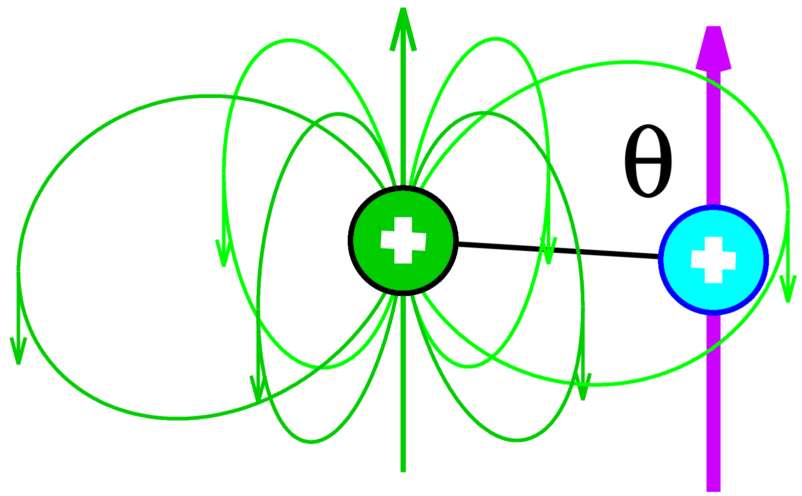
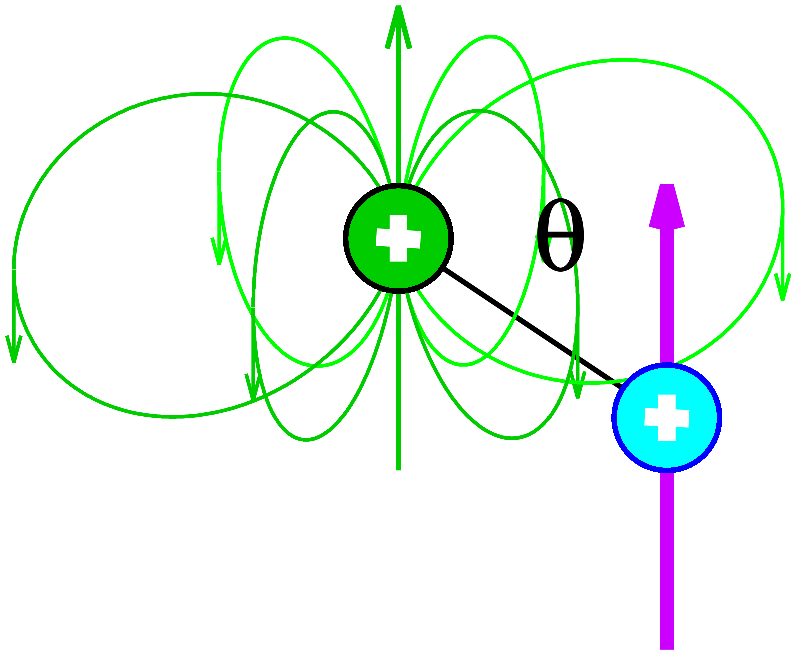
Lecture 6: Ensemble of non-interacting spins

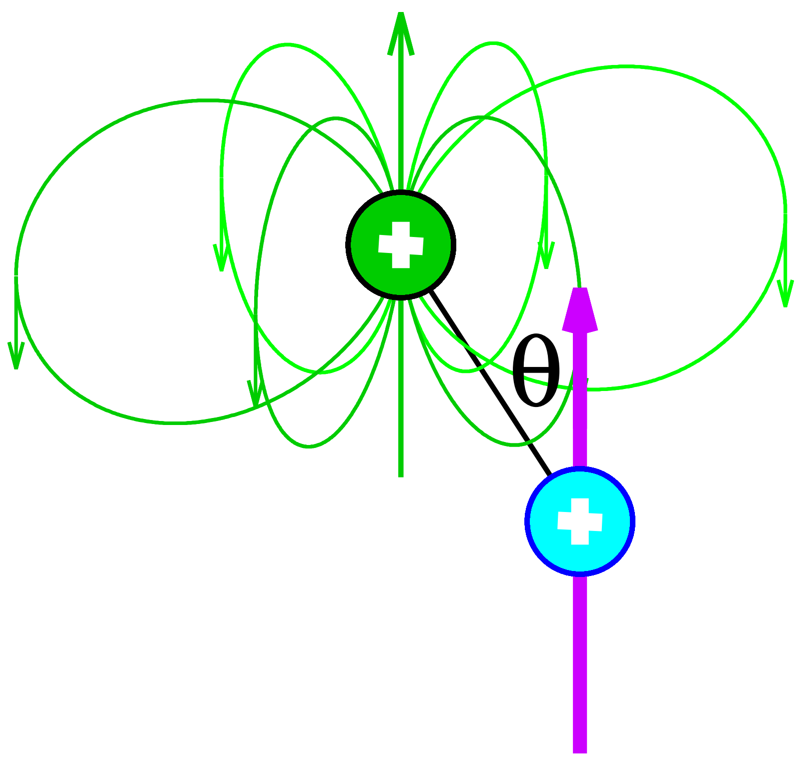
Classical interacting spin magnetic moments



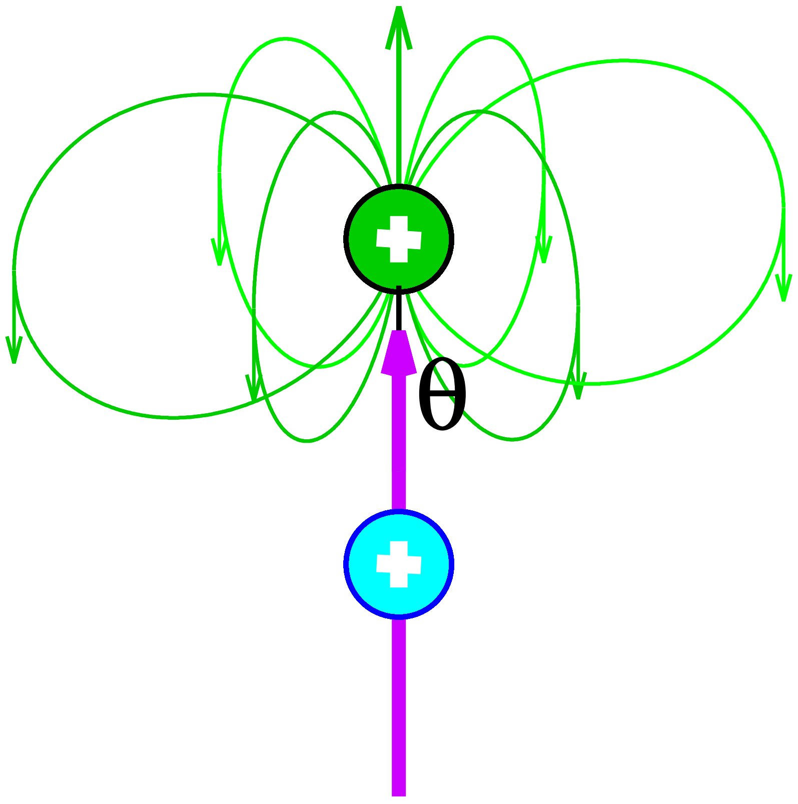
Classical interacting spin magnetic moments



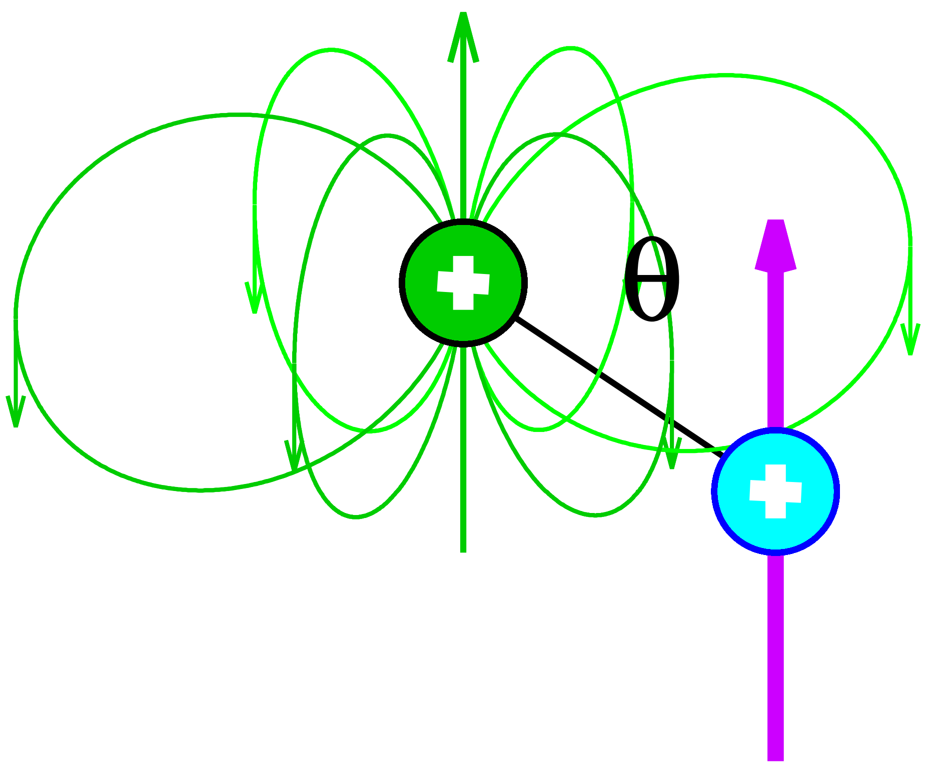
Classical interacting spin magnetic moments



Classical interacting spin magnetic moments

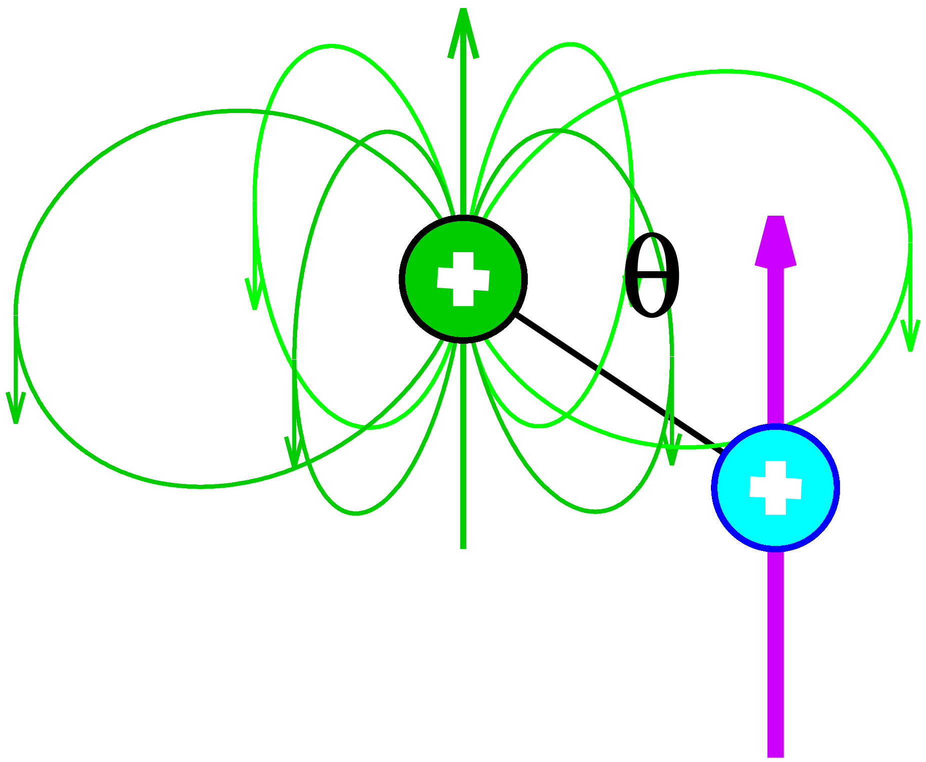


Classical interacting spin magnetic moments



$$\begin{pmatrix} B_{2,x} \\ B_{2,y} \\ B_{2,z} \end{pmatrix} = \frac{\mu_0}{4\pi r^5} \begin{pmatrix} 3r_x^2 - r^2 & 3r_x r_y & 3r_x r_z \\ 3r_x r_y & 3r_y^2 - r^2 & 3r_y r_z \\ 3r_x r_z & 3r_y r_z & 3r_z^2 - r^2 \end{pmatrix} \cdot \begin{pmatrix} \mu_{2,x} \\ \mu_{2,y} \\ \mu_{2,z} \end{pmatrix}$$

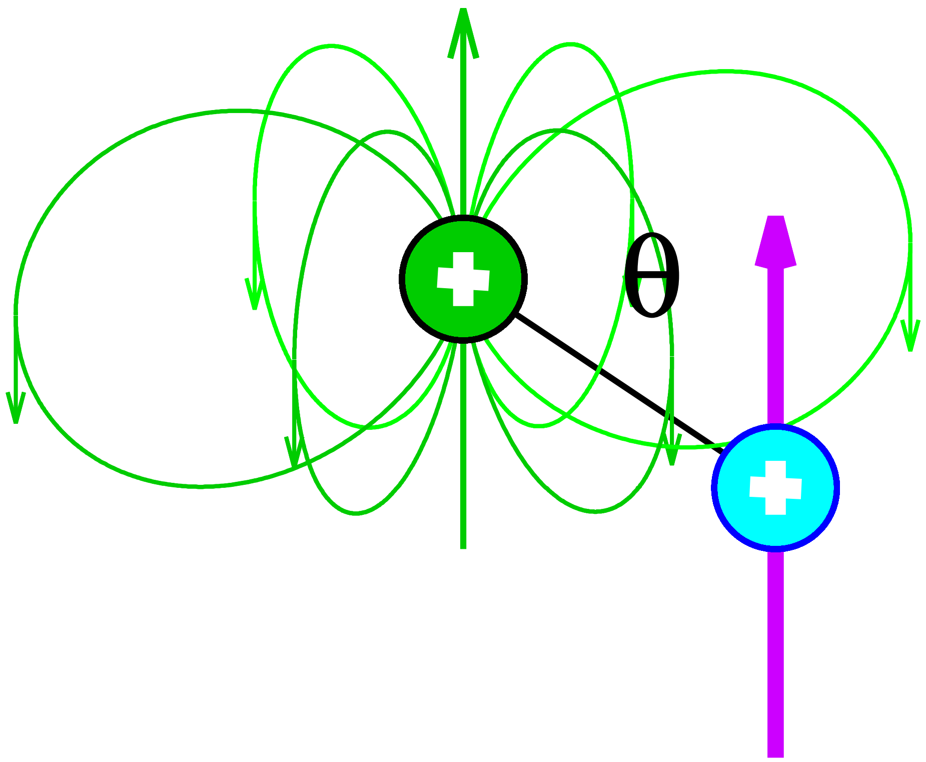
Classical interacting spin magnetic moments



$$\mathcal{E} = -\vec{\mu}_1 \cdot \vec{B}_2 = -\begin{pmatrix} \mu_{1,x} & \mu_{1,y} & \mu_{1,z} \end{pmatrix} \cdot \begin{pmatrix} B_{2,x} \\ B_{2,y} \\ B_{2,z} \end{pmatrix} =$$

$$-\frac{\mu_0}{4\pi r^5} \begin{pmatrix} \mu_{1,x} & \mu_{1,y} & \mu_{1,z} \end{pmatrix} \cdot \begin{pmatrix} 3r_x^2 - r^2 & 3r_x r_y & 3r_x r_z \\ 3r_x r_y & 3r_y^2 - r^2 & 3r_y r_z \\ 3r_x r_z & 3r_y r_z & 3r_z^2 - r^2 \end{pmatrix} \cdot \begin{pmatrix} \mu_{2,x} \\ \mu_{2,y} \\ \mu_{2,z} \end{pmatrix}$$

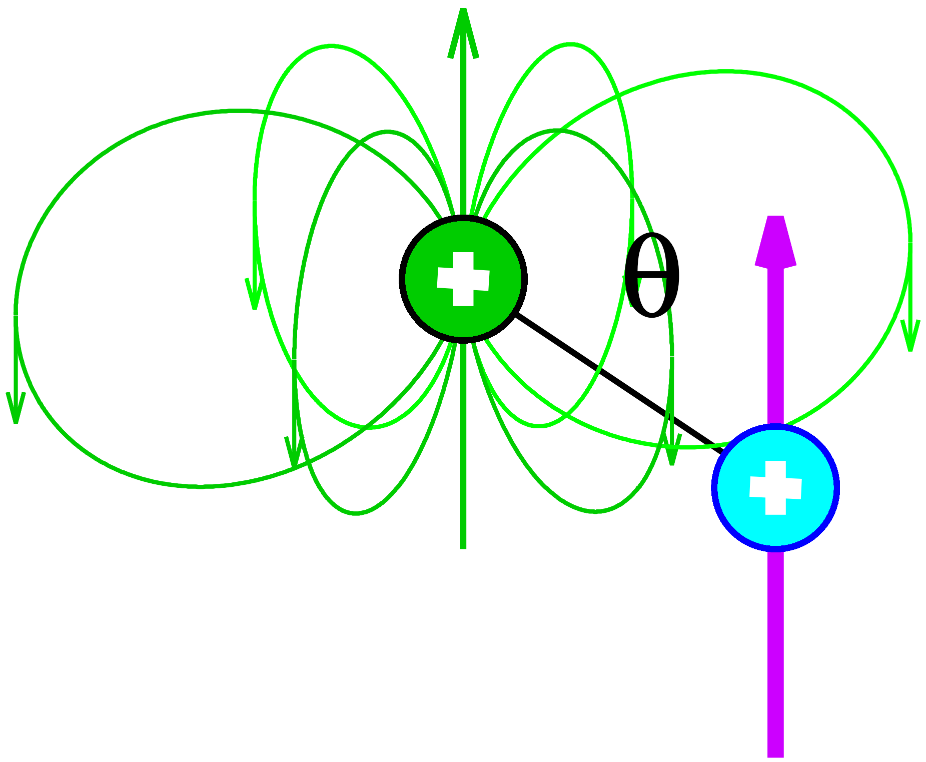
Classical interacting spin magnetic moments



$$\mathcal{E} = -\begin{pmatrix} \mu_{1,x} & \mu_{1,y} & \mu_{1,z} \end{pmatrix} \cdot \underline{D} \cdot \begin{pmatrix} \mu_{2,x} \\ \mu_{2,y} \\ \mu_{2,z} \end{pmatrix} =$$

$$-\frac{\mu_0}{4\pi r^5} \begin{pmatrix} \mu_{1,x} & \mu_{1,y} & \mu_{1,z} \end{pmatrix} \cdot \begin{pmatrix} 3r_x^2 - r^2 & 3r_x r_y & 3r_x r_z \\ 3r_x r_y & 3r_y^2 - r^2 & 3r_y r_z \\ 3r_x r_z & 3r_y r_z & 3r_z^2 - r^2 \end{pmatrix} \cdot \begin{pmatrix} \mu_{2,x} \\ \mu_{2,y} \\ \mu_{2,z} \end{pmatrix}$$

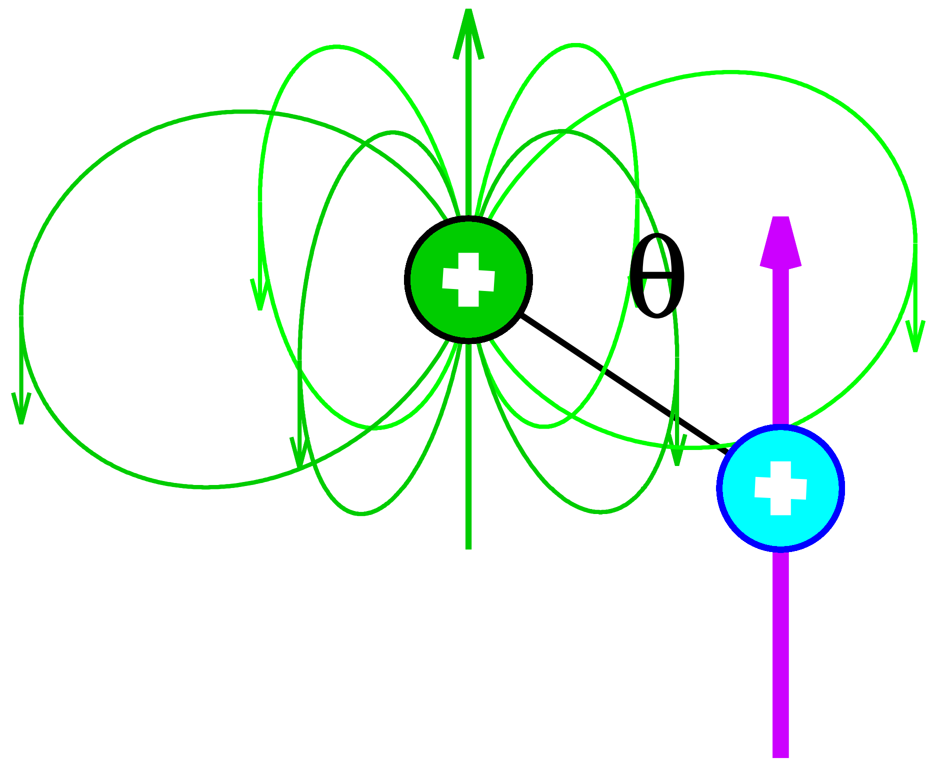
QM interacting spin magnetic moments



$$\hat{H}_D = -\begin{pmatrix} \hat{\mu}_{1,x} & \hat{\mu}_{1,y} & \hat{\mu}_{1,z} \end{pmatrix} \cdot \underline{D} \cdot \begin{pmatrix} \hat{\mu}_{2,x} \\ \hat{\mu}_{2,y} \\ \hat{\mu}_{2,z} \end{pmatrix} =$$

$$-\frac{\mu_0 \gamma_1 \gamma_2}{4\pi r^5} \begin{pmatrix} \hat{I}_{1,x} & \hat{I}_{1,y} & \hat{I}_{1,z} \end{pmatrix} \cdot \begin{pmatrix} 3r_x^2 - r^2 & 3r_x r_y & 3r_x r_z \\ 3r_x r_y & 3r_y^2 - r^2 & 3r_y r_z \\ 3r_x r_z & 3r_y r_z & 3r_z^2 - r^2 \end{pmatrix} \cdot \begin{pmatrix} \hat{I}_{2,x} \\ \hat{I}_{2,y} \\ \hat{I}_{2,z} \end{pmatrix}$$

