

XI. Resonant absorption and a.c. Stark shift

Equations to be used:

$$|i\rangle = |n_i L_i S J_i I F_i M_{F_i}\rangle, \quad |f\rangle = |n_f L_f S J_f I F_f M_{F_f}\rangle, \quad M_{F_f} = M_{F_i} + \mu$$

$$d_{fi} = (-1)^{L_f+S+J_i+J_f+I+F_i} \sqrt{(2J_f+1)(2J_i+1)(2F_i+1)} C_{F_i M_{F_i} 1 \mu}^{F_f M_{F_f}} \times \\ \times \begin{Bmatrix} J_i & I & F_i \\ F_f & 1 & J_f \end{Bmatrix} \begin{Bmatrix} L_i & S & J_i \\ J_f & 1 & L_f \end{Bmatrix} \langle n_f L_f || \hat{d} || n_i L_i \rangle$$

$$\langle n_f L_f S J_f I F_f || \hat{d} || n_i L_i S J_i I F_i \rangle = (-1)^{J_f+I+F_i+1} \sqrt{(2F_f+1)(2F_i+1)} \times \\ \times \begin{Bmatrix} J_i & I & F_i \\ F_f & 1 & J_f \end{Bmatrix} \langle n_f L_f S J_f || \hat{d} || n_i L_i S J_i \rangle$$

$$\langle n_f L_f S J_f || \hat{d} || n_i L_i S J_i \rangle = (-1)^{L_f+S+J_i+1} \sqrt{(2J_f+1)(2J_i+1)} \begin{Bmatrix} L_i & S & J_i \\ J_f & 1 & L_f \end{Bmatrix} \langle n_f L_f || \hat{d} || n_i L_i \rangle$$

$$C_{\alpha\alpha 1\beta}^{c\gamma}$$

c	$\beta = 1$	$\beta = 0$	$\beta = -1$
$a + 1$	$\left[\frac{(c + \gamma - 1)(c + \gamma)}{(2c - 1)2c} \right]^{1/2}$	$\left[\frac{(c + \gamma)(c - \gamma)}{(2c - 1)c} \right]^{1/2}$	$\left[\frac{(c - \gamma - 1)(c - \gamma)}{(2c - 1)2c} \right]^{1/2}$
a	$-\left[\frac{(c + \gamma)(c - \gamma + 1)}{2c(c + 1)} \right]^{1/2}$	$\frac{\gamma}{[c(c + 1)]^{1/2}}$	$\left[\frac{(c + \gamma + 1)(c - \gamma)}{2c(c + 1)} \right]^{1/2}$
$a - 1$	$\left[\frac{(c - \gamma + 1)(c - \gamma + 2)}{(2c + 2)(2c + 3)} \right]^{1/2}$	$-\left[\frac{(c + \gamma + 1)(c - \gamma + 1)}{(c + 1)(2c + 3)} \right]^{1/2}$	$\left[\frac{(c + \gamma + 2)(c + \gamma + 1)}{(2c + 2)(2c + 3)} \right]^{1/2}$

$$\begin{aligned}
 C_{\alpha\alpha b\beta}^{c\gamma} &= (-1)^{a+b-c} C_{b\beta a\alpha}^{c\gamma} = (-1)^{a-\alpha} \sqrt{\frac{2c+1}{2b+1}} C_{\alpha\alpha c-\gamma}^{b-\beta} = (-1)^{a-\alpha} \sqrt{\frac{2c+1}{2b+1}} C_{c\gamma a-\alpha}^{b\beta} = \\
 &= (-1)^{b+\beta} \sqrt{\frac{2c+1}{2a+1}} C_{c-\gamma b\beta}^{a-\alpha} = (-1)^{b+\beta} \sqrt{\frac{2c+1}{2a+1}} C_{b-\beta c\gamma}^{a\alpha}
 \end{aligned}$$

$$C_{\alpha\alpha b\beta}^{c\gamma} = (-1)^{a+b-c} C_{a-\alpha b-\beta}^{c-\gamma}$$

