Evaluation of the matrix elements for radiative transitions

The transition matrix element for electic dipole transition is proportional to $|\langle e|\mathbf{E}\cdot\mathbf{r}|g\rangle|^2$ where $|e\rangle$ and $|g\rangle$ are described by some angular momentum quantum numbers. First consider the simplest case $|g\rangle = |l, m_l\rangle$ - a single uncoupled electron. We introduce polarization vector $\mathbf{E} = E_0\varepsilon$ and expand the vector product in terms in spherical tensor operators

$$\mathbf{E}\cdot\mathbf{r} = E_0 \sum_{\rho=-1}^{1} (-1)^{\rho}\varepsilon_{\rho} r_{-\rho} \tag{1}$$

here

$$\varepsilon_1 = -\frac{1}{\sqrt{2}}(\varepsilon_x + i\varepsilon_y) \tag{2}$$

$$\varepsilon_0 = \varepsilon_z \tag{3}$$

$$\varepsilon_{-1} = \frac{1}{\sqrt{2}}(\varepsilon_x - i\varepsilon_y) \tag{4}$$

and similar for components of $\mathbf{r}$. Therefore,

$$\langle lm_l|\mathbf{E}\cdot\mathbf{r}|l', m_l'\rangle = E_0 \sum_{\rho} (-1)^{\rho}\varepsilon_{\rho} \langle lm_l|r_{-\rho}|l', m_l'\rangle \tag{5}$$

Here $r_{-\rho}$ is a component of a tensor of rank 1 (i.e. vector) and can be evaluated using a general relationship for expectation value of a tensor operator

$$\langle lm|T_{kq}|l', m'\rangle = (-1)^{l-m}(l||T_k||l') \begin{pmatrix} l & k & l' \\ -m & q & m' \end{pmatrix} \tag{6}$$

The expression in the parenthesis is the Wigner 3j symbol and $(l||T_k||l')$ is known as the reduced matrix element. Eq. (6) is known as the Wigner-Eckart Theorem. The 3j symbol is related to the usual Clebsch-Gordon coefficient coupling two angular momenta j_1 and j_2 to a total momentum j by

$$(j_1 j_2 m_1 m_2|j_1 j_2 j m) = (-1)^{-j_1+j_2-m}\sqrt{2j+1} \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & -m \end{pmatrix} \tag{7}$$

To calculate the reduced matrix element $(l||r||l')$ we can first experes it in terms of spherical harmonics, $r_{\rho} = \sqrt{4\pi/3}rY_{1\rho}$. Then one can do the angular integral explicitly for one particular value of ρ and use Wigner-Eckart theorem to calculate the reduced matrix element. In general,

$$(l||Y_k||l') = (-1)^l \sqrt{\frac{(2l+1)(2l'+1)(2k+1)}{4\pi}} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix} \tag{8}$$

Finally, we get $(l||r||l') = \langle r\rangle (l-l')\sqrt{l_{\max}}$, where $l_{\max} = \max(l, l')$ and $l' = l\pm 1$. The reduced matrix element is equal to zero if $l' \neq l\pm 1$. Therefore a dipole transition has to change l quantum number. Here $\langle r\rangle$ is the purely radial matrix element between the two states, $\langle r\rangle = \int R_g(r)R_e(r)r^3dr$. Hence

$$\langle lm_l|\mathbf{E}\cdot\mathbf{r}|l', m_l'\rangle = E_0 \langle r\rangle \sqrt{l_{\max}} \sum_{\rho} (-1)^{\rho+l-m}(l-l') \begin{pmatrix} l & 1 & l' \\ -m & -\rho & m' \end{pmatrix} \varepsilon_{\rho} \tag{9}$$

$$|\langle e|\mathbf{E}\cdot\mathbf{r}|g\rangle|^2 = \langle lm_l|\mathbf{E}\cdot\mathbf{r}|l', m_l'\rangle \langle l'm_l'|\mathbf{E}^*\cdot\mathbf{r}|l, m_l\rangle = E_0^2 \langle r\rangle^2 l_{\max} \times \tag{10}$$

$$\sum_{\rho,\rho'} (-1)^{\rho+\rho'+l+l'-m-m'+1} \begin{pmatrix} l & 1 & l' \\ -m & -\rho & m' \end{pmatrix} \begin{pmatrix} l' & 1 & l \\ -m' & -\rho' & m \end{pmatrix} \varepsilon_{\rho}\varepsilon^*_{\rho'} \tag{11}$$

