EXA-2017

E2 electric quadrupole spectrum of H2+

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Presenting results obtained with

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Precision spectroscopy of molecular hydrogen ions (MHI)

Possible types of transitions:

- E1 electric dipole
- E2 electric quadrupole
- Forbidden E1
- 2-photon electric
- ...

Precision spectroscopy of MHI

Theoretical calculation of E1, E2, forbidden E1 and 2-photon spectra of H_2^+ and HD^+, incl. Zeeman, AC-DC Stark and light shift, etc.

QED effects of high order taken into account.

Determining the electron-to-proton(deuteron) mass ratio; other fundamental constants

Transitions with lowest response to external fields selected.

Designing molecular clocks

New physics: 5th force, time variability of m_e/m_p…

Spectroscopy of heteronuclear ions

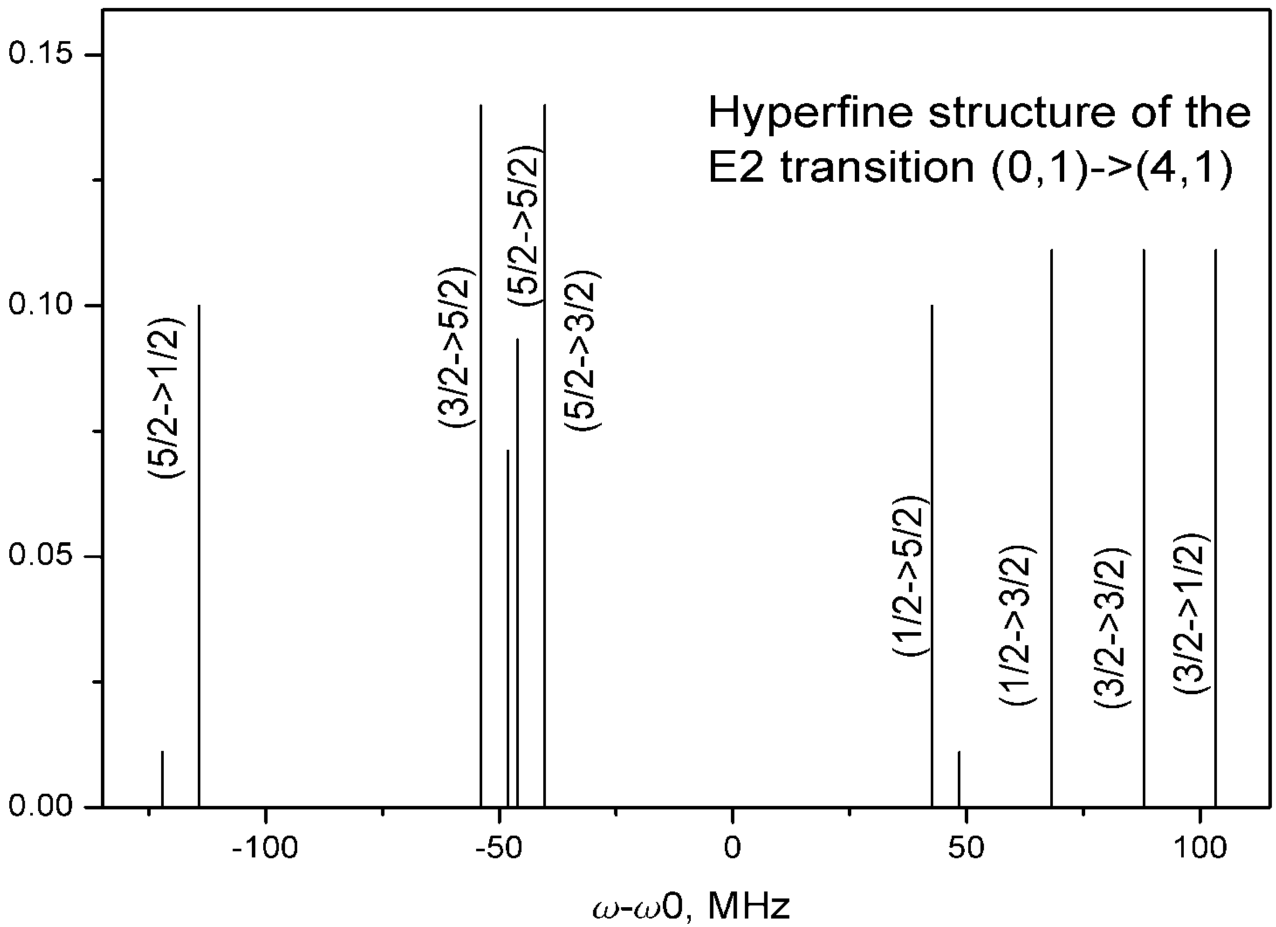
Transitions in HD^+:

- E1 (electric dipole)
- 2-photon electric
- E2 electric quadrupole

Already evaluated (Korobov, Karr, earlier…):

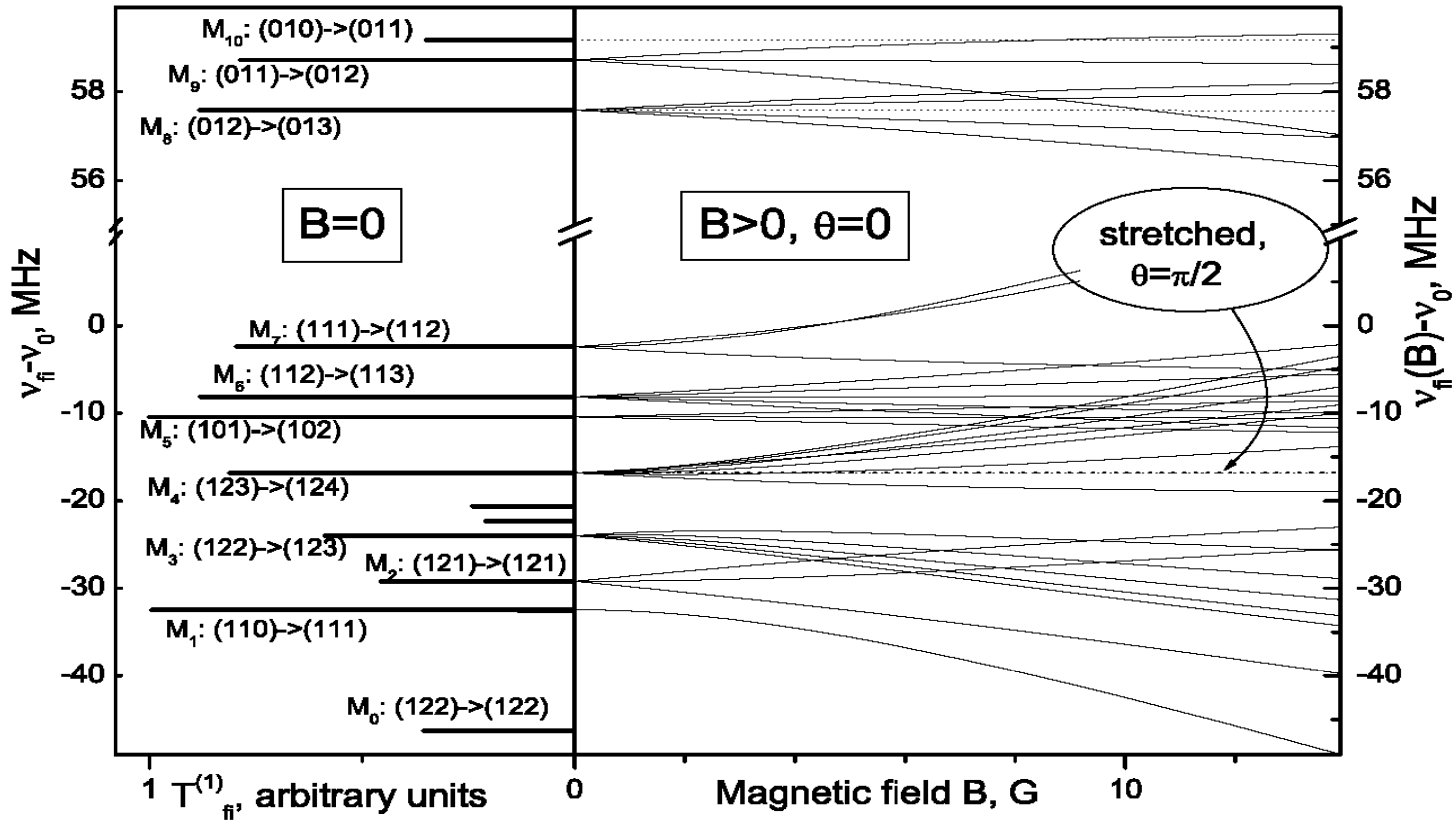
- QED/relativistic corrections at ppt level,
- HFS at ppm level
- Systematic effects (Zeeman, AC/DC Stark, BBR)

HFS of E2 spectra in HD^+



Precision spectroscopy of HD^+

Selection of HF lines for molecular clocks



Precision spectroscopy of H_2^+

Possible transitions:

- ~~E1 (electric dipole)~~
  → **Forbidden E1**
- 2-photon electric
- E2 electric quadrupole
- ...
- ...