$$\sum_{\alpha\beta\delta} C_{a\alpha}^{c\gamma} C_{b\beta}^{e\epsilon} C_{d\delta}^{d\delta} C_{a\alpha}^{f\varphi} = \kappa_1 \Pi_{cd} C_{c\gamma}^{e\epsilon} C_{f\varphi} \begin{Bmatrix} a & b & c \\ e & f & d \end{Bmatrix},$$

$$\sum_{\alpha\beta\delta} C_{b\beta}^{a\alpha} C_{c\gamma}^{d\delta} C_{b\beta}^{e\epsilon} C_{a\alpha}^{f\varphi} = \kappa_1 \frac{\Pi_{add}}{\Pi_e} C_{c\gamma}^{e\epsilon} C_{f\varphi} \begin{Bmatrix} a & b & c \\ e & f & d \end{Bmatrix},$$

$$\sum_{\sigma\beta\delta} C_{b\beta}^{c\gamma} C_{a\alpha}^{e\epsilon} C_{d\delta}^{d\delta} C_{a\alpha}^{f\varphi} = \kappa_2 \Pi_{cd} C_{c\gamma}^{e\epsilon} C_{f\varphi} \begin{Bmatrix} a & b & c \\ e & f & d \end{Bmatrix},$$

$$\sum_{\alpha\beta\delta} (-1)^{a-\alpha} C_{a\alpha}^{c\gamma} C_{b\beta}^{e\epsilon} C_{d\delta}^{d\delta} C_{d\delta}^{f\varphi} C_{a-\alpha}^{f\varphi} = \kappa_1 \Pi_{cf} C_{c\gamma}^{e\epsilon} C_{f\varphi} \begin{Bmatrix} a & b & c \\ e & f & d \end{Bmatrix},$$

$$\sum_{\alpha\beta\delta} (-1)^{b+\beta} C_{a\alpha}^{c\gamma} C_{b\beta}^{d\delta} C_{b-\beta}^{e\epsilon} C_{a\alpha}^{f\varphi} = \kappa_1 \frac{\Pi_{cdd}}{\Pi_e} C_{c\gamma}^{e\epsilon} C_{f\varphi} \begin{Bmatrix} a & b & c \\ e & f & d \end{Bmatrix},$$

$$\sum_{\alpha\beta\delta} (-1)^{a-\alpha} C_{b\beta}^{c\gamma} C_{a\alpha}^{e\epsilon} C_{b\beta}^{d\delta} C_{d\delta}^{f\varphi} C_{a-\alpha}^{f\varphi} = \kappa_2 \Pi_{cf} C_{c\gamma}^{e\epsilon} C_{f\varphi} \begin{Bmatrix} a & b & c \\ e & f & d \end{Bmatrix},$$

$$\sum_{\alpha\beta\delta} (-1)^{b+\beta} C_{b-\beta}^{a\alpha} C_{c\gamma}^{e\epsilon} C_{d\delta}^{d\delta} C_{a\alpha}^{f\varphi} = \kappa_1 \Pi_{ad} C_{c\gamma}^{e\epsilon} C_{f\varphi} \begin{Bmatrix} a & b & c \\ e & f & d \end{Bmatrix},$$

$$\sum_{\alpha\beta\delta} (-1)^{a-\alpha} C_{a\alpha}^{b\beta} C_{c-\gamma}^{e\epsilon} C_{d\delta}^{d\delta} C_{a\alpha}^{f\varphi} = \kappa_1 \Pi_{bd} C_{c\gamma}^{e\epsilon} C_{f\varphi} \begin{Bmatrix} a & b & c \\ e & f & d \end{Bmatrix},$$

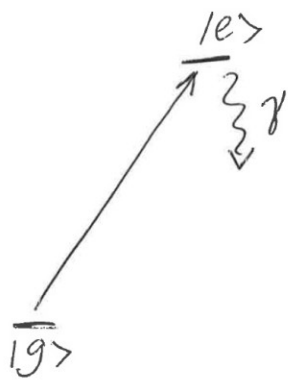
$$\kappa_1 = (-1)^{b+c+d+f},$$

$$\kappa_2 = (-1)^{a+b+e+f}$$

These expressions are easily derived from the sum of products of four CG symbols, that follows from the definition of the 6j-symbol. Multiply

both sides by $C_{c\gamma}^{e\epsilon} C_{f\varphi}$ and take a sum over γ and φ .

