

# Perturbed oscillator strengths of one-electron system atoms

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## Abstract

—Oscillator strength (OS) and its perturbations in one electron system atoms are studied in this paper numerically by using the Numerov method.

OS is a measure of electron transition probability between the two transition energy levels in an atom. One electron system atoms, or in other words, Hydrogen like atoms, are the main subjects to be discussed and compared, on account of their simple structures which have a single electron in the outer shell.

Perturbation theory (PT) was used in this paper to study OS under perturbation of Zeeman Effect (ZE) which occurs when atoms are under the influence of magnetic fields. The three types of ZE that are perturbed separately are Normal Zeeman Effect (NZE), Internal Zeeman effect (IZE) and Anomalous Zeeman effect (AZE).

The results have shown the varied OS patterns under different perturbations while the magnetic field strength increases. Moreover, further corrections to the energy levels of hydrogen like atoms are required since Spin-orbit (SO) coupling was the only factor considered in this paper. For instance, Fine structure and hyper-fine structure will give better approximation of OS.

**Index Terms**— OS, PT, ZE, NZE, IZE, AZE, SO coupling

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## 1. Introduction

OS  $f_{ka}$  is a dimensionless quantity [1] representing the probability of an electron to be transited in an atom. When  $f_{ka} > 0$ , absorption occurs where the electron jumps to a higher energy level after absorbing a photon with a certain energy. Else ways, emission happens if  $f_{ka} < 0$ . Emission is a reversed process of absorption; it has one electron dropped to a lower shell by emitting a photon. OS is an important definition in quantum atomic model because it contributes in determining the half time of atoms and the broadness of the spectral lines.

This project focus on computing and investigating the allowed transitions within an atom. The allowed transitions can be understood as the ones that have high OS, whereas the forbidden transitions are unlikely to happen. For an allowed transition, the major component of  $f_{ka}$  is the transition moment integral (TMI)

$\int \psi_k^* \hat{r} \psi_a d\tau$  [2]. This integral comprises the product of the initial and final wave functions and a position vector.

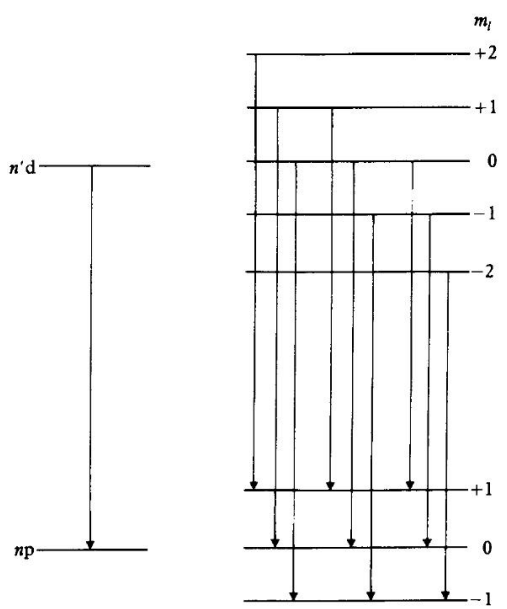
A wave function contains three parts of information about a particle, namely: radial part  $P_{nl}$ ; angular part  $Y_{lm_l}$ ; spin part  $\chi_{sm_s}$ . The radial wave function depends on  $n$  (principal quantum number) and  $l$  (orbital angular momentum quantum number). The angular part has dependency on both  $l$  and  $m_l$  (magnetic orbital angular momentum quantum number). Lastly, the spin of a particle is dependent on  $s$  (spin quantum number) and  $m_s$  (magnetic spin quantum number). Numerov method is a type of “step-by-step method” where it can find the third neighbouring point by knowing the first and the second point in the equation. This method was introduced to find the numerical solution of an electron wave function.

## PT

OS varies under different conditions which are brought by applying PT to the same atom. PT comprises mathematical methods that give an approximate solution to a problem. Another way to apprehend it is that PT deals with the changes induced in a system by a “small” disturbance [2].

The PT used in this paper is to study the effect on OS when magnetic field has taken into account. A well-known phenomenon in the influence of a magnetic field is the ZE. This effect describes the fact that multiple equally spaced splitting in spectral lines of a hydrogen atom once a uniform external magnetic field has penetrated. Three types of ZE were discussed as follows.

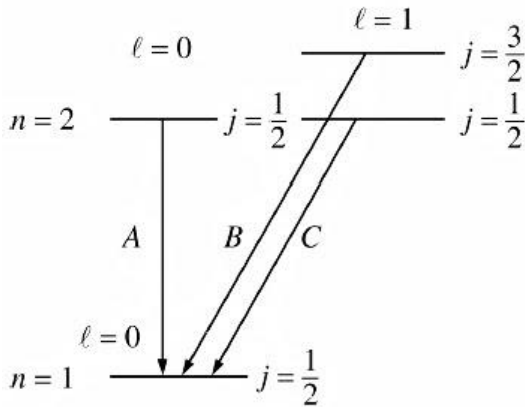
## NZE



**Fig.1** [2] Schematic of the energy levels and emissions of electrons from  $n'd$  to  $np$  where  $m_l$  can go down by one in each possible transition. When there is no magnetic field present, electron emission occurs when  $n'd$  to  $np$  and the energy is  $h\nu$ . Lines of  $m_l$  indicate splittings of the energy level with magnetic field present. For instance,  $n'd$  energy level splits into five where  $m_l = +2, +1, 0, -1, -2$ . In the same sense,  $np$  splits into three states, where  $m_l = +1, 0, -1$ .

NZE [5] is a phenomenon that has a single energy level splitting into several identically spaced new energy levels. NZE only occurs under the assumption that SO coupling is negligible in comparison to the external magnetic field. Therefore, the spin part of the wave function does not take into the calculation. The total angular momentum quantum number  $J$  is the sum of orbital angular momentum quantum number  $L$  and spin quantum number  $S$ . In this special case,  $J$  is equivalent to  $L$ .

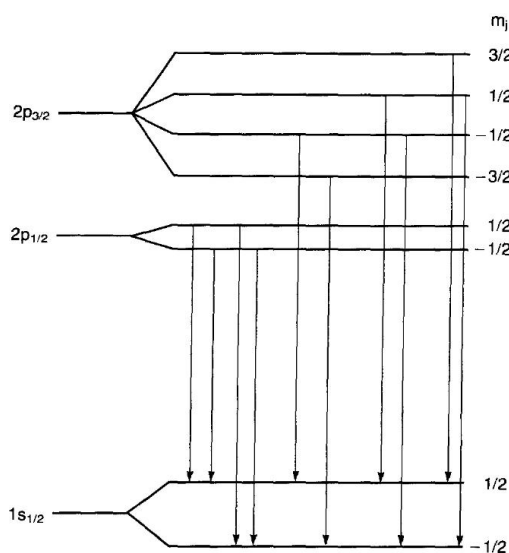
## IZE



**Fig.2** [3] Schematic of the energy levels and emissions of electrons when SO interaction causes IZE. From the graph, energy level  $2p_1$  splits into two lines where  $j = \frac{3}{2}, \frac{1}{2}$ .