Forbidden E1-transitions in H_2^+

In molecules with identical nuclei

$$p.(-1)^{L+I+m} = 1$$

L: orbital momentum

I: total nuclear spin

p: exchange of nuclei parity. $\boxed{p=1, m=0 \text{ in LO appr.}}$

Dipole transitions: forbidden in non-relativistic approximation, but allowed due to parity breaking terms in the spin Hamiltonian.

Forbidden E1-transitions in H_2^+

First-order corrections to the wave-function of the final state

$$|(pvL)IFJJ_z\rangle^{(1)} = \sum |(v'L'p')I'F'JJ_z\rangle \frac{\langle (v'L'p')I'F'JJ_z|U^{spin}|(pvL)IFJJ_z\rangle}{E-E'}$$

are coupled by the electric dipole moment to the unperturbed w. f. of the initial state!

Transition intensity suppressed by α^2

Calculation of forbidden E1 spectra: in progress

Two-photon transitions in $H2+$

- Stectrum calculated in earlier works by J.-Ph. Karr, V.I.Korobov, etc.
- Evaluated the main systematic effects (Zeeman, Stark, BBR,…)
- Considered the cases of linear and circular laser light polarization

Precision spectroscopy of H_2^+

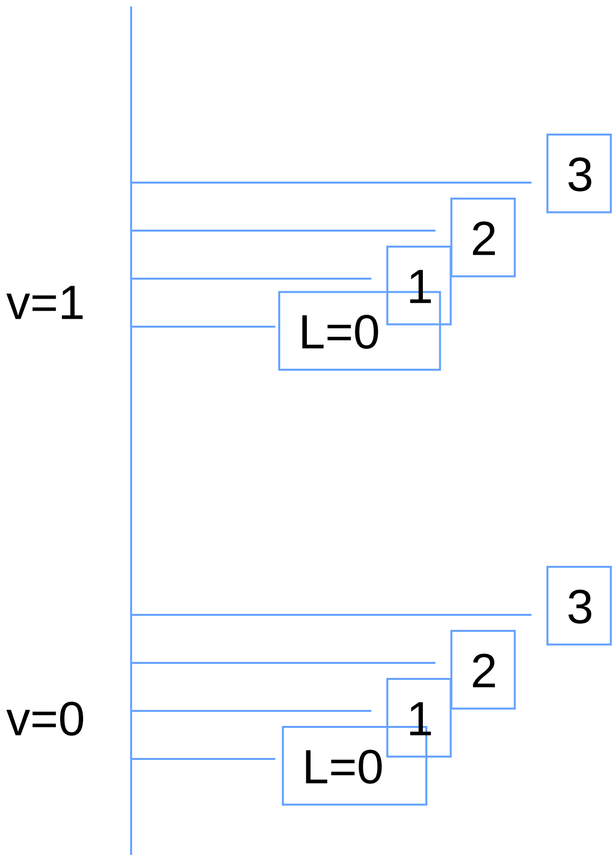
Our current interest:

- ...
- $\boxed{\textbf{E2 electric quadrupole}}$
    - *Transition frequencies*
    - *Transition Intensity*

A paper in preparation

(with P.Danev, V.Korobov, S.Schiller)

H_2^+ energy levels

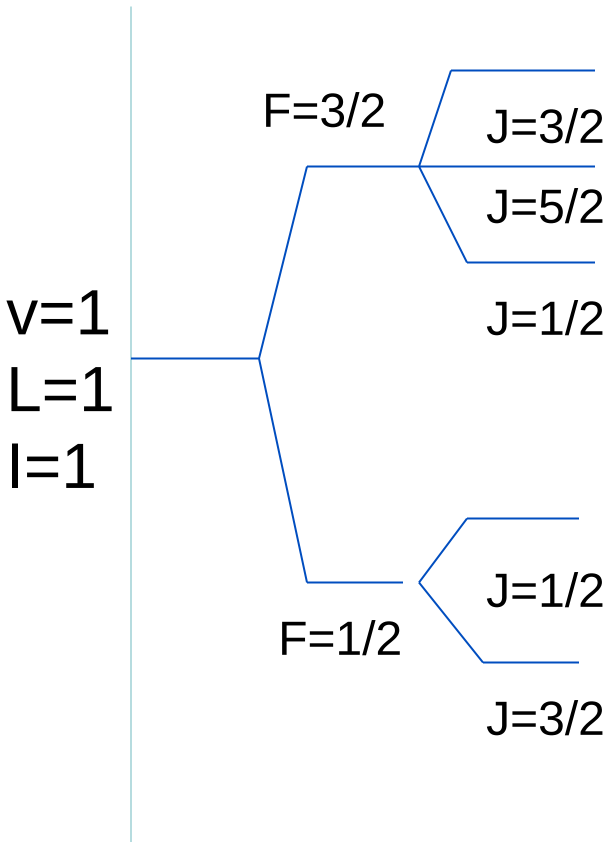


Non-relativistic picture

$$H^{nr} = \sum_i \frac{P_i^2}{2m_i} + \sum_{i<j} \frac{Z_i Z_j}{|r_i - r_j|}$$

Accuracy of the non-relativistic values:

Leading order QED & HFS

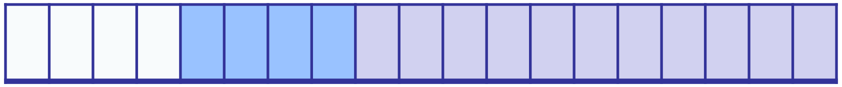


Breit interaction, 1st order

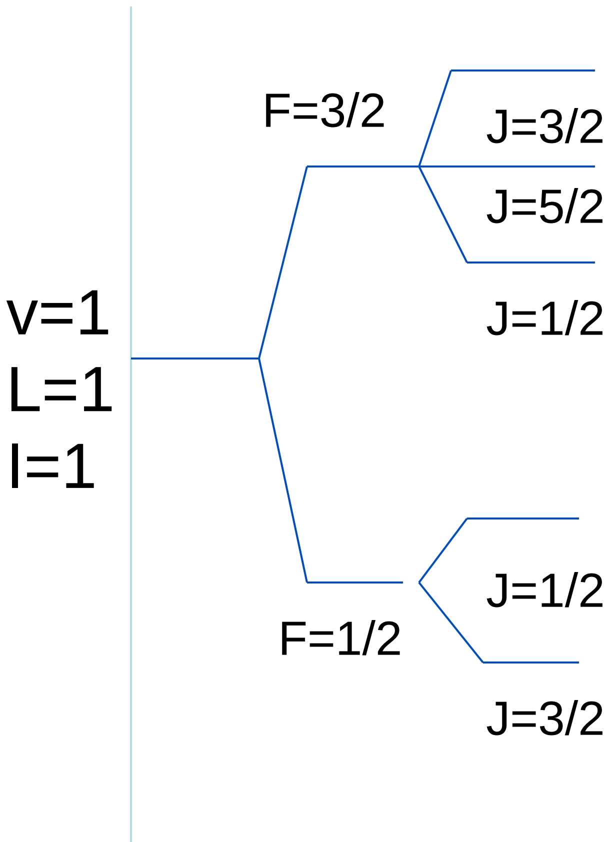
$\mathbf{S}_{p1}+\mathbf{S}_{p2}=\mathbf{I}$, $\mathbf{I}+\mathbf{S}_{e}=\mathbf{F}$, $\mathbf{F}+\mathbf{L}=\mathbf{J}$

$$H = H^{nr} + U^{spin} + U^{rel}$$

Breit contributions in 1st order of P.T.:



