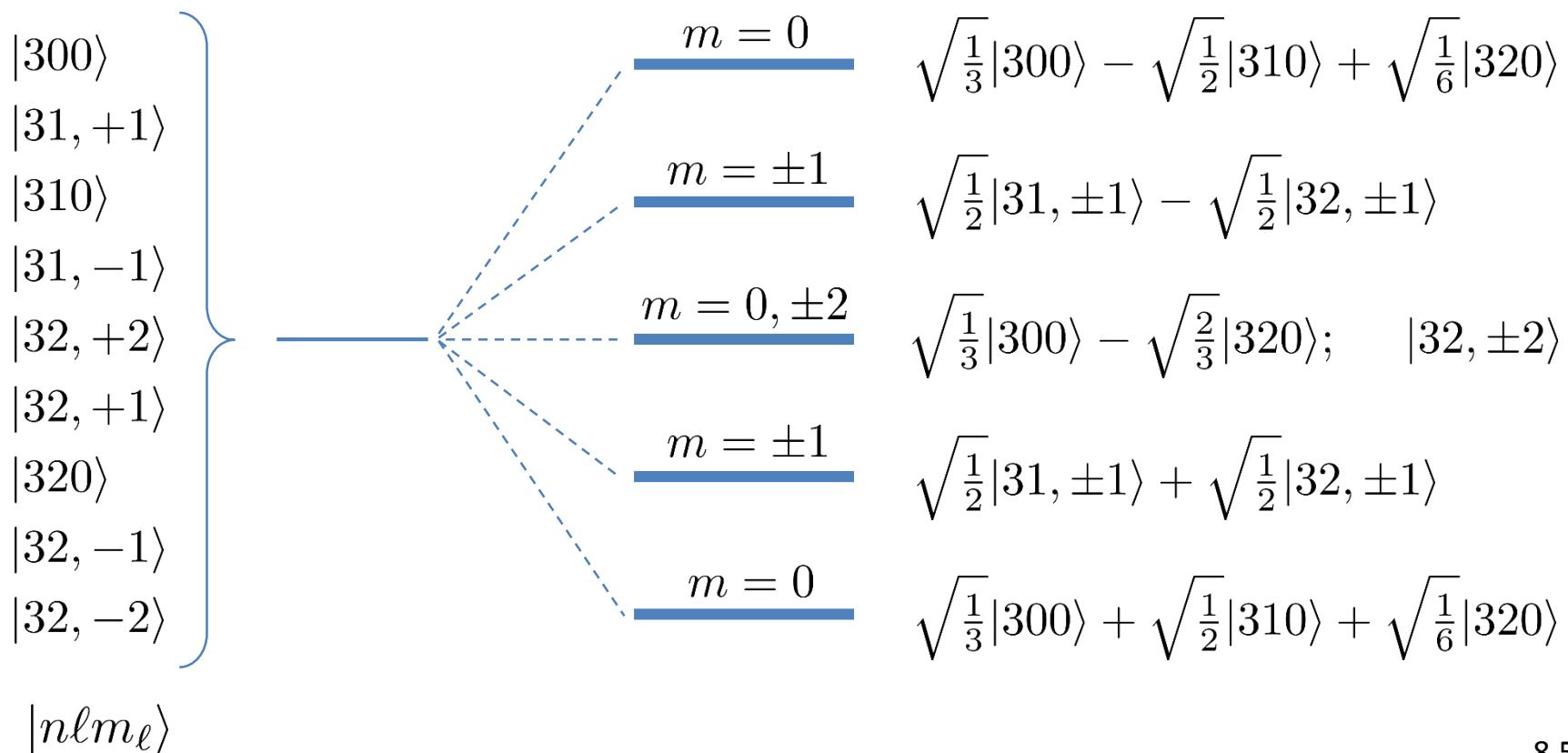
## Linear Stark effect : hydrogen $n = 3$

[ EXAMPLES SHEET ]

- For the  $n = 3$  level, the non-zero matrix elements are :

$$\langle 300|z|310\rangle, \quad \langle 320|z|310\rangle, \quad \langle 32,+1|z|31,+1\rangle, \quad \langle 32,-1|z|31,-1\rangle$$

- A strong electric field splits the  $n = 3$  level into **5** equally spaced levels :



## Stark effect : the general case

- As the electric field strength is reduced :
  - the energy corrections become smaller, eventually becoming comparable to those due to fine structure and the Lamb shift
  - a combined analysis of all relevant perturbations (electric field, fine structure, Lamb shift) is needed
- For the  $n = 2$  level of hydrogen, the  $2S_{1/2}$ ,  $2P_{1/2}$  and  $2P_{3/2}$  levels must be considered together
  - involves the diagonalisation of an  $8 \times 8$  matrix

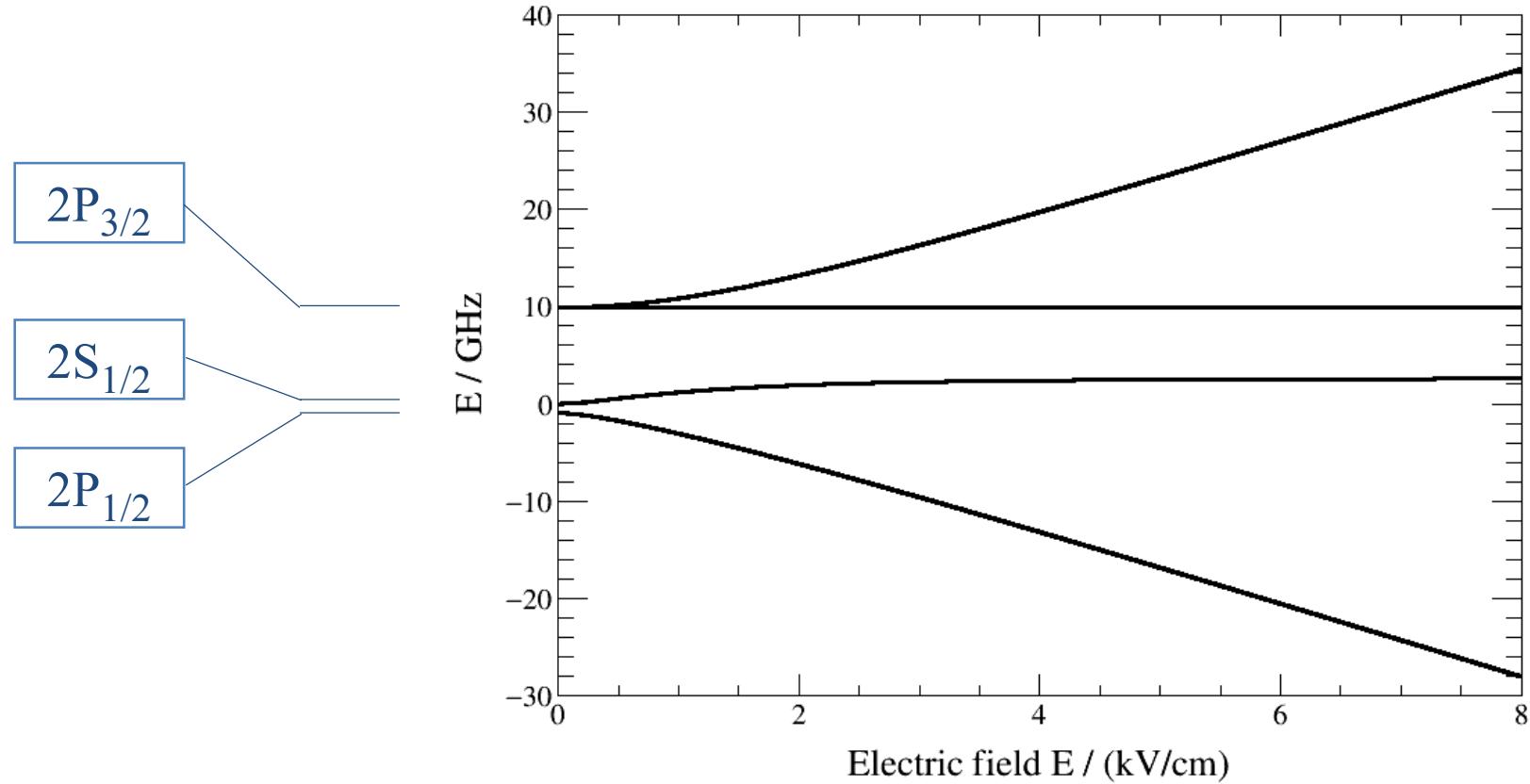
Similarly, for the  $n = 3$  level, the  $3S_{1/2}$ ,  $3P_{1/2}$ ,  $3P_{3/2}$ ,  $3D_{3/2}$  and  $3D_{5/2}$  levels must be considered together