SO coupling, a magnetic interaction between spin and orbital magnetic moments [4], causes IZE. These moments are arisen by the spin (S) and orbital (L) motion of an electron.

## AZE



**Fig.3** [2] Schematic of the energy levels and emissions of electrons when AZE occurs. The spectral lines can be splitted under the selection rules of  $J$  and  $m_j$ . ( $\Delta J = 0, \pm 1$ ,  $\Delta m_j = 0, \pm 1$ )

Polarisation of the emissions follow the same patterns as NZE. For instance,  $2p_{3/2}$  energy level splits in to four where  $m_j =$

$$\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}.$$

AZE [5] is most likely to be observed in a weak external magnetic field when the SO coupling is dominant. The spaces between each split spectral line are no longer equal, because the spacing is proportional to magnetic field strength. The orbital magnetic moment gives rise to an interaction with the magnetic field proportional to  $\vec{M} \times \vec{B}$ , where  $\vec{B}$  is the magnetic field vector.

## One electron system atom

A hydrogen-like atom or a one electron system atom is any atomic nucleus with one electron in the outer energy level and thus is isoelectronic with hydrogen [6]. For instance, the nuclei charge of a neutral sodium atom is +11 and it will have 11 electrons with -1 charge each. However, it can be treated as a one electron system owing to the only electron from the 3s orbital which is the outer shell. Ten inner electrons with a total charge -10 and the nuclei with charge +11 are treated as the centre of the atom. The charge of this new centre, "z" is +1. Sodium atoms will have one electron in the outer shell behave just like hydrogen atoms.

Coulomb–Buckingham (CB) potential [7], the general form of the potential model for different hydrogen like atoms, has three major parts. They are Born-Mayer (BM) potential [8], Coulomb potential (CP) and polarization. BM potential is the repulsion part of the CB potential. The origin of the repulsion is the interpenetration of the closed electron shells [9], because there are repulsion forces between electrons in particular when some part of the electron shells overlap. There is an exponential decay of repulsion when the distance between shells increases. CP of one electron system atoms matches with the formula of hydrogen atoms entirely, on account of the fact that the centre of the atom has overall charge +1 which is the same as the

core of a hydrogen atom. Polarization is not taken into account in hydrogen atoms, because the attraction between the only outer electron and the centre proton cannot change the shape of the core. However, the other hydrogen like atoms have the cores to be comprised of nuclei and electron shells, so that the attraction force is strong enough to change the shape of the electron clouds to have polarization energy. The Coulomb potential of a one electron system atom is exactly the same as the one in a hydrogen atom.

Another factor that is considered regarding other hydrogen like atoms is quantum defect. Quantum defect accounts for the difference between the energy of a weakly bound highly excited electron bound to a positive ion core in Rydberg atoms. Investigations in a general model for one electron system atoms are included in this paper, such as sodium atoms.

## 2. Method

### Unperturbed average OS (UAOS) for H atom

An effective one-electron system atom is comprised of an atomic core and one valence electron. In the case of hydrogen, this description is exact. Therefore, UAOS is developed upon the case for Hydrogen atom since there is no quantum defect need to be concerned.

The wave function that describes an electron can be written in terms of spherical polar coordinates  $(r, \theta, \phi)$  as  $\psi(r) = R(r)Y_{lm}(\theta, \phi)$  (1)

where we shall use the radial function,  $R(r)$ , in the form,

$$R(r) = \frac{1}{r} P_{nl}(r) \quad (2)$$

In a spherically symmetric potential the TISE [5] is

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V(r) \right] \psi(r, \theta, \phi) = E \psi(r, \theta, \phi) \quad (3)$$

where the del squared operator in spherical coordinates is  $\nabla^2 = \frac{1}{r^2} \left[ \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) - \frac{L^2}{\hbar^2} \right]$  and the solution of the wave function is constructed of two parts: angular and radial part.

Since the electron is in bound state, TISE is reduced to a second order differential equation in atomic units

$$\left[ \frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - 2V(r) - \frac{1}{n^{*2}} \right] P_{nl}(r) = 0, \quad (4)$$

where  $V(r)$  is the potential that describes the interaction between  $A^+$  and  $e^-$ . In the case of hydrogen,  $V(r) = -\frac{1}{r}$  and  $n^* = n$ . In the general case  $V(r)$  is a modified Coulomb potential and

$$n^* = n - \mu_{nl}, \quad (5)$$

where  $\mu$  is called the quantum defect. For a given value of  $l$ ,  $\mu_{nl}$  varies slowly with  $n$ .

The differential equation in (4) is of the form

$$\frac{d^2 y}{dx^2} + f(x)y = 0 \quad (6)$$

A suitable mathematical approximation method called the Numerov method applies to second-order differential equations without the first-order derivatives. This method was introduced to find the numerical solution of  $P_{nl}$ . In equation (7) below, where  $f$  refers to  $f(x)$  in equation (6) and  $y$  represents  $P_{nl}$ ,

$$\left(1 + \frac{h^2 f_{n+1}}{12}\right) y_{n+1} - \left(2 - \frac{10h^2 f_n}{12}\right) y_n + \left(1 + \frac{h^2 f_{n-1}}{12}\right) y_{n-1} = 0 \quad (7)$$

where  $n = 1, 2, \dots$ . [10]

This is a step-by-step method; we start out at small  $x$  with two values of  $y(x)$ ,  $y_0$  and  $y_1$  say, and then (7) gives  $y_2$  and hence  $y_1$  and  $y_2$  gives  $y_3$  etc.

In this case, bound state wave functions satisfy the boundary conditions

$$P_{nl}(r) \propto r^{l+1} \text{ as } r \rightarrow 0; P_{nl}(r) \propto r^{n^*} \exp\left(\frac{-r}{n^*}\right) \text{ as } r \rightarrow \infty. \quad (8)$$

At the centre of the atom, the wave function is zero owing to the fact that no electron can be at the centre of the nuclei. Therefore, the first value of  $y$  was set to be 0, the second value was a small value (0.1) to start over the step-by-step method. Since the second value is only an approximation, it is verified until it matches with the experimental result. Hydrogen's wave function should decrease to 0 while the radius increases, since the  $e^{-x}$  term indicates an exponential decay. A defect remained unsolved with this method is the assumption that no electron wave function exist further than a chosen large distance.

