Κβαντική Μηχανική Ι.

Πρόβλημα 9.4 : Βρείτε σε πρώτη τάξη της θεωρίας διαταραχών την διόρθωση στην θεμελιώδη ενέργεια ενός μονο-ηλεκτρονικού ατόμου λόγω του πεπερασμένου μεγέθους του πυρήνα. Θεωρείστε ότι ο πυρήνας είναι μια ομογενής σφαίρα φορτίου Ze και ακτίνας R και όλο το φορτίο βρίσκεται στην επιφάνειά της. Αν $R = Z^{\frac{1}{3}}\ 10^{-15}\ m$ βρείτε ποσοστιαία πόσο σημαντική είναι αυτή η διόρθωση.

Solution

9.4 According to Gauss' law the potential outside the spherical shell is that of a point-like charge Ze,

$$V_{\text{outside}} = -\frac{Ze}{r} \ \ , \ \ r > R \tag{1}$$

while inside it is constant, as there is no electric field. This constant is determined by continuity at $r = R$ and therefore

$$V_{\text{inside}} = -\frac{Ze}{R} \ \ , \ \ r < R \tag{2}$$

We consider now as our unperturbed problem the Hydrogen-like atom with a Coulomb potential

$$H_0 = -\frac{\hbar^2}{2m}\vec{\nabla}^2 - \frac{Ze^2}{r} \tag{3}$$

If we write the Hamiltonian for our problem as

$$H = H_0 + \Delta V \tag{4}$$

then

$$\Delta V = \begin{cases} 0, & r > R, \\ \\ \frac{Ze^2}{r} - \frac{Ze^2}{R}, & r < R \end{cases} \tag{5}$$

Note that ΔV is non-negative everywhere.

To compute now the first correction to the ground state energy in perturbation theory we must calculate the matrix element of the perturbation in the unperturbed ground-state wave-function.

$$E_0^{(1)} = \langle 1,0,0|\Delta V|1,0,0\rangle = \int d^3r\ \Delta V\ |\psi_{1,0,0}(r)|^2 \tag{6}$$

The ground state energy of the unperturbed problem is

$$E_0^{(0)} = -\frac{mZ^2e^4}{2\hbar^2} = -\frac{Ze^2}{2a} = -\frac{Z^2e^2}{2a_0} \ \ , \ \ a_0 = \frac{\hbar^2}{me^2} = a\ Z \tag{7}$$

where a is the Bohr radius and a_0 is the Bohr radius for the hydrogen atom. The unperturbed normalized ground state wave-function is

$$\psi_{1,0,0} = \frac{1}{\sqrt{\pi a^3}}e^{-\frac{r}{a}} = \frac{Z^{\frac{3}{2}}}{\sqrt{\pi a_0^3}}\ e^{-Z\frac{r}{a_0}} \tag{8}$$

We may now compute

$$E_0^{(1)} = \frac{1}{\pi a^3}\int_0^\infty r^2 dr \int d\Omega \; \Delta V \; e^{-\frac{2r}{a}} = Ze^2 \frac{4\pi}{\pi a^3}\int_0^R r^2 dr \; \left(\frac{1}{r} - \frac{1}{R}\right) \; e^{-\frac{2r}{a}} \tag{9}$$

where in the second step we integrated over the angles using

$$\int d\Omega \equiv \int_0^\pi \sin\theta \; d\theta \; \int_0^{2\pi} d\phi = 4\pi \tag{10}$$

and we restricted the radial integral in $[0, R]$ as ΔV is zero otherwise. The radial integral can be written as

$$E_0^{(1)} = \frac{4Ze^2}{a^3}\left[I_1(a,R) - \frac{I_2(a,R)}{R}\right] \tag{11}$$

where

$$I_n(a,R) \equiv \int_0^R r^n \; e^{-\frac{2r}{a}} \; dr \tag{12}$$

We can collectively compute such integrals by establishing first a recurrence relation, relating I_n for different n. We first define a new dimensionless variable u so that

$$r = Ru \;\; , \;\; I_n = R^{n+1}\mathcal{I}_n\left(\frac{R}{a}\right) \;\; , \;\; \mathcal{I}_n(\lambda) = \int_0^u du \; u^n e^{-2\lambda u} \tag{13}$$

By taking a derivative with respect to λ we obtain

$$\frac{d\mathcal{I}_n(\lambda)}{d\lambda} = -2\mathcal{I}_{n+1}(\lambda) \qquad \rightarrow \qquad \mathcal{I}_{n+1}(\lambda) = -\frac{1}{2}\frac{d\mathcal{I}_n(\lambda)}{d\lambda} \tag{14}$$

We can easily compute $\mathcal{I}_0$ by direct integration

$$\mathcal{I}_0(\lambda) = \int_0^1 du \; e^{-2\lambda u} = -\frac{e^{-2\lambda u}}{2\lambda}\Big|_0^1 = \frac{1-e^{-2\lambda}}{2\lambda} \tag{15}$$

