

2 ONE-ELECTRON ATOMS

2.1 THE BOHR ATOM

The postulates:

1. The electron moves in circular classical orbits about the nucleus without radiating
2. The angular momentum L is quantized.

$$L = n\hbar \quad \hbar = h/2\pi \text{ and } n=1,2,3,\dots, \quad (1)$$

Coulomb force between nucleus and electron is balanced by the centripetal force. Assuming the nucleus is infinitely heavy

$$\frac{Ze^2}{4\pi\epsilon_0 R^2} = \frac{m_e v^2}{R} \quad (2)$$

From the quantization of L , $L = n\hbar$ we get

$$v = \frac{n\hbar}{m_e R} \quad r_n = \frac{4\pi\epsilon_0 \hbar^2 n^2}{Ze^2 m_e} \quad (3)$$

we can now work out the For $n = 1$, $r_{n=1} = \frac{4\pi\epsilon_0 \hbar^2}{Ze^2 m_e}$. For $Z = 1$ (hydrogen) this is called the BOHR RADIUS. We can eliminate r in the equation for the velocity:

$$v_n = \frac{Ze^2}{4\pi\epsilon_0 n\hbar} \quad (4)$$

Knowing v and r we can work out the total kinetic energy, T , for each quantum state, since $T = \frac{1}{2}m_e v^2$ and the potential energy, V , since $V = -\frac{Ze^2}{4\pi\epsilon_0 r}$: Put these, with r and v given above, in TOTAL ENERGY:

$$E = T + V \quad (5)$$

you get

$$E_n = -\frac{m_e}{2\hbar^2} \left[\frac{Ze^2}{4\pi\epsilon_0} \right]^2 \frac{1}{n^2} \quad (6)$$

for $n = 1, 2, 3, \dots$. Note that the energy is negative, since we have a bound state.

2.1.1 TRANSITIONS

If the electron jumps from an initial state i with n_i to a final state j with n_j , we have:

$$h\nu_{if} = |E_{n_i} - E_{n_f}| = \left| \frac{m_e}{2\hbar^2} \left[\frac{Ze^2}{4\pi\epsilon_0} \right]^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \right| \quad (7)$$

$n_i < n_f$, the photon will be absorbed and the process is called excitation, $n_i > n_f$ the photon will be emitted and the process is de - excitation.

The wavelength of the photon will be:

$$\frac{1}{\lambda_{if}} = \frac{\nu_{if}}{c} = \left| \frac{m_e}{4\pi\hbar^3 c} \left[\frac{Ze^2}{4\pi\epsilon_0} \right]^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \right| \quad (8)$$

Similar to formula empirically determined by Rydberg for the H spectrum:

$$\frac{1}{\lambda_{if}} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (9)$$

$R=109677.58 \text{ cm}^{-1}$ is the observed **Rydberg constant**, note the dimensions. The Bohr model predicts:

$$R_\infty = \frac{m_e}{4\pi\hbar^3 c} \left[\frac{e^2}{4\pi\epsilon_0} \right]^2 = 109737 \text{ cm}^{-1} \quad (10)$$

(the symbol ∞ makes reference to the fact that we are assuming the mass of the nucleus to be infinite). The discrepancy is $\simeq 5 \times 10^{-4}$.

2.2 LYMAN, BALMER AND PASCHEN SPECTRAL SERIES

- Lyman series $n = 2, 3, 4, 5 \dots \rightarrow n = 1$ (u.v.)
- Balmer series $n = 3, 4, 5 \dots \rightarrow n = 2$ (optical)
- Paschen series $n = 4, 5 \dots \rightarrow n = 3$ (Infra Red)

See figure 2.1. The limit of the Lyman series is 912 \AA (in u.v.) corresponding to the ionisation energy of hydrogen $R_\infty = 109737 \text{ cm}^{-1}$.

