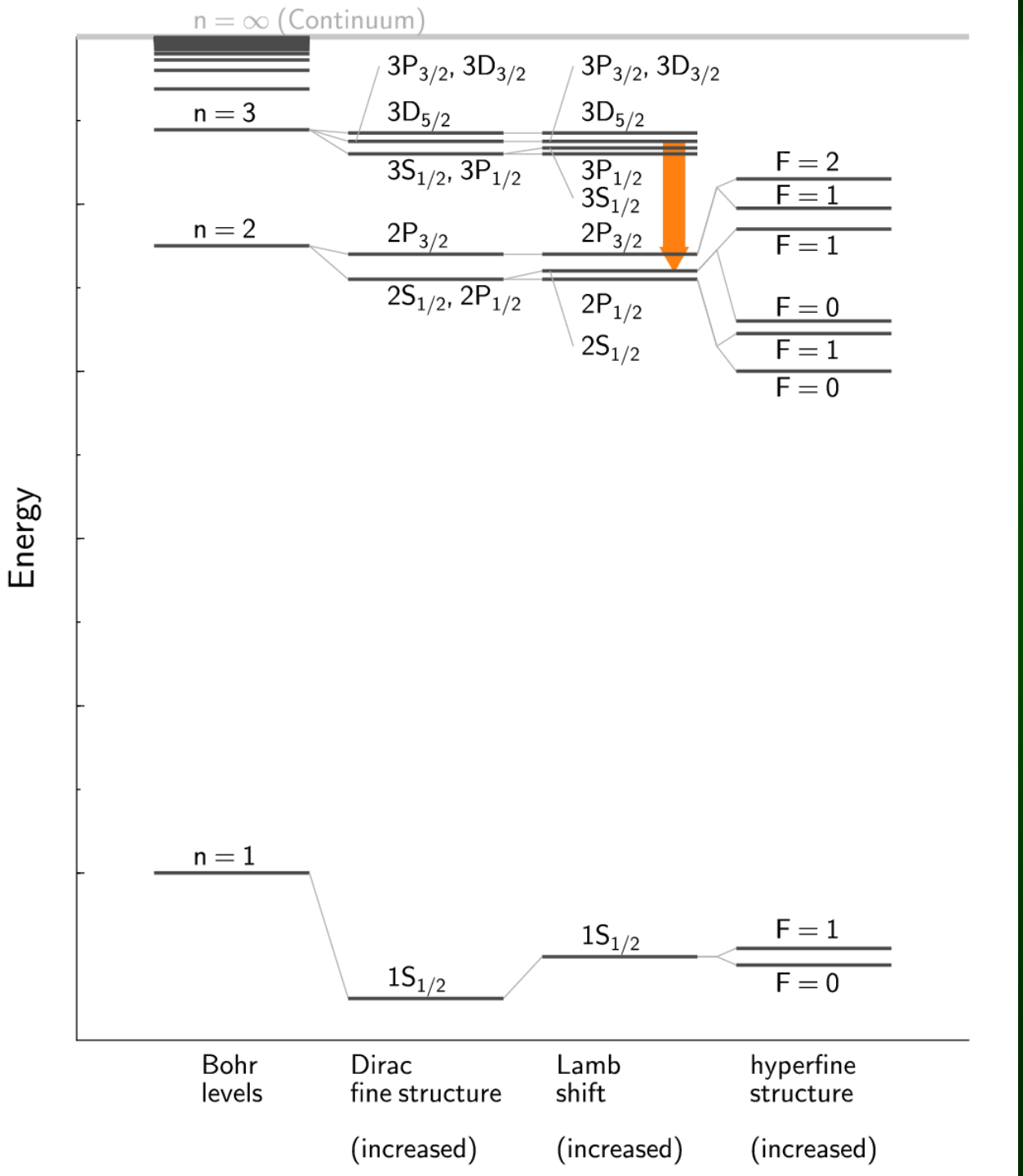
The Hydrogen atom
Fine structure


n = ∞ (Continuum)
n = 3
n = 2
n = 1
3P3/2, 3D3/2
3D5/2
3S1/2, 3P1/2
2P3/2
2S1/2, 2P1/2
1S1/2
3P3/2, 3D3/2
3D5/2
3P1/2
3S1/2
2P3/2
2P1/2
2S1/2
1S1/2
F = 2
F = 1
F = 1
F = 0
F = 1
F = 0
F = 1
F = 0
Energy
Bohr levels
Dirac fine structure
(increased)
Lamb shift
(increased)
hyperfine structure
(increased)