The resonant excitation



Schrödinger equation describing excitation from the ground state $|g\rangle$ to the optically excited state $|e\rangle$.

$$|\Psi(t)\rangle = a_g(t)|g\rangle + a_e(t)|e\rangle$$

$$i\dot{a}_g = -\left(\frac{\vec{d}_{eg}\vec{E}}{\hbar}\right)^* a_e$$

$$i\dot{a}_e = -(\Delta + i\gamma)a_e - \frac{\vec{d}_{eg}\vec{E}}{\hbar} a_g$$

Detuning $\Delta = \omega - \omega_{eg}$
 2γ is the decay rate (into non-observable states, formally speaking).

Without defining other quantum numbers, $|e\rangle = |F_e M_e\rangle$, $|g\rangle = |F_g M_g\rangle$

$$M_e = M_g + \mu, \quad \mu = 0, \pm 1$$

$$d_{eg} = \frac{C_{F_g M_g 1 \mu}^{F_e M_e}}{\sqrt{2F_e + 1}} \langle F_e || d || F_g \rangle$$

Assume that \vec{E} contains only the polarization component that drives the transition $|g\rangle \leftrightarrow |e\rangle$:

$$\begin{aligned} \vec{E} &= \vec{e}^{-\mu} E_{-\mu} e^{-i\omega t} + c.c. = \\ &= \vec{e}_{\mu} (-1)^{\mu} E_{-\mu} e^{-i\omega t} + c.c. \end{aligned}$$

$$\text{Intensity } I = 2c\epsilon_0 |E_{-\mu}|^2$$

Assumption: only one polarization component is present!

In the rotating wave approximation

$$i\dot{a}_g = (-1)^{\mu+1} \hbar^{-1} (\text{deg } E_{-\mu})^* a_e$$

$$i\dot{a}_e = -(\Delta + i\gamma)a_e + (-1)^{\mu+1} \hbar^{-1} \text{deg } E_{-\mu} a_g$$

If the e.m. field does not saturate the transition, i.e., if

$$\left| \frac{\text{deg } E_{-\mu}}{\hbar} \right| \ll \min(|\Delta|, \gamma)$$

$$\text{then } a_e \approx \frac{(-1)^{\mu+1}}{\hbar(\Delta + i\gamma)} \text{deg } E_{-\mu} a_g$$

Adiabatic elimination of the excited state

Energy shift and width of the ground state irradiated by resonant light

$$\dot{a}_g = (-i \Delta \omega_{\text{Stark}} - W) a_g$$

a. c. Stark shift

$$\Delta \omega_{\text{Stark}} \equiv \frac{\Delta E_{\text{Stark}}}{\hbar} = \frac{\Delta}{\Delta^2 + \gamma^2} \left| \frac{\text{deg } E - \mu}{\hbar} \right|^2$$

Optically induced width of $|g\rangle$ (imaginary correction to the energy, divided by \hbar):

$$W = \frac{\gamma}{\Delta^2 + \gamma^2} \left| \frac{\text{deg } E - \mu}{\hbar} \right|^2$$

$$|a_g(t)|^2 = |a_g(0)|^2 \exp(-2Wt)$$

$2W =$ decay rate of the state $|g\rangle =$
 $=$ photon scattering rate

Absorption cross-section, by definition,

$$\sigma = \frac{\text{Scattered energy}}{\text{Intensity}} = \frac{2W\hbar\omega}{I}$$

$$\sigma = \frac{1}{1 + (\Delta/\gamma)^2} \sigma_0,$$

where the cross-section exactly at resonance ($\Delta = 0$) is

$$\begin{aligned} \sigma_0 &= 2\hbar\omega \left| \frac{\text{deg } E - \mu}{\hbar} \right|^2 / (\gamma \cdot 2c\epsilon_0 |E_{-\mu}|^2) = \\ &= \frac{|\text{deg}|^2 \omega}{\hbar c \epsilon_0 \gamma} \approx \frac{|\text{deg}|^2 \omega_{\text{eg}}}{\hbar c \epsilon_0 \gamma} \end{aligned}$$

