Lecture 14

Hydrogen-like atom-II

Study Goal of This Lecture

- Energy levels

- Atomic orbitals

14.1   Recall

Recall for hydrogen-like atoms, the Hamiltonian is

$$\hat{H} = \frac{-\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - \frac{Ze^2}{4\pi\epsilon\sqrt{x^2 + y^2 + z^2}}. \tag{14.1}$$

The Schrödinger equation:

$$\hat{H}\psi = E\psi, \tag{14.2}$$

can be solved in the spherical coordinates to yield

$$\psi(r,\theta,\phi) = R_{nl}(r)Y_l^m(\theta,\phi). \tag{14.3}$$

Make sure you understand why $R(r)$ depends on n and l.

The energy levels describe the spectrum of hydrogen here, we often rewrite E_n in a few other constants:

$$\begin{aligned}
E_n &= \frac{m_e e^4 Z^2}{2(4\pi\epsilon_0)^2\hbar^2 n^2} \\
&= -\frac{Z^2}{2n^2}\frac{e^2}{4\pi\epsilon_0 a_0},
\end{aligned} \tag{14.4}$$

where a_0 is Bohr radius, it is the most probable distance of the electron from the nucleus for the hydrogen 1s orbital,

$$a_0 = \frac{(4\pi\epsilon)\hbar^2}{m_e e^2}. \tag{14.5}$$

And E_h is the Hartree energy,

$$E_h = \frac{e^2}{4\pi\epsilon_0 a_0}. \tag{14.6}$$

Note that $a_0 \simeq 0.53\text{Å}$ and one Hartree$\simeq 27.2$eV,

$$\therefore E_n = -\frac{1}{2}\frac{Z^2}{\hbar^2}E_h. \tag{14.7}$$

14.2 Hydrogen Atom Spectrum

In spectroscopy, we often use "wavelength" or "wavenumbers" to describe transitions. In this case,

$$\Delta E = h\nu = \frac{2\pi\hbar c}{\lambda} = 2\pi\hbar c\tilde{\nu} = E_{n2} - E_{n1}, \tag{14.8}$$

consider the emission

$$\begin{aligned}\therefore \tilde{\nu}_{n_1 \to n_2} &= \frac{1}{2\pi\hbar c} \times \frac{\mu e^4 Z^2}{2(4\pi\epsilon_0)^2\hbar^2} \times \left(\frac{-1}{n_2^2} + \frac{1}{n_1^2}\right) \\ &= RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right).\end{aligned} \tag{14.9}$$

$$R = \frac{\mu e^4}{4\pi c(4\pi\epsilon_0)^2\hbar^3} \simeq 13.6\text{eV, : Rydberg constant.} \tag{14.10}$$

The real R slightly depends on the nuclear atomic number. The above equation also defines the ionization energy, the energy required to take the electron in the groundstate to $n = \infty$.

$$E_i = \frac{R \cdot Z^2}{n_i^2} \tag{14.11}$$

$$n = 1 : -109678 \ cm^{-1}$$

$$n = 2 : -27420 \ cm^{-1}$$

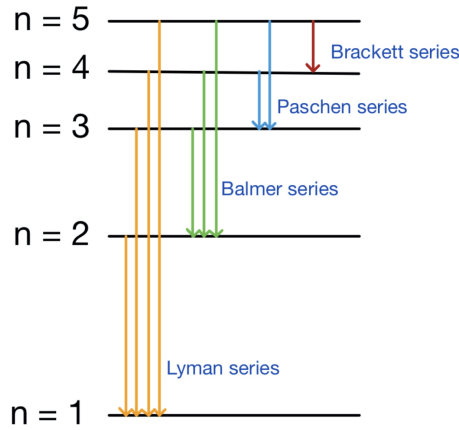$$n = 3 : -12186 \ cm^{-1}$$

$$n = 4 : -6855 \ cm^{-1}$$

Figure 14.1: Hydrogen atom spectrum.

14.2.1 Atomic Orbital

Now we are ready to consider the eigenfunctions,

$$\psi_{n,l,m_l,} = R_{nl}(r)Y_l^{m_l}(\theta,\phi). \tag{14.12}$$

Eigenfunctions of the electron are:

The s,p,d,f terminology is due to historical reason. It comes from Bohr's H-atom model.

$$\textbf{1s: } R_{1s} = 2\Big(\frac{Z}{a_0}\Big)^{\frac{3}{2}} e^{\frac{-Zr}{a_0}}, \ Y_0^0(\theta,\phi) = \frac{1}{2\sqrt{\pi}},$$

$$\textbf{2s: } R_{2s} = \frac{1}{\sqrt{2}}\Big(\frac{Z}{a_0}\Big)^{\frac{3}{2}}(1 - \frac{Zr}{2a_0})e^{\frac{-Zr}{2a_0}}, \ Y_0^0(\theta,\phi) = \frac{1}{2\sqrt{\pi}},$$

$$\textbf{2p: } R_{2p} = \frac{1}{2\sqrt{6}}\Big(\frac{Z}{a_0}\Big)^{\frac{5}{2}} r e^{\frac{-Zr}{2a_0}}, \ \begin{matrix} Y_1^0(\theta,\phi) = \Big(\frac{3}{4\pi}\Big)^{\frac{1}{2}}\cos\theta, \\ Y_1^{\pm1}(\theta,\phi) = \Big(\frac{3}{8\pi}\Big)^{\frac{1}{2}}\sin\theta e^{\pm i\phi}. \end{matrix}$$

