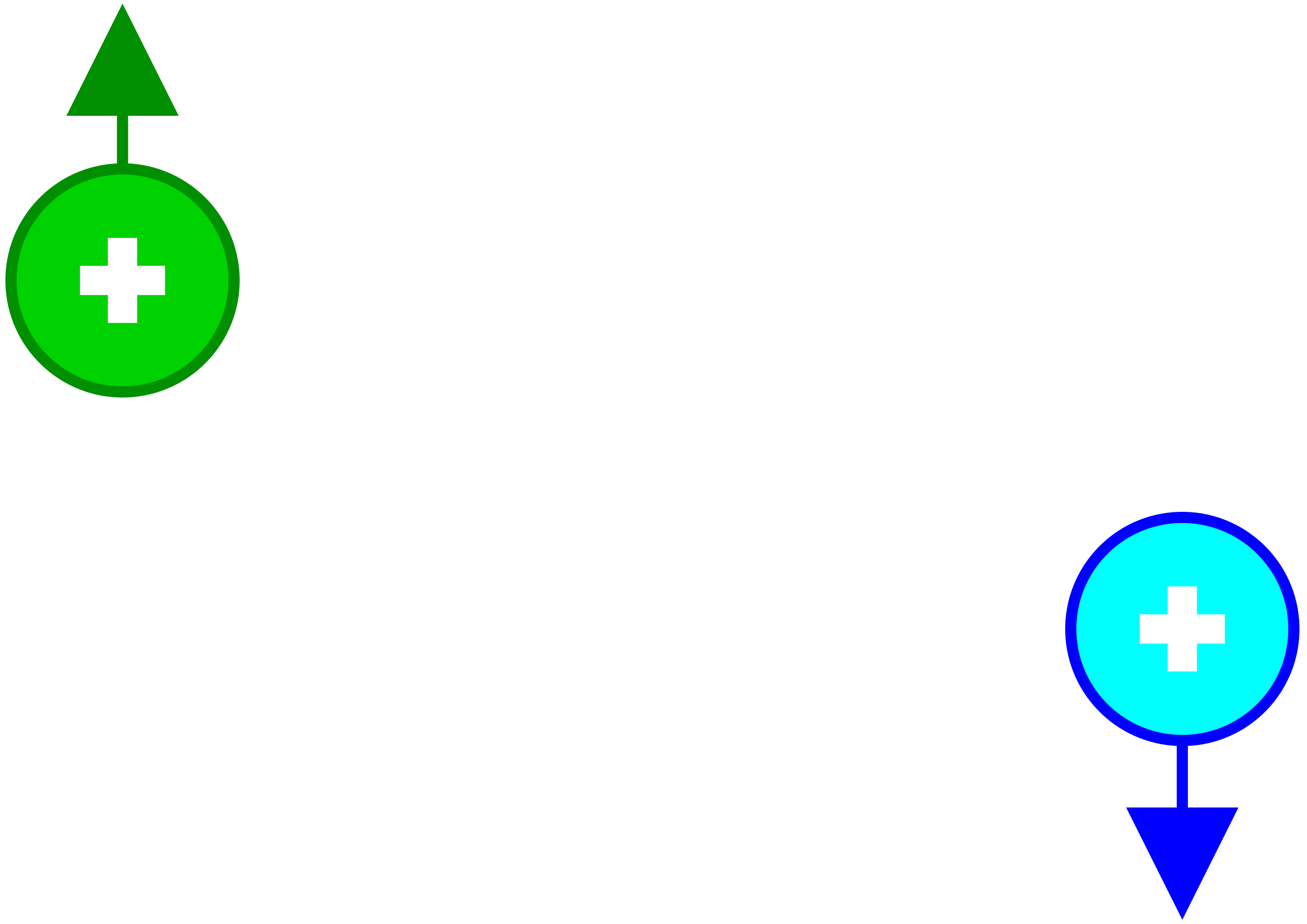
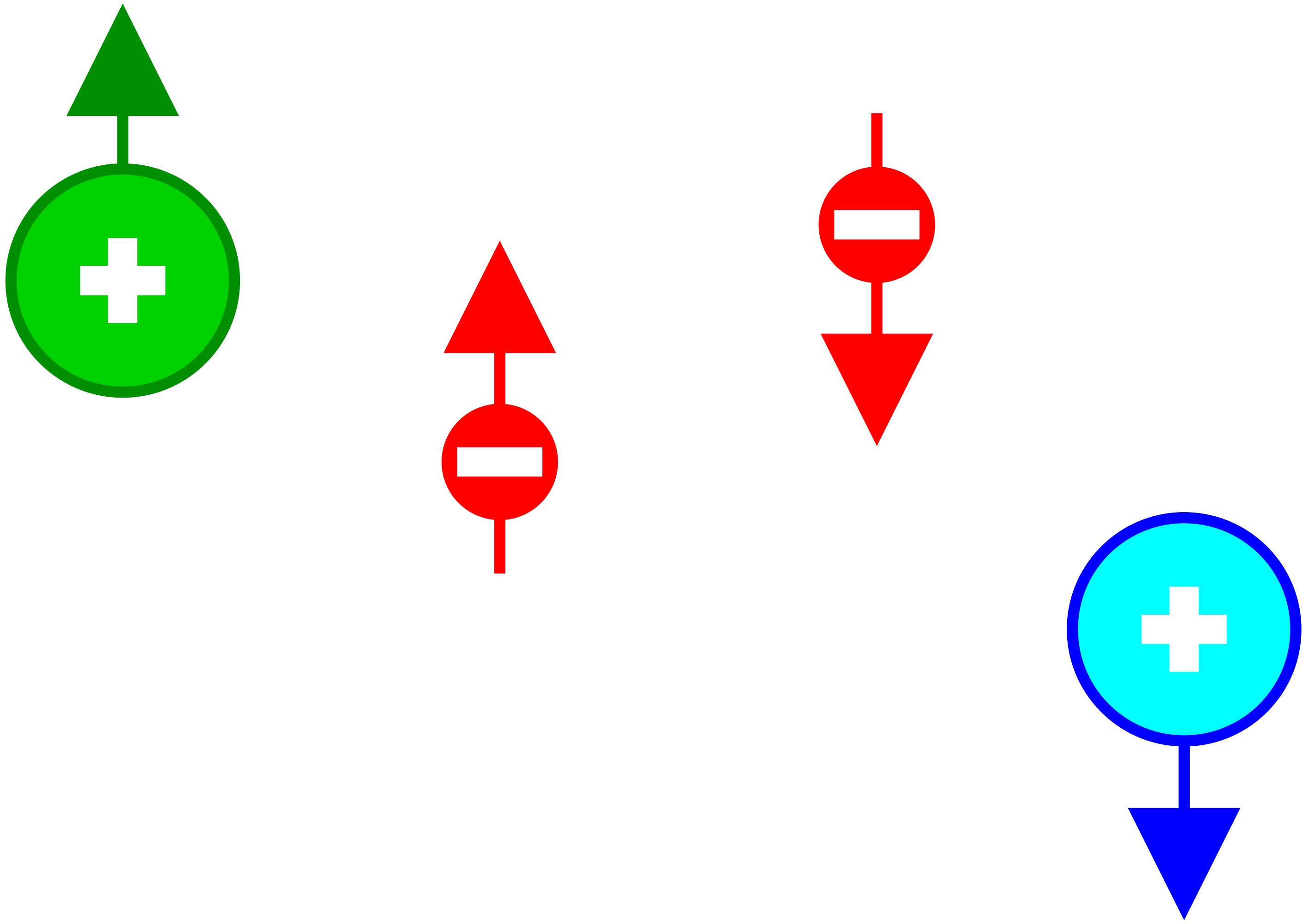
Lecture 10: J-coupling, spin echoes

Direct dipole–dipole coupling



J-coupling (indirect, through-bond)