Partial width (corresponding to the radiative decay $|e\rangle \rightarrow |g\rangle$):

$$\gamma_{\text{eg}} = \frac{|\text{deg}|^2}{6\pi\epsilon_0\hbar} \left(\frac{\omega_{\text{eg}}}{c} \right)^3$$

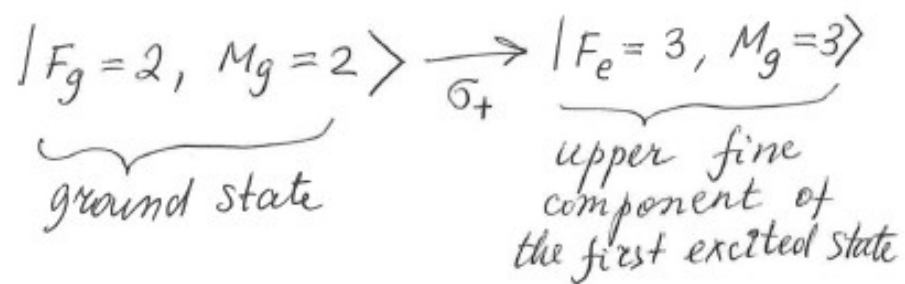
$\gamma =$ Sum of all partial width
 (sum over all final states of radiative decay)

$$\sigma_0 = \frac{3}{2\pi} \lambda^2 \frac{\gamma_{\text{eg}}}{\gamma},$$

where $\lambda = \frac{2\pi c}{\omega_{\text{eg}}} =$ wavelength of resonant radiation

The maximum possible value of $\sigma = \frac{3}{2\pi} \lambda^2$ is obtained for alkali atoms on a cycling transition in D_2 -line, where the optically excited state has only one decay channel.

For 87Rb :



In a case of D_1 - or D_2 -line (when $|e\rangle$ is the first electronic excited state, that decays to sublevels of the ground state only)

$$\frac{\gamma_{eg}}{\gamma} = |C_{F_g M_g 1 \mu}^{F_e M_e}|^2 (2L_e + 1) \times \\ \times (2J_e + 1)(2J_g + 1)(2F_g + 1) \times \\ \times \left\{ \begin{matrix} J_e & I & F_e \\ F_g & 1 & J_g \end{matrix} \right\}^2 \left\{ \begin{matrix} L_e & S & J_e \\ J_g & 1 & L_g \end{matrix} \right\}^2$$

Here we recalled that, after all summations

$$\gamma = \frac{|\langle n_g L_g || \hat{d} || n_e L_e \rangle|^2}{6\pi\epsilon_0 \hbar (2L_e + 1)} \left(\frac{\omega_{eg}}{c}\right)^3$$

Stark shift

a. c. Stark shift: single resonant level

$$\omega_{\text{Stark}} = \frac{\Delta}{\gamma} W = \frac{\Delta}{\gamma} \frac{\sigma I}{2\hbar\omega}$$

$$\sigma = \frac{1}{1 + (\Delta/\gamma)^2} \sigma_0 = \frac{1}{1 + (\Delta/\gamma)^2} \frac{3\lambda^2}{2\pi} \frac{\gamma_{\text{eg}}}{\gamma} =$$

$$= \frac{1}{1 + (\Delta/\gamma)^2} \sigma_{\text{max}} \frac{\gamma_{\text{eg}}}{\gamma}$$

In the practically important case $|\Delta| \gg \gamma$ (but we still consider Δ that is small compared to the hyperfine splitting of the excited state)

We have

$$\omega_{\text{Stark}} \approx \frac{\gamma}{\Delta} \frac{\gamma_{\text{eg}}}{\gamma} \frac{\sigma_{\text{max}} I}{2\hbar\omega}$$

All the state/polarization dependence is in

$$\frac{\gamma_{\text{eg}}}{\gamma} = \left| C_{F_g M_g 1 \mu}^{F_e M_e} \right|^2 (2L_e + 1)(2J_e + 1)(2J_g + 1)(2F_g + 1) \times$$

$$\times \left\{ \begin{matrix} J_e & I & F_e \\ F_g & 1 & J_g \end{matrix} \right\}^2 \left\{ \begin{matrix} L_e & S & J_e \\ J_g & 1 & L_g \end{matrix} \right\}^2$$

