THE CENTERAL FIELD APPROXIMATION FOR MANY ELECTRON ATOMS

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ACRONYMS AND ABBREVIATIONS

CFA	centeral field approximation
e	electron
Eq.	equation

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BIOGRAPHICAL SKETCH

The author,Wondwosun Assemahagn was born on october 1985 in west Hararge zone, Tulo woreda Hirna town, Oromiya regional state. He attended his elementary and junior education at Hirna number one elementary and junior school, and attended his secondary school education at Hirna senior secondary school. Following his completion of secondary school education in 2002, he was joined Adama teacher's training college in 2003 and graduate with diploma in physics in 2004. Soon after graduation he was employed at Hirna, west Hararege zone in Oromiya regional state as a teacher. He continued to upgrade his professional qualification and graduate with B.Ed. degree in physics major and mathematics minor from Dilla university in 2009. He then joined the school of graduate studies at Haramaya university in July, 2013 to pursue his M.Sc. degree in quantum physics.

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ABSTRACT

The solution to the Schrodinger equation in case of Hydrogen atom (single particle) can be solved exactly. But if we consider many electron atoms the Schrodinger equation could not solved exactly due to the electron-electron term makes the solution inseparable in single-particle coordinates. However, we can estimate the solutions using different methods. so from those methods the Central Field Approximation provides an excellent starting point to deal with a many-electron system and even if further improvements on this are available and often employed, the Central Field Approximation scheme itself serves a very large number of applications. A set of Quantum defect were also performed and the results have been compared with that of the experimental values. the term quantum defect is a measure of the difference betwen an energy level and the corresponding one in hydrogen. That is the extent to which an outer (valence) electron of a given angular momentum penetrates the inner shell of the atom. While comparing the experimental and calculated values, we have stressed the role of centeral field approximation in Quantum defect theory, some suggestions for improvement of the results are also disscussed.

Keywords: *Schrodinger Equation, Centeral Field Approximation, Separation of Variable, Quantum Defect.*

1. INTRODUCTION

1.1. Back ground of the study

It is well-known that the first model of the electronic structure of atoms based on the idea of quantization of the angular momentum was proposed by Niels Bohr in the year 1913. Bohr"s model was based on the planetary model of Kepler, but the Bohr-Kepler orbits are indefensible since an orbit requires a simultaneous description of position and momentum of the electron which correspond to mutually incompatible observables. The Bohr-model thus had to give way to formal quantum theory based on the Schrodinger equation and the Heisenberg's principle of uncertainty.

The Schrodinger equation for the Hydrogen atom has exact analytical solution, but an atom consisting of two or more electrons poses a formidable challenge. Quantum elementary particles such as in a many-electron system are fundamentally identical, and one cannot track the temporal dynamics of each electron separately when it is in the company of another. The two electrons are indistinguishable; a ''two-electron'' system can therefore be best described essentially only as a ''two-electron'' wave function. This certainly does not mean that the ''two-electron-system'' becomes a fundamental particle! The fundamental particle in this case also is of course the individual single electron itself, since the two-electron can be written as a product of single-electron wave functions, but the form of the product function must respect the indistinguishability of the two electrons.

In this thesis many-electron atoms have been described by simply presuming that the central forces dominate the motion of the individual electrons. This central field approximation allows the separation of variables, which makes it possible to continue the practice of describing the atoms in terms of single electron orbitals with quantum numbers n and l. This means that the atomic state can be characterized by specifying the electron configuration. The configuration with the lowest energy (strongest binding) corresponds to the ground state.

For atoms with more than one electron the Pauli principle limits the occupation of the orbitals. two electrons are said to be equivalent if they carry the same quantum numbers n and l

(irrespective of the magnetic quantum numbers m_l and m_s). When a shell contains the maximum number of electrons consistent with the Pauli principle it is called closed or fully filled.

The Coulomb interaction dominates by orders of magnitude over all other terms in the atomic Hamiltonian. Therefore, to calculate the ground state energy the electronic charge has to be distributed across the atom as accurately as possible. In atomic systems this is best done with the self-consistent (Hartree method).

The central field approximation provides - in hindsight - the justification for treating the alkali atoms as hydrogen-like atoms.

1.2. Statement of the Problem

It is not possible to find the exact solution for many electron schrodinger equation since the hamiltonian is much more complicated and the mutual electrostatic repulsion of the N electrons is prevents us from separating the equation into a set of N individual equations. Further from this it is also too large to treat as a small perturbation. That is why we use some approximation method. So the centeral field approximation makes the hamiltonian of many electron atoms separate in to two parts. The radial part approximate at the center and the remaining part is possible to treat as a small perturbation.