Notice that the angular part wavefunction of p-orbital is complex. In chemistry, we frequently use real-value spherical harmonic:

$$\psi_{p_z} = R_{2p} \times Y_1^0(\theta,\phi),$$

$$\psi_{p_x} = R_{2p} \times \frac{1}{\sqrt{2}}\Big[Y_1^{+1}(\theta,\phi) + Y_1^{-1}(\theta,\phi)\Big] = R_{2p} \times \sqrt{\frac{3}{4\pi}}\sin\theta\cos\phi, \tag{14.13}$$

$$\psi_{p_y} = R_{2p} \times \frac{1}{\sqrt{2}}\Big[Y_1^{+1}(\theta,\phi) - Y_1^{-1}(\theta,\phi)\Big] = R_{2p} \times \sqrt{\frac{3}{4\pi}}\sin\theta\sin\phi.$$

Note that ψ_{p_x}, ψ_{p_y} are not eigenfunctions of $\hat{L}_z$, but still eigenfunctions of $\hat{L}^2 \Rightarrow$ Eigenfunctions of $\hat{H}$.

We can write down the $3s, 3p, 3d \cdots$ vice versa. If you are interested in know-ing it, see the textbook. These are the "stable" states for a single eletron moving around a positive charge and denotes Hydrogen-like "atomic orbitals" $\Rightarrow$ In quantum mechanics, orbitals are defined as "one-electron" wavefunction.

Note that these functions are normalized and orthogonal to each other, i.e.

$$\int |\psi|^2 d\tau = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |\psi(x, y, z)|^2 dx dy dz$$
$$= \int_{0}^{\infty} \int_{0}^{\pi} \int_{0}^{2\pi} |R_{nl}(r)|^2 |Y_l^m(\theta, \phi)|^2 r^2 \sin\theta d\phi d\theta dr \qquad (14.14)$$
$$= \int_{0}^{\infty} |R_{nl}(r)|^2 r^2 dr \underbrace{\int_{0}^{\pi} \int_{0}^{2\pi} |Y_l^m(\theta, \phi)|^2 \sin\theta d\theta d\phi}_{=1}.$$

Therefore, the nomralization condition requires that

$$\int_{0}^{\infty} |R_{nl}(r)|^2 r^2 dr = 1, \qquad (14.15)$$

the probability density is

$$P(r) = |R_{nl}(r)|^2 r^2. \qquad (14.16)$$

$P(r)$ is called radial probability density functions, it is the probability density of finding a electron at distance r from the nuclei. The factor r^2 comes from the surface.

It is impossible to directly visualize ψ, but we can gain a good understanding of its functional form by plotting radial and angular functions seperately.

14.2.2 Radial distribution function

Now let's gain a rough idea(qualitative) about the radial distribution function First, the $1s$ function $R_{1,0}(r)$ along the x-direction looks like:
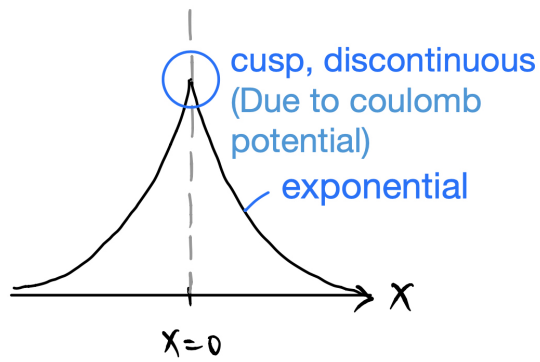
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cusp, discontinuous
(Due to coulomb potential)

exponential

X

$X = 0$

Figure 14.2: Radial function $R_{1,0}$

and for others:

density distribution

R_{1s}

r^2

$\implies \quad |\overset{2}{R}| \cdot \overset{2}{r}$
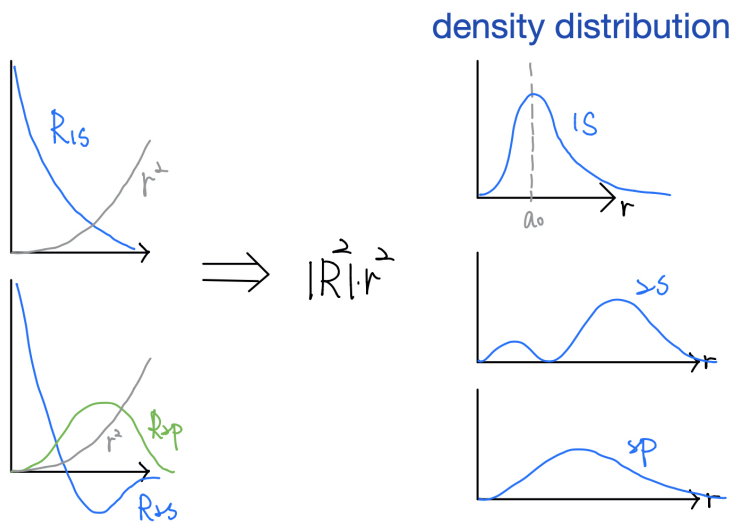
r^2 R_{2p}

R_{2s}

$1s$

a_0 r

$2s$ r

$2p$ r

Figure 14.3: Radial distribution function of $1s$, $2s$ and $2p$.

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Now we define the following terms:

Terms	Name	Remark
ψ_{nlm}	H-like atomic orbitals	Eigenstates of the Hamiltonian
$|\psi_{nlm}|^2$	One electron probability density	
$R_{nl}(r)$	Radial function	No physical meaning
$r^2 R_{nl}(r)^2$	Radial probability distribution function	
$s, p, d, \cdots$	Denoting $l = 0, 1, 2, \cdots$ orbitals	Used in chemistry

For more contents, see the slides!