

In these notes, we fill the gaps between equation (7.41) and equation (7.46).

We start with the 1st-order perturbed energy shift (eq 7.41)

$$\Delta_{(1s)^2} = \left\langle \frac{e^2}{r_{12}} \right\rangle_{(1s)^2} = \iint d^3x_1 d^3x_2 \frac{Z^6}{\pi^2 a_0^6} e^{-2Z(r_1+r_2)/a_0} \frac{e^2}{r_{12}} \quad (1)$$

Let $\angle_{r_1, r_2} = \gamma$, then

$$\begin{aligned} \frac{1}{r_{12}} &= \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos \gamma}} \\ &= \frac{1}{r_{>} \sqrt{1 - 2 \cos \gamma \left(\frac{r_{\leq}}{r_{>}} \right) + \left(\frac{r_{\leq}}{r_{>}} \right)^2}} \end{aligned} \quad (2)$$

But recall $g(x, t) = (1 - 2tx + t^2)^{-1/2}$, for $x, t \in [-1, 1]$ is the generating function for the Legendre polynomials

$$(1 - 2tx + t^2)^{-1/2} = \sum_l P_l(x) t^l \quad (3)$$

thus (2) becomes equation (7.42)

$$\frac{1}{r_{12}} = \frac{1}{r_{>}} \sum_l P_l(\cos \gamma) \left(\frac{r_{\leq}}{r_{>}} \right)^l = \sum_l \frac{r_{\leq}^l}{r_{>}^{l+1}} P_l(\cos \gamma) \quad (4)$$

Next, we can use the Addition Theorem of spherical harmonics (proved in earlier notes)

$$P_l(\cos \gamma) = \frac{4\pi}{2l+1} \sum_m Y_l^{m*}(\theta_1, \phi_1) Y_l^m(\theta_2, \phi_2) \quad (5)$$

Insert (4),(5) back into (1) and do the double integral in spherical coordinates,

$$\Delta_{(1s)^2} = \frac{Z^6 e^2}{\pi^2 a_0^6} \int r_1^2 dr_1 \int r_2^2 dr_2 e^{-2Z(r_1+r_2)/a_0} \sum_{l,m} \frac{r_{\leq}^l}{r_{>}^{l+1}} \frac{4\pi}{2l+1} \int d\Omega_1 \int d\Omega_2 Y_l^{m*}(\theta_1, \phi_1) Y_l^m(\theta_2, \phi_2) \quad (6)$$

Next, notice

$$\int d\Omega Y_l^m(\theta, \phi) = \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta C_l^m e^{im\phi} P_l^m(\cos \theta) \quad (7)$$

where the ϕ integral will vanish unless $m = 0$, in which case the θ integral in (7) becomes (let $y = \cos \theta$)

$$\int_{-1}^1 dy P_l(y) = \int_{-1}^1 dy P_l(y) \overbrace{P_0(y)}^{=1} = 2\delta_{l0} \quad (8)$$

Recall $C_{l=0}^{m=0} = 1/\sqrt{4\pi}$, so we have

$$\int d\Omega Y_l^m(\theta, \phi) = \frac{4\pi}{\sqrt{4\pi}} \delta_{l0} \delta_{m0} = \sqrt{4\pi} \delta_{l0} \delta_{m0} \quad (9)$$

Now plugging (9) back into (6) produces

$$\Delta_{(1s)^2} = \frac{Z^6 e^2}{\pi^2 a_0^6} (4\pi)^2 \overbrace{\int r_1^2 dr_1 \int r_2^2 dr_2 e^{-2Z(r_1+r_2)/a_0} \frac{1}{r_{>}}}^R \quad (10)$$

where the radial integral is equivalent to

$$\begin{aligned} R &= \int_0^\infty r_1^2 dr_1 \left\{ \left[\int_0^{r_1} r_2^2 dr_2 e^{-2Z(r_1+r_2)/a_0} \frac{1}{r_1} \right] + \left[\int_{r_1}^\infty r_2^2 dr_2 e^{-2Z(r_1+r_2)/a_0} \frac{1}{r_2} \right] \right\} \quad (\text{define } \beta \equiv \frac{2Z}{a_0}) \\ &= \int_0^\infty r_1 dr_1 e^{-\beta r_1} \underbrace{\int_0^{r_1} r_2^2 dr_2 e^{-\beta r_2}}_A + \int_0^\infty r_1 dr_1 e^{-\beta r_1} \underbrace{\int_{r_1}^\infty r_2 dr_2 e^{-\beta r_2}}_B \end{aligned} \quad (11)$$