In practice, integrating outwards from the origin for  $P_{nl}(r)$  breaks down when  $P_{nl}(r)$  begins to decrease exponentially. To avoid this difficulty, we can also start out at large values and use the step-by-step method in the inward direction. The two solutions can then be matched at an intermediate point using

$$\frac{1}{P_{nl}} \frac{dP_{nl}}{dr} \Big|_{r=r_0}, \quad (9)$$

where  $\frac{dP_{nl}}{dr} \Big|_{r=r_0}$  is the first order derivative of the radial wave function at a certain radius  $r_0$ .  $\frac{1}{P_{nl}}$  is multiplied to normalise the first derivative so that the value of the first derivative is independent of any scaling factors.

The merging of two wave functions into one continuous curve was achieved by obtaining the intermediate point. This point was found when two curves have the same shape and no difference in magnitude at a certain radius. Since the first derivative of a figure determines its shape, the continuity of the shape of two graphs can therefore being found by the first order derivative calculation as follows:

$$\frac{1}{P_{nl1}} \frac{dP_{nl1}}{dr} \Big|_{r=r_0} - \frac{1}{P_{nl2}} \frac{dP_{nl2}}{dr} \Big|_{r=r_0} = 0 \quad (10)$$

where  $P_{nl1}$  is the wave function with correct initial value, whereas,  $P_{nl2}$  is the one with boundary condition applied at large radius. Their subtraction of the normalised first order derivatives at the same point should be 0 when their shapes are identical.

The final step was to normalise the radial wave function, the absolute values of  $P_{nl}(r)$  are fixed by using the normalization condition

$$\int_0^\infty P_{nl}(r)^2 dr = 1. \quad (11)$$

Since the numerical solution of the radial wave function of hydrogen atoms was found, studying OS became feasible. The following equation defines the UAOS:

$$f(nl \rightarrow n'l') = \frac{2}{3} (E_{n'l'} - E_{nl}) C_{l'} \left| \int_0^\infty P_{nl}(r) r P_{n'l'}(r) dr \right|^2 \quad (12)$$

where  $C_{l'} = \frac{\max(l, l')}{2l+1}$ ,  $E_{n'l'} > E_{nl}$ ,  $l' = l+1$ , both  $E_{n'l'}$  and  $E_{nl}$  are in atomic units,  $E_{n'l'} = \frac{-1}{2n'^2}$  (energy of the electron after transition),  $E_{nl} = \frac{-1}{2n^2}$  (energy of the electron before transition).

Considering the only numerical component in (6) is the TMI  $\int_0^\infty P_{nl}(r) r P_{n'l'}(r) dr$ , thus, comparing both numerical and analytical solutions of TMI examines the validity of unperturbed OS. Obtaining the analytical solution of TMI requires to know the analytical form of radial wave functions  $P_{nl}(r)P_{n'l'}(r)$ . For simplicity, only the transition of an electron from 1s to 2p orbital was studied and their analytical solutions were found as [2]:

$$P_{1s}(r) = -2re^{-r} \quad (13)$$

$$P_{2p}(r) = -\frac{1}{2\sqrt{6}}r^2e^{-\frac{r}{2}} \quad (14)$$

### Einstein A coefficient

When there is no electromagnetic field to stimulate the emission of electron in the atom, the excited level in the atom will decay spontaneously. The rate of this spontaneous decay,  $\Gamma_{spon}$ , is the same as Einstein A coefficient where electron transition occurs from excited state to ground state. In mathematical interpretation, the above relationship can be written as:

$$\Gamma_{spon} = A_{ka}, \quad (15)$$

Where  $A_{ka}$  indicates the Einstein A coefficient used is for transition from excited state (level a) to ground state (level k).

Besides, Einstein A coefficient is mathematically defined in terms of OS as follows:

$$A_{ka} = \frac{2\hbar\alpha(\omega_{ka})^2}{mc^2} |f_{ka}| \quad (16)[11]$$

Where  $\omega_{ka}$  is the angular frequency,  $\omega_{ka} = \frac{(E_k - E_a)}{\hbar}$  [2];  $\alpha$  is the fine structure constant,  $\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c}$  [2];  $\epsilon_0$  is the permittivity of the vacuum.

From the rate of decay, the lifetime of the excited state  $\tau_{spon}$  is deduced.  $\tau_{spon}$  is the inverse of this decay rate. The equation for calculating lifetime is as follows:

$$\tau_{spon} = \frac{1}{\Gamma_{spon}}. \quad (17)$$

Therefore, in a multi-level system, the rate of spontaneous decay  $\Gamma_i$  is the sum of Einstein A coefficients in all possible decays to all allowed final states. The equation is written as:

$$\Gamma_i = \sum_f A_{if}. \quad (18)$$

As a result, the total lifetime of an excited state in a multi-level system is

$$\tau_i = \frac{1}{\Gamma_i} = [\sum_f A_{if}]^{-1} \quad (19)$$

Where  $A_{if}$  means the electron transition is from an initial state to a final state.

## OS with NZE

We now need to consider explicitly the separate  $nlm$  states. Then equation (11) is replaced by

$$f(nlm \rightarrow n'l'm')$$

$$= \frac{2}{3} (E_{n'l'm'} - E_{nlm}) \left| \int_0^\infty P_{nl}(r) Y_{lm}^*(\theta, \phi) \left(\frac{4\pi}{3}\right)^{\frac{1}{2}} r Y_{1\mu}(\theta, \phi) P_{n'l'}(r) Y_{l'm'}(\theta, \phi) r \sin(\theta) dr d\theta d\phi \right|^2 \quad (20)$$

The integral over the angular variables can be done analytically. The explicit expressions required are given below.

$$\begin{aligned} I &= \int_0^\infty Y_{lm}^*(\theta, \phi) \left(\frac{4\pi}{3}\right)^{\frac{1}{2}} (\theta, \phi) Y_{1\mu}(\theta, \phi) Y_{l'm'}(\theta, \phi) \sin(\theta) d\theta d\phi \\ &= [(2l+1)(2l'+1)]^{\frac{1}{2}} (-1)^m \begin{pmatrix} l & 1 & l' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & 1 & l' \\ -m & \mu & m' \end{pmatrix}, \end{aligned} \quad [12](21)$$

For the case of zero external magnetic field, it is

$$f(nl \rightarrow n'l') = \frac{1}{(2l+1)} \sum_{mm'\mu} f(nlm \rightarrow n'l'm') \quad [2](22)$$

Where we have summed over final states  $m'$  and averaged over initial states  $m$  (there are  $(2l+1)$  degenerate  $m$  states). We have also summed over the different components of the vector  $r$ . In what follows, I give the general analysis but you don't need to bother with the details. We need the quantity

$$\frac{1}{(2l+1)} \sum_{mm'\mu} I^2 = (2l'+1) \begin{pmatrix} l & 1 & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \sum_{mm'\mu} \begin{pmatrix} l & 1 & l' \\ -m & \mu & m' \end{pmatrix}^2 = (2l'+1) \begin{pmatrix} l & 1 & l' \\ 0 & 0 & 0 \end{pmatrix}^2 = C_l, l' = l \pm 1 \quad (23)$$

See equation (12). Then from (22) and (23) we recover the result (12).

