Quantum Mechanics

Cheatsheet and Summary

Contents

1 Basic starters

Photon energy and momentum
A-level stuff:

$$E = hf = pc \tag{1}$$

Definition of a wavenumber

$$k = \frac{2\pi}{\lambda} \tag{2}$$

Compton scattering, know how to derive it:

$$\Delta\lambda = \frac{h}{mc}(1 - \cos\theta) \tag{3}$$

The uncertainty principle
Components of position $\mathbf{r}$ and momentum $\mathbf{p}$ cannot be known with absolute precision at the same time. We can never know x and p_x with precision better than $\frac{\hbar}{2}$:

$$\Delta q \Delta p_q \geq \frac{\hbar}{2} \tag{4}$$

From the classical wave equation, we can move to the Schrodinger Equation, where we want $E \propto p^2$. The time dependent schrodinger eqation (TDSE) is given as:

$$i\hbar\partial_t \Psi = \hat{H}\Psi \tag{5}$$

where $\hat{H}$ is the hamiltonian operator. Using separation of variables, we can obtain the time independent Schrodinger equation (TISE):

$$\hat{H}\psi = E\psi \tag{6}$$

with the full solution of the TDSE as:

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r})e^{\frac{-iE}{\hbar}t} \tag{7}$$

2 Postulate 1 - The wavefunction

A wavefunction exists & contains all the information about a system
In quantum mechanics, we use the wavefunction to describe the universe in terms of a mathematical object Ψ. "The wavefunction contains all the dynamical information about the system it describes."[1] Ψ is complex, and is difficult to ascribe it to a physical interpretation. It is just a database of the universe, where our observations can determine its various properties from it.

The Born Rule It is given as the following:

$$\int_{-\infty}^{\infty} \Psi^*\Psi d\tau = 1 \tag{8}$$

In all space, the wavefunction and its complex conjugate forms an orthonormal set, where the both are the same, resulting in one. This is analogous to multiplying the basis vectors, where $i \cdot i = 1$. The normalisation constant can be found using the above.

Boundary Conditions of Ψ

1. Continuous, single-valued functions of position $\underline{r}$ and time t. Continuous means there are no jumps, gaps, discontinuity or undefined points.

2. The first derivative of Ψ should be continuous, except for the infinite discontinuity for the potential energy function. I.e. $\partial_\tau \Psi$ is continuous.

3. The squared modulus of the function over all values of position should be finite.

$$\int_{-\infty}^{\infty} |f(x)|^2 d\tau < \infty \tag{9}$$

This is to ensure that:

- Infinity does not occur in $\partial_\tau^2 \Psi$
- Ψ can be normalized.
- Probability of finding the property of a particle is unambiguously defined, or not defined clearly, so that other quantities can be calculated from Ψ.

3 Postulate 2 - Extracting data

We can extract information from the wavefunction by applying an operator.
Consider the following:

$$\hat{Q}\phi_n = q_n\phi_n \tag{10}$$

Where $\hat{Q}$ is the operator, ϕ_n is the eigenfunction, and q is the eigenvalue of the corresponding eigenfunction being acted on the operator, which is the measurement result. $\hat{Q}$ should be **linear** and **Hermitian** to each observed quantity. Hermitian operators guarantee real eigenvalues, as the observables have to be real/physical. For an operator to be Hermitian, the following identity has to be satisfied:

$$\int f^* \hat{Q} g \, d\tau = \int g (\hat{Q} f)^* d\tau \tag{11}$$

when provided f and g are well-behaved functions, which vanish at infinity.

Exercise
Proof if some operators are Hermitian, as in notes.
For linearity, the following has to be satisfied:

$$\hat{Q}(c_1 f_1 + c_2 f_2) = c_1 \hat{Q}(f_1) + c_2 \hat{Q} f_2 \tag{12}$$

where $c_n \in C$.

The effect of measurement
Critically, after a measurement is made the wave function must be an eigenfunction of the system. The wavefunction Φ before the measurement may not be the same as the one after the measurement ϕ. The act of measurement changes the wavefunction, IF the system is not in some eigenstate. The same result can be measured if we immediately measure again the same quantity, as the system is now in an eigenstate of the operator.