→ involves the diagonalisation of an  $18 \times 18$  matrix

This can only be done numerically

## Stark effect : hydrogen $n = 2$

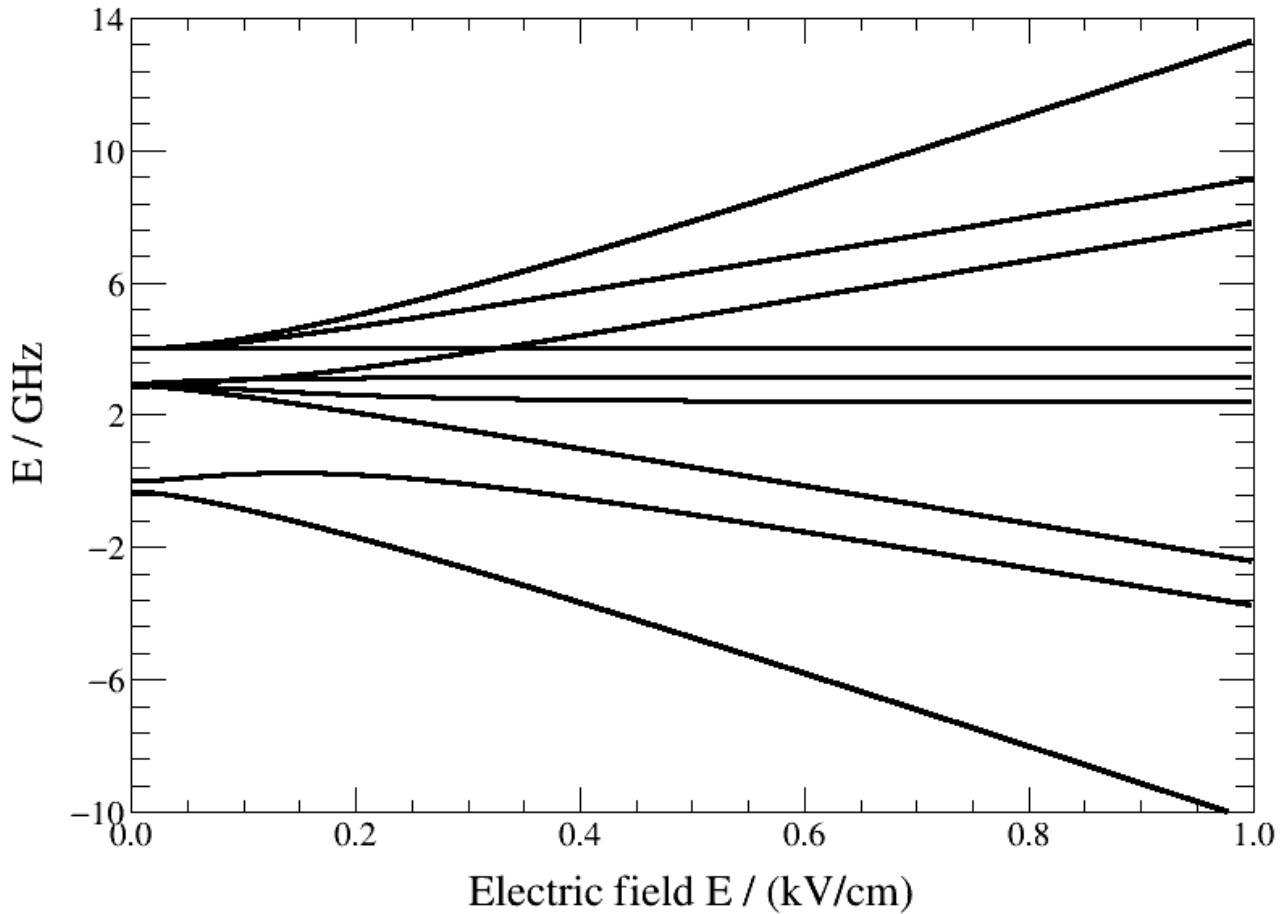
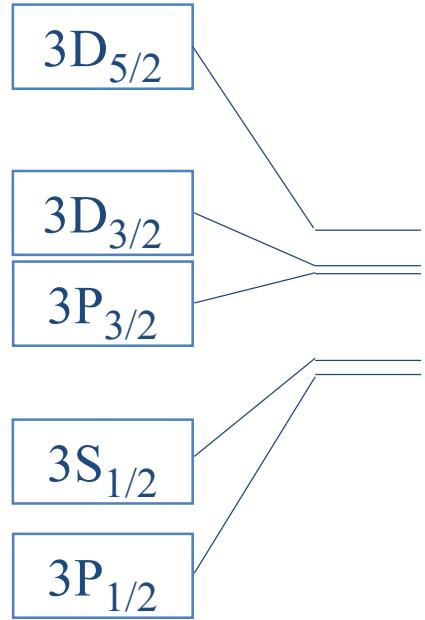
- Evolution with electric field strength for the  $n = 2$  level of hydrogen :



- At high electric field, this asymptotically approaches the 3 equally separated levels found from the linear Stark effect analysis (slide 8.50)  
A remnant of the original fine-structure splitting is also always present

## Stark effect : hydrogen $n = 3$

- Similarly, for the  $n = 3$  level of hydrogen (via an  $18 \times 18$  matrix) :

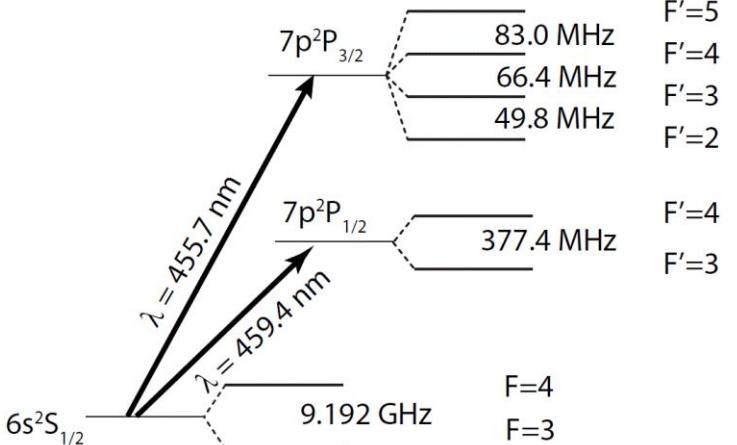


- Asymptotically approaches the **5** equally separated levels of slide 8.51 (with a remnant of the original fine-structure splitting also present)

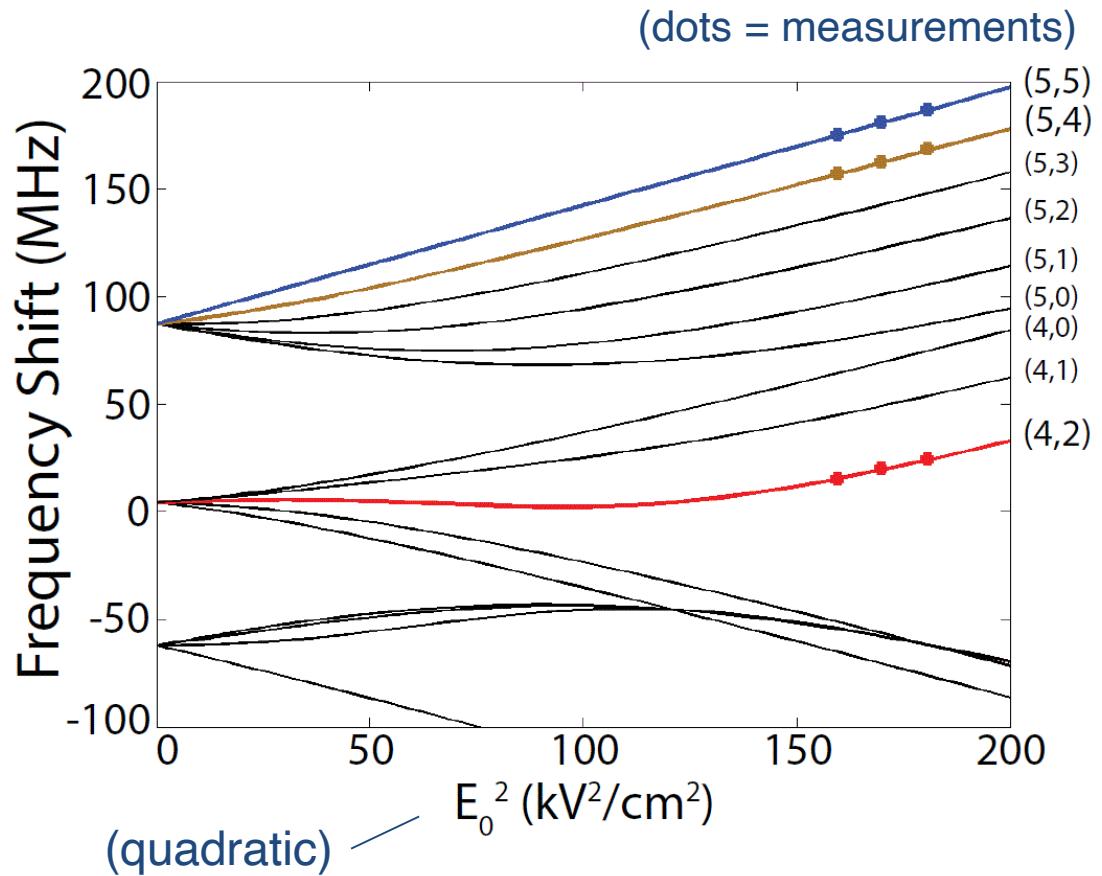
## Stark effect : cesium hyperfine

- A recent (2014) measurement of the Stark effect in atomic cesium :

[G. Toh et al., Phys. Rev. A 89 \(2014\) 042512 \(arXiv:1901.00574\)](#)



(see slide 3.75)



- Motivation: test theoretical calculations of the reduced matrix elements and atomic polarisabilities

$$\langle 7P \parallel \hat{r} \parallel 6D \rangle, \dots$$

# Molecular Structure

- A molecule consists of electrons,  $n = 1, 2, 3, \dots$  and nuclei,  $N = a, b, c, \dots$ , moving in a potential set up by all the other charges
- Because the nuclei have a much greater mass than the electrons, we can treat the electrons and nuclei separately
  - the *Born-Oppenheimer approximation*
    - to study the eigenstates of the electron system, treat the nuclei as being in fixed positions  
( → *this course* )
    - to study nuclear motion (molecular rotations and vibrations), assume that the electrons adjust instantly to changes in nuclear positions  
( → *not this course* )

## The Born-Oppenheimer Approximation

- The Hamiltonian for a molecule is of the form

$$\hat{H} = \sum_{n=1,2,\dots} \frac{\hat{\mathbf{p}}_n^2}{2m_e} + \sum_{N=a,b,\dots} \frac{\hat{\mathbf{p}}_N^2}{2m_N} + V(\{\mathbf{r}_n\}, \{\mathbf{R}_N\})$$

$$\hat{\mathbf{p}}_n = -i\hbar\nabla_n ; \quad \hat{\mathbf{p}}_N = -i\hbar\nabla_N$$

- In the Born-Oppenheimer approximation, the Schrödinger equation is

$$\left[ -\frac{\hbar^2}{2m_e} \sum_{n=1,2,\dots} \nabla_n^2 + V(\{\mathbf{r}_n\}, \{\mathbf{R}_N\}) \right] \Psi(\{\mathbf{r}_n\}, \{\mathbf{R}_N\}) = E(\{\hat{\mathbf{R}}_N\}) \Psi(\{\mathbf{r}_n\}, \{\mathbf{R}_N\})$$

