7.7: Appendix - Magnetic Dipole and Electric Quadrupole Transitions

The second term in the expansion in eq. (6.39) leads to magnetic dipole and electric quadrupole transitions, which we will describe here. The interaction potential is

$V^{(2)}(t) = -\frac{q}{m}\left[iA_0(\hat{\varepsilon}\cdot\bar{p})(\bar{k}\cdot\bar{r})e^{-i\omega t} - iA_0^*(\hat{\varepsilon}\cdot\bar{p})(\bar{k}\cdot\bar{r})e^{i\omega t}\right]$

We can use the identity

$$\begin{aligned}(\hat{\varepsilon}\cdot\bar{p})(\bar{k}\cdot\bar{r}) &= \hat{\varepsilon}\cdot(\overline{pr})\cdot\bar{k} \\ &= \frac{1}{2}\hat{\varepsilon}\,(\overline{pr}-\overline{rp})\bar{k} + \frac{1}{2}\hat{\varepsilon}\,(\overline{pr}+\overline{rp})\bar{k}\end{aligned}$$

to separate V(t) into two distinct light–matter interaction terms:

$$V^{(2)}(t) = V^{(2)}_{mag}(t) + V^{(2)}_{Q}(t) \tag{7.7.1}$$

$$V^{(2)}_{mag}(t) = \frac{-iq}{2m}\hat{\varepsilon}\cdot(\overline{pr}-\overline{rp})\cdot\bar{k}\left(A_0e^{-i\omega t} + A_0^*e^{i\omega t}\right) \tag{7.7.2}$$

$$V^{(2)}_{Q}(t) = \frac{-iq}{2m}\hat{\varepsilon}\cdot(\overline{pr}+\overline{rp})\cdot\bar{k}\left(A_0e^{-i\omega t} + A_0^*e^{i\omega t}\right) \tag{7.7.3}$$

where the first $V^{(2)}_{\text{mag}}$ gives rise to magnetic dipole transitions, and the second $V^{(2)}_{Q}$ leads to electric quadrupole transitions.

For the notation above, $\overline{pr}$ represents an outer product (tensor product $\bar{p}:\bar{r}$), so that

$$\hat{\varepsilon}\cdot(\overline{pr})\cdot\bar{k} = \begin{pmatrix}\varepsilon_x & \varepsilon_y & \varepsilon_z\end{pmatrix}\begin{pmatrix}p_xr_x & p_xr_y & p_xr_z \\ p_yr_x & p_yr_y & p_yr_z \\ p_zr_x & p_zr_y & p_zr_z\end{pmatrix}\begin{pmatrix}k_x \\ k_y \\ k_z\end{pmatrix} \tag{7.7.4}$$

This expression is meant to imply that the component of r that lies along k can influence the magnitude of p along ε. Alternatively this term could be written $\sum_{a,b=x,y,z}\varepsilon_a\left(p_ar_b\right)k_b$. These interaction potentials can be simplified and made more intuitive. Considering first eq. 7.7.2, we can use the vector identity $(\bar{A}\times\bar{B})\cdot(\bar{C}\times\bar{D}) = (\bar{A}\times\bar{C})(\bar{B}\times\bar{D}) - (\bar{A}\times\bar{D})(\bar{B}\times\bar{C})$ to show

$$\begin{aligned}\frac{1}{2}\hat{\varepsilon}\cdot(\overline{pr}-\overline{rp})\cdot\bar{k} &= \frac{1}{2}[(\hat{\varepsilon}\cdot\bar{p})(\bar{r}\cdot\bar{k}) - (\hat{\varepsilon}\cdot\bar{r})(\bar{p}\cdot\bar{k})] = \frac{1}{2}[(\bar{k}\cdot\hat{\varepsilon})\cdot(\bar{r}\times\bar{p})] \\ &= \frac{1}{2}(\bar{k}\times\hat{\varepsilon})\cdot\bar{L}\end{aligned}$$

For electronic spectroscopy, $\bar{L}$ is the orbital angular momentum. Since the vector $\bar{k}\times\hat{\varepsilon}$ describes the direction of the magnetic field $\bar{B}$, and since $A_0 = B_0/2ik$

$$V^{(2)}_{md}(t) = \frac{-q}{2m}\bar{B}(t)\cdot\bar{L} \quad \bar{B}(t) = \bar{B}_0\cos\omega t \tag{7.7.5}$$

$\bar{B}\cdot\bar{L}$ more generally is $\bar{B}\cdot(\bar{L}+2\bar{S})$ when considering the spin degrees of freedom. In the case of an electron,

$$\frac{q\bar{L}}{m} = \frac{2c}{\hbar}\beta\bar{L} = \frac{2c}{\hbar}\bar{\mu}_{mag} \tag{7.7.6}$$

where the Bohr magneton

$$\beta = \sum_i e\hbar/2m_ic, \text{and} \bar{\mu}_{mag} = \beta\bar{L} \tag{7.7.7}$$

is the magnetic dipole operator. So we have the form for the magnetic dipole interaction

$$V^{(2)}_{mag}(t) = -\frac{c}{\hbar}\bar{B}(t)\cdot\bar{\mu}_{mag} \tag{7.7.8}$$

For electric quadrupole transitions, once can simplify eq. 7.7.3 by evaluating matrix elements for the operator $(\overline{pr}+\overline{rp})$.

$$\overline{pr}+\overline{rp} = \frac{im}{\hbar}[[H_0,\bar{r}]\,\bar{r} - \bar{r}\,[\bar{r},H_0]] = \frac{-im}{\hbar}[\bar{r}\bar{r},H_0] \tag{7.7.9}$$

and

$$V_Q^{(2)}(t) = \frac{-q}{2\hbar} \hat{\varepsilon} \cdot [\bar{r}\bar{r}, H_0] \cdot \bar{k} \left(A_0 e^{-i\omega t} + A_0^* e^{i\omega t} \right) \tag{7.7.10}$$

Here $\bar{r}\bar{r}$ is an outer product of vectors. For a system of many charges (i), we define the quadrupole moment, a traceless second rank tensor

$$\begin{gathered} \bar{Q} = \sum_i q_i \bar{r} \otimes \bar{r} \\ Q_{mn} = \sum_i q_i \left(3 r_{mi} \cdot r_{ni} - r_i^2 \delta_{mn} \right) \quad m, n = x, y, z \end{gathered} \tag{7.7.11}$$

Now, using $A_0 = E_0 / 2i\omega$ eq. (7.7.10) becomes

$$V(t) = -\frac{1}{2i\hbar\omega} \bar{E}(t) \cdot \left[\bar{\bar{Q}}, H_0 \right] \cdot \hat{k} \quad \bar{E}(t) = \bar{E}_0 \cos \omega t \tag{7.7.12}$$

Since the matrix element $\langle k | [Q, H_0] | \ell \rangle = \hbar \omega_{k\ell} \bar{\bar{Q}}_{k\ell}$, we can write the electric quadrupole transition moment as

$$\begin{aligned} V_{k\ell} &= \frac{i E_0 \omega_{k\ell}}{2\omega} \langle k | \hat{\varepsilon} \cdot \bar{\bar{Q}} \cdot \hat{k} | \ell \rangle \\ &= \frac{i E_0 \omega_{k\ell}}{2\omega} \bar{\bar{Q}}_{k\ell} \end{aligned}$$