4   Postulate 3 - Identifying the operator

This section tells us how to construct an operator. Main idea: from classical to quantum; from variables to operators. For the position operator in 3 dimensions:

$$\hat{\mathbf{R}} = \mathbf{r} \tag{13}$$

and for the momentum operator also in 3 dimensions:

$$\hat{\mathbf{P}} = i\hbar\nabla \tag{14}$$

The energy operator can be expressed as the Hamiltonian operator:

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}, t) \tag{15}$$

where the potential V depends on the problem we are looking at.

Exercise
Try to derive energy, momentum, and angular momentum operators, as per the notes.

5   Square well problems

Notes and Boundary Conditions

1. Know the range of integration

2. Know the potential of the regions

3. ψ at the "walls" of the box should be zero

4. ψ and its derivative ψ' should be continuous everywhere, more specifically, at the ends of the box.

5. In the case of a finite square well, ψ out of the well should be a decaying function, so it does not diverge at infinity(tunnelling).

6. Remember to find the normalization constants.

6   Plane waves and particle flux

6.1   Plane wave

The solution should be as follows:
$$\psi(x) = Ae^{ikx} \tag{16}$$

Note that plane wave solutions are not square integrable. For a function to be square integrable:

$$\int_{\infty}^{\infty} |\psi(x)|^2 = \text{finite} \tag{17}$$

where in the case of a plane wave, it is not square integrable, as we will be integrating the mod squared of the normalization constant A from minus to plus infinity, which leads us to the concept of particle flux.

6.2 Particle flux/Current density ($\Gamma(x)$)

Here, we are treating the plane wave not as just one particle, but a beam of particles, so we integrate the plane wave solution within an arbitrary length a to b, where ab is the average distance between the particles. The normalization constant A, will give the number of partcles per unit length. If we set this amplitude constant to 1, we will have one particle per unit length. Net flux passing through the region a to b can be given by flux entering - leaving:

$$\Gamma_{net} = \Gamma(a) - \Gamma(b) \tag{18}$$

From this we can derive an equation for particle flux (derive as exercise as per notes)

$$\Gamma(x) = \frac{i\hbar}{2m}(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi*}{\partial x}) \tag{19}$$

The particle flux of a plane wave of $\Psi(x,t) = Ae^{i(kx-\omega t)}$ is:

$$\Gamma(x) = \frac{\hbar k}{m}|A|^2 \tag{20}$$

where the $\frac{\hbar k}{m}$ term denotes the velocit of the particle, as in quantum mechanics, $p = \hbar k$.

Probabilities for reflection & transmittance
The probability for reflection R and transmission T is defined as follows:

$$R = |\frac{\Gamma_{reflected}}{\Gamma_{incident}}| \tag{21}$$

$$T = |\frac{\Gamma_{transmitted}}{\Gamma_{incident}}| \tag{22}$$

Note that $R + T = 1$ for checking.

7 Quantum tunnelling

Using what we know about flux and transmittance, consider a particle travelling from left to right across a potential V_0, with an energy E either greater or lower than V_0, but never zero. The results can be obtained by applying the boundary conditions imposed, thus finding the constants, similar to previous sections:

- Continuity of ψ and $\psi\prime$ at the edges of the potential well, x = 0 or x=a

- Square integrable wavefunctions, doesnt diverge to infinity

For $0 < E \leq V_0$:
$$T = \frac{16E(V_0 - E)}{V_0^2}e^{-2\kappa a} \tag{23}$$

and for E $\geq V_0$:
$$T = \frac{16k^2 k_{II}^2}{|(k + k_{II})^2 e^{-ik_{II}a} - (k - k_{II})^2 e^{-ik_{II}a}|^2} \tag{24}$$

Classically, we would expect the particle to have 100% transmittance T if E $\geq V_0$, and 0% T, if $0 < E \leq V_0$. However in QM, if you dont have enough energy to go over the barrier, you can still probably go over the barrier; if have enough energy to go over the barrier, you might not be able to go over the barrier.
See also the application of this, from the scanning tunnelling microscope.

8 1-D eignenvalue problems

Looking at problem with non-zero potential V.