Now if a magnetic field is applied the energies of the perturbed states given by

$$E_{nlm} = E_{nl} + \mu_e B_m, \quad (24)$$

Where  $\mu_e$  is the Bohr magneton, it is defined as follows:

$$\mu_e = \frac{e\hbar}{2m_e} = 9.27400949 \times 10^{-24} J T^{-1} = 2.127 \times 10^{-6} E_H T^{-1} \quad (25)$$

Where  $E_H$  is the energy in atomic units since  $E_H = 4.35974417 \times 10^{-18} J$ .  $B$  is the field in units of  $T$  (Tesla) and so from (24) and (25),  $\mu_e B_m$  can be expressed in atomic units of energy.

We can now rewrite (20) using (21) and (24) in the form

$$\begin{aligned} &f(nlm \rightarrow n'l'm') \\ &= \frac{2}{3} [E_{n'l'} - E_{nl} + \mu_e B(m' - m)] \left| \int_0^\infty P_{nl}(r) P_{n'l'}(r) dr \right|^2 \\ &\times (2l+1)(2l'+1) \left[ \begin{pmatrix} l & 1 & l' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & 1 & l' \\ -m & \mu & m' \end{pmatrix} \right]^2, \end{aligned} \quad (26)$$

And the algebraic coefficients can be evaluated using the following relations

$$\begin{pmatrix} J+1 & J & 1 \\ M & -M-1 & 1 \end{pmatrix} = (-1)^{J-M-1} \left[ \frac{(J-M)(J-M+1)}{(2J+3)(2J+2)(2J+1)} \right]^{\frac{1}{2}}, \quad [12](27)$$

$$\begin{pmatrix} J+1 & J & 1 \\ M & -M & 0 \end{pmatrix} = (-1)^{J-M-1} \left[ \frac{(J+M+1)(J-M+1)2}{(2J+3)(2J+2)(2J+1)} \right]^{\frac{1}{2}}, \quad [12](28)$$

Together with the general relations ( $|m_j| \leq j; i = 1, 2, 3$ )

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \begin{pmatrix} j_1 & j_2 & j_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix} (-1)^{j_1+j_2+j_3}; \quad [12](29)$$

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = 0 \text{ unless } m_1 + m_2 + m_3 = 0 \quad [12](30)$$

Finally, on using (12)

$$f(nlm \rightarrow n'l'm') = \left[ 1 + \frac{\mu_e B(m'-m)}{E_{n'l'} - E_{nl}} \right] \begin{pmatrix} l & 1 & l' \\ -m & \mu & m' \end{pmatrix}^2 (2l+1) f(nl \rightarrow n'l'). \quad (31)$$

Therefore, the perturbed oscillator strengths are related to the field-free ones simply through algebraic coefficients and field  $B$ .

### OS with INZ

$$\Delta E = \frac{1}{2} \hbar^2 < \xi(r) > [j(j+1) - l(l+1) - s(s+1)], \quad \xi(r) = \frac{1}{2m^2 c^2} \frac{1}{r} \frac{dV}{dr}. \quad [2](32)$$

If  $V(r)$  is in atomic units of energy (a.u.) and  $r$  is in units of  $a_0$

$$\Delta E(a, u) = \frac{1}{4} \alpha^2 [j(j+1) - l(l+1) - s(s+1)] < \frac{1}{r} \frac{dV}{dr} >, \quad (33)$$

Where  $\alpha$  is the fine structure constant.

The integral for the dipole moment in equation (20) can be re-expressed in terms of the total angular momentum  $J = L + S$ . We introduce the bra and ket notation,  $< \dots |$  and  $|\dots >$ , to label the atomic states so that for example  $|nlm >$  corresponds to the wave function  $\frac{1}{r} P_{nl}(r) Y_{lm}(\theta, \phi)$  and

$$< nlm | n'l'm' > = \int_0^\infty P_{nl}(r) r P_{n'l'}(r) dr \int Y_{lm}^*(\theta, \phi) Y_{l'm'}(\theta, \phi) \sin(\theta) d\theta d\phi. \quad (34)$$

In order to obtain wave function with total angular momentum quantum number  $j$  we couple states  $|nlm >$  and  $|sm_s >$  together so that

$$|nl_j m_j > = \sum_{mm_s} C_m^l \quad C_{m_s}^s \quad C_{m_j}^j |nlm > |sm_s >, \quad (35)$$

Where

$$C_m^l \quad C_{m_s}^s \quad C_{m_j}^j = (-1)^{l-s-m_j} (2j+1)^{\frac{1}{2}} \begin{pmatrix} l & s & j \\ m & m_s & m_j \end{pmatrix} \quad [13](36)$$

The dipole moment does not depend on spin, and so it is

$$\begin{aligned} D &\equiv < nl_j m_j | \left( \frac{4\pi}{3} \right)^{\frac{1}{2}} r Y_{1\mu}(\theta, \phi) | n'l'j'm_j' > \\ &= \sum_{mm_s} C_m^l \quad C_{m_s}^s \quad C_{m_j}^j \quad C_{m'}^{l'} \quad C_{m_s'}^{s'} \quad C_{m_j'}^{j'} < nlm | \left( \frac{4\pi}{3} \right)^{\frac{1}{2}} r Y_{1\mu}(\theta, \phi) | n'l'm' > \end{aligned} \quad (37)$$



on using equation (21). By examining the sum over  $mm'm_s$ , it is shown as

$$\begin{aligned}
S &= \sum_{mm'm_s} (-1)^{l-s+m_j} (-1)^{l'-s+m'_j} \begin{pmatrix} l & s & j \\ m & m_s & -m_j \end{pmatrix} \begin{pmatrix} l' & s & j' \\ m' & m_s & -m'_j \end{pmatrix} \begin{pmatrix} l & 1 & l' \\ -m & \mu & m' \end{pmatrix} (-1)^m \\
&= \sum_{mm'm_s} (-1)^{l-s+m_j+l'-s+m'_j+m} \begin{pmatrix} l & s & j \\ m & m_s & -m_j \end{pmatrix} \begin{pmatrix} l' & s & j' \\ m' & m_s & -m'_j \end{pmatrix} \begin{pmatrix} l & 1 & l' \\ -m & \mu & m' \end{pmatrix} \\
&= \sum_{mm'm_s} (-1)^n \begin{pmatrix} j' & s & l' \\ -m'_j & -m_s & -m' \end{pmatrix} (-1)^{j'+s+l'} \begin{pmatrix} l & 1 & l' \\ -m & \mu & m' \end{pmatrix} \begin{pmatrix} l & s & j \\ m & m_s & -m_j \end{pmatrix}
\end{aligned} \tag{38}$$

