1.   Calculate the radial distribution function $\{RDR = r^2 R^2(r)\}$ for the 1s and 2s state of the hydrogen atom. Determine the locations (i.e. values of r) of its minima and maxima for both 1s and 2s in terms of a_0. What do these minima signify?

Solution

Wavefunctions of H-atom are:

$$\psi_{1s} = cons\tan t.e^{-\left(\frac{r}{a_0}\right)} \quad \& \quad \psi_{2s} = cons\tan t.\left(2 - \frac{r}{a_0}\right)e^{-\left(\frac{r}{2a_0}\right)}$$

$$\psi_{1s}(r,\theta,\phi) = const.R_{n,l}(r)\gamma_{l_{m_l}}(\theta,\phi) \text{ Where } a_0 \text{ is Bohr radius}$$

$$\psi_{2s}(r,\theta,\phi) = const.R_{n,l}(r)\underbrace{\gamma_{l_{m_l}}(\theta,\phi)}_{cons\tan t}$$

$$RDR = P(r) = r^2 R^2(r)$$

For 1s : $P(r) = (const.)^2 .r^2 e^{-\frac{2r}{a_0}}$

For 2s : $P(r) = (const.)^2 .r^2 \left(2 - \frac{r}{a_0}\right)^2 e^{-\frac{r}{a_0}}$

For the minimum condition: $\dfrac{dP(r)}{dr} = 0 \quad \& \quad \dfrac{d^2 P(r)}{dr^2} = +ve$

$\therefore$ For 1s case : $\left(2re^{-2r/a_0} - \dfrac{2}{a_0}r^2 e^{-2r/a_0}\right) = 0$

$$2re^{-\frac{2r}{a_0}}\left(1 - \frac{r}{a_0}\right) = 0$$

We ignore $r = \infty$ solution.

$$\therefore \quad r = 0 \quad \& \quad r = a_0$$

For $r = a_0 \Rightarrow$ not minimum but maximum since 2nd derivative is –ve.

For 2s: $2r\left(2 - \dfrac{r}{a_0}\right)^2 e^{-r/a_0} + 2r^2\left(2 - \dfrac{r}{a_0}\right)\left(-\dfrac{1}{a_0}\right)e^{-r/a_0} + r^2\left(2 - \dfrac{r}{a_0}\right)^2\left(-\dfrac{1}{a_0}\right)e^{-r/a_0} = 0$

We get shows as: $r = 0$

For 2nd case: $\left(2 - \dfrac{r}{a_0}\right) = 0 \Rightarrow r = 2a_0$ We again ignore $r = \infty$

$2\left(2 - \dfrac{r}{a_0}\right) - \dfrac{2r}{a_0} - \dfrac{r}{a_0}\left(2 - \dfrac{r}{a_0}\right) = 0$

$\dfrac{r^2}{a_0^2} - \dfrac{6r}{a_0} + 4 = 0$

$r^2 - 6a_0 r + 4a_0^2 = 0$

Then gives result $\left(3 \pm \sqrt{5}\right)a_0$ where in the second derivative is –ve
$\therefore$ These are maxima & not minima.

We have $r = 2a_0$ where there is a node i.e. the minima position!

Only minimum for 1s is the origin (r=0).
For *2s* one of the minima is the origin while the other signifies the node.

2. Find the total degeneracy of the energy level with $E = -\dfrac{13.6}{n^2} eV$ given the constraints:

$m_1 = 0, \pm 1, \pm 2, ... \pm l, \quad l = 0,1,2,3...(n-1)$ and $n = 1,2,3...$

Solution

Total degeneracy for level n

$$= \sum_{l=0}^{n-1}(2l+1) = 2 \times \sum_{l=0}^{n-1} l + \sum_{l=0}^{n-1} 1 = \frac{2n(n-1)}{2} + n = n^2$$

3. The vibrations of the diatomic molecule $^1H\,^{35}Cl$ are better described by a Morse oscillator with the energy levels:

$$E_n = \tilde{v}\left(n+\frac{1}{2}\right) - \tilde{v}\,\tilde{x}\left(n+\frac{1}{2}\right)^2$$

With $\tilde{x} = \dfrac{hc\tilde{v}}{4D}$. The dissociation energy $D = 440.2\ kJ\ mol^{-1}$ and $\tilde{v} = 2886\ cm^{-1}$.

The energies are measured in cm^{-1} (wavenumbers).
  (i)   Calculate the values of $\tilde{x}$ and hence $\tilde{v}\,\tilde{x}$.
  (ii)   Estimate the zero-point energy (in wavenumbers).
  (iii) How many bound vibrational states are supported by this Morse oscillator?