We see from the analytic expressions for $C_{F_g M_g 1 \mu}^{F_e M_e}$, that the squares of these C.-G.-coefficients depend on M_g quadratically:

$$\left| C_{F_g M_g 1 \mu}^{F_e M_e} \right|^2 = \alpha_0 + \alpha_1 M_g + \alpha_2 M_g^2$$

What is the (mathematical) physics behind?

$$\omega_{\text{Stark}} = \left(C_{F_g M_g 1 \mu}^{F_e M_e} \right)^2 \tilde{\omega}_0$$

$\tilde{\omega}_0 \propto I$ = what remains after factorizing out $\left(C_{F_g M_g 1 \mu}^{F_e M_e} \right)^2$.

Calculating ω_{Stark} for $|F_g M_g\rangle$ sublevel of the ground state and the known polarization μ , we can formally add a sum:

$$\omega_{\text{Stark}} = \sum_{M_e} \left(C_{F_g M_g 1 \mu}^{F_e M_e} \right)^2 \tilde{\omega}_0,$$

where only the term with $M_e = M_g + \mu$ contributes

$$C_{F_g M_g 1 \mu}^{F_e M_e} = (-1)^{1+\mu} \sqrt{\frac{2F_e+1}{2F_g+1}} C_{F_g M_g 1-\mu}^{F_e M_e} = (-1)^{F_e-F_g+\mu} \sqrt{\frac{2F_e+1}{2F_g+1}} C_{F_e M_e 1-\mu}^{F_g M_g}$$

$$\omega_{Stark} = \sum_{M_e} (-1)^{F_e-F_g+\mu} \sqrt{\frac{2F_e+1}{2F_g+1}} \times C_{F_g M_g 1-\mu}^{F_e M_e} C_{F_g M_g 1 \mu}^{F_e M_e} \tilde{\omega}_0$$

Consider the direction vector

$$\vec{n} = \sin\theta \cos\varphi \vec{e}_x + \sin\theta \sin\varphi \vec{e}_y + \cos\theta \vec{e}_z$$

and its cyclic components as an irreducible tensor of rank 1

Analogously to matrix elements of the dipole moment operator (actually, for a single outer electron $\vec{d} = -e r \vec{n}$), we obtain

$$\langle F_e M_e | n_\mu | F_g M_g \rangle = (-1)^{L_e+S+J_e+J_g+I+F_g} \times C_{F_g M_g 1 \mu}^{F_e M_e} \sqrt{(2J_e+1)(2J_g+1)(2F_g+1)} \times \begin{Bmatrix} J_g & I & F_g \\ F_e & 1 & J_e \end{Bmatrix} \begin{Bmatrix} L_g & S & J_g \\ J_e & 1 & L_e \end{Bmatrix} \langle L_e || n || L_g \rangle$$

It is known that

$$\langle L_e || n || L_g \rangle = \sqrt{2L_g+1} C_{L_g 0 1 0}^{L_e 0}$$

Recall also

$$\begin{aligned} & \begin{Bmatrix} J_g & I & F_g \\ F_e & 1 & J_e \end{Bmatrix} = \begin{Bmatrix} J_g & 1 & J_e \\ F_e & I & F_g \end{Bmatrix} = \\ & = \begin{Bmatrix} F_e & I & J_e \\ J_g & 1 & F_g \end{Bmatrix} = \begin{Bmatrix} F_e & 1 & F_g \\ J_g & I & J_e \end{Bmatrix} \end{aligned}$$

and analogous relations for

$$\begin{Bmatrix} L_g & S & J_g \\ J_e & 1 & L_e \end{Bmatrix}$$

Recall the angular-momentum dependence of $\tilde{\omega}_0 = \frac{\gamma_{0g}}{\gamma} \tilde{\omega}_{sc}$,

where $\tilde{\omega}_{sc}$ does not depend on F_e, F_g etc (scalar):

$$\omega_{Stark} = (-1)^\mu \sum_{M_e} \langle F_g M_g | n_{-\mu} | F_e M_e \rangle \langle F_e M_e | n_{\mu} | F_g M_g \rangle$$

