Appendix A

One-Electron Theory of Magnetic Dichroism

Electric dipole operator

In order to calculate the transition probabilities for a particular light polarization in a general experimental geometry, the electric dipole operator and the electronic wave function are written in terms of spherical harmonics. We starting from the electric dipole operator in the form:

$$T_\epsilon = \vec{r} \cdot \vec{\epsilon} = x\epsilon_x + y\epsilon_y + z\epsilon_z \tag{A.1}$$

We express the coordinate vectors of the electron and the light polarization:

$$\vec{r} = r\hat{r} = r\left[\left(\frac{x}{r}\right)\hat{\epsilon}_x + \left(\frac{y}{r}\right)\hat{\epsilon}_y + \left(\frac{z}{r}\right)\hat{\epsilon}_z\right] \tag{A.2}$$

and

$$\vec{\epsilon} = \epsilon_x\hat{e}_x + \epsilon_y\hat{e}_y + \epsilon_z\hat{e}_z. \tag{A.3}$$

With the help of the spherical harmonics, the coordinate unit vector can be written as:

$$\begin{aligned}
\hat{r} &= \sqrt{\frac{4\pi}{3}}\left[\left(\frac{Y_1^{-1} - Y_1^1}{\sqrt{2}}\right)\hat{e}_x + i\sqrt{\frac{4\pi}{3}}\left(\frac{Y_1^1 + Y_1^{-1}}{\sqrt{2}}\right)\hat{e}_y + \sqrt{\frac{4\pi}{3}}Y_1^0\hat{e}_z\right] \\
&= \sqrt{\frac{4\pi}{3}}\left(Y_1^{-1}\hat{e}_+ - Y_1^1\hat{e}_- + Y_1^0\hat{e}_z\right)
\end{aligned} \tag{A.4}$$

Here we used

$$\frac{x}{r} = \sqrt{\frac{4\pi}{3}}\left(\frac{Y_1^{-1} - Y_1^1}{\sqrt{2}}\right),\ \frac{y}{r} = i\sqrt{\frac{4\pi}{3}}\left(\frac{Y_1^1 + Y_1^{-1}}{\sqrt{2}}\right),\ \frac{z}{r} = \sqrt{\frac{4\pi}{3}}Y_1^0 \tag{A.5}$$

and introduced the convenient new basis vectors

$$\hat{e}_+ = \frac{\hat{e}_x + i\hat{e}_y}{\sqrt{2}},\ \hat{e}_- = \frac{\hat{e}_x - i\hat{e}_y}{\sqrt{2}}. \tag{A.6}$$

One can now rewrite the light polarization vector:

$$\vec{\epsilon} = \epsilon_+ \hat{e}_+ + \epsilon_- \hat{e}_- + \epsilon_z \hat{e}_z, \tag{A.7}$$

with

$$\epsilon_+ = \frac{\epsilon_x - i\epsilon_y}{\sqrt{2}},\ \epsilon_- = \frac{\epsilon_x + i\epsilon_y}{\sqrt{2}}, \tag{A.8}$$

and one arrives at the dipole operator in the form:

$$T_\epsilon = \vec{r} \cdot \vec{\epsilon} = r\sqrt{\frac{4\pi}{3}} \left(-Y_1^1 \epsilon_+ + Y_1^{-1} \epsilon_- + Y_1^0 \epsilon_z\right). \tag{A.9}$$

The dipole operator written in this way is conveniently applied to cases in which CP light propagates along the z axis or z-polarized LP light propagates in the xy plane.

We proceed further in the generalization of the expression for an arbitrary geometry. To define the polarization, one first needs the photon propagation direction, defined by $(\theta_q,\ \phi_q)$, and second, the relative magnitude and phase difference between two orthogonal components of the electric fields. The unit vector of polarization in spherical coordinates is written in terms of the angles α and δ

$$\hat{\epsilon} = \cos\alpha\ \hat{e}_\theta + \sin\alpha\ e^{i\delta} \hat{e}_\phi. \tag{A.10}$$

Now, the normalized electric-dipole operator for general photon polarization and propagation direction takes the form:

$$\vec{r} \cdot \hat{\epsilon} = \sqrt{\frac{4\pi}{3}} \left(Y_1^{-1} \hat{e}_+ - Y_1^1 \hat{e}_- + Y_1^0 \hat{e}_z\right) \cdot \left(\cos\alpha\ \hat{e}_\theta + \sin\alpha\ e^{i\delta} \hat{e}_\phi\right), \tag{A.11}$$

where

$$\begin{aligned} \hat{e}_\theta &= \cos\theta_q\ \cos\phi_q\ \hat{e}_x + \cos\theta_q\ \sin\phi_q\ \hat{e}_y - \sin\theta_q\ \hat{e}_z \\ \hat{e}_\phi &= -\sin\phi_q\ \hat{e}_x + \cos\phi_q\ \hat{e}_y. \end{aligned} \tag{A.12}$$