J-coupling Hamiltonian

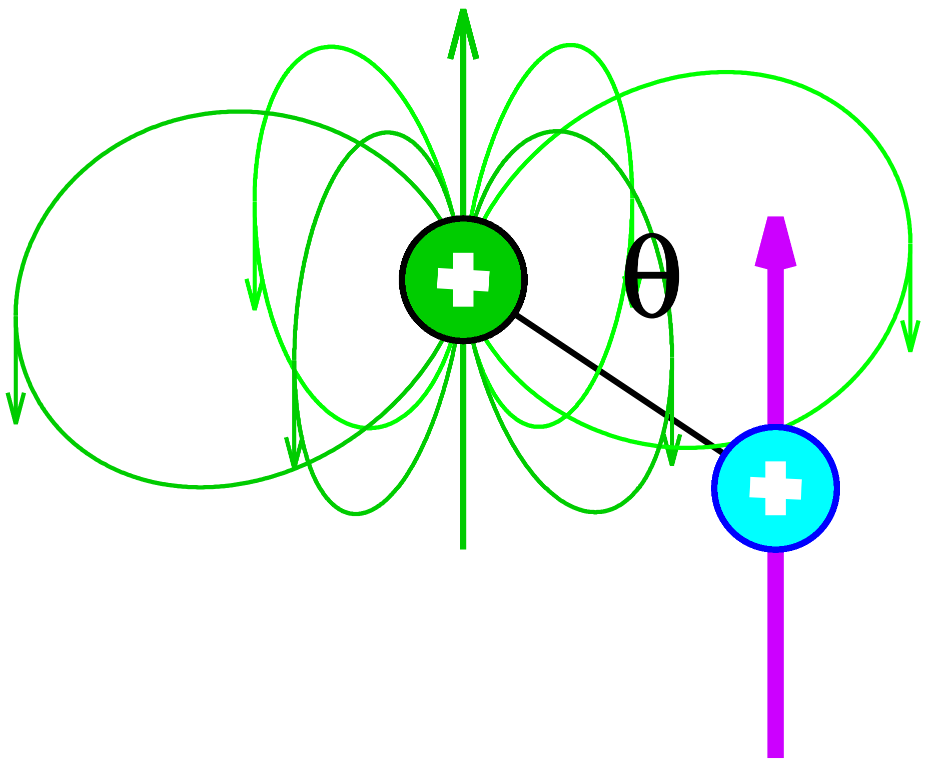
$$\begin{pmatrix} B_{2,x} \\ B_{2,y} \\ B_{2,z} \end{pmatrix} = -\frac{2\pi}{\gamma_1 \gamma_2} \begin{pmatrix} J_{xx} & J_{xy} & J_{xz} \\ J_{yx} & J_{yy} & J_{yz} \\ J_{zx} & J_{zy} & J_{zz} \end{pmatrix} \cdot \begin{pmatrix} \mu_{2,x} \\ \mu_{2,y} \\ \mu_{2,z} \end{pmatrix}$$

$$\mathcal{E} = -\vec{\mu}_1 \cdot \vec{B}_2 = \frac{2\pi}{\gamma_1 \gamma_2} \begin{pmatrix} \mu_{1,x} & \mu_{1,y} & \mu_{1,z} \end{pmatrix} \cdot \underline{J} \cdot \begin{pmatrix} \mu_{2,x} \\ \mu_{2,y} \\ \mu_{2,z} \end{pmatrix}$$

$$\hat{H}_J = 2\pi \begin{pmatrix} \hat{I}_{1,x} & \hat{I}_{1,y} & \hat{I}_{1,z} \end{pmatrix} \cdot \underline{J} \cdot \begin{pmatrix} \hat{I}_{2,x} \\ \hat{I}_{2,y} \\ \hat{I}_{2,z} \end{pmatrix} =$$

$$2\pi \begin{pmatrix} \hat{I}_{1,x} & \hat{I}_{1,y} & \hat{I}_{1,z} \end{pmatrix} \cdot \begin{pmatrix} J_{xx} & J_{xy} & J_{xz} \\ J_{yx} & J_{yy} & J_{yz} \\ J_{zx} & J_{zy} & J_{zz} \end{pmatrix} \cdot \begin{pmatrix} \hat{I}_{2,x} \\ \hat{I}_{2,y} \\ \hat{I}_{2,z} \end{pmatrix}$$

J-coupling Hamiltonian

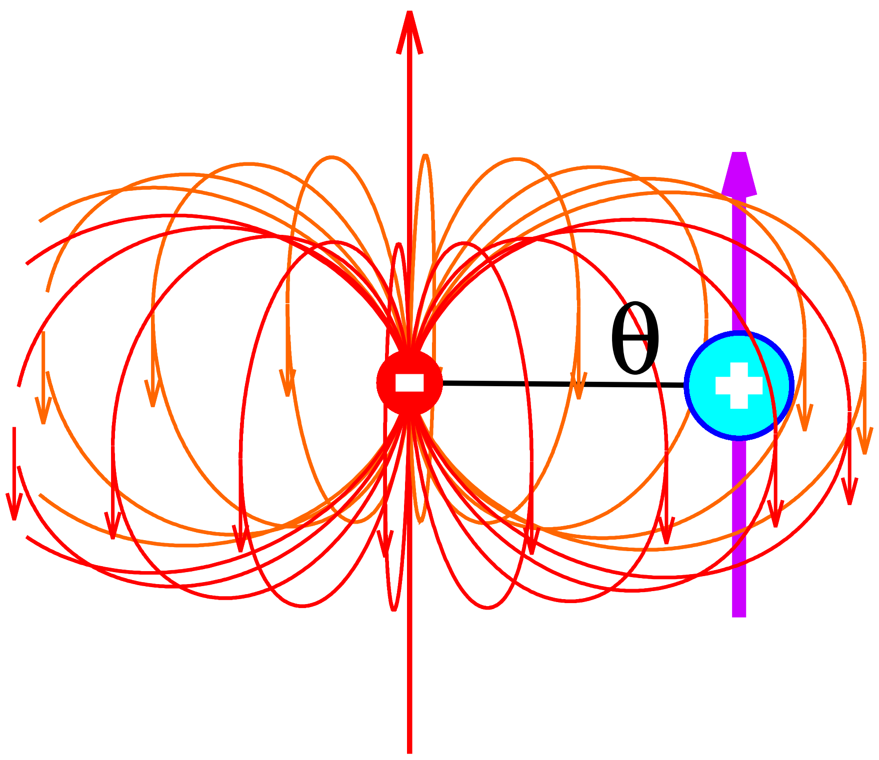


$$\hat{H}_J = 2\pi(J_{xx}\hat{I}_{1,x}\hat{I}_{2,x} + J_{xy}\hat{I}_{1,x}\hat{I}_{2,y} + J_{xz}\hat{I}_{1,x}\hat{I}_{2,z}$$

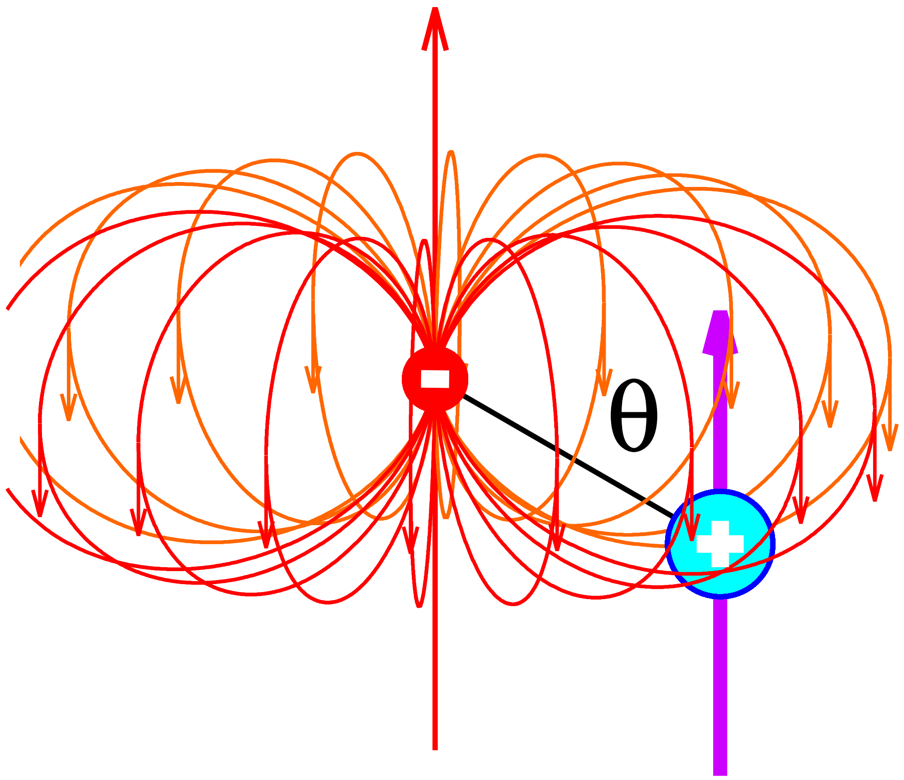
$$+J_{yx}\hat{I}_{1,y}\hat{I}_{2,x} + J_{yy}\hat{I}_{1,y}\hat{I}_{2,y} + J_{yz}\hat{I}_{1,y}\hat{I}_{2,z}$$

$$+J_{zx}\hat{I}_{1,z}\hat{I}_{2,x} + J_{zy}\hat{I}_{1,z}\hat{I}_{2,y}J_{zz}\hat{I}_{1,z}\hat{I}_{2,z}$$