$$\times \frac{(2L_e+1)(-1)^{L_e-L_g} \tilde{\omega}_{sc}}{\sqrt{(2L_e+1)(2L_g+1)} C_{L_g 0 1 0}^{L_e 0} C_{L_e 0 1 0}^{L_g 0}}$$

$$C_{L_g 0 1 0}^{L_e 0} = (-1)^{L_e-L_g} \sqrt{\frac{2L_e+1}{2L_g+1}} C_{L_e 0 1 0}^{L_g 0}$$

$$\omega_{Stark} = (-1)^\mu \sum_{M_e} \langle F_g M_g | n_{-\mu} | F_e M_e \rangle \langle F_e M_e | n_{\mu} | F_g M_g \rangle$$

$$\times \tilde{\omega}_{sc} / |C_{L_e 0 1 0}^{L_g 0}|^2$$

$\sum_{M_e=-F_e}^{F_e} |F_e M_e \rangle \langle F_e M_e|$ is a scalar (IR tensor of rank 0).

$$\omega_{Stark} = (-1)^\mu \langle F_g M_g | P_{-\mu} n_{\mu} | F_g M_g \rangle \frac{\tilde{\omega}_{sc}}{|C_{L_e 0 1 0}^{L_g 0}|^2}$$

$$P_{-\mu} = n_{-\mu} \sum_{M_e=-F_e}^{F_e} |F_e M_e \rangle \langle F_e M_e|$$

$$P_{\mu'} n_{\mu} = \sum_{k=0}^2 C_{1\mu' 1\mu}^{k\mu'+\mu} \{P \otimes n\}_{k\mu'+\mu}$$

$$\{P \otimes n\}_{k\mu'+\mu} = \sum_{\mu_1 \mu_2} C_{1\mu_1 1\mu_2}^{k\mu'+\mu} P_{\mu_1} n_{\mu_2}$$

Therefore

$$\omega_{Stark} = \sum_{k=0}^2 (-1)^{F_e-F_g+\mu} C_{1-\mu 1\mu}^{k0} \sqrt{\frac{2F_e+1}{2F_g+1}}$$

$$\times \sum_{M_e M_1 M_2} C_{1\mu_1 1\mu_2}^{k0} C_{F_e M_e 1 M_1}^{F_g M_g} C_{F_g M_g 1 M_2}^{F_e M_e} \tilde{\omega}_0$$

$$= \sum_{k=0}^2 (-1)^{F_e+F_g+k+\mu} C_{F_g M_g k 0}^{F_g M_g} C_{1-\mu 1\mu}^{k0} \times$$

$$\times \sqrt{\frac{2k+1}{2F_g+1}} (2F_e+1) \left\{ \begin{matrix} 1 & 1 & k \\ F_g & F_g & F_e \end{matrix} \right\} \tilde{\omega}_0$$

$$\left\{ \begin{matrix} 1 & 1 & k \\ F_g & F_g & F_e \end{matrix} \right\} = \left\{ \begin{matrix} F_g & F_g & k \\ 1 & 1 & F_e \end{matrix} \right\}$$

F_g, F_g, k must obey the triangle rule.

$k=0$ component is always present

$k=1$; for $F_g \geq \frac{1}{2}$

$k=2$; for $F_g \geq 1$

$$C_{1010}^{10} = 0$$

Hence, $k=1$ component is present for $\mu = \pm 1$ only.

$k=0$ gives scalar polarizability (no dependence on M_g)

$k=1$ gives vector polarizability $\propto M_g$

$k=2$ gives tensor polarizability $\propto 3M_g^2 - F_g(F_g+1)$

Consider in more detail the case of $k=0$

$$C_{1-\mu 1 \mu}^{00} = \frac{(-1)^{1-\mu}}{\sqrt{3}}, \quad C_{F_g M_g F_g M_g 00}^{F_g M_g} = 1$$

$$\left\{ \begin{matrix} 1 & 1 & 0 \\ F_g & F_g & F_e \end{matrix} \right\} = \frac{(-1)^{1+F_e+F_g}}{\sqrt{3}(2F_g+1)}$$

$F_e + F_g$ is integer, therefore

$$(-1)^{F_e+F_g+\mu} C_{F_g M_g F_g M_g 00}^{F_g M_g} C_{1-\mu 1 \mu}^{00}$$

$$\times \sqrt{\frac{1}{2F_g+1}} (2F_e+1) \left\{ \begin{matrix} 1 & 1 & 0 \\ F_g & F_g & F_e \end{matrix} \right\} \tilde{\omega}_0 =$$

$$= \frac{2F_e+1}{3(2F_g+1)} \tilde{\omega}_0$$

has the same sign as $\tilde{\omega}_0$, i.e., the same sign as Δ .

