Hydrogen Dipole matrix elements using the Factorization method

Factorization formula(s)

First we assume the relativistic (spinor) hydrogen wavefunction [Eq. (7.4.89) of Biedernharn-Louck book]:

$$\phi_{Ekm}(\mathbf{r}) = R_{El(k)}(r)\chi_{km}(\Omega) = R_{El(k)}(r)\mathbf{Y}^{l_k \frac{1}{2}}_{j_k m}(\Omega),$$

with $\mathbf{Y}^{l_k \frac{1}{2}}_{j_k m}(\Omega)$ given by (6.57) for the spin-1/2 case.

The values of l_k are related with k and l as:

$$\kappa > 0 \quad \rightarrow \quad \begin{cases} l(\kappa) & = \kappa = l \\ l(-\kappa) & = \kappa - 1 = l - 1 \end{cases} \tag{1}$$

$$\kappa < 0 \quad \rightarrow \quad \begin{cases} l(\kappa) & = -\kappa - 1 = l \\ l(-\kappa) & = -\kappa = l + 1 \end{cases} \tag{2}$$

Since the spinor part is fully determined from the κ, m values we focus on the radial part. Taken into account various symmetry properties we may arrive at the below (relativistic) formula as is expressed in 7.4.100 of Biedernharn-Louck book:

$$\left[1 - \kappa\left(\frac{d}{dr} + \frac{k+1}{r}\right)\right] R_{\eta l(\kappa)}(r) = \left[1 - \varepsilon\frac{k^2}{\eta^2}\right]^{1/2} R_{\eta l(-\kappa)}(r) \tag{3}$$

$$\tag{4}$$

$$\eta = \begin{cases} n = 1, 2, \cdots, & E = -1/n^2 < 0, \quad \varepsilon = +1 \\ 1, & E = 0, \quad \varepsilon = 0 \\ \frac{1}{k} > 0 & E = k^2 > 0, \quad \varepsilon = -1 \end{cases} \tag{5}$$

From the above relation we may obtain a recurrence relation for the radial part of the corresponding (non-relativistic) radial functions:

$$\left[1+(l+1)\left(\frac{d}{dr}-\frac{l}{r}\right)\right]R_{\eta l}(r)=\left[1-\varepsilon\frac{(l+1)^2}{\eta^2}\right]^{1/2}R_{\eta l+1}(r) \tag{6}$$

$$\left[1-l\left(\frac{d}{dr}+\frac{l+1}{r}\right)\right]R_{\eta l}(r)=\left[1-\varepsilon\frac{l^2}{\eta^2}\right]^{1/2}R_{\eta l-1}(r) \tag{7}$$

Let's take the latter equation (Equation 7) and substitute $l\to l+1$; then we instead get:

$$\left[1-(l+1)\left(\frac{d}{dr}+\frac{l+2}{r}\right)\right]R_{\eta l+1}(r)=\left[1-\varepsilon\frac{(l+1)^2}{\eta^2}\right]^{1/2}R_{\eta l}(r)$$

Now we continue by substitution of the $P_{\eta l}(r)$ radial function, defined by:

$$R_{\eta l}(r)=\frac{1}{r}P_{\eta l}(r)$$

In this case the recurrence relation becomes:

$$\left[1-(l+1)\left(\frac{d}{dr}+\frac{l+1}{r}\right)\right]P_{\eta l+1}(r)=\left[1-\varepsilon\frac{(l+1)^2}{\eta^2}\right]^{1/2}P_{\eta l}(r)$$

This is one of the two main equations for the recurrence relation for $P_{\eta l}(r)$; Multiplying both sides with $P_{\eta' l}(r)$ and integrating over the radial variable we find,

$$\langle P_{\eta' l}|P_{\eta l+1}\rangle-(l+1)\langle P_{\eta' l}|\left(\frac{d}{dr}+\frac{l+1}{r}\right)|P_{\eta l+1}\rangle=\delta_{\eta'\eta}\left[1-\varepsilon\frac{(l+1)^2}{\eta^2}\right]^{1/2}$$

since the radial functions $R_{\eta l}(r)$ are assumed orthonormalized (orthogonal because are solutions of the same radial Hamiltonian); note that we define:

$$\langle P_{\eta' l}|P_{\eta l+1}\rangle:=\int_0^\infty dr\,P_{\eta' l}(r)P_{\eta l+1}(r)=\int_0^\infty dr\,r^2R_{\eta' l}(r)R_{\eta l+1}(r)$$

