

Lecture 5: Bohr Hydrogenic Quantification

$$\begin{cases} \Delta x = \Delta r = 2\pi r \\ \Delta p = p/n = \begin{cases} 0 & \dots n \rightarrow \infty \dots \text{atomic frontier} \\ \infty & \dots n \rightarrow 0 \dots \text{atomic kern} \end{cases} \end{cases} \quad (1.)$$

$$rp = \hbar n, \quad n=1,2,\dots \quad (1.)$$

$$E = T(p) + V(r)$$

$$= \frac{p^2}{2m_0} - \frac{Ze_0^2}{4\pi\epsilon_0} \frac{1}{r} = \frac{p^2}{2m_0} - \frac{Ze_0^2}{4\pi\epsilon_0 \hbar} \frac{p}{n} \quad (1.)$$

$$\left(\frac{\partial E}{\partial p} \right)_{optimum} = 0 \quad (1.)$$

$$\begin{cases} p_{opt,n} = \frac{e_0^2 m_0}{4\pi\epsilon_0 \hbar} \left(\frac{Z}{n} \right) \\ r_{opt,n} = \frac{4\pi\epsilon_0 \hbar^2}{e_0^2 m_0} \left(\frac{n^2}{Z} \right) \\ E_{opt,n} = -\frac{1}{2} \frac{e_0^4 m_0}{(4\pi\epsilon_0)^2 \hbar^2} \left(\frac{Z}{n} \right)^2 = -\frac{1}{2} \frac{Z^2}{n^2} [a.u.] \end{cases} \quad (1.)$$

Worth introducing a fundamental chemical-physical energy constant, namely the atomic unit or the hartree (Hartree) as:

$$1a.u. \equiv 1E_h (\text{hartree}) = \frac{e_0^4 m_0}{(4\pi\epsilon_0)^2 \hbar^2} \equiv 2R_\infty hc \equiv m_0 c^2 \alpha^2 \cong 27.2eV \quad (1.)$$

with R_∞ the Rydberg constant:

$$R_\infty = \frac{m_0 e_0^4}{8c\epsilon_0^2 \hbar^3} = \frac{m_0 c \alpha^2}{2h} [m^{-1}],$$

and were

$$\alpha = \frac{e_0^2}{4\pi\epsilon_0} \frac{1}{\hbar c} \cong \frac{1}{137}$$

is introduced as the fine-structure (universal) constant.

The energetic terms, i.e. kinetic and potential energy provided by the Bohr hydrogenic quantification, looks like:

$$T_{opt,n} = \frac{p_{opt,n}^2}{2m_0} = \frac{1}{2} \frac{e_0^4 m_0}{(4\pi\epsilon_0)^2 \hbar^2} \left(\frac{Z}{n}\right)^2 = \frac{e_0^2}{4\pi\epsilon_0} \frac{Z}{2r_{opt,n}} = -\frac{1}{2} V_{opt,n} = -E_{opt,n}$$

while fulfilling the virial relationships at the atomic level.

For the sake of completeness, the *virial theorem* can be rather elementary be proved by assuming the total energy composed by kinetic and potential terms depending on the second and first power of the space displacement about the equilibrium position, respectively, i.e.

$$E_{tot} = E_{kin} + E_{pot}, E_{kin} \propto x^2; E_{pot} \propto x;$$

Then, if the space is parametrically inflated (rescaled) as

$$x \rightarrow \lambda x, \lambda \in \mathfrak{R}$$

one has now from the energy

$$E_{tot}^\lambda = \lambda^2 E_{kin} + \lambda E_{pot}$$

whereas the equilibrium condition now demands:

$$\left. \frac{\partial E_{tot}^\lambda}{\partial \lambda} \right|_{\lambda=1} = 0$$

leading with the general relationship:

$$E_{kin} = -0.5 E_{pot} = -E_{tot}$$

that is the virial theorem affirms on.

Note that also for the central potential, as for any other, the potential energy variation is correctly considered as being proportional with the space displacement from the equilibrium position, as above, since it may always be written as related with the associated work through the consecrated relationship:

$$\Delta E_{pot} = \mathbf{F} \cdot \Delta \mathbf{x} = -\partial_x V(x) \cdot \Delta \mathbf{x};$$

Thus, the above demonstration of the virial theorem holds in general.