QM interacting spin magnetic moments

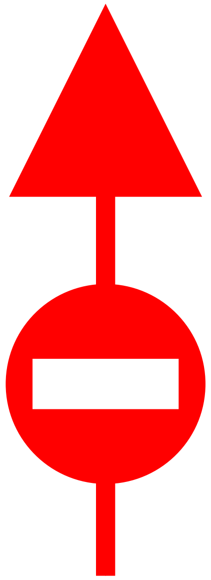


$$\hat{H}_D = -\frac{\mu_0 \gamma_1 \gamma_2}{4\pi r^5}((3r_x^2 - r^2)\hat{I}_{1,x}\hat{I}_{2,x} + 3r_x r_y \hat{I}_{1,x}\hat{I}_{2,y} + 3r_x r_z \hat{I}_{1,x}\hat{I}_{2,z}$$

$$+3r_y r_x \hat{I}_{1,y}\hat{I}_{2,x} + (3r_y^2 - r^2)\hat{I}_{1,y}\hat{I}_{2,y} + 3r_y r_z \hat{I}_{1,y}\hat{I}_{2,z}$$

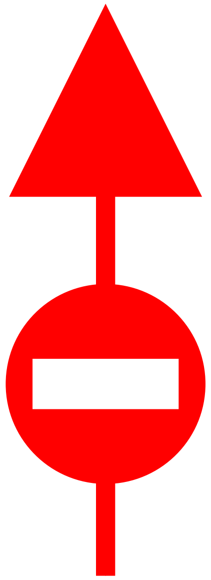
$$+3r_z r_x \hat{I}_{1,z}\hat{I}_{2,x} + 3r_z r_y \hat{I}_{1,z}\hat{I}_{2,y}(3r_z^2 - r^2)\hat{I}_{1,z}\hat{I}_{2,z}$$

1 particle:



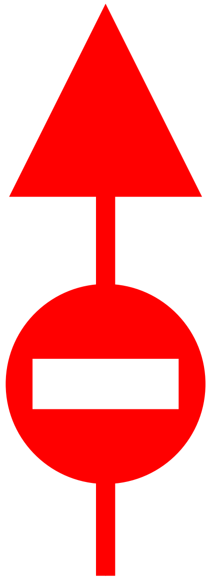
$$\Psi(x, y, z, c_\alpha)$$

1 particle:



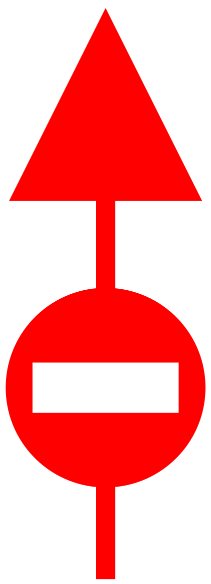
$$\Psi(x, y, z, c_\alpha)$$

1 particle:



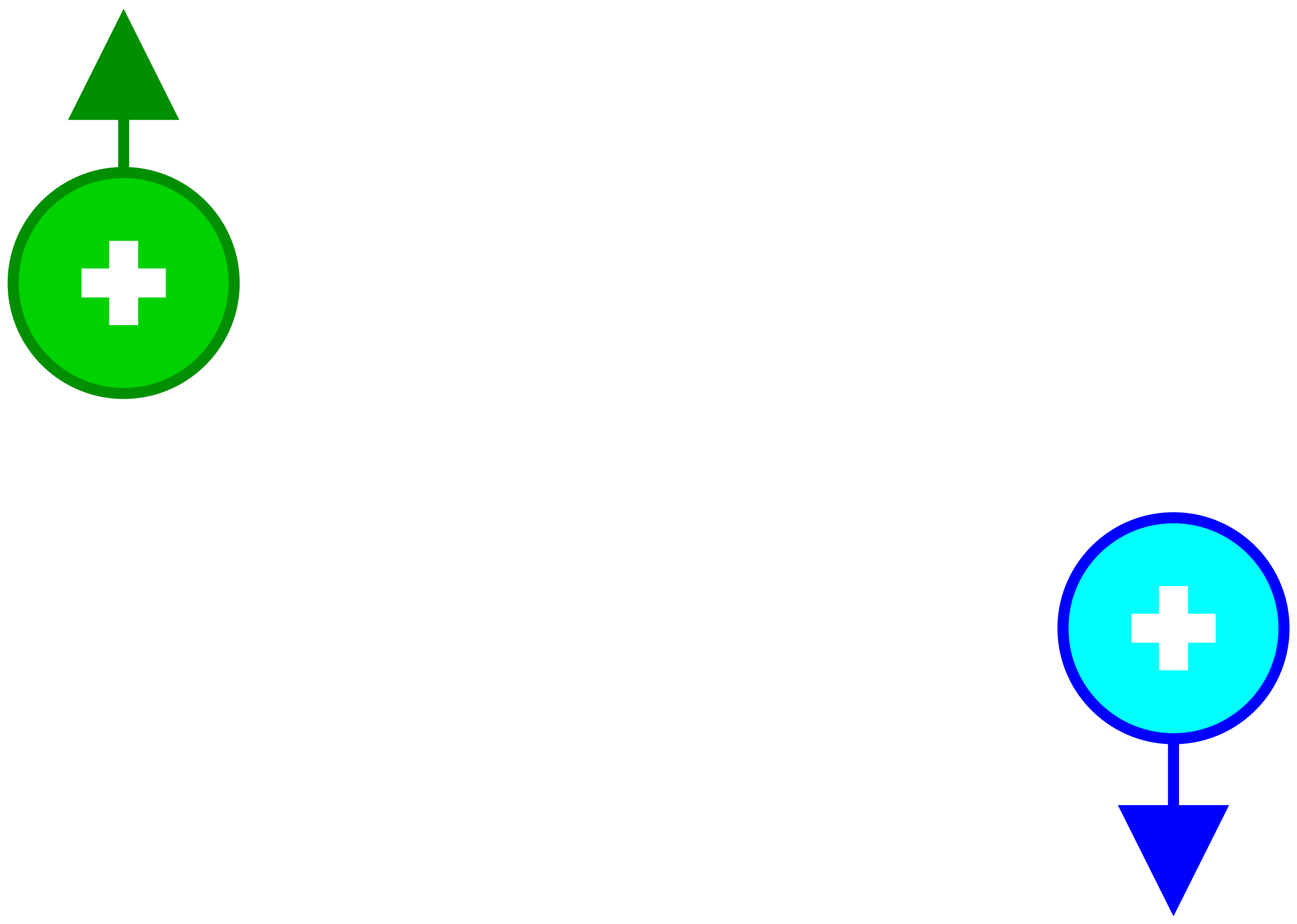
$$\Psi = \phi(x, y, z) \cdot \psi(c_\alpha)$$

1 particle:



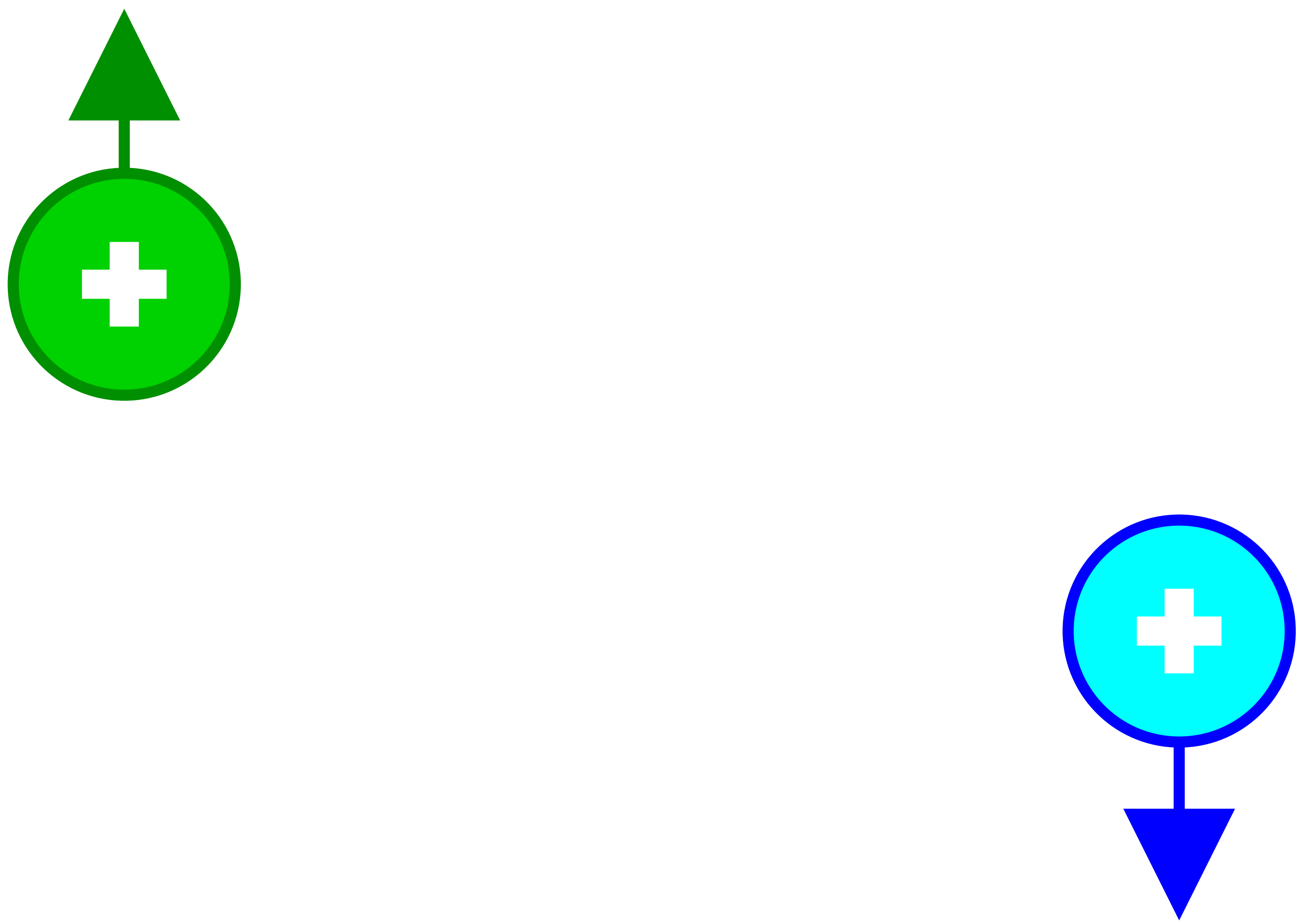
$$\Psi = \phi(x, y, z) \cdot \begin{pmatrix} c_\alpha \\ c_\beta \end{pmatrix}$$

2 particles = 1 pair:



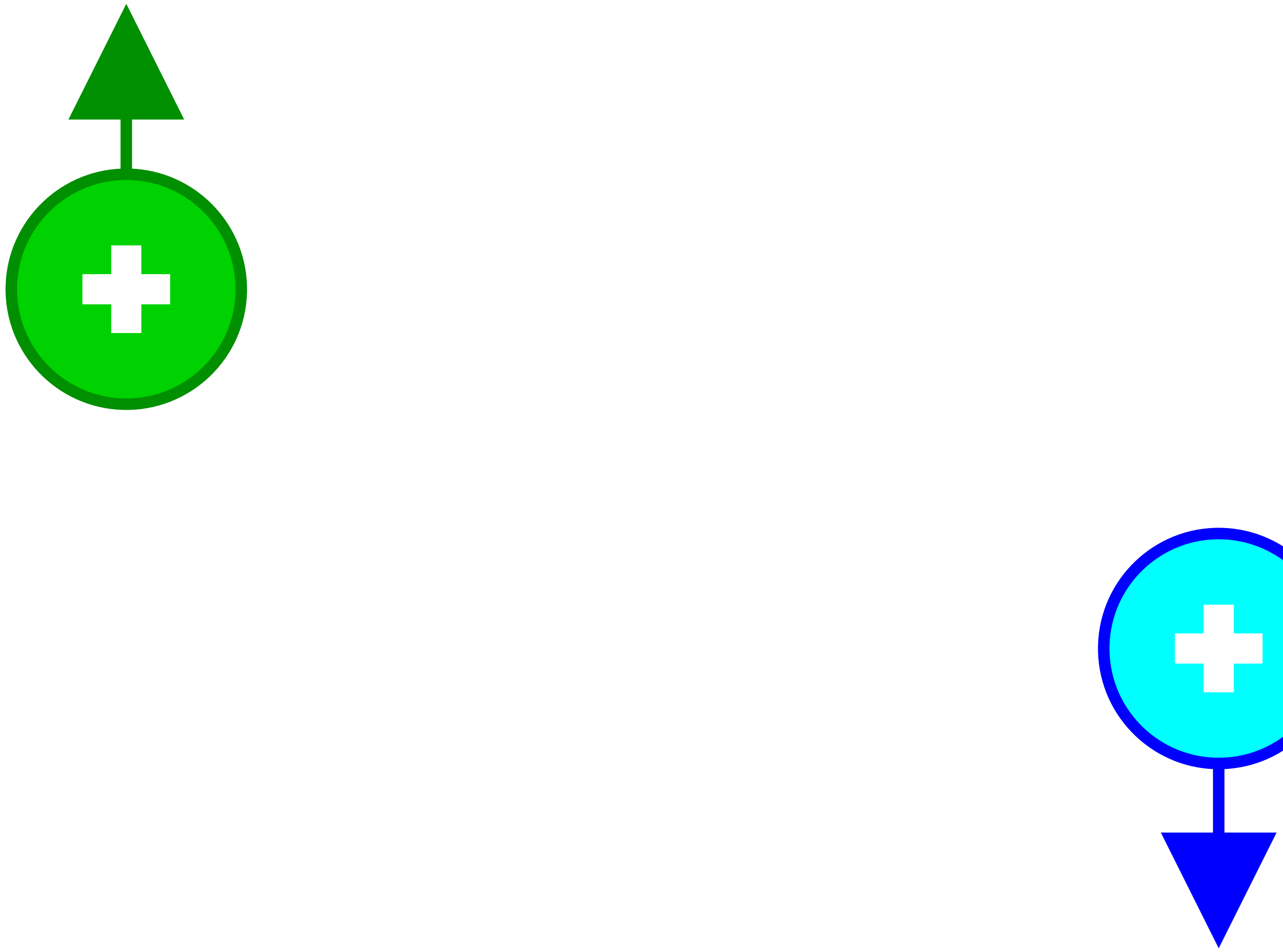
$$\Psi(x_1, y_1, z_1, x_2, y_2, z_2, c_{\alpha,1}, c_{\alpha,2})$$

2 particles = 1 pair:



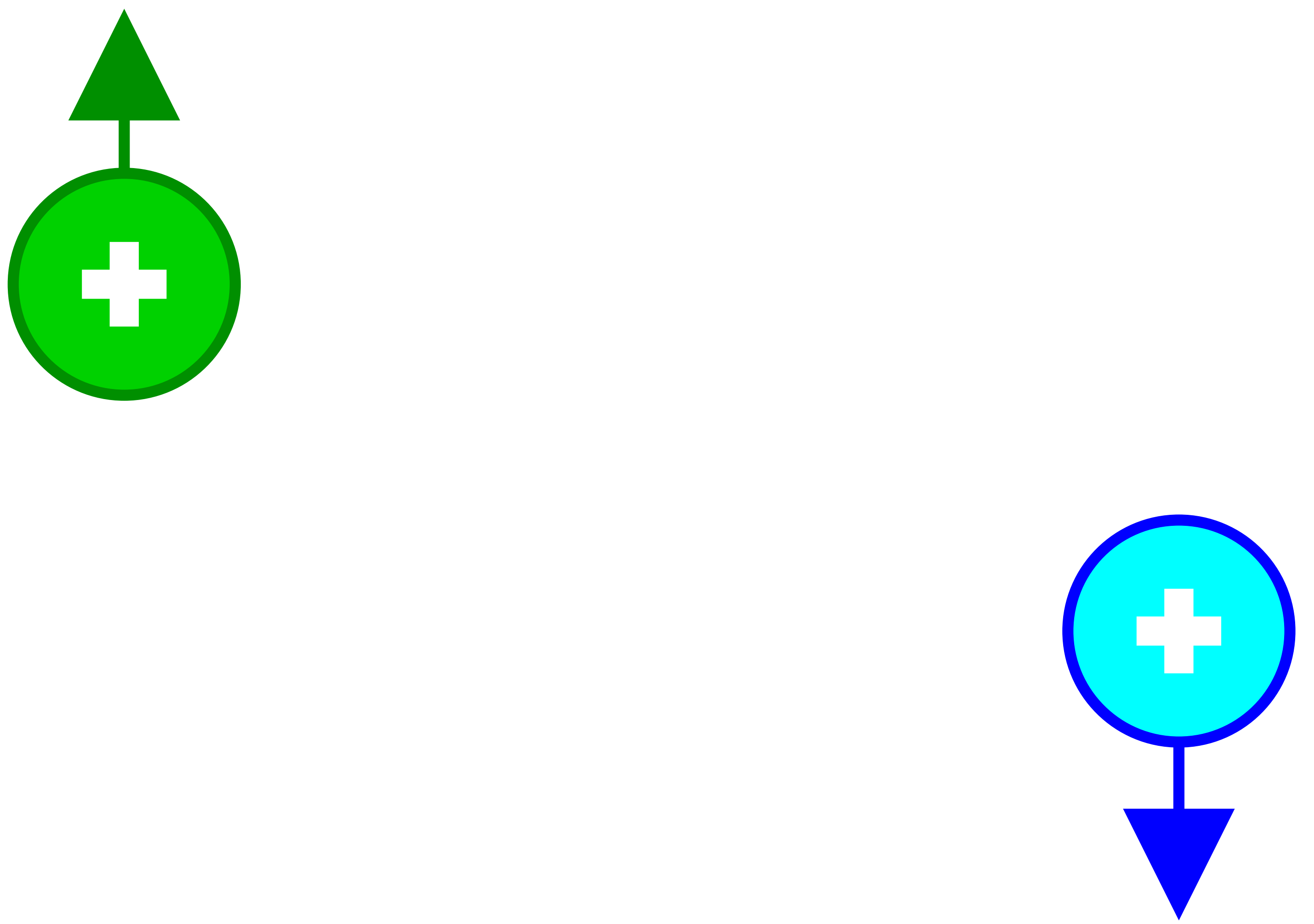
$$\Psi(x_1, y_1, z_1, x_2, y_2, z_2, c_{\alpha,1}, c_{\alpha,2})$$

2 particles = 1 pair:



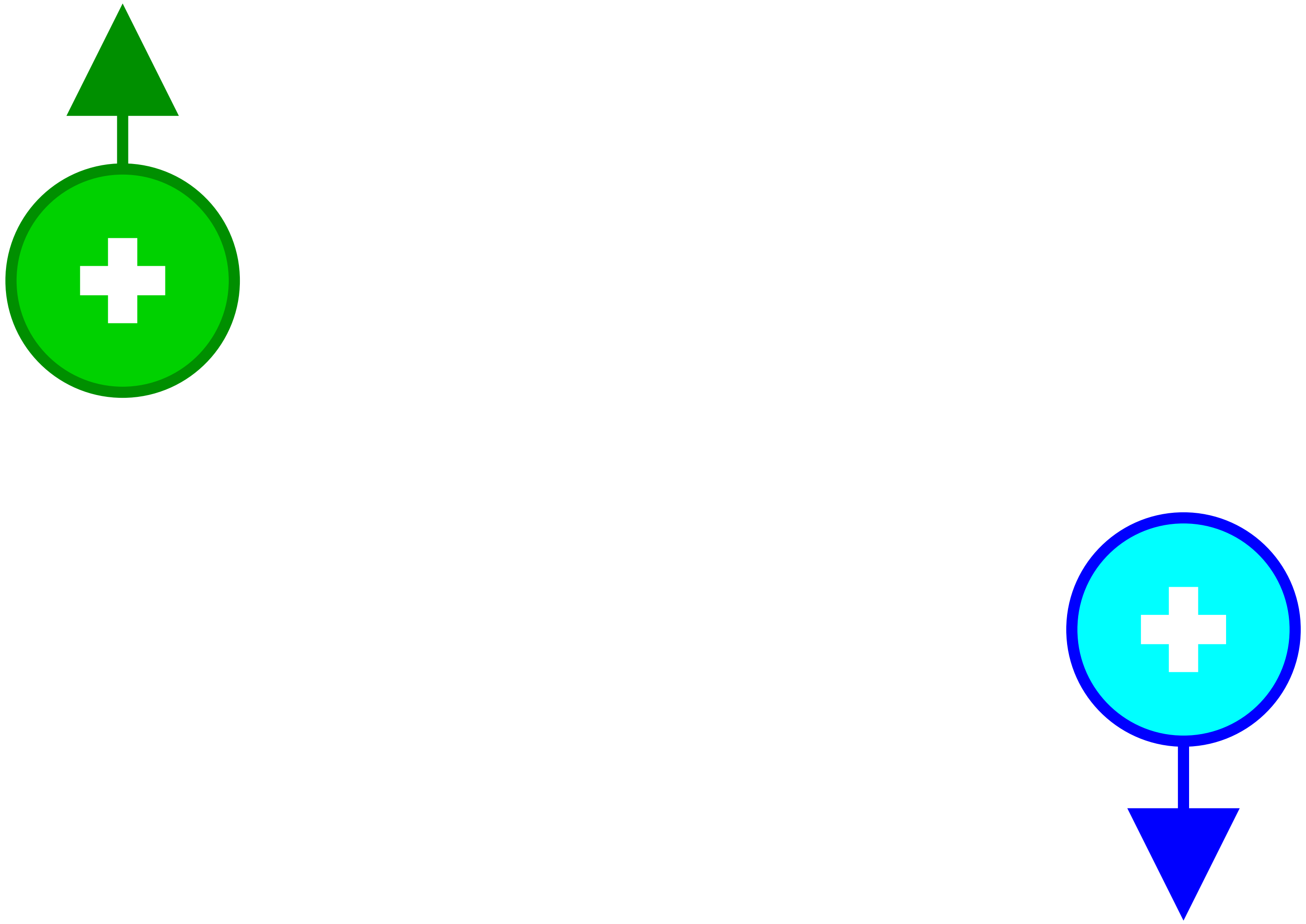
$$\Psi = \phi(x_1, y_1, z_1, x_2, y_2, z_2) \cdot \psi(c_{\alpha,1}, c_{\alpha,2})$$

2 particles = 1 pair:



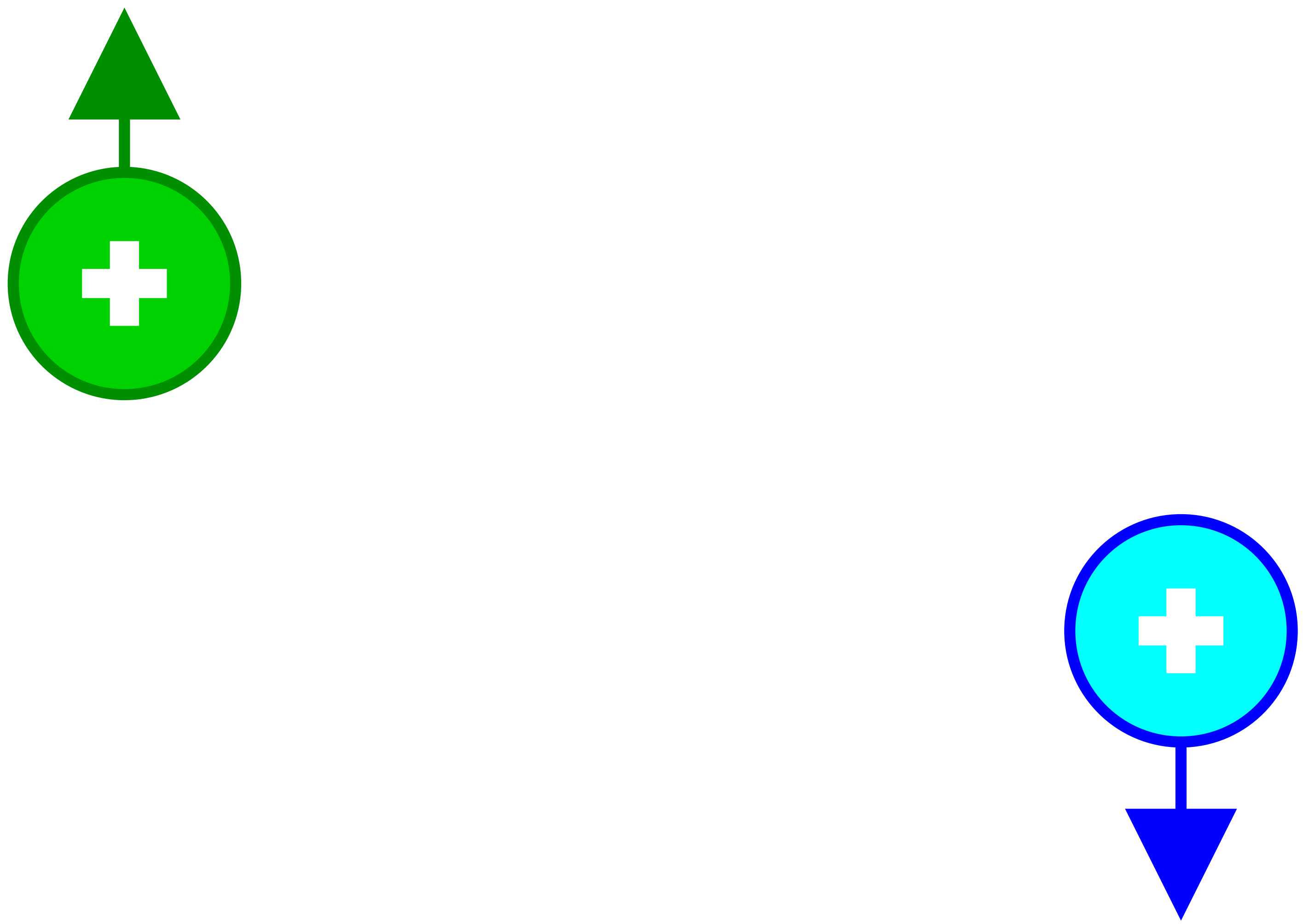
$$\Psi = \phi(x_1 \ldots) \cdot \psi_1(c_{\alpha,1}) \cdot \psi_2(c_{\alpha,2})$$

2 particles = 1 pair:



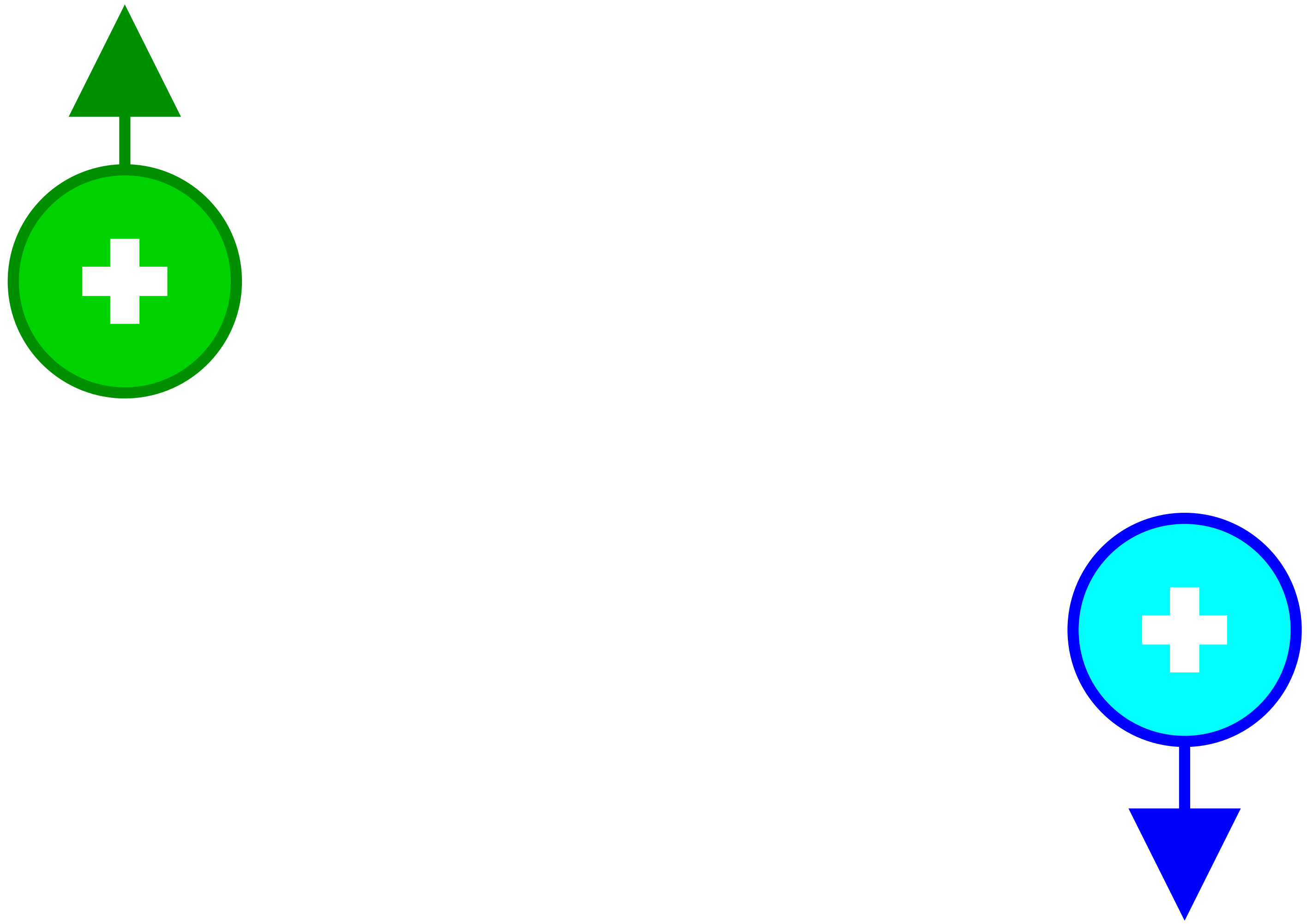
$$\Psi = \phi(x_1 \ldots) \cdot \begin{pmatrix} c_{\alpha,1} \\ c_{\beta,1} \end{pmatrix} \cdot \psi_2(c_{\alpha,2})$$

2 particles = 1 pair:



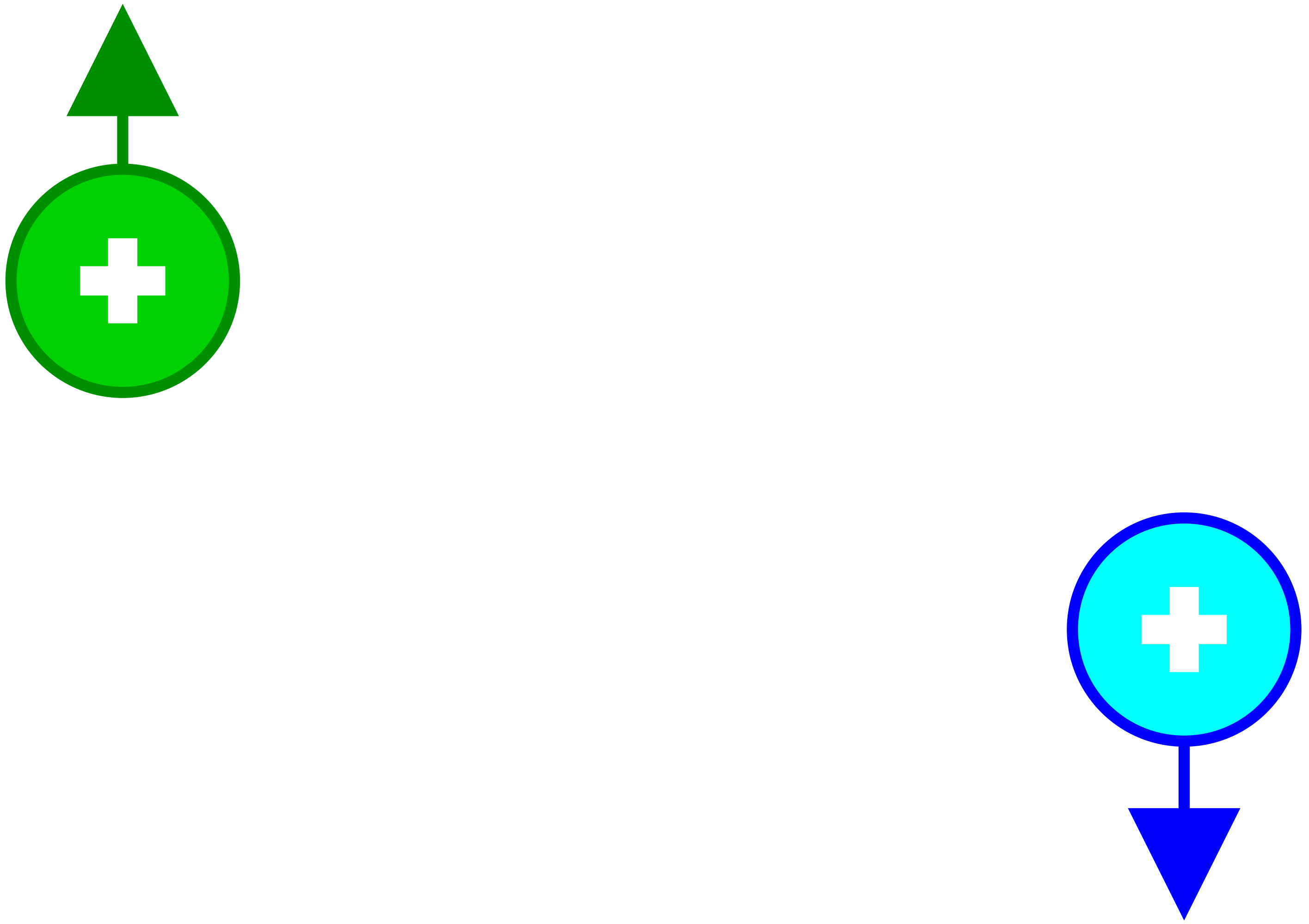
$$\Psi = \phi(x_1 \ldots) \cdot \begin{pmatrix} c_{\alpha,1} \cdot \psi_2(c_{\alpha,2}) \\ c_{\beta,1} \cdot \psi_2(c_{\alpha,2}) \end{pmatrix}$$

2 particles = 1 pair:



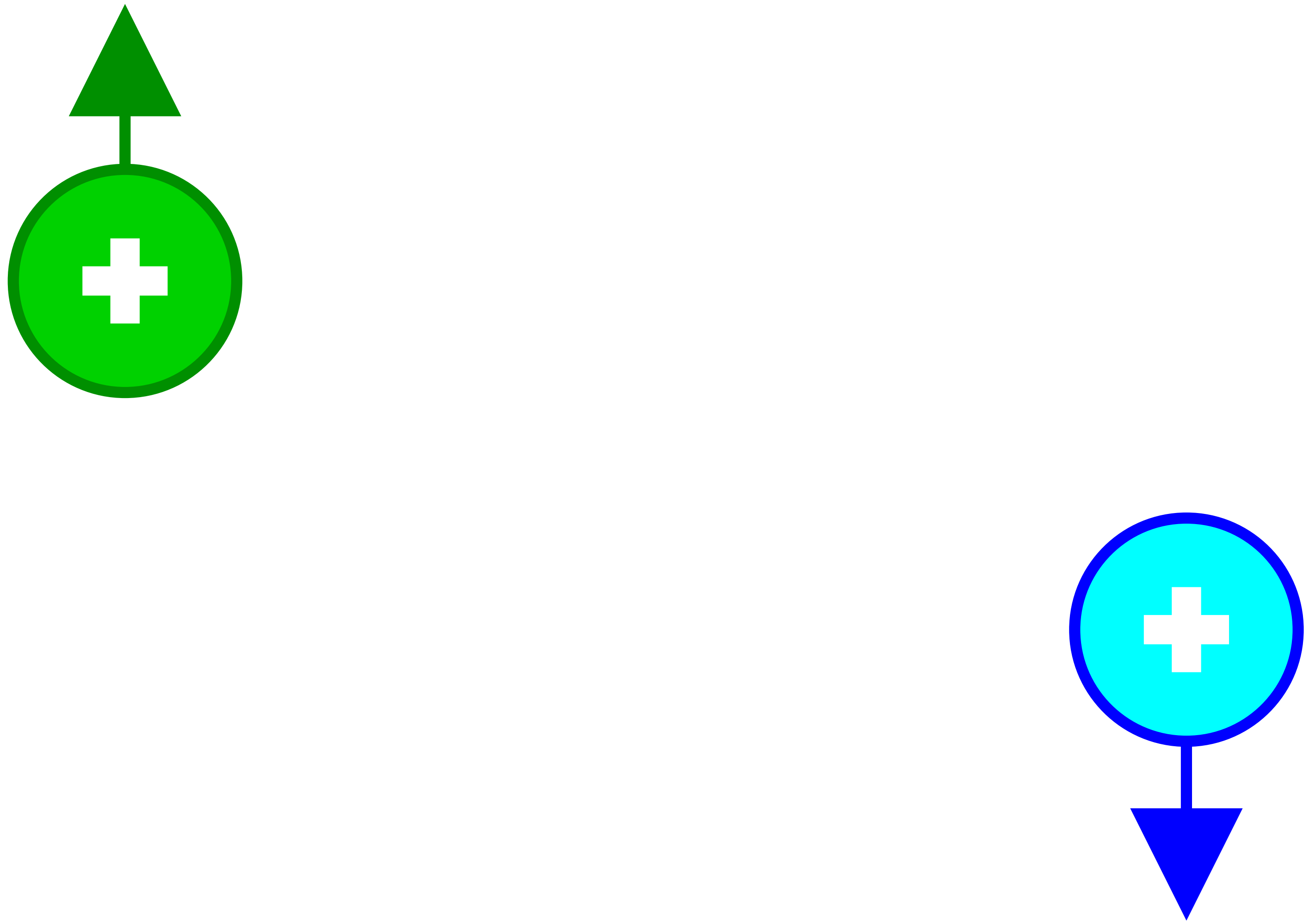
$$\Psi = \phi(x_1 \ldots) \cdot \begin{pmatrix} c_{\alpha,1} \begin{pmatrix} c_{\alpha,2} \\ c_{\beta,2} \end{pmatrix} \\ c_{\beta,1} \begin{pmatrix} c_{\alpha,2} \\ c_{\beta,2} \end{pmatrix} \end{pmatrix}$$

2 particles = 1 pair:



$$\Psi = \phi(x_1 \ldots) \cdot \begin{pmatrix} c_{\alpha,1} c_{\alpha,2} \\ c_{\alpha,1} c_{\beta,2} \\ c_{\beta,1} c_{\alpha,2} \\ c_{\beta,1} c_{\beta,2} \end{pmatrix}$$

2 particles = 1 pair:



$$\Psi = \phi(x_1 \ldots) \cdot \begin{pmatrix} c_{\alpha\alpha} \\ c_{\alpha\beta} \\ c_{\beta\alpha} \\ c_{\beta\beta} \end{pmatrix}$$

Direct product of wave functions (vectors)

$$\begin{pmatrix} c_{\alpha,1} \\ c_{\beta,1} \end{pmatrix} \otimes \begin{pmatrix} c_{\alpha,2} \\ c_{\beta,2} \end{pmatrix} = \begin{pmatrix} c_{\alpha,1} \begin{pmatrix} c_{\alpha,2} \\ c_{\beta,2} \end{pmatrix} \\ c_{\beta,1} \begin{pmatrix} c_{\alpha,2} \\ c_{\beta,2} \end{pmatrix} \end{pmatrix} = \begin{pmatrix} c_{\alpha,1} c_{\alpha,2} \\ c_{\alpha,1} c_{\beta,2} \\ c_{\beta,1} c_{\alpha,2} \\ c_{\beta,1} c_{\beta,2} \end{pmatrix} \equiv \begin{pmatrix} c_{\alpha\alpha} \\ c_{\alpha\beta} \\ c_{\beta\alpha} \\ c_{\beta\beta} \end{pmatrix}$$