Relativistic effect – the Klein-Gordon equation

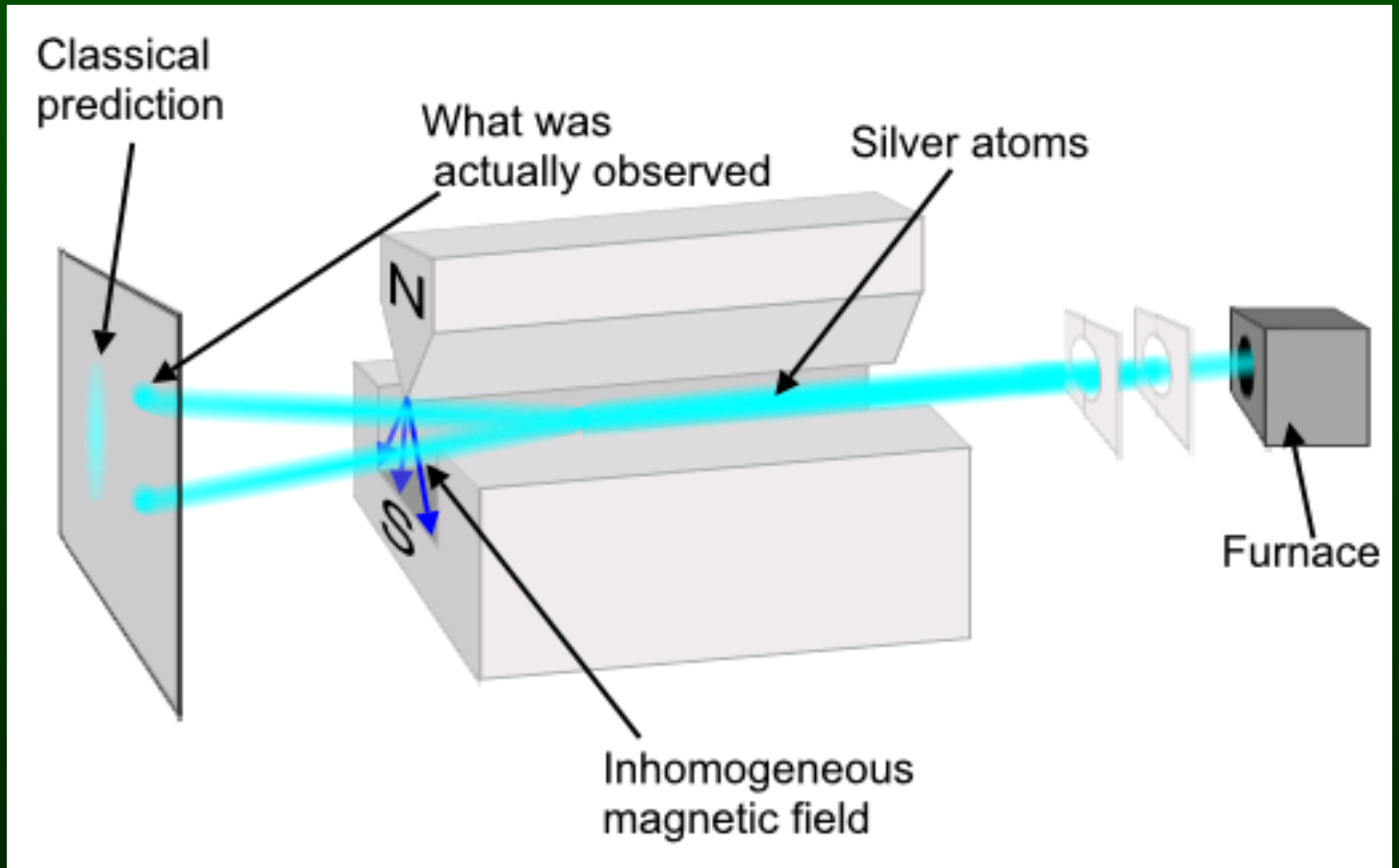
$$E_{n,l} = -\frac{RhcZ^2}{n^2}\left[1 + \frac{\alpha^2 Z^2}{n^2}\left(\frac{n}{l+1/2} - \frac{3}{4}\right)\right]$$

$$\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c} = \frac{1}{137}$$

the fine structure constant

The spin of the electron

- s=1/2



The Dirac equation

$$i\frac{\partial \Psi}{\partial t} = \hat{H}_D \Psi$$

$$\hat{H}_D = eV + \hat{\alpha}(\hat{\mathbf{p}} - e\vec{A})c + \hat{\beta} m_0 c^2$$

$\hat{\alpha} = (\hat{\alpha}_x, \hat{\alpha}_y, \hat{\alpha}_z)$ and $\hat{\beta}$ act only on the spin

The solution for hydrogen

$$E = m_0 c^2 \left[1 + \left(\frac{\alpha Z}{n - j - 1/2 + \sqrt{(j + 1/2)^2 - \alpha^2 Z^2}} \right)^2 \right]^{-1/2}$$

- **The total angular momentum** $\mathbf{J} = \mathbf{L} + \mathbf{S}.$
- **The energy depends on j!**
- **Second-order approximation**

$$E_{n,j} = -\frac{RhcZ^2}{n^2}\left[1 + \frac{Z^2\alpha^2}{n^2}\left(\frac{n}{j+1/2} - \frac{3}{4}\right)\right]$$