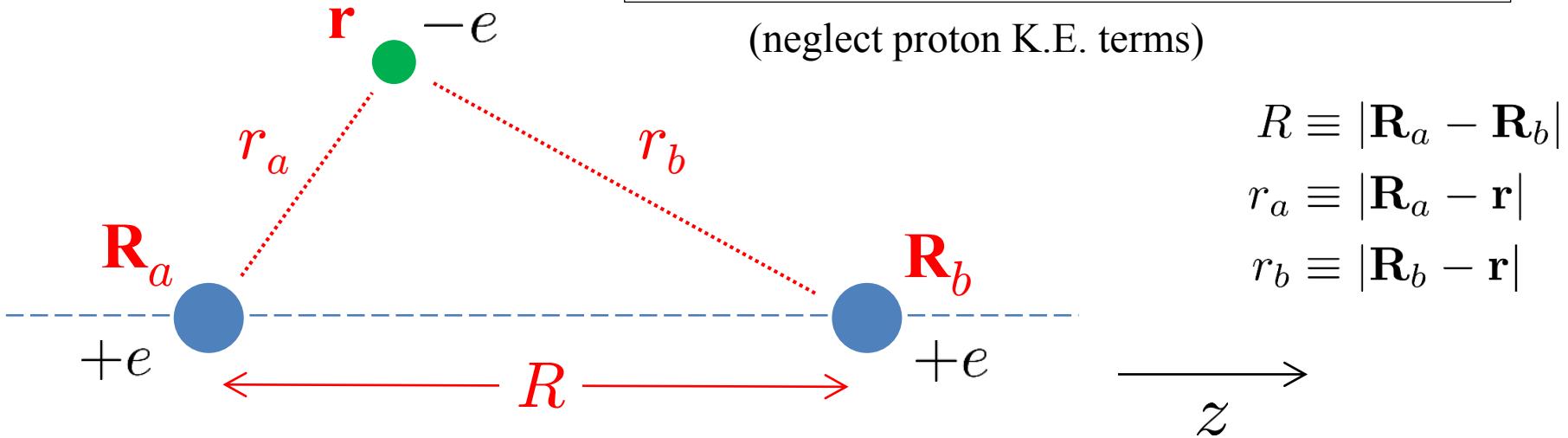
As the *molecular conformation* is varied, by changing the nuclear positions  $\mathbf{R}_a, \mathbf{R}_b, \dots$ , the ground state energy  $E_0$  can be minimised to find the *equilibrium conformation* for those positions

- We first consider the molecular ion  $\text{H}_2^+$  ; then the hydrogen molecule  $\text{H}_2$

# The $H_2^+$ ion

- The  $H_2^+$  ion is the simplest of all molecules – two protons at  $\mathbf{R}_a$ ,  $\mathbf{R}_b$ , plus an electron at  $\mathbf{r}$  :

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla_r^2 + \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{R} - \frac{1}{r_a} - \frac{1}{r_b} \right)$$



- Schrödinger's equation can be solved *exactly* using elliptical polar coordinates; the solution can be written in closed form, but is complicated

D. R. Bates, K. Ledsham + A. L. Stewart, Phil. Trans. R. Soc. Lond. A246 (1953) 215

We will not pursue further the calculation of the exact solution ...

## The $H_2^+$ ion (2)

- Instead, we use the *Rayleigh-Ritz* variational method, since this can be applied also to other molecules, and compare with the true answer

As the trial wavefunction, we take a linear combination of two hydrogen-like ground state atomic wavefunctions :

$$\psi_{\text{trial}}(\mathbf{r}; R, Z') = \alpha_a \psi_a(\mathbf{r}) + \alpha_b \psi_b(\mathbf{r})$$

$$\psi_{a,b}(\mathbf{r}) = \left( \frac{\beta^3}{\pi} \right)^{1/2} \exp(-\beta|\mathbf{R}_{a,b} - \mathbf{r}|) ; \quad \beta \equiv \frac{Z'}{a_0}$$

- Explicitly, the trial wavefunction is

$$\psi(x, y, z) = \sqrt{\frac{\beta^3}{\pi}} [\alpha_a e^{-\beta r_a} + \alpha_b e^{-\beta r_b}]$$

where, orienting the  $z$  axis through the two protons :

$$\begin{aligned} \mathbf{R}_a &= (0, 0, -R/2) & r_a^2 &= x^2 + y^2 + (z + R/2)^2 \\ \mathbf{R}_b &= (0, 0, +R/2) & r_b^2 &= x^2 + y^2 + (z - R/2)^2 \end{aligned}$$

## The $H_2^+$ ion (3)

- For this choice of trial wavefunction, there are **4** variational parameters :
  - the coefficients  $\alpha_a$  and  $\alpha_b$
  - the proton-proton separation  $R$
  - an effective nuclear charge  $Z'$

The variational method requires us to minimise the energy  $E(\alpha_a, \alpha_b, R, Z')$  to find the overall minimum energy  $E_{\min}$

In chemistry, with  $Z' = 1$ , the trial wavefunction is an example of a *molecular orbital* (MO), and the approximation method is known as

*Linear Combination of Atomic Orbitals* (LCAO)

- To apply the variational method, we follow a two-step procedure :
  - 1) Use Rayleigh-Ritz (slides 2.50-2.53) to find the coefficients  $\alpha_a$  and  $\alpha_b$  for any given values of  $R$  and  $Z'$  (this can be done analytically)
  - 2) Scan the energy  $E(R, Z')$  to find the overall minimum energy  $E_{\min}$  (this can only be done numerically)

## The $H_2^+$ ion (4)

- For any given values of  $R$  and  $Z'$ , the coefficients  $\alpha_a$  and  $\alpha_b$  can be obtained by solving the Rayleigh-Ritz secular equation

$$\det(H - E_{\min} S) = 0$$

where  $H$  and  $S$  are (symmetric)  $2 \times 2$  matrices

$$S = \begin{pmatrix} 1 & S_{ab} \\ S_{ba} & 1 \end{pmatrix} ; \quad H = \begin{pmatrix} H_{aa} & H_{ab} \\ H_{ba} & H_{bb} \end{pmatrix}$$

with matrix elements (note that  $|\psi_a\rangle$  and  $|\psi_b\rangle$  are not orthogonal)

$$S_{aa} = S_{bb} = 1, \quad S_{ab} = S_{ba} = \langle \psi_a | \psi_b \rangle$$

$$H_{aa} = \langle \psi_a | \hat{H} | \psi_a \rangle = H_{bb} = \langle \psi_b | \hat{H} | \psi_b \rangle$$

$$H_{ab} = H_{ba} = \langle \psi_b | \hat{H} | \psi_a \rangle$$

- The secular equation for the energy  $E$  is therefore

$$\begin{vmatrix} H_{aa} - E & H_{ab} - ES_{ab} \\ H_{ab} - ES_{ab} & H_{aa} - E \end{vmatrix} = 0$$

## The $H_2^+$ ion (5)

- The resulting eigenstates have  $\alpha_a = \pm \alpha_b$  :

“g” = *gerade* (even)

“u” = *ungerade* (odd)

$$\psi_g = \frac{\psi_a + \psi_b}{\sqrt{2(1 + S_{ab})}}$$

$$E_g = \frac{H_{aa} + H_{ab}}{1 + S_{ab}}$$

$$\psi_u = \frac{\psi_a - \psi_b}{\sqrt{2(1 - S_{ab})}}$$

$$E_u = \frac{H_{aa} - H_{ab}}{1 - S_{ab}}$$

The eigenstate  $\psi_g$  ( $\psi_u$ ) is even (odd) under the interchange  $a \leftrightarrow b$

- For each of these two cases, we can then vary  $R$  and  $Z'$ , and look for the overall minima of the energies

$$E_{g,u}(R, Z') = \frac{H_{aa} \pm H_{ab}}{1 \pm S_{ab}}$$

## The $H_2^+$ ion (6)

- The integrations needed to evaluate the matrix elements

$$S_{ab} = \langle \psi_a | \psi_b \rangle ; \quad H_{aa} = \langle \psi_a | \hat{H} | \psi_a \rangle ; \quad H_{ab} = \langle \psi_a | \hat{H} | \psi_b \rangle$$

can be carried out using prolate spheroidal coordinates, for example

*For completeness*, analytic expressions for the integrals involved are given in Appendix B

- For all values of  $R$  and  $Z'$ , the lowest energy state turns out to be  $|\psi_g\rangle$  :

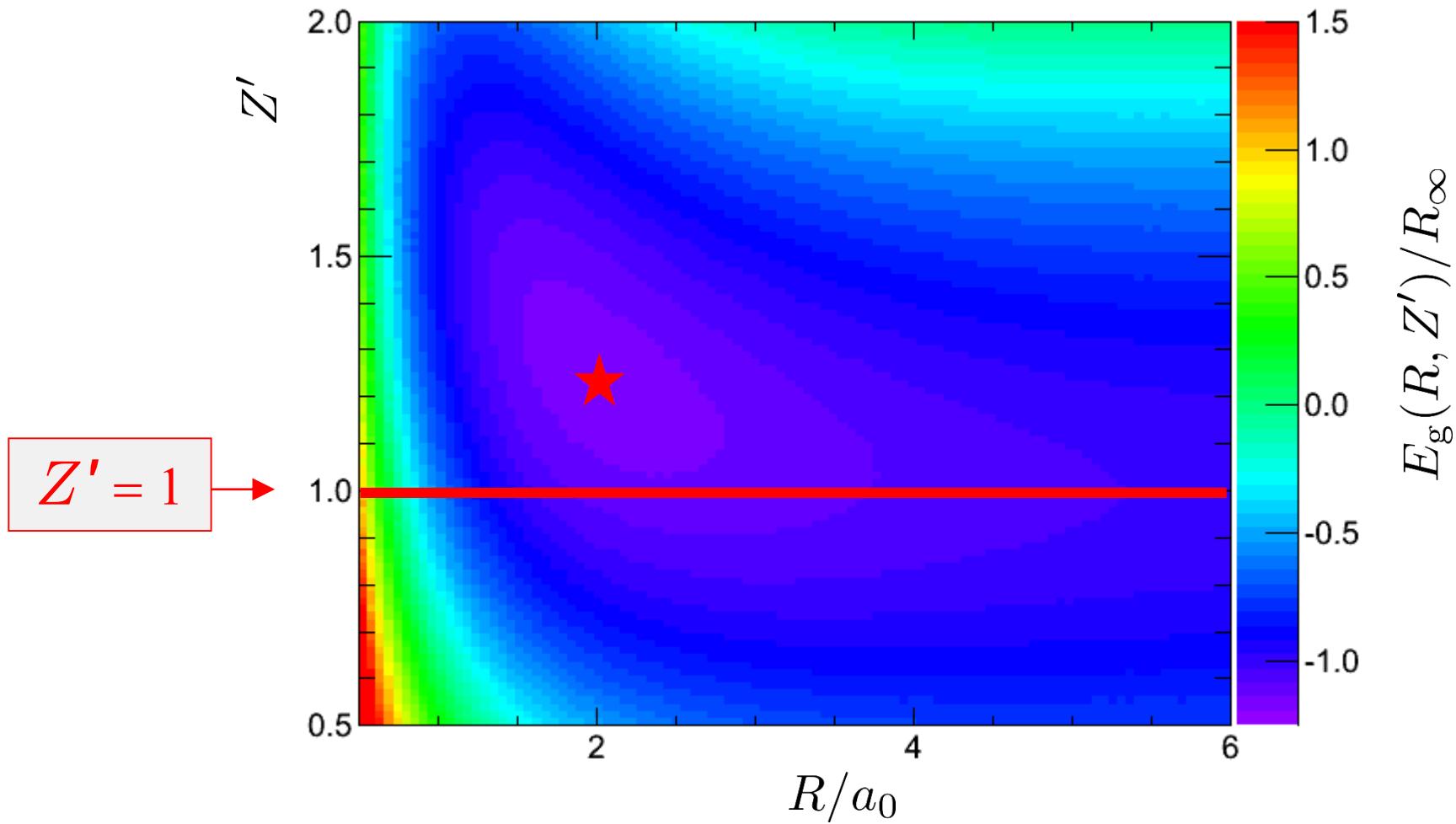
$$\frac{H_{aa} + H_{ab}}{1 + S_{ab}} < \frac{H_{aa} - H_{ab}}{1 - S_{ab}} ; \quad E_g(R, Z') < E_u(R, Z')$$