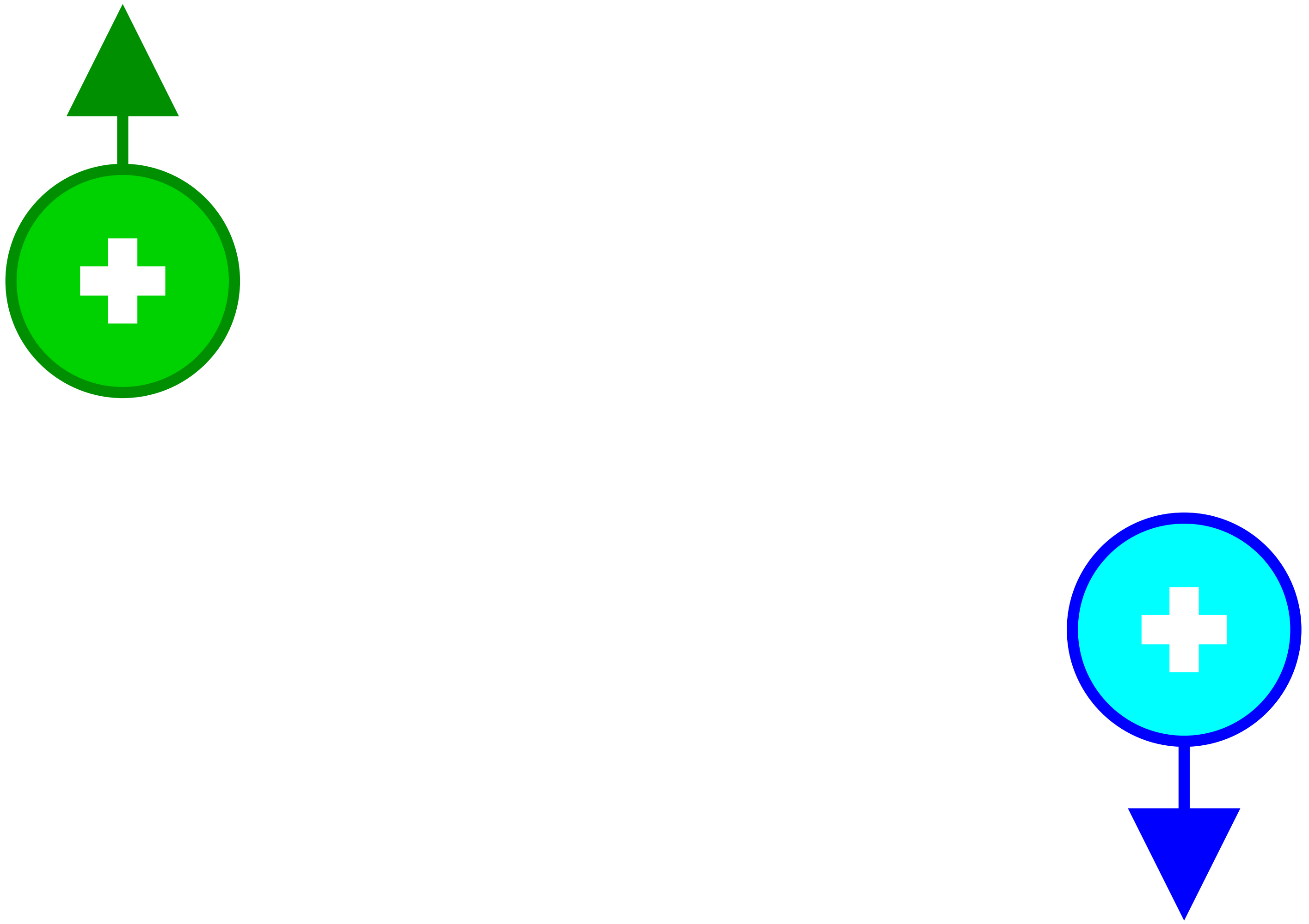
Direct product of matrices

$$\hat{A} \otimes \hat{B} = \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \otimes \begin{pmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{pmatrix} =$$

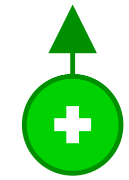
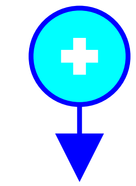
$$\begin{pmatrix} A_{11} \begin{pmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{pmatrix} & A_{12} \begin{pmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{pmatrix} \\ A_{21} \begin{pmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{pmatrix} & A_{22} \begin{pmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{pmatrix} \end{pmatrix} =$$

$$\begin{pmatrix} A_{11}B_{11} & A_{11}B_{12} & A_{12}B_{11} & A_{12}B_{12} \\ A_{11}B_{21} & A_{11}B_{22} & A_{12}B_{21} & A_{12}B_{22} \\ A_{21}B_{11} & A_{21}B_{12} & A_{22}B_{11} & A_{22}B_{12} \\ A_{21}B_{21} & A_{21}B_{22} & A_{22}B_{21} & A_{22}B_{22} \end{pmatrix}$$

2 particles = 1 pair:



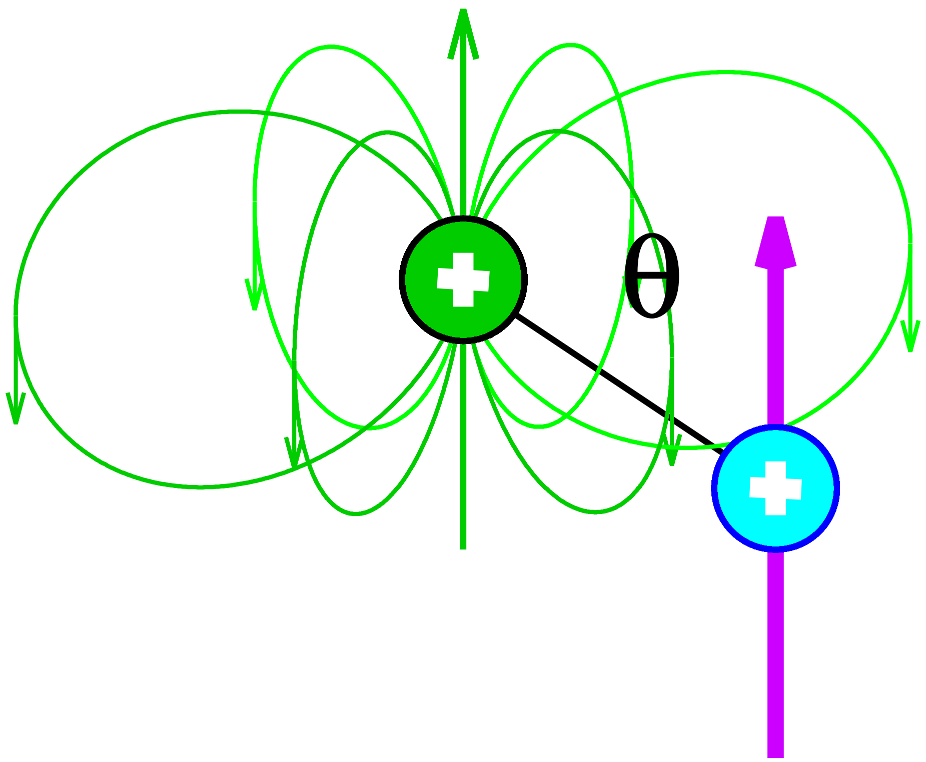
$$\psi_1\psi_2 = \begin{pmatrix} c_{\alpha\alpha} \\ c_{\alpha\beta} \\ c_{\beta\alpha} \\ c_{\beta\beta} \end{pmatrix}$$

1 000 000 000 000 000 000 000 000 000 000 pairs   :

$$\hat{\rho} = \begin{pmatrix} \overline{c_{\alpha\alpha}c^*_{\alpha\alpha}} & \overline{c_{\alpha\alpha}c^*_{\alpha\beta}} & \overline{c_{\alpha\alpha}c^*_{\beta\alpha}} & \overline{c_{\alpha\alpha}c^*_{\beta\beta}} \\ \overline{c_{\alpha\beta}c^*_{\alpha\alpha}} & \overline{c_{\alpha\beta}c^*_{\alpha\beta}} & \overline{c_{\alpha\beta}c^*_{\beta\alpha}} & \overline{c_{\alpha\beta}c^*_{\beta\beta}} \\ \overline{c_{\beta\alpha}c^*_{\alpha\alpha}} & \overline{c_{\beta\alpha}c^*_{\alpha\beta}} & \overline{c_{\beta\alpha}c^*_{\beta\alpha}} & \overline{c_{\beta\alpha}c^*_{\beta\beta}} \\ \overline{c_{\beta\beta}c^*_{\alpha\alpha}} & \overline{c_{\beta\beta}c^*_{\alpha\beta}} & \overline{c_{\beta\beta}c^*_{\beta\alpha}} & \overline{c_{\beta\beta}c^*_{\beta\beta}} \end{pmatrix}$$

4×4 matrix $\Rightarrow$ 16 4×4 basis matrices

Products of spin operators in Hamiltonian



$$\hat{H}_D = -\frac{\mu_0 \gamma_1 \gamma_2}{4\pi r^5}((3r_x^2 - r^2)\hat{I}_{1,x}\hat{I}_{2,x} + 3r_x r_y \hat{I}_{1,x}\hat{I}_{2,y} + 3r_x r_z \hat{I}_{1,x}\hat{I}_{2,z}$$

$$+3r_y r_x \hat{I}_{1,y}\hat{I}_{2,x} + (3r_y^2 - r^2)\hat{I}_{1,y}\hat{I}_{2,y} + 3r_y r_z \hat{I}_{1,y}\hat{I}_{2,z}$$

$$+3r_z r_x \hat{I}_{1,z}\hat{I}_{2,x} + 3r_z r_y \hat{I}_{1,z}\hat{I}_{2,y}(3r_z^2 - r^2)\hat{I}_{1,z}\hat{I}_{2,z}$$

Product operators as basis

$$2 \cdot \mathscr{I}_t(1) \otimes \mathscr{I}_t(2) = \mathscr{I}_t(12) \tag{1}$$
$$2 \cdot \mathscr{I}_x(1) \otimes \mathscr{I}_t(2) = \mathscr{I}_{1x}(12) \tag{2}$$
$$2 \cdot \mathscr{I}_y(1) \otimes \mathscr{I}_t(2) = \mathscr{I}_{1y}(12) \tag{3}$$
$$2 \cdot \mathscr{I}_z(1) \otimes \mathscr{I}_t(2) = \mathscr{I}_{1z}(12) \tag{4}$$
$$2 \cdot \mathscr{I}_t(1) \otimes \mathscr{I}_x(2) = \mathscr{I}_{2x}(12) \tag{5}$$
$$2 \cdot \mathscr{I}_t(1) \otimes \mathscr{I}_y(2) = \mathscr{I}_{2y}(12) \tag{6}$$
$$2 \cdot \mathscr{I}_t(1) \otimes \mathscr{I}_z(2) = \mathscr{I}_{2z}(12) \tag{7}$$
$$2 \cdot \mathscr{I}_x(1) \otimes \mathscr{I}_x(2) = 2\mathscr{I}_{1x}\mathscr{I}_{2x}(12) \tag{8}$$
$$2 \cdot \mathscr{I}_x(1) \otimes \mathscr{I}_y(2) = 2\mathscr{I}_{1x}\mathscr{I}_{2y}(12) \tag{9}$$
$$2 \cdot \mathscr{I}_x(1) \otimes \mathscr{I}_z(2) = 2\mathscr{I}_{1x}\mathscr{I}_{2z}(12) \tag{10}$$
$$2 \cdot \mathscr{I}_y(1) \otimes \mathscr{I}_x(2) = 2\mathscr{I}_{1y}\mathscr{I}_{2x}(12) \tag{11}$$
$$2 \cdot \mathscr{I}_y(1) \otimes \mathscr{I}_y(2) = 2\mathscr{I}_{1y}\mathscr{I}_{2y}(12) \tag{12}$$
$$2 \cdot \mathscr{I}_y(1) \otimes \mathscr{I}_z(2) = 2\mathscr{I}_{1y}\mathscr{I}_{2z}(12) \tag{13}$$
$$2 \cdot \mathscr{I}_z(1) \otimes \mathscr{I}_x(2) = 2\mathscr{I}_{1z}\mathscr{I}_{2x}(12) \tag{14}$$
$$2 \cdot \mathscr{I}_z(1) \otimes \mathscr{I}_y(2) = 2\mathscr{I}_{1z}\mathscr{I}_{2y}(12) \tag{15}$$
$$2 \cdot \mathscr{I}_z(1) \otimes \mathscr{I}_z(2) = 2\mathscr{I}_{1z}\mathscr{I}_{2z}(12), \tag{16}$$

Product operators as basis: examples

$$2 \cdot \mathscr{I}_t(1) \otimes \mathscr{I}_t(2) = 2 \cdot \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \cdot \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \equiv \mathscr{I}_t$$

$$2 \cdot \mathscr{I}_x(1) \otimes \mathscr{I}_t(2) = 2 \cdot \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \cdot \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \equiv \mathscr{I}_{1x}$$

$$2 \cdot \mathscr{I}_t(1) \otimes \mathscr{I}_x(2) = 2 \cdot \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \cdot \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \equiv \mathscr{I}_{2x}$$

Density matrix: interpretation

$$\hat{\rho} = \begin{pmatrix} \overline{c_{\alpha\alpha}c^*_{\alpha\alpha}} & \overline{c_{\alpha\alpha}c^*_{\alpha\beta}} & \overline{c_{\alpha\alpha}c^*_{\beta\alpha}} & \overline{c_{\alpha\alpha}c^*_{\beta\beta}} \\ \overline{c_{\alpha\beta}c^*_{\alpha\alpha}} & \overline{c_{\alpha\beta}c^*_{\alpha\beta}} & \overline{c_{\alpha\beta}c^*_{\beta\alpha}} & \overline{c_{\alpha\beta}c^*_{\beta\beta}} \\ \overline{c_{\beta\alpha}c^*_{\alpha\alpha}} & \overline{c_{\beta\alpha}c^*_{\alpha\beta}} & \overline{c_{\beta\alpha}c^*_{\beta\alpha}} & \overline{c_{\beta\alpha}c^*_{\beta\beta}} \\ \overline{c_{\beta\beta}c^*_{\alpha\alpha}} & \overline{c_{\beta\beta}c^*_{\alpha\beta}} & \overline{c_{\beta\beta}c^*_{\beta\alpha}} & \overline{c_{\beta\beta}c^*_{\beta\beta}} \end{pmatrix}$$

$$\hat{\rho} = C_t\mathscr{I}_t + C_{1x}\mathscr{I}_{1x} + C_{1y}\mathscr{I}_{1y} + C_{1z}\mathscr{I}_{1z} + C_{2x}\mathscr{I}_{2x} + C_{2y}\mathscr{I}_{2y} + \ldots$$

Matrices $\mathscr{I}_t, \mathscr{I}_{1x}, \mathscr{I}_{1y}, \mathscr{I}_{1z}, \mathscr{I}_{2x}, \mathscr{I}_{2y} \ldots$:
features (polarizations) of the mixed state

Coefficients $C_t, C_{1x}, C_{1y}, C_{1z}, C_{2x}, C_{2y} \ldots$:
how much individual features contribute to the actual state

Density matrix: populations

4 populations (real numbers),

3 independent ($\overline{c_{\alpha\alpha}c^*_{\alpha\alpha}} + \overline{c_{\alpha\beta}c^*_{\alpha\beta}} + \overline{c_{\beta\alpha}c^*_{\beta\alpha}} + \overline{c_{\beta\beta}c^*_{\beta\beta}} = 1$):

$$\hat{\rho} = \begin{pmatrix} \overline{c_{\alpha\alpha}c^*_{\alpha\alpha}} & \overline{c_{\alpha\alpha}c^*_{\alpha\beta}} & \overline{c_{\alpha\alpha}c^*_{\beta\alpha}} & \overline{c_{\alpha\alpha}c^*_{\beta\beta}} \\ \overline{c_{\alpha\beta}c^*_{\alpha\alpha}} & \overline{c_{\alpha\beta}c^*_{\alpha\beta}} & \overline{c_{\alpha\beta}c^*_{\beta\alpha}} & \overline{c_{\alpha\beta}c^*_{\beta\beta}} \\ \overline{c_{\beta\alpha}c^*_{\alpha\alpha}} & \overline{c_{\beta\alpha}c^*_{\alpha\beta}} & \overline{c_{\beta\alpha}c^*_{\beta\alpha}} & \overline{c_{\beta\alpha}c^*_{\beta\beta}} \\ \overline{c_{\beta\beta}c^*_{\alpha\alpha}} & \overline{c_{\beta\beta}c^*_{\alpha\beta}} & \overline{c_{\beta\beta}c^*_{\beta\alpha}} & \overline{c_{\beta\beta}c^*_{\beta\beta}} \end{pmatrix}$$

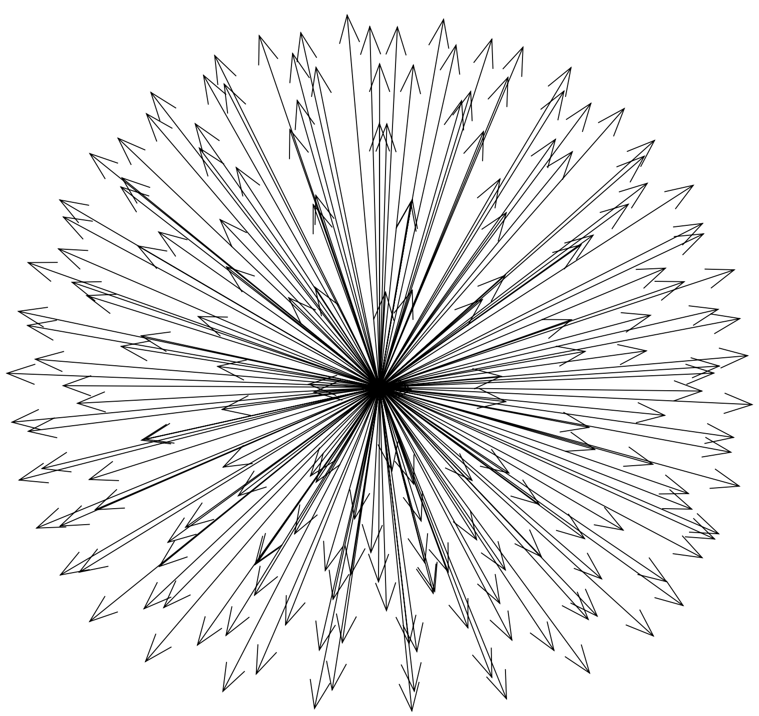
or

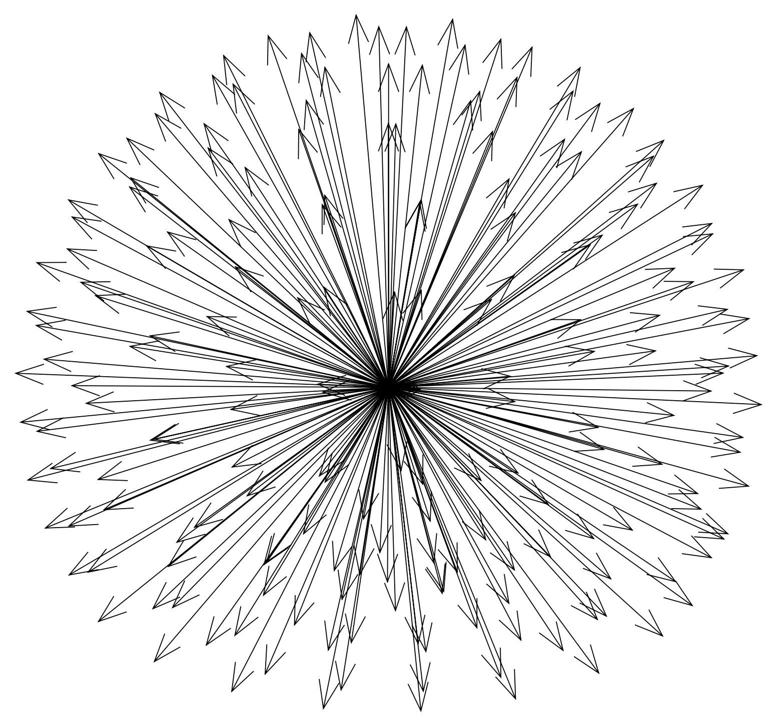
$$\mathscr{I}_t = \frac{1}{2}\begin{pmatrix} +1 & 0 & 0 & 0 \\ 0 & +1 & 0 & 0 \\ 0 & 0 & +1 & 0 \\ 0 & 0 & 0 & +1 \end{pmatrix} \qquad \mathscr{I}_{1z} = \frac{1}{2}\begin{pmatrix} +1 & 0 & 0 & 0 \\ 0 & +1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

$$\mathscr{I}_{2z} = \frac{1}{2}\begin{pmatrix} +1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & +1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \qquad 2\mathscr{I}_{1z}\mathscr{I}_{2z} = \frac{1}{2}\begin{pmatrix} +1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & +1 \end{pmatrix}$$