Stationary perturbational method

$$H = H^0 + H' \tag{1}$$

The eigenstates and eigenfunctions of H^0 are known

If E_k^0 is non-degenerated

$$H^0 \Psi_k = E_k^0 \Psi_k. \tag{2}$$

First-order correction

$$E_k^{(1)} = \langle \Psi_k | H' | \Psi_k \rangle = H'_{kk} \tag{3}$$

Eigenfunctions

$$(H^0 - E_k^0)\Psi_k^{(1)} + (H' - E_k^{(1)})\Psi_k = 0. \tag{4}$$

$$\Psi_k^{(1)} = \sum_{m \neq k} \frac{H'_{mk}}{E_k - E_m} \Psi_m \tag{5}$$

If E_k^0 is degenerated

$$H^0\Psi_{kr} = E_k^0\Psi_{kr}; \qquad r = \overline{1,g}, \tag{8}$$

ahol g – degree of degeneration

$$\langle\Psi_{kr}|\Psi_{ks}\rangle = \delta_{rs}; \qquad r,s = \overline{1,g}. \tag{9}$$

The first-order corrections are given by

$$\begin{vmatrix} \langle\Psi_{k1}|H'|\Psi_{k1}\rangle - E_k^{(1)} & \langle\Psi_{k1}|H'|\Psi_{k2}\rangle & \cdots & \langle\Psi_{k1}|H'|\Psi_{kg}\rangle \\ \langle\Psi_{k2}|H'|\Psi_{k1}\rangle & \langle\Psi_{k2}|H'|\Psi_{k2}\rangle - E_k^{(1)} & \cdots & \langle\Psi_{k2}|H'|\Psi_{kg}\rangle \\ \vdots & \vdots & & \vdots \\ \langle\Psi_{kg}|H'|\Psi_{k1}\rangle & \langle\Psi_{kg}|H'|\Psi_{k2}\rangle & \cdots & \langle\Psi_{kg}|H'|\Psi_{kg}\rangle - E_k^{(1)} \end{vmatrix} = 0. \tag{10}$$

Roots: $E_{k1}^{(1)}, E_{k2}^{(1)}, \ldots, E_{kg}^{(1)}$.

If Ψ_{kr} are the eigenfunctions belonging to different eigenvalues of H', the matrix of H' will be diagonal.

The perturbational treatment of the relativistic effect

If the Dirac equation is expanded in terms of v^2/c^2, one obtains 3 correction terms:

- the relativistic correction of the kinetic energy

$$H_1 = -\frac{1}{8}\frac{p_e^4}{m^3c^2}$$

- the Darwin-term (only for l=0)

$$H_D = \frac{\pi e^2 \hbar^2}{2m_e^2 c^2}\delta^3(\vec{r})$$

- the spin-orbit interaction term

$$H_{LS} = A(r)\mathbf{LS}$$

$$\begin{aligned} A(r) &= \frac{\alpha^2}{2}\frac{1}{r}\frac{dV}{dr} \\ &= \frac{\alpha^2}{2}\frac{Z}{r^3}. \end{aligned}$$

Perturbation theory for a degenerate level

Is desirable that the perturbation LS to be diagonal

This is valid in the representation $|lsjm_j>$,

because L_2, S_2, J_2 and J_z commute with LS.

We write the scalar product as

$$\mathbf{LS} = \frac{1}{2}(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2)$$

The diagonal matrix element is

$$\begin{aligned} E_{LS} &= \langle nlsjm_j|\frac{1}{2}A(r)(\mathbf{J}^2-\mathbf{L}^2-\mathbf{S}^2)|nlsjm_j\rangle \\ &= \frac{1}{2}\langle nlsjm_j|A(r)|nlsjm_j\rangle \\ &\quad \times[j(j+1)-l(l+1)-s(s+1)], \end{aligned}$$

It can be calculated analytically

$$\langle nlsjm_j|A(r)|nlsjm_j\rangle = \frac{\alpha^2}{2}\frac{Z^4}{n^3 l(l+1/2)(l+1)}$$

Finally

$$E_{LS} = -E_n \frac{(Z\alpha)^2}{2nl(l+1/2)(l+1)}\left[j(j+1)-l(l+1)-\frac{3}{4}\right]$$

