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 $\Psi(q_1, q_2, \ldots q_N, t)$

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. Relativistic effects modify the Z-dependence as Z increases.

1.2.4 Transition to quantum mechanics

A particle wavefunction: $\psi(\boldsymbol{r}, t)$
Schrödinger equation: $i\hbar\frac{\partial\psi}{\partial t}\psi(\boldsymbol{r}, t) = H\psi(\boldsymbol{r}, t)$
Hamiltonian: $\hat{H}(\boldsymbol{p}, \boldsymbol{r}) = \frac{1}{2m}\boldsymbol{p}^2 + V(\boldsymbol{r}), \quad \boldsymbol{p} \to -i\hbar\Delta, \quad \boldsymbol{r} \to \boldsymbol{r}$
$V(\boldsymbol{r}) \to$ potential energy of an electron at a distance $r = |\boldsymbol{r}|$

$$V(\boldsymbol{r}) = -\frac{Ze^2}{4\pi\varepsilon r}$$

which could deduce the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\Delta^2 - \frac{Ze^2}{4\pi\varepsilon r}$$

and whoes energies are given by the formula

$$\varepsilon_{nl} = -\frac{mZ^2e^4}{32\pi^2\varepsilon_0^2\hbar^2n^2}$$

The orbital angular momentum vector $\boldsymbol{l}$, and $\boldsymbol{l}^2$ takes the values $l(l+1)\hbar^2$, l_z takes the $2l+1$ values $m\hbar$. Due to Rydberg's formula $R = mZ^2e^4/32\pi^2\varepsilon_0^2\hbar^2$, from the energy relation could deduce that $\langle T_n\rangle = -E_n$, and $T_n = mv^2/2$, get the relation

$$\frac{v_n}{c} = \frac{\alpha Z}{n}$$

where $\alpha = e^2/4\pi\varepsilon_0\hbar c$ is the dimensionless fine structure constant.

In spherical polar coordinates

$$\psi_{nlm}(\boldsymbol{r}, t) = \text{const.}\frac{P_{nl}(r)}{r}Y_l^m(\theta, \phi)$$

1.2.5 Sommerfeld's relativistic orbits and Dirac's wave equation

In the Kepler problem, the particle speed attains its maximum at closest approach to the centre of force

$$\frac{v_{max}}{c} = \frac{k}{c|\boldsymbol{l}|}(1+\varepsilon), \qquad \varepsilon > 0$$

v_{max} is inversely proportional to $|\boldsymbol{l}|$, so the largest effects in states with the lowest angular momentum.

A particle moving in some reference frame with velocity $\boldsymbol{u}$ has four-momentum p^u

$$p^0 = \frac{E}{c} = mc\gamma(u), \quad p^i = mu^i\gamma(u), \quad i = 1, 2, 3.$$

where $\gamma(u) = 1/\sqrt{1-u^2/c^2}$ and u^i are the Cartesian components of $\boldsymbol{u}$.

Dirac' relativistic wave equation for hydrogenic atoms:

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi, \qquad \hat{H} = c\boldsymbol{\alpha}\cdot\boldsymbol{p} + \beta mc^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$