Microscopic argument for SO coupling:

Consider an (accelerated!) frame in which the electron is stationary and is circled by the nucleus. The nucleus looks like a current ring with current \( I = \frac{e}{\tau} \) (here assumed \( \tau = 1 \)) and radius \( R \). Its field is \( B = \frac{m_0 I}{2\tau} \) at the origin.

We can put this in terms of the orbital angular momentum of the electron \( L = 2\pi m r^2 \); \( R \):

\[
\vec{B} = \frac{m_0 eL}{4\pi mr^3} = \left( \frac{1}{4\pi \varepsilon_0} \right) \frac{e}{mc^2 r^3} \vec{L}.
\]

The energy of the electron spin in this frame is

\[
-\vec{\alpha} \cdot \vec{b} = \frac{ge\vec{S} \cdot \vec{B}}{2m} \quad g \approx 2
\]

and we are left with

\[
H = \left( \frac{e^2}{4\pi \varepsilon_0} \right) \left( \frac{1}{m^2 c^2 r^2} \right) \vec{L} \cdot \vec{S}.
\]

The only error introduced by working in this accelerated frame is a factor of 2. We can write the final answer as

\[
H = \left( \frac{e^2}{4\pi \varepsilon_0} \right) \frac{1}{2mc^2 r} \frac{d}{dr} \left( \frac{1}{2} \right) \vec{E} \cdot \vec{S}.
\]
Resolving an \( \alpha \)-fold degeneracy in \( \mathcal{PT} \):

\[
\langle \chi_{nr}^{(0)} | \chi_{ns}^{(0)} \rangle = \delta_{rs}, \quad r, s = 1, \ldots, \alpha
\]

\[
\chi_{nr} = \sum_{\alpha} \lambda_{nr}^{(0)} + \lambda_{nr}^{(1)} + \lambda_{nr}^{(2)} + \ldots
\]

\[
E_{nr} = E_{n}^{(0)} + \lambda_{n}^{(1)} + \lambda_{n}^{(2)} + \ldots
\]

We write \( \chi_{nr}^{(0)} \) rather than \( \chi_{nr} \) because the correct zeroth-order wave function may be a nontrivial combination of our original basis states.

\[
\chi_{nr}^{(0)} = \sum_{s=1}^{\alpha} c_{rs} \chi_{ns}^{(0)}
\]

\[
\chi_{nr}^{(1)} = \sum_{k} a_{nrs}^{(1)} \chi_{ks}^{(0)}
\]

Substitute in \( H_{0} \chi_{nr}^{(1)} + H \chi_{nr}^{(0)} = E_{n}^{(0)} \chi_{nr}^{(1)} + E_{nr}^{(1)} \chi_{nr}^{(0)} \)

\[
\rightarrow \sum_{k} a_{nrs}^{(1)} \left( E_{k}^{(0)} - E_{n}^{(0)} \right) \chi_{ks}^{(0)} + \sum_{s} c_{rs} \left( H - E_{nr}^{(1)} \right) \chi_{ns}^{(0)} = 0.
\]

Form inner product with \( \chi_{nu}^{(0)} \times \) to get

\[
\sum_{k} a_{nrs}^{(1)} \left( E_{k}^{(0)} - E_{n}^{(0)} \right) \chi_{nu}^{(0)} \chi_{ks}^{(0)} + \sum_{s} c_{rs} \left( H_{nu,ns} - E_{nr}^{(1)} \right) \chi_{nu}^{(0)} \chi_{ns}^{(0)} = 0.
\]

In first term, only get non-zero selection products if \( nu = ks \), but then energies are the same. We are left with the second part, which looks like a matrix equation.
\[ \sum_{s=1}^{\infty} C_{rs} \left[ H'_{nu,ns} - E_{nr}^{(u)} \delta_{vs} \right] = 0 \quad v = 1, \ldots, \infty \]

At fixed \( r \) and \( E_{nr}^{(u)} \), this is a system of \( \infty \) equations for \( \infty \) unknowns \( C_{r1}, C_{r2}, C_{r3}, \ldots \).