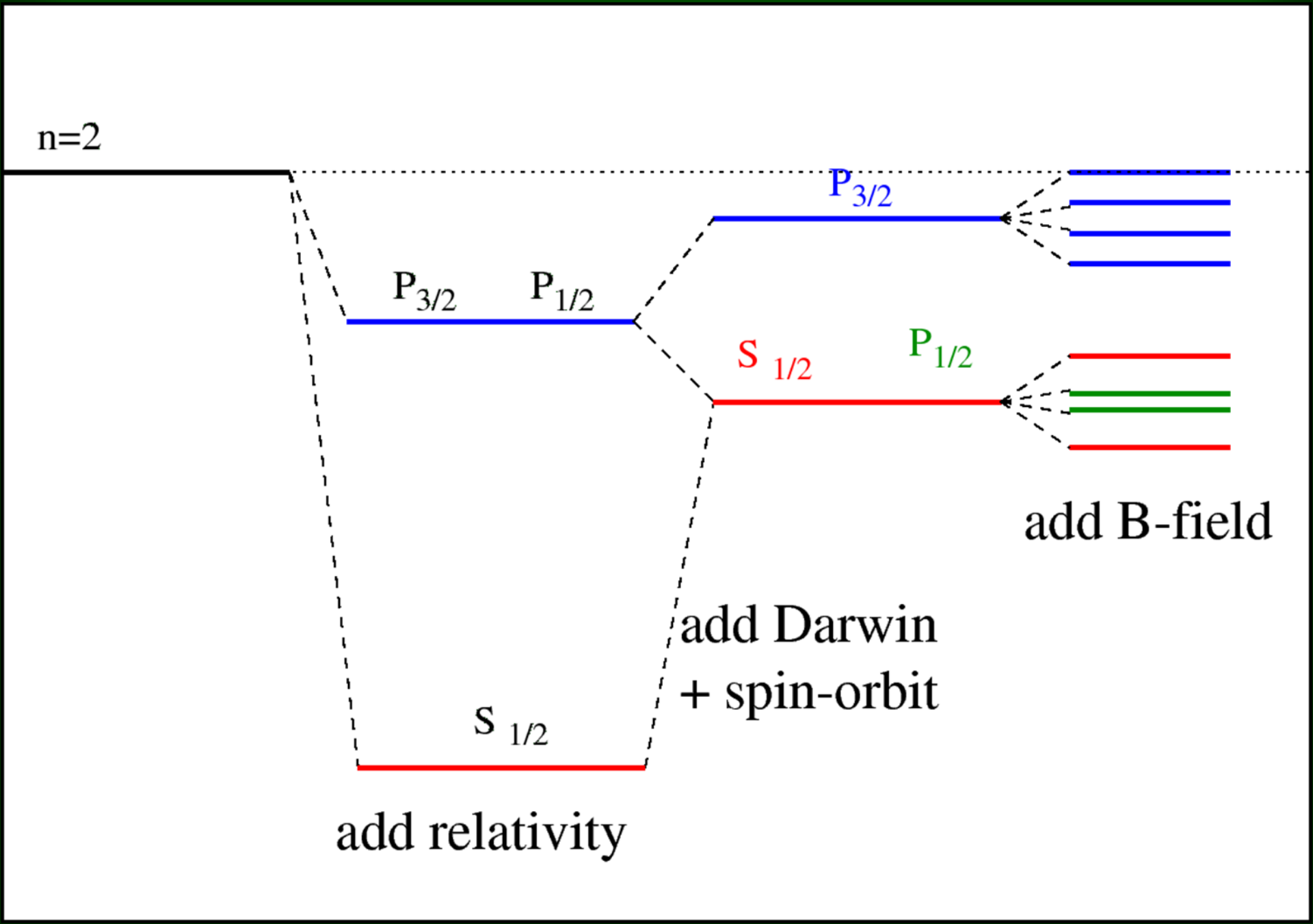
$$\langle \psi_{nlm} | H_1 | \psi_{nlm} \rangle = + \frac{E_n^{(0)^2}}{2mc^2} \left[3 - \frac{4n}{\ell + \frac{1}{2}} \right]$$

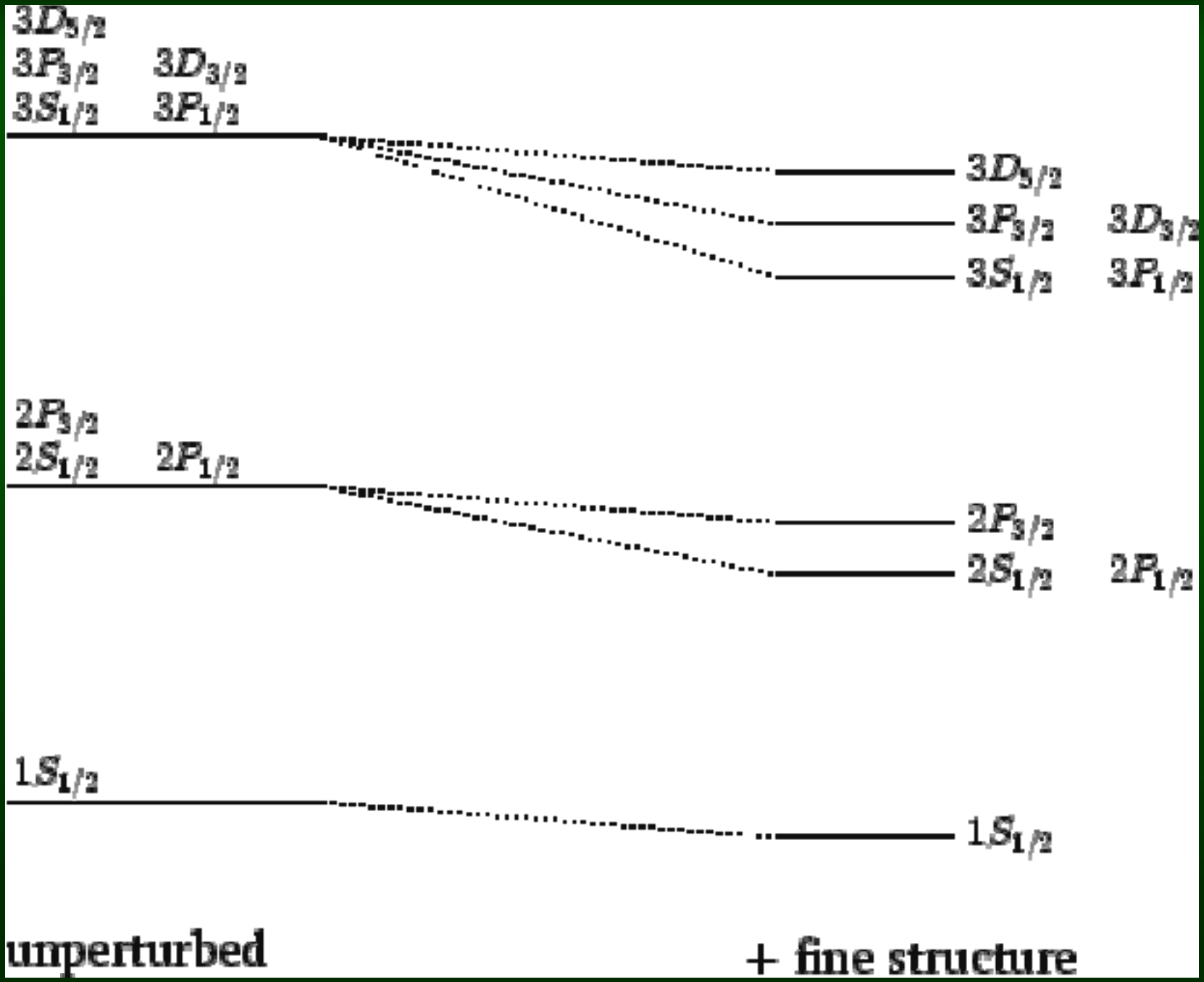
$$\langle H_D \rangle_{n00} = \frac{4e^2\hbar^2}{8n^3 a_0^3 m^2 c^2} = \frac{e^2\hbar^2\alpha^2 m^2 c^2}{2n^3 a_0 m^2 c^2 \hbar^2} = \frac{2nE_n^2}{mc^2}$$