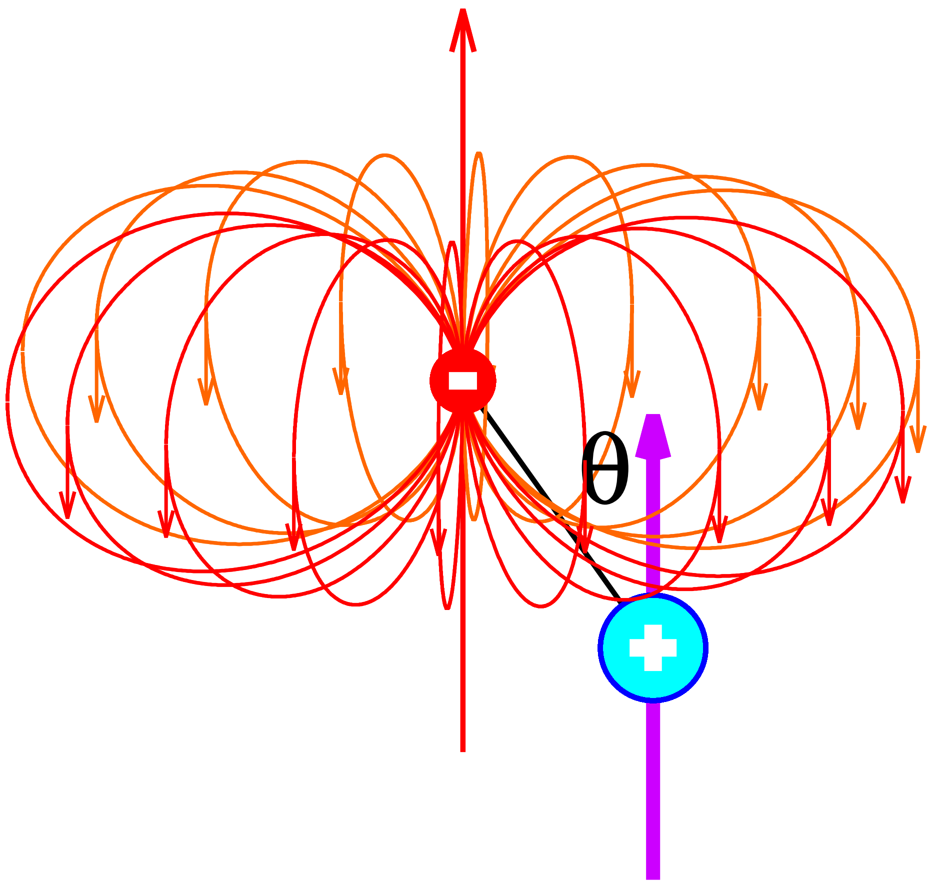
Classical nucleus-electron interaction



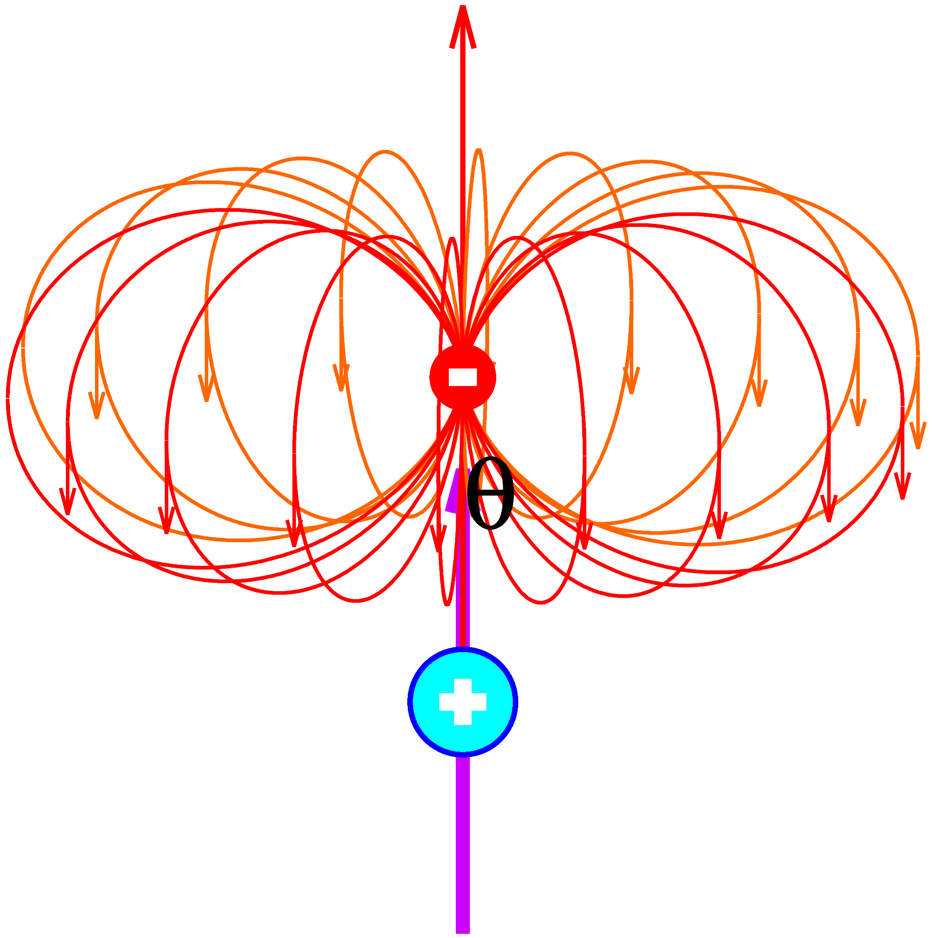
Classical nucleus-electron interaction



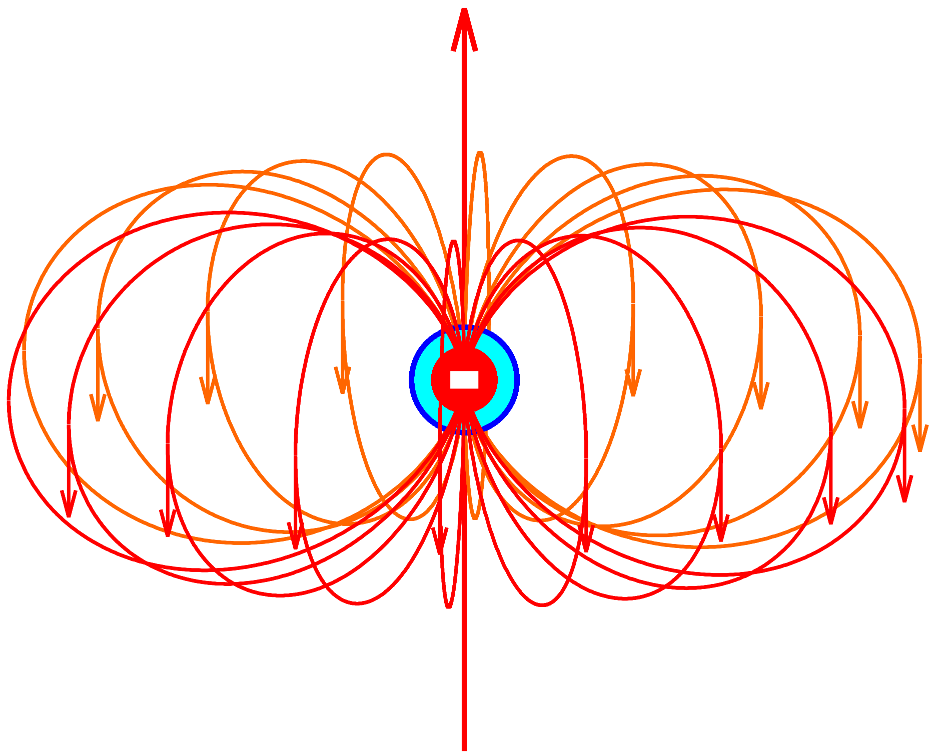
Classical nucleus–electron interaction