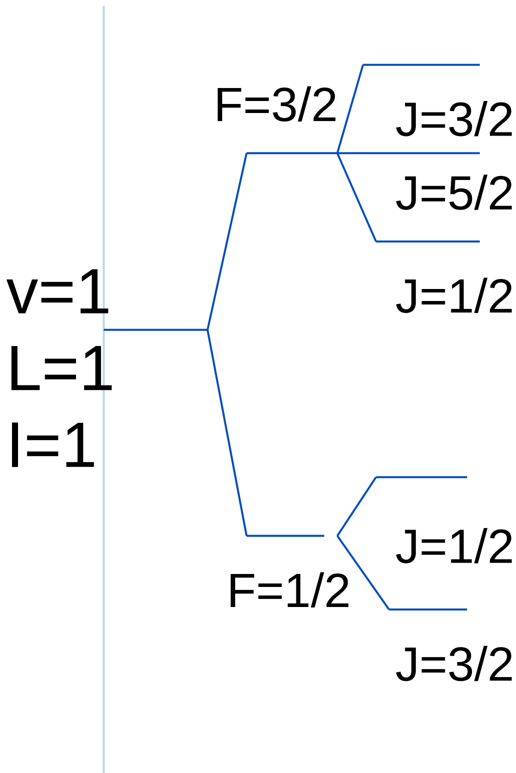
Higher order QED & HFS



Breit interaction, 2nd order, higher order QED terms and relativistic corrections

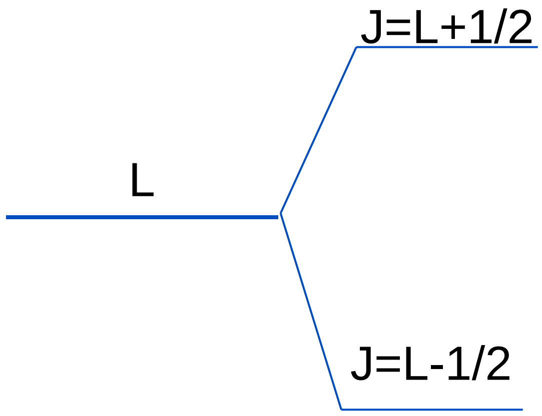
Various QED and relativistic contributions

Hyperfine structure for odd L



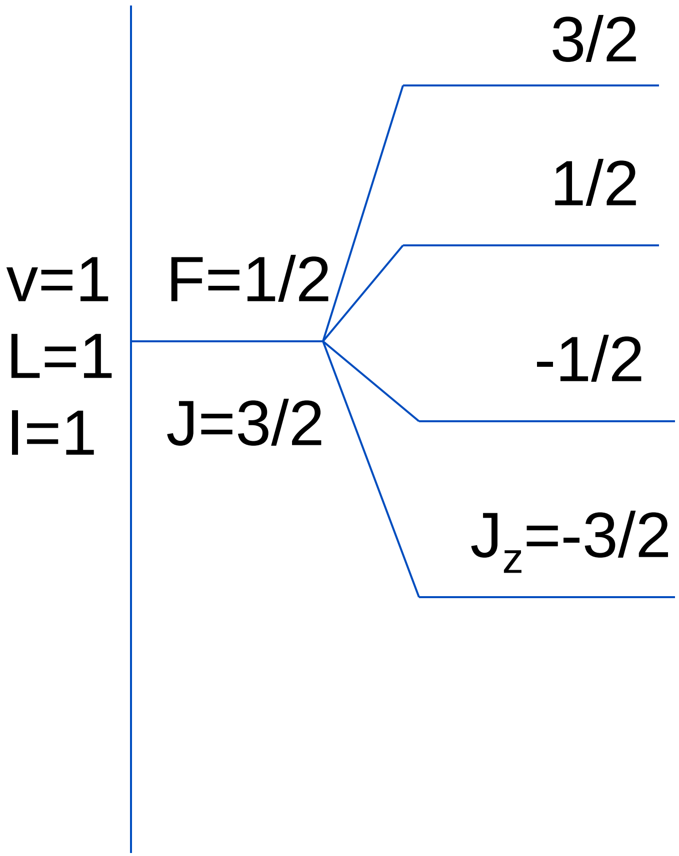
		E	E		φ	E		φ	E
v L	$J=$	$L-3/2$	$L-1/2$			$L+1/2$			$L+3/2$
	$F=$	$3/2$	$1/2$	$3/2$		$1/2$	$3/2$		$3/2$
0 1			-910.6980	385.3687	-0.038903	-930.3732	481.9234	-0.0156	474.0763
1 1			-887.1909	377.9657	-0.037356	-905.7253	468.4956	-0.0151	461.2282
2 1			-865.4856	371.2588	-0.035781	-882.9269	456.0493	-0.0145	449.3273
8 1			-767.8240	344.3925	-0.025481	-779.3412	398.8163	-0.0107	394.8271
0 3		341.5241	-894.6020	423.6046	-0.061855	-941.0438	489.4960	-0.0421	507.2270
1 3		336.8955	-871.9908	413.6522	-0.059480	-915.6828	475.5481	-0.0407	492.3526
2 3		332.8336	-851.1450	404.5273	-0.057050	-892.2046	462.6063	-0.0392	478.5158
3 3		329.3264	-831.9595	396.1856	-0.054560	-870.4878	450.6022	-0.0376	465.6422
8 3		320.0235	-758.1833	365.1210	-0.040899	-785.0303	402.7612	-0.0288	413.6433

Hyperfine structure for even L



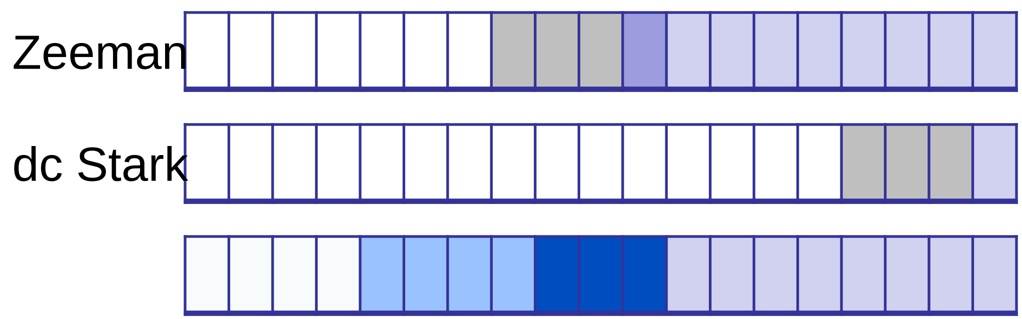
v L	$J=L-1/2$	$J=L+1/2$
0 2	-63.2438	42.1625
1 2	-59.3574	39.5716
2 2	-55.6487	37.0992
3 2	-52.0943	34.7295
4 2	-48.6718	32.4479
5 2	-45.3600	30.2400
0 4	-103.2355	82.5884
1 4	-96.8707	77.4966
2 4	-90.7937	72.6350
3 4	-84.9660	67.9728
4 4	-79.3509	63.4807

External fields effects



$$H = H^{nr} + U^{spin} + U^{rel}$$
$$+ U^{Zee}(B) + U^{St}(E)$$
$$+ U^{Q}(\nabla E) + \ldots$$

For typical external fields:
B~1G, E=200 V/m



E2-transition probability (Nrel)