$$E_{LS} = -E_n \frac{(Z\alpha)^2}{2nl(l+1/2)(l+1)} \left[j(j+1) - l(l+1) - \frac{3}{4} \right]$$

Adding these contributions, the terms depending on l cancel out.

$$E_{nlm} = E_n^{(0)} + \frac{E_n^{(0)^2}}{2mc^2} \left[3 - \frac{4n}{j + \frac{1}{2}} \right]$$


n=2
P3/2
P3/2
P1/2
S 1/2
P1/2
add B-field
add Darwin
+ spin-orbit
S 1/2
add relativity


$3D_{5/2}$
$3P_{3/2}$ $3D_{3/2}$
$3S_{1/2}$ $3P_{1/2}$
$2P_{3/2}$
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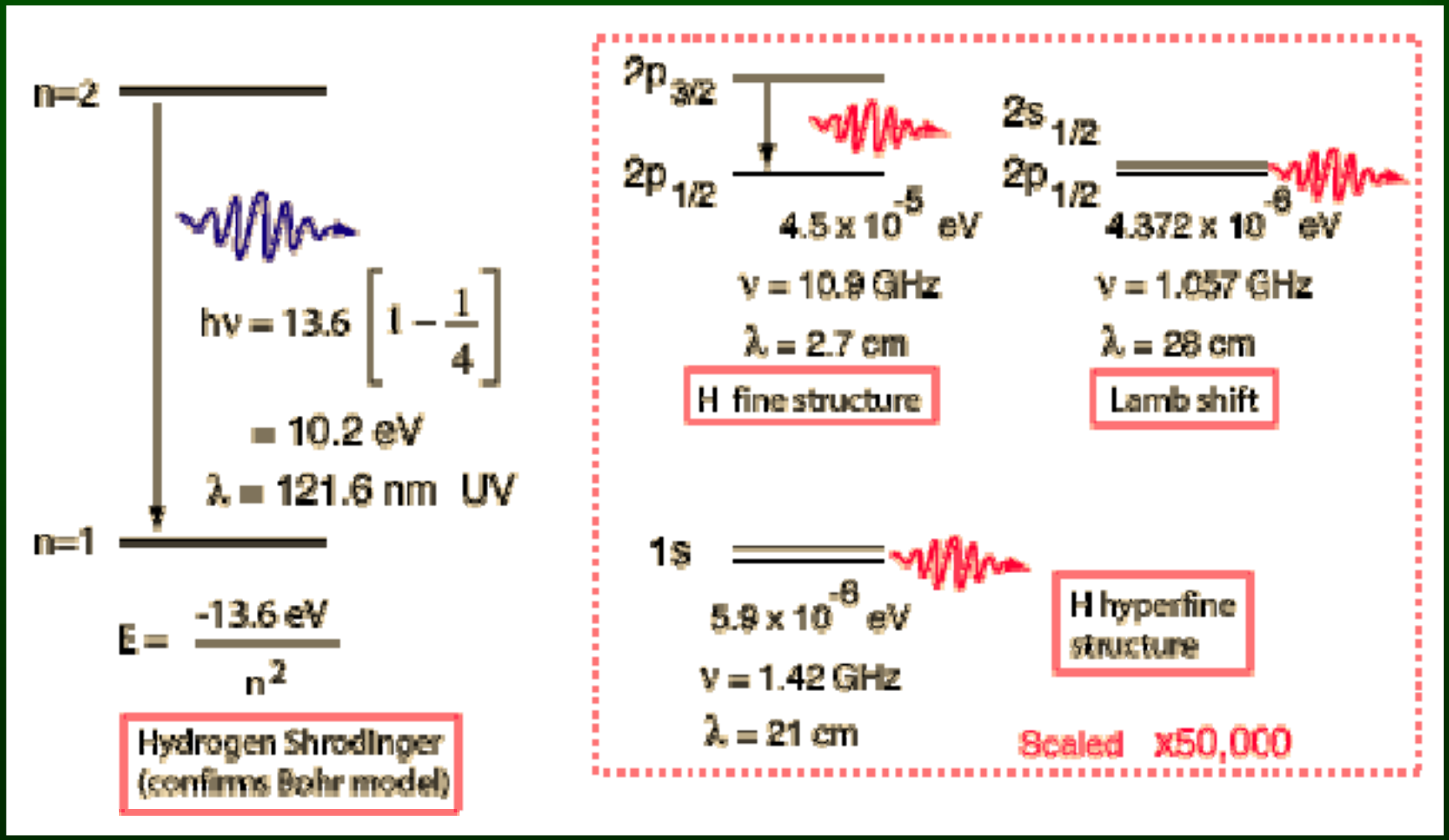
$2P_{3/2}$
$2S_{1/2}$ $2P_{1/2}$
$1S_{1/2}$
unperturbed
+ fine structure