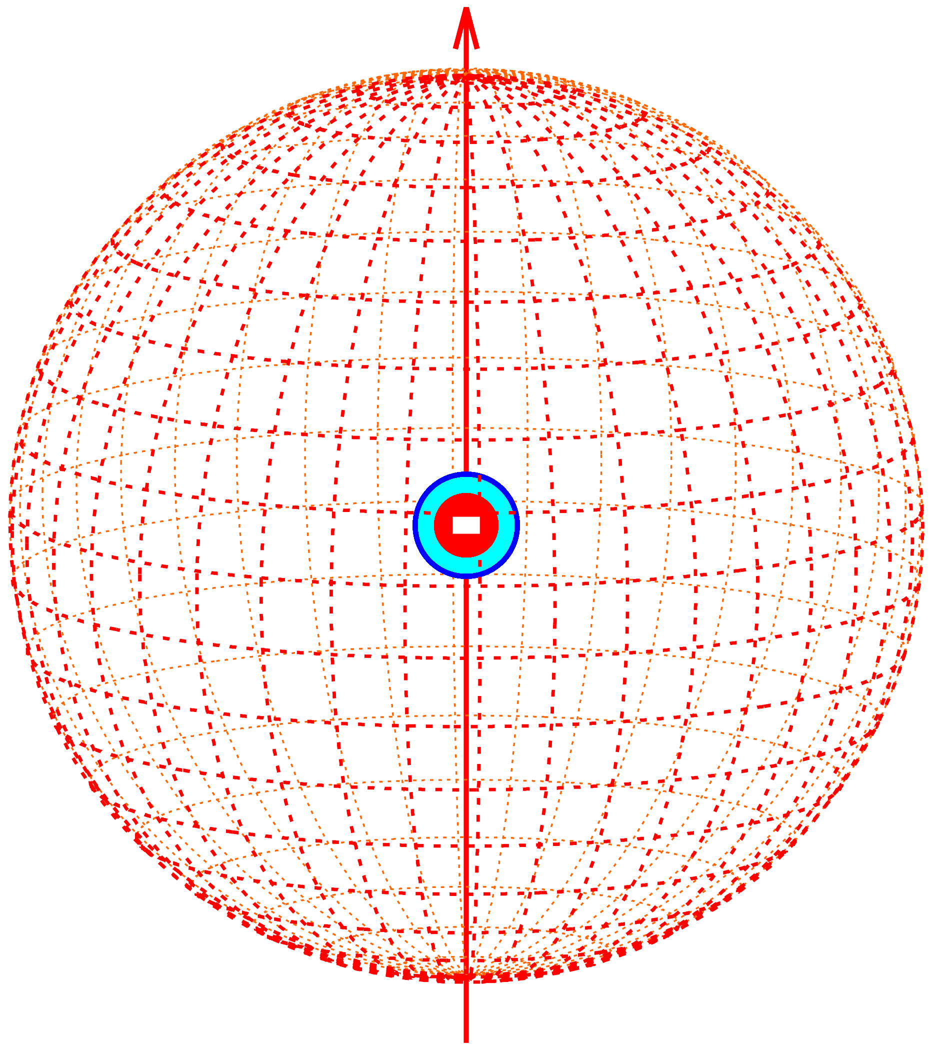
Classical nucleus–electron interaction



Classical nucleus–electron interaction

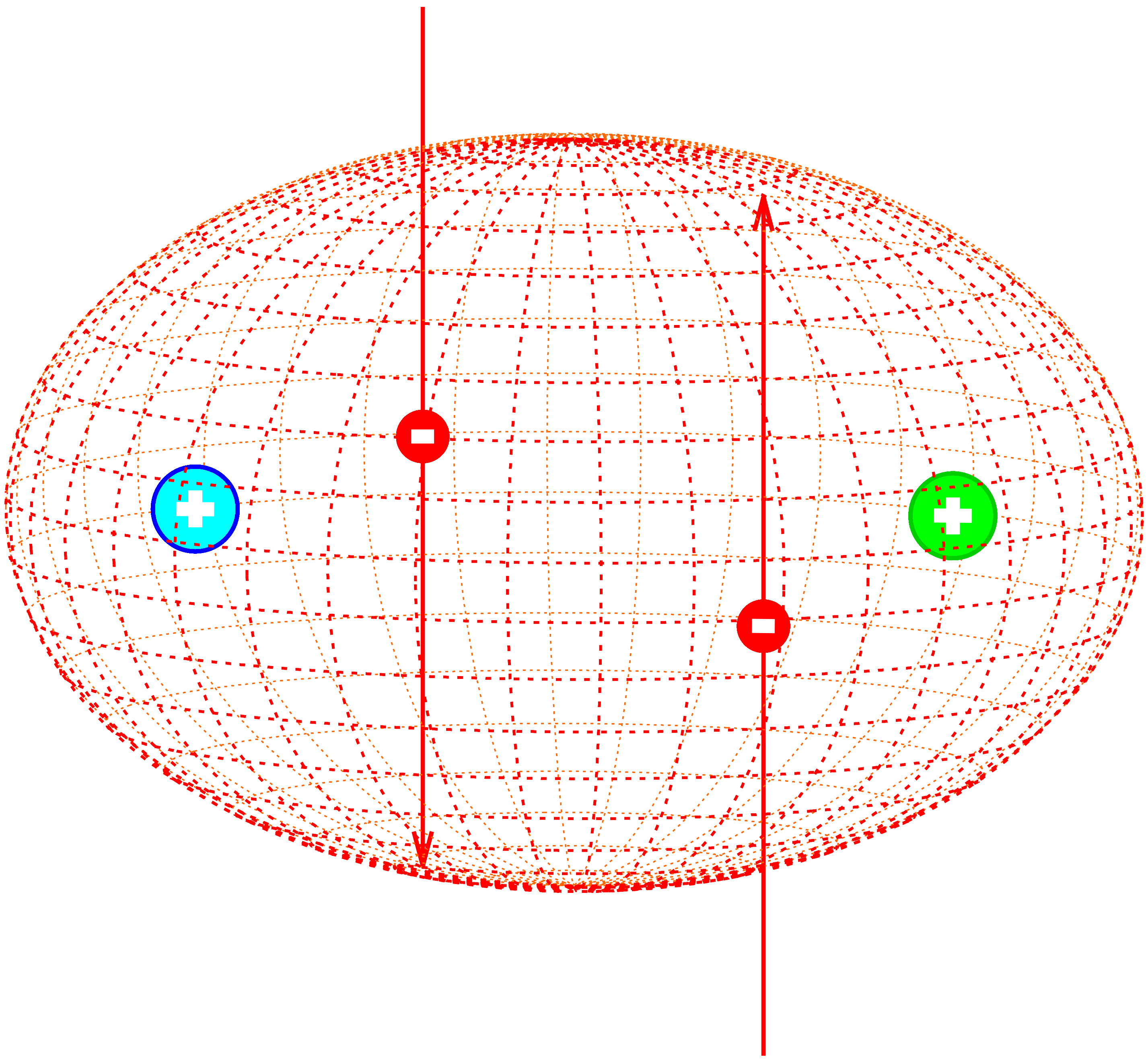


Fermi interaction

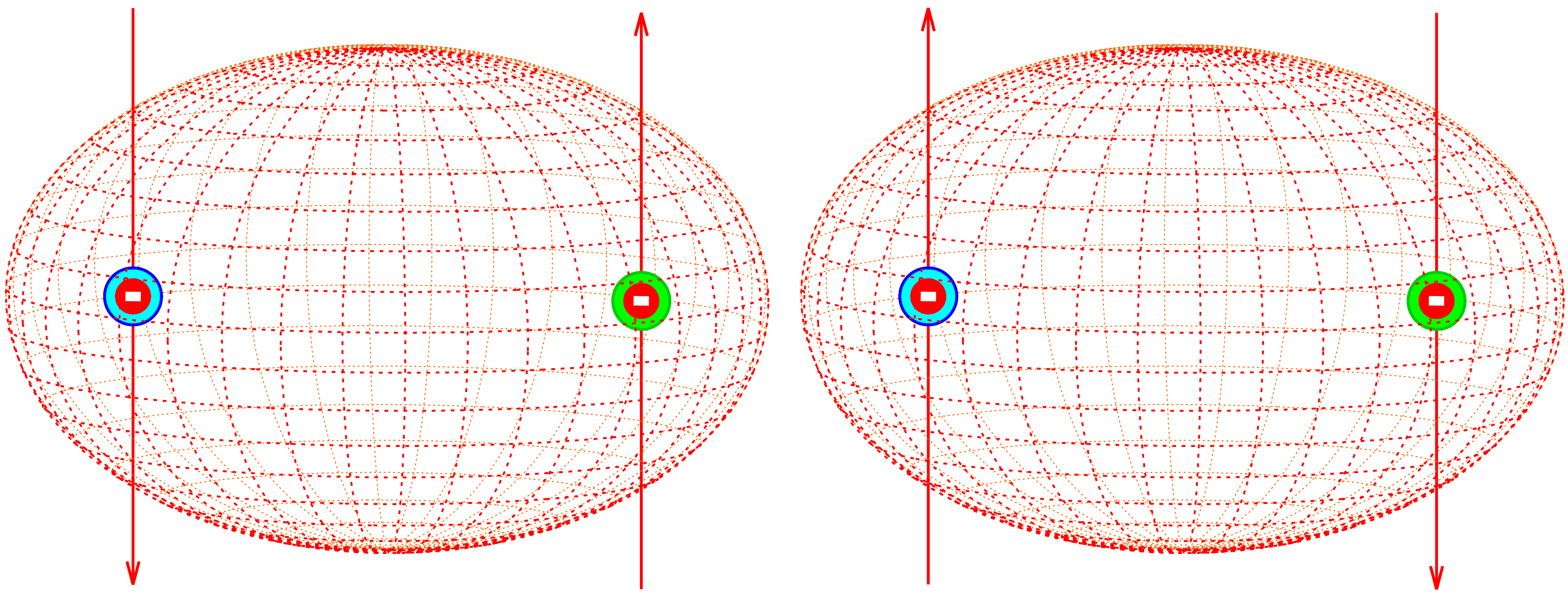