Nontrivial solutions result if the determinant of the quantity in square brackets, considered as a square matrix \( M \) with indices \( s \) and \( v \), vanishes:

\[ \det \left( H'_{nu,ns} - E_{nr}^{(u)} \delta_{vs} \right) = 0 \]

\( \uparrow \)

identity matrix

But this is exactly the condition that \( E_{nr}^{(u)} \) be an eigenvalue of \( H'_{nu,ns} \), the matrix of \( H' \) in the degenerate subspace.
SPONTANEOUS EMISSION from b→a transition

Number of atoms going b→a per unit time:

\[ N_{ab} = A_{ab} N_b + B_{ab} N_b \rho(\omega_{ba}) \]

\[ A_{ab} = \text{spontaneous emission (to be found)} \]
\[ B_{ab} = \text{stimulated emission} \]

\[ = B_{ba} = \frac{n^2}{3h^2 \varepsilon_0} |D_{ba}|^2 = \frac{c W_{ba}}{I(\omega_{ba})} \]

\( I(\omega_{ba}) = \text{energy density per unit freq.} \)

\[ \rho(\omega_{ba}) = \frac{I(\omega_{ba})}{2} \]
\[ N_{ba} = B_{ba} N_a \rho(\omega_{ba}) \]

At equilibrium

\[ \dot{N}_b = N_{ab} \]

\[ \Rightarrow \frac{N_a}{N_b} = \frac{A_{ab} + B_{ab} \rho(\omega_{ba})}{B_{ba} \rho(\omega_{ba})} \]

If this is in thermal equilibrium with radiation at temp \( T \), then

\[ \frac{N_a}{N_b} = e^{-\frac{(E_a - E_b)}{kT}} = e^{\frac{h \omega_{ba}}{kT}} \]

so

\[ \rho(\omega_{ba}) = \frac{A_{ab}}{B_{ba} \exp(h \omega_{ba}/kT) - B_{ab}} \]
We can compare this to the famous "Planck distribution" for thermal radiation (see Physics 112 or Bransden)

\[ \beta(w_{ba}) = \frac{\hbar w_{ba}^3}{\pi^2 c^3} \frac{1}{\exp(\hbar w_{ba}/kT) - 1} \]

and these look the same if

\[ B_{ab} = B_{ba} \] (which we knew already)

and

\[ A_{ab} = \frac{\hbar w_{ba}^3}{\pi^2 c^3} B_{ab} \]

\[ \Rightarrow W_{ab} = \frac{w_{ba}^3 1D_{ba}^2}{3\pi c^3 h E_0} \]
\[
\frac{\delta S}{\delta E} = \frac{1}{T} \quad (S = k_B \ln \Omega, \ \Omega = \# \text{ of states available at energy } E)
\]

Imagine "thermal contact" between reservoir at temperature \( T \). Energy can flow back and forth, but total \( E \) is conserved.

2-state system  Reservoir
\[E_a\quad E_0\]
\[E_b\quad E_0 - (E_b - E_a)\]

The probability to find in state A or B is determined by the number of configurations of the reservoir:

- two-state system is reservoir configs
- \[N_\text{in A} = \frac{S(E_0)}{k_B}\]
- \[N_\text{in B} = \frac{S(E_0 - E_b + E_a)}{k_B}\]

Expand the exponent, assuming \( E_b - E_a \) is small compared to reservoir energy scales:

\[
S(E_0 - E_b + E_a)/k_B = S(E_0) + (E_a - E_b) \left( \frac{\delta S}{\delta E} \right)_{E} \frac{k_B}{k_B}
\]

so
\[
\frac{N_B}{N_A} = e^{-(E_b - E_a)/k_B T} = \frac{S(E_0)/k_B - (E_b - E_a)/k_B T}{N_A}
\]