The best *overall* upper bound on the ground state energy is thus obtained by minimising  $E_g$  :

$$E_0 \leq \min_{Z', R} [E_g(R, Z')]$$

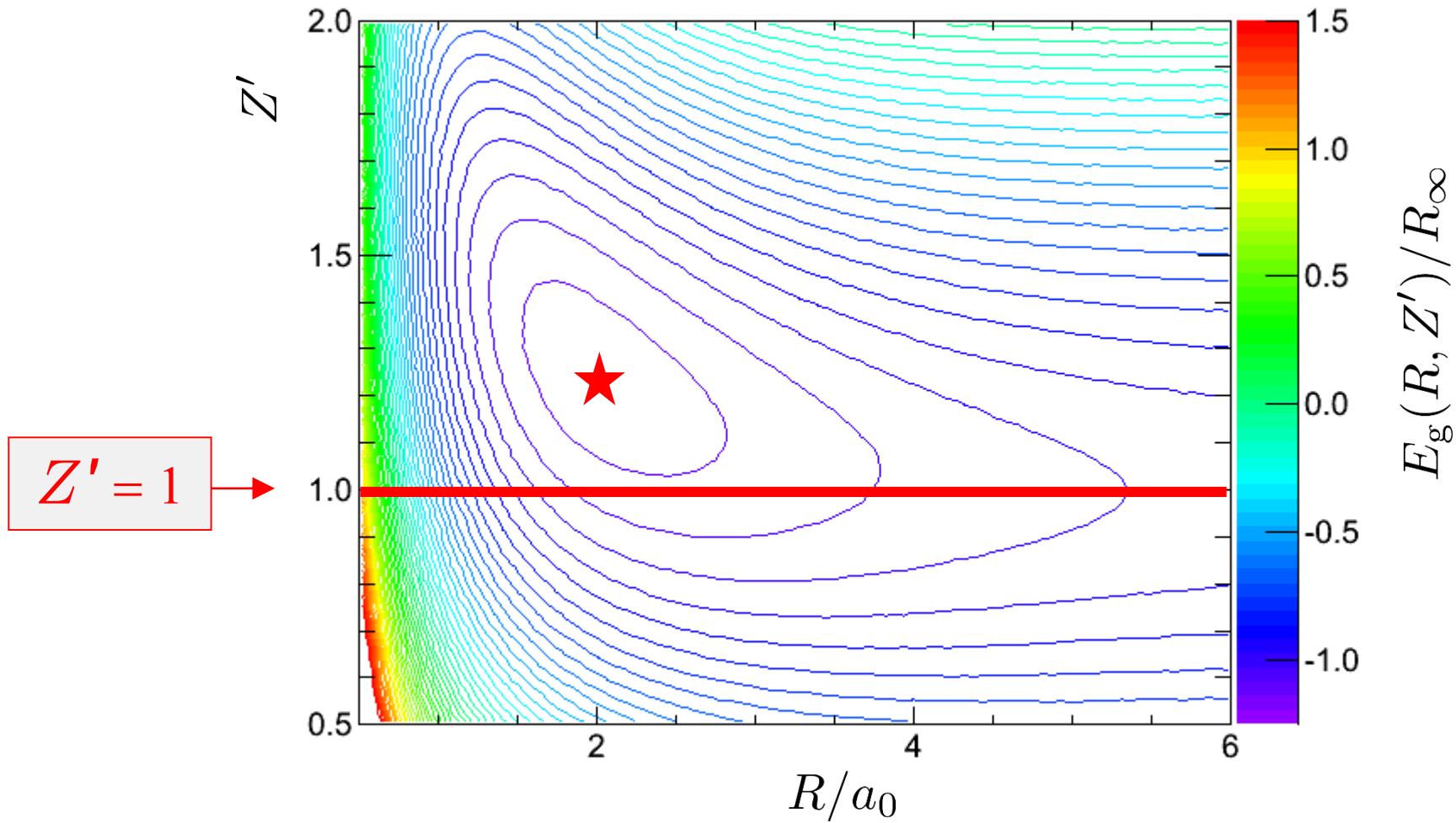
This minimum can be obtained numerically by scanning the plot below ...

## The $H_2^+$ ion (7)



- The energy  $E_g(Z', R)$  is found to have a single, stable minimum at  $(R/a_0, Z') = (2.002, 1.238)$  with  $E_{\min} = -(1.173)R_\infty$

## The $H_2^+$ ion (7)



- The energy  $E_g(Z', R)$  is found to have a single, stable minimum at  $(R/a_0, Z') = (2.002, 1.238)$  with  $E_{\min} = -(1.173)R_\infty$

## The $H_2^+$ ion (8)

- The proton-proton separation, and bound state energy, are thus predicted to be

$$R_0 = 106.0 \text{ pm} ; \quad E_0 \leq -(1.173)R_\infty = -15.96 \text{ eV}$$

Since  $E_0 < 0$ , the  $H_2^+$  ion is (correctly!) predicted to exist as a bound state

The effective nuclear charge at the minimum is  $Z' = 1.238$

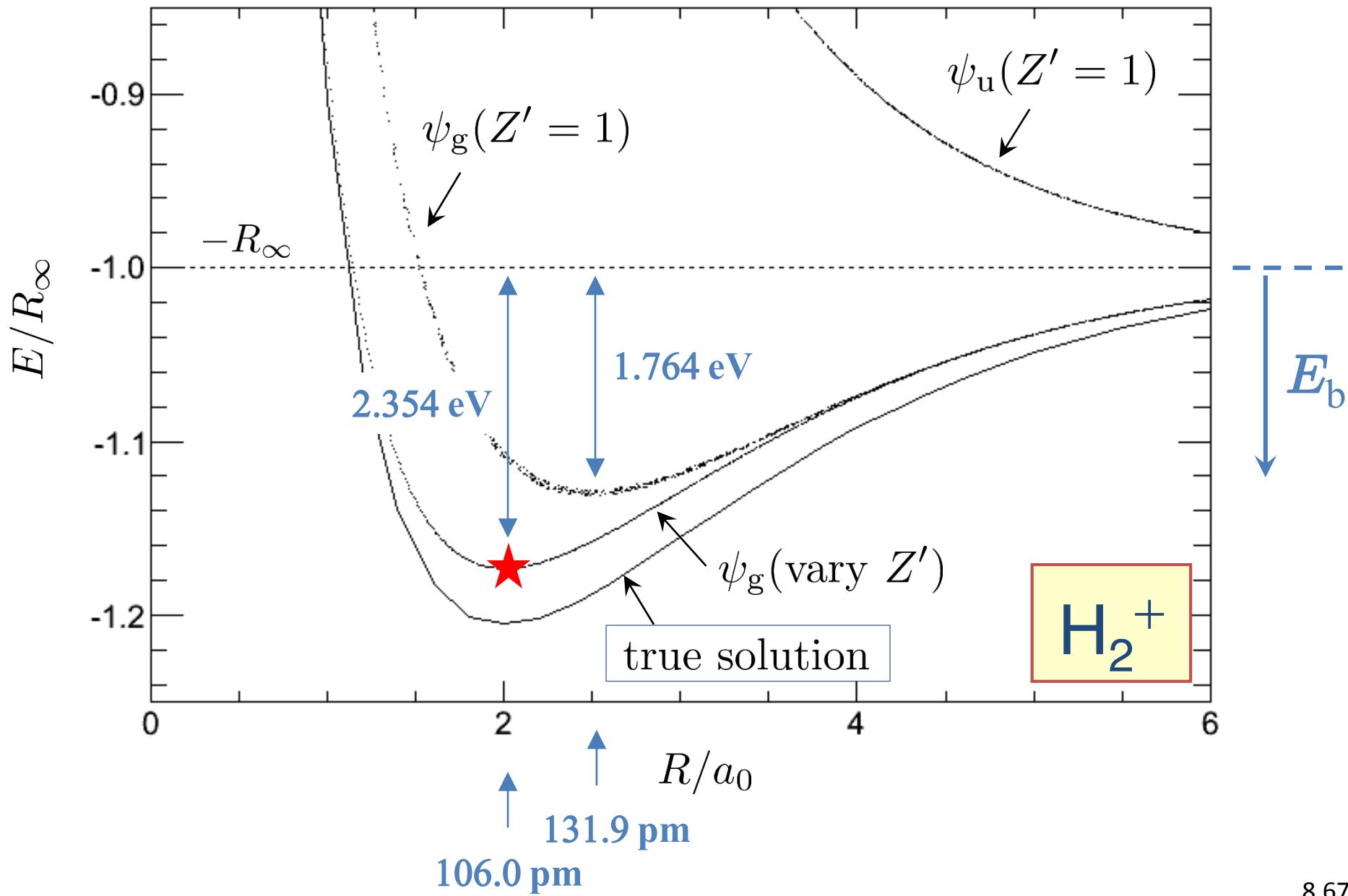
- The predicted separation  $R_0$  is very close to the true value, but the true molecule is more tightly bound (by about 0.4 eV) :

$$R_{\text{exact}} = 106.0 \text{ pm} ; \quad (E_0)_{\text{true}} = -(1.206)R_\infty = -16.4 \text{ eV}$$

- We can gain further insight by considering the prediction from the variational method as a function of the proton separation  $R$  :

i.e. vary  $R$ , and minimise the energy  $E_g$  at each value of  $R$

## The $H_2^+$ ion (9)



## The $H_2^+$ ion (10)

- For infinite proton separation ( $R \rightarrow \infty$ ), we find that

$$E_0(R) \rightarrow -R_\infty \approx -13.6 \text{ eV} \quad \text{as } R \rightarrow \infty$$

i.e. for infinite proton separation, the state of lowest energy is a ground state H atom plus a proton