$$\hat{H}_\mathsf{F} = -\frac{2\mu_0}{3}\left(\hat{\vec{\mu}}_\mathsf{n}\cdot\hat{\vec{\mu}}_\mathsf{e}\right)\ \psi^2(0)$$

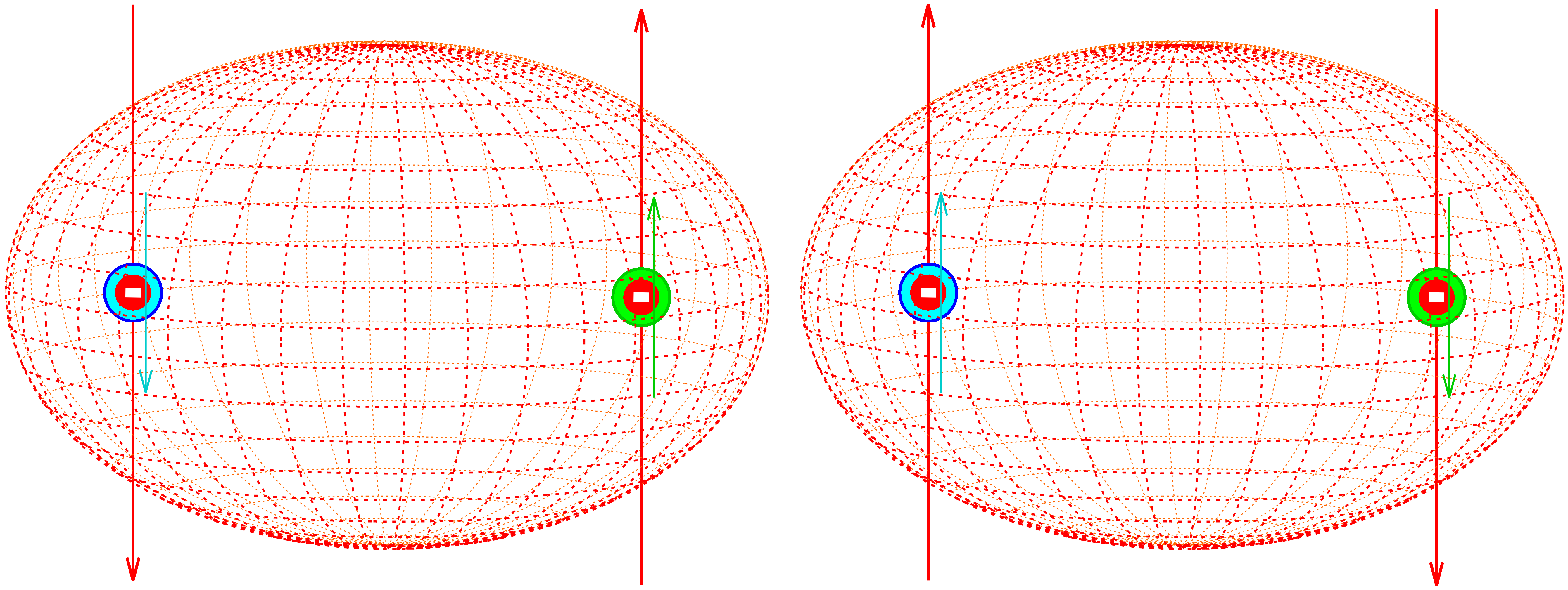
J-coupling



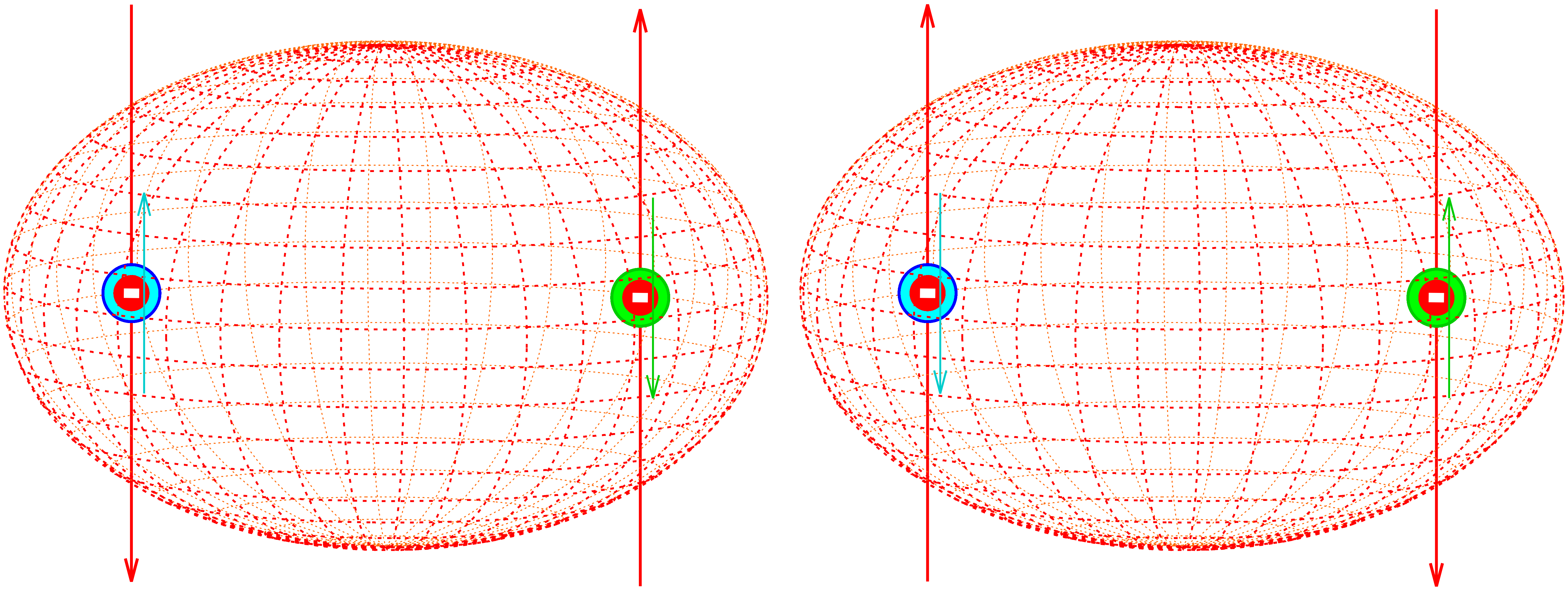
Stationary state of unperturbed σ electrons



