Practice Problem #1

1) The Hamiltonian is given by

$$H = \frac{\vec{p}^{\,2}}{2m} - Ze^2 \int d^3r' \frac{\rho_N(r')}{|\vec{r}-\vec{r}'|},$$

since the charge of the nucleus is Ze, we have $\int d^3r\, \rho_N(r) = 1$.

Consider the integral

$$\int d^3r' \frac{\rho_N(r')}{|\vec{r}-\vec{r}'|} = \int_0^\infty dr' r'^2 \rho_N(r') \underbrace{\int_0^{2\pi} d\varphi'}_{=2\pi} \times$$

$$\times \underbrace{\int_{-1}^{+1} d(\cos\theta') \frac{1}{\left[r^2+r'^2-2rr'\cos\theta'\right]^{1/2}}}$$

$$= \frac{2}{-2rr'}\left[\sqrt{r^2+r'^2-2rr'\cos\theta'}\right]\Bigg|_{\cos\theta'=}^{+}$$

$$= \frac{-1}{rr'}\left[|r-r'| - (r+r')\right]$$

$$= -\frac{2\pi}{r}\int_0^\infty dr'\, r' \rho_N(r')\left[|r-r'| - (r+r')\right]$$

$$= \frac{4\pi}{r}\int_0^r dr'\, r'^2 \rho_N(r') + 4\pi\int_r^\infty dr'\, r' \rho_N(r')$$

1) Continuing

$$\int d^3r' \frac{\rho_N(r')}{|\vec{r}-\vec{r}'|} = \frac{1}{r}\overbrace{\int_0^\infty dr' r'^2 \int_{4\pi} d\Omega'}^{\int d^3r'} \rho_N(r')$$

$$+ 4\pi \int_r^\infty dr' \left(r' - \frac{r'^2}{r}\right) \rho_N(r')$$

$$= \frac{1}{r}\underbrace{\int d^3r' \rho_N(r')}_{=1} + 4\pi \int_r^\infty dr' r' \left(1 - \frac{r'}{r}\right) \rho_N(r')$$

So
$$\int d^3r' \frac{\rho_N(r')}{|\vec{r}-\vec{r}'|} = \frac{1}{r} + \underbrace{4\pi \int_r^\infty dr' r' \left(1 - \frac{r'}{r}\right) \rho_N(r')}_{\text{due to nuclear finite size}}$$

So

$$H = \underbrace{\frac{\vec{p}^2}{2m} - \frac{Ze^2}{r}}_{H_0} + \underbrace{- 4\pi Z e^2 \int_r^\infty dr' r' \left(1 - \frac{r'}{r}\right) \rho_N(r')}_{H'}$$

If nucleus is point-like, then $\rho_N(r') = \delta^3(\vec{r}')$ and $H' = 0$. Hence H' is the energy due to finite size effects of nucleus.

1.) R-S perturbation theory gives the first order energy shifts by finding the eigenvalues of the matrix elements in the H_0 eigenbasis of H'.

Now the eigenstates of H_0 are

$$H_0 |n,l,m\rangle = E_n^0 |n,l,m\rangle, \quad n=1,2\ldots$$

with

$$E_n^0 = -\frac{mc^2(Z\alpha)^2}{2}\frac{1}{n^2}$$

$$\vec{L}^2 |n,l,m\rangle = l(l+1)\hbar^2 |n,l,m\rangle$$

$$, \quad l = 0,1,\ldots,n-1$$

$$L_z |n,l,m\rangle = m\hbar |n,l,m\rangle,$$

$$m = -l,\ldots,+l.$$

Thus we need the matrix elements

$$\langle n,l,m| H' |n,l',m'\rangle$$

1.) $\langle n,l,m|H'|n,l',m'\rangle$

$$= -4\pi Ze^2\int d^3r\, \underbrace{\psi^*_{nlm}(\vec{r})}_{=R_{nl}(r)Y_l^m(\theta,\varphi)} \int_r^\infty dr'\, r'\left(1-\frac{r'}{r}\right)\rho_N(r')\, \times \underbrace{\psi_{nl'm'}(\vec{r})}_{=R_{nl'}(r)Y_{l'}^{m'}(\theta,\varphi)}$$

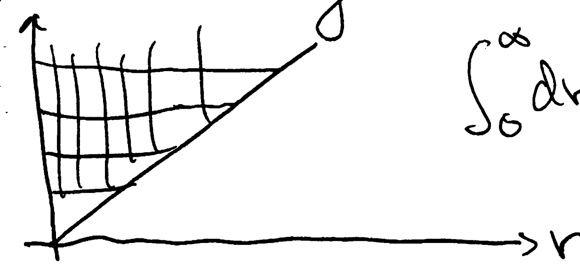
$$= -4\pi Ze^2\int_0^\infty dr\, r^2 R^*_{nl}(r) R_{nl'}(r)\, \times$$