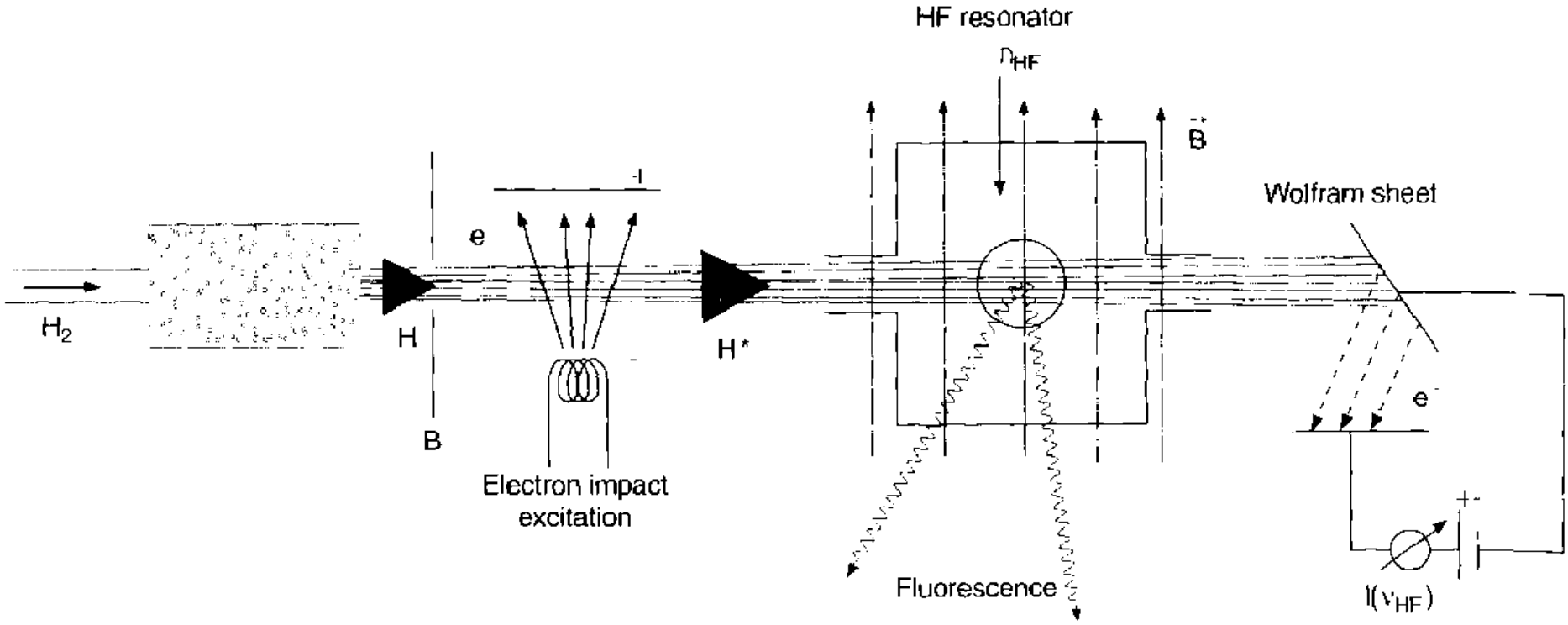
The difference between the two splitted levels (the spin-orbit splitting)

$$\begin{aligned}
\Delta E_{LS} &= E_{LS}(j = l + \frac{1}{2}) - E_{LS}(j = l - \frac{1}{2}) \\
&= -E_n \frac{(Z\alpha)^2}{2nl(l+1/2)(l+1)} \left[(l+\frac{1}{2})(l+\frac{3}{2}) - (l+\frac{1}{2})(l-\frac{1}{2}) \right] \\
&= -E_n \frac{(Z\alpha)^2}{nl(l+1)} \qquad (2.7
\end{aligned}$$