No polarization

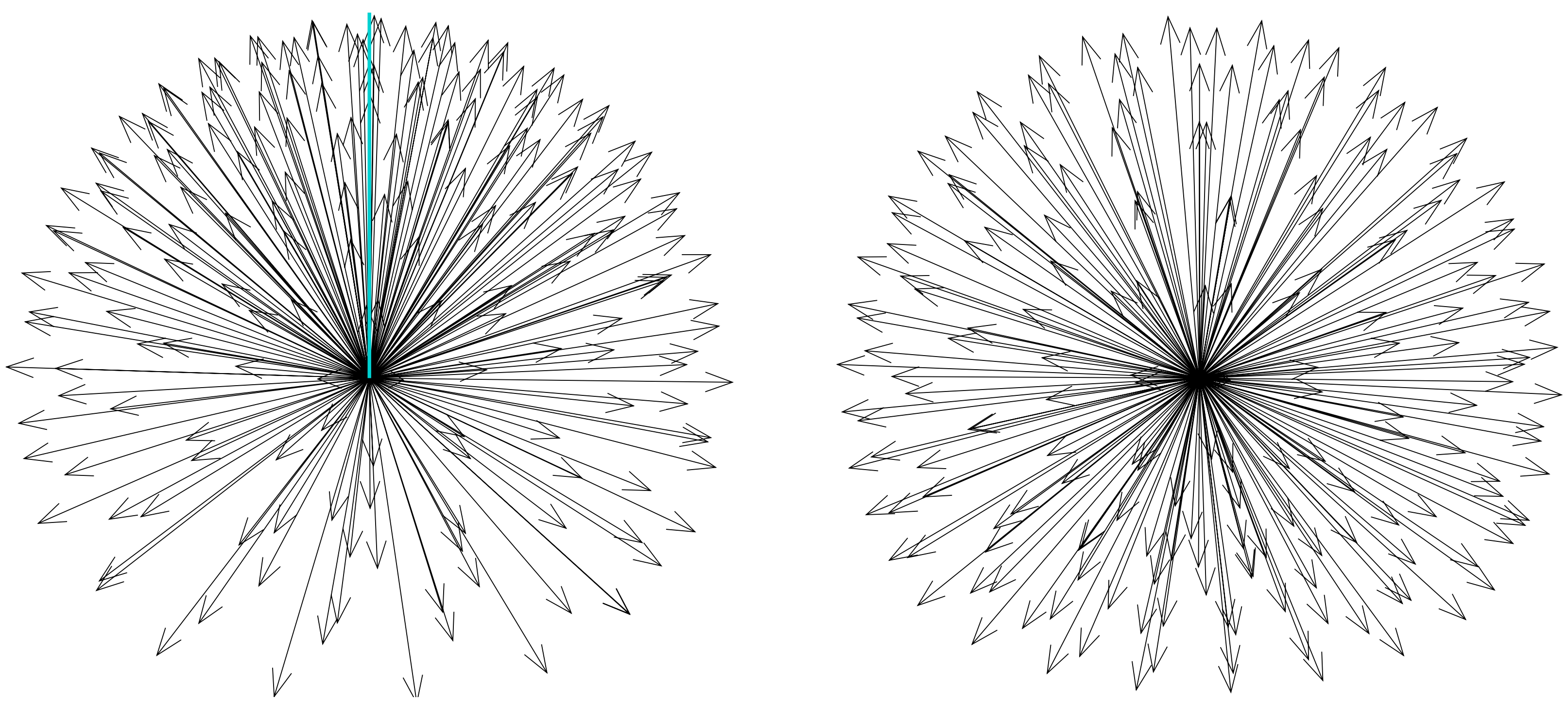
$$\mathscr{I}_t = \frac{1}{2}\begin{pmatrix} +1 & 0 & 0 & 0 \\ 0 & +1 & 0 & 0 \\ 0 & 0 & +1 & 0 \\ 0 & 0 & 0 & +1 \end{pmatrix}$$





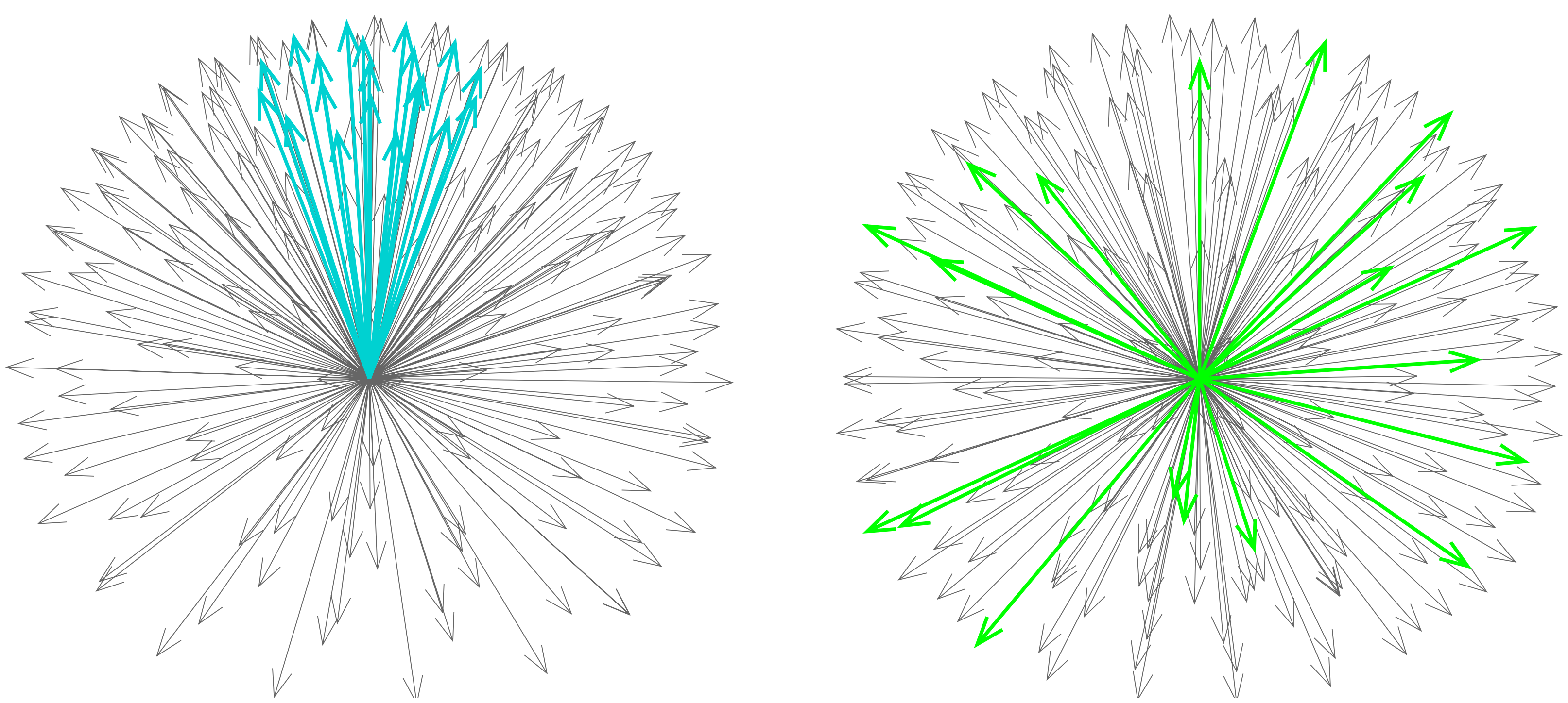
Longitudinal polarization of $\vec{\mu}_1$, regardless of $\vec{\mu}_2$

$$\mathscr{I}_{1z} = \frac{1}{2}\begin{pmatrix} +1 & 0 & 0 & 0 \\ 0 & +1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$



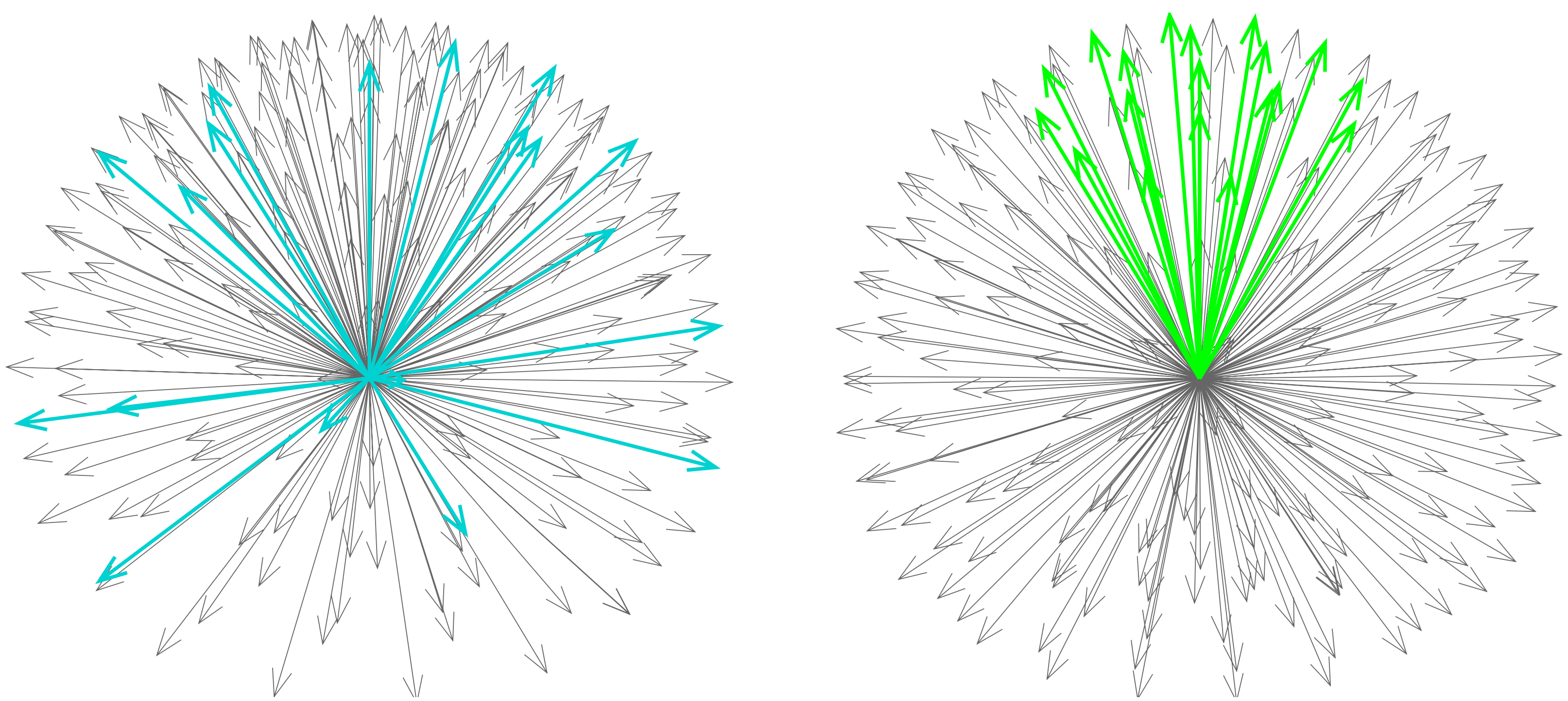
Longitudinal polarization of $\vec{\mu}_1$, regardless of $\vec{\mu}_2$

$$\mathscr{I}_{1z} = \frac{1}{2}\begin{pmatrix} +1 & 0 & 0 & 0 \\ 0 & +1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$



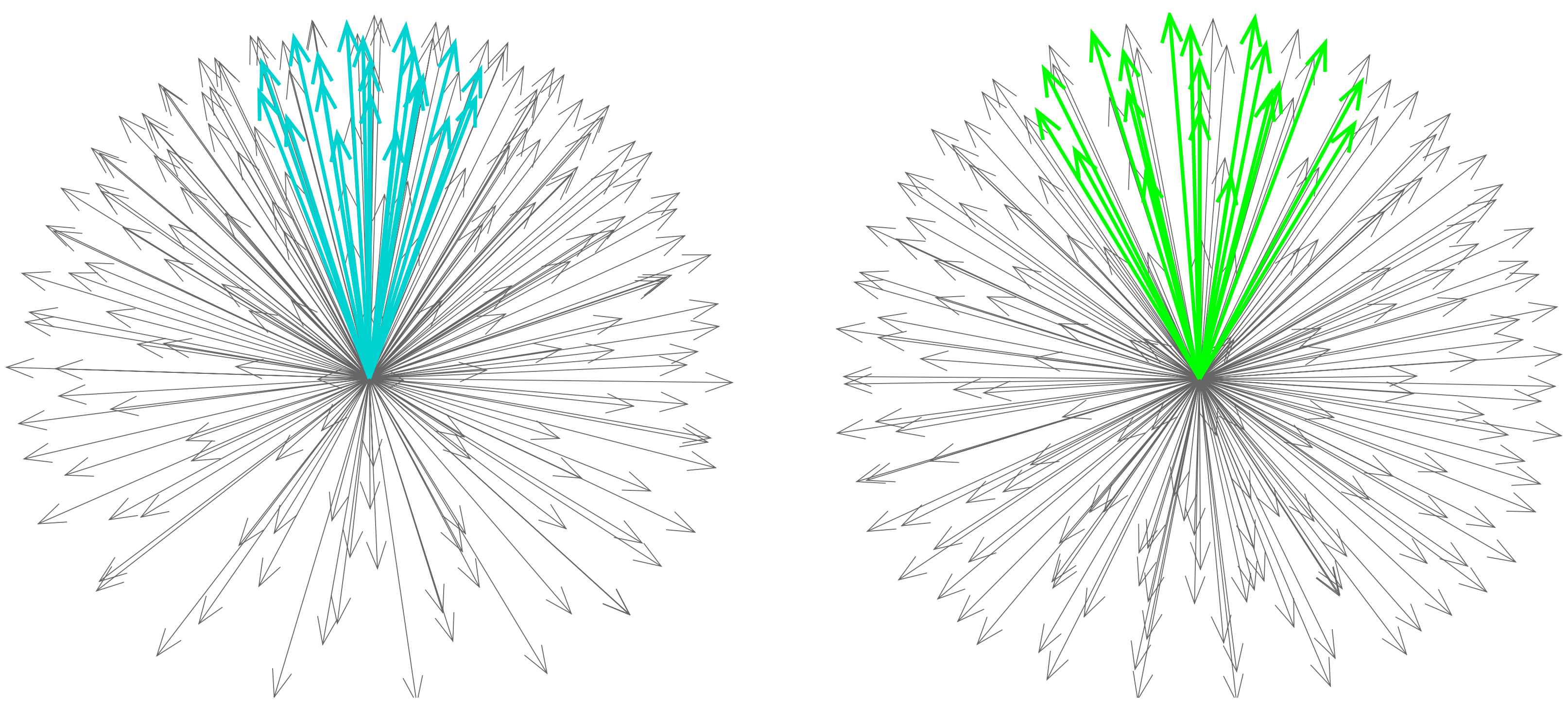
Longitudinal polarization of $\vec{\mu}_2$, regardless of $\vec{\mu}_1$

$$\mathscr{I}_{2z} = \frac{1}{2}\begin{pmatrix} +1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & +1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$



Coupled longitudinal polarizations of $\vec{\mu}_1$ and $\vec{\mu}_2$

$$2\mathscr{I}_{1z}\mathscr{I}_{2z} = \frac{1}{2}\begin{pmatrix} +1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & +1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$



Density matrix: coherences

12 coherences (complex numbers: 12 real, 12 imaginary),

6 independent ($\overline{c_{\alpha\alpha}c^*_{\alpha\beta}} = \overline{c_{\alpha\beta}c^*_{\alpha\alpha}}$ etc.):

$$\hat{\rho} = \begin{pmatrix} \overline{c_{\alpha\alpha}c^*_{\alpha\alpha}} & \overline{c_{\alpha\alpha}c^*_{\alpha\beta}} & \overline{c_{\alpha\alpha}c^*_{\beta\alpha}} & \overline{c_{\alpha\alpha}c^*_{\beta\beta}} \\ \overline{c_{\alpha\beta}c^*_{\alpha\alpha}} & \overline{c_{\alpha\beta}c^*_{\alpha\beta}} & \overline{c_{\alpha\beta}c^*_{\beta\alpha}} & \overline{c_{\alpha\beta}c^*_{\beta\beta}} \\ \overline{c_{\beta\alpha}c^*_{\alpha\alpha}} & \overline{c_{\beta\alpha}c^*_{\alpha\beta}} & \overline{c_{\beta\alpha}c^*_{\beta\alpha}} & \overline{c_{\beta\alpha}c^*_{\beta\beta}} \\ \overline{c_{\beta\beta}c^*_{\alpha\alpha}} & \overline{c_{\beta\beta}c^*_{\alpha\beta}} & \overline{c_{\beta\beta}c^*_{\beta\alpha}} & \overline{c_{\beta\beta}c^*_{\beta\beta}} \end{pmatrix}$$

or purely real/imaginary

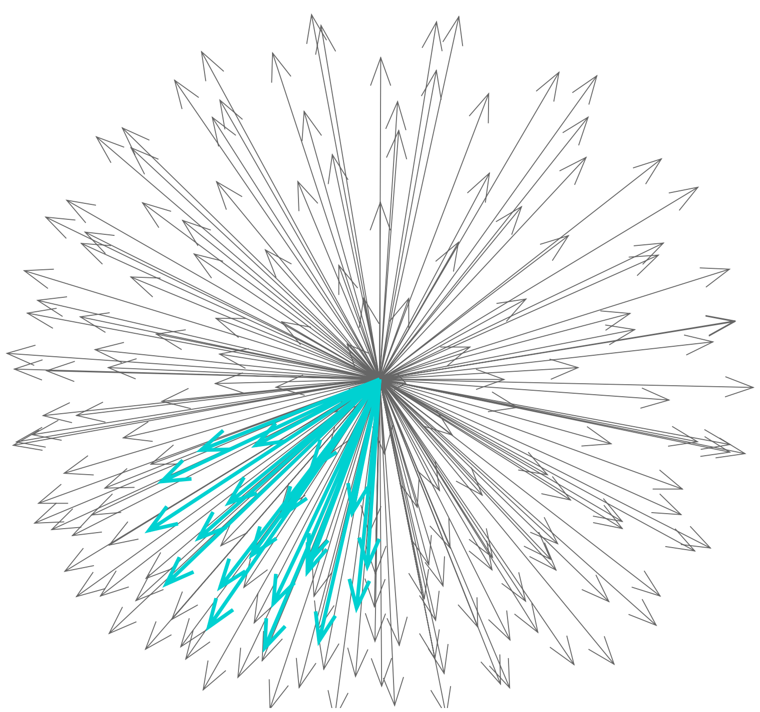
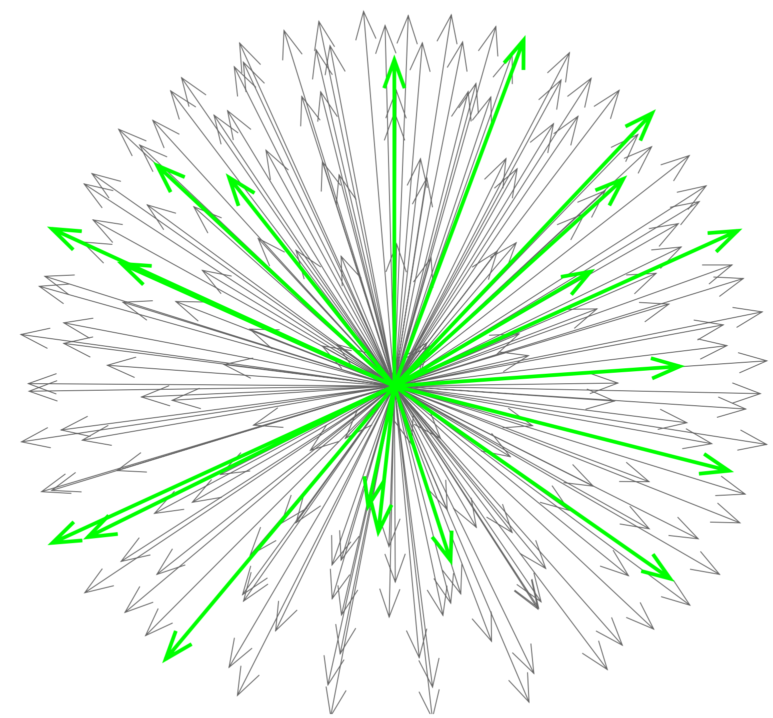
$$\frac{1}{2}\begin{pmatrix} 0 & 0 & +1 & 0 \\ 0 & 0 & 0 & +1 \\ +1 & 0 & 0 & 0 \\ 0 & +1 & 0 & 0 \end{pmatrix} \quad \frac{1}{2}\begin{pmatrix} 0 & 0 & +1 & 0 \\ 0 & 0 & 0 & -1 \\ +1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix} \quad \frac{1}{2}\begin{pmatrix} 0 & 0 & -\mathrm{i} & 0 \\ 0 & 0 & 0 & -\mathrm{i} \\ +\mathrm{i} & 0 & 0 & 0 \\ 0 & +\mathrm{i} & 0 & 0 \end{pmatrix} \quad \frac{1}{2}\begin{pmatrix} 0 & 0 & -\mathrm{i} & 0 \\ 0 & 0 & 0 & +\mathrm{i} \\ +\mathrm{i} & 0 & 0 & 0 \\ 0 & -\mathrm{i} & 0 & 0 \end{pmatrix}$$

$$\frac{1}{2}\begin{pmatrix} 0 & +1 & 0 & 0 \\ +1 & 0 & 0 & 0 \\ 0 & 0 & 0 & +1 \\ 0 & 0 & +1 & 0 \end{pmatrix} \quad \frac{1}{2}\begin{pmatrix} 0 & +1 & 0 & 0 \\ +1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \end{pmatrix} \quad \frac{1}{2}\begin{pmatrix} 0 & -\mathrm{i} & 0 & 0 \\ +\mathrm{i} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\mathrm{i} \\ 0 & 0 & +\mathrm{i} & 0 \end{pmatrix} \quad \frac{1}{2}\begin{pmatrix} 0 & -\mathrm{i} & 0 & 0 \\ +\mathrm{i} & 0 & 0 & 0 \\ 0 & 0 & 0 & +\mathrm{i} \\ 0 & 0 & -\mathrm{i} & 0 \end{pmatrix}$$

$$\frac{1}{2}\begin{pmatrix} 0 & 0 & 0 & +1 \\ 0 & 0 & +1 & 0 \\ 0 & +1 & 0 & 0 \\ +1 & 0 & 0 & 0 \end{pmatrix} \quad \frac{1}{2}\begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & +1 & 0 \\ 0 & +1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix} \quad \frac{1}{2}\begin{pmatrix} 0 & 0 & 0 & -\mathrm{i} \\ 0 & 0 & +\mathrm{i} & 0 \\ 0 & -\mathrm{i} & 0 & 0 \\ +\mathrm{i} & 0 & 0 & 0 \end{pmatrix} \quad \frac{1}{2}\begin{pmatrix} 0 & 0 & 0 & -\mathrm{i} \\ 0 & 0 & -\mathrm{i} & 0 \\ 0 & +\mathrm{i} & 0 & 0 \\ +\mathrm{i} & 0 & 0 & 0 \end{pmatrix}$$