A total energy  $E = 0$  corresponds to *all* constituents (the two protons and the electron) being infinitely separated :

$$R \rightarrow \infty , \quad r_a \rightarrow \infty , \quad r_b \rightarrow \infty$$

- The *molecular binding energy*,  $E_b$ , is defined relative to this asymptotic energy :

$$E_b \equiv -R_\infty - E_0(R)$$

Thus  $E_b > 0$  for a molecular bound state

The overall minimum from the variational method corresponds to a (positive) binding energy given by

$$E_b = -R_\infty + (1.173)R_\infty = +(0.173)R_\infty = 2.354 \text{ eV}$$

## The $H_2^+$ ion (11)

- The states  $|\psi_g\rangle$  and  $|\psi_u\rangle$  are orthonormal, and diagonalise the Hamiltonian :

For  $|\psi_g\rangle$  the two atomic wavefunctions interfere *constructively*, giving enhanced electron density between the two protons, thereby screening the proton charge and reducing the p-p repulsion  $\rightarrow$  **bonding**

For  $|\psi_u\rangle$  the two atomic wavefunctions interfere *destructively*, giving no screening  $\rightarrow$  not a bound state

The standard labelling of the molecular orbitals is

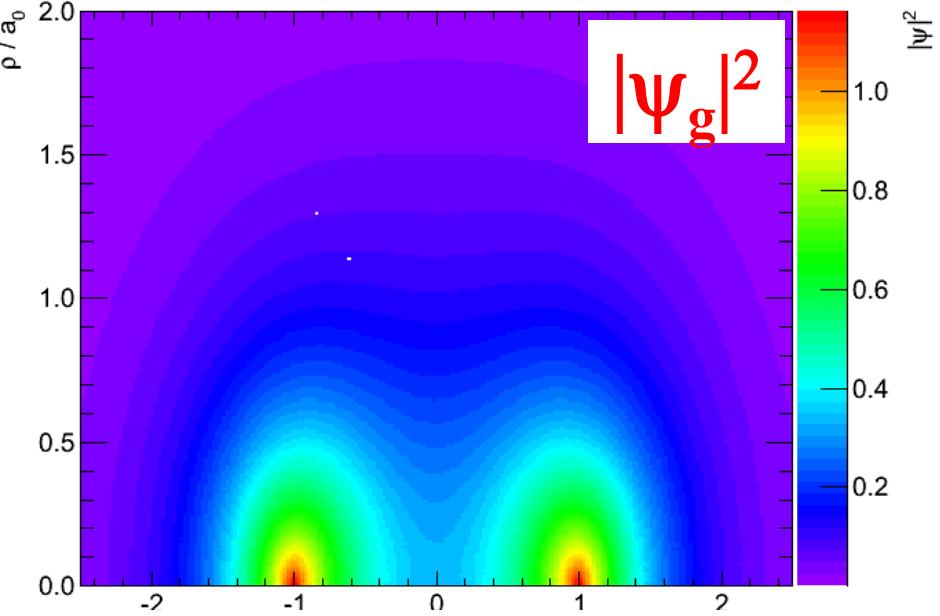
$|\psi_g\rangle, |\psi_u\rangle$  are denoted  $\sigma_g, \sigma_u^*$  (\* = antibonding)

- The next slide shows plots of  $|\psi|^2$  and the probability density, in cylindrical polar coordinates  $(\rho, \phi, z)$  :

$$P(z, \rho) = \rho |\psi(\rho, \phi, z)|^2 ; \quad \int_{-\infty}^{+\infty} \int_0^\infty P(z, \rho) dz d\rho = 1$$

(bonding)

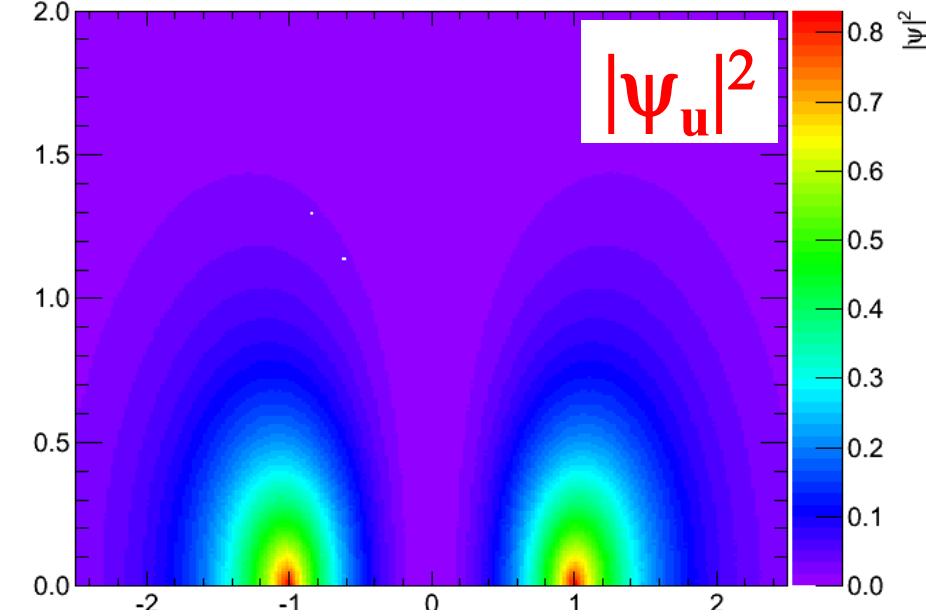
$$\psi_g$$



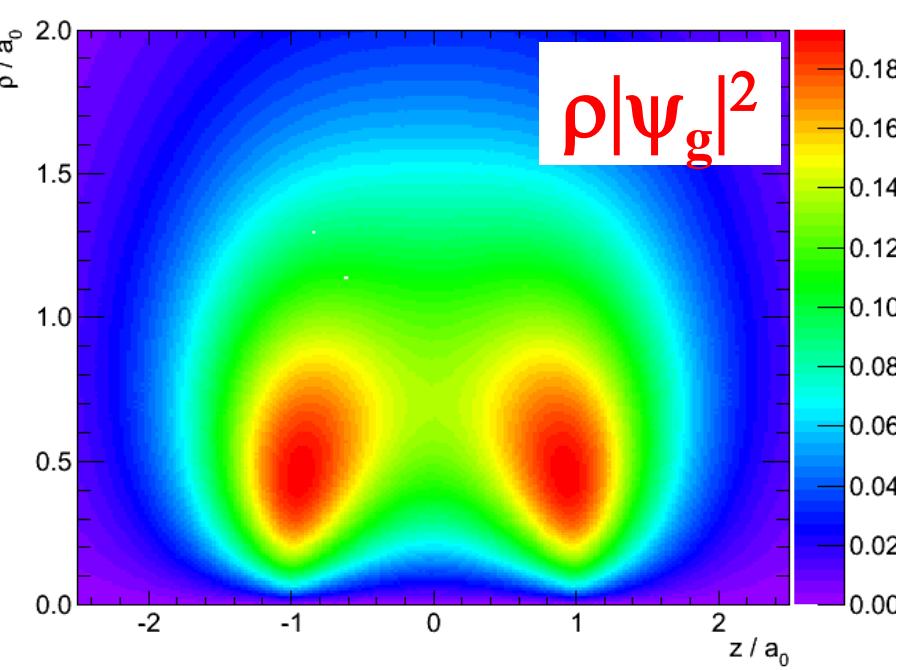
$$|\psi_g|^2$$

$$\psi_u$$

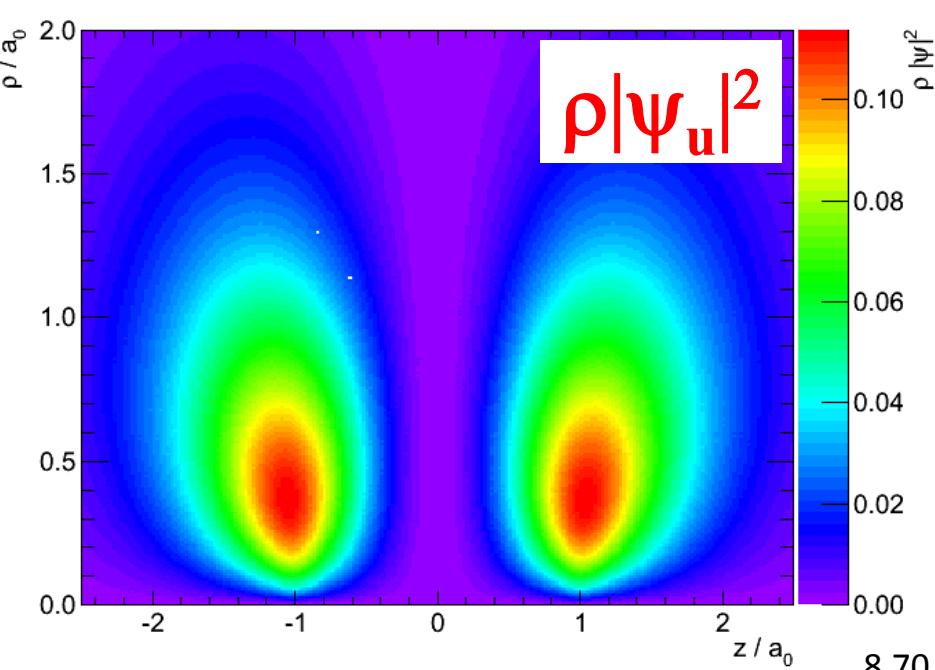
(antibonding)



$$|\psi_u|^2$$



$$\rho|\psi_g|^2$$



$$\rho|\psi_u|^2$$

## The $H_2^+$ ion : Summary

	$R_0$	$E_b$
LCAO ( $Z' = 1$ )	0.132 nm	1.764 eV
Vary $Z'$	0.106 nm	2.354 eV
True solution	0.106 nm	2.80 eV