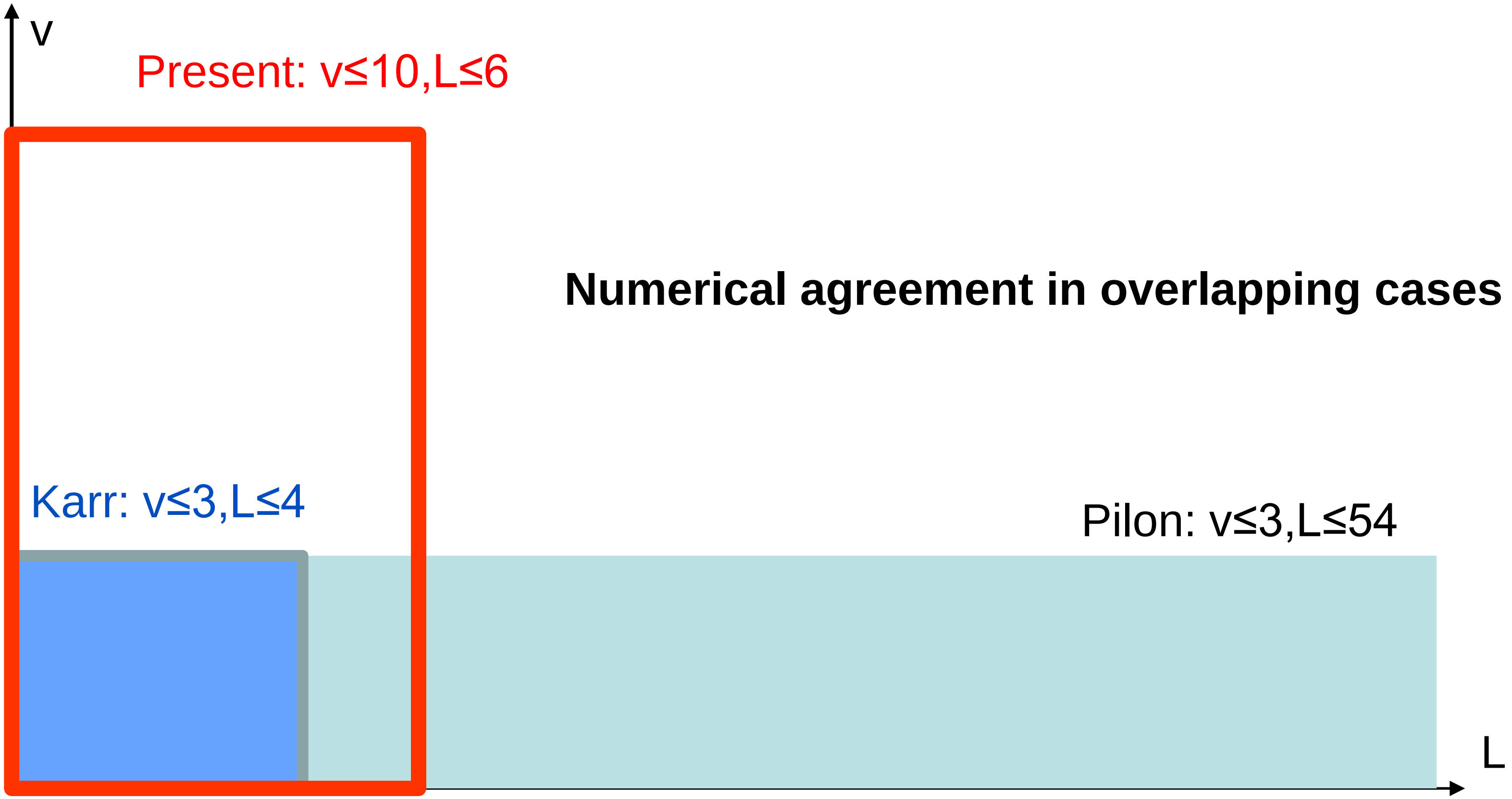
$$\mathcal{P}_{vLL\to v'L'L'_z}(t)$$
$$= 2\pi\, t\, \delta(\omega_{fi}-\omega)\, \frac{\omega_{fi}^2}{4\hbar^2(2L'+1)} \boxed{\langle v'L'||\tilde{Q}||vL\rangle^2} \left(C^{L'L'_z}_{LL_z,2q}\right)^2 \left|\tilde{T}^q\right|^2,$$

$$T = (\mathbf{A}\otimes\mathbf{k})^{(2)},\;\; \tilde{T}^q = \sum_{q_1 q_2} C1q_1,1q_2{}^{2q}\, \tilde{A}_0^{q_1}\, \tilde{k}^{q_2}, \quad q = L'_z - L_z,$$

Nontrivial calculation: <u>the matrix element</u>!

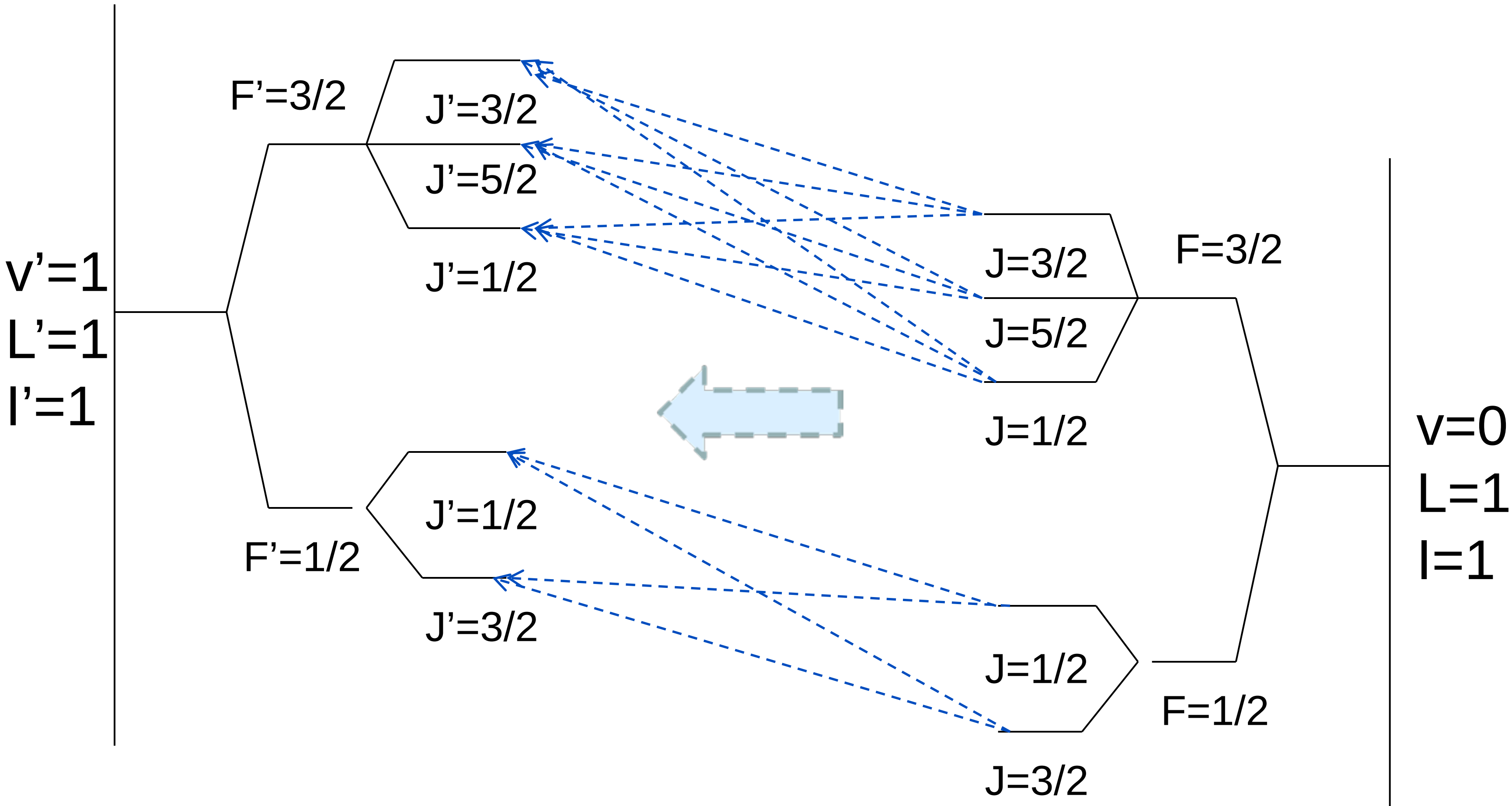
Preceding calculations: Moss *et al*., Pilon & Baye, Karr, Korobov *et al*.

Comparison with earlier works



Numerical agreement in overlapping cases

Hyperfine structure of E2 spectra



$$\omega_{f\leftarrow i} = (E_{v'L'I'F'J'} - E_{vLIFJ})/\hbar$$

E2-transition probability with HFS

$$\mathcal{P}_{if}(t) = t\,\frac{\pi}{2\hbar}\delta(E_{v'L'} - E_{vL})$$
$$\times\omega^2_{v'L',vL}\,\langle v'L'\|\tilde{Q}\|vL\rangle^2$$
$$\times(2J+1)\left(\sum_{IF}(-1)^{J+L+F}\beta^{v'L'N'J'}_{IF}\,\beta^{vLNJ}_{IF}\begin{Bmatrix} J' & 2 & J \\ L & F & L' \end{Bmatrix}\right)^2$$
$$\times\left(C^{J'J'_z}_{JJ_z,2q}\right)^2\,|\tilde{T}^q|^2,\quad q = J'_z - J_z$$

$$\beta^{vLNJ}_{IF}:\quad N \to F',\ \beta^{vLNJ}_{IF} \to \beta^J_{F'F} = \begin{Bmatrix} \cos\varphi & \sin\varphi \\ -\sin\varphi & \cos\varphi \end{Bmatrix}$$

$$T = (\mathbf{A}\otimes\mathbf{k})^{(2)},\ \tilde{T}^q = \sum_{q_1q_2} C1q_1,1q_2{}^{2q}\,\tilde{A}^{q_1}_0\,\tilde{k}^{q_2},\quad q = L'_z - L_z,$$