2.2.1 THE CORRESPONDENCE PRINCIPLE

In the limit of large quantum numbers $n \rightarrow \infty$, QM results should tend to the classical results.

2.2.2 EFFECTS OF FINITE NUCLEAR MASS

The mass of the nucleus is not infinite. Corrections due to the finite mass are important, e.g. the spectral line frequencies differ for D and H.

So, we consider the REDUCED MASS, μ , in the Bohr atom.

DEFINITION: the reduced mass, μ is the effective mass of a system once the Centre of Mass motion is separated off.

Consider the proton and electron system as a rigid rotor, separation r and note that $M_p/m_e = 1836$ and $\underline{r} = \underline{r}_e - \underline{R}_p$. The Centre of Mass remains at rest. It is at the origin, so taking moments,

$$M_p \underline{R}_p + m_e \underline{r}_e = 0, \quad (11)$$

$$\underline{R}_p = -\frac{m_e}{m_e + M_p} \underline{r} \quad \text{and} \quad \underline{r}_e = \frac{M_p}{m_e + M_p} \underline{r} \quad (12)$$

Then, for the angular momentum, L :

$$L = m_e \omega r_e^2 + M_p \omega R_p^2 = \mu \omega r^2 = \mu v r. \quad (13)$$

where $\mu = \frac{m_e M_p}{(m_e + M_p)}$ is the reduced mass.

In the Bohr atom expressions we **replace** m_e **by** μ . In general we can approximate $\mu \sim m_e$, but the difference accounts for the difference between R and R_∞ , and can be important. We have for each atom a different value of R .

2.2.3 ASSESMENT OF THE BOHR MODEL

Predictions for energy levels of H and other one-electron (hydrogenic) atoms are good. Could not explain quantitatively transitions between states. It could not be extended to other atoms, even helium, but it does work well for hydrogenic atoms, with only one electron such as He^+ or Li^{2+} .

2.3 ATOMIC UNITS AND WAVENUMBERS

2.3.1 ATOMIC UNITS “a.u.”

When working with atoms it is convenient to use a new set of units.

We define:

- unit of mass = m_e
- unit of charge = e
- unit of length=Bohr radius = a_0

So $\hbar = 4\pi\epsilon_0 = a_0 = e = m_e = 1$.

Put these in eqs above and find that:

$$r_n = \frac{n^2}{Z} . \quad (14)$$

$Z = 1$ and $n = 1$ we have $r_1 = a_0 = 1$,

the BOHR RADIUS, $a_0 = 0.529 \times 10^{-10}$ a.u. The energy is given by

$$E_n = -\frac{Z^2}{2n^2} . \quad (15)$$

The ground state energy of hydrogen for infinite mass is: $E_{n=1} = -1/2$ a.u. ... or -13.605 eV... or -2.18×10^{-18} J... .

The atomic unit of energy is also called the **Hartree**: 1 Hartree= 1 a.u. =27.21 eV

The speed of the e^- in the ground (lowest) state of H is:

$$v = \frac{e^2}{4\pi\epsilon_0\hbar} = 1 \text{ a.u.} = \alpha c \quad (16)$$

where $\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \simeq \frac{1}{137}$ is fine structure constant.

The speed of light is $\simeq 137$ a.u..

Can also use: $R_\infty = |E_{n=1}|$, the RYDBERG CONSTANT. The ∞ refers to infinite mass. Then

$$E_n = -R_\infty \frac{Z^2}{n^2} \quad \left(\text{strictly, } E_n = -R_\infty \frac{\mu}{m_e} \frac{Z^2}{n^2} \right). \quad (17)$$

Note: the ionisation energy of hydrogen is $|E_{n=1}|$ since it is the energy which must be supplied to the atom in its *ground state to remove the electron*.

Another energy unit can be defined: *Rydberg* = $\frac{1}{2}$ Hartree

2.3.2 SPECTROSCOPIC UNITS: WAVENUMBERS

Wavenumbers or cm^{-1} are the units favoured by spectroscopists.

