86(9): Comparison of Hydrogen and Helium

Hydrogen

The Schrödinger equation of H is:

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi - \frac{e^2}{4\pi\epsilon_0 r}\psi = E\psi \quad -(1)$$

which can be written as:

$$\frac{1}{r}\frac{\partial^2 r\psi}{\partial r^2} + \frac{1}{r^2}\Lambda^2\psi + \frac{\mu e^2}{2\pi\epsilon_0\hbar^2 r}\psi = -\frac{2\mu E}{\hbar^2}\psi \quad -(2)$$

where:

$$\Lambda^2 Y = -l(l+1)Y \quad -(3)$$

The solution of eq. (1) is written as:

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi). \quad -(4)$$

From eqs. (2) to (4): $\quad -(5)$

$$\frac{1}{r}\frac{\partial^2}{\partial r^2}(rRY) - \frac{1}{r^2}l(l+1)RY + \frac{\mu e^2}{2\pi\epsilon_0\hbar^2 r}RY = -\left(\frac{2\mu E}{\hbar^2}\right)RY$$

which is

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2P}{dr^2} - V_{eff}^{(0)}P = EP} \quad -(6)$$

where

$$V_{eff}^{(0)} = \frac{-e^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2} \quad -(7)$$

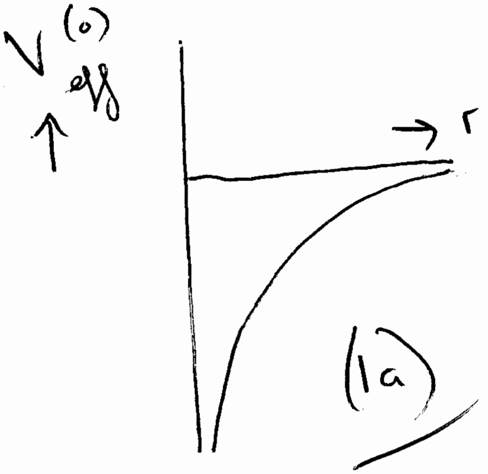
2) The first part is the Coulomb attraction (minus sign) and the second part is the centrifugal repulsion (positive sign).

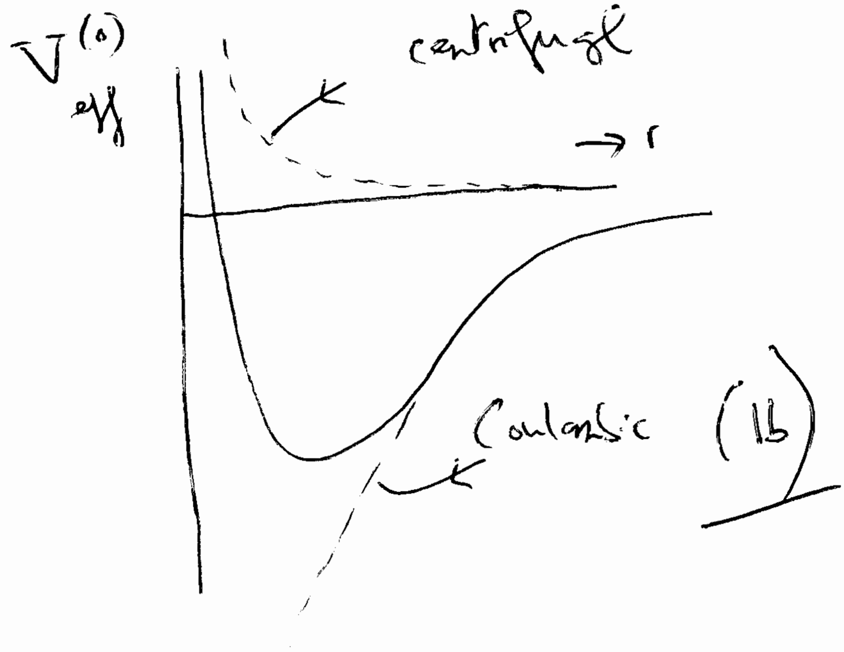
S Orbitals

In this case:

$$\ell = 0 \quad -(8)$$

so for all the s orbitals the potential is attractive as in Fig 1a. For other orbitals it is a combination as in Fig 1b.





P Orbitals

In this case:

$$\ell = 1 \quad -(9)$$

and the complete potential is as in Fig 1b.