Where  $n = l - s + m_j + l' - s + m'_j + m$

Now from Edmonds p.95 equation (6.2.8)

$$\begin{aligned}
&\sum_{\mu_1 \mu_2 \mu_3} (-1)^{l_1+l_2+l_3+\mu_1+\mu_2+\mu_3} \begin{pmatrix} j_1 & l_2 & l_3 \\ m_1 & \mu_2 & -\mu_3 \end{pmatrix} \begin{pmatrix} l_1 & j_2 & l_3 \\ -\mu_1 & m_2 & \mu_3 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & j_3 \\ \mu_1 & -\mu_2 & m_3 \end{pmatrix} \\
&= \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3 \\ l_1 & l_2 & l_3 \end{pmatrix}
\end{aligned} \tag{39}$$

and so on using (38) and (39)

$$S = (-1)^{m_j+j'+l'} \begin{pmatrix} j' & 1 & j \\ m'_j & \mu & -m_j \end{pmatrix} \begin{pmatrix} j' & 1 & j \\ l & s & l' \end{pmatrix} \tag{40}$$

Finally, from (37) and (40)

$$D = S[(2l+1)(2l'+1)(2j+1)(2j'+1)]^{\frac{1}{2}} \begin{pmatrix} l & 1 & l' \\ 0 & 0 & 0 \end{pmatrix} \int_0^\infty P_{nl}(r) r P_{n'l'}(r) dr \tag{41}$$

The V-C coefficient in (40) has  $m_j$  dependence, so that there are  $(2j+1)$  degenerate  $m_j$  states.

$$f(nlj \rightarrow n'l'j') = \frac{1}{2j+1} \sum_{m_j m'_j \mu} f(nlj m_j \rightarrow n'l'j' m'_j) \tag{42}$$

OS with SO coupling or IZE:

$$\begin{aligned}
&f(nlj \rightarrow n'l'j') \\
&= \frac{2}{3} [(E_{n'l'} - E_{nl}) - (\Delta E'_{so} - \Delta E_{so})] \left| \int_0^\infty P_{nl}(r) r P_{n'l'}(r) dr \right|^2 (2j'+1)(2l'+1) \begin{pmatrix} l & 1 & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} j' & 1 & j \\ l & s & l' \end{pmatrix}^2 \\
&= \frac{2}{3} [(E_{n'l'} - E_{nl}) - (\Delta E'_{so} - \Delta E_{so})] \left| \int_0^\infty P_{nl}(r) r P_{n'l'}(r) dr \right|^2 C'_l (2j'+1) \begin{pmatrix} j' & 1 & j \\ l & s & l' \end{pmatrix}^2
\end{aligned} \tag{43}$$

### OS with AZE

The formula below shows how to calculate OS with AZE, which is related to  $g(j)$ .

$$\begin{aligned}
&f(nlj m_j \rightarrow n'l'j' m'_j) \\
&= \frac{2}{3} [(E_{n'l'} - E_{nl}) + (\Delta E'_{so} - \Delta E_{so}) + \mu B(g(j')m'_j - g(j)m_j)] D^2
\end{aligned} \tag{44}$$

$$g(j) = 1 + \frac{j(j+1)+s(s+1)-l(l+1)}{2j(j+1)}$$

### OS in effective one-electron atoms

Effective one-electron atoms model is particularly applicable when  $A^+$  is a closed shell system, e.g.  $A \equiv Li, Na, K, \dots$ , the alkalis. In this part, a model potential for effective one-electron atomic systems was built and  $Na$  was studied as an example.

The formula used to calculate potential is given as,

$$V_{a,b}(r) = -Z \left( \frac{1}{r} + \delta_0 + \delta_1 r + \delta_2 r^2 + \delta_3 r^3 \right) \exp(-\gamma r) - \frac{\alpha}{2r^4} [\chi_2(\beta r)]^2 - \frac{z}{r}, \quad (45)$$

Where

$$\chi_2(x) \equiv 1 - (1 + x + \frac{x^2}{2}) \exp(-x). \quad (46) [14]$$

As seen from equation (41), the potential depends on  $r$  which is the distance between the electron and the central atom. The potential experiences an exponential decay due to the term  $\exp(-\gamma r)$ . One variable  $\chi_2$  has  $x$  dependence which also exhibits exponential decay when  $x$  increases because of  $\exp(-x)$ .

The parameters used in this paper to calculate the potential of Sodium atoms are given below: [14]

$$Z = 10$$

$$z = 1$$

$$\gamma = 3.032459521675$$

$$\delta_0 = -0.1648757105954$$

$$\delta_1 = 0.5254039623026$$

$$\delta_2 = 0.03225926765253$$

$$\delta_3 = 0.05746004991888$$

$$\beta = 4.790960043258$$

$$\alpha = 0.9448$$

### 3. Results

#### UAOS of hydrogen like atoms

Results of average OS without any perturbation in one electron system atom are given in the table below. The model was set up to calculate oscillator strength of electron transition from  $np$  to  $n's$ .

	1s	2s	3s	4s
2p	-0.13904146	0	+0.01219668	+0.03620382
3p	-0.02642399	-0.1458527	0	+0.61689115
4p	-0.00968431	-0.03450623	-0.16302348	0
5p	-0.00465598	-0.01408716	-0.04083802	-0.18352021
6p	-0.00260534	-0.00726896	-0.01737421	-0.04685877
7p	-0.00160804	-0.00428243	-0.00926204	-0.02030567
8p	-0.00106338	-0.00275006	-0.00560435	-0.01100725

**Table 1.** A table shows the oscillator strength in unperturbed hydrogen system when  $np$  goes to  $n's$ .

There is no probability for electron transition to occur when  $n = n'$  so OS is zero at the same energy level. OS has negative sign when  $n > n'$ , indicating emission of the electron in bound state. On the other hand, absorption process takes place when  $n < n'$ . For emission processes, when the difference between the initial and final  $n$  values increase, negative OS increases exponentially to reach 0.

	3s	4s	5s	6s
3p	-0.32235007	+0.17318412	+0.01346186	+0.00421422
4p	-0.00448902	-0.48277469	+0.31934188	+0.02183381

<b>5p</b>	-0.00066774	-0.01475262	-0.62659584	+0.46152335
<b>6p</b>	-0.00020851	-0.00317524	-0.02436396	-0.76611602
<b>7p</b>	-0.00008435	-0.00116373	-0.0056581	-0.03291388
<b>8p</b>	-0.00004206	-0.00056004	-0.00221527	-0.00805830

**Table 2.** This table contains the values of unperturbed oscillator strength in a sodium atom. The electron transition is from np to n's. The quantum defect values of sodium atoms used in this calculation can be found in appendix A.

Unlike hydrogen atoms, the outer single electron in a sodium atom can only go through emission process at the third energy level or the level above it. This is because the first and the second shells are fully occupied with electrons. Another result that sodium atoms differ from hydrogen atoms is the fact that emission transitions can even take place at the same energy level in sodium atoms, such as electron transferring from 3p to 3s. Moreover, the transition probability reach the maximum value when n remains the same during emission process.