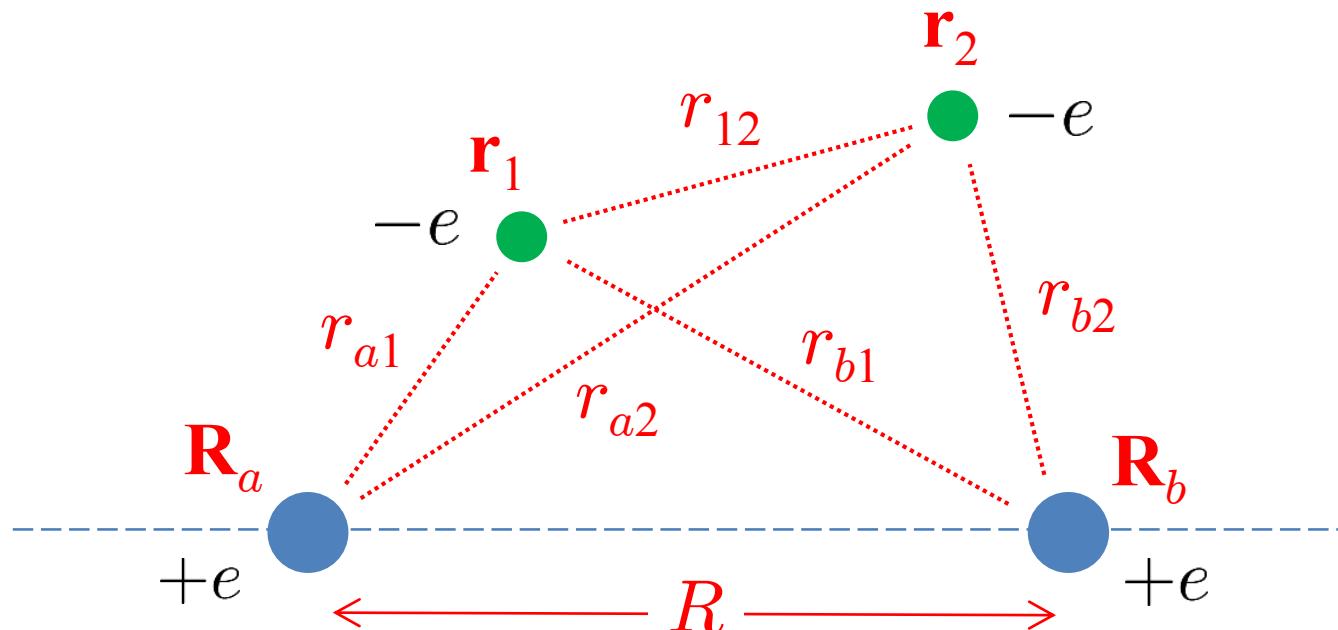
- Introducing a variable effective nuclear charge  $Z'$  gives an excellent prediction for the proton separation
- The true molecule is more tightly bound than the prediction
- The above estimates can be improved further by using more atomic orbitals and/or more variational parameters

# The $H_2$ Molecule

- $H_2$  is not a trivial extension of  $H_2^+$ , and cannot be solved exactly :

$$\hat{H} = -\frac{\hbar^2}{2m_e} (\nabla_1^2 + \nabla_2^2) + \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{R} + \frac{1}{r_{12}} - \frac{1}{r_{a1}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} - \frac{1}{r_{b2}} \right)$$

$$R = |\mathbf{R}_a - \mathbf{R}_b| ; \quad r_{12} = |\mathbf{r}_1 - \mathbf{r}_2| ; \quad r_{a1} = |\mathbf{R}_a - \mathbf{r}_1| , \dots$$



## The H<sub>2</sub> molecule (2)

- The H<sub>2</sub> Hamiltonian is a sum of two *independent* H<sub>2</sub><sup>+</sup> Hamiltonians, plus a term

$$\frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r_{12}} - \frac{1}{R} \right)$$

- In the absence of this term, the H<sub>2</sub> eigenstates are products of two H<sub>2</sub><sup>+</sup> molecular orbitals :

$$\psi_g(\mathbf{r}_1)\psi_g(\mathbf{r}_2) , \quad \psi_g(\mathbf{r}_1)\psi_u(\mathbf{r}_2) , \quad \psi_u(\mathbf{r}_1)\psi_g(\mathbf{r}_2) , \quad \psi_u(\mathbf{r}_1)\psi_u(\mathbf{r}_2)$$

- We would expect the first of these to be the ground state :

$$\psi_g(\mathbf{r}_1)\psi_g(\mathbf{r}_2) = \frac{1}{2(1 + S_{ab})} [\psi_a(\mathbf{r}_1) + \psi_b(\mathbf{r}_1)] [\psi_a(\mathbf{r}_2) + \psi_b(\mathbf{r}_2)]$$

- The two-electron state  $|\psi_g(\mathbf{r}_1)\rangle|\psi_g(\mathbf{r}_2)\rangle$  is *symmetric* under  $1 \leftrightarrow 2$ , so must be combined with the *antisymmetric*  $S = 0$  spin singlet state :

$$|\psi\rangle = \psi_g(\mathbf{r}_1)\psi_g(\mathbf{r}_2) \times \frac{1}{\sqrt{2}} (|\uparrow\rangle_1|\downarrow\rangle_2 - |\downarrow\rangle_1|\uparrow\rangle_2)$$

## The $H_2$ molecule (3)

- We again use the variational method to estimate the ground state energy, taking the trial wavefunction to be  $|\Psi_g(\mathbf{r}_1)\rangle|\Psi_g(\mathbf{r}_2)\rangle$ , with a variable effective nuclear charge  $Z'$  :

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{\beta^3/\pi}{2(1+S)} [e^{-\beta r_{a1}} + e^{-\beta r_{b1}}] [e^{-\beta r_{a2}} + e^{-\beta r_{b2}}]$$

where

$$r_{a1}^2 = x_1^2 + y_1^2 + (z_1 + R/2)^2 \quad r_{a2}^2 = x_2^2 + y_2^2 + (z_2 + R/2)^2$$

$$r_{b1}^2 = x_1^2 + y_1^2 + (z_1 - R/2)^2 \quad r_{b2}^2 = x_2^2 + y_2^2 + (z_2 - R/2)^2$$

$$S = \left(1 + \beta R + \frac{1}{3}(\beta R)^2\right) e^{-\beta R} \quad \beta \equiv \frac{Z'}{a_0}$$

- The variational method requires that we minimise the expectation value

$$\langle E \rangle = \langle g; g | \hat{H} | g; g \rangle \propto \langle a + b; a + b | \hat{H} | a + b; a + b \rangle$$

as a function of the variational parameters :  $R, Z'$

The integrals required can again be evaluated analytically, and are again given *for completeness* in Appendix B

## The H<sub>2</sub> molecule (4)

- For H<sub>2</sub>, the *molecular binding energy*  $E_b$  is defined in relation to two infinitely separated ground state H atoms :
- Fixing  $Z' = 1$  corresponds to the *molecular orbital* (MO) approach, and gives a minimum with

$$R = R_0 = 85.2 \text{ pm}, \quad E_b = 2.70 \text{ eV}$$

( $E_b > 0$  : the H<sub>2</sub> molecule exists !)

- Varying the effective nuclear charge  $Z'$  gives an improved energy minimum at

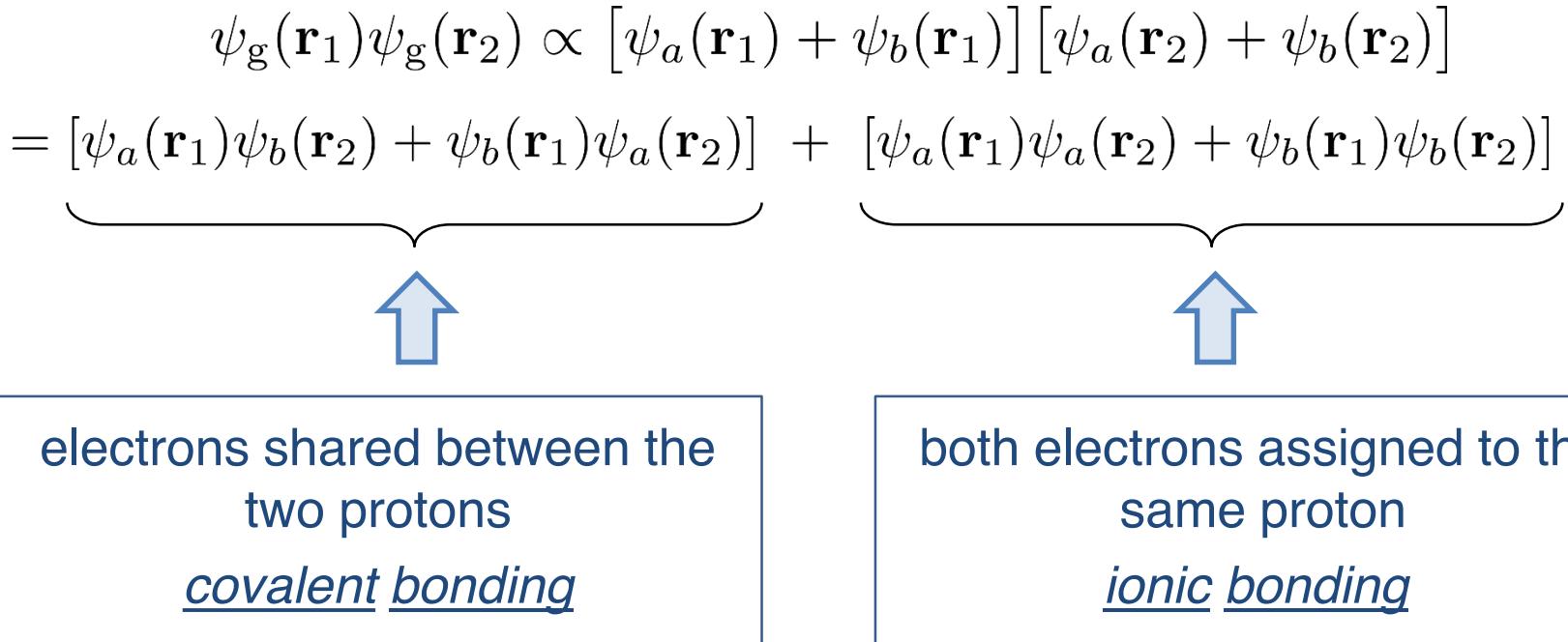
$$R_0 = 73.0 \text{ pm}, \quad E_b = 3.49 \text{ eV} \quad (Z' = 1.192)$$

However the true molecule is significantly more tightly bound than this :

$$R_0 = 74.1 \text{ pm}, \quad E_b = 4.75 \text{ eV}$$

## The H<sub>2</sub> molecule (5)

- Basic problem:  $\Psi_g \Psi_g$  is not a good representation of the true ground state  
Expanding out the product  $\Psi_g \Psi_g$  gives



- The above equation suggests *equal* covalent and ionic contributions :
  - we are equally likely to get an H<sup>+</sup> and an H<sup>-</sup> ion when we split the molecule, as we are to get two H atoms  
(which is unlikely due to electron-electron repulsion)