Have dimension *Length*⁻¹.

Advantage: if the energies of quantum states are given in this unit one can rapidly infer the wavelength.

Using $E = h\nu = hc/\lambda$ we get

$$\lambda^{-1} = Z^2 \tilde{R}_\infty \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right]. \quad (18)$$

Now \tilde{R}_∞ defines the unit of the WAVENUMBER. We usually drop the tilde.

To get the energy in different units we can use $E_n = R_\infty Z^2/n^2$ with:

- $R_\infty = 109737 \text{ cm}^{-1}$
- $R_\infty = \frac{1}{2} \text{ a.u.}$
- $R_\infty = 13.605 \text{ eV}$

So 1 a.u. of energy = 27.2 eV = 219475 cm^{-1}

1 eV = 0.0368 a.u. = 8065.48 cm^{-1}

1 cm^{-1} = 1.239×10^{-4} eV = 0.0456×10^{-4} a.u.

2.4 REVIEW OF QUANTUM ANGULAR MOMENTUM AND SPHERICAL HARMONICS

Classically, orbital angular momentum, \underline{L} , is given by

$$\underline{L} = \underline{r} \times \underline{p} \quad \text{so that} \quad L_x = yp_z - zp_y, \quad \text{etc ...} \quad (19)$$

Quantum mechanically we use the momentum operator $\hat{p} = -i\hbar\nabla$ and \hat{r} which give \hat{L} whose components and length are given by

$$\hat{L}_x = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right), \quad \text{etc and} \quad \hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \quad (20)$$

The **commutation relations** are $[\hat{L}_i, \hat{L}_j] = i\hbar\hat{L}_k$, i, j, k stand for x, y and z , i.e. $[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z$ so that the components of \hat{L} **cannot be assigned definite values simultaneously** (unless $\hat{L} = 0$).

However, $[\hat{L}^2, \hat{L}_j] = 0$, i.e. $[\hat{L}^2, \hat{L}_x] = 0$ so that we can have **simultaneous eigenfunctions of \hat{L}^2 and one component of \hat{L}** (note in general we choose \hat{L}_z). To understand this, picture \hat{L} precessing about the z -axis (can always rotate reference frame for this to be the case).

It is easier to use **spherical polar coordinates**, r, θ, ϕ (see text books for diagram, but note mathematics books often interchange θ and ϕ !).

$$\begin{aligned} x &= r \sin \theta \cos \phi & 0 \leq r \leq \infty \\ y &= r \sin \theta \sin \phi & 0 \leq \theta \leq \pi \\ z &= r \cos \theta & 0 \leq \phi \leq 2\pi \end{aligned}$$

which gives

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi} \quad \text{and} \quad \hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \quad (21)$$

The simultaneous eigenfunctions of \hat{L}^2 and \hat{L}_z are called **spherical harmonics**, $Y_{lm}(\theta, \phi)$ and the eigenvalue equations are

$$\hat{L}^2 Y_{lm}(\theta, \phi) = l(l+1)\hbar^2 Y_{lm}(\theta, \phi) \quad \hat{L}_z Y_{lm}(\theta, \phi) = m\hbar Y_{lm}(\theta, \phi) \quad (22)$$

where $l = 0, 1, 2, \dots$ are the **orbital angular momentum quantum numbers** and $m (= m_l) = 0, \pm 1, \pm 2, \pm 3, \dots, \pm l$ are the **orbital angular momentum magnetic quantum numbers** and there are $2l + 1$ values.

So we find that angular momentum is quantized but not in the same way as in the Bohr picture where we had $L = n\hbar$.

The **Spherical Harmonics**: $Y_{lm}(\theta, \phi) = \Theta_{lm}(\theta)\Phi_m(\phi)$.

