

# Physic 521: Problem Set 2

## Solutions

### Problem 1: Hydrogenic atoms and atomic units

Two oppositely charged particles:

- Charge 1 (negative)  $q_1 = -z_1 e$ , mass  $m_1$
- Charge 2 (positive)  $q_2 = z_2 e$ , mass  $m_2$

Coulomb interaction  $V(r) = \frac{q_1 q_2}{r} = -z_1 z_2 \frac{e^2}{r}$

Relative motion Hamiltonian:  $\hat{H}_{rel} = \frac{\hat{p}_{rel}^2}{2\mu} + V(r)$ ,  $\mu = \frac{m_1 m_2}{m_1 + m_2}$

Atomic units (I will use  $\sim$  for 'hydrogenic' atomic units)

- Length  $\tilde{a}_0 = \frac{\hbar^2}{\mu q_1 q_2} = \frac{\hbar^2}{\mu z_1 z_2 e^2} = \left( \frac{m_e}{\mu z_1 z_2} \right) \left( \frac{\hbar^2}{m_e e^2} \right)$

$$\Rightarrow \tilde{a}_0 = \frac{m_e}{\mu z_1 z_2} (5.3 \text{ \AA})$$

- Energy  $\tilde{E}_0 = \frac{q_1 q_2}{a_0} = \left( \frac{\mu z_1 z_2}{m_e} \right) \left( \frac{m_e e^4}{\hbar^2} \right) = \left( \frac{\mu}{m_e} z_1 z_2 \right) (27.2 \text{ eV})$

- Time  $\tilde{t}_0 = \frac{\hbar}{E_0} = \left( \frac{m_e}{\mu z_1 z_2} \right) \left( \frac{\hbar^3}{m_e e^4} \right) = \left( \frac{m_e}{\mu z_1 z_2} \right) (2.43 \times 10^{-19} \text{ s})$

- Momentum  $\tilde{p}_0 = \frac{\hbar}{\tilde{a}_0} = \left( \frac{\mu}{m_e} z_1 z_2 \right) \left( \frac{m_e e^2}{\hbar} \right) = \left( \frac{\mu}{m_e} z_1 z_2 \right) (2.0 \times 10^{-19} \text{ g cm/s})$

- Internal E-field at particle  $\tilde{E}_0 = \frac{q_2}{\tilde{a}_0^2} = \left( \frac{\mu z_1 z_2}{m_e} \right)^2 z_2 \frac{m_e e^5}{\hbar^4} = \left[ \left( \frac{\mu z_1 z_2}{m_e} \right)^2 z_2 \right] 5.7 \times 10^9 \frac{\text{V}}{\text{cm}}$   
or  $1.7 \times 10^2 \frac{\text{statvolt}}{\text{cm}}$

- Velocity  $\frac{\tilde{v}_0}{c} = \frac{\tilde{p}_0}{\mu c} = \left( \frac{z_1 z_2 m_e}{\mu} \right) \frac{e^2}{\hbar c} = (z_1 z_2) \alpha = (z_1 z_2) \frac{1}{137}$   
non-relativistic assumption

Aside: Helpful factoid:  $r_{class} = \alpha \lambda_{compton} = \alpha^2 a_0$

where  $r_{class} = \frac{e^2}{m_e c^2}$  (classical electron radius)  
 $\lambda_{comp} = \frac{\hbar}{m_e c}$  (Compton wavelength)

(Internal B-field at 1)  $\vec{B}_0 = \frac{q_2 \vec{v}_2}{r_0} = \frac{\vec{v}_2}{c} \vec{E}_0 = (z_1 z_2) \alpha \vec{E}_0$

$$\Rightarrow \vec{B}_0 = \left(\frac{\mu}{m_e}\right)^2 (z_1^3 z_2^4) \frac{m^2 e^7}{h^5 c} = \left(\frac{\mu}{m_e}\right)^2 (z_1^3 z_2^4) \times 10^5 \text{ Gauss}$$

(Magnetic moment of 1)  $\vec{\mu}_0 = (\text{Current}) \frac{(\text{Area})}{c} = \left(\frac{q_1 v_1}{r_0}\right) \left(\frac{a_0^2}{c}\right)$

$$\Rightarrow \vec{\mu}_0 = \left(\frac{m_e z_1}{\mu}\right) \left(\frac{eh}{m_e c}\right) = \left(\frac{m_e z_1}{\mu}\right) (1.85 \times 10^{-20} \frac{\text{erg}}{\text{Gauss}})$$