1. Constant factor

constant

$$
\begin{aligned}
\mathcal{P}_{if}(t) &= \boxed{t\,\frac{\pi}{2\hbar}\delta(E_{v'L'}-E_{vL})} \\
&\times \omega^2_{v'L',vL}\,\langle v'L'||\tilde{Q}||vL\rangle^2 \\
&\times (2J+1)\left(\sum_{IF}(-1)^{J+L+F}\beta^{v'L'N'J'}_{IF}\,\beta^{vLNJ}_{IF}\begin{Bmatrix} J' & 2 & J \\ L & F & L' \end{Bmatrix}\right)^2 \\
&\times \left(C^{J'J'_z}_{JJ_z,2q}\right)^2\,|\tilde{T}^q|^2, \quad q = J'_z - J_z
\end{aligned}
$$

Difference of the **Coulomb** energies

2. Nonrelativistic factor

constant

nonrelativistic

$$\mathcal{P}_{if}(t) = \boxed{t\,\frac{\pi}{2\hbar}\delta(E_{v'L'} - E_{vL})}$$
$$\times\boxed{\omega^2_{v'L',vL}\,\langle v'L'||\tilde{Q}||vL\rangle^2}$$
$$\times(2J+1)\left(\sum_{IF}(-1)^{J+L+F}\beta^{v'L'N'J'}_{IF}\beta^{vLNJ}_{IF}\begin{Bmatrix} J' & 2 & J \\ L & F & L' \end{Bmatrix}\right)^2$$
$$\times\left(C^{J'J'_z}_{JJ_z,2q}\right)^2\,|\tilde{T}^q|^2, \quad q = J'_z - J_z$$

Matrix elements with the non-relativistic wave functions

3. Hyperfine factor

constant

nonrelativistic

Hyperfine structure

$$
\begin{aligned}
\mathcal{P}_{if}(t) = & \boxed{t\,\frac{\pi}{2\hbar}\delta(E_{v'L'} - E_{vL})} \\
& \times \boxed{\omega^2_{v'L',vL}\,\langle v'L'\|\tilde{Q}\|vL\rangle^2} \\
& \times \boxed{(2J+1)\left(\sum_{IF}(-1)^{J+L+F}\beta^{v'L'N'J'}_{IF}\beta^{vLNJ}_{IF}\begin{Bmatrix} J' & 2 & J \\ L & F & L' \end{Bmatrix}\right)^2} \\
& \times \left(C^{J'J'_z}_{JJ_z,2q}\right)^2 |\tilde{T}^q|^2, \quad q = J'_z - J_z
\end{aligned}
$$

Sum rule: if HF interactions are switched off, nonrelativistic ntensities are reproduces!