Eventually we obtain the following relation:

$$\boxed{(l+1)\langle P_{\eta' l}|\left(\frac{d}{dr}+\frac{l+1}{r}\right)|P_{\eta l+1}\rangle=\langle P_{\eta' l}|P_{\eta l+1}\rangle-\delta_{\eta'\eta}\left[1-\varepsilon\frac{(l+1)^2}{\eta^2}\right]^{1/2}} \tag{8}$$

Also, by making the change $l \rightarrow l-1$ in (Equation 6) we obtain instead:

$$\boxed{l\langle P_{\eta' l}|\left(\frac{d}{dr}-\frac{l}{r}\right)|P_{\eta l-1}\rangle = \delta_{\eta'\eta}\left[1-\varepsilon\frac{l^2}{\eta^2}\right]^{1/2} - \langle P_{\eta' l}|P_{\eta l-1}\rangle} \tag{9}$$

Note that we can arrive at the same relation if we instead have started from (Equation 8), changing $l \rightarrow l-1$ and then using the boundary conditions (BCs) (also swapping the $\eta \leftrightarrow \eta'$ between the states) to write:

$$P_{\eta l}(a)P_{\eta l'}(b) = P_{\eta l}(a)P_{\eta l}(b),$$

which hold for our case of infinitely extended space ($P(0) = 0$ and $P(r \rightarrow \infty) \rightarrow 0$). The latter BCs (needed to ensure the self-adjointess of the momentum operator), require $\langle P_{\eta l}|P'_{\eta l'}\rangle = -\langle P'_{\eta l}|P_{\eta l'}\rangle$.

We notice that the second term in the LHS of (Equation 8 and Equation 9) is the radial dipole operator in the velocity gauge for transitions $l \rightarrow l+1$ and $l \rightarrow l-1$ respectively; then we can write:

$$d^{(v)}_{\eta' l;\eta l+1} = \frac{1}{l+1}\left[\langle P_{\eta' l}|P_{\eta l+1}\rangle - \delta_{\eta'\eta}\left[1-\varepsilon\frac{(l+1)^2}{\eta^2}\right]^{1/2}\right] \tag{10}$$

and

$$d^{v}_{\eta' l;\eta l-1} = -\frac{1}{l}\left[\langle P_{\eta' l}|P_{\eta l-1}\rangle - \delta_{\eta'\eta}\left[1-\varepsilon\frac{l^2}{\eta^2}\right]^{1/2}\right]$$

We then reach at the important conclusion that for the calculation of the dipole matrix elements we only need to calculate the overlap integrals between the involved states; this makes redundant the calculation of matrix elements between states and their derivatives as well as non-diagonal matrix elements of the $1/r$

In the below we give few specific examples for the case of hydrogen.

Note: need to check whether the below relation holds generally:

$$\langle P_{nl}|(\frac{d}{dr}+\frac{l+1}{r})|P_{nl+1}\rangle = 0,$$

if non-zero it would correspond to a transition (say EM transition) with a static field ($\omega = 0$), with the exchange of angular momentum ($l = 1$) without exchanging energy.