2x "Bohr magneton"

Now for each of the cases given:

(i) Hydrogen:  $z_1 = z_2 = 1$   $m_1 = m_e$   $m_2 = m_p \Rightarrow \mu \approx m_e$

(ii) Heavy ion:  $z_1 = 1, z_2 = 50$ ,  $\mu \approx m_e$

(iv) Muonium:  $z_1 = z_2 = 1$   $m_1 \approx 200 m_e$   $m_2 = m_p = 2000 m_p \Rightarrow \mu \approx 190 m_e$

(iv) Positronium  $z_1 = z_2 = 1$   $m_1 = m_2 = m_e \Rightarrow \mu = \frac{1}{2} m_e$

### Summary

	$\tilde{a}_0$ length	$\tilde{E}_0$ energy	$\tilde{t}_0$ time	$\tilde{p}_0$ momentum	$\tilde{v}_0/c$ velocity	$\tilde{E}_0$ electric	$\tilde{B}_0$ magnetic	$\tilde{\mu}_0$ mag moment
Hydrogen	5.3 Å	27.2 eV	$2.4 \times 10^{-17}$ s	$2 \times 10^{-19} \text{ g cm/s}$	$\alpha = \frac{1}{137}$	$5.7 \times 10^9 \text{ V/cm}$	$10^5 \text{ G}$	$1.85 \times 10^{-20} \text{ erg/G}$
4x ionized Ti	0.1 Å	360 eV	$4.8 \times 10^{-19}$ s	$10^{-17} \text{ g cm/s}$	0.36	$7.1 \times 10^{14} \text{ V/cm}$	$10^{11} \text{ G}!$	$1.85 \times 10^{-20} \text{ erg/G}$
Muon + proton	0.03 Å	4876 eV	$1.8 \times 10^{-19}$ s	$3.6 \times 10^{-17} \text{ g cm/s}$	1.31!?	$1.8 \times 10^{14} \text{ V/cm}$	$3.29 \times 10^9 \text{ G}$	$3.3 \times 10^{-28} \text{ erg/G}$
Positronium	10.6 Å	13.6 eV	$4.8 \times 10^{-17}$ s	$10^{-18} \text{ g cm/s}$	$2\alpha = 0.014$	$1.4 \times 10^9 \text{ V/cm}$	$\frac{1}{4} \times 10^5 \text{ G}$	$3.7 \times 10^{-20} \text{ erg/G}$

## Problem 2: Radial Expectation Values for Hydrogen

(a) We seek the mean value of  $r$  for  $(n, l, m)$

$$= \langle r \rangle_{nlm} = \int_0^{\infty} dr r^3 R_{nl}(r) \underbrace{\int_0^{\pi} d\theta \int_0^{2\pi} d\phi}_{=1} |\Psi_{nlm}(\theta, \phi)|^2$$

where  $R_{nl}(r) = \sqrt{N_{nl}} \left(\frac{2Z}{na_0}\right)^{3/2} e^{-\rho/2} \rho^l L_{n-l}^{2l+1}(\rho)$

$\rho = \frac{2Zr}{na_0}$        $N_{nl}$  = normalization constant

By brute force, we use the method given in Appendix 3 of B&J based on the generating function

$$U_p(\rho, s) = (-s)^p \frac{e^{-\rho s / (1-s)}}{(1-s)^{p+1}} = \sum_{q=p}^{\infty} \frac{L_q^p(\rho)}{q!} s^q$$

$$\therefore \langle r \rangle_{nl} = N_{nl} \left(\frac{na_0}{2Z}\right) \int_0^{\infty} d\rho \rho^{2l+3} e^{-\rho} \left[ L_{n-l}^{2l+1}(\rho) \right]^2$$

Now  $\int_0^{\infty} e^{-\rho} \rho^{\alpha} U_p(\rho, s) U_p(\rho, t) d\rho$

$$= \sum_{q=p}^{\infty} \sum_{q'=p}^{\infty} \frac{s^q t^{q'}}{q! q'} I_{pq, pq'}^{\alpha}$$

where  $I_{pq, pq'}^{\alpha} = \int_0^{\infty} e^{-\rho} \rho^{\alpha} \left[ L_q^p(\rho) \right]^2 d\rho$

Thus,  $\langle r \rangle_{nl} = N_{nl} \frac{na_0}{2Z} I_{pq, pq'}^{\alpha}$        $p = 2l+1$   
 $q = n-l$   
 $\alpha = p+2$