See figures 2.3, 2.4, 2.5 and 2.8.

are separable in functions of θ and ϕ , where $\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\phi}$ and $\Theta_{lm}(\theta)$ is proportional to $P_l^m(\cos\theta)$, the Associated Legendre Polynomial.

The parity of $Y_{lm}(\theta, \phi)$. The parity operator, \hat{P} , corresponds to an inversion of a vector \underline{r} through the origin and is defined by the relation

$$\hat{P}f(\underline{r}) = f(-\underline{r}) \quad (23)$$

If $\hat{P}f(\underline{r}) = +f(\underline{r})$ **EVEN function.**

If $\hat{P}f(\underline{r}) = -f(\underline{r})$ **ODD function.**

The **parity** of $Y_{lm}(\theta, \phi)$ is $(-1)^l$ and

$Y_{lm}(\theta, \phi)$ is EVEN if l is even and ODD if l is odd.

2.5 REVIEW OF QUANTUM TREATMENT OF ONE-ELECTRON ATOMS

Time-independent Schrödinger eq. for one electron-atoms (in a. u.)

$$\hat{H}\Psi_{nlm}(\underline{r}) = \left[-\frac{1}{2}\nabla^2 - \frac{Z}{r} \right] \Psi_{nlm}(\underline{r}) = E_n \Psi_{nlm}(\underline{r}) \quad (24)$$

where $\Psi_{nlm}(\underline{r}) = R_{nl}(r)Y_{lm}(\theta, \phi)$ can be written as a product of the radial and angular eigenfunction of \hat{H} .

Radial Wavefunction

$R_{nl}(r) = N_{nl}e^{-\rho/2}\rho^l L_{nl}(\rho)$ where we used **scaled variables**: $\rho = \frac{2Z}{n}r$

N_{nl} is a constant for given n, l and Z .

$L_{nl}(\rho)$ are the Associated Laguerre Polynomials.

For large ρ the exponential term, $e^{-\rho/2}$, dominates so that as $\rho \rightarrow \infty$ we have $R_{nl} \rightarrow 0$. So:

- as $r \rightarrow \infty$ we have $R_{nl} \rightarrow 0$, as expected since the e^- is bound to the atom.
- The larger Z the faster the exponential decay, the e^- is closer to the nucleus.
- The larger n , the slower the decay. Excited states are more extended.
- For normalized wavefunction

$$\int |\Psi_{nlm}|^2 d\tau = \int_0^\infty |R_{nl}(r)|^2 r^2 dr \int_0^{2\pi} \int_0^\pi |Y_{lm}(\theta\phi)|^2 \sin\theta d\theta d\phi = 1 \quad (25)$$

- $r^2 R_{nl}^2$ gives the **probability density** of finding the e^- at a distance r from the nucleus. So to 'visualize' the radial function we can look at the integrand of the radial integral as shown in figures for H atom (figure 2.3). We do not have a well defined orbit as in the Bohr model.
- Number of peaks in $r^2 R_{nl}^2$ is equal to $n - l$ (From Laguerre Polynomial).
- For a given n the probability of finding the e^- near the nucleus decreases as l increases, because the centrifugal barrier pushes the e^- out. So the low- l orbitals are called penetrating.

The energy eigenvalues obtained by solving the Schrödinger eq. are

$$E_n = -\frac{1}{2n^2} \left(\frac{Ze^2}{4\pi\epsilon_0} \right) \frac{\mu}{\hbar^2} \quad (26)$$

The result is the same as in the Bohr model, E_n depends on n , but for each value of n we have n values of l ($=0,1,2,\dots,n-1$) and for each each value of l we have $(2l + 1)$ values of m ($0, \pm 1, \pm 2, \pm 3, \dots, \pm l$). In quantum mechanics solution for H, we have for each energy several quantum states \rightarrow **Degeneracy**.