$$\times \int_r^\infty dr'\, r'\left(1-\frac{r'}{r}\right)\rho_N(r') \underbrace{\int_{4\pi} d\Omega\, Y_l^{m*}(\theta,\varphi)\, Y_{l'}^{m'}(\theta,\varphi)}_{=\delta_{ll'}\delta_{mm'}}$$

$$= -4\pi Ze^2 \delta_{ll'}\delta_{mm'} \int_0^\infty dr \int_r^\infty dr'\, |R_{nl}(r)|^2 \times$$

$$\times\, r r'(r-r')\rho_N(r')$$

Now change order of integration



$$\int_0^\infty dr \int_r^\infty dr' = \int_0^\infty dr' \int_0^{r'} dr$$

1.) So we obtain

$$\langle n, l, m | H' | n, l', m' \rangle$$

$$= -4\pi Z e^2 \delta_{ll'} \delta_{mm'} \int_0^\infty dr' \, r' \rho_N(r') \int_0^{r'} dr \times$$

$$\times r(r-r') |R_{nl}(r)|^2$$

Now the nucleus is much smaller than the Bohr radius, so $\rho_N(r')$ goes to zero rapidly for small r', hence the r'-integral has its contribution from small r' only. If r' is small so is r in the r-integral; for r small Taylor expand the $|R_{nl}(r)|^2$ integrand

$$|R_{nl}(r)|^2 = |R_{nl}(0)|^2 + r\left(\frac{d}{dr}|R_{nl}(r)|^2\Big|_{r=0}\right) + \cdots$$

$\Longrightarrow$

$$\int_0^{r'} dr \, r(r-r') |R_{nl}(r)|^2$$

$$= |R_{nl}(0)|^2 \underbrace{\int_0^{r'} dr \, r(r-r')}_{= -\frac{1}{6} r'^3} + \left(\frac{d}{dr}|R_{nl}(r)|^2\right)\Bigg|_{r=0} \overbrace{\int_0^{r'} dr \, r^2 (r-r')}^{= -\frac{1}{12} r'^4} + \cdots$$

1.) $\int_0^{r'} dr\, r(r-r')|R_{n\ell}(r)|^2$

$$= -\frac{1}{6}|R_{n\ell}(0)|^2 r'^3 - \frac{1}{12}\left(\frac{d}{dr}|R_{n\ell}(r)|^2\right)\bigg|_{r=0} r'^4 + \cdots$$

$\Rightarrow$

$\langle n,\ell,m|H'|n,\ell',m'\rangle$

$$= \delta_{\ell\ell'}\delta_{mm'}\frac{4\pi Ze^2}{6}\Big\{|R_{n\ell}(0)|^2\int_0^\infty dr'\, r'^4 \rho_N(r')$$

$$+ \frac{1}{2}\left(\frac{d}{dr}|R_{n\ell}(r)|^2\right)\bigg|_{r=0}\int_0^\infty dr'\, r'^5 \rho_N(r') + \cdots\Big\}$$

Define $\langle r_N^k\rangle = \int d^3r\, r^k \rho_N(r) = 4\pi\int_0^\infty dr\, r^{k+2}\rho_N(r)$

1.) So

$$\langle n,l,m|H'|n,l',m'\rangle = \delta_{ll'}\delta_{mm'}\frac{Ze^2}{6}\times$$

$$\times\left\{|R_{nl}(0)|^2\langle r_N^2\rangle + \frac{1}{2}\left(\frac{d}{dr}|R_{nl}(r)|^2\right)\Bigg|_{r=0}\langle r_N^3\rangle + \dots\right\}$$

Only keep lowest order term

$$R_{nl}(0) = R_{n0}(0)\delta_{l0} = 2\left(\frac{Z}{na_0}\right)^{3/2}\delta_{l0},$$

Only $l=0$, s-states have an energy shift in this order. If $l=0 \Rightarrow m=0$. Thus

$$\langle n,l,m|H'|n,l',m'\rangle$$

$$=\delta_{ll'}\delta_{mm'}\delta_{l0}\delta_{m0}\,\frac{2}{3}\frac{Z^4e^2}{n^3a_0^3}\langle r_N^2\rangle$$

Using $a_0 = \frac{\hbar}{mc\alpha}$; $\alpha = \frac{e^2}{\hbar c}$ this becomes

1c) $$\boxed{\begin{aligned}&\langle n,l,m|H'|n,l',m'\rangle \\ &= \delta_{ll'}\delta_{mm'}\delta_{l0}\delta_{m0}\ \frac{2}{3}\ \frac{m^3c^4(Z\alpha)^4}{\hbar^2 n^3}\langle r_N^2\rangle\end{aligned}}$$

Neglecting $O(\langle r_N^3\rangle)$ terms, only S-states get shifted

$$\boxed{\begin{aligned}\Delta E_{ns} &= \langle n,l=0,m=0|H'|n,l=0,m=0\rangle \\ &= \frac{2}{3}\ \frac{m^3c^4(Z\alpha)^4}{\hbar^2 n^3}\langle r_N^2\rangle\end{aligned}}$$