Except the transition between the same energy level, the emission processes in a hydrogen atom is 10-100 times stronger than the same transitions in a sodium atom. This is owing to the fact that the outer electron in the sodium atom is more tightly bounded to the centre of the atom which is a combination of electrons and a +11 charged nuclei. Therefore, the outer electron in sodium is harder to be emitted.

Despite having the same z value for both sodium and hydrogen atoms, the charge of a sodium nuclei is 11 times larger than hydrogen's. This big nuclei charge provides a huge attraction towards the electron nearby and causes the results that are in table 2. If the outer electron is further away from the centre of the sodium atom, the whole atom could be treated as a hydrogen atom. In this scenario, OS values for the same transition in both sodium and hydrogen atoms would be similar.

### Einstein A coefficient

The lifetime of each excited states in a neutral hydrogen atom differs. Einstein A coefficients are required to measure the lifetimes using the equation (46). Results are shown below in table 3 and 4.

State		$A_{if} \text{ } 10^8 \text{s}^{-1}$			Sum of $A_{if} \text{ } 10^8 \text{s}^{-1}$	Lifetime $10^{-8} \text{s}$
Initial	final	n=1	n=2	n=3		
2s	np	-	-	-	-	$\infty$
2p	ns	6.282	-	-	6.282	0.159
3s	np	-	0.061	-	0.061	16.393
3p	ns	1.677	0.226	-	1.903	0.525

3d	np	-	0.647	-	0.647	1.546
4s	np	-	0.025	0.018	0.043	23.256
4p	ns	0.684	0.097	0.031	0.815	1.227
	nd	-	-	0.003		
4d	np	-	0.206	0.070	0.276	3.623
4f	nd	-	-	0.138	0.138	7.246

**Table 3.** Lifetimes of excited states in hydrogen. The first two columns shows the initial and final sub-shells that at spontaneous emission processes take place. The following 3<sup>rd</sup>, 4<sup>th</sup> and 5<sup>th</sup> columns give the values of Einstein A coefficient in unit of  $10^8 \text{s}^{-1}$  when  $n=1, 2, 3$  respectively. Knowing the total amount of Einstein A coefficient for each sub-shell in the 6<sup>th</sup> column, gives the lifetime information of corresponding sub-shells (see the last column).

Level	2s	2p	3s	3p	3d	4s	4p	4d	4f
Lifetime $10^{-8} \text{s}$	$\infty$	0.159	16.393	0.525	1.546	23.256	1.227	3.623	7.246

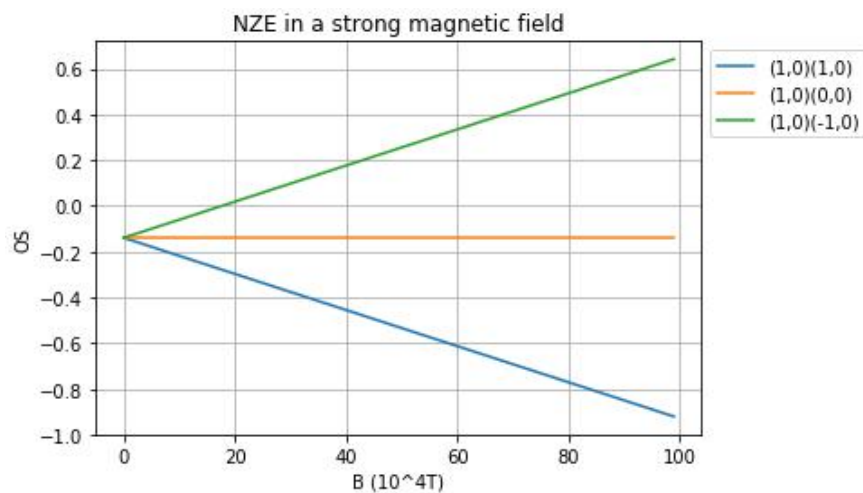
**Table 4.** Lifetimes of the sub shells of a hydrogen atom.

Ignoring 2s orbital, the lifetimes of the energy state becomes longer when  $n$  gets higher. For instance, the lifetime of the 3s orbital,  $16.393 \times 10^{-8} \text{s}$ , is less than the lifetime of 4s orbital which is  $23.256 \times 10^{-8} \text{s}$ . However, the lifetime of the 2s orbital in hydrogen atoms is infinite. According to the experimental data, the real lifetime of 2s is  $1/7 \text{s}$  [1] which is a very long time in comparison with the lifetimes in unit of  $10^{-8} \text{s}$ .

When  $n$  remains the same, the order of the orbital lifetimes from the longest to the shortest is ns, nf, nd, np. This pattern suggests that s orbital is the most stable one, whereas, p orbital is the least.

## NZE

NZE occurs in a strong magnetic field, because SO coupling becomes negligible in comparison to the external strong B field. The graph below shows NZE of a hydrogen atom without SO coupling in a strong magnetic field.



**Fig.4** A figure showing the behaviour of OS under NZE in a strong magnetic field. OS calculated is going under emission process from  $n=2$  to  $n=1$  with  $ml$  values equals to -1, 0, 1 respectively. Also, SO coupling has not taken into account in this case. The strength of the magnetic field has unit  $10^4$  T. The label of each line has two brackets which contains the electron emission information of  $l$  and  $ml$  respectively, for example, Label “(1,0)(1,0)” stands for the transition between P with  $ml=1$  to S with  $ml=0$ .

The 2P orbital in a hydrogen atom splits into three equally spaced new energy levels under NZE. They are  $ml=1, 0, -1$ . Electrons in these three new sub-shells have different chances going through emission processes to arrive at the ground level. Fig. 4 shows the OS from these three 2P sub-shells to 1S.

When the strength of the magnetic field equals to 0 T, the three OS values  $ml=1, 0, -1$  are all equal to -0.13904146. The line “(1,0)(0,0)” is independent on the variation of magnetic field strength, because  $ml$  has no change in the emission process. The other two lines “(1,0)(1,0)” and “(1,0)(-1,0)” vary linearly with the magnetic field. The pattern shows that OS increases linearly if the  $ml$  value increase by 1.

## IZE

OS is corrected with SO coupling in this section. Due to the correction, one p orbit in a neutral hydrogen atom splits into two orbitals which are off by a small amount of energy. They are  $p_{1/2}$  and  $p_{3/2}$  orbitals. The subscript represents the value of total angular momentum quantum number  $j$  which has the relation  $j=|l+s| \dots |l-s|$ . In this case, the only electron in the hydrogen atom has a half spin number, so that it gives the two values of  $j$  that are  $3/2$  and  $1/2$ .

The table below gives the perturbed OS in each sub shells.