Using appendix eq (A3.20)

$$\int_0^{\infty} e^{-t} t^{\alpha} \mathcal{U}_p(p, s) \mathcal{U}_p(p, t) = \underset{\text{integer}}{\alpha!} \frac{(1-s)^{\alpha+1}}{(1-s)^{p+1}} \frac{(1-t)^{\alpha+1}}{(1-t)^{p+1}} \frac{(st)^p}{(1-st)^{\alpha+1}}$$

Using binomial

$$= \frac{(1-s)^{\alpha+1}}{(1-s)^{p+1}} \frac{(1-t)^{\alpha+1}}{(1-t)^{p+1}} \sum_{k=0}^{\infty} \frac{(\alpha+k)!}{k!} \frac{(st)^{\alpha+k}}{(1-st)^{\alpha+k+1}}$$

Plug in  $\alpha = p+2$

$$\Rightarrow = (1-s)^2 (1-t)^2 \sum_{k=0}^{\infty} \frac{(p+2+k)!}{k!} (st)^{k+p}$$

$$= (1+s^2-2s)(1+t^2-2t) \sum_{q=p}^{\infty} \frac{(q+2)!}{(q-p)!} (st)^q$$

$$= \sum_{q=p}^{\infty} \sum_{q'=p}^{\infty} \frac{I_{p, p}^{\alpha=p+2}}{q! q'!} s^q t^{q'}$$

Equating the coefficients where  $q = q'$

$$\Rightarrow I_{p, p}^{\alpha=p+2} = (q!)^2 \left[ \frac{(q+2)!}{(q-p)!} + \frac{4(q+1)!}{(q-p-1)!} + \frac{q!}{(q-2-p)!} \right]$$

$$= \frac{(q!)^3}{(q-p)!} \left[ (q+2)(q+1) + 4(q+1)(q-p) + (q-p)(q-p) \right]$$

Now, according to the appendix 3 A3.25

with  $p=2l+1$ ,  $q=n+l \Rightarrow N_{nz} = \frac{(q-p)!}{(q!)^3 (2q-p+1)}$

Putting it all together

$$\langle r \rangle_{nl} = \frac{na_0}{2Z} \left[ \frac{(q+2)(q+1) + 4(q+1)(q-p) + (q-p)(q-p-1)}{2q-p+1} \right]$$

Plug in  $p=2l+1$   $q=n+l$

$$\Rightarrow \langle r \rangle_{nl} = \frac{na_0}{2Z} \left[ 3n - \frac{2(l+1)}{n} \right]$$

$$\boxed{\langle r \rangle_{nl} = \frac{n^2 a_0}{Z} \left[ 1 + \frac{1}{2} \left( 1 - \frac{2(l+1)}{n^2} \right) \right]}$$

phew! What a mess

(b) For circular states  $\Rightarrow$  max angular momentum  
(no radial kinetic energy)  $\Rightarrow l=n-1$

$$\Rightarrow \langle r \rangle_{nl} = \frac{n^2 a_0}{Z} \left[ 1 + \frac{1}{2} \left[ 1 - \frac{n(n-1)}{n^2} \right] \right] \xrightarrow[n \rightarrow \infty]{0} a_0$$

$$\Rightarrow \langle r \rangle_{nl} = n^2 \frac{a_0}{Z}$$

The Bohr result.

### (c) Feynman-Hellman

Consider expectation value as function of parameters

$$\langle n_r, \xi | \hat{H}(\xi) | n_r, \xi \rangle = E_{n_r}(\xi)$$

Take partial w.r.t. some  $\xi$

$$\Rightarrow \left( \frac{\partial}{\partial \xi} \langle n_r, \xi | \right) \hat{H}(\xi) | n_r, \xi \rangle + \langle n_r, \xi | \hat{H} \left( \frac{\partial}{\partial \xi} | n_r, \xi \rangle \right) + \langle n_r, \xi | \frac{\partial \hat{H}(\xi)}{\partial \xi} | n_r, \xi \rangle = \frac{\partial E_{n_r}(\xi)}{\partial \xi}$$

But  $\hat{H}(\xi) | n_r, \xi \rangle = E_{n_r}(\xi) | n_r, \xi \rangle$  and adjoint

$$\rightarrow \text{First two terms} = E_{n_r} \frac{\partial}{\partial \xi} (\langle n_r, \xi | n_r, \xi \rangle) = 0$$

same normalization

$$\Rightarrow \boxed{\langle n_r, \xi | \frac{\partial \hat{H}(\xi)}{\partial \xi} | n_r, \xi \rangle = \frac{\partial E_{n_r}(\xi)}{\partial \xi}}$$