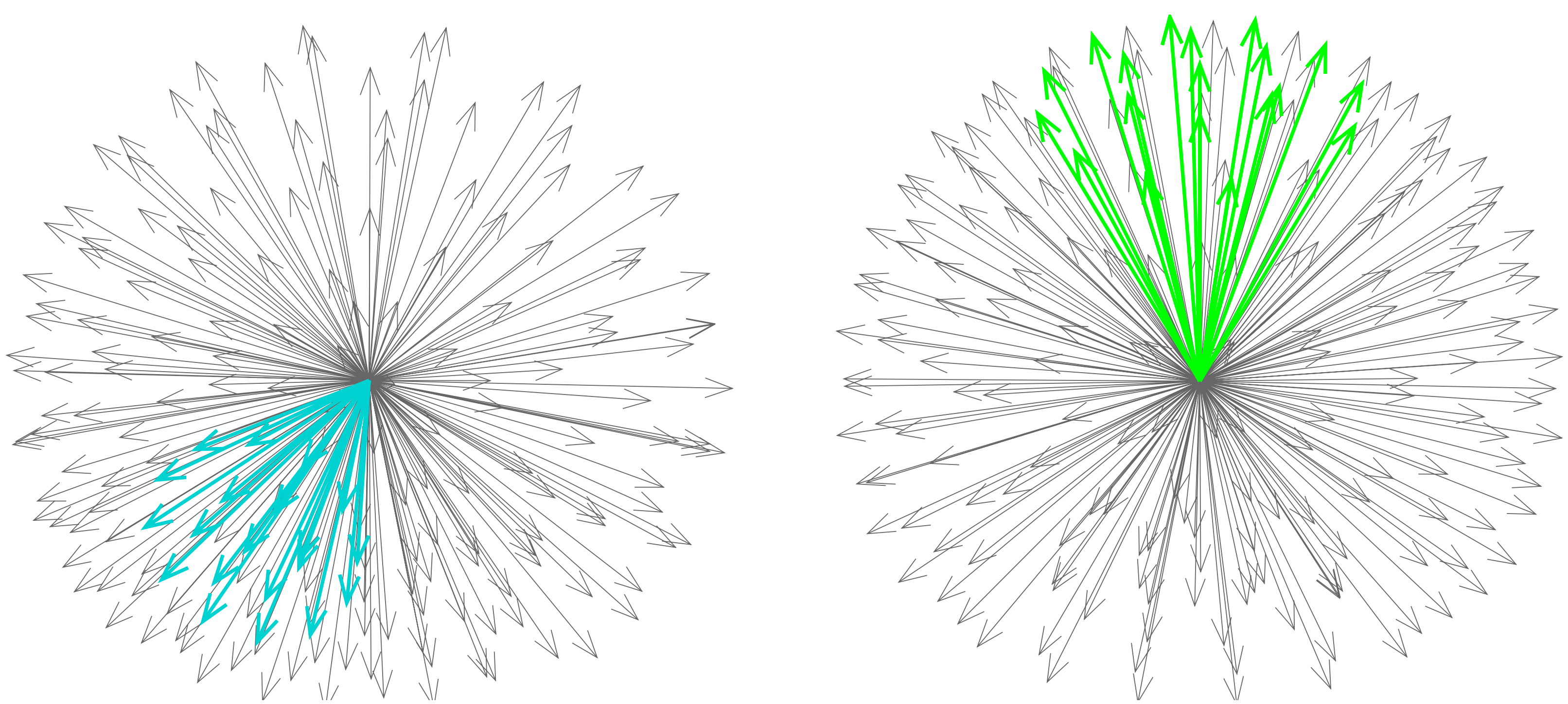
Transverse polarization of $\vec{\mu}_1$ (direction x), regardless of $\vec{\mu}_2$

$$\mathscr{I}_{1x} = \frac{1}{2}\begin{pmatrix} 0 & 0 & +1 & 0 \\ 0 & 0 & 0 & +1 \\ +1 & 0 & 0 & 0 \\ 0 & +1 & 0 & 0 \end{pmatrix}$$

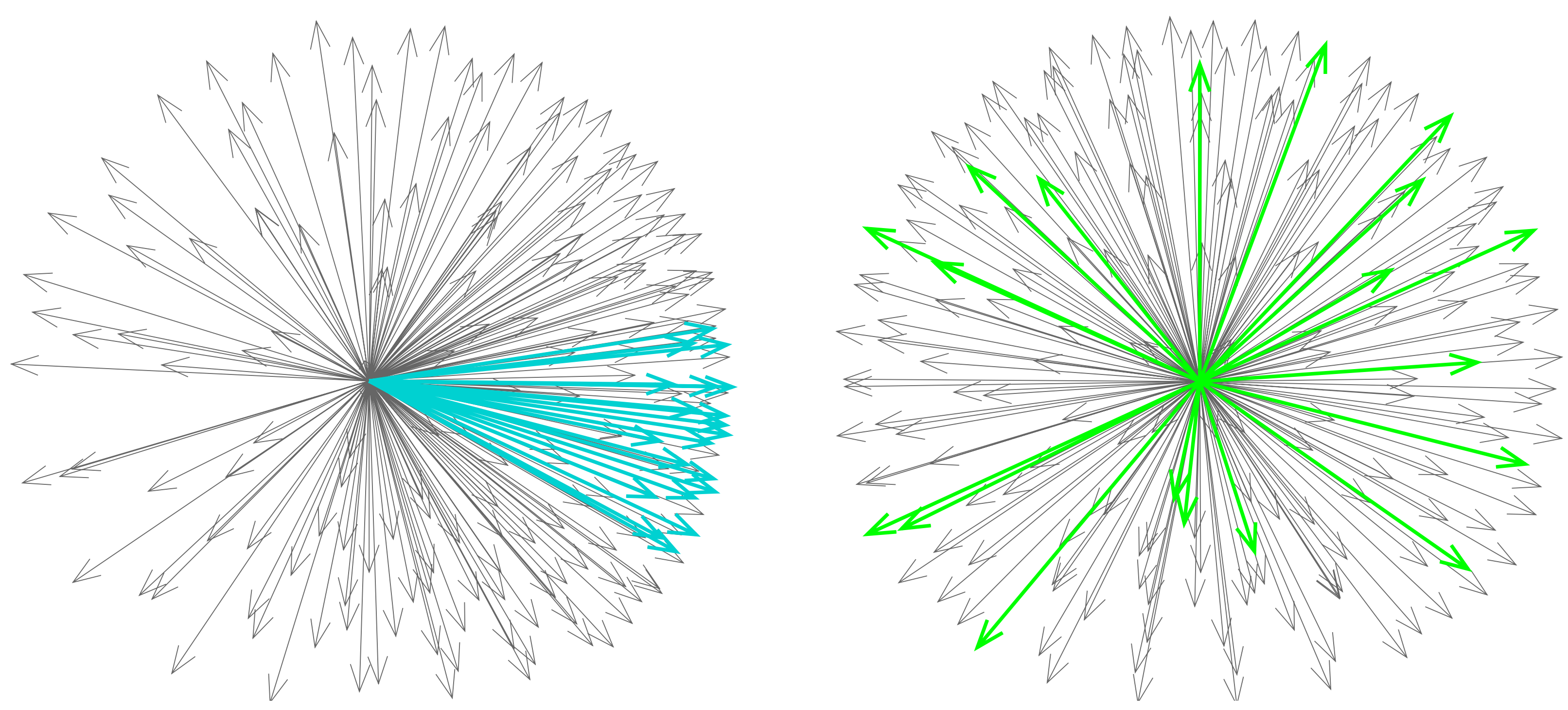
Transverse polarization of $\vec{\mu}_1$ (direction x) coupled with longitudinal polarization of $\vec{\mu}_2$

$$2\mathscr{I}_{1x}\mathscr{I}_{2z} = \frac{1}{2}\begin{pmatrix} 0 & 0 & +1 & 0 \\ 0 & 0 & 0 & -1 \\ +1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}$$



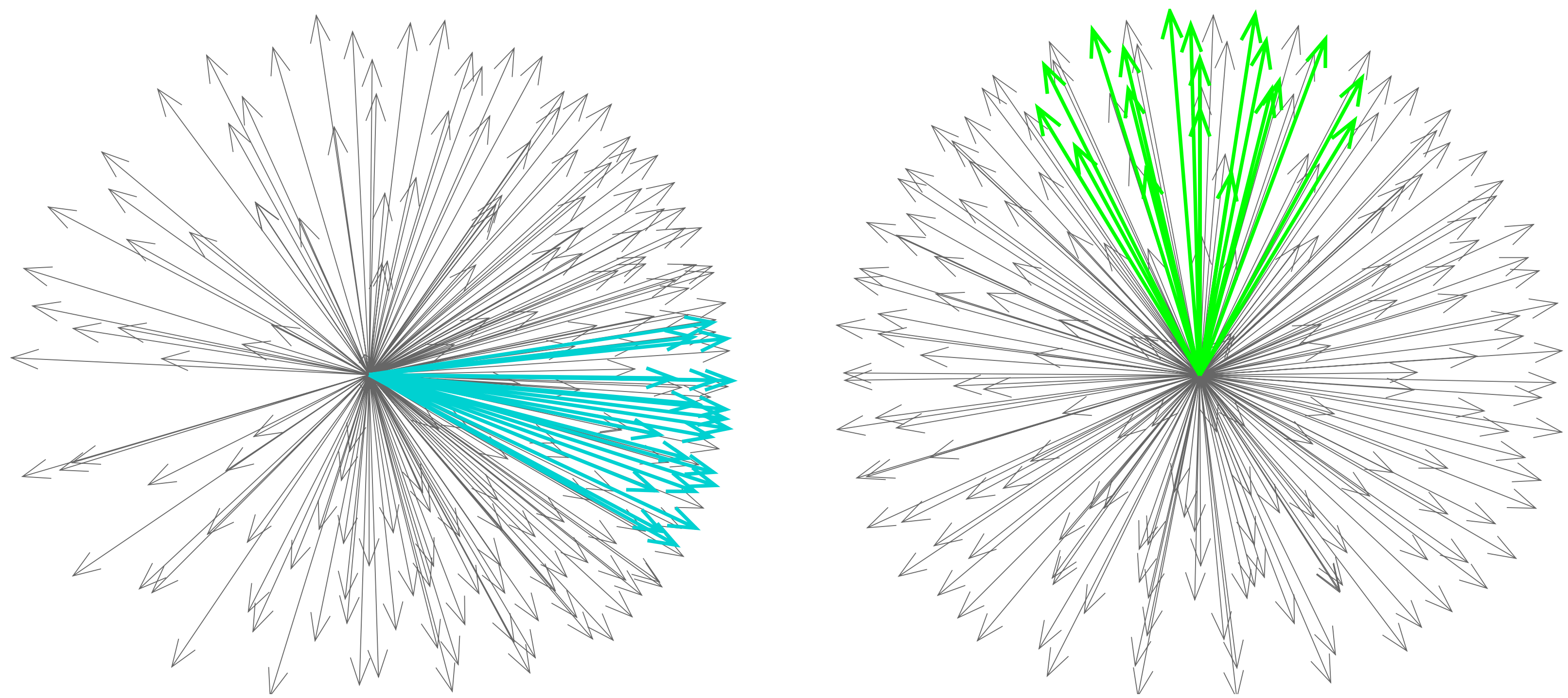
Transverse polarization of $\vec{\mu}_1$ (direction y), regardless of $\vec{\mu}_2$

$$\mathscr{I}_{1y} = \frac{\mathrm{i}}{2}\begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \\ +1 & 0 & 0 & 0 \\ 0 & +1 & 0 & 0 \end{pmatrix}$$



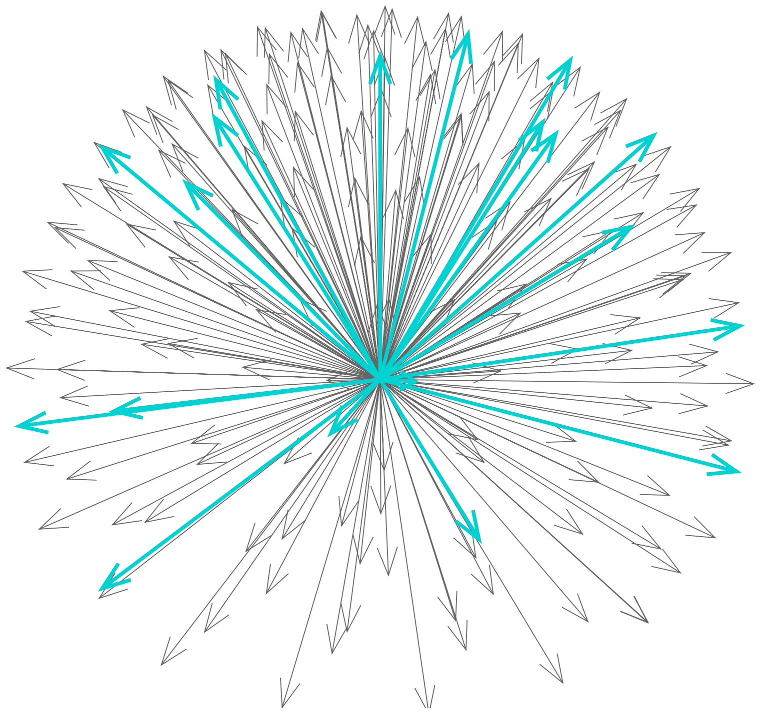
Transverse polarization of $\vec{\mu}_1$ (direction y) coupled with longitudinal polarization of $\vec{\mu}_2$

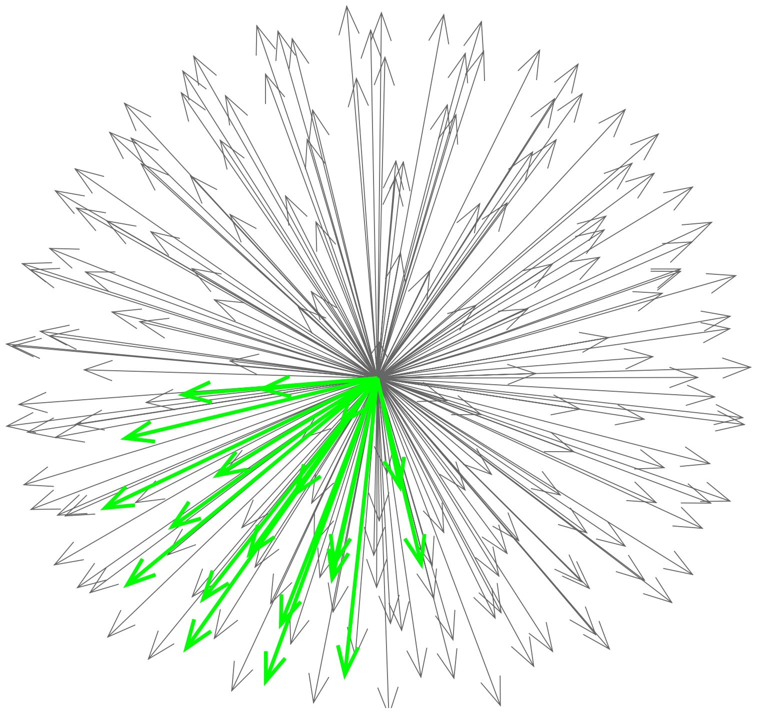
$$2\mathscr{I}_{1y}\mathscr{I}_{2z} = \frac{\mathrm{i}}{2}\begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & +1 \\ +1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}$$



Transverse polarization of $\vec{\mu}_2$ (direction x), regardless of $\vec{\mu}_1$

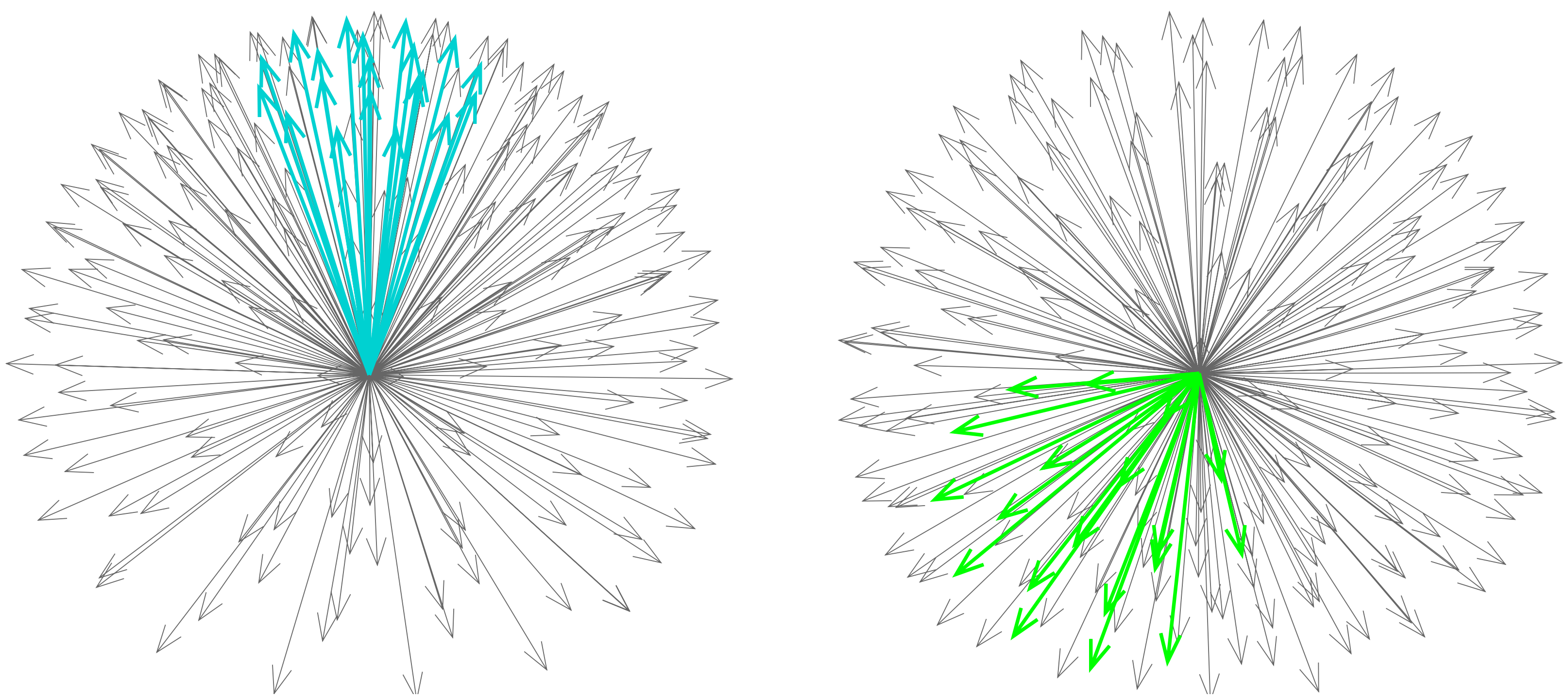
$$\mathscr{I}_{2x} = \frac{1}{2}\begin{pmatrix} 0 & +1 & 0 & 0 \\ +1 & 0 & 0 & 0 \\ 0 & 0 & 0 & +1 \\ 0 & 0 & +1 & 0 \end{pmatrix}$$





