Relativistic Quantum Theory of Atoms and Molecules

1 Relativity in atomic and molecular physics

1.1 Elementary ideas

nuclei $\longrightarrow$ point mass a-th nucleus $\longrightarrow Z_a e$

The moving particles interact according to Coulomb's law:

$$-\frac{Z_e e^2}{4\pi\varepsilon_0 r^2} \qquad \text{nucleus a – electrons}$$

$$\frac{e^2}{4\pi\varepsilon_0 r^2} \qquad \text{electron – electron}$$

$$\frac{Z_a Z_b e^2}{4\pi\varepsilon_0 r^2} \qquad \text{nuclei a–b repel each other}$$

The electronic intrinsic angular momentum – spin $\boldsymbol{s}$

$$\boldsymbol{s} = \frac{1}{2}\hbar\boldsymbol{\sigma} \qquad \boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$$

Note: $\boldsymbol{s}^2$ and s_z have eigenfunction. $\sigma - -spinlabel$

N indistinguishable electrons system wavefunction $\Psi(q_1, q_2, \dots q_N, t)$

Spin-Orbit Coupling $\longrightarrow \boldsymbol{j} = \boldsymbol{l} + \boldsymbol{s}$

1.2 The one-electron atom

1.2.1 Classical Kepler orbits

$$\frac{1}{r} = \frac{mk}{|\boldsymbol{l}|^2}\{1 + \varepsilon\cos(\theta + \alpha)\} \qquad k = \frac{Ze^2}{4\pi\varepsilon_0} \qquad \varepsilon = \sqrt{1 + \frac{2E|\boldsymbol{L}|^2}{mk^2}}$$

- $-\frac{mk}{2|\boldsymbol{l}|^2} \leqslant E < 0 \quad \Longrightarrow \quad 0 \leqslant \varepsilon < 1$

$$\Longrightarrow \begin{cases} r = \dfrac{|\boldsymbol{l}|^2}{mk(1+\varepsilon)} & \text{closest approach} \\ r = \dfrac{|\boldsymbol{l}|^2}{mk(1-\varepsilon)} & \text{maximum distance} \end{cases}$$

When $\varepsilon = 0 \quad \Longrightarrow \quad r = \frac{l^2}{mk} \quad \Longrightarrow \quad E = -\frac{mk}{2|\boldsymbol{l}|^2}$.

- $E = 0 \quad \Longrightarrow \quad \varepsilon = 1 \quad \Longrightarrow$ orbit is a parabola.
- $E > 0 \quad \Longrightarrow \quad \varepsilon > 1 \quad \Longrightarrow$ orbit is hyperbola.

$$r_{min} = \frac{|\boldsymbol{l}|^2}{mk(1 + varepsilon)} \qquad v_{max} = \frac{|\boldsymbol{l}|}{mr_{min}}$$

1.2.2 The Bohr atom

$$E = \frac{1}{2}\langle V\rangle = -\langle T\rangle$$

Where E is the energy of particle, $\langle T \rangle$ is the orbital average of the kinetic energy and $\langle V \rangle$ is the potential energy.

The frequencies of the spectral lines could be fitted to Rydberg's formula:

$$\nu = R\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

The transition energy between two states: $E_n = -\frac{R}{n^2}$

1.2.3 X-ray spectra and Moseley's Law

The square root of the frequency of each corresponding X-ray line was approximately proportional to Z.