(d) Now we can use the clever trick

$$\bullet \text{ Let } \xi = e^2 \Rightarrow \frac{\partial \hat{H}}{\partial e^2} = \frac{-Z}{r} \quad \frac{\partial E_{n_r}}{\partial e^2} = \frac{2}{e^2} E_{n_r}$$

$$\Rightarrow Z \langle n_r, \xi | \frac{1}{r} | n_r, \xi \rangle = \frac{2}{e^2} E_{n_r} = \frac{2}{e^2} \left( -Z^2 \frac{e^2}{2a_0 n^2} \right)$$

$$\Rightarrow \boxed{\langle \frac{1}{r} \rangle_{n\ell} = \frac{Z}{a_0 n^2}} \quad \checkmark$$

• Let  $\xi = r \Rightarrow \frac{\partial \hat{H}}{\partial r} = \frac{(2l+1)\hbar^2}{2m_e r^2} \quad \frac{\partial E}{\partial l} = -\frac{2}{n} E_n$

$$\Rightarrow (l + \frac{1}{2}) \frac{\hbar^2}{m_e} \left\langle \frac{1}{r^2} \right\rangle_{nl} = -\frac{2}{n} \frac{Z^2}{-2\hbar^2} \left( \frac{c^2}{a_0} \right)$$

$$\Rightarrow \left\langle \frac{1}{r^2} \right\rangle_{nl} = \frac{Z^2}{n^3(l + \frac{1}{2})} \frac{m_e e^2}{\hbar a_0} \quad \left[ = \left( \frac{Z}{a_0} \right)^2 \frac{1}{n^3(l + \frac{1}{2})} \right]$$

• Consider  $\left\langle \left[ \frac{\partial}{\partial r}, \hat{A} \right] \right\rangle_{nlm} = \left\langle nlm | \frac{\partial}{\partial r} \hat{A} - \hat{A} \frac{\partial}{\partial r} | nlm \right\rangle$   
 $= 0$  since  $\hat{A}|nlm\rangle = E_n |nlm\rangle$

Now

$$\langle nlm | \hat{H} = \langle nlm | E_n$$

Now  $\left\langle \left[ \frac{\partial}{\partial r}, \hat{H} \right] \right\rangle = \frac{\hbar^2 l(l+1)}{2m} \left\langle \left[ \frac{\partial}{\partial r}, \frac{1}{r^2} \right] \right\rangle - Ze^2 \left\langle \left[ \frac{\partial}{\partial r}, \frac{1}{r} \right] \right\rangle$

Now  $\left[ \frac{\partial}{\partial r}, \frac{1}{r^2} \right] f = \frac{\partial}{\partial r} \left( \frac{f}{r^2} \right) - \frac{1}{r^2} \frac{\partial f}{\partial r} = -\frac{2f}{r^3}$

$$\left[ \frac{\partial}{\partial r}, \frac{1}{r} \right] f = \frac{\partial}{\partial r} \left( \frac{f}{r} \right) - \frac{1}{r} \frac{\partial f}{\partial r} = -\frac{f}{r^2}$$

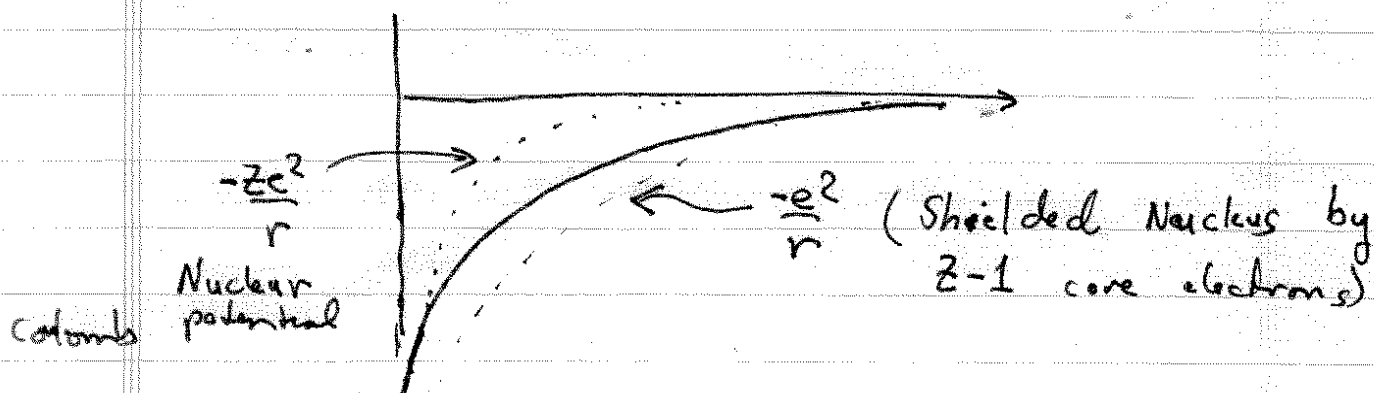
$$\Rightarrow \left\langle \left[ \frac{\partial}{\partial r}, \hat{H} \right] \right\rangle = -\frac{\hbar^2 l(l+1)}{m} \left\langle \frac{1}{r^3} \right\rangle + Ze^2 \left\langle \frac{1}{r^2} \right\rangle = 0$$