4. Laser polarization factor

constant

nonrelativistic

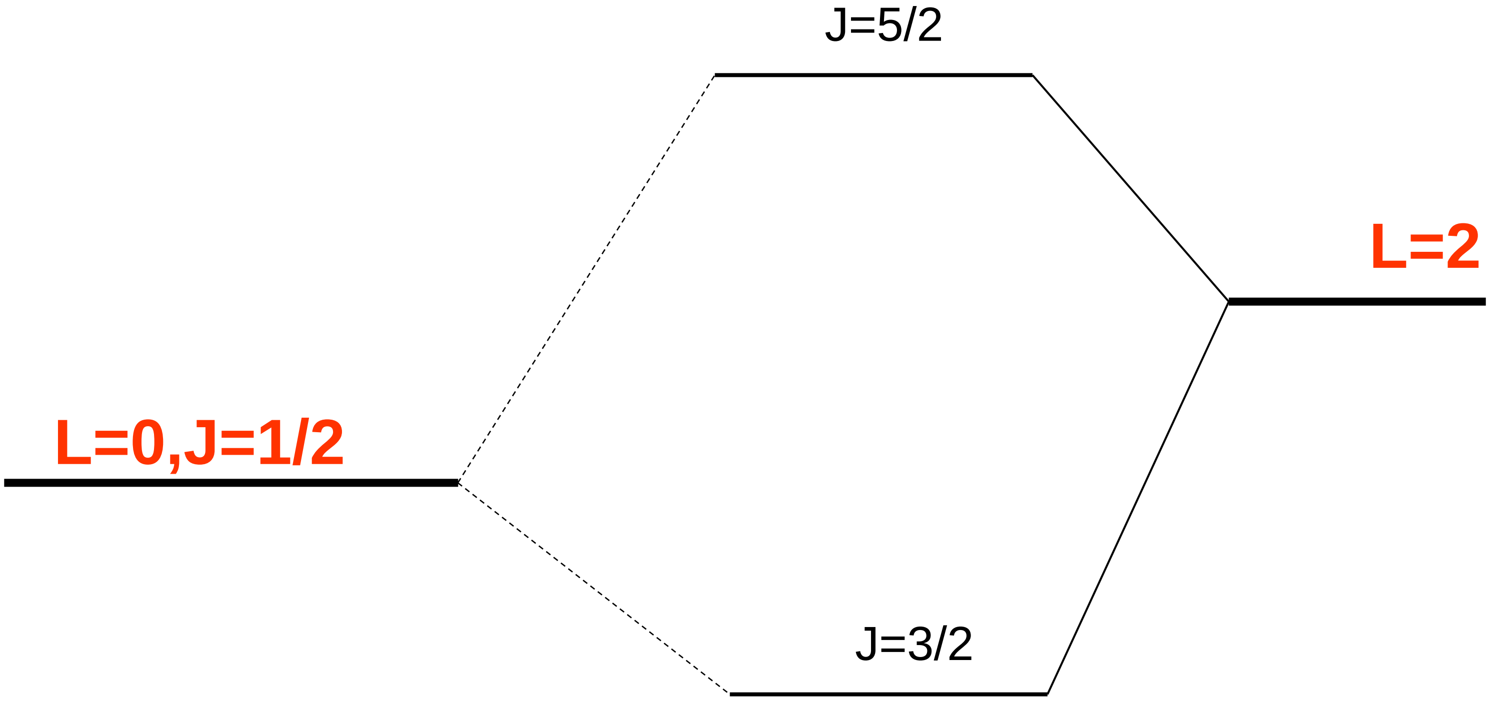
Hyperfine structure

polarization

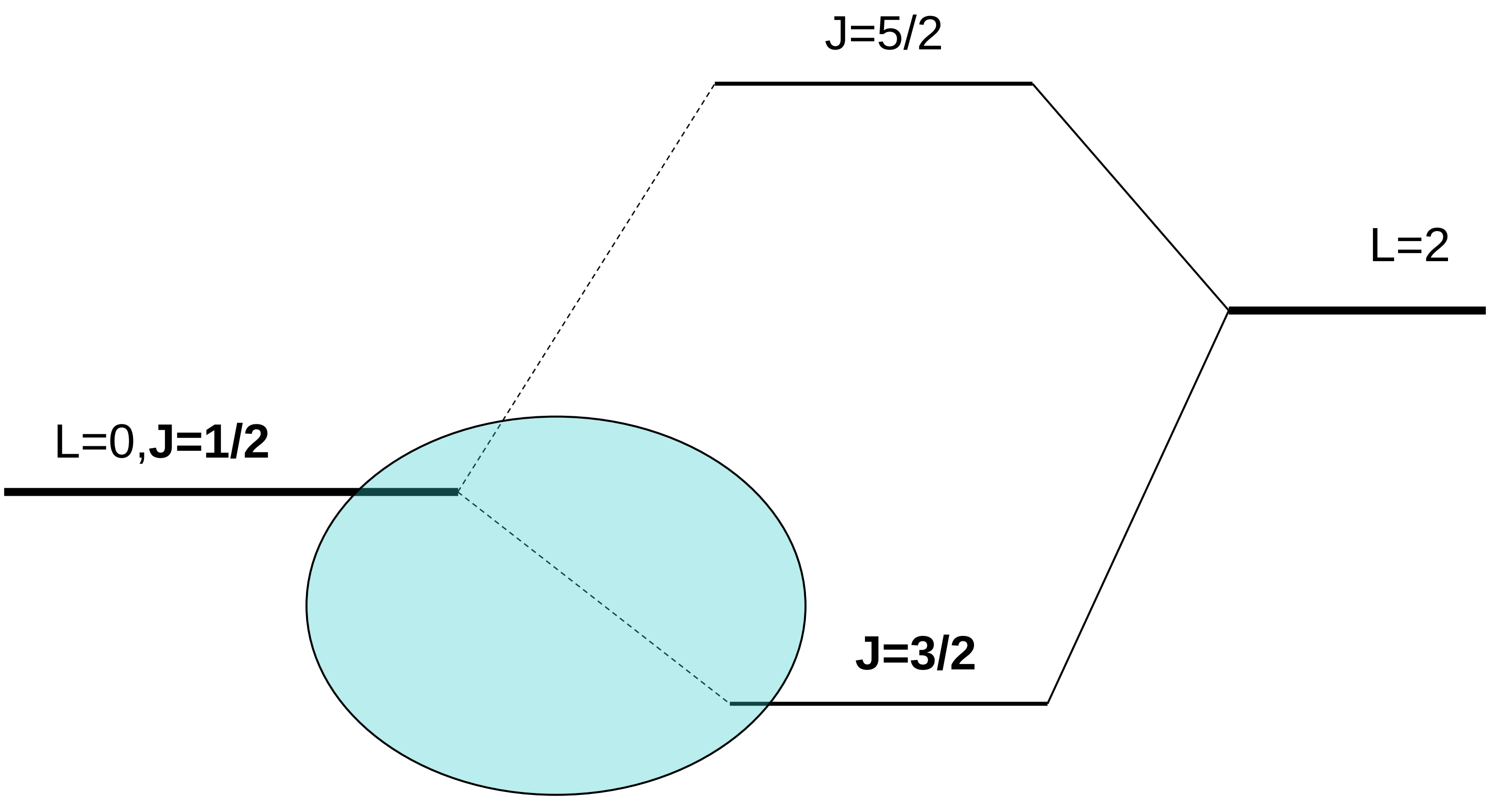
$$\mathcal{P}_{if}(t) = \boxed{t\,\frac{\pi}{2\hbar}\delta(E_{v'L'} - E_{vL})}$$
$$\times \boxed{\omega^2_{v'L',vL}\,\langle v'L'||\tilde{Q}||vL\rangle^2}$$
$$\times \boxed{(2J+1)\left(\sum_{IF}(-1)^{J+L+F}\beta^{v'L'N'J'}_{IF}\beta^{vLNJ}_{IF}\begin{Bmatrix} J' & 2 & J \\ L & F & L' \end{Bmatrix}\right)^2}$$
$$\times \boxed{\left(C^{J'J'_z}_{JJ_z,2q}\right)^2\,|\tilde{T}^q|^2}, \quad q = J'_z - J_z$$

Sum rules:
If the levels are degenerate with respect to J_z,
The hyperfine structure is reproduced, and
Laser polarization effects disappear

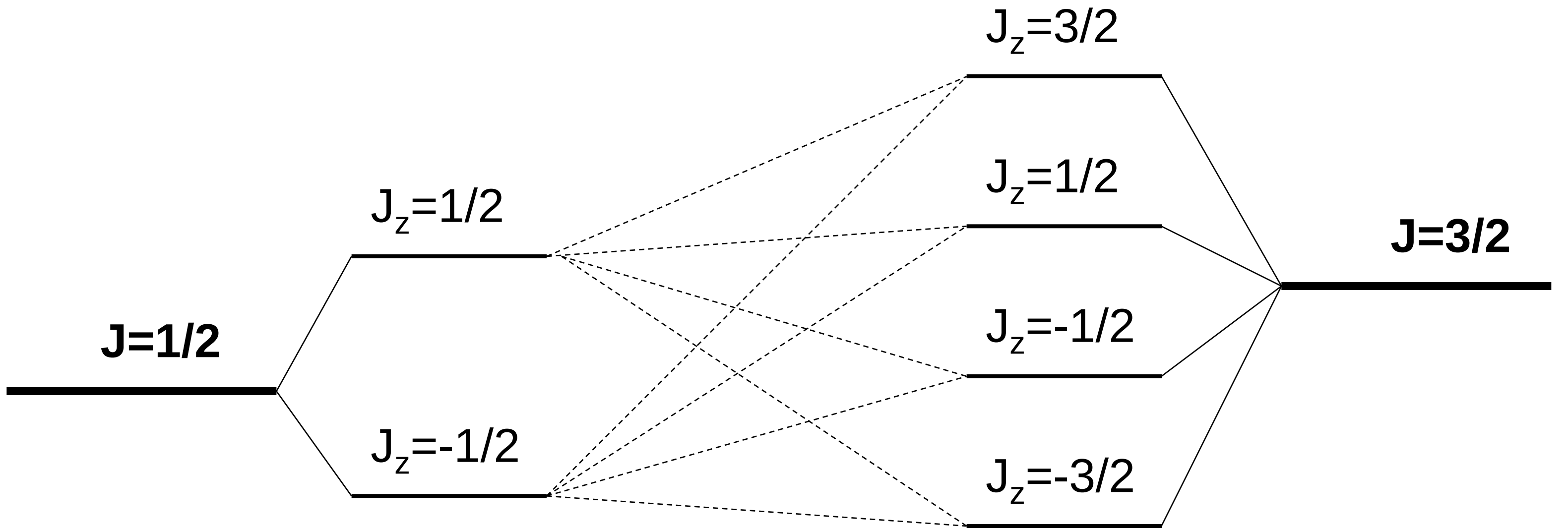
Simple example: hfs of E2-lines



Hyperfine structure of E2-lines



HF + Zeeman splitting



E2 transition rate (intensities)

$dP_{i\to f}/dt=$

$(\pi/2h)\ \delta(E_{v'L'}-E_{vL})$ (e.c.)

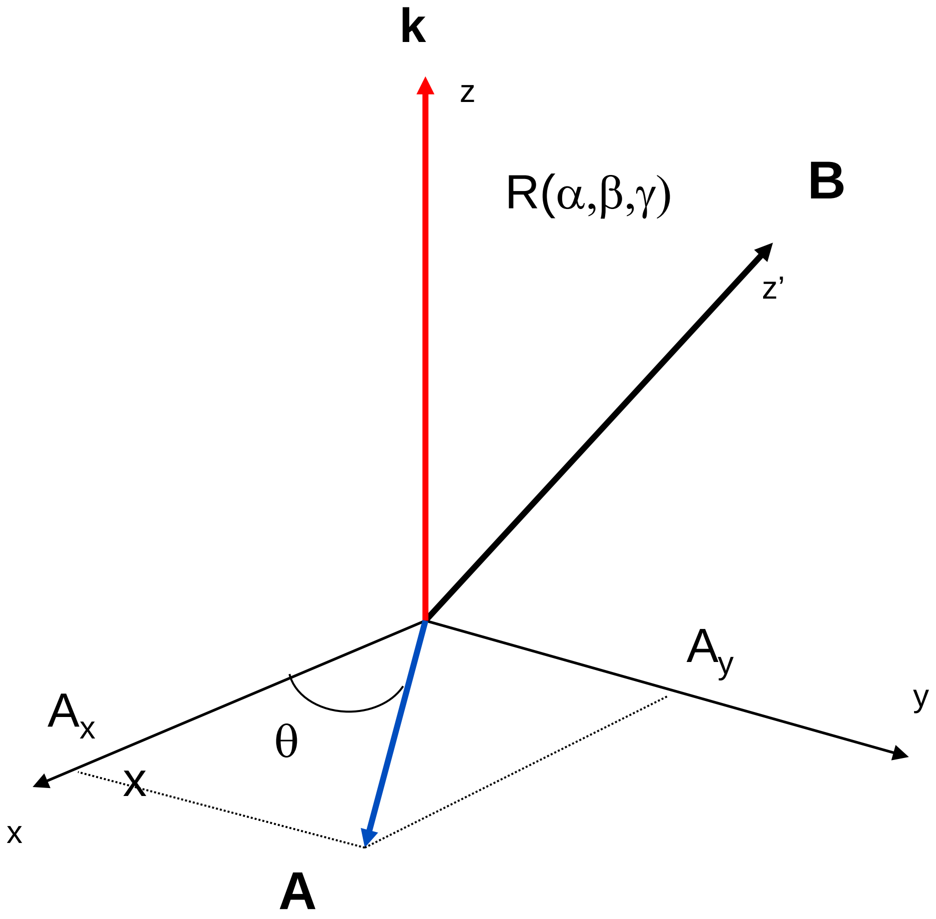
$\times\ \omega_{v'L',vL}^{2}\ \langle v'L'||Q||vL\rangle^2$ (nrel)

$\times\ F_{I'S'J',ISJ}$ (hfs)