Normalized Radial Wavefunctions for Hydrogen

First we resume the properties for the hydrogen wavefunction. As usual, we use atomic units $\hbar = m_e = e = 1/4\pi\varepsilon_0 = 1$). We also assume, the radial wavefunctions $R_{nl}(r) $ are normalized such that:

$$\int_0^\infty |R_{nl}(r)|^2 r^2 \, dr = 1$$

let's take the the $2s \to 3p$ transition; the two radial (reduced) functions are given by,

$$P_{20}(r) = \frac{1}{2\sqrt{2}}(2-r)e^{-r/2}, \qquad P_{31}(r) = \frac{4}{81\sqrt{6}} r(6-r)e^{-r/3}$$

We apply (Equation 8) for this case with $\varepsilon = -1, \eta = 0, 1, 2, ...$ and $(n', l) = (2, 0) \to (n, l) = (3, 1)$; since the energy differs we have $\delta_{\eta'\eta=0}$ and need to verify the below equation:

$$(0+1)\left(\langle P_{20}|P'_{31}\rangle + \langle P_{20}|\frac{0+1}{r}|P_{31}\rangle\right) = \langle P_{20}|P_{31}\rangle \quad \to \quad \langle P_{20}|P'_{31}\rangle + \langle P_{20}|\frac{1}{r}|P_{31}\rangle = \langle P_{20}|P_{31}\rangle \tag{11}$$

The integrations for the given radial functions are quite straightforward to obtain by various means:

$$\langle P_{20}|P'_{31}\rangle = \frac{88128}{3125} \times \frac{1}{2\sqrt{2}} \times \frac{4}{81\sqrt{6}} \tag{12}$$

$$\langle P_{20}|\frac{1}{r}|P_{31}\rangle = \frac{5184}{3125} \times \frac{1}{2\sqrt{2}} \times \frac{4}{81\sqrt{6}} \tag{13}$$

$$\langle P_{20}|P_{31}\rangle = \frac{93312}{3125} \times \frac{1}{2\sqrt{2}} \times \frac{4}{81\sqrt{6}} \tag{14}$$

It's not difficult that to see that (Equation 11) holds since 88128 + 5184 = 93312.

We can also check the case where the principal quantum number is the same; for example the validity of (Equation 8) for $\eta = n = 3, l = 0 \to 1$ (so, $\varepsilon = 1$),

$$(0+1)\langle P_{30}|\left(\frac{d}{dr} + \frac{0+1}{r}\right)|P_{31}\rangle = \langle P_{30}|P_{31}\rangle - \left[1 - \frac{(0+1)^2}{3^2}\right]^{1/2}$$

The LHS is identically zero, so it remains to show that,

$$\langle P_{30}|P_{31}\rangle = \frac{\sqrt{8}}{3}$$

We have for the integral

$$\langle P_{30}|P_{31}\rangle = \int_0^\infty dr \frac{2}{81\sqrt{3}} r\left(27-18r+2r^2\right)e^{-r/3} \times \frac{8}{27\sqrt{6}}, r\left(1-\frac{r}{6}\right)e^{-r/3}$$

(n = 1)

- (l = 0)

$$R_{10}(r) = 2e^{-r}$$

(n = 2)

- (l = 0)

$$R_{20}(r) = \frac{1}{\sqrt{2}}\left(1-\frac{r}{2}\right)e^{-r/2}$$

- (l = 1)

$$R_{21}(r) = \frac{1}{2\sqrt{6}}\, r\, e^{-r/2}$$

(n = 3)

- (l = 0)

$$R_{30}(r) = \frac{2}{81\sqrt{3}} \left(27 - 18r + 2r^2\right) e^{-r/3}$$

- (l = 1)

$$R_{31}(r) = \frac{8}{27\sqrt{6}}\, r \left(1 - \frac{r}{6}\right) e^{-r/3}$$

- (l = 2)

$$R_{32}(r) = \frac{4}{81\sqrt{30}}\, r^2\, e^{-r/3}$$

(n = 4)

- (l = 0)

$$R_{40}(r) = \frac{1}{96\sqrt{6}} \left(96 - 72r + 12r^2 - r^3\right) e^{-r/4}$$

- (l = 1)

$$R_{41}(r) = \frac{1}{96\sqrt{30}}\, r \left(48 - 18r + r^2\right) e^{-r/4}$$

- (l = 2)

$$R_{42}(r) = \frac{1}{768\sqrt{5}}\, r^2\, (12 - r)\, e^{-r/4}$$

- (l = 3)

$$R_{43}(r) = \frac{1}{768\sqrt{35}}\, r^3\, e^{-r/4}$$