Using (14) we can now compute

$$\mathcal{I}_1(\lambda) = -\frac{1}{2}\frac{d\mathcal{I}_0(\lambda)}{d\lambda} = -\frac{1}{2}\left[-\frac{1}{2\lambda^2}(1-e^{-2\lambda}) + \frac{2}{2\lambda}e^{-2\lambda}\right] = \frac{1-(1+2\lambda)e^{-2\lambda}}{4\lambda^2} \tag{16}$$

$$\mathcal{I}_2(\lambda) = -\frac{1}{2}\frac{d\mathcal{I}_1(\lambda)}{d\lambda} = \frac{1-(1+2\lambda+2\lambda^2)e^{-2\lambda}}{4\lambda^3} \tag{17}$$

using (14)-(17) we can rewrite (11) as

$$E_0^{(1)} = \frac{4Ze^2}{a^3}\left[R^2\mathcal{I}_1\left(\frac{R}{a}\right) - \frac{R^3\mathcal{I}_2\left(\frac{R}{a}\right)}{R}\right] = \frac{4Ze^2}{a}\frac{R^2}{a^2}\left[\mathcal{I}_1\left(\frac{R}{a}\right) - \mathcal{I}_2\left(\frac{R}{a}\right)\right] = \tag{18}$$

$$= \frac{4Ze^2}{a}\frac{R^2}{a^2}\frac{\frac{R}{a} - 1 + \left(1+\frac{R}{a}\right)e^{-2\frac{R}{a}}}{4\frac{R^3}{a^3}}$$

We may now estimate the ratio $\frac{R}{a}$ using $R = \frac{10^{-15} \; m}{Z^{\frac{1}{3}}}$

$$\frac{R}{a} = Z\frac{R}{a_0} \simeq Z^{\frac{2}{3}}\frac{10^{-15} \;\; m}{0.5 \; 10^{-10} \;\; m} \simeq 2\times 10^{-5} \; Z^{\frac{2}{3}} \tag{19}$$

where the Bohr radius is $a_0 \simeq 0.5 \times 10^{-10} m$. Therefore, even for large nuclear charge $Z \sim 100$ the ratio $R/$ is a small number. We can therefore simplify our result in (18) by expanding it for small R/a using

$$\mathcal{I}_1\left(\frac{R}{a}\right) - \mathcal{I}_2\left(\frac{R}{a}\right) = \frac{1}{6} - \frac{1}{6}\frac{R}{a} + \mathcal{O}\left(\frac{R^2}{a^2}\right) \tag{20}$$

so that

$$E_0^{(1)} = \frac{4Ze^2}{6a}\frac{R^2}{a^2}\left[1 + \mathcal{O}\left(\frac{R}{a}\right)\right] \simeq \frac{2}{3}\frac{Ze^2}{a}\frac{R^2}{a^2} = \frac{2Z^4e^2}{3a_0}\frac{R^2}{a_0^2} \tag{21}$$

To check the validity of perturbation theory we have to compare the leading value of the ground state energy to the correction and see if the correction is relatively small

$$\left|\frac{E_0^{(1)}}{E_0^{(0)}}\right| = \frac{\frac{2Ze^2}{3a}\frac{R^2}{a^2}}{\frac{Ze^2}{2a}} = \frac{4}{3}\frac{R^2}{a^2} \simeq \frac{16}{3} \times 10^{-10}\ Z^{\frac{4}{3}} \tag{22}$$

which for all relevant Z up to 150, is a very small number.

The integral

$$I' = \int_0^R r^2 dr\ \left(\frac{1}{r} - \frac{1}{R}\right)\ e^{-\frac{2r}{a}} = R^2 \int_0^1 du\ \left(u - u^2\right) e^{-2\frac{R}{a}u} \tag{23}$$

can be also computed approximately directly. In the second step in (23) we changed variables to $u = \frac{r}{R}$. Because $R \ll a$ the exponential over the whole integration range is close to one. We can therefore expand it inside the integral

$$(u-u^2)\ e^{-2\frac{R}{a}u} = (u-u^2)(1-2\frac{R}{a}u-\frac{1}{2!}4\left(\frac{R}{a}\right)^2 u^2+\cdots) = u-u^2-2(u^2-u^3)\frac{R}{a}+\mathcal{O}\left[\left(\frac{R}{a}\right)^2\right] \tag{24}$$

Therefore

$$\begin{aligned} I' = R^2 \int_0^1 du \left[u - u^2 - 2(u^2 - u^3)\frac{R}{a} + \mathcal{O}\left[\left(\frac{R}{a}\right)^2\right]\right] &= \\ = R^2\left[\frac{u^2}{2} - \frac{u^3}{3} - 2\left(\frac{u^3}{3} - \frac{u^4}{4}\right)\frac{R}{a} + \mathcal{O}\left[\left(\frac{R}{a}\right)^2\right]\right]_0^1 &= \\ = R^2\left[\frac{1}{2} - \frac{1}{3} - 2\left(\frac{1}{3} - \frac{1}{4}\right)\frac{R}{a} + \mathcal{O}\left[\left(\frac{R}{a}\right)^2\right]\right] &= \\ = \frac{R^2}{6}\left[1 - \frac{R}{a} + \mathcal{O}\left[\left(\frac{R}{a}\right)^2\right]\right] & \end{aligned} \tag{25}$$

which agrees with (20).