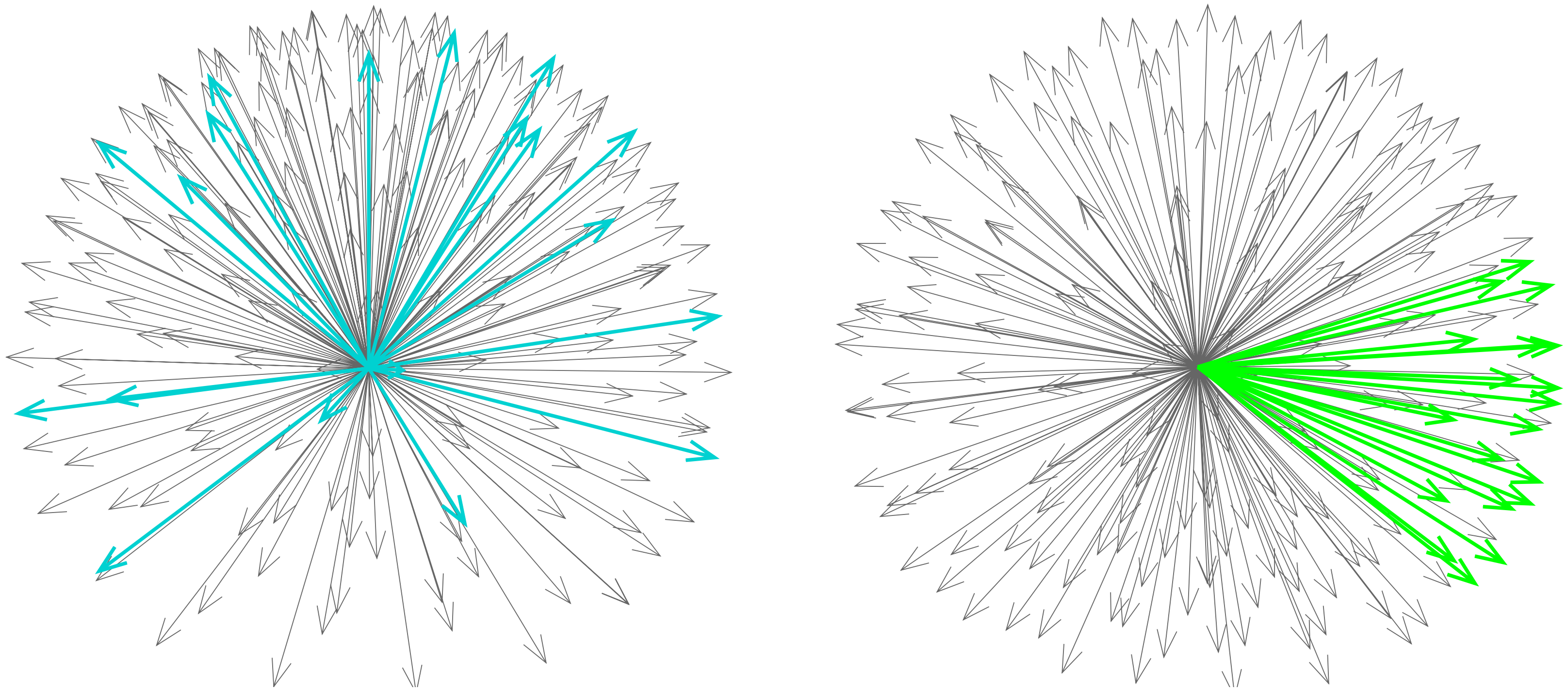
Transverse polarization of $\vec{\mu}_2$ (direction x) coupled with longitudinal polarization of $\vec{\mu}_1$

$$2\mathscr{I}_{1z}\mathscr{I}_{2x} = \frac{1}{2}\begin{pmatrix} 0 & +1 & 0 & 0 \\ +1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \end{pmatrix}$$



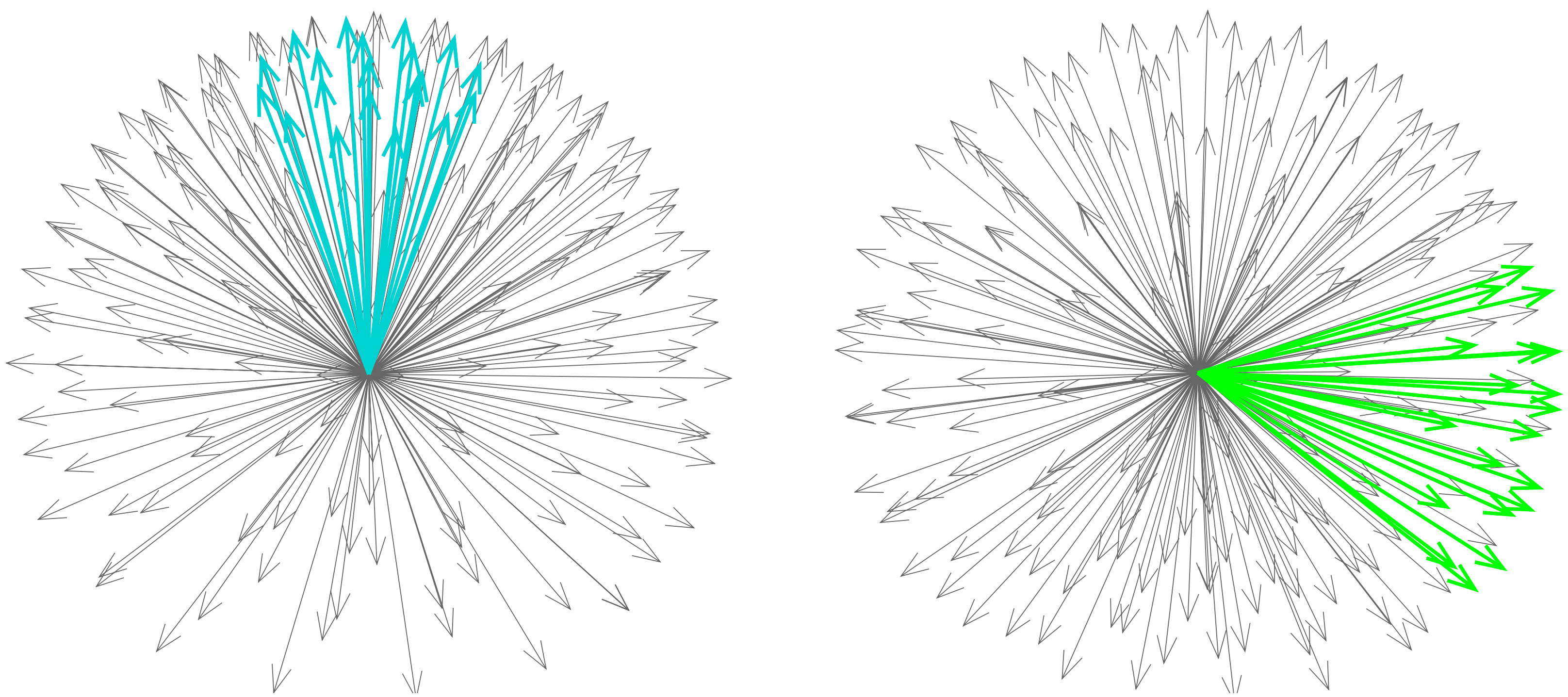
Transverse polarization of $\vec{\mu}_2$ (direction y), regardless of $\vec{\mu}_1$

$$\mathscr{I}_{2y} = \frac{\mathrm{i}}{2}\begin{pmatrix} 0 & -1 & 0 & 0 \\ +1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & +1 & 0 \end{pmatrix}$$



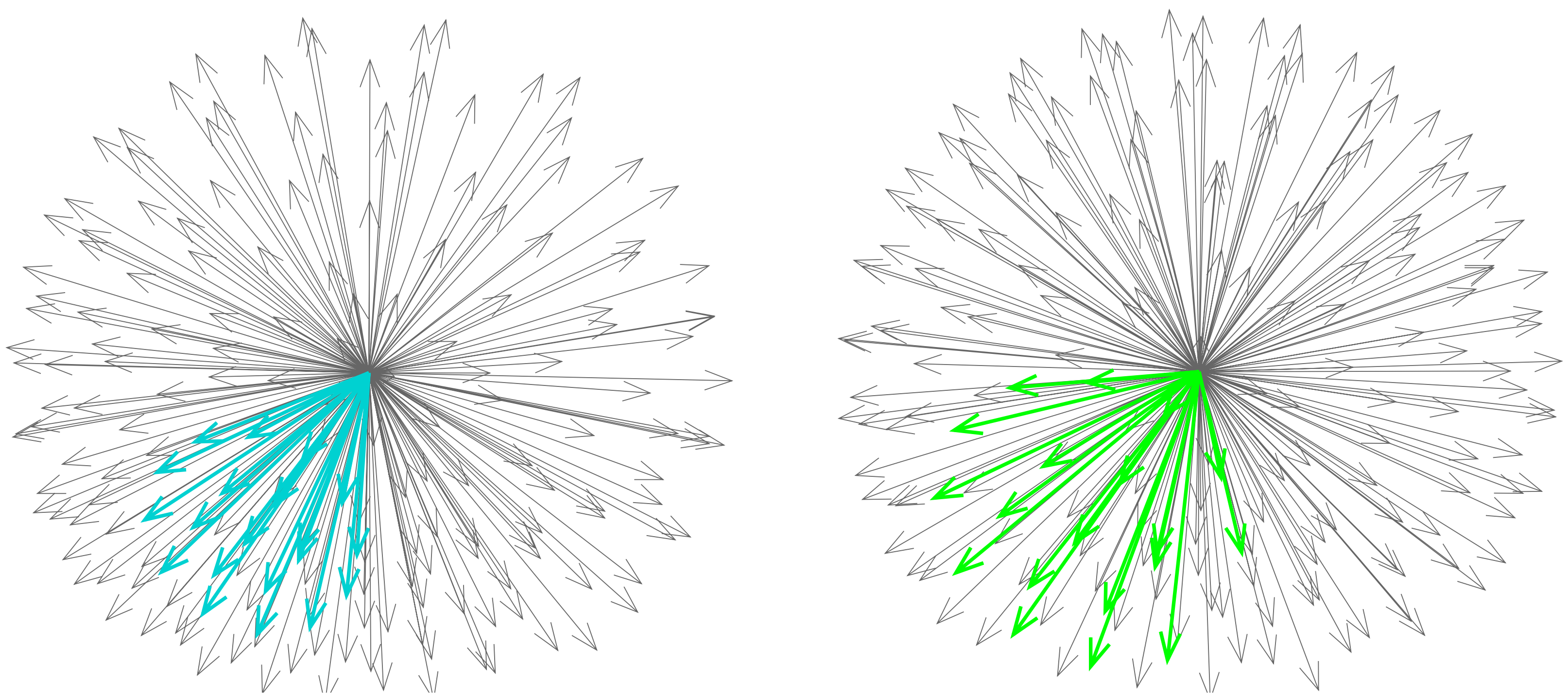
Transverse polarization of $\vec{\mu}_2$ (direction y) coupled with longitudinal polarization of $\vec{\mu}_1$

$$2\mathscr{I}_{1z}\mathscr{I}_{2y} = \frac{\mathrm{i}}{2}\begin{pmatrix} 0 & -1 & 0 & 0 \\ +1 & 0 & 0 & 0 \\ 0 & 0 & 0 & +1 \\ 0 & 0 & -1 & 0 \end{pmatrix}$$



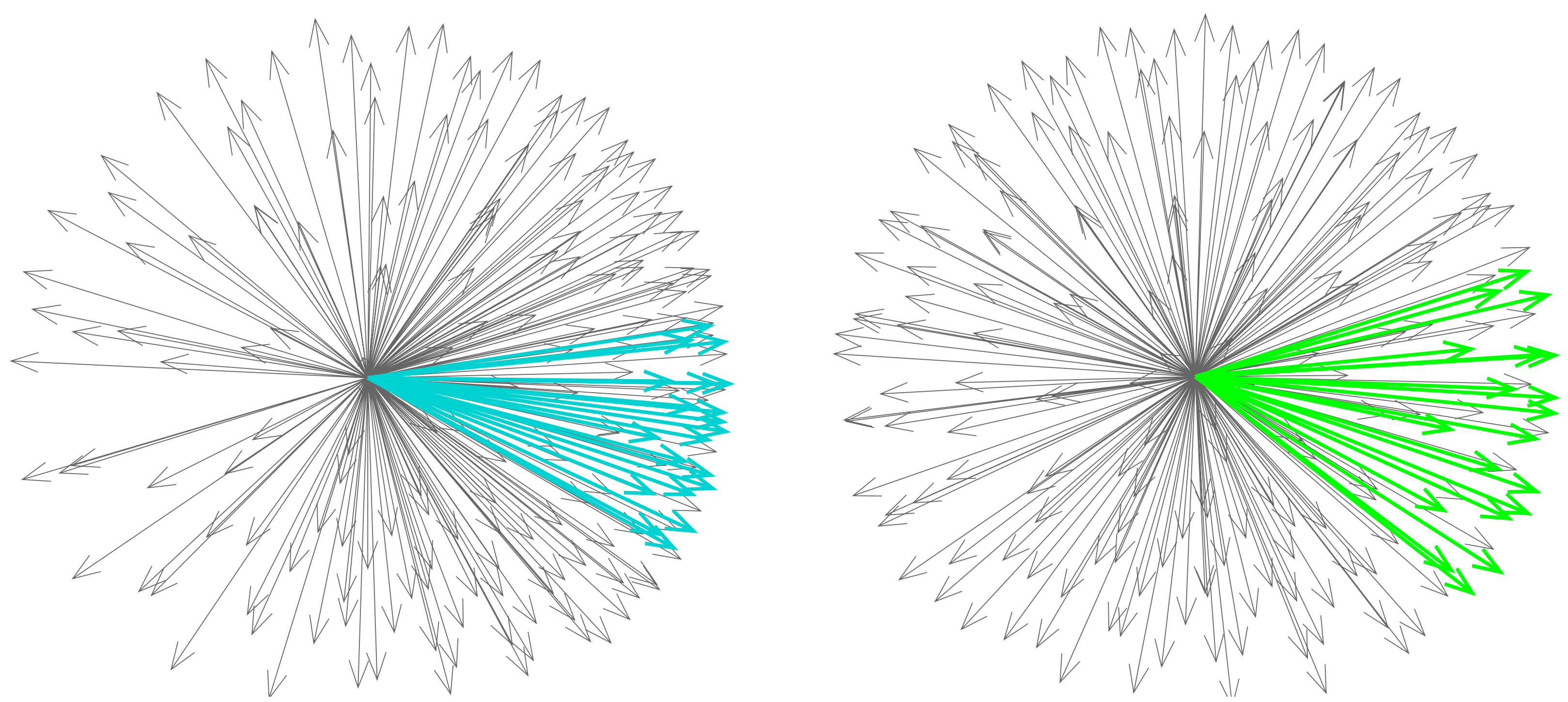
Coupled transverse polarization of $\vec{\mu}_1$ and $\vec{\mu}_2$ in direction x

$$2\mathscr{I}_{1x}\mathscr{I}_{2x} = \frac{1}{2}\begin{pmatrix} 0 & 0 & 0 & +1 \\ 0 & 0 & +1 & 0 \\ 0 & +1 & 0 & 0 \\ +1 & 0 & 0 & 0 \end{pmatrix}$$



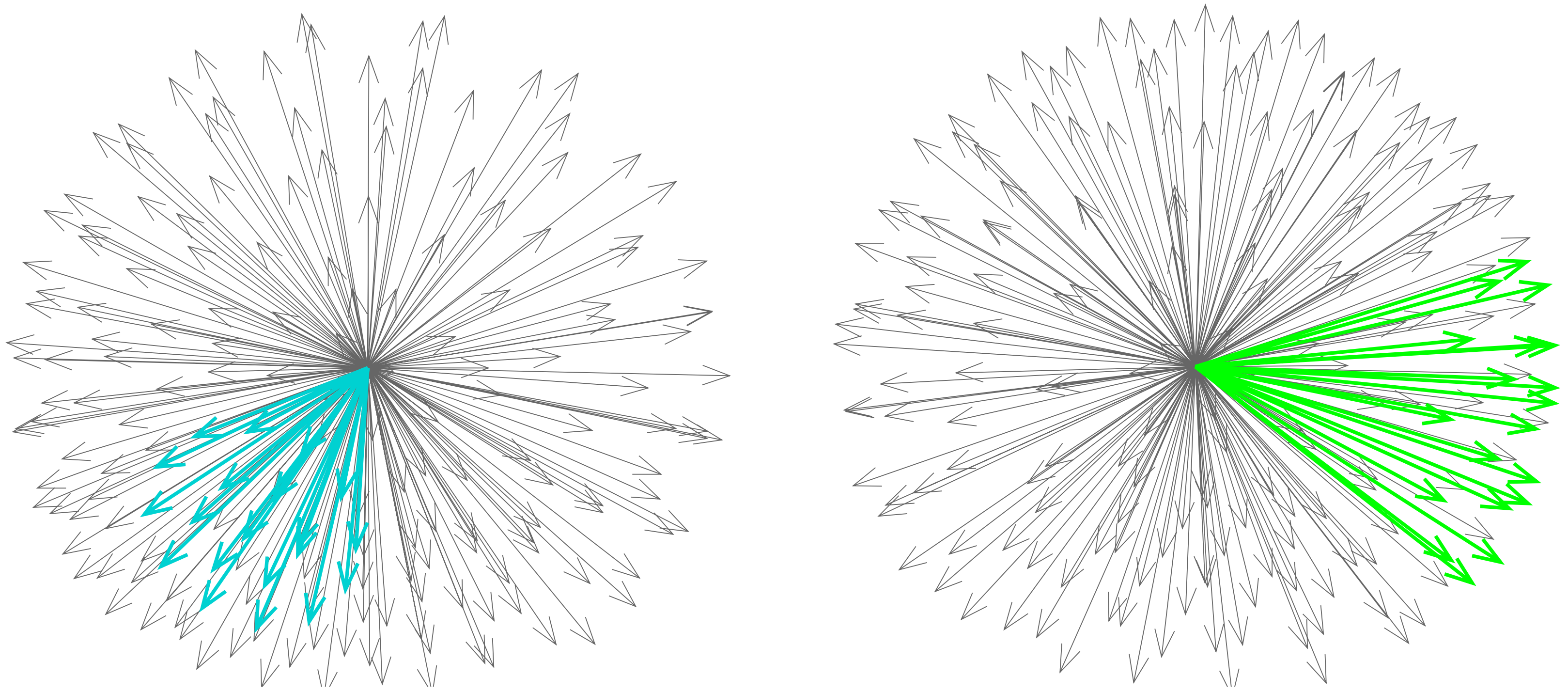
Coupled transverse polarization of $\vec{\mu}_1$ and $\vec{\mu}_2$ in direction y

$$2\mathscr{I}_{1y}\mathscr{I}_{2y} = \frac{1}{2}\begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & +1 & 0 \\ 0 & +1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix}$$



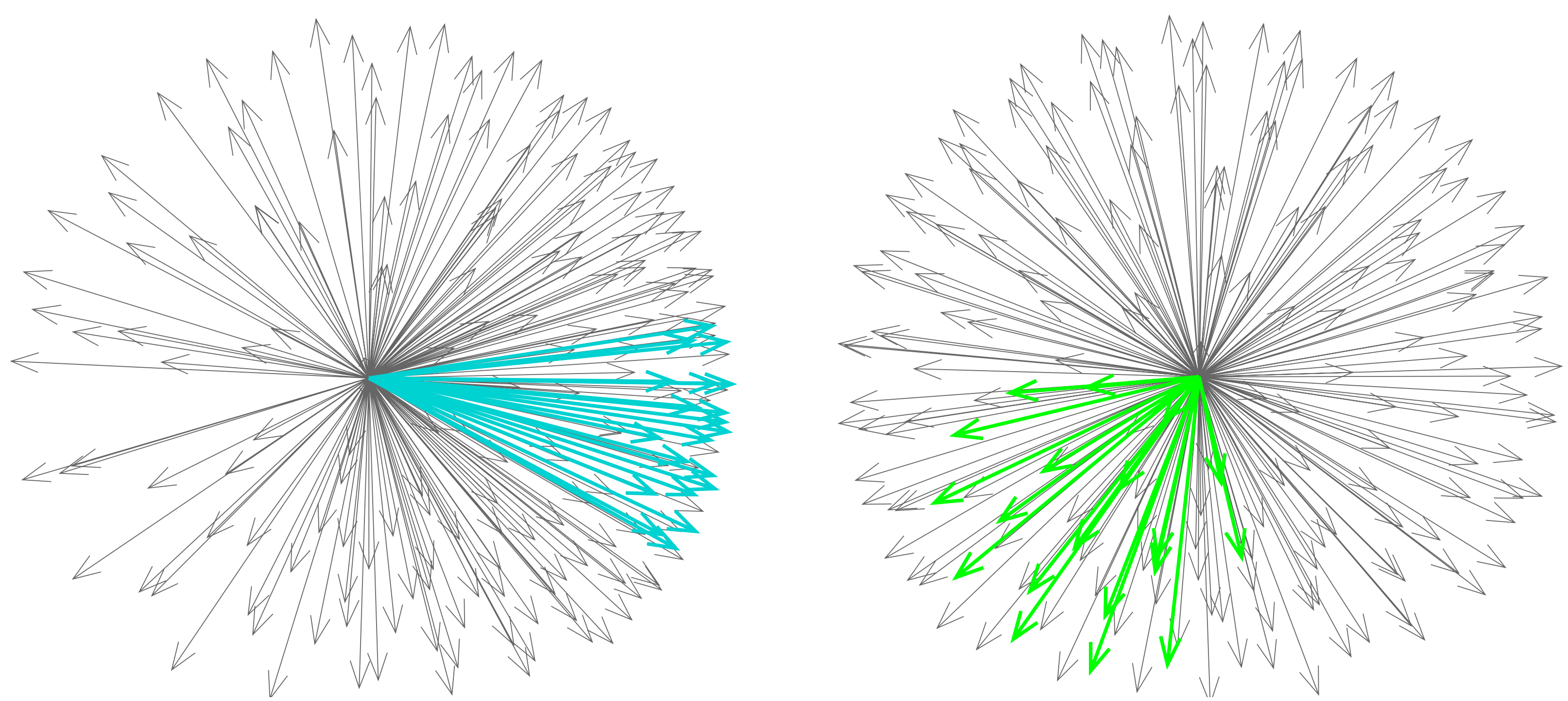
Transverse x polarization of $\vec{\mu}_1$ coupled with transverse y polarization of $\vec{\mu}_2$

$$2\mathscr{I}_{1x}\mathscr{I}_{2y} = \frac{\mathrm{i}}{2}\begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & +1 & 0 \\ 0 & -1 & 0 & 0 \\ +1 & 0 & 0 & 0 \end{pmatrix}$$



Transverse y polarization of $\vec{\mu}_1$ coupled with transverse x polarization of $\vec{\mu}_2$

$$2\mathscr{I}_{1y}\mathscr{I}_{2x} = \frac{\mathrm{i}}{2}\begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \\ 0 & +1 & 0 & 0 \\ +1 & 0 & 0 & 0 \end{pmatrix}$$



WHAT REMAINS?