For general integration range $[u, v]$,

$$\begin{aligned}
\int_u^v r e^{-\lambda r} dr &= -\frac{1}{\lambda} e^{-\lambda r} r \Big|_u^v + \frac{1}{\lambda} \int_u^v e^{-\lambda r} dr \\
&= -\frac{1}{\lambda} e^{-\lambda r} r \Big|_u^v - \frac{1}{\lambda^2} e^{-\lambda r} \Big|_u^v \\
&= -\left(\frac{1}{\lambda} e^{-\lambda r} r + \frac{1}{\lambda^2} e^{-\lambda r} \right) \Big|_u^v
\end{aligned} \tag{12}$$

$$\begin{aligned}
\int_u^v r^2 e^{-\lambda r} dr &= -\frac{1}{\lambda} e^{-\lambda r} r^2 \Big|_u^v + \frac{1}{\lambda} \int_u^v e^{-\lambda r} 2r dr && \text{(by (12))} \\
&= -\left(\frac{1}{\lambda} e^{-\lambda r} r^2 + \frac{2}{\lambda^2} e^{-\lambda r} r + \frac{2}{\lambda^3} e^{-\lambda r} \right) \Big|_u^v
\end{aligned} \tag{13}$$

Then the A, B in (11) can be evaluated as

$$A = -\left(\frac{1}{\beta} e^{-\beta r_1} r_1^2 + \frac{2}{\beta^2} e^{-\beta r_1} r_1 + \frac{2}{\beta^3} e^{-\beta r_1} - \frac{2}{\beta^3} \right) \tag{14}$$

$$B = \frac{1}{\beta} e^{-\beta r_1} r_1 + \frac{1}{\beta^2} e^{-\beta r_1} \tag{15}$$

Now the radial integral (11) becomes

$$\begin{aligned}
R &= \int_0^\infty -dr_1 \left(\frac{1}{\beta} e^{-2\beta r_1} r_1^3 + \frac{2}{\beta^2} e^{-2\beta r_1} r_1^2 + \frac{2}{\beta^3} e^{-2\beta r_1} r_1 - \frac{2}{\beta^3} e^{-\beta r_1} r_1 \right) + \int_0^\infty dr_1 \left(\frac{1}{\beta} e^{-2\beta r_1} r_1^3 + \frac{1}{\beta^2} e^{-2\beta r_1} r_1^2 \right) \\
&= -\frac{1}{\beta^2} \int_0^\infty e^{-2\beta r_1} r_1^2 dr_1 - \frac{2}{\beta^3} \int_0^\infty e^{-2\beta r_1} r_1 dr_1 + \frac{2}{\beta^3} \int_0^\infty e^{-\beta r_1} r_1 dr_1 && \text{(by (12), (13))} \\
&= -\frac{1}{\beta^2} \frac{2}{(2\beta)^3} - \frac{2}{\beta^3} \frac{1}{(2\beta)^2} + \frac{2}{\beta^3} \frac{1}{\beta^2} \\
&= \frac{5}{4\beta^2} \\
&= \frac{5}{128} \frac{a_0^5}{Z^5}
\end{aligned} \tag{16}$$

Plug back to (10), we eventually get

$$\begin{aligned}
\Delta_{(1s)^2} &= \frac{Z^6 e^2}{\pi^2 a_0^6} (4\pi)^2 \frac{5}{128} \frac{a_0^5}{Z^5} \\
&= \frac{5}{4} \frac{e^2}{a_0}
\end{aligned} \tag{17}$$