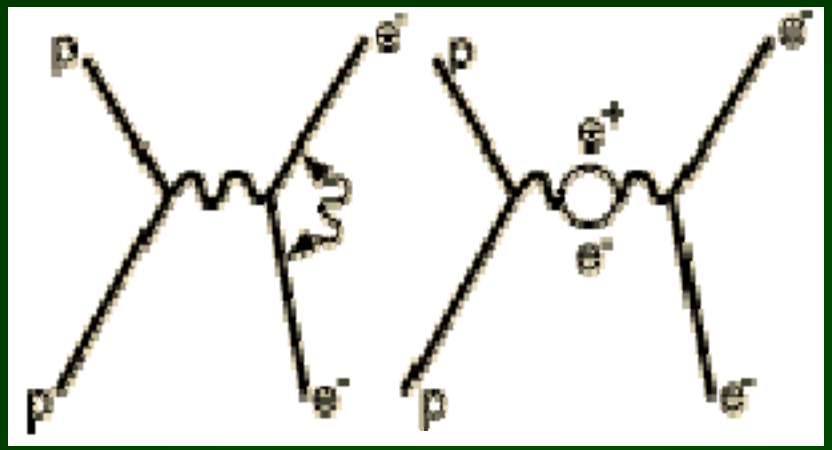
Lamb shift – quantum field theory



The Lamb shift experiment



Slight changes in the electromagnetic force



$$\Delta E_{\text{Lamb}} = \alpha^5 m_e c^2 \frac{k(n,0)}{4n^3} \text{ for } \ell = 0$$

$$\Delta E_{\text{Lamb}} = \alpha^5 m_e c^2 \frac{1}{4n^3} \left[k(n,\ell) \pm \frac{1}{\pi(j+\frac{1}{2})(\ell+\frac{1}{2})} \right] \text{ for } \ell \neq 0 \text{ and } j = \ell \pm \frac{1}{2},$$

Hyperfine splitting

- The magnetic momentum of the nucleus

$$\vec{\mu}_N = \frac{Zeg_N}{2M_N c}\vec{I}$$

- The interaction with the magnetic moment of the electron (for I=0)

$$\Delta E = \left\langle \frac{e}{mc}\vec{S}\cdot\vec{B} \right\rangle = \frac{4}{3}(Z\alpha)^4 \left(\frac{m}{M_N}\right)(mc^2)g_N \frac{1}{n^3}\frac{\vec{S}\cdot\vec{I}}{\hbar^2}$$

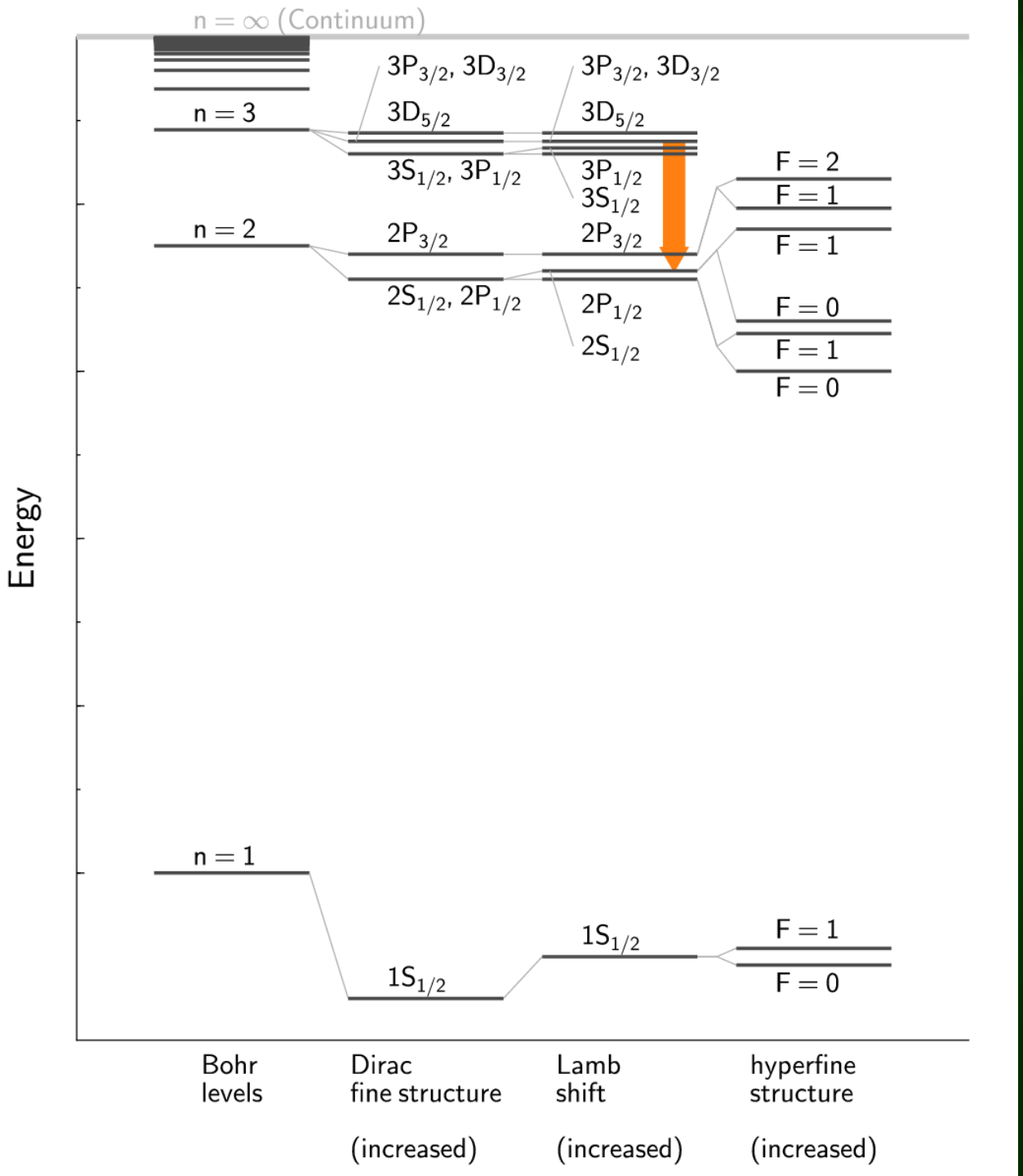
$$\Delta E = \tfrac{2}{3}(Z\alpha)^4 \left(\tfrac{m}{M_N}\right)(mc^2)g_N \tfrac{1}{n^3}\left(f(f+1)-\tfrac{3}{2}\right) \equiv \tfrac{A}{2}\left(f(f+1)-\tfrac{3}{2}\right)$$