8.1 Simple Harmonic Oscillator

In the example of the SHO, $V =]\frac{kx^2}{2}$, where k is the spring constant. Solving the TISE involves some change in variables, using the Frobenius Method from MMIII, and introducing the Hermite polynomials $H(y)$, also from MMIII, as we want the series solution to truncate/vanish at some term, so the wavefunction is finite and normalisable. The eigenfunction can be written as:

$$\phi_n(x) = A_n H_n(\sqrt{\frac{m\omega_0}{\hbar}}x)e^{\frac{-m\omega_0 x^2}{2\hbar}} \tag{25}$$

or with a slight change of variable, letting $y = \sqrt{\frac{m\omega_0}{\hbar}}x$

$$\phi_n(y) = H_n(y)e^{\frac{-y^2}{2}} \tag{26}$$

The energy eigenvalue is given as:

$$E_n = \hbar\omega_0(n + \frac{1}{2}) \tag{27}$$

See graphs from P.chem and QM notes, or the Atkins textbook.

9 Perturbation theory

To be specific: 1$^{\text{st}}$ order, time independent, non-degenerate
We can see perturbations as some adjustments made to our system. For example, for the particle in a box, we can see the perturbations as the lumps or corrections made to the box. We will we only interested in the first order of the system.
After some derivations, the First order correction using perturbation theory can be written as:

$$E_n^{(1)} = \int \phi_n^{(0)*} \hat{H}' \phi_n^{(0)} d\tau \tag{28}$$

10 Periodic potentials

10.1 Perioidic Infinite square well

Just think of this as an infinite square well, but have some perturbation caused by the Coulomb potentials. Using the following assumptions:

- Born Oppenheimer Approximation; consider the motion of the electrons of a fixed lattice

- Independent electrons, we do not consider electron-electron interaction.

- One dimensional

And we add one more condition, which is the periodic boundary condition: For a periodic potential,$V(x) = V(x+na)$, a particle moving to the right side of the N$^{\text{th}}$ state finds itself back to the 1$^{\text{th}}$ one:

$$\psi(x + Na) = \psi(x) \tag{29}$$

Subject to boundary conditions, the eigenfunction will be:

$$\psi(x + Na) = \psi(x)e^{ika} \tag{30}$$

with $k = \frac{2\pi a}{Na}$
Fermi energy refers to the unoccupied level just above the topmost filled level.

10.2 Bloch's Theorem

The eigenfunctions of the Schrödinger equation for a periodic potential are the product of a plane wave, e^{ika} times a function $u(x)$ with the periodicity of the lattice. i.e.:

$$\psi(x) = u(x)e^{ika} \tag{31}$$

where u(x) has the period of the lattice, i.e.:

$$u(x) = u(x + a) \tag{32}$$

The quantity k is known as the crystal wave number.
The corresponding quantity $\hbar k$ is known as the crystal momentum.
The alternative form of Bloch's Theorem after some change of variables can be given by equation 30.

10.3 The Kronig-Penny Model

With the periodic boundary conditions and Bloch waves concepts, this model investigates the dispersion relation for a periodic potential. By applying boundary conditions like those of the infinite square well, and solve the simultaneous equations using matricies, we get for the Kronig-Penny Model:

$$\frac{\beta^2 - \alpha^2}{2\alpha\beta} \sinh(\beta b) \sin(\alpha a) + \cosh(\beta b) \cos(\alpha a) = \cos(k(a+b)) \tag{33}$$

10.3.1 Replacing barriers using the Dirac Delta function

We want to replace the potential barriers of height h and width b to Dirac-Delta functions. With the strength $V_0 = \int_0^b h dx$. We are shrinking b $\to$ 0 and increasing h $\to \infty$. The dirac-delta potential can be given as:

$$\int_\infty^\infty V_0 \delta(x - x_0) = V_0 \tag{34}$$

and the periodic potential function becomes:

$$V(x) = V_0 \sum_n \delta(x - x_0) \tag{35}$$

These results for the dirac-delta function potentials can be subbed back in to the Kronig Penny model, resulting in:

$$\frac{mV_0}{\alpha\hbar^2} \sin \alpha a + \cos \alpha a = \cos ka \tag{36}$$

10.4 Implications of the Kronig Penny Model

Case 1: $V_0 \to 0$
Free particle dispersion with $E = \frac{\hbar^2 k^2}{2m}$

Case 2: $V_0 \to \infty$
Particle in an infinite square well with $E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$, with a as the width of the box.

Generally
$\alpha = \frac{\sqrt{2mE}}{\hbar^2}$, L.H.S of equation 36 oscillates, and only takes values between $\pm$ 1, hence called the allowed energy band. Values exceeding ± 1 are forbidden,hence called the forbidden energy gaps, or Band Gaps.