	SO	Perturbed OS	Perturbed AOS	UAOS
1s-2p	$1s_{1/2}-2p_{3/2}$	0.2780825	0.41712437	0.41712437
	$1s_{1/2}-2p_{1/2}$	0.13904187		
1s-3p	$1s_{1/2}-3p_{3/2}$	0.05284795	0.07927196	0.07927196
	$1s_{1/2}-3p_{1/2}$	0.02642401		
1s-4p	$1s_{1/2}-4p_{3/2}$	0.01936861	0.02905292	0.02905292
	$1s_{1/2}-4p_{1/2}$	0.00968431		
1s-5p	$1s_{1/2}-5p_{3/2}$	0.00931197	0.01396795	0.01396795
	$1s_{1/2}-5p_{1/2}$	0.00465598		
1s-6p	$1s_{1/2}-6p_{3/2}$	0.00521068	0.00781601	0.00781601
	$1s_{1/2}-6p_{1/2}$	0.00260534		
1s-7p	$1s_{1/2}-7p_{3/2}$	0.00321609	0.00482413	0.00482413
	$1s_{1/2}-7p_{1/2}$	0.00160804		
1s-8p	$1s_{1/2}-8p_{3/2}$	0.00212748	0.00319122	0.00319015
	$1s_{1/2}-8p_{1/2}$	0.00106374		
1s-9p	$1s_{1/2}-9p_{3/2}$	0.00153922	0.00230883	0.00222078

	$1s_{1/2}-9p_{1/2}$	0.00076961		
1s-10p	$1s_{1/2}-10p_{3/2}$	0.00156688	0.00235033	0.00160875
	$1s_{1/2}-10p_{1/2}$	0.00078344		
1s-11p	$1s_{1/2}-11p_{3/2}$	0.00159323	0.00238984	0.00120305
	$1s_{1/2}-11p_{1/2}$	0.00079661		
1s-12p	$1s_{1/2}-12p_{3/2}$	0.00196958	0.00295437	0.00092338
	$1s_{1/2}-12p_{1/2}$	0.00098479		
1s-13p	$1s_{1/2}-13p_{3/2}$	0.00190107	0.0028516	0.00072428
	$1s_{1/2}-13p_{1/2}$	0.00095053		
1s-14p	$1s_{1/2}-14p_{3/2}$	0.00190205	0.00285307	0.00058093
	$1s_{1/2}-14p_{1/2}$	0.00095102		
1s-15p	$1s_{1/2}-15p_{3/2}$	0.00234347	0.00351521	0.00051145
	$1s_{1/2}-15p_{1/2}$	0.00117174		

**Table 5.** This table compares the values of unperturbed OS and perturbed OS that is under the effect of SO coupling with the method of LS coupling. The first column gives the orbit where absorption process occurs. Every transition starts with 1s orbit and ends at  $n'p$  ( $n' \neq n$ ), eg. 1s-8p. The second column represents the splitting of orbitals due to SO coupling. For example, one p orbit in a neutral hydrogen atom can split into two orbitals,  $p_{1/2}$  and  $p_{3/2}$ , which are off by small amount of energy. The subscript is the total angular momentum quantum number  $j$ . OS for different  $j$  are shown in the third column which are all positive numbers. Summing up the OS values from  $1s_{1/2}$  to both  $p_{1/2}$  and  $p_{3/2}$  states separately in column 4, and comparing to the unperturbed oscillator strength (column 5), their value starts to differ at the transition from 1s to 8p orbitals.

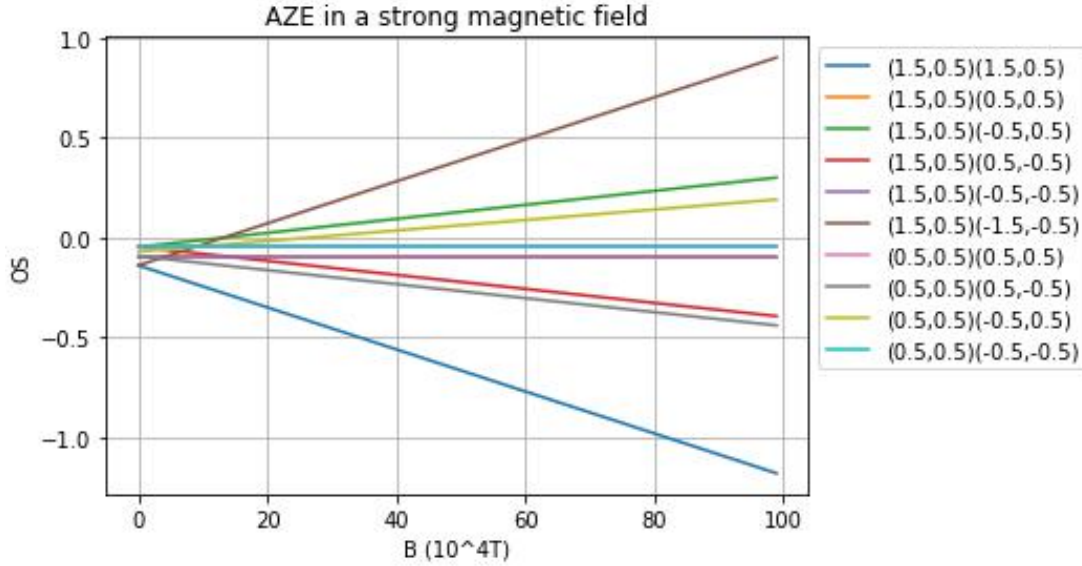
The first correlation that can be spot in table 9 is the decline of the UAOS when  $n'$  increases. This is because the absorption process is less likely to happen if the gap between initial and final  $n$  quantum numbers gets greater. Secondly, the perturbed OS of the absorption process “ $1s_{1/2}-n'p_{3/2}$ ” is twice as much as the perturbed OS of “ $1s_{1/2}-n'p_{1/2}$ ”.

Moreover, summation of the OS from the two split sub-shells  $p_{1/2}$  and  $p_{3/2}$  with a division of weight  $2l+1$  gives an average OS which is independent of magnetic quantum numbers. Since s orbital corresponding to  $l=0$ , the degenerate weight  $2l+1$  equals to 1. Therefore, the average OS after SO coupling correction is the sum of the OS of “ $1s_{1/2}-n'p_{3/2}$ ” and “ $1s_{1/2}-n'p_{1/2}$ ”. Comparing with the unperturbed OS, SO coupling has no effect on OS until the transitions after “1s-8p”. For example, the corrected OS is higher than the unperturbed one by  $1.07 \times 10^{-6}$  from the transition “1s-8p”. In the transition range of “1s-9p” and “1s-14p”, the unperturbed OS decreases exponentially from 0.00222078 to 0.00058093, whereas the corrected OS fluctuates between 0.002 and 0.003. The results shows that the addition of the SO coupling introduces a new portion of energy that is very weak in hydrogen atoms.

An Anomaly is found in the transition “1s-15p”, corrected OS arises to 0.00351521 by  $6.62 \times 10^{-4}$ . Such huge increase is unexpected, thus, it might be a numerical mistake which is created by computer. After all, the transition “1s-15p” gives a very small OS value, precision can be a big issue at this level. An improved method, JJ coupling, could be applied to measure OS when the electron gets far away from the nuclei.