$\times\ \langle J'J'_z|JJ_z,2q\rangle^2\ |T^q|^2,\ q=J'_z-J_z$ (pol)

where $\boxed{T=(A\otimes k)^{(2)}}$

Parameterization of T



$$\mathbf{A}=|\mathbf{A}|(\cos\theta, \sin\theta\, e^{i\varphi}, 0)$$

Dependence of $|T_q|$ on 4 angles

Euler: α, β; polarization parameters: θ, φ

$$
\begin{aligned}
|\tilde{T}_{\pm 2}|^2 = \; & \frac{1}{64}\sin^2\beta \; (12 + 4\cos 2\beta - 2\cos 2(\alpha - \theta) + \cos 2(\alpha - \beta - \theta) + \cos 2(\alpha + \beta - \theta) \\
& -2\cos 2(\alpha + \theta) + \cos 2(\alpha - \beta + \theta) + \cos 2(\alpha + \beta + \theta)) \\
& -\frac{1}{8}\sin 2\alpha \sin 2\theta \sin^4\beta \cos\varphi \mp \frac{1}{8}\sin 2\beta \sin 2\theta \sin\beta \sin\varphi
\end{aligned}
$$

$$
\begin{aligned}
|\tilde{T}_{\pm 1}|^2 = \; & \frac{1}{64}(8 + 4\cos 2\beta + 4\cos 4\beta \\
& -\cos 2(\alpha - \beta - \theta) - \cos 2(\alpha + \beta - \theta) - \cos 2(\alpha - \beta + \theta) - \cos 2(\alpha + \beta + \theta) \\
& +\cos 2(\alpha - 2\beta - \theta) + \cos 2(\alpha - 2\beta + \theta) + \cos 2(\alpha + 2\beta - \theta) + \cos 2(\alpha + 2\beta + \theta)) \\
& -\frac{1}{8}\sin 2\alpha \sin 2\theta \sin^2\beta (1 + \cos 2\beta)\cos\varphi \mp \frac{1}{8}\sin 2\theta (\cos\beta + \cos 3\beta)\sin\varphi
\end{aligned}
$$

$$
|\tilde{T}_0|^2 = \frac{3}{32}\sin^2 2\beta (2 + \cos 2(\alpha - \theta) + \cos 2(\alpha + \theta)) + \frac{3}{16}\sin 2\alpha \sin^2 2\beta \sin 2\theta \cos\varphi
$$

No 4th angle in linear polarization

$$|T_{\pm 2}|^2 = \frac{1}{32}\sin^2\beta\,(6+\cos(2(\alpha-\theta-\beta))+\cos(2(\alpha-\theta+\beta))-2\cos(2(\alpha-\theta))+2\cos(2\beta))$$

$$|T_{\pm 1}|^2 = \frac{1}{32}\,(4+\cos(2(\alpha-\theta-2\beta))+\cos(2(\alpha-\theta+2\beta))$$

$$-\cos(2(\alpha-\theta-\beta))-\cos(2(\alpha-\theta+\beta))+2\cos(2\beta)+2\cos(4\beta))$$

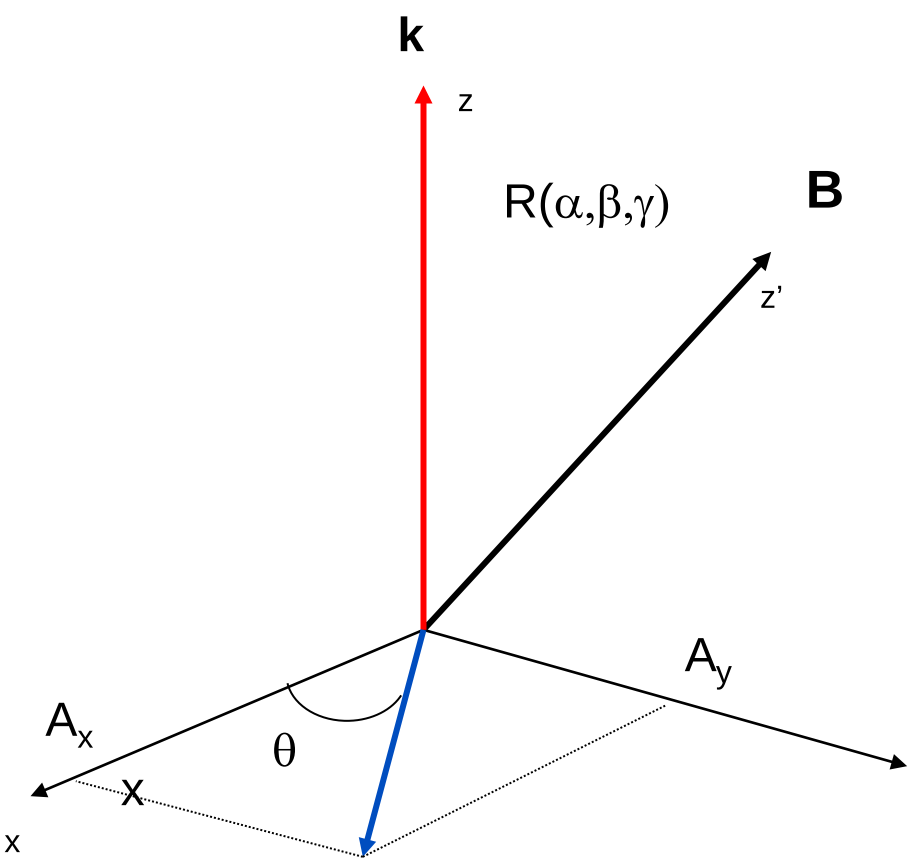
$$|T_0|^2 = \frac{3}{8}\sin^2(2\beta)\cos^2(\alpha-\theta)$$

No 4th angle in linear polarization

- Only the difference

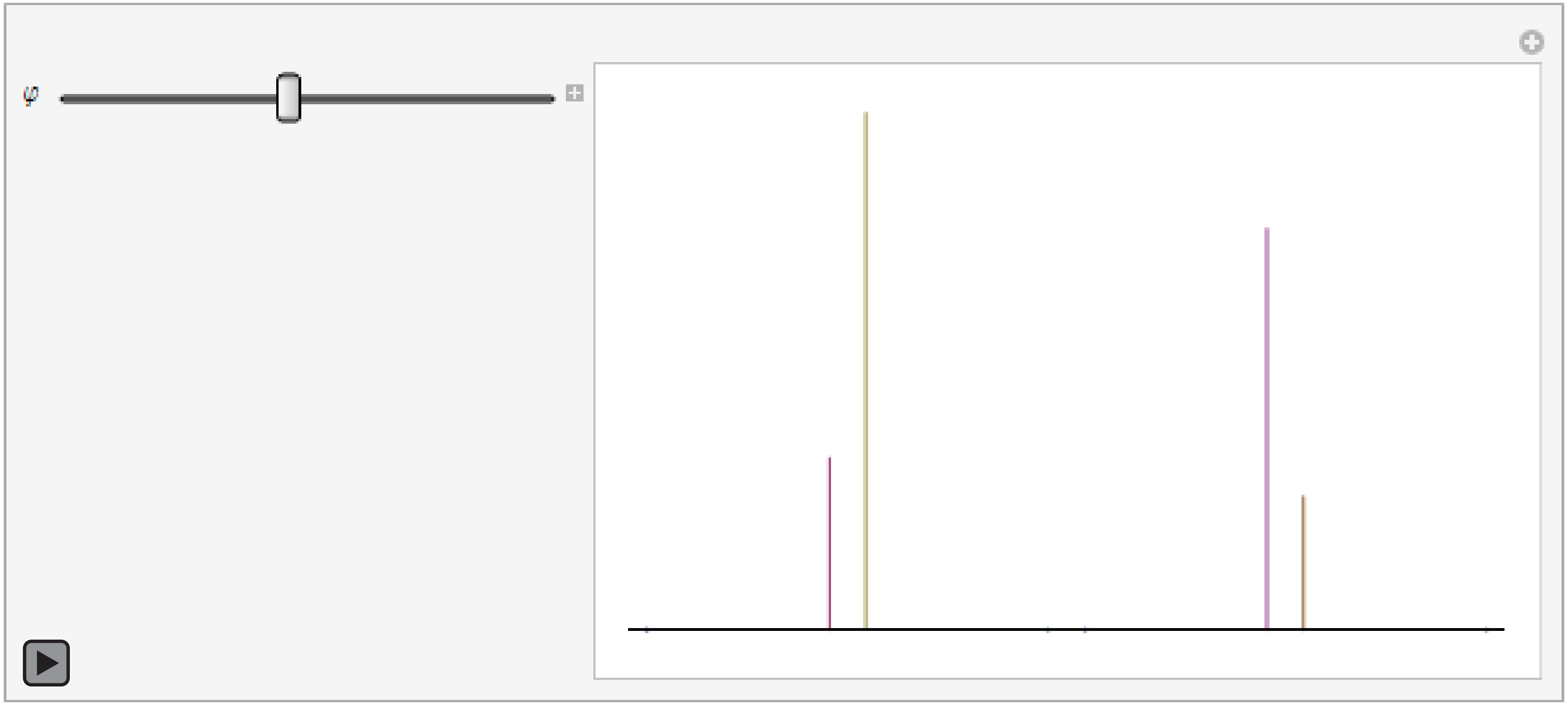
  α - θ

  appears in the case of linearly polarization of the laser
- α appears for circular or elliptic polarization