$$\Rightarrow \left\langle \frac{1}{r^3} \right\rangle_{nl} = \frac{Ze^2 m_e}{l(l+1)\hbar^2} \left\langle \frac{1}{r^2} \right\rangle = \frac{Z}{a_0} \frac{1}{l(l+1)} \left\langle \frac{1}{r^2} \right\rangle_{nl}$$

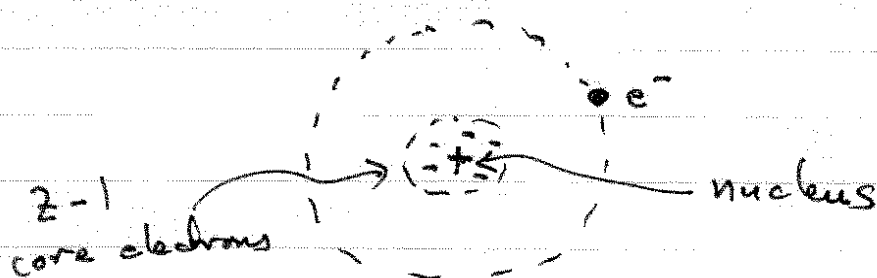
### Problem 3: Spectrum of multielectron atoms

In the mean field approximation, we ignore electron correlations and then obtain a spherically symmetric charge distribution. The total potential seen by the valence electron is then the sum of the Coulomb potential due to the attraction to the nucleus plus the repulsive potential due to the other "core" electrons

$$V(r) = V_{\text{nucleus}}(r) + V_{\text{core}}(r)$$



In a Bohr like picture for an alkali with one valence electron



The question is thus, how much does the wave function associated with the valence electron penetrate the core?



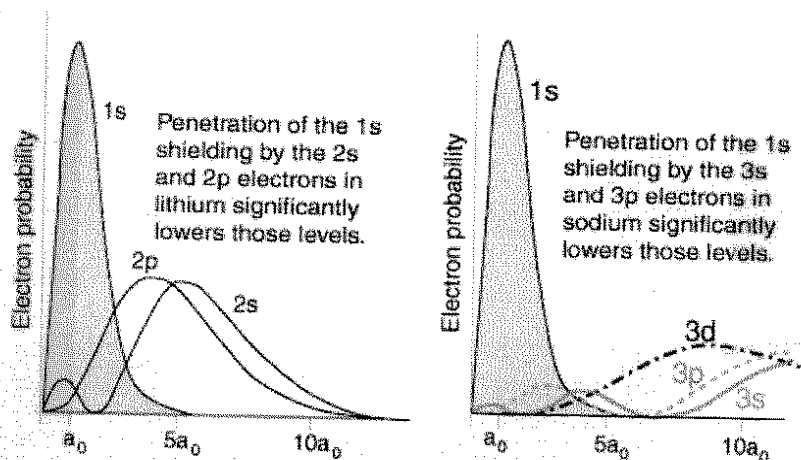
Since the potential is still spherically symmetric, the set  $\{n, l, m\}$  are still "good quantum numbers". Because the radial wave functions associated with different  $l$  will have different support inside the core, the energy will be different. In particular, we expect the  $s$ -states ( $l=0$ ) to have the lowest energy for a given  $n$ , since these are more peaked near the origin.

