The Bohr model (of the one electron atom or ion) (1913)

- Solved the problem of radiative stability of atoms.
- Proposed the existence of stationary states, before mathematical procedure (Schrödinger Eq., etc.) was discovered, which was not until ~1925.
- Semiclassical reasoning: blend of new quantum ideas and classical mechanics.

Consider an electron of mass $m$, charge $-e$ orbiting a nucleus of charge $Ze$ ($Z = \text{atomic} \# = \#\text{protons}$). For simplicity, assume uniform circular motion.

Angular momentum: $L = mvr$

2nd Law: $F = ma \Rightarrow a = \frac{-v^2}{r}$ (centripetal acc)

Potential and force

$$V(r) = -\frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{r} \quad (\text{SI units})$$

$$F(r) = -\frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{r^2} \Rightarrow \vec{F} = - \vec{F} V$$

So, 2nd Law becomes

$$\frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{r^2} = \frac{mv^2}{r} \quad (1)$$

Total energy:

$$E = \frac{mv^2}{2} - \frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{r}$$

$$= \left(\frac{1}{2} - 1\right) \frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{r} \quad \text{(from Eq.}(1)\))$

$$E = -\frac{1}{2} \frac{Ze^2}{4\pi\varepsilon_0 r} \quad (2)$$

Bohr's idea (in the language of de Broglie):

Integer \# of wavelengths must fit in orbit,

$$2\pi r = n\lambda$$
For a matter wave, $\lambda = \frac{\hbar}{p} = \frac{\hbar}{mv}$, nonrelativistic.

So,

$$2\pi r = \frac{\hbar}{mv}$$

$\Rightarrow$ $L = mvr = n\hbar$

Quantization of angular momentum.

What is $r_n$? (Needed to find $E_n$ in Eq. (2) above.)

$$m^2 v^2 r^2 = \frac{Z e^2}{4\pi \varepsilon_0} m r$$ (from Eq. (1))

$$n^2 \hbar^2 = \frac{Z e^2}{4\pi \varepsilon_0} m r_n$$

$$r_n = \frac{n^2 \hbar^2}{Z_e^2} \frac{4\pi \varepsilon_0 \hbar^2}{m e^2}$$

where $a_o = \frac{4\pi \varepsilon_0 \hbar^2}{m e^2}$ (Bohr radius) = 0.5292 Å

Energy levels (from Eq. (2)):

$$E_n = -\frac{Z^2}{n^2} E_R, \quad n = 1, 2, 3, \ldots$$

where

$$E_R = \left(\frac{e^2}{4\pi \varepsilon_0}\right)^2 \frac{m}{2\hbar^2} = 13.6 \text{ eV} \quad \text{(Rydberg energy unit)}.$$
Supplement on gradient + Laplacian in orthogonal coordinates

Recall, in Cartesian coordinates

\[ \nabla f = \left( \frac{\partial f}{\partial x}, \frac{\partial f}{\partial y}, \frac{\partial f}{\partial z} \right) \] gradient of \( f(\mathbf{x}) \), \hspace{1cm} (1)

\[ \nabla^2 f = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} \] Laplacian of \( f(\mathbf{x}) \), \hspace{1cm} (2)

\[ \nabla \cdot \mathbf{\hat{d}} = \frac{\partial g_x}{\partial x} + \frac{\partial g_y}{\partial y} + \frac{\partial g_z}{\partial z} \] divergence of \( \mathbf{\hat{d}}(\mathbf{x}) \). \hspace{1cm} (3)

Eq. (2) follows from (1) and (3) for \( \mathbf{\hat{d}} = \nabla f \).

Orthogonal coordinate systems

Coordinates are orthogonal if the length element is

\[ ds^2 = h_1^2 dx_1^2 + h_2^2 dx_2^2 + h_3^2 dx_3^2, \]

with no cross terms, for some scale factors \( h_i \). Examples:

\[ \begin{align*}
    ds^2 &= dx^2 + dy^2 + dz^2 \quad h_x, h_y, h_z = 1, 1, 1 \text{ \hspace{1cm} cartesian} \\
    ds^2 &= d\rho^2 + \rho^2 d\phi^2 + dz^2 \quad h_{\rho}, h_{\phi}, h_z = 1, r, 1 \text{ \hspace{1cm} cylindrical} \\
    ds^2 &= dr^2 + r^2 d\theta^2 + r^2 \sin^2 \theta d\phi^2 \quad h_r, h_\theta, h_\phi = 1, r, r \sin \theta \text{ \hspace{1cm} spherical} 
\end{align*} \]

The gradient and Laplacian can be shown to be

\[ \nabla = \frac{x_1}{h_1} \frac{\partial}{\partial x_1} + \frac{x_2}{h_2} \frac{\partial}{\partial x_2} + \frac{x_3}{h_3} \frac{\partial}{\partial x_3} \]

\[ \nabla^2 = \frac{1}{h_1 h_2 h_3} \left[ \frac{\partial}{\partial x_1} \left( h_2 h_3 \frac{\partial}{\partial x_1} \right) + \frac{\partial}{\partial x_2} \left( h_1 h_3 \frac{\partial}{\partial x_2} \right) + \frac{\partial}{\partial x_3} \left( h_1 h_2 \frac{\partial}{\partial x_3} \right) \right]. \]
Spherical case: \((x_1, x_2, x_3) = (r, \theta, \phi)\)

\[
\nabla = \hat{r} \frac{\partial}{\partial r} + \hat{\theta} \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{\phi} \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi}
\]

\[
\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}
\]

Note that the unit vectors \(\hat{r}, \hat{\theta}, \hat{\phi}\) point in different directions at different points in space, so cannot "square the components of \(\nabla\)" to obtain the Laplacian \(\nabla^2\). Need to differentiate the unit vectors too.

Transformations between cartesian, cylindrical, and spherical coords.

\[
\begin{align*}
\text{Cylindrical} & : (r, \phi, z) \quad \text{to} \quad (x, y, z) \\
\rho &= \sqrt{x^2 + y^2}, \quad x = \rho \cos \phi, \\
\phi &= \arctan \left( \frac{y}{x} \right), \quad y = \rho \sin \phi.
\end{align*}
\]

\[
\begin{align*}
\text{Spherical} & : (r, \theta, \phi) \quad \text{to} \quad (x, y, z) \\
r &= \sqrt{x^2 + y^2 + z^2}, \quad x = r \sin \theta \cos \phi, \\
\theta &= \arccos \left( \frac{r}{r} \right), \quad y = r \sin \theta \sin \phi, \\
\phi &= \arctan \left( \frac{y}{x} \right), \quad z = r \cos \theta.
\end{align*}
\]

(Note: \(\frac{\partial}{\partial \phi} = -\frac{x}{\rho^2} + \frac{y}{\rho^2 \sin \theta} + \frac{z}{\rho^2 \sin^2 \theta} \)

\[
\text{spherical} = -r \sin \theta \sin \phi \frac{\partial}{\partial x} + r \sin \theta \cos \phi \frac{\partial}{\partial y} + \frac{\partial}{\partial \phi}
\]

Can use this to show \(-\imath \frac{\partial}{\partial \phi} = \hat{\phi} \).

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