1.3. Objective of the Study

General objective

The general objective of this study is to solve the schrodinger equation of many electron atoms.

Specific objectives

- ✓ To solve the schrodinger equation of N-electron atoms under centeral field approximation method.
- ✓ To calculate the ionization energy of alkali metal elements.
- ✓ To compare the calculated ionization energy of alkali metals with expermental result.

1.4. Significance of the Study

The Central Field Approximation gives a zero-order Hamiltonian $\hat{H}_O$ that allows to solve the Schrödinger equation and thus find a set of zero-order wave functions ψ_{ij}. The hope is that treat the residual electrostatic interaction (i.e. the non-central bit of the electron-electron repulsion) as a small perturbation, $\hat{H}_O$. The change to the energy would be found using the functions ψ_{ij}. It also provides an excellent starting point to deal with a many-electron system and even if further improvements on this are available and often employed, the Central Field Approximation scheme itself serves a very large number of applications. The methodology is applicable not only to atoms or ions, but is readily extended to study other many-body systems, including molecules, clusters, solids etc.

2. LITERATURE REVIEW

2.1 The Time-dependent and Time-independent Schrodinger Equations

2.1.1. The Time-dependent Schrodinger Equation

The time-dependent schrodinger equation involves the hamiltonian operator Ĥ and is formulated thus:

$$\hat{\mathrm{H}}\Psi(\mathrm{X,t}) = i\hbar\frac{\partial\Psi}{\partial t} \tag{2.1}$$

X stands for all the coordinates. If we define the energy operator Ê by

$$\widehat{\mathrm{E}} \equiv i\hbar\frac{\partial}{\partial t} \tag{2.2}$$

We see that we can write the time-dependent schrodinger equation as

$$\hat{\mathrm{H}}\Psi(\mathrm{X,t}) = \widehat{\mathrm{E}}\Psi(\mathrm{X,t}) \tag{2.3}$$

Do not confuse this with an eigen value equation; the right hand side has an operator Ê, not a scalar value E.

2.1.2. The Time-independent Schrodinger Equation

For time-independent problems the Hamiltonian operators does not explicitly depend on the time t, i.e, $\hat{\mathrm{H}} \equiv \hat{\mathrm{H}}(\mathrm{x,y,z}),$ we must have the probability density $\Psi\Psi*$ independent of time. This requires that we write $\Psi(\mathrm{x,y})$ as a product of factors,one involving the time only, and the other involving the other coordinates. If this function is to satisfy the time-dependet schrodinger equation, it is easy to show that the time-dependent part must be of the form $e^{-iEt/\hbar}$. We than have

$$\Psi(\mathrm{X,t}) = \psi(\mathrm{x}) \times e^{-iEt/\hbar} \tag{2.4}$$

$$\Psi*(\mathrm{x,t}) = \psi*(\mathrm{x}) \times e^{iEt/\hbar} \tag{2.5}$$

$\Psi(\mathrm{X,t})\Psi*(\mathrm{x,t}) = \psi(\mathrm{x})\psi*(\mathrm{x})$ is independent of time. And also that since Et/ $\hbar$ must be dimensionless, and $\hbar/t$ has units of energy, the parameter E must have units of energy. We can substitute equ. (2.4) in equ. (2.1) and show that

$$\hat{\mathrm{H}}\psi(\mathrm{x}) = E\psi(\mathrm{x}) \tag{2.6}$$

This is the time-independent schrodinger equation, we see that in this case the wave-function ψ is an eigen function of the Hamiltonian operator with E as its eigen value. Equ.(2.6) is colled the time-independent schrodinger equation and ψ time-independent wave function. This is the equation that we use when the Hamiltonian operator does not explicitly depend on the time and the system does not change with time (stationary). In cases like the interaction of molecules with light, the Hamiltonian operator depends explicitly on time, i.e $\hat{\mathrm{H}} \equiv \hat{\mathrm{H}}(\mathrm{x,y,z,t})$, the wave function $\Psi(\mathrm{X,t})$ can not be factored according to equ. (2.4) and we now have to use the time-dependent wave equation. We then calculate the energy of the system by the recipe.

$$\mathrm{E} \equiv \langle\hat{\mathrm{H}}\rangle \tag{2.7}$$

$$= \left\langle\Psi(x,y,z,t)\middle|\hat{\mathrm{H}}(\mathrm{x,y,z,t})\middle|\Psi(x,y,z,t)\right\rangle \tag{2.8}$$

This is in accordance with the recipe in quantum mechanics that any measured observable $\mathcal{O}$ for a system described by a wave function Ψ is to be compared with the quantum mechanical a verage of the corresponding operator $\hat{\mathcal{O}}$, written as $\langle\hat{\mathcal{O}}\rangle_\Psi$, or more briefly, $\langle\hat{\mathcal{O}}\rangle$ which stands for (in Dirac's notation) $\langle\Psi|\hat{\mathcal{O}}|\Psi\rangle$.