A nice description of this is given at the url:

<http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/orbdep.html>

## Origin of Orbital Quantum Number Dependence of Electron Energies

When the wavefunctions for electrons with different orbital quantum numbers are examined, it is found that there is a different amount of penetration into the region occupied by the  $1s$  electrons. This penetration of the shielding  $1s$  electrons exposes them to more of the influence of the nucleus and causes them to be more tightly bound, lowering their associated energy states.



In the case of lithium, the  $2s$  electron shows more penetration inside the first Bohr radius and is therefore lower than the  $2p$ . In the case of sodium with two filled shells, the  $3s$  electron penetrates the inner shielding shells more than the  $3p$  and is significantly lower in energy.

(b) Coarse but solvable model

$$V(r) = -\frac{e^2}{r} + \frac{A}{r^2}$$

Radial eq.

$$-\frac{1}{2} \frac{d^2 u}{d\bar{r}^2} + \left( \frac{l(l+1) + \bar{A}}{2\bar{r}^2} - \frac{1}{\bar{r}} \right) u = -\epsilon u$$

where  $\bar{r} = \frac{r}{a_0}$   $\epsilon = -E / \frac{e^2}{a_0}$  binding energy  
Bohr radius

$$\bar{A} = \frac{2A}{\hbar^2}$$

This is the same form of the radial equation as for Hydrogen, except  $l(l+1) \rightarrow l(l+1) + \bar{A}$

Thus let  $s(s+1) = l(l+1) + \bar{A}$

Making the Ansatz (as we did for Hydrogen)

$$u(\bar{r}) = \bar{r}^{s+1} e^{-K\bar{r}} F(\bar{r}) \quad K = \sqrt{2\epsilon}$$

We arrive at the Laguerre eq. with eigenfunction  $L_{n_r}^{2s+1}(K\bar{r})$

Eigenvalue  $K = \frac{1}{n_r + s + 1} = \sqrt{2\epsilon}$

$$\Rightarrow \epsilon = \frac{1}{2(n_r + s + 1)^2} \quad (\text{Next Page})$$

$$\rightarrow E = \frac{-R}{2(n_r + s + 1)^2} \quad R = \frac{e^2}{2a_0} = 13.6 \text{ eV}$$

Now we must solve for  $s$  in terms of  $l$  and  $A$ :

$$s^2 + s - (l(l+1) + \bar{A}) = 0$$

$$\Rightarrow s = -\frac{1}{2} + \frac{1}{2} \sqrt{1 + (4l(l+1) + \frac{8mA^2}{\hbar^2})}$$

↑  
must choose (+)-sign to make  $s > 0$

$$\Rightarrow s+1 = \frac{1}{2} \left( 1 + \sqrt{(2l+1)^2 + \frac{8mA^2}{\hbar^2}} \right)$$

$$\therefore E_{n_r, l} = \frac{-R}{\left[ n_r + \frac{1}{2} \left( 1 + \sqrt{(2l+1)^2 + \frac{8mA^2}{\hbar^2}} \right) \right]^2}$$

Check  $A \rightarrow 0$   $E_{n_r, l} = \frac{-R}{(n_r + l + 1)^2}$  as expected

Performing a power series expansion

$$E_{n_r, l} = \frac{-R}{(n_r + l + 1)^2} + \frac{R(2A)}{(n_r + l + 1)^3 (2l + 1)}$$

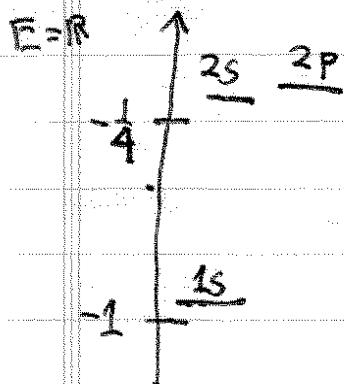
⏟  
Perturbation #

(Next Page)

⊙ In terms of principle q-number:

$$E_{n,l} = -\frac{R}{n^2} \left( 1 - \frac{\bar{A}}{(l+\frac{1}{2})n} \right)$$

Sketch:



← degeneracy broken

$2s$  is lower energy than  $2p$

Note  $\frac{R\bar{A}}{n^3(l+\frac{1}{2})}$

follows from first order perturbation theory

$$E^{(1)} = \langle n,l | \frac{A}{r^2} | n,l \rangle = \frac{\hbar^2 \bar{A}}{2ma_0^2} \langle n,l | \frac{1}{r^2} | n,l \rangle$$

$$= R\bar{A} \frac{1}{n^3(l+\frac{1}{2})} \quad \text{as expected.}$$