## The H<sub>2</sub> molecule (6)

- We can allow the covalent / ionic composition to vary by introducing an extra variational parameter  $\lambda$  for the ionic part :

$$[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)] + \lambda [\psi_a(\mathbf{r}_1)\psi_a(\mathbf{r}_2) + \psi_b(\mathbf{r}_1)\psi_b(\mathbf{r}_2)]$$

The case  $\lambda = 0$  where the ionic part is dropped completely is known as the *valence band (VB) approximation* :

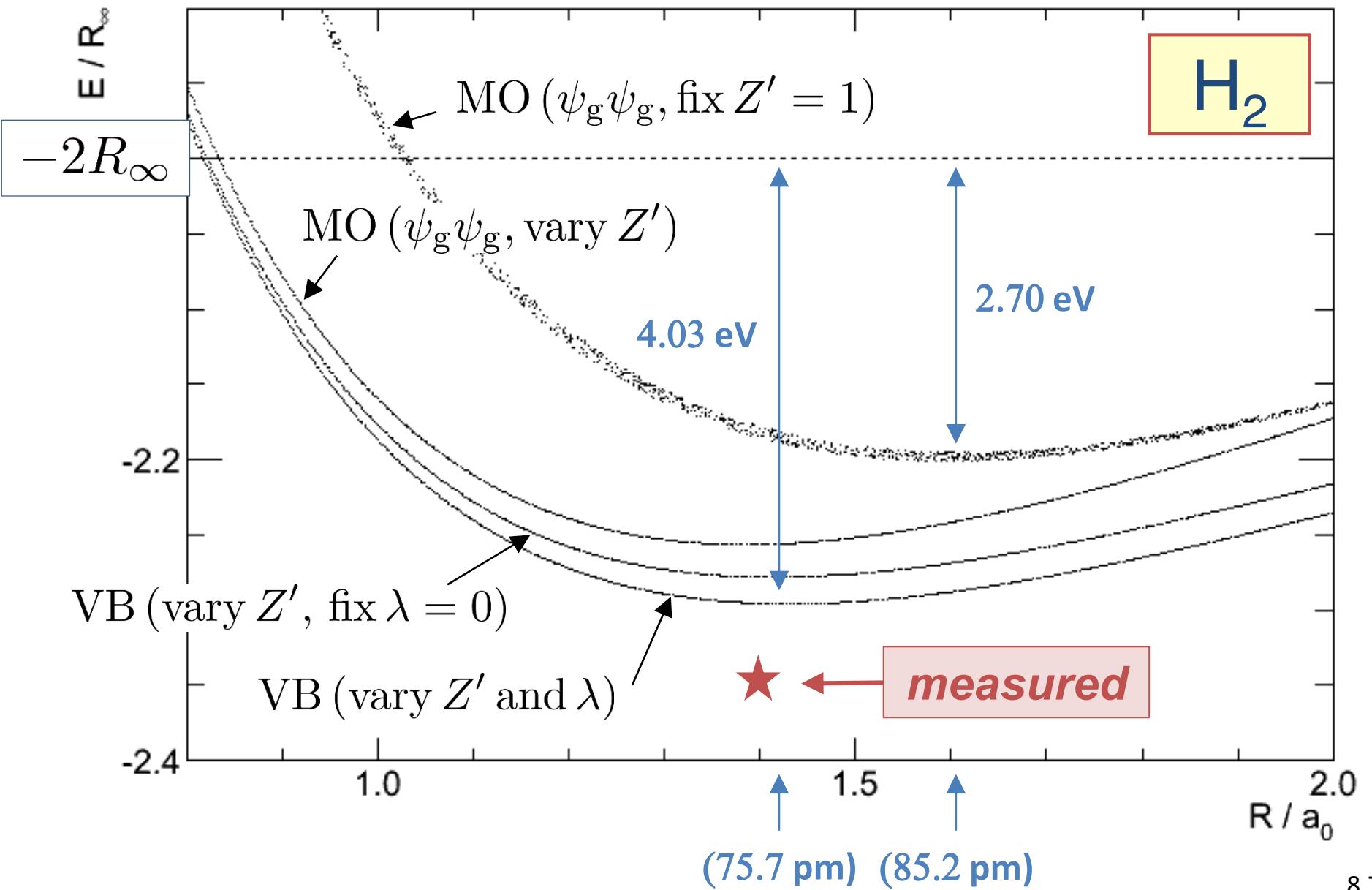
$$\psi_{\text{VB}} \propto [\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)]$$

- Including the extra parameter  $\lambda$ , the variational method now gives :

$$R_0 = 75.7 \text{ pm}, \quad E_b = 4.03 \text{ eV}, \quad \lambda = 0.26 \quad (Z' = 1.195)$$

- we obtain an improved lower bound (4.03 eV) on the binding energy, but still significantly below the measured value (4.75 eV)
- the optimal value  $\lambda = 0.26$  corresponds to a  $\lambda^2 = 7.0\%$  probability for the ionic part

## The $H_2$ molecule (7)



## The $H_2$ molecule : Summary

- The results so far are summarised in the first four rows of the table below :

trial wavefunction	fix	vary	$Z'$	$\lambda$	$R/\text{pm}$	$\text{BE/eV}$
MO	$Z', \lambda$	$R$	1.0	1.0	85.2	2.70
MO, variable charge	$\lambda$	$Z', R$	1.192	1.0	73.0	3.49
VB, variable charge variable $\lambda$ and charge	$\lambda$	$Z', R$	1.167	0.0	74.6	3.78
		$\lambda, Z', R$	1.195	0.26	75.7	4.03
James & Coolidge					74.1	$4.73 \pm 0.02$
Experiment					74.1	4.75

The MO,VB approach gives a reasonable understanding of bonding in  $H_2$ , but the predicted binding energy is still about 0.7 eV too small

- need more variational parameters and improved trial wavefunctions
- James & Coolidge (1933) used trial wavefunctions motivated by those used for the successful calculations of the helium atom
  - 30 variational parameters brings us within 0.02 eV of the measured binding energy

## The H<sub>2</sub> molecule : state of the art

- Fast-forward 86 years : a new (2019) experimental measurement of the H<sub>2</sub> dissociation energy, with a relative precision of about  $1 \times 10^{-10}$  :

Experiment : 35999.582834(11) cm<sup>-1</sup>

$$(1 \text{ cm}^{-1} \approx 1.24 \times 10^{-4} \text{ eV})$$

Theory : 35999.582820(26) cm<sup>-1</sup>

[N. Hölsch et al., Phys. Rev. Lett. 122 \(2019\) 103002 \(arXiv:1902.09471\)](#)

[M. Puchalski et al., Phys. Rev. Lett. 122 \(2019\) 103003 \(arXiv:1812.02980\)](#)

- Measurement and theory are now approaching a precision where the H<sub>2</sub> molecule can contribute to determinations of the proton radius

*(“This agreement between experiment and theory at the accuracy level of better than 1 MHz ... unprecedented in molecular physics.”)*

# Appendices

- *Appendix A :*

The second-order perturbation theory calculation of the quadratic Stark effect for hydrogen :

$$\Delta E_{100}^{(2)} = -\frac{9}{4}(4\pi\epsilon_0)\mathcal{E}^2 a_0^3$$

- *Appendix B :*

Summary of integrals involved in  $\text{H}_2^+$  and  $\text{H}_2$  variational calculations

## A : The Quadratic Stark Effect

- The second-order correction to the ground state energy of the hydrogen atom in an electric field was given on slide 8.45 as

$$\Delta E_{100}^{(2)} = \sum_{n \geq 2, \ell, m} \frac{|\langle n\ell m | e\mathcal{E}z | 100 \rangle|^2}{E_1^{(0)} - E_n^{(0)}} \quad (8.82.1)$$

where the zeroth-order eigenstate energies are

$$E_n^{(0)} = -\frac{1}{n^2} R_\infty$$

- This (infinite) summation can in fact be evaluated exactly; the trick is to find an operator  $F$  which satisfies the equation

$$z|0\rangle = (\hat{F}\hat{H}_0 - \hat{H}_0\hat{F})|0\rangle \quad (8.82.2)$$

where  $|0\rangle = |100\rangle$  is the unperturbed hydrogen ground state

## A : The quadratic Stark effect (2)

- If such an operator  $\hat{F}$  could be found, we would then have, for any zeroth-order state  $|k\rangle$ ,

$$\langle k|z|0\rangle = \langle k|\hat{F}\hat{H}_0|0\rangle - \langle k|\hat{H}_0\hat{F}|0\rangle = (E_0^{(0)} - E_k^{(0)})\langle k|\hat{F}|0\rangle$$

The infinite summation in equation (8.82.1) can then be written as

$$\begin{aligned} \sum_{k \neq 0} \frac{|\langle k|z|0\rangle|^2}{E_0^{(0)} - E_k^{(0)}} &= \sum_{k \neq 0} \langle 0|\hat{z}|k\rangle \langle k|\hat{F}|0\rangle \\ &= \langle 0|\hat{z}\hat{F}|0\rangle - \langle 0|\hat{z}|0\rangle \langle 0|\hat{F}|0\rangle \end{aligned}$$

where the last step uses the completeness relation in the form

$$\hat{I} = \sum_k |k\rangle \langle k| = |0\rangle \langle 0| + \sum_{k \neq 0} |k\rangle \langle k|$$

- Since (from parity)  $\langle 0|\hat{z}|0\rangle = 0$

we then obtain

$$\sum_{k \neq 0} \frac{|\langle k|z|0\rangle|^2}{E_0^{(0)} - E_k^{(0)}} = \langle 0|\hat{z}\hat{F}|0\rangle \quad (8.83.1)$$

## A : The quadratic Stark effect (3)

- Consider the operator  $F$  defined as

$$\hat{F} \equiv -\frac{m_e a_0}{\hbar^2} \left( \frac{r}{2} + a_0 \right) z \quad (8.84.1)$$

We can now check that this operator indeed satisfies equation (8.82.2)  
(more satisfyingly, we would write (8.80.2) as a differential equation, and  
then solve for  $F$ )

- Using

$$\hat{H}_0 |0\rangle = -R_\infty |0\rangle$$

gives

$$\hat{F} \hat{H}_0 |0\rangle = -R_\infty \hat{F} |0\rangle = R_\infty \frac{m_e a_0}{\hbar^2} \left( \frac{r}{2} + a_0 \right) z |0\rangle$$