For the 3j symbol to be non-zero we need $-m-\rho+m'=0$ and $-m'-\rho'+m=0$. So, $\rho = m'-m = -\rho'$. Also by symmetry of the 3j symbols

$$\begin{pmatrix} l & 1 & l' \\ -m & -\rho & m' \end{pmatrix} = (-1)^{l+l'+\rho} \begin{pmatrix} l' & 1 & l \\ m' & -\rho & -m \end{pmatrix} = \begin{pmatrix} l' & 1 & l \\ -m' & \rho & m \end{pmatrix} \tag{12}$$

So,

$$|\langle lm|\mathbf{E}\cdot\mathbf{r}|l'm'\rangle|^2 = E_0^2 \langle r\rangle^2 l_{\max}(-1)^{l+l'-m-m'+1} \begin{pmatrix} l & 1 & l' \\ -m & m-m' & m' \end{pmatrix}^2 \varepsilon_{m'-m}\varepsilon^*_{m-m'} \tag{13}$$

As an example, calculate

$$|\langle 00|\mathbf{E}\cdot\mathbf{r}|11\rangle|^2 = -E_0^2 \langle r\rangle^2 l_{\max} \begin{pmatrix} 0 & 1 & 1 \\ 0 & -1 & 1 \end{pmatrix}^2 \varepsilon_1\varepsilon^*_{-1} = -\frac{E_0^2 \langle r\rangle^2 l_{\max}}{3}\varepsilon_1\varepsilon^*_{-1} \tag{14}$$

Note that ε^*_{-1} refers to the complex conjugate of the field, not the spherical tensor, $\varepsilon^*_{-1} = (\varepsilon^*_x - i\varepsilon^*_y)/\sqrt{2}$.

If the light is right circularly polarized, $\varepsilon_R = -(\widehat{x} + i\widehat{y})/\sqrt{2}$, then one gets $\varepsilon_1\varepsilon^*_{-1} = -1$ and $|\langle 00|\mathbf{E}\cdot\mathbf{r}|11\rangle|^2 = E_0^2 \langle r\rangle^2 l_{\max}/3$. For left circularly or linearly polarized light $\varepsilon_1\varepsilon^*_{-1} = 0$. Similarly,

$$|\langle 00|\mathbf{E}\cdot\mathbf{r}|10\rangle|^2 = E_0^2 \langle r\rangle^2 l_{\max} \begin{pmatrix} 1 & 1 & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 \varepsilon_0\varepsilon^*_0 = E_0^2 \langle r\rangle^2 l_{\max}\varepsilon_z^2/3$$

In more general case, the quantum state is described by additional quantum numbers, for example, $|l,s,j,I,F,m_F\rangle$, where $j=l+s$ and $F=j+I$. To evaluate the transition matrix element in this case one first uses the Wigner-Eckert therem to get a reduced matrix element

$$\langle l,s,j,I,F,m|T_{kq}|l',s,j',I,F',m'\rangle = (-1)^{F-m}(l,s,j,I,F||T_k||l',s,j',I,F') \begin{pmatrix} F & k & F' \\ -m & q & m' \end{pmatrix} \tag{15}$$

Then one looks for the interaction of the operator T_k with the angular momenta involved. In the case of $T_k = r$, there is only interaction with orbital angular momentum, not electron or nuclear spin. There is a general relationship for reduced matrix elements

$$(J_1,J_2,J||T_k||J_1',J_2,J') = (-1)^{J_1+J_2+J'+k}(J_1||T_k||J_1')\sqrt{(2J+1)(2J'+1)} \begin{Bmatrix} J_1 & J & J_2 \\ J' & J_1' & k \end{Bmatrix} \tag{16}$$

when the operator T_k commutes with J_2 but not J_1.The quantity in $\{\}$ is the 6j symbol. In the case of $|l,s,j,I,F,m_F\rangle$ state, one needs to apply this relationship twice, first to get $(l,s,j||T_k||l',s,j')$ and then $(l||T_k||l')$.

This general method allows one to calculate transition matrix elements as well as any other operator represented in terms of spherical tensor components.