### Strong field limit

The following discussion is about the AZE in a strong magnetic field with the range from 0 to  $10^6$  T. The occurrence of AZE requires OS under SO coupling perturbation as well as an external magnetic field. Measuring the behaviour of OS in a hydrogen atom when the magnetic field strength increase gradually aids with the study of AZE.



**Fig.5** A figure showing the behaviour of OS with AZE in a strong magnetic field regime. OS values calculated are going under emission process from  $n=2$  to  $n=1$  with SO coupling. The strength of the magnetic field has unit  $10^4$  T. The label of each line has two brackets which contains the electron emission information of  $j$  and  $m_j$  respectively, for example, label “(1.5, 0.5)(0.5, -0.5)” stands for the transition between  $P_{3/2}$  with  $m_j=1/2$  to  $S_{1/2}$  with  $m_j=-1/2$ .

In a strong magnetic field, OS of emission process from each sub-shell has linear behaviour when the strength of the field increases. In addition, 10 lines of OS merged into 5 evenly spaced major lines with the growth of B field. NZE has occurred at this stage, on account of the fact that SO coupling is too weak in comparison to the strength of the magnetic field.

The 4 overlapped lines with label “(1.5, 0.5)(0.5, 0.5)”, “(1.5, 0.5)(-0.5, -0.5)”, “(0.5, 0.5)(0.5, 0.5)” and “(0.5, 0.5)(-0.5, -0.5)” have no variation with the change of magnetic field. A resemblance between these four lines are their fixed  $m_j$  values throughout the emission process. Therefore, the strength of the magnetic field is independent on OS if  $m_j$  value doesn't change between electron transitions.

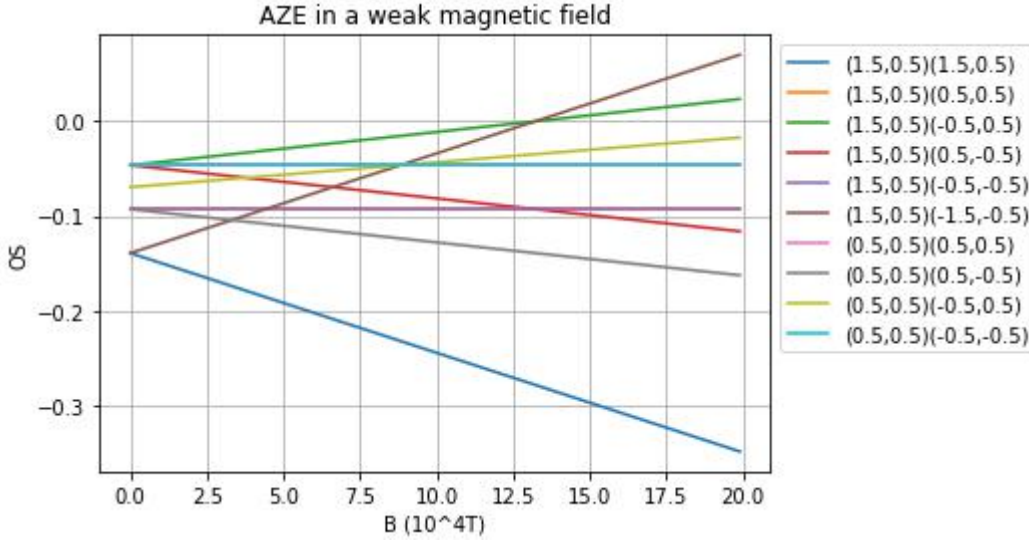
Besides, the OS lines which have their  $m_j$  value increased by 1 after emission process grow linearly with the increasing strength of the magnetic field, while the ones that have  $m_j$  value decreased decline. In more details, the rate of changing in OS is higher if the initial  $m_j$  values are 1.5 or -1.5 rather than 0.5 or -0.5.

Both fig.5 and fig.4 show the OS of a hydrogen atom in a strong magnetic field. Despite fig.5 has taken SO coupling into account, OS values behave in a similar fashion as the ones in fig.4 in a strong magnetic field. The major difference is the fact that the OS with SO coupling correction suggests more routes of electron emission would happen and more detailed energy splitting would appear after correction.



### Weak field limit

The effect of SO coupling to OS is more significant in a weak magnetic field region. Therefore, AZE is nothing alike NZE in such case. The following figure shows the AZE in a magnetic field with the range of 0 T to  $2 \times 10^5$  T. In general, such range is way too strong for a weak B field limit. However, it is weak enough to just review the different behaviour of AZE to NZE.



**Fig.6** A figure showing the behaviour of OS with AZE in a weaker magnetic field regime compared to fig.5. The strength of the magnetic field has unit  $10^4$  T. The label of each line follows the same rules that described in fig.5.

When there is no magnetic field, the ten lines of OS initiate at four points with OS values: -0.13904125, -0.09269417, -0.04634708, -0.06952093. With the increase of magnetic field in the unit of  $10^4$  T, the ten electron emission lines in the 2p orbital behave the same way as the pattern described for AZE in a strong magnetic field. However, because each line has varied starting point and they are interacting with each other when B field changes.

In comparison to NZE in fig.4, the spacing between the lines are uneven at the same magnetic strength in fig.6. This is owing to the extra energy from SO coupling.

## 4. Discussion and conclusion

### Conclusion

OS is a powerful definition to study the electron transition with varied perturbations. The first mathematical tool used to obtain UAOS is the Numerov method which provides the wave function of an electron numerically. Despite its high efficiency, it can introduce some numerical mistakes due to programming. Another mathematical approach that was applied in this paper is the perturbation theory. In the scenario of finding OS under NZE or AZE, instead of resolving the wave function in (4) with the additional energy that is from the external magnetic field, perturbation of the B field is directly applied to the UAOS. Therefore, the new perturbed OS is written in terms of UAOS. Three types of perturbations were discussed in this paper.

The first perturbation corrects the UAOS of a hydrogen-like atom with SO coupling without external B field. The corrected AOS overcomes the UAOS when n increases, because the additional energy from SO coupling

becomes more dominant while the electron is further away from the nuclei.

Secondly, the phenomenon of NZE is observed in any hydrogen-like atom if SO coupling is negligible when an external B field is present. OS with the perturbation of NZE has linear behaviour when the strength of the magnetic field increases. In addition, the space between each split of OS is even.

The last one is AZE. Alike NZE, the splitting spaces between OS are even when SO coupling is weaker than the B field which is  $1 \times 10^6$  T. However, OS lines intersect with each other and NZE has disappeared while the strength of the magnetic field is decreased to a range in between 0 and  $2 \times 10^5$  T. The range of the magnetic field studied in this paper is in strong field region, but AZE appears in a relatively weaker B field in comparison to the one in NZE.

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