We will recall that in Dirac's notation

$$\langle f|\hat{O}|g\rangle \equiv \int f^*(x)\left[\hat{O}g(x)\right]d\tau \tag{2.9}$$

$d\tau$ is the volume element for the coordinate system considered:dxdydz for cartesian coordinates, $r^2 sin\theta dr d\theta d\phi$ for spherical coordinates. The integral will be a multiple integeral, and you have to use the limits of integration. You will see that the integrand is obtained by first operating *g* with the operator $\widehat{O}$ and multiplying the result with the complex conjugate of *f*.

2.2. Operators

We will recall that the Hamiltonian operator is obtained from the Hamiltonian of classical mechanics by substituting from the momenta and coordinates in the classical Hamiltonian by the cooresponding operators. We will also recall that any function of the coordinates and momenta has a corresponding operator,obtained by substituting for any coordinate q_i the corresponding operator $\hat{q}_i \equiv q_i$ (i.e, operation by $\hat{q}_i$ is the same as multiplying by the value of q_i) and the momentum operator $\hat{p}_i \equiv -i\hbar\frac{\partial}{\partial q_i} = \frac{\hbar}{i}\frac{\partial}{\partial q_i}$ where q_i is the coordinate conjugate to the momentum p_i. It is convenient to introduce the time operator $\hat{t} \equiv t$, i.e, operation with $\hat{t}$ has the same effect as multiplying by *t*. We will also recall that the result of successive operation by two operators $\widehat{O}_1$ and $\widehat{O}_2$ depends on the order, i.e $\widehat{O}_2\widehat{O}_1 \neq \widehat{O}_1\widehat{O}_2$. The difference between these is referred to as the commutator of the two operators, denoted by $[\widehat{O}_1, \widehat{O}_2]$:

$$[\widehat{O}_1, \widehat{O}_2] \equiv \widehat{O}_1\widehat{O}_2 - \widehat{O}_2\widehat{O}_1 \qquad (2.10)$$

When the commutator of two operators is zero,then the order of operation does not matter and the operators are said to commute. We will recall that

$$\widehat{L}^2 = \hbar^2\ell(\ell+1)y_\ell^m \qquad (2.11)$$

$$\widehat{L}_z y_\ell^m = m_\ell y_\ell^m \qquad (2.12)$$

We see that the spherical harmonic function y_ℓ^m is eigen function of both the operator corresponding to the square of the angular momentum, $\hat{L}^2$, and the operator corresponding to the z-component of the angular momentum operator $\hat{L}_z$. Using this we should be easily able to verify that $[L^2, L_z] = 0$. This is a general feature; when two operators commute, it is possible to find a set of functions that are simultaneously eigen functions of both operators. This has the consequence that the quantities corresponding to both operators can be measured simultaneously with out error.

When two oprators do not commute, it is not possible to find functions which are eigen functions of both operators, and the quantities corresponding to the operators can not be measured simultaneously with accuracy. As examples of operators that do not commute, we have

$$[\hat{X}, \hat{P}_X] = i\hbar \tag{2.13}$$

$$[\hat{E}, \hat{t}] = i\hbar \tag{2.14}$$

$$[\hat{L}_X, \hat{L}_y] = i\hbar\hat{L}_z \tag{2.15}$$

$$[\hat{L}_y, \hat{L}_Z] = i\hbar\hat{L}_X \tag{2.16}$$

$$[\hat{L}_Z, \hat{L}_X] = i\hbar\hat{L}_y \tag{2.17}$$

Particularly important are operators that commute with the Hamiltonian operator. Stationary state wave functions are eigen functions of the Hamiltonian operator, so that only quantities whose operators commute with the Hamiltonian can be measured accurately. For operators that do not commute with the Hamiltonian, we seek the averages of these operators,and the standard deviation will give a measure of the ''spread''. Thus,for the $\hat{X}$ operator, which does not commute with the Hamiltonian,

$$\langle X_{op} \rangle \equiv \langle \psi | X | \psi \rangle \tag{2.18}$$

$$\langle X_{op}^2\rangle \equiv \langle\psi|X^2|\psi\rangle \tag{2.19}$$

$$\langle P_{X,op}\rangle \equiv \left\langle\psi\middle|-i\hbar\frac{\partial}{\partial x}\middle|\psi\right\rangle \tag{2.20}$$

$$\langle P_{X,op}^2\rangle \equiv \left\langle\psi\middle|-\hbar^2\frac{\partial^2}{\partial x^2}\middle|\psi\right\rangle \tag{2.21}$$