We have used the identities

$$(\hat{e}_\pm)^* \cdot \hat{e}_\theta = \frac{e^{\mp i\phi_q}}{\sqrt{2}} \cos\theta_q;\ (\hat{e}_\pm)^* \cdot \hat{e}_\phi = \frac{\mp i e^{\mp i\phi_q}}{\sqrt{2}}. \tag{A.13}$$

We now arrive at the expression for the polarization coefficients in terms of the parameters $\theta_q,\ \phi_q,\ \alpha,\ \beta$ describing general experiment geometries:

$\langle\Psi_{k\uparrow}\vert$	$\langle\Psi_{k\downarrow}\vert$	$\vert j,m_j\rangle$
$-\frac{3}{2}\widetilde{R}_2\sin^2\theta_k e^{2i\phi_k}$	0	$\vert\frac{3}{2},\ \frac{3}{2}\rangle$
$\sqrt{3}\widetilde{R}_2\sin\theta_k\cos\theta_k e^{i\phi_k}$	$-\sqrt{\frac{3}{4}}\widetilde{R}_2\sin^2\theta_k e^{2i\phi_k}$	$\vert\frac{3}{2},\ \frac{1}{2}\rangle$
$-\sqrt{\frac{1}{3}}[\widetilde{R}_0+\frac{1}{2}\widetilde{R}_2(3\cos^2\theta_k-1)]$	$\sqrt{3}\widetilde{R}_2\sin\theta_k\cos\theta_k e^{i\phi_k}$	$\vert\frac{3}{2},\ -\frac{1}{2}\rangle$
0	$-[\widetilde{R}_0+\frac{1}{2}\widetilde{R}_2(3\cos^2\theta_k-1)]$	$\vert\frac{3}{2},\ -\frac{3}{2}\rangle$
$\sqrt{\frac{3}{2}}\widetilde{R}_2\sin\theta_k\cos\theta_k e^{i\phi_k}$	$\sqrt{\frac{3}{2}}\widetilde{R}_2\sin^2\theta_k e^{2i\phi_k}$	$\vert\frac{1}{2},\ \frac{1}{2}\rangle$
$-\sqrt{\frac{2}{3}}[\widetilde{R}_0+\frac{1}{2}\widetilde{R}_2(3\cos^2\theta_k-1)]$	$-\sqrt{\frac{3}{2}}\widetilde{R}_2\sin\theta_k\cos\theta_k e^{i\phi_k}$	$\vert\frac{1}{2},\ -\frac{1}{2}\rangle$

Table A.1: Dipole transition matrix elements, $\widehat{T}_\epsilon = rY_1^1$ for PE from p-level. From Ref. [38].

$\langle\Psi_{k\uparrow}\vert$	$\langle\Psi_{k\downarrow}\vert$	$\vert j,m_j\rangle$
$-[\widetilde{R}_0+\frac{1}{2}\widetilde{R}_2(3\cos^2\theta_k-1)]$	0	$\vert\frac{3}{2},\ \frac{3}{2}\rangle$
$-\sqrt{3}\widetilde{R}_2\sin\theta_k\cos\theta_k e^{-i\phi_k}$	$-\sqrt{\frac{1}{3}}[\widetilde{R}_0+\frac{1}{2}\widetilde{R}_2(3\cos^2\theta_k-1)]$	$\vert\frac{3}{2},\ \frac{1}{2}\rangle$
$-\sqrt{\frac{3}{4}}\widetilde{R}_2\sin^2\theta_k e^{-2i\phi_k}$	$-\sqrt{3}\widetilde{R}_2\sin\theta_k\cos\theta_k e^{-i\phi_k}$	$\vert\frac{3}{2},\ -\frac{1}{2}\rangle$
0	$-\frac{3}{2}\widetilde{R}_2\sin^2\theta_k e^{-2i\phi_k}$	$\vert\frac{3}{2},\ -\frac{3}{2}\rangle$
$-\sqrt{\frac{3}{2}}\widetilde{R}_2\sin\theta_k\cos\theta_k e^{-i\phi_k}$	$\sqrt{\frac{2}{3}}[\widetilde{R}_0+\frac{1}{2}\widetilde{R}_2(3\cos^2\theta_k-1)]$	$\vert\frac{1}{2},\ \frac{1}{2}\rangle$
$-\sqrt{\frac{3}{2}}\widetilde{R}_2\sin^2\theta_k e^{-2i\phi_k}$	$\sqrt{\frac{3}{2}}\widetilde{R}_2\sin\theta_k\cos\theta_k e^{-i\phi_k}$	$\vert\frac{1}{2},\ -\frac{1}{2}\rangle$