- This tidies up as

$$\hat{F} \hat{H}_0 |0\rangle = \frac{1}{2} \left( \frac{r}{2a_0} + 1 \right) z |0\rangle \quad (8.84.2)$$

## A : The quadratic Stark effect (4)

- We also have

$$\begin{aligned}\hat{H}_0 \hat{F} &= \left( \frac{\hbar^2}{2m_e} \nabla^2 + \frac{e^2}{4\pi\epsilon_0 r} \right) \frac{m_e a_0}{\hbar^2} \left( \frac{r}{2} + a_0 \right) z \\ &= \frac{a_0}{2} \nabla^2 \left( \frac{r}{2} + a_0 \right) z + \frac{1}{r} \left( \frac{r}{2} + a_0 \right) z \\ &= \frac{a_0}{2} \nabla^2 \left( \frac{r}{2} + a_0 \right) r \cos \theta + \left( \frac{r}{2} + a_0 \right) \cos \theta\end{aligned}$$

- Using the ground state wavefunction

$$|0\rangle = \left( \frac{1}{\pi a_0^3} \right)^{1/2} e^{-r/a_0}$$

and

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2} \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right)$$

some straightforward but tedious algebra then gives

$$\hat{H}_0 \hat{F} |0\rangle = -\frac{1}{2} \left( -\frac{r}{2a_0} + 1 \right) z |0\rangle \quad \text{(8.85.1)}$$

## A : The quadratic Stark effect (5)

-- Combining equations (8.84.2) and (8.85.1) then gives, as required :

$$(\hat{F}\hat{H}_0 - \hat{H}_0\hat{F})|0\rangle = z|0\rangle$$

-- With the operator  $F$  as in equation (8.84.1), equation (8.83.1) becomes

$$\sum_{k \neq 0} \frac{|\langle k|z|0\rangle|^2}{E_0^{(0)} - E_k^{(0)}} = -\langle 0|\hat{z}\frac{m_e a_0}{\hbar^2} \left(\frac{r}{2} + a_0\right) z|0\rangle \quad (8.86.1)$$

-- For an arbitrary function  $f(r)$ , we have

$$\langle 0|f(r)x^2|0\rangle = \langle 0|f(r)y^2|0\rangle = \langle 0|f(r)z^2|0\rangle = \frac{1}{3}\langle 0|f(r)r^2|0\rangle$$

Equation (8.86.1) above is therefore

$$\begin{aligned} \sum_{k \neq 0} \frac{|\langle k|z|0\rangle|^2}{E_0^{(0)} - E_k^{(0)}} &= -\frac{1}{3}\langle 0|\frac{m_e a_0}{\hbar^2} \left(\frac{r}{2} + a_0\right) r^2|0\rangle \\ &= -\frac{m_e a_0}{3\hbar^2} \left(\frac{1}{2}\langle r^3\rangle_0 + a_0\langle r^2\rangle_0\right) \end{aligned} \quad (8.86.2)$$

## A : The quadratic Stark effect (6)

- The expectation values for the ground state of hydrogen are

$$\langle r^2 \rangle_0 \equiv \langle 0 | r^2 | 0 \rangle = 3a_0^2 ; \quad \langle r^3 \rangle_0 \equiv \langle 0 | r^3 | 0 \rangle = \frac{15}{2}a_0^3$$

Substituting into equation (8.86.2) then gives

$$\Delta E_{100}^{(2)} = \sum_k \frac{|\langle k | e\mathcal{E}z | 0 \rangle|^2}{E_0^{(0)} - E_k^{(0)}} = -e^2 \mathcal{E}^2 \frac{m_e a_0}{3\hbar^2} \left( \frac{15}{4}a_0^3 + 3a_0^3 \right)$$

- Hence we finally obtain the second-order correction to the hydrogen atom ground state energy as

$$\boxed{\Delta E_{100}^{(2)} = -\frac{9}{4}(4\pi\epsilon_0)\mathcal{E}^2 a_0^3}$$

(8.87.1)

## B : Molecular integrals

- For  $\text{H}_2^+$ , the Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla_r^2 + \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{R} - \frac{1}{r_a} - \frac{1}{r_b} \right)$$

where

$$R = |\mathbf{R}_a - \mathbf{R}_b| , \quad r_a = |\mathbf{R}_a - \mathbf{r}| , \quad r_b = |\mathbf{R}_b - \mathbf{r}|$$

- For a trial wavefunction basis consisting of

$$\psi_a(\mathbf{r}) = \sqrt{\frac{\beta^3}{\pi}} e^{-\beta r_a} , \quad \psi_b(\mathbf{r}) = \sqrt{\frac{\beta^3}{\pi}} e^{-\beta r_b} ; \quad \beta \equiv \frac{Z'}{a_0}$$

the variational method requires evaluation of the overlap integral

$$S_{ab} = \langle \psi_a | \psi_b \rangle$$

and the matrix elements

$$H_{aa} = \langle \psi_a | \hat{H} | \psi_a \rangle ; \quad H_{ab} = \langle \psi_a | \hat{H} | \psi_b \rangle$$

## B : Molecular integrals (2)

- Explicitly, the overlap integral required is

$$\langle \psi_a | \psi_b \rangle = \frac{\beta^3}{\pi} \int e^{-\beta(r_a + r_b)} d^3 \mathbf{r} \equiv S$$

This can be evaluated analytically using prolate spheroidal coordinates, for example, with the result

$$S = \left( 1 + \beta R + \frac{1}{3}(\beta R)^2 \right) e^{-\beta R}$$

- The matrix elements  $H_{aa}$  and  $H_{ab}$  require the component integrals

$$\langle \psi_a | \nabla^2 | \psi_a \rangle , \quad \langle \psi_b | \nabla^2 | \psi_a \rangle$$

$$\langle \psi_a | (1/r_a) | \psi_a \rangle , \quad \langle \psi_b | (1/r_a) | \psi_a \rangle , \quad \langle \psi_b | (1/r_a) | \psi_b \rangle$$

For example :

$$\langle \psi_b | \nabla^2 | \psi_a \rangle = \frac{\beta^3}{\pi} \int e^{-\beta r_b} \nabla_r^2 (e^{-\beta r_a}) d^3 \mathbf{r}$$

$$\langle \psi_b | (1/r_a) | \psi_a \rangle = \frac{\beta^3}{\pi} \int \frac{1}{r_a} e^{-\beta(r_b + r_a)} d^3 \mathbf{r}$$

## B : Molecular integrals (3)

- These integrals can again be evaluated analytically, with the results

$$\langle \psi_a | \nabla_r^2 | \psi_a \rangle = -\beta^2$$

$$\langle \psi_b | \nabla_r^2 | \psi_a \rangle = \beta^2(S + K)$$

$$\langle \psi_a | (1/r_a) | \psi_a \rangle = \beta$$

$$\langle \psi_b | (1/r_a) | \psi_a \rangle = -\beta K/2$$

$$\langle \psi_b | (1/r_a) | \psi_b \rangle = -\beta J/2$$

where

$$K = -2\beta R (1 + \beta R) e^{-\beta R}$$

$$J = -\frac{2}{\beta R} [1 - (1 + \beta R)e^{-2\beta R}]$$

## B : Molecular integrals (4)

- For molecular hydrogen, H<sub>2</sub>, the Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m_e} (\nabla_1^2 + \nabla_2^2) + \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{R} + \frac{1}{r_{12}} - \frac{1}{r_{a1}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} - \frac{1}{r_{b2}} \right)$$

where

$$r_{12} = |\mathbf{r}_1 - \mathbf{r}_2| , \quad r_{a1} = |\mathbf{R}_a - \mathbf{r}_1| , \quad r_{a2} = |\mathbf{R}_a - \mathbf{r}_2| , \quad \dots$$

- The variational method requires evaluation of the matrix element

$$\langle a + b; a + b | \hat{H} | a + b; a + b \rangle$$

where

$$\begin{aligned} |a + b; a + b\rangle &= \psi_{a+b}(\mathbf{r}_1)\psi_{a+b}(\mathbf{r}_2) \\ &= [\psi_a(\mathbf{r}_1) + \psi_b(\mathbf{r}_1)] [\psi_a(\mathbf{r}_2) + \psi_b(\mathbf{r}_2)] \\ &= \frac{\beta^3/\pi}{2(1+S)} [e^{-\beta r_{a1}} + e^{-\beta r_{b1}}] [e^{-\beta r_{a2}} + e^{-\beta r_{b2}}] \end{aligned}$$

## B : Molecular integrals (5)

- Multiplying out, all the component integrals required have already been evaluated for  $\text{H}_2^+$ , except for those arising from the  $1/r_{12}$  term in  $H$  :

$$\langle a; b | (1/r_{12}) | a; b \rangle ; \quad \langle a; b | (1/r_{12}) | b; a \rangle$$

where

$$|a; b\rangle = \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) ; \quad |b; a\rangle = \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)$$

$$\psi_a(\mathbf{r}_1) = \sqrt{\frac{\beta^3}{\pi}} e^{-\beta r_{a1}} , \quad \psi_b(\mathbf{r}_2) = \sqrt{\frac{\beta^3}{\pi}} e^{-\beta r_{b2}}$$

- These integrals can again be evaluated in prolate spheroidal coordinates

This gives the first integral as

$$\langle a; b | (1/r_{12}) | a; b \rangle = \beta J'/2$$

where

$$J' = \frac{2}{\beta R} - \left[ \frac{2}{\beta R} + \frac{11}{4} + \frac{3}{2}\beta R + \frac{1}{3}(\beta R)^2 \right] e^{-2\beta R}$$

## B : Molecular integrals (6)

-- The second integral is

$$\langle a; b | (1/r_{12}) | b; a \rangle = \beta K'/2$$

where

$$K' = \frac{2}{5} \left[ - \left( -\frac{25}{8} + \frac{23}{4}\beta R + 3(\beta R)^2 + \frac{1}{3}(\beta R)^3 \right) e^{-2\beta R} + \frac{6}{\beta R} [S^2(C + \ln(\beta R)) + (S')^2 \text{Ei}(-4\beta R) - 2SS' \text{Ei}(-2\beta R)] \right]$$

$$S' = \left( 1 - \beta R + \frac{1}{3}(\beta R)^2 \right) e^{\beta R}$$

and  $C$  is *Euler's constant*,

$$C = \int_0^1 \frac{1 - e^{-t}}{t} dt - \int_1^\infty \frac{e^{-t}}{t} dt \approx 0.577215664901533$$

and  $\text{Ei}(-x)$  is the *exponential integral*, defined as

$$\text{Ei}(-x) = - \int_x^\infty \frac{e^{-t}}{t} dt \quad (x \neq 0)$$