10.5 Band Gaps

Determining the full E(k) relationship, the below equation, as from equation 36 should be solved numerically and plotted parametrically:

$$\arccos\left(\frac{mV_0}{\sqrt{2mE}\hbar}\sin\left(\frac{\sqrt{2mEa}}{\hbar}\right) + \cos\left(\frac{\sqrt{2mEa}}{\hbar}\right)\right) = ka \tag{37}$$

Band gaps are developed at $ka = n\pi$, which define the zone edges, i.e. the region between $k = \frac{n\pi}{a}$. The first zone (n=1) is called the Brillouin zone.

Rules for the bands
These bands have dsicrete allowed values of k, and filling up with electrons according to the Pauli Exclusion Principle.

Metals
Band is partially filled, the Fermi Energy E_F, which is the energy of the highest allowed occupied energy level, is higher than the band gap. When energy is applied, electron is excited above E_F, therefore we have a free electron, and hence metals are conductors

Semi-Conductors
Electrons is just filled up to the bottom of the band gap, hence E_F is just at the bottom of the band gap. To have electrons, energy supplied has to be bigger than the band gap, or up to the conductor band, to conduct electricity

Insulators
Very large band gaps (>3eV)

10.5.1 Reduced zone schemes

Band structures are usually plotted in the "reduced" zone scheme, i.e., the centre, where the bands are folded back into the Brillouin Zone.

11 Postulate 4 - Linear Combinations and Probability

In summary: We can represent any general wave function for a given system as a linear combination of the eigenfunctions of the system:

$$\psi = \sum_n a_n \phi_n \tag{38}$$

The quantity, $|a_n|^2$ tells us the probability that a measurement of the wave function will yield the result q_n. Meaning, the probability that the wave function is in the state ϕ_n after the measurement.

11.1 Orthogonal Eigenfunctions

Defined as:

$$\int \phi_n^* \phi_m d\tau = 0 (n \neq m) \tag{39}$$

11.2 Orthonormal Eigenfunctions

If ϕ_i is normalised, orthonomal eigenfunctions are defined as:

$$\int \phi_m^* \phi_n d\tau = \delta_{n,m} \tag{40}$$

11.3 Complete Sets

Kind of like Fourier series in MMIII

Definition

- Eigenfunctions ϕ_n of a Hermitian Operator form a <u>complete set</u>.

- Any well behaved function can be expanded as a linear combination of the eigenfunction

$$\psi = \sum_n a_n \phi_n \tag{41}$$

- If we know ψ, ϕ_n of an orthonormal set, we can determine a_n, which we pick n=m:

$$a_m = a_n = \int \phi_n^* \psi d\tau \tag{42}$$

11.4 Basis and definition for Postulate 4

Basis
$|a_n|^2$ is the probability of finding the system in state ϕ_n.

Definition
When a measurement of a physical variable represented by a Hermitiam Operator $\hat{Q}$, is carried out on a system of which the wavefunction ϕ, the probability of the result being equal to a particular eigenvalue q_m is $|a_n|^2$.

11.5 Expectation values

The average value, when a set of repeated measurements is carried out on an identical system, is called the expectation value, with:

$$\left\langle \hat{Q} \right\rangle = \int \psi^* \hat{Q} \psi d\tau = \langle \psi | \hat{Q} | \psi \rangle = \sum_n |a|^2 q_n \tag{43}$$

11.6 Commutation Relations

This is just saying: can we switch the order of multiplication of the two operators. In general, they do not commute. Defining the commutation relationship:

$$\left[\hat{A}, \hat{B} \right] = \hat{A}\hat{B} - \hat{B}\hat{A} \tag{44}$$

If commute:

$$\left[\hat{A}, \hat{B} \right] = -\left[\hat{B}, \hat{A} \right] = 0 \tag{45}$$

If not, then $\neq 0$. Below is the commutation relationships of the position and momentum operator in 3D, with i,j = 1=x,2=y,3=z, :

$$\left[\hat{X}_i, \hat{X}_j \right] = 0 \tag{46}$$

$$\left[\hat{P}_i, \hat{P}_j \right] = 0 \tag{47}$$

$$\left[\hat{P}_i, \hat{X}_j \right] = -i\hbar\delta_{ij} \tag{48}$$

11.7   Compatible Operators of physical observables

Two physical observables are said to be compatible IF the operators representing them have a common set of eigenfunctions:

1. If one quantity is measured, the resulting wavefunction of the system will be in one of the common eigenfunctions

2. A subsequent measurement of the other quantity will have a completely predictable result.

Compatible operators commute, i.e. $\left[\hat{A}, \hat{B}\right] = 0$. Acting $\hat{A}$ on ψ gives eigenfunction ϕ, and acting $\hat{B}$ on ϕ gives eigenfunction ϕ as well, assuming non-degenerate eigenfunctions.