- The splitting

$$\Delta E_{f=1} - \Delta E_{f=0} = \frac{4}{3}(Z\alpha)^4 \left(\frac{m}{M_N}\right)(mc^2)g_N \frac{1}{n^3}$$

- For the ground state

$$\lambda = 2\pi\frac{\hbar c}{E} = 2\pi\frac{1973}{5.84\times10^{-6}}\mathring{A} = 2\times10^9\mathring{A} = 21.2\ \mathrm{cm}$$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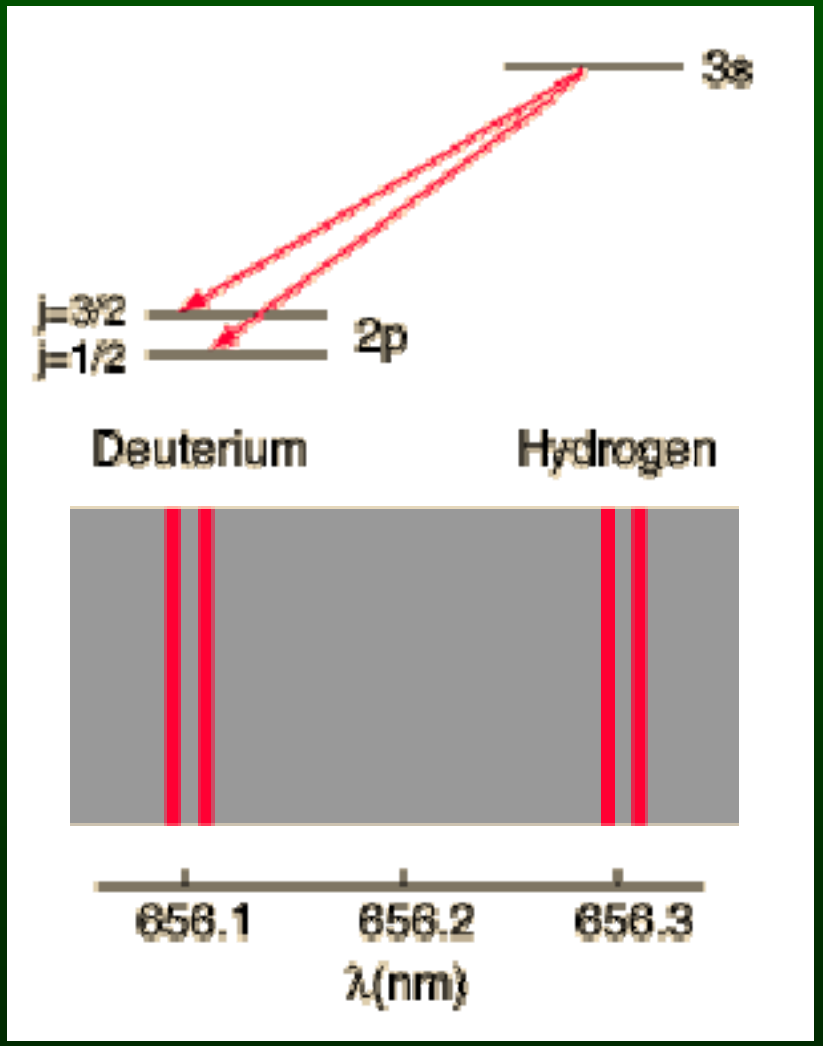
Isotope shift (different reduced mass)