Solution

$$\tilde{x} = \frac{hc\tilde{v}}{4D} = \frac{6.63 \times 10^{-34}\ Js \times 3 \times 10^{10}\ cms^{-1} \times 6.023 \times 10^{23} \times 2886\ cm^{-1}}{4 \times 440.2 \times 10^3\ J} \approx 0.0196$$

$$\text{(dimensionless)}$$

$$\therefore\ \tilde{v}\,\tilde{x} \approx (0.0196)\ (2886\ cm^{-1}) \approx 56.7\ cm^{-1}$$

$$\therefore\ E_n = \left[2886\left(n+\frac{1}{2}\right) - 56.7\left(n+\frac{1}{2}\right)^2\right] cm^{-1}$$

$$\therefore\ \text{Zero Point Energy:}\quad E_0 \cong 1428.8\ cm^{-1}$$

Spacing between adjacent levels : $\Delta E = E_{n+1} - E_n$

$\therefore$ $\Delta E = 2886 - 113.4\ (n+1)$

Last bound state when $\Delta E \approx 0$

$$\Rightarrow n_{max} \approx \frac{2886}{113.4} - 1 \approx 25$$

$\therefore$ roughly 26 bound states supported.

$$n = 0,1,2,.....,n_{max}$$

4.   The first ionization potential of Na is about 5.14 eV. Assume that the energy level of the outer electron (3s) can be represented by a hydrogen-like formula with some effective nuclear charge Z'. Calculate the value of Z'.

Solution

For hydrogen-like system :

$$E_n = \frac{-13.6}{n^2} Z'^2\ eV$$

$\therefore$ For 3s e^- of Na : $n = 3$

$\therefore$ $\frac{13.6}{9} Z'^2 \approx 5.14$

$\Rightarrow$ $Z' \approx \sqrt{\frac{9 \times 5.14}{13.6}} \approx \underline{1.84}$

($Z' > 1 \Rightarrow$ inner e^-s do not completely screen the nuclear charge)

5.   In case of the He atom, it is not possible to solve the Schrodinger equation exactly. Justify this statement by writing out the full Hamiltonian for the He-atom (in atomic units). What is the approximation made in the Hamiltonian so written to make the problem solvable?

Solution

Full Hamiltonian for the He-atom (in atomic units) is:

$$H = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

1 & 2 represent the two electrons.

The electron-electron repulsion term $\frac{1}{r_{12}}$ is responsible for making it impossible to implement separation of variables and not allowing to solve the Schrodinger equation exactly.

The approximation made in the Hamiltonian is to ignore the electron-electron repulsion term $\frac{1}{r_{12}}$ which enables us to solve this multi-electron problem to be solved as two independent electron problems.

6.   Four, noninteracting, electrons are confined in a two-dimensional square box of length L=100 pm, which follow the Pauli exclusion principle, i.e. not more than two electrons are occupied in the same orbital.

    i.   Calculate the ground state energy of the system (in *Joules*).
    ii.   What is the longest wavelength transition (in *nm*)?
    iii.   Suppose that the Pauli exclusion principle is ignored. Estimate the error that result in determining the longest wavelength.

Solution

For particle in square box of side L :

$$E_{n_1 n_2} = \frac{\pi^2 \hbar^2}{2m_e L^2}\left(n_1^2 + n_2^2\right); \quad n_1 = 1,2,.....$$

$$n_2 = 1,2,.....$$

Ground state: particles 1 & 2 are in $n_1 = 1$, $n_2 = 1$

and particles 3 & 4 in $n_1 = 1, n_2 = 2$ $\left(or, n_1 = 2, n_2 = 1\right)$

$$\therefore \ E_{total,gs} = \frac{\pi^2\hbar^2}{2m_eL^2}(2+2+5+5) = \frac{7\pi^2\hbar^2}{m_eL^2} = \frac{7}{4}\times\frac{h^2}{m_eL^2}$$

$$\approx \frac{7\times10\times10^{-68}}{10^{-30}\times10^{-20}} \approx 7\times10^{-17}\,J$$

(1,3) ———— ⋮ ———— (3,1) $\lambda_{long} \ \Rightarrow \quad (1,2)\rightarrow(2,2)$

———— (2,2)

(2,1) —↑———↑↑—↑—— (1,2) $\therefore \ \Delta E = E_{22} - E_{21} = \frac{3\pi^2\hbar^2}{2m_eL^2}$

(1,1) —↑↓————

$$\approx \frac{3\times10\times10^{-68}}{2\times10^{-30}\times10^{-20}} = 1.5\times10^{-17}\,J$$

$$\therefore \ \lambda_{long} = \frac{hc}{\Delta E} = \frac{6.63\times10^{-34}\times3\times10^8}{1.5\times10^{-17}} \ = \ 1.33\times10^{-8}\,m = 13.3 \text{ nm}$$

Pauli exclusion ignored $\Rightarrow$ all 4 electrons in (1,1) state.

Then, $\Delta E = E_{21} - E_{11} = \frac{3\pi^2\hbar^2}{2m_eL^2}$ $\qquad\qquad \therefore$ No error.