11.8   Degenerate eigenfunctions

Definition

If 2 or more eigenfunctions share the same eigenvalue, then they are degenerate. Any linear combination of them is also an egeinfunction with the same eigenvalue:

$$\hat{Q} \sum_n c_n \phi_n = q \sum_n c_n \phi_n \tag{49}$$

12   Postulate 5 - Time evolution of the wave function

In summary: The time evolution of the wave function when it remains undisturbed is governed by TDSE, as per equation 5. For systems where the potential is time independent ($V(\mathbf{r}, t) \equiv V(\mathbf{r})$). The general time dependent eigenfunctions are given as follows:

$$\Psi(\mathbf{r}, t) = \sum_n a_n \phi_n(x) e^{\frac{-i\hbar E_n}{\hbar}} \tag{50}$$

Note that E_i depends on ϕ_n when t=0, so that:

$$\Psi(x, 0) = \sum_n^\infty a_n \phi_n(x) \tag{51}$$

Given V(x) and $\Psi(x, 0)$:

1. Solve TISE and determine ϕ_n and E_n.

2. Determine coefficients a_n which determines equation 51.

3. Construct $\Psi(x, t)$, tack onto each term its characteristic time dependence.

If $|\Psi(x, t)|^2 \neq |\Psi(x, 0)|^2$, then it is not a stationary state. Wavefunctions are not stationary in general.

12.1   Rate of change of expectation value

$$\frac{d\left\langle \hat{Q} \right\rangle}{dt} = \left\langle \frac{\partial \hat{Q}}{\partial t} \right\rangle + \frac{1}{i\hbar} \left\langle \left[\hat{Q}, \hat{H}\right] \right\rangle \tag{52}$$

First term corresponds to the intrinsic time dependence of the operator. Second term corresponds to the time dependence from changing wavefunctions.

13   Angular Momentum

The operator for angular momentum $\hat{L}$ is:

$$\hat{\mathbf{L}} = -i\hbar \mathbf{r} \times \nabla \tag{53}$$

with the squared operator as the dot product of the two angular momenta vectors:

$$\hat{\mathbf{L}}^2 = \hat{L_x}^2 + \hat{L_y}^2 + \hat{L_z}^2 \tag{54}$$

For commutation relationships, we have cyclic permutations:

$$\left[\hat{L_x}, \hat{L_y} \right] = i\hbar \hat{L_z} \tag{55}$$

$$\left[\hat{L_y}, \hat{L_z} \right] = i\hbar \hat{L_x} \tag{56}$$

$$\left[\hat{L_z}, \hat{L_x} \right] = i\hbar \hat{L_y} \tag{57}$$

$$\left[\hat{L}^2, \hat{L_i} \right] = 0 \tag{58}$$

We can see that different components to not commute, therefore we can't find simultaneous eigenfunctions of all 3 components of angular momentum. That is saying, if a system is an eigenstate of one component, it cannot simultaneosly be in an eigenstate of either one of the other components.

Oppositley, we can find simultaneous eigenfunctions of the square magnitude as from commutation relationship 58. Hence, total angular momentum can be measured compatibly with any one component.

13.1   Operators for angular momenta using spherical coordinates

13.1.1   Angular momentum of the z-component

$$\hat{L_z} = -i\hbar \frac{\partial}{\partial \phi} \tag{59}$$

with eigenvalues:

$$\hat{L_z}\psi = m\hbar\psi \tag{60}$$

where m = -l,...,-1,0,1,...l

13.1.2   Squared Angular momentum

$$\hat{L}^2 = -\hbar \left(\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} (\sin\theta \frac{\partial}{\partial\theta}) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right) \tag{61}$$

with eigenvalues:

$$\hat{L}^2\psi = l(l+1)\hbar^2\psi \tag{62}$$

where l = 0,1,2,...