The radiative corrections are now incorporated

3) into this model as follows:

$$-\frac{\hbar^2}{2\mu}\left(1+\frac{\alpha}{4\pi}\right)^2\frac{d^2P}{dr^2} - \bar{V}_{eff}^{(0)}P = EP \quad -(10)$$

which is equivalent by hypothesis to:

$$-\frac{\hbar^2}{2\mu}\frac{d^2P}{dr^2} - \bar{V}_{eff}\underline{P} = E\underline{P} \quad -(11)$$

where:

$$\bar{V}_{eff} = \frac{e^2}{4\pi\epsilon_0(r+r_{vac})} - \frac{\ell(\ell+1)\hbar^2}{2\mu(r+r_{vac})^2} \quad -(12)$$

To first order in α:

$$-\frac{\hbar^2\alpha}{4\pi\mu}\frac{d^2P}{dr^2} = \left(\bar{V}_{eff}^{(0)} - \bar{V}_{eff}\right)P \quad -(13)$$

where $\underline{P} = \underline{P}_0$ — (14)

is hydrogen-like.

Helium Atom

This consists of two electrons and two protons. One electron is $\underline{r_1}$ from the nucleus, and one is at $\underline{r_2}$ from the nucleus. The inter-electron distance is $\underline{r_{12}}$. The Schrödinger

4) equation of helium is:

$$\hat{H}\phi(\underline{r}_1, \underline{r}_2) = E\phi(\underline{r}_1, \underline{r}_2) \quad -(15)$$

where:

$$\phi(\underline{r}_1, \underline{r}_2) = \phi_{n_1 l_1 m_{l_1}} \phi_{n_2 l_2 m_{l_2}} \quad -(16)$$

This is too complicated to be solved analytically, so perturbation theory is used. It is assumed that there is an unperturbed hamiltonian which is ~~a~~ sum of two hydrogen-like hamiltonians:

$$\boxed{H^{(0)} = H_1 + H_2} \quad -(17)$$

where.

$$H_i = -\frac{\hbar^2}{2m_e}\nabla_i^2 - \frac{2e^2}{4\pi\epsilon_0 r_i}. \quad -(18)$$

The assumption (17) means that ~~the~~ wave function is a product:

$$\boxed{\phi(\underline{r}_1, \underline{r}_2) = \phi(\underline{r}_1)\phi(\underline{r}_2)} \quad -(19)$$

<u>Proof</u>

Let $H_i\phi(r_i) = E_i\phi(r_i)$ $-(20)$

then:

$$(H_1 + H_2)\phi(\underline{r}_1, \underline{r}_2) = (H_1 + H_2)\phi(\underline{r}_1)\phi(\underline{r}_2)$$

5)

$$= \left(H_1 \phi(\underline{r}_1)\right)\phi(\underline{r}_2) + \phi(\underline{r}_1)\left(H_2 \phi(\underline{r}_2)\right)$$

$$= \left(E_1 \phi(\underline{r}_1)\right)\phi(\underline{r}_2) + \left(E_2 \phi(\underline{r}_1)\right)\phi(\underline{r}_2)$$

$$= (E_1 + E_2)\,\phi(\underline{r}_1, \underline{r}_2) \quad -(22)$$

<u>Q.E.D.</u>

The total unperturbed energy levels of helium are:

$$E = -4hcR_\infty\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right) \quad -(23)$$

<u>Radiative Corrections</u>

The first step is to develop eq. (18), and write it as:

$$H_i = -\frac{\hbar^2}{2m_e}\frac{d^2}{dr_i^2} - V^{(0)}_{eff, i} \quad -(24)$$

$$-(25)$$

where

$$V^{(0)}_{eff, i} = -\frac{e^2}{2\pi\epsilon_0 r_i} + \frac{l(l+1)\hbar^2}{m_e r_i^2}$$

There is a factor of two because two electrons are attracted to two protons. So there are

6) two H like equations:

$$-\frac{\hbar^2}{2m_e}\frac{d^2 \rho}{dr_i^2} - V^{(0)}_{eff,i}\,\rho = E_i \rho \quad -(26)$$

with

$$\rho = \rho(\underline{r}_1, \underline{r}_2) = \rho(\underline{r}_1)\,\rho(\underline{r}_2) \quad -(27)$$

These two equations are:

$$-\frac{\hbar^2}{2m_e}\frac{d^2 \rho}{dr_1^2} - V^{(0)}_{eff,1}\,\rho = E_1 \rho \quad -(28)$$

$$-\frac{\hbar^2}{2m_e}\frac{d^2 \rho}{dr_2^2} - V^{(0)}_{eff,2}\,\rho = E_2 \rho \quad -(29)$$

where:

$$V^{(0)}_{eff,1} = -\frac{e^2}{2\pi\epsilon_0 r_1} + \frac{l(l+1)\hbar^2}{m r_1^2} \quad -(30)$$

$$V^{(0)}_{eff,2} = -\frac{e^2}{2\pi\epsilon_0 r_2} + \frac{l(l+1)\hbar^2}{m r_2^2} \quad -(31)$$

Radiative corrections are incorporated into eqns. (28) and (29) as in eqns. (10) to (14).