A general case

Polarizabilities (\mathbf{u} the e.m. field polarization unit vector):

- Scalar ($k=0$) const
- Vector ($k=1$) $\propto [\mathbf{u}^* \times \mathbf{u}] \hat{\mathbf{J}}$
- Tensor ($k=2$) $\propto \left[(\mathbf{u} \hat{\mathbf{J}})(\mathbf{u}^* \hat{\mathbf{J}}) + (\mathbf{u}^* \hat{\mathbf{J}})(\mathbf{u} \hat{\mathbf{J}}) - \frac{2}{3} \hat{\mathbf{J}}^2 \right]$

See, e.g., Fam Le Kien,
Scheeweiß & Rauschenbeutel,
PRA **88**, 033840 (2013)

Prefactors?

hyper
 If $|\Delta|$ is much larger than the fine splitting of the upper state, this detuning may be considered as (approximately) equal for all F_e 's for a given fine-structure level. Then we can sum up over F_e .

$$\omega_{\text{Stark}} = \sum_{F_e M_e} (-1)^M \langle F_g M_g | \hat{n}_{-\mu} | F_e M_e \rangle \langle F_e M_e | \hat{n}_{\mu} | F_g M_g \rangle \times \frac{\tilde{\omega}_{\text{sc}}}{|C_{L_{e0}^{Lg0}}|_{10}^2}$$

$$|F_e M_e\rangle = \sum_{M_J M_I} C_{J_e M_{J_e} I M_I}^{F_e M_e} |J_e M_{J_e}\rangle |I M_I\rangle$$

$$|F_g M_g\rangle = \sum_{M_J M_I} C_{J_g M_{J_g} I M_I}^{F_g M_g} |J_g M_{J_g}\rangle |I M_I\rangle$$

\hat{n}_{μ} does not act on nuclear-spin degrees of freedom.

Omitting the details,

$$\omega_{\text{Stark}} = \sum_{k=0}^2 \omega_{\text{Stark}}^{(k)}, \quad \text{where}$$

$$\omega_{\text{Stark}}^{(k)} \propto C_{F_g M_g k 0}^{F_g M_g} \begin{Bmatrix} J_g & J_g & k \\ F_g & F_g & I \end{Bmatrix} \begin{Bmatrix} 1 & 1 & k \\ J_g & J_g & J_e \end{Bmatrix}$$

This means that not only F_g, F_e, k , but also J_g, J_e, k must satisfy the triangle rule. This means that for alkali atoms ($J_g = 1/2$) and detunings much larger than the hyperfine splitting of the 1st excited state ($|\Delta| \gg 2\pi \cdot 1 \text{ GHz}$) only $k=0$ and $k=1$ give non-zero shift (scalar and vector polarizability)

If the absolute value of the detuning is even much larger than the fine splitting of the excited state ($|\Delta| \gg 2\pi \cdot 10 \text{ THz}$), then

$$\omega_{\text{Stark}}^{(k)} \propto \begin{Bmatrix} 1 & 1 & k \\ L_g & L_g & L_e \end{Bmatrix} = \begin{Bmatrix} L_g & L_g & k \\ 1 & 1 & L_e \end{Bmatrix}$$

This means that L_g, L_g, k must satisfy the triangle rule. For alkali atoms ($L_g = 0$) in this regime the Stark shift is characterized by scalar polarizability ($k = 0$) only.

In particular, the d.c. Stark shift (in a static electric field, $\omega = 0$) is always scalar ($k = 0$).

However, the static polarizability, unlike the near-resonant case, is determined by the size of the atom.