Favorable state of electron-coupled nuclei



Unavorable state of electron-coupled nuclei



Scalar coupling

$$\hat{H}_J = 2\pi \begin{pmatrix} \hat{I}_{1,x} & \hat{I}_{1,y} & \hat{I}_{1,z} \end{pmatrix} \cdot \begin{pmatrix} J_{xx} & J_{xy} & J_{xz} \\ J_{yx} & J_{yy} & J_{yz} \\ J_{zx} & J_{zy} & J_{zz} \end{pmatrix} \cdot \begin{pmatrix} \hat{I}_{2,x} \\ \hat{I}_{2,y} \\ \hat{I}_{2,z} \end{pmatrix}$$

$$2\pi \begin{pmatrix} J_{xx} & J_{xy} & J_{xz} \\ J_{yx} & J_{yy} & J_{yz} \\ J_{zx} & J_{zy} & J_{zz} \end{pmatrix} \longrightarrow 2\pi \begin{pmatrix} J_{XX} & 0 & 0 \\ 0 & J_{YY} & 0 \\ 0 & 0 & J_{ZZ} \end{pmatrix}$$

$$= 2\pi \frac{J_{XX} + J_{YY} + J_{ZZ}}{3} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = 2\pi J \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$J = (J_{XX} + J_{YY} + J_{ZZ})/3$ isotropic constant (**scalar**)

$(2J_{ZZ} - J_{YY} - J_{XX})/6 = 0$ no anisotropy

$(J_{XX} - J_{YY})/2 = 0$ no rhombicity

$$\hat{H}_J = \pi J \left(2\hat{I}_{1z}\hat{I}_{2z} + 2\hat{I}_{1x}\hat{I}_{2x} + 2\hat{I}_{1y}\hat{I}_{2y}\right)$$

J-coupling constants

- $^{1}J(^{31}\text{P-}^{1}\text{H}) < 700\,\text{Hz}$
- $^{1}J(^{13}\text{C-}^{1}\text{H})$ 140 Hz to 200 Hz
- $^{1}J(^{15}\text{N-}^{1}\text{H})$ $-90\,\text{Hz}$
- $^{1}J(^{13}\text{C-}^{13}\text{C})$ 30 Hz to 60 Hz
- $^{3}J(^{1}\text{H-}^{1}\text{H}) < 15\,\text{Hz}$ torsion angle

Secular approximation

- isotropic $\underline{J}$: no ensemble averaging is needed

- $\gamma_1 = \gamma_2$ **and** $\delta_{\mathrm{i},1} \approx \delta_{\mathrm{i},2}$ (*strong coupling*):

$$\hat{H}_J = \pi J \left(2\hat{I}_{1z}\hat{I}_{2z} + 2\hat{I}_{1x}\hat{I}_{2x} + 2\hat{I}_{1y}\hat{I}_{2y}\right)$$

- $\gamma_1 \neq \gamma_2$ **or** $|\delta_{\mathrm{i},1} - \delta_{\mathrm{i},2}|B_0 \gg 2\pi|J|$ (*weak coupling*):

$$\hat{H}_J = 2\pi J \hat{I}_{1z}\hat{I}_{2z} = \pi J \left(2\hat{I}_{1z}\hat{I}_{2z}\right)$$

Density matrix at thermal equilibrium

Diagonal elements:

$$P^{\mathrm{eq}}_{\alpha\alpha} \approx \frac{1}{4} + \gamma_1(1+\delta_{\mathrm{i},1})\frac{B_0\hbar}{8k_{\mathrm{B}}T} + \gamma_2(1+\delta_{\mathrm{i},2})\frac{B_0\hbar}{8k_{\mathrm{B}}T} - \frac{\pi J\hbar}{16k_{\mathrm{B}}T}$$

$$P^{\mathrm{eq}}_{\alpha\beta} \approx \frac{1}{4} + \gamma_1(1+\delta_{\mathrm{i},1})\frac{B_0\hbar}{8k_{\mathrm{B}}T} - \gamma_2(1+\delta_{\mathrm{i},2})\frac{B_0\hbar}{8k_{\mathrm{B}}T} + \frac{\pi J\hbar}{16k_{\mathrm{B}}T}$$

$$P^{\mathrm{eq}}_{\beta\alpha} \approx \frac{1}{4} - \gamma_1(1+\delta_{\mathrm{i},1})\frac{B_0\hbar}{8k_{\mathrm{B}}T} + \gamma_2(1+\delta_{\mathrm{i},2})\frac{B_0\hbar}{8k_{\mathrm{B}}T} + \frac{\pi J\hbar}{16k_{\mathrm{B}}T}$$

$$P^{\mathrm{eq}}_{\beta\beta} \approx \frac{1}{4} - \gamma_1(1+\delta_{\mathrm{i},1})\frac{B_0\hbar}{8k_{\mathrm{B}}T} - \gamma_2(1+\delta_{\mathrm{i},2})\frac{B_0\hbar}{8k_{\mathrm{B}}T} - \frac{\pi J\hbar}{16k_{\mathrm{B}}T}$$

$\pi J < 0.00001\ \gamma B_0$,

$|\delta_{\mathrm{i},1}| < 0.00002\ (^{1}\mathrm{H})$, $|\delta_{\mathrm{i},2}| < 0.0002\ (^{13}\mathrm{C}, ^{15}\mathrm{N})$

$$\hat{\rho}^{\mathrm{eq}} = \tfrac{1}{2}\left(\mathscr{I}_t + \kappa_1\mathscr{I}_{1,z} + \kappa_2\mathscr{I}_{2,z}\right), \qquad \kappa_j = \frac{\gamma_j B_0\hbar}{4k_{\mathrm{B}}T}$$

Density matrix evolution

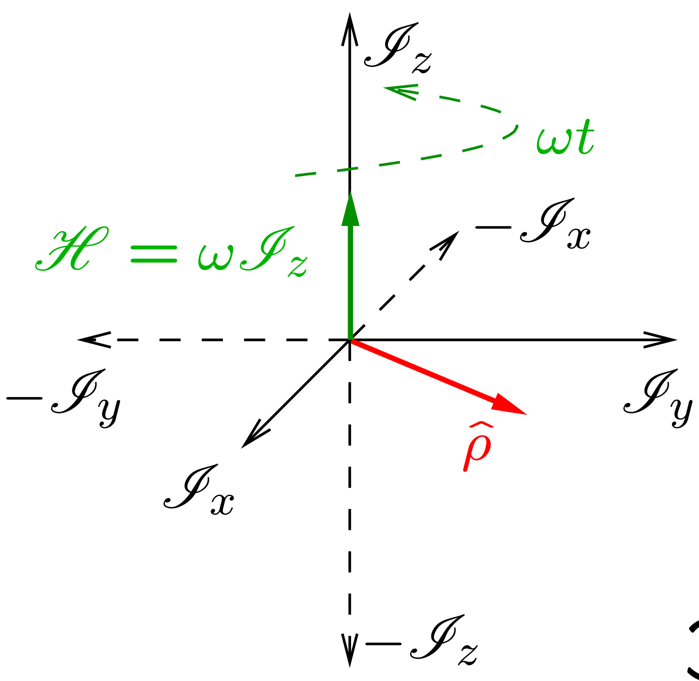
$$\mathscr{H} = \Omega_1 \mathscr{I}_{1z} + \Omega_2 \mathscr{I}_{2z} + \pi J \left(2\mathscr{I}_{1z}\mathscr{I}_{2z} + 2\mathscr{I}_{1x}\mathscr{I}_{2x} + 2\mathscr{I}_{1y}\mathscr{I}_{2y} \right)$$

$$\Omega_1 = -\gamma_1 B_0 (1 + \delta_{\mathrm{i},1}), \qquad \Omega_2 = -\gamma_2 B_0 (1 + \delta_{\mathrm{i},2})$$