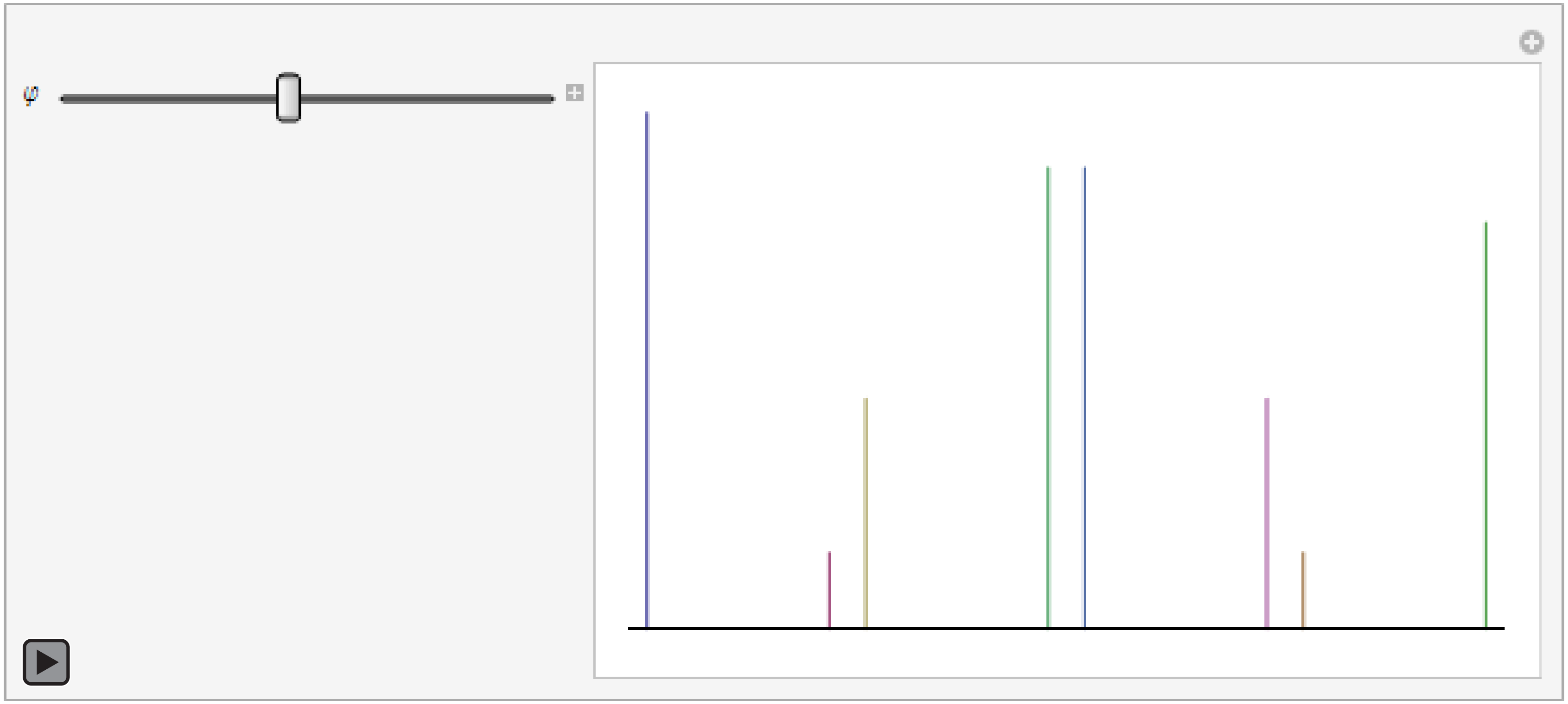


Varying φ, α=0,θ=π/4, β=0

B||k, no dependence on φ for B⊥k

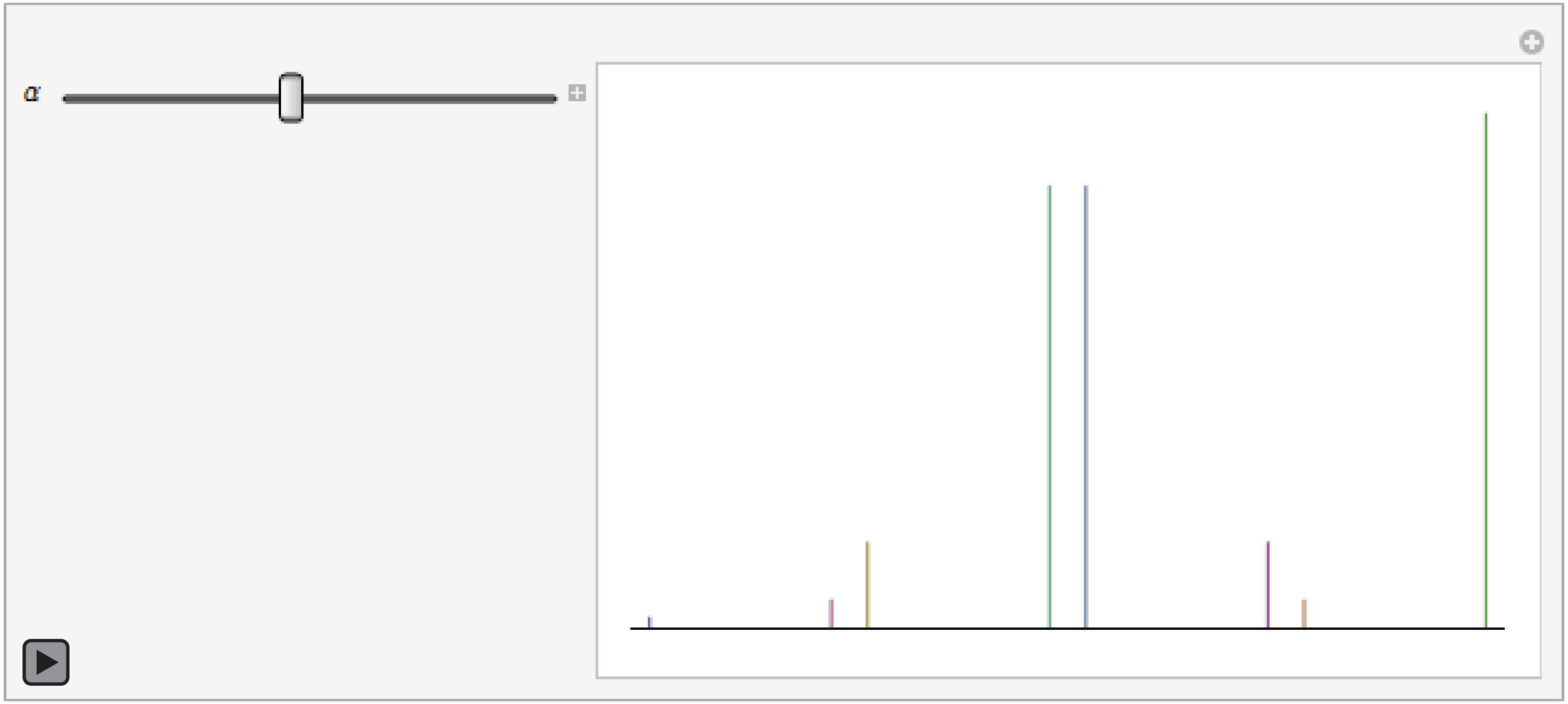


Varying φ, α=0,θ=π/4, β= π/4



Varying α, $\varphi = \pi/2$, $\theta=\pi/4$, $\beta= \pi/4$

No dependence on α for B||k



Varying β, random α, φ; $\theta=\pi/6$