Lecture 12: Hydrogenic Ground State

Let be the stationary radial trial wave-function with two-parameters:

$$\psi_Z(C,\alpha,r) = C\exp(-\alpha r)$$

to be determined throughout imposing it the normalization and eigen-energy variational constraints.

Based on the general "Slater" type formula (see Appendix)

$$I_k(m) = \int_0^\infty r^k e^{-mr} dr = \frac{k!}{m^{k+1}}, \ \forall k \in \mathbf{N} \,\&\, m \in \mathbf{C}, \mathrm{Re}(m) > 0$$

the wave-function radial normalization gives:

$$1 = \int_0^\infty \psi_Z^* \psi_Z r^2 dr = C^2 \int_0^\infty e^{-2\alpha r} r^2 dr = C^2 \frac{2!}{(2\alpha)^3} = \frac{C^2}{4\alpha^3}$$

from where the normalization constants is yield and the trial wave-function takes the intermediate form:

$$\psi_Z(\alpha,r) = 2\alpha^{3/2}\exp(-\alpha r)$$

to be further considered for employing variational principle on the eigen-energy:

$$E_Z(\alpha) = \int_0^\infty \psi_Z^*(\alpha,r)\hat{H}\psi_Z(\alpha,r) r^2 dr$$

with the hydrogenic Hamiltonian

$$\hat{H}_Z = -\frac{\hbar^2}{2m_0}\nabla^2 - \frac{Ze_0^2}{r}, \ e_0^2 = \frac{e^2}{4\pi\varepsilon_0}$$

to be fully considered in radial-spherical coordinates; however, for the Laplacian term the involved integral can be easier evaluated through applying the Gauss surface-to-volume integral transformation (law) while counting the null contribution of the wave-function on the infinite expanded integrated surface; thus one can write:

$$0 = \int_{\Sigma\to\infty} (\psi^* \nabla \psi) d\Sigma_V = \int \nabla(\psi^* \nabla \psi) dV = \int \psi^* \nabla^2 \psi dV + \int \nabla \psi^* \nabla \psi dV$$

from where follows the relationship:

$$\int \psi^* \nabla^2 \psi dV = -\int \left|\nabla \psi\right|^2 dV$$

that has the immediate correspondent in radial operators:

$$\int_0^\infty \psi^* \nabla_r^2 \psi \, r^2 dr = -\int_0^\infty \left|\partial_r \psi\right|^2 r^2 dr \, .$$

With this the above average energy integral becomes:

$$E_Z(\alpha) = 2\frac{\alpha^5 \hbar^2}{m_0}\int_0^\infty e^{-2\alpha r} r^2 dr - 4\alpha^3 Z e_0^2 \int_0^\infty e^{-2\alpha r} r dr$$

$$= 2\frac{\alpha^5 \hbar^2}{m_0}\frac{2!}{2^3 \alpha^3} - 4\alpha^3 Z e_0^2 \frac{1}{2^2 \alpha^2}$$

$$= \frac{\alpha^2 \hbar^2}{2m_0} - \alpha Z e_0^2 \, ,$$

while through the variational principle

$$0 = \partial_\alpha E_Z(\alpha) = \frac{\alpha \hbar^2}{m_0} - Z e_0^2$$

one finally gets also the α -parameter with the form recuperating the inverse of first Bohr radius:

$$\alpha = \frac{Z e_0^2 m_0}{\hbar^2} = \frac{1}{a_0}$$

with the help of which either the first radial wave-function expression

$$\psi_Z(r) = 2 a_0^{-3/2} \exp\left(-r / a_0\right)$$

as well as the first Bohr-(eigen) energy (for the first quantum number in hydrogen atoms)

$$E_{Z,n=1} = -\frac{Z^2 e_0^4 m_0}{2\hbar^2} = -\frac{Z^2 e^4 m_0}{2\left(4\pi\varepsilon_0\right)^2 \hbar^2} = -\frac{Z^2 e^4 m_0}{8\varepsilon_0^2 h^2}$$

are obtained, in fully agreement with previous phenomenological Bohr and wave-function Schrödinger approaches.

Appendix

- $I_k(m)=\int_0^\infty r^k e^{-mr}dr=\frac{k!}{m^{k+1}}$, $\forall k\in\mathbf{N}\,\&\,m\in\mathbf{C},\mathrm{Re}(m)>0$ … Slater radial integral

Proof: $$I_k(m)=\int_0^\infty \frac{d^k\left(e^{-mr}\right)}{d(-m)^k}dr=(-1)^k\frac{d^k}{dm^k}\int_0^\infty e^{-mr}dr=(-1)^k\frac{d^k}{dm^k}\left[-\frac{1}{m}e^{-mr}\right]_0^\infty$$

$$=(-1)^k\frac{d^k}{dm^k}\left(m^{-1}\right)=(-1)^k(-1)^k k!m^{-1-k}=\frac{k!}{m^{k+1}}$$