13.2   Derivations from MMIII

The derivation can be taken from the MMIII and QM notes. Basically, we start from using spherical polar coordinates for the laplacian, given by:

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \tag{63}$$

and the scalar quadruple product:

$$(A \times B) \cdot (C \times D) = (A \cdot C)(B \cdot D) - (A \cdot D)(B \cdot C) \tag{64}$$

and then the commutation relationship:

$$[r\partial_r, \partial_r r]f = 0 \tag{65}$$

to get that $\hat{L}^2$ is dependant only on the angular behaviour. Then we find the eigenvalue for $\hat{L}_z$, we apply the boundary condition that $\Phi(\phi + 2\pi) = \Phi(\phi)$, thus finding qunatum number m to be m = ±1,±2, ±3 and so on.

Then we get the eigenvalue and its equation for $\hat{L}^2$ using Legendre Polynomials, with the eigenvalue = $l(l+1)\hbar^2$, and common eigenfunction between the two operators being the spherical harmonic solutions:

$$Y_{lm}(\theta, \phi) = (-1)^m [\frac{(2l+1)}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}]^{\frac{1}{2}} P_l^m(\cos\theta)e^{im\phi} \tag{66}$$

with the associated Legendre functions being:

$$P_l^m(\mu) \equiv (1-\mu^2)^{\frac{|m|}{2}} (\frac{d}{d\mu})^{|m|} P_l(\mu) \tag{67}$$

and the associated Legendre polynomials:

$$P_l(\mu) \equiv \frac{1}{2^l l!} (\frac{d}{d\mu})^l (\mu^2 - 1)^l \tag{68}$$

14   3-D Potentials

14.1   3D particle in a box

using solutions for the 1D problem, we get for the energy:

$$E_n = \frac{\hbar^2 \pi^2}{8ma}(n_x^2 + n_y^2 + n_z^2) \tag{69}$$

with the eigenfunction

$$\phi_{n_x n_y n_z} = \sqrt{\frac{1}{a^3}} \begin{bmatrix} \sin \\ \cos \end{bmatrix} (\frac{n_x \pi x}{2a}) \begin{bmatrix} \sin \\ \cos \end{bmatrix} (\frac{n_y \pi y}{2a}) \begin{bmatrix} \sin \\ \cos \end{bmatrix} (\frac{n_z \pi z}{2a}) \tag{70}$$

The cos is used if n is odd, and sin is used if n is even.

Degeneracy
Energy can have the same value for 2 different sets of eigenvalues (e.g. $n_x = n_y = 1$, $n_z = 2$)

14.2   The hydrogenic atom

Using separation of variable, and in spherical coordinates. The hamiltonian can be given by:

$$\hat{H} = -\frac{\hbar^2}{2m_e} \frac{1}{r^2} \frac{\partial}{\partial r}(r^2 \frac{\partial}{\partial r}) + \frac{\hat{L}^2}{2m_e r^2} - \frac{Ze^2}{4\pi\epsilon_0 r} \tag{71}$$

Also note that:

$$\left[\hat{H}, \hat{L}^2\right] = 0 \tag{72}$$

$$\left[\hat{H}, \hat{L}_z\right] = 0 \tag{73}$$

$$\left[\hat{L}_z, \hat{L}^2\right] = 0 \tag{74}$$

Therefore the 3 are compatible operators, meaning we can find a common set of eigenfunctions, and we can measure the total L, L_z and energy compatibly.

With a change of variable: $R(r) = \chi(r)/r$, we get for the TISE:

$$\frac{-\hbar^2}{2m_e} \frac{d^2\chi}{dr^2} + (\frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} - \frac{Ze^2}{4\pi\epsilon_0 r})\chi = E\chi \tag{75}$$

with $V_{eff}(r) = \frac{l(l+1)}{r^2} - \frac{Ze^2}{4\pi\epsilon_0 r}$ being the effective potential.