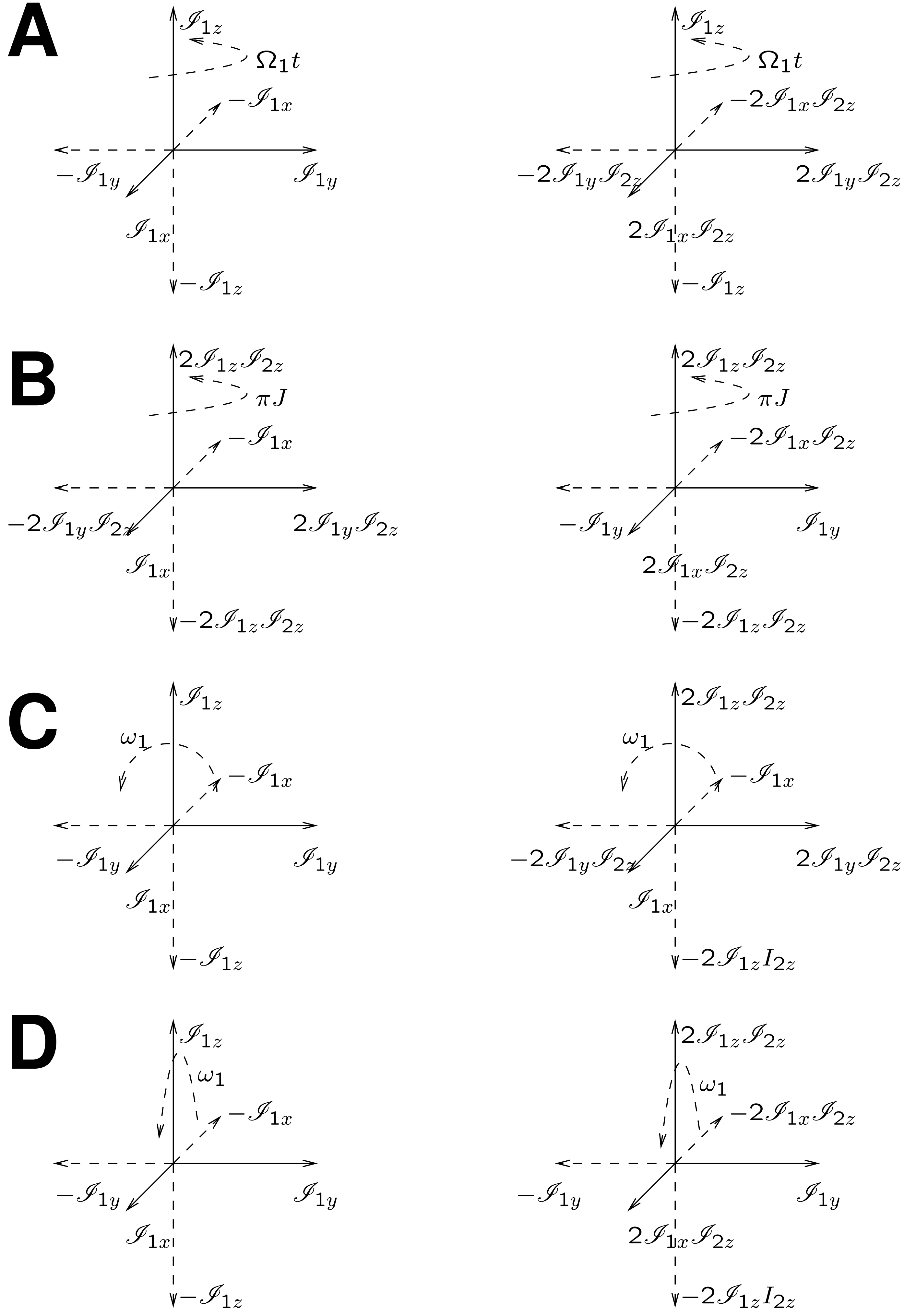
Weak coupling: $\mathscr{H} = \Omega_1 \mathscr{I}_{1z} + \Omega_2 \mathscr{I}_{2z} + \pi J \left(2\mathscr{I}_{1z}\mathscr{I}_{2z} \right)$

$\mathscr{I}_{1z}$, $\mathscr{I}_{2z}$, $2\mathscr{I}_{1z}\mathscr{I}_{2z}$ commute $\Rightarrow$

$$[\mathscr{I}_j, \mathscr{I}_k] = \mathrm{i}\mathscr{I}_l \quad \Rightarrow \quad \hat{\rho} = c\mathscr{I}_j \longrightarrow c\mathscr{I}_j \cos(\omega t) + c\mathscr{I}_l \cos(\omega t)$$



3× for $\mathscr{I}_l = \mathscr{I}_{1z}, \mathscr{I}_{2z}, 2\mathscr{I}_{1z}\mathscr{I}_{2z}$ in any order



A
$\mathscr{I}_{1z}$
$\Omega_1 t$
$-\mathscr{I}_{1x}$
$-\mathscr{I}_{1y}$
$\mathscr{I}_{1y}$
$\mathscr{I}_{1x}$
$-\mathscr{I}_{1z}$
$\mathscr{I}_{1z}$
$\Omega_1 t$
$-2\mathscr{I}_{1x}\mathscr{I}_{2z}$
$-2\mathscr{I}_{1y}\mathscr{I}_{2z}$
$2\mathscr{I}_{1y}\mathscr{I}_{2z}$
$2\mathscr{I}_{1x}\mathscr{I}_{2z}$
$-\mathscr{I}_{1z}$
B
$2\mathscr{I}_{1z}\mathscr{I}_{2z}$
πJ
$-\mathscr{I}_{1x}$
$-2\mathscr{I}_{1y}\mathscr{I}_{2z}$
$2\mathscr{I}_{1y}\mathscr{I}_{2z}$
$\mathscr{I}_{1x}$
$-2\mathscr{I}_{1z}\mathscr{I}_{2z}$
$2\mathscr{I}_{1z}\mathscr{I}_{2z}$
πJ
$-2\mathscr{I}_{1x}\mathscr{I}_{2z}$
$-\mathscr{I}_{1y}$
$\mathscr{I}_{1y}$
$2\mathscr{I}_{1x}\mathscr{I}_{2z}$
$-2\mathscr{I}_{1z}\mathscr{I}_{2z}$
C
$\mathscr{I}_{1z}$
ω_1
$-\mathscr{I}_{1x}$
$-\mathscr{I}_{1y}$
$\mathscr{I}_{1y}$
$\mathscr{I}_{1x}$
$-\mathscr{I}_{1z}$
$2\mathscr{I}_{1z}\mathscr{I}_{2z}$
ω_1
$-\mathscr{I}_{1x}$
$-2\mathscr{I}_{1y}\mathscr{I}_{2z}$
$2\mathscr{I}_{1y}\mathscr{I}_{2z}$
$\mathscr{I}_{1x}$
$-2\mathscr{I}_{1z}I_{2z}$
D
$\mathscr{I}_{1z}$
ω_1
$-\mathscr{I}_{1x}$
$-\mathscr{I}_{1y}$
$\mathscr{I}_{1y}$
$\mathscr{I}_{1x}$
$-\mathscr{I}_{1z}$
$2\mathscr{I}_{1z}\mathscr{I}_{2z}$
ω_1
$-2\mathscr{I}_{1x}\mathscr{I}_{2z}$
$-\mathscr{I}_{1y}$
$\mathscr{I}_{1y}$
$2\mathscr{I}_{1x}\mathscr{I}_{2z}$
$-2\mathscr{I}_{1z}I_{2z}$

Density matrix evolution

$\hat{\rho}$ after a 90° pulse: $\hat{\rho}(\mathrm{b}) = \frac{1}{2}\mathscr{I}_t + \frac{1}{2}\kappa(-\mathscr{I}_{1y} - \mathscr{I}_{2y})$

$$\mathscr{I}_{1t} \longrightarrow \mathscr{I}_{1t} \longrightarrow \mathscr{I}_{1t}$$

$$-\mathscr{I}_{1y} \longrightarrow \begin{cases} -c_1 \mathscr{I}_{1y} \longrightarrow \begin{cases} -c_1 c_J \ \mathscr{I}_{1y} \\ +c_1 s_J \ 2\mathscr{I}_{1x}\mathscr{I}_{2z} \end{cases} \\ +s_1 \mathscr{I}_{1x} \longrightarrow \begin{cases} +s_1 c_J \ \mathscr{I}_{1x} \\ +s_1 s_J \ 2\mathscr{I}_{1y}\mathscr{I}_{2z} \end{cases} \end{cases}$$

$$-\mathscr{I}_{2y} \longrightarrow \begin{cases} -c_2 \mathscr{I}_{2y} \longrightarrow \begin{cases} -c_2 c_J \ \mathscr{I}_{2y} \\ +c_2 s_J \ 2\mathscr{I}_{2x}\mathscr{I}_{1z} \end{cases} \\ +s_2 \mathscr{I}_{2x} \longrightarrow \begin{cases} +s_2 c_J \ \mathscr{I}_{2x} \\ +s_2 s_J \ 2\mathscr{I}_{2y}\mathscr{I}_{1z} \end{cases} \end{cases}$$