Table A.2: Dipole transition matrix elements, $\widehat{T}_\epsilon = rY_1^{-1}$.

$$\begin{aligned}
\epsilon_+ &= \frac{e^{-i\phi_q}}{\sqrt{2}}[\cos\alpha\ \cos\theta_q - i\sin\alpha\ e^{i\delta}] \\
\epsilon_- &= \frac{e^{i\phi_q}}{\sqrt{2}}[\cos\alpha\ \cos\theta_q + i\sin\alpha\ e^{i\delta}] \\
\epsilon_z &= -\cos\alpha\ \sin\theta_q
\end{aligned} \tag{A.14}$$

One can see that the electric dipole operator for an arbitrary choice of light can be represented by a linear combination of spherical harmonic functions. RCP light propagating in z direction ($\theta_q = 0^0$), with $\alpha = 45^0$ and $\delta = 90^0$ ($|\epsilon_+| = 1$), corresponds to $T_\epsilon \sim Y_1^1$, i.e. the photon angular momentum and the wave vector q are parallel. LP light propagating along x direction ($\theta_q = 90^0,\ \phi_q = 0^0$), with $\alpha = 90^0$, $\delta = 0^0$, gives $\hat{\epsilon} = \hat{e}_y$; consequently $T_\epsilon \sim i\left(Y_1^1 + Y_1^{-1}\right) \sim y$.

Dipole transition matrix elements

Dipole transition matrix elements, calculated for the basis set $|j, m_j\rangle$, with $j = \frac{1}{2}, \frac{3}{2}$ and for particular light polarizations ($rY_1^1,\ rY_1^{-1},\ rY_1^0$), are presented

$\langle\Psi_{k\uparrow}\vert$	$\langle\Psi_{k\downarrow}\vert$	$\vert j,m_j\rangle$
$\sqrt{\frac{9}{2}}\widetilde{R}_2\sin\theta_k\cos\theta_k e^{i\phi_k}$	0	$\vert\frac{3}{2},\ \frac{3}{2}\rangle$
$\sqrt{\frac{2}{3}}[\widetilde{R}_0-\widetilde{R}_2(3\cos^2\theta_k-1)]$	$\sqrt{\frac{3}{2}}\widetilde{R}_2\sin\theta_k\cos\theta_k e^{i\phi_k}$	$\vert\frac{3}{2},\ \frac{1}{2}\rangle$
$-\sqrt{\frac{3}{2}}\widetilde{R}_2\sin\theta_k\cos\theta_k e^{-i\phi_k}$	$\sqrt{\frac{2}{3}}[\widetilde{R}_0-\widetilde{R}_2(3\cos^2\theta_k-1)]$	$\vert\frac{3}{2},\ -\frac{1}{2}\rangle$
0	$-\sqrt{\frac{9}{2}}\widetilde{R}_2\sin\theta_k\cos\theta_k e^{-i\phi_k}$	$\vert\frac{3}{2},\ -\frac{3}{2}\rangle$
$\sqrt{\frac{1}{3}}[\widetilde{R}_0-\widetilde{R}_2(3\cos^2\theta_k-1)]$	$-\sqrt{3}\widetilde{R}_2\sin\theta_k\cos\theta_k e^{i\phi_k}$	$\vert\frac{1}{2},\ \frac{1}{2}\rangle$
$-\sqrt{3}\widetilde{R}_2\sin\theta_k\cos\theta_k e^{-i\phi_k}$	$-\sqrt{\frac{1}{3}}[\widetilde{R}_0-\widetilde{R}_2(3\cos^2\theta_k-1)]$	$\vert\frac{1}{2},\ -\frac{1}{2}\rangle$

Table A.3: Dipole transition matrix elements, $\widehat{T}_\epsilon = rY_1^0$.

in the Tables A.1, A.2, A.3. In the tables, θ_k, ϕ_k describe the emitted electrons. The $\widetilde{R}_l$ are defined as $\widetilde{R}_l = R_l e^{i\delta_l}$, with R_l being the radial part of the matrix element for the dipole-allowed final-state channels:

$$R_l = \int_0^\infty f_{kl}(r) r^3 f_{nl}(r) dr \tag{A.15}$$

δ_l denotes the phase of the outgoing photoelectron wave of orbital character l. For some elements, the matrix elements and the phase shifts have been tabulated by Goldberg, Fadley, and Kono [40].