WHAT CHANGES?

Hamiltonian

In the absence of radio waves:

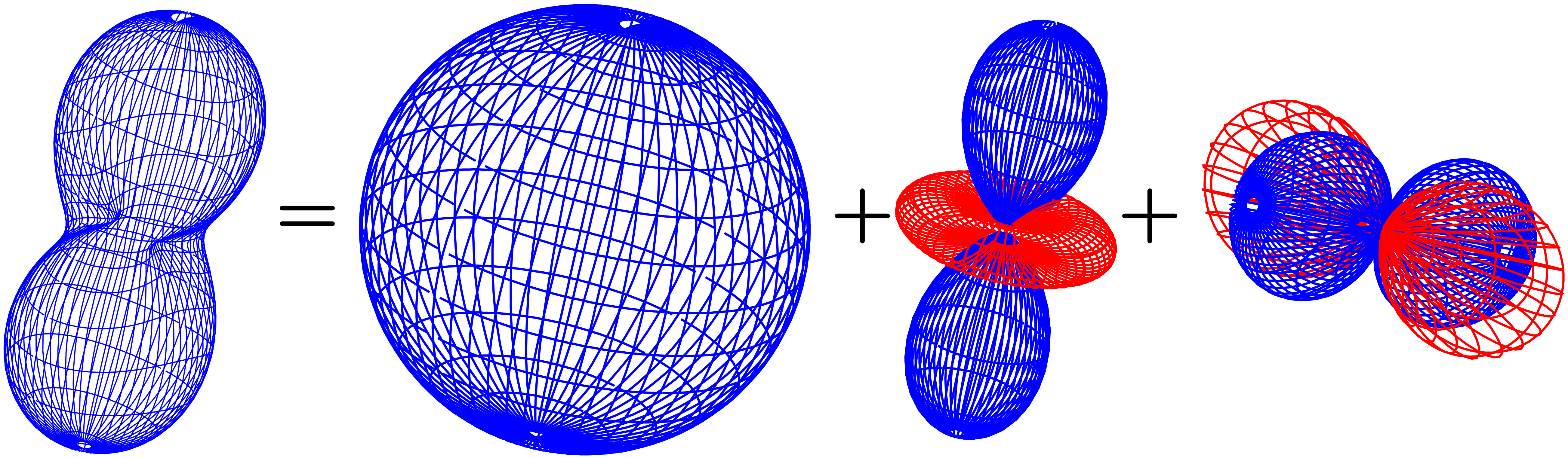
$$\hat{H} = \hat{H}_0 + \hat{H}_D$$

$$\hat{H} = \underbrace{-\gamma_1 B_0 \hat{I}_{1z} - \gamma_2 B_0 \hat{I}_{2z} + \hat{H}_{\delta,1} + \hat{H}_{\delta,2}}_{\hat{H}_0} + \hat{H}_D$$

In the presence of radio waves ($B_1 \gg B_2$):

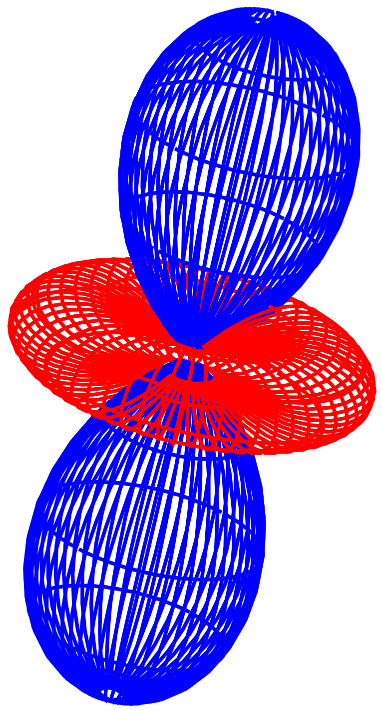
$$\hat{H} \approx \hat{H}_1$$

Hamiltonian of chemical shift



$$\hat{H}_{\delta} = \hat{H}_{\delta,\mathrm{i}} + \hat{H}_{\delta,\mathrm{a}} + \hat{H}_{\delta,\mathrm{r}}$$

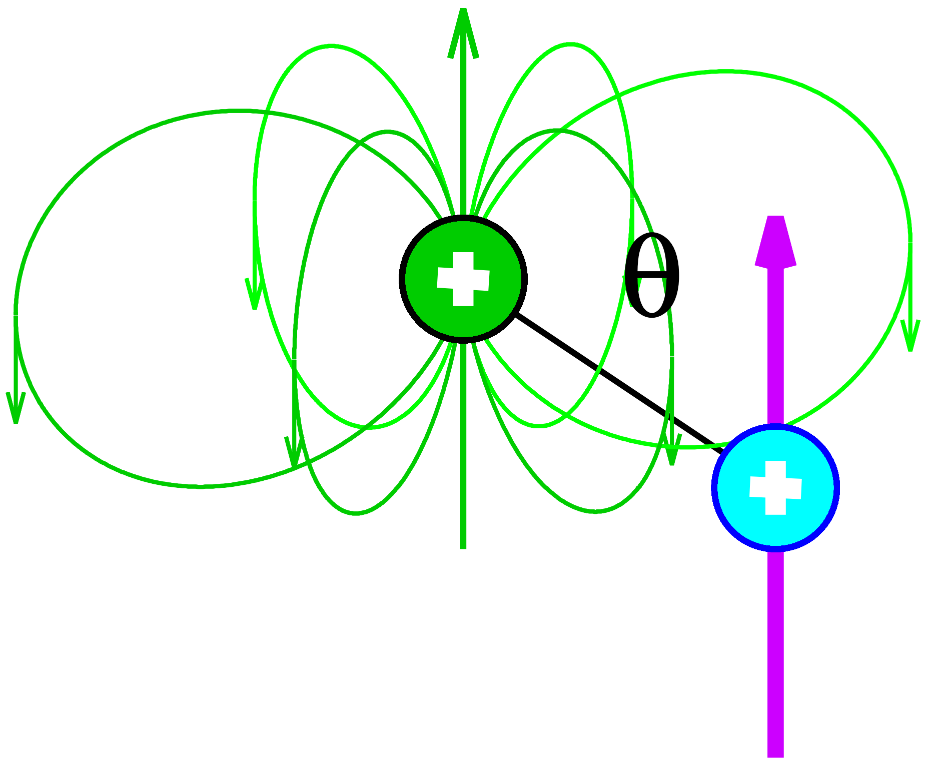
Hamiltonian of chemical shift anisotropy



$$\hat{H}_{\delta,\mathrm{a}} = -\begin{pmatrix} \hat{\mu}_x & \hat{\mu}_y & \hat{\mu}_z \end{pmatrix} \cdot \underline{\delta_{\mathrm{a}}} \cdot \begin{pmatrix} 0 \\ 0 \\ B_0 \end{pmatrix} =$$

$$-\gamma\delta_{\mathrm{a}} \begin{pmatrix} \hat{I}_x & \hat{I}_y & \hat{I}_z \end{pmatrix} \cdot \begin{pmatrix} 3a_x^2 - 1 & 3a_xa_y & 3a_xa_z \\ 3a_xa_y & 3a_y^2 - 1 & 3a_ya_z \\ 3a_xa_z & 3a_ya_z & 3a_z^2 - 1 \end{pmatrix} \cdot \begin{pmatrix} 0 \\ 0 \\ B_0 \end{pmatrix}$$

Hamiltonian of dipolar coupling



$$\hat{H}_D = -\begin{pmatrix} \hat{\mu}_{1,x} & \hat{\mu}_{1,y} & \hat{\mu}_{1,z} \end{pmatrix} \cdot \underline{D} \cdot \begin{pmatrix} \hat{\mu}_{2,x} \\ \hat{\mu}_{2,y} \\ \hat{\mu}_{2,z} \end{pmatrix} =$$

$$-\frac{\mu_0 \gamma_1 \gamma_2}{4\pi r^5} \begin{pmatrix} \hat{I}_{1,x} & \hat{I}_{1,y} & \hat{I}_{1,z} \end{pmatrix} \cdot \begin{pmatrix} 3r_x^2 - r^2 & 3r_x r_y & 3r_x r_z \\ 3r_x r_y & 3r_y^2 - r^2 & 3r_y r_z \\ 3r_x r_z & 3r_y r_z & 3r_z^2 - r^2 \end{pmatrix} \cdot \begin{pmatrix} \hat{I}_{2,x} \\ \hat{I}_{2,y} \\ \hat{I}_{2,z} \end{pmatrix}$$

Chemical shift Hamiltonian

Isotropic component (independent of orientation):

$$\hat{H}_{\delta,\mathrm{i}} = -\gamma B_0 \delta_{\mathrm{i}} (\hat{I}_z)$$

Anisotropic (axially symmetric) component (depends on ϑ, φ):

$$\hat{H}_{\delta,\mathrm{a}} = -\gamma B_0 \delta_{\mathrm{a}} (3 \sin\vartheta \cos\vartheta \cos\varphi \hat{I}_x + 3 \sin\vartheta \cos\vartheta \sin\varphi \hat{I}_y + (3\cos^2\vartheta - 1)\hat{I}_z)$$

Rhombic (asymmetric) component (depends on ϑ, φ, χ):

$$\begin{aligned}\hat{H}_{\delta,\mathrm{r}} = -\gamma B_0 \delta_{\mathrm{r}} (\quad & (-\cos 2\chi \sin\vartheta \cos\vartheta \cos\varphi + \sin 2\chi \sin\vartheta \cos\vartheta \sin\varphi)\hat{I}_x + \\ & (-\cos 2\chi \sin\vartheta \cos\vartheta \sin\varphi - \sin 2\chi \sin\vartheta \cos\vartheta \cos\varphi)\hat{I}_y + \\ & ((\cos 2\chi \sin^2\vartheta)\hat{I}_z)\end{aligned}$$

Secular approximation and averaging

Recall chemical shift Hamiltonian:

Isotropic component:

$$\hat{H}_{\delta,\mathrm{i}} = -\gamma B_0 \delta_{\mathrm{i}} (\hat{I}_z)$$

Anisotropic (axially symmetric) component:

$$\hat{H}_{\delta,\mathrm{a}} = -\gamma B_0 \delta_{\mathrm{a}} (3 \sin\vartheta \cos\vartheta \cos\varphi \hat{I}_x + 3 \sin\vartheta \cos\vartheta \sin\varphi \hat{I}_y + (3\cos^2\vartheta - 1)\hat{I}_z)$$

Rhombic (asymmetric) component:

$$\begin{aligned}\hat{H}_{\delta,\mathrm{r}} = -\gamma B_0 \delta_{\mathrm{r}} (\quad & (-\cos 2\chi \sin\vartheta \cos\vartheta \cos\varphi + \sin 2\chi \sin\vartheta \cos\vartheta \sin\varphi)\hat{I}_x + \\ & (-\cos 2\chi \sin\vartheta \cos\vartheta \sin\varphi - \sin 2\chi \sin\vartheta \cos\vartheta \cos\varphi)\hat{I}_y + \\ & ((\cos 2\chi \sin^2\vartheta)\hat{I}_z)\end{aligned}$$

Hamiltonian in presence of dipolar coupling

In the absence of radio waves in isotropic liquid (on time scales $\gg$ ns, not relaxation!):

$$\hat{H} = -\gamma_1(1+\delta_{\mathrm{i},1})B_0 - \gamma_2(1+\delta_{\mathrm{i},2})B_0 = \hat{H}_0$$

$$\hat{H} = \hat{H}_0$$

In the presence of radio waves ($B_1 \gg B_2$):

$$\hat{H} \approx \hat{H}_1$$

Liouville - von Neumann equation

$$\frac{\mathrm{d}\hat{\rho}}{\mathrm{d}t} = \mathrm{i}(\hat{\rho}\mathscr{H} - \mathscr{H}\hat{\rho}) = \mathrm{i}[\hat{\rho}, \mathscr{H}] = -\mathrm{i}[\mathscr{H}, \hat{\rho}]$$

If $\hat{\rho} = c\mathscr{I}_j$, $\mathscr{H} = \omega\mathscr{I}_l$, and $[\mathscr{I}_j, \mathscr{I}_k] = \pm\mathrm{i}\mathscr{I}_l$, $\hat{\rho}$ evolves as

$$\hat{\rho} = c\mathscr{I}_j \quad \longrightarrow \quad c\mathscr{I}_j\cos(\omega t) \pm c\mathscr{I}_k\sin(\omega t)$$

THE SAME FORM

$\Rightarrow$ **new commutators:**

$[\mathscr{I}_{nx}, \mathscr{I}_{ny}] = \mathrm{i}\mathscr{I}_{nz}, \quad [\mathscr{I}_{ny}, \mathscr{I}_{nz}] = \mathrm{i}\mathscr{I}_{nx}, \quad [\mathscr{I}_{nz}, \mathscr{I}_{nx}] = \mathrm{i}\mathscr{I}_{ny}$

$[\mathscr{I}_{nj}, 2\mathscr{I}_{nk}\mathscr{I}_{n'l}] = 2[\mathscr{I}_{nj}, \mathscr{I}_{nk}]\mathscr{I}_{n'l}$

$[2\mathscr{I}_{nj}\mathscr{I}_{n'l}, 2\mathscr{I}_{nk}\mathscr{I}_{n'm}] = [\mathscr{I}_{nj}, \mathscr{I}_{nk}]\delta_{lm} + [\mathscr{I}_{n'l}, \mathscr{I}_{n'm}]\delta_{jk}$

$\mathscr{I}_j, \mathscr{I}_k, \mathscr{I}_l$ **are product operators**

$\Rightarrow$ **rotation in 3D subspace of 16D operator space**

Discussed later in the course (not needed now because dipolar coupling averages to zero in isotropic liquids)

Operator of measured quantity

$$M_+ = M_{1+} + M_{2+} = M_{1x} + \mathsf{i}M_{1y} + M_{2x} + \mathsf{i}M_{2y}$$

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

$$\hat{M}_+ = \mathcal{N}\left(\gamma_1\hat{I}_{1+}\gamma_2\hat{I}_{2+}\right)$$

MINOR INTUITIVE MODIFICATION

Thermal equilibrium as the initial state

$$\hat{\rho}^{\mathrm{eq}} = \begin{pmatrix} \frac{1}{4} + \frac{\gamma_1 B_0 \hbar}{8k_\mathrm{B}T} + \frac{\gamma_2 B_0 \hbar}{8k_\mathrm{B}T} & 0 & 0 & 0 \\ 0 & \frac{1}{4} + \frac{\gamma_1 B_0 \hbar}{8k_\mathrm{B}T} - \frac{\gamma_2 B_0 \hbar}{8k_\mathrm{B}T} & 0 & 0 \\ 0 & 0 & \frac{1}{4} - \frac{\gamma_1 B_0 \hbar}{8k_\mathrm{B}T} + \frac{\gamma_2 B_0 \hbar}{8k_\mathrm{B}T} & 0 \\ 0 & 0 & 0 & \frac{1}{4} - \frac{\gamma_1 B_0 \hbar}{8k_\mathrm{B}T} - \frac{\gamma_2 B_0 \hbar}{8k_\mathrm{B}T} \end{pmatrix}$$

$$= \frac{1}{4}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} + \frac{\gamma_1 B_0 \hbar}{8k_\mathrm{B}T}\begin{pmatrix} +1 & 0 & 0 & 0 \\ 0 & +1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} + \frac{\gamma_2 B_0 \hbar}{8k_\mathrm{B}T}\begin{pmatrix} +1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & +1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

$$= \frac{1}{2}\left(\mathscr{I}_t + \kappa_1 \mathscr{I}_{1,z} + \kappa_2 \mathscr{I}_{2,z}\right),$$

SAME APPROACH AS FOR ISOLATED NUCEI,

just applied to both magnetic moments

No effect of dipolar coupling (exact in isotropic liquids)

Relaxation due to dipolar coupling

Bloch-Wangsness-Redfield theory applicable

dipolar coupling: different Hamiltonian, large effect

$$\text{dipolar } b = -\frac{\mu_0\gamma_1\gamma_2\hbar}{4\pi r^3}$$

$$\frac{\mathrm{d}\Delta\langle M_{1z}\rangle}{\mathrm{d}t} = -\frac{b^2}{8}(6J(\omega_{0,1})+2J(\omega_{0,1}-\omega_{0,2})+12J(\omega_{0,1}+\omega_{0,2}))\Delta\langle M_{1z}\rangle$$
$$+\ \frac{b^2}{8}(2J(\omega_{0,1}-\omega_{0,2})-12J(\omega_{0,1}+\omega_{0,2}))\Delta\langle M_{2z}\rangle$$
$$= -R_{a1}\Delta\langle M_{1z}\rangle - R_{x}\Delta\langle M_{2z}\rangle$$

$$\frac{\mathrm{d}\Delta\langle M_{2z}\rangle}{\mathrm{d}t} = -\frac{b^2}{8}(6J(\omega_{0,2})+2J(\omega_{0,1}-\omega_{0,2})+12J(\omega_{0,1}+\omega_{0,2}))\Delta\langle M_{2z}\rangle$$
$$+\ \frac{b^2}{8}(2J(\omega_{0,1}-\omega_{0,2})-12J(\omega_{0,1}+\omega_{0,2}))\Delta\langle M_{1z}\rangle$$
$$= -R_{a2}\Delta\langle M_{2z}\rangle - R_{x}\Delta\langle M_{1z}\rangle$$

$$\frac{\mathrm{d}\langle M_{1+}\rangle}{\mathrm{d}t} = -\frac{b^2}{8}(4J(0)+3J(\omega_{0,1})+6J(\omega_{0,2})$$
$$+J(\omega_{0,1}-\omega_{0,2})+6J(\omega_{0,1}+\omega_{0,2}))\langle M_{1+}\rangle$$
$$= -\left(R_{0,1}+\frac{1}{2}R_{a1}\right)\langle M_{1+}\rangle = -R_{2,1}\langle M_{1+}\rangle$$

Differences of dipole-dipole relaxation

Hamiltonian of dipolar coupling vs. chemical shift:

$2\mathscr{I}_{1x}\mathscr{I}_{2z}, 2\mathscr{I}_{1y}\mathscr{I}_{2z}, 2\mathscr{I}_{1z}\mathscr{I}_{2x}, 2\mathscr{I}_{1z}\mathscr{I}_{2y}$ like $\mathscr{I}_{1x}, \mathscr{I}_{1y}, \mathscr{I}_{2x}, \mathscr{I}_{2y}$

$2\mathscr{I}_{1x}\mathscr{I}_{2x}, 2\mathscr{I}_{1y}\mathscr{I}_{2y}, 2\mathscr{I}_{1x}\mathscr{I}_{2y}, 2\mathscr{I}_{1y}\mathscr{I}_{2x}, 2\mathscr{I}_{1z}\mathscr{I}_{2z}$ new

$b^2 = \left(\frac{\mu_0\gamma_1\gamma_2\hbar}{4\pi r^3}\right)^2 \gg (\gamma_1 B_0 \delta_{\mathrm{a},1})^2$ if 2 is attached proton

$+2J(\omega_{0,1} - \omega_{0,2}) + 12J(\omega_{0,1} + \omega_{0,2})$ in $R_{\mathrm{a}1}$ and $R_{\mathrm{a}2}$

The whole $R_{\mathrm{x}} \propto 2J(\omega_{0,1} - \omega_{0,2}) - 12J(\omega_{0,1} + \omega_{0,2})$

cross-relaxation (mutual dependence)

Nuclear Overhauser Effect (NOE)

$+6J(\omega_{0,2})$ in $R_{0,1}$