14.2.1 Atomic units

$$\hbar = 1$$
$$m_e = 1$$
$$e = 1$$
$$\frac{1}{4\pi\epsilon_0} = 1$$
$$a_0 = 5.29 \times 10^{-11} \text{m}$$
$$E_H = 27.21 \ eV$$
$$V_{eff} = \frac{l(l+1)}{2r^2} - \frac{Z}{r}$$

We can also define energy levels as:

$$E_n = -\frac{Z^2}{2n^2} \tag{76}$$

Energy is specified by n only, therefore has a degeneracy:

$$2\sum_{l=0}^{n-1}(2l+1) = 2n^2 \tag{77}$$

Notice how to solve the radial equation from F to χ back to R, using Frobenius's method from MM3:

$$R(r) = \frac{\chi(r)}{r} = \frac{F(r)e^{-\kappa r}}{r} \tag{78}$$

$$F(r) = \sum_{p=0} c_p r^{p+l+1} \tag{79}$$

$$c_p = 2\frac{(\frac{Z}{n})(p+l) - Z}{(p+l+1)(p+l) - l(l+1)}c_{p-1} \tag{80}$$

Note also that the spherical harmonics are already normalized, so

$$\int_0^\infty |R_{nl}(r)|^2 r^2 dr = 1 \tag{81}$$

The r^2 part comes from the Jacobian determinant / from spherical polar coordinates.

15   Electron spin total angular momentum

15.1   A semiclassical approach

We will be using a semi-classical approach, borrowing the Bohr model. Imagine an electron orbiting the nucleus, and that orbit behaves like a current loop. From E&M, current loops give a magnetic moment μ. The classical magnetic moment is given by:

$$\boldsymbol{\mu} = -\frac{e\hbar}{2m_e\hbar} = -\frac{\mu_B}{\hbar}\mathbf{L} \tag{82}$$

Where μ_B is the Bohr magneton. Notice the sign, which says that the magnetic moment is opposite of the angular momentum. The magnetic potential energy can be given by:

$$V_{magnetic} = \frac{\mu_B}{\hbar}\mathbf{L} \cdot \mathbf{B} \tag{83}$$

Getting the magnetic moment operator:

$$\boldsymbol{\mu} = -\frac{\mu_B}{\hbar}\hat{\mathbf{L}} \tag{84}$$

and the magnetic potential operator:

$$\hat{H}_{magnetic} = \frac{\mu_B}{\hbar}\hat{\mathbf{L}} \cdot \mathbf{B} \tag{85}$$

15.2 Splitting energy levels, the Zeeman effect

Using 1th order, non-degenerate, perturbation, we get for the first order perturbed energy as:

$$E_n^{(1)} = m\mu_B B_z \tag{86}$$

where m is the magnetic angular momentum quantum number. We can see that for a Hydrogen having some quantum state defined by the quantum numbers, and having it be inside a uniform magnetic field in the z-direction, we will have a split of energy levels with $\delta E = m\mu_B B_z$, which is the Zeeman effect.

15.3 The Stern-Gerlach experiment

Shows us that the electron has an intrinsic angular momentum, aka spin.
We would expect odd number of beam deflections according to the allowed values of m, but instead, there are 2 groups of atoms deflected in opposite directions experimentally.

15.4 Intrinsic magnetic moment for electrons

Operator can be given by:

$$\hat{\boldsymbol{\mu}}_s = -g_s \frac{\mu_B}{\hbar} \hat{\boldsymbol{S}} \tag{87}$$

with $g_s = 2$, and $\hat{\mu_{sz}}$ having allowed values of $g_s\mu_B m_s$, m_s being the magnetic quantum number. Considering an atom in a B-filed, we must take into account spin and orbital momenta:

$$\hat{H} = \hat{H}^{(0)} + \frac{\mu_B}{\hbar} \mathbf{B} \cdot (\hat{\mathbf{L}} + 2\hat{\mathbf{S}}) \tag{88}$$

The eigenfcuntion for the spin momentum is $m_s\hbar$.
The total angular momentum J can be obtained by vector addition of orbital angular momentum (L) and intrinsic angular momentum(S).

15.5 Complete set of quantum numbers

Quantum Number	Name	Allowed Values
n	principle QN	n = 1,2,3...
l	orbital angular momentum QN	l = 0,1,2,...,n-1
m/m_l	magnetic QN	-l,...-1,0,1,...,+l
m_s	magnetic spin QN	$\pm\frac{1}{2}$
s	spin	$\frac{1}{2}$
j	total angular momentum	$\left\|l - \frac{1}{2}\right\|, l + \frac{1}{2}$
m_j	projection of j on the z-component	-j,...,+j

Table 1: Table of qunatum numbers

References

[1] Atkins, and De Paula. Atkins' Physical Chemistry / Peter Atkins, Julio De Paula. Tenth ed. 2014.