Hence the total number of states with the same E_n , i.e. **total degeneracy** with respect to l and m is

$$\sum_{l=0}^{n-1} (2l + 1) = n^2 \quad (27)$$

Spectroscopic notation. Each level is labelled by nl where l is represented by a letter

$$\begin{array}{cccccc} l = & 0 & 1 & 2 & 3 & 4 & \dots \\ & s & p & d & f & g & \end{array}$$

s stands for 'sharp', p for 'principal', d for 'diffuse' and f for 'fundamental'.

So the ground state (g.s.) of H is labelled $1s$, the first excited states $2s$ and $2p$. Transitions between states with any Δn are allowed but as we will see there is a restriction on l and m ; $\Delta l = \pm 1$ and $\Delta m = 0, \pm 1$ (called electric-dipole selection rule). Also we label the n quantum numbers by

$$\begin{array}{cccccc} n = & 1 & 2 & 3 & 4 & \dots \\ & K & L & M & N & \end{array}$$

2.6 ELECTRON SPIN AND ANTIPARTICLES

As experimental techniques improved, many transitions were found to exhibit what became known as *fine structure* e.g., the $2p \rightarrow 1s$ transition in atomic hydrogen was found to be a doublet. This led to the assignment of an additional quantum number to the electron, *spin*, s , associated with its intrinsic angular momentum, \hat{S} (remember these are operators), such that (in analogy with \hat{L}) we obtain the eigenvalue expressions:

$$\hat{S}^2 \chi_{sm_s} = s(s+1)\hbar^2 \chi_{sm_s} \quad \text{with } s = \frac{1}{2} \quad (28)$$

$$\hat{S}_z \chi_{sm_s} = m_s \hbar \chi_{sm_s} \quad \text{with } m_s = \pm \frac{1}{2}. \quad (29)$$

and the spin eigenfunctions χ_{sm_s} are called spinors.

So, the total wavefunction of the H atom is:

$$\Psi_{nlm_l m_s}(\underline{r}) = \underbrace{R_{nl}(r)}_{\text{radial}} \underbrace{Y_{lm_l}(\theta, \phi)}_{\text{angular}} \underbrace{\chi_{m_s}}_{\text{spin}}. \quad (30)$$

The theoretical justification for spin eventually emerged through Dirac's relativistic theory of quantum mechanics. The same theory lead to the prediction of antiparticles.

In order to make the Schrödinger equation consistent with the relativistic relation $E^2 = c^2p^2 + m^2c^4$

and to allow for the conservation of angular momentum in a central potential, $V(r)$, Dirac found that he had to allow the electron an *extra* angular momentum, the spin \hat{S} , such that the total angular momentum, $\hat{J} = \hat{L} + \hat{S}$, is a constant in a central field of force.

Dirac's theory (1930) also predicted that the allowed values of the total relativistic energy for a *free* electron are:

$$E = \pm\sqrt{c^2p^2 + m^2c^4}, \quad (31)$$

where c is the speed of light, p and m the momentum and rest mass of the electron, respectively.

If these negative energy states do exist, what prevents ($E > 0$) electrons from jumping to such lower energy states? Dirac removed this difficulty by proposing that the negative energy states are usually full, so that the Pauli Exclusion Principle (see next section) prevents further transitions.

The normal state of the vacuum then consists of an infinite density of negative energy electrons. If an electron with $E < 0$ is excited to a state with $E > 0$, the *hole* left behind (or absence of a negatively charged electron with negative mass and negative kinetic energy) would manifest itself as a particle with $E > 0$, charge $+e$, and mass equal to the mass of an electron. This antiparticle of the electron—the positron—was observed a few years later (Anderson 1932, Blackett and Occhialini 1933).

The excitation of an electron from a state with $E < 0$ to one with $E > 0$ state is known as e^-e^+ pair production; it is an endothermic process requiring $E \geq 2mc^2$. The reverse is known as annihilation. This is an exothermic process releasing energy, most commonly through the emission of two γ -rays with $E \geq 511$ keV each.