$$c_1 = \cos(\Omega_1 t) \qquad s_1 = \sin(\Omega_1 t)$$

$$c_2 = \cos(\Omega_2 t) \qquad s_2 = \sin(\Omega_2 t)$$

$$c_J = \cos(\pi J t) \qquad s_J = \sin(\pi J t)$$

Spectrum

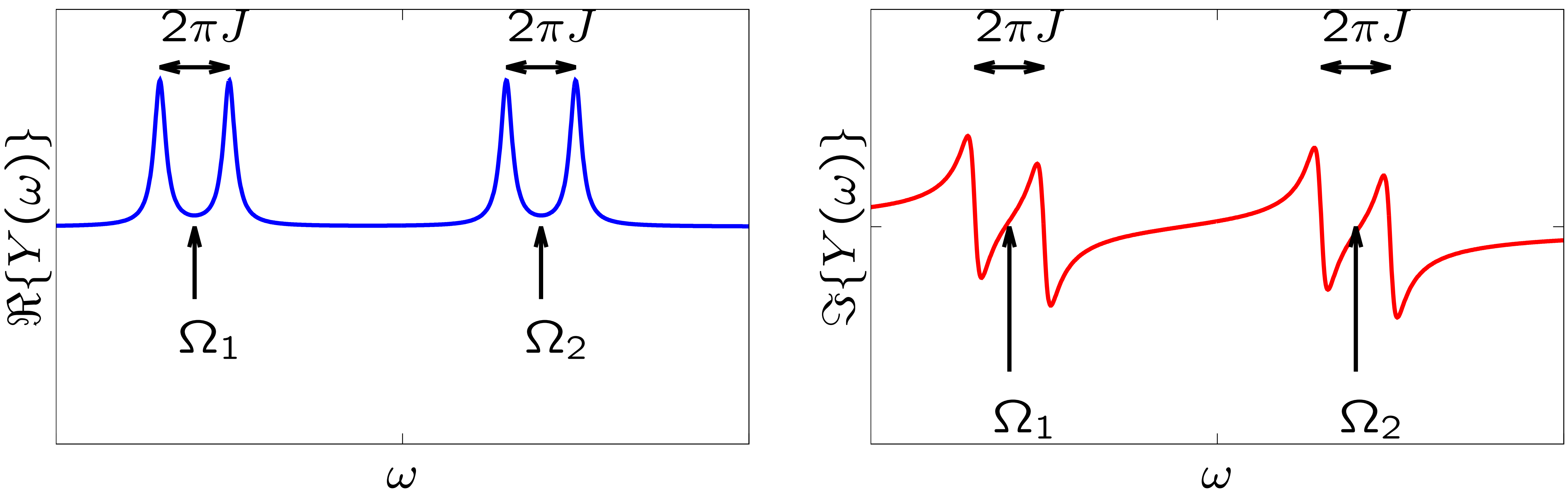
$$\widehat{M}_+ = \mathcal{N}\left(\gamma_1(\widehat{I}_{1x} + \mathrm{i}\widehat{I}_{1y}) + \gamma_2(\widehat{I}_{2x} + \mathrm{i}\widehat{I}_{2y})\right)$$

$$\begin{aligned}\mathrm{Tr}\left\{\mathscr{I}_{nx}(\mathscr{I}_{nx} + \mathrm{i}\mathscr{I}_{ny})\right\} &= 1\\ \mathrm{Tr}\left\{\mathscr{I}_{ny}(\mathscr{I}_{nx} + \mathrm{i}\mathscr{I}_{ny})\right\} &= \mathrm{i}\end{aligned}$$

$$\langle M_+\rangle = \mathrm{Tr}\{\widehat{\rho}(t)\widehat{M}_+\} \propto$$
$$\frac{\kappa}{4}\left(\mathrm{e}^{-R_{2,1}t}\left(\mathrm{e}^{\mathrm{i}(\Omega_1-\pi J)t} + \mathrm{e}^{\mathrm{i}(\Omega_1+\pi J)t}\right) + \mathrm{e}^{-R_{2,2}t}\left(\mathrm{e}^{\mathrm{i}(\Omega_2-\pi J)t} + \mathrm{e}^{\mathrm{i}(\Omega_2+\pi J)t}\right)\right)$$

$$\Re\{Y(\omega)\} = \frac{\mathcal{N}\gamma^2\hbar^2 B_0}{16k_\mathrm{B}T}\left(\frac{R_{2,1}}{R_{2,1}^2 + (\omega-\Omega_1+\pi J)^2} + \frac{R_{2,1}}{R_{2,1}^2 + (\omega-\Omega_1-\pi J)^2}\right.$$
$$\left. + \frac{R_{2,2}}{R_{2,2}^2 + (\omega-\Omega_2+\pi J)^2} + \frac{R_{2,2}}{R_{2,2}^2 + (\omega-\Omega_2-\pi J)^2}\right)$$

Spectrum

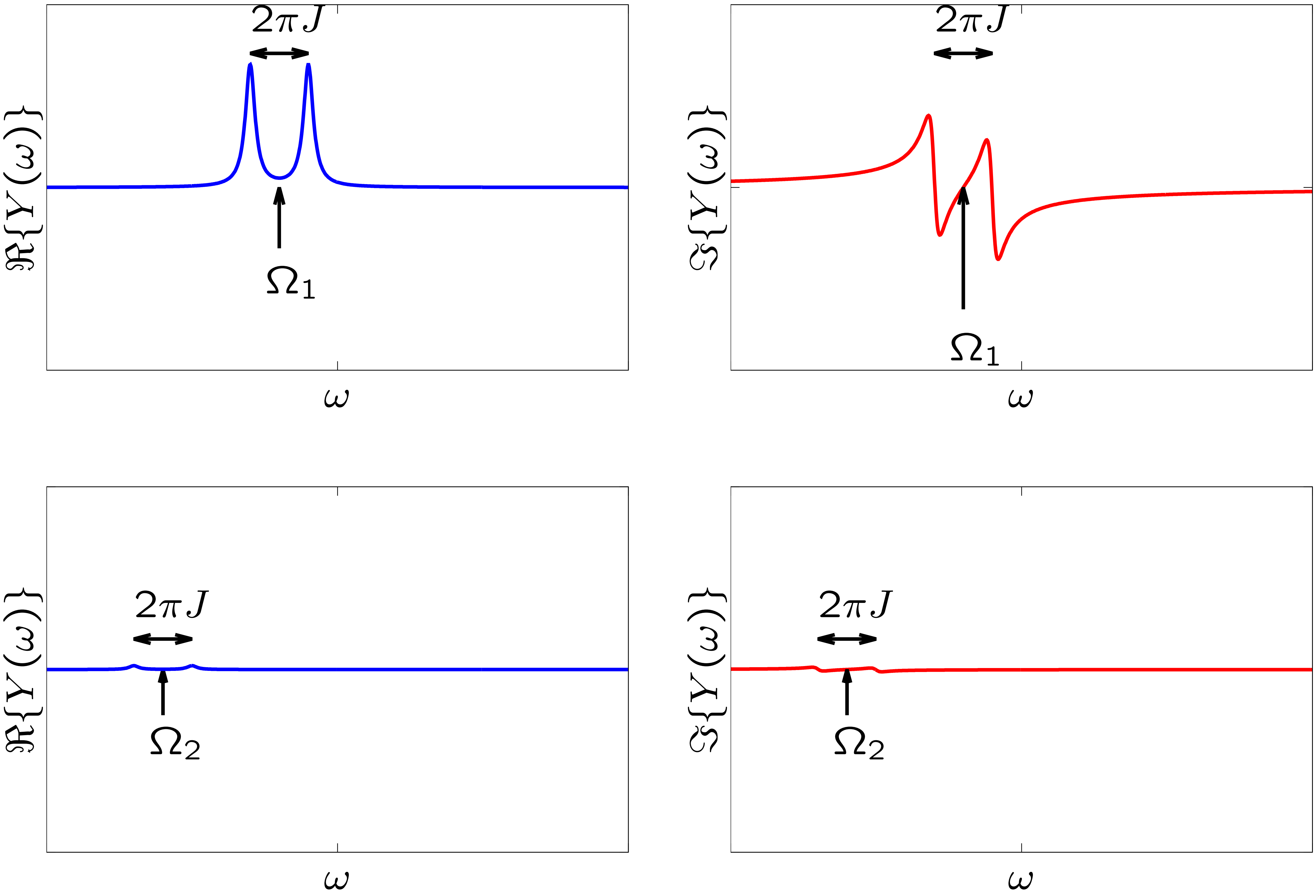


Homo- and heteronuclear pairs

Homonuclear: $\gamma_1 = \gamma_2$, $\mathscr{I}_{1j}, \mathscr{I}_{2j}$, e.g. $^{1}\mathrm{H}$–$^{1}\mathrm{H}$

Heteronuclear: $\gamma_1 \neq \gamma_2$, $\mathscr{I}_{j}, \mathscr{S}_{j}$, e.g. $^{1}\mathrm{H}$–$^{13}\mathrm{C}$

Homo- and heteronuclear pairs



HOMEWORK:

Spin echoes

Sections 10.5–10.8

Spin echoes