372(2) : <u>Evaluation for $l = 0$ States</u>

First check that the lagrangian result:

$$\nabla^2 \phi = -\frac{1}{a_0}\left(\frac{2}{r} - \frac{1}{n^2 a_0}\right)\phi \quad -(1)$$

is the same as the hamiltonian result for the H atom. Eq. (1) is:

$$\nabla^2 \phi + \frac{2}{a_0 r}\phi = \frac{1}{n^2 a_0^2}\phi \quad -(2)$$

where the Bohr radius is:

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} \quad -(3)$$

Therefore:

$$\nabla^2 \phi + \frac{me^2}{2\pi\epsilon_0\hbar^2 r}\phi = \frac{m^2 e^4}{16\pi^2\epsilon_0^2\hbar^4 n^2}\phi \quad -(4)$$

$$= -\frac{2mE}{\hbar^2}\phi$$

where the total energy is:

$$E = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2 n^2} \quad -(5)$$

Eq. (4) is the same as Eq. (4.3.4) of Atkins, "Molecular Quantum Mechanics" (OUP, 2nd edition, 1983):

$$\frac{d^2 P}{dr^2} + \frac{2m}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r} - l(l+1)\frac{\hbar^2}{2mr^2}\right)P = -\frac{2mE}{\hbar^2}P \quad -(6)$$

where

$$P = r\phi(r) \quad -(7)$$

, where $\phi(r)$ is the radial wavefunction. Eq. (6) is interpreted with the effective potential:

$$V_{eff} = \frac{-e^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2mr^2} \quad -(8)$$

where

$$L^2\phi = l(l+1)\hbar^2\phi \quad -(9)$$

so the classical equivalent of eq. (8) is:

$$V_{eff} = -\frac{e^2}{4\pi\epsilon_0 r} + \frac{L^2}{2mr^2} \quad -(10)$$

which is the sum of an attractive Coulombic potential and a repulsive centrifugal potential:

$$U(\text{centrifugal}) = \frac{l(l+1)\hbar^2}{2mr^2} \quad -(11)$$

When

$$l = 0 \quad -(12)$$

$$\frac{d^2P}{dr^2} + \frac{me^2}{2\pi\epsilon_0\hbar^2 r}P \sim 0 \quad -(13)$$

so

$$P \sim Ar + \frac{1}{2}Ar^2 \quad -(14)$$

and

$$\phi(r) \sim A \quad -(15)$$

which is a non-zero constant.

There is a non zero probability of finding the electron at the nucleus.

Therefore eq. (1) gives the correct radial

3) wavefunctions of the H atom. The analytical solutions of eq. (1) are related to the associated Laguerre functions, and are:

$$\phi(r) = -\left(\frac{2Z}{na_0}\right)\left(\frac{(n-l-1)!}{2n[(n+l)!]^3}\right)\rho^{l} L_{n+l}^{2l+1}(\rho)\, e^{-\rho/2} \quad -(16)$$

where

$$\rho = \left(\frac{2Z}{na_0}\right) r \quad -(17)$$

for H-like radial wavefunctions of atomic number Z. So eq. (1) is true for all H-like atoms.

for atomic H: $Z = 1$ $-(18)$

For $n = 1$, $l = 0$ (1s)

$$\phi_{10}(r) = \frac{2}{a_0^{3/2}} \exp(-\rho/2) \quad -(19)$$

For $n = 2$, $l = 0$ (2s)

$$\phi_{20}(r) = \frac{1}{2\sqrt{2}\, a_0^{3/2}} (2-\rho) \exp(-\rho/2) \quad -(20)$$

For $n = 2$, $l = 1$ (2p)

$$\phi_{21}(r) = \frac{1}{a^{3/2}} \frac{\rho}{2\sqrt{6}} \exp(-\rho/2) \quad -(21)$$

and so on.