We can calculate $\Delta x \equiv \left[\langle X_{op}^2\rangle - \langle X_{op}\rangle^2\right]^{1/2}$ and $\Delta P_X \equiv \left[\langle P_{x,op}^2\rangle - \langle P_{x,op}\rangle^2\right]^{1/2}$ and verify, for a case for which ψ is known (for example, the particle in a box), Heisenberg's uncertainty principle:

$$\Delta x\Delta P_X \geq \hbar/2 \tag{2.22}$$

2.3. Perturbation-Theory

Perturbation theory is a method for solving a problem interms of the solutions for a very similar problem. Suppose that we has solved the time-independent schrodinger wave equation for a problem with Hamiltonian $\hat{H}^{(0)}$. Let the solution be $\psi_1^{(0)}$, $\psi_2^{(0)}$, $\psi_3^{(0)}$, $\cdots$ with corresponding energy leveles $E_1^{(0)}$, $E_2^{(0)}$, $E_3^{(0)}$, $\cdots$. This means that $\hat{H}^{(0)}\psi_1^{(0)} = E_1^{(0)}\psi_1^{(0)}$, $\hat{H}^{(0)}\psi_2^{(0)} = E_2^{(0)}\psi_2^{(0)}$, $\cdots$ $\hat{H}^{(0)}\psi_i^{(0)} = E_n^{(0)}\psi_i^{(0)}$. We assume that the solutions are not degenerate; when there is degerency the equations given below will have to be modified slightly.

The superfix (0) represent the unperturbed problem, and subscripts 1,2,... represent the ground state, the first excited state, etc. Thus $\hat{H}^{(0)}$ is the Hamiltonian for the unperturbed problem, $\psi_1^{(0)}$ is the ground state wave function for the unperturbed problem, and $E_3^{(0)}$ is the energy of the second excited state for the unperturbed problem.

Let the Hamiltonian for the problem we are interested in (the perturbed problem) be of the for $\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}$, where $\hat{H}^{(1)}$ is small compared to $\hat{H}^{(0)}$. It is resonable to suppose that the solutions for the perturbed problem will be close in some sense to the solutions of the unperturbed problem. We make use of the following fact: the solutions $\psi_n^{(0)}$ for the unperturbed problem form a complete set, i.e., any arbitrary function, in particular the wave functions for the perturbed problem, can be written as a linear sum of these, our assumption can be formulated thus:

$$\psi_n = \psi_n^{(0)} + \sum_{i \neq n} C_i \, \psi_n^{(0)} \tag{2.23}$$

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \dots \tag{2.24}$$

In effect we the writting down a correction for both ψ_n and E_n the form of a series. We will see that many of the higher correction terms will be small so that we are left with a few corrections terms only. Note that ψ_n is not normalized.

We summarize the final results

- As a result of the perturbations the wave functions are a ‘’mixture’’ of the solutions for the unperturbed problem. For every n, the perturbed wave function ψ_n is largely the unperturbed wave function $\psi_n^{(0)}$ with a little admixture of the other unperturbed wave functions.
- The coefficient C_i is a measure of how much $\psi_i^{(0)}$ makes a contribution to (has got ‘’mixed in to’’) $\psi_n^{(0)}$. Its contribution to the probability density function will be proportional to C_i^2.
- The value of C_i may be calculated from

$$C_i = \frac{\left\langle \psi_n^{(0)} \middle| \hat{\mathrm{H}}^{(1)} \middle| \psi_n^{(0)} \right\rangle}{E_n^{(0)} - E_i^{(0)}} \qquad i \neq n \tag{2.25}$$

Thuse the coefficient C_i, the coefficient of $\psi_i^{(0)}$ in ψ_n, is equal to the matrix element of the perturbation $\hat{\mathrm{H}}^{(1)}$ between the unperturbed wave function $\psi_i^{(0)}$ and $\psi_n^{(0)}$ divided by the energy difference between ith and nth unperturbed leveles. If the matrix element is zero(for symmetry reasons,for example), then C_i is zero. Because of the energy term in the denominator,the leveles close to n make a greater contribution than those further away.

- The first order correction to the energy, $E_n^{(1)}$ is given by the average of the perturbation $\hat{H}^{(1)}$ over the unperturbed wave function $\psi_n^{(0)}$:

$$E_n^{(1)} = \langle \hat{H}^{(1)} \rangle_{\psi_n^{(0)}} \tag{2.26}$$

$$= \left\langle \psi_n^{(0)} \middle| \hat{H}^{(1)} \middle| \psi_n^{(0)} \right\rangle \tag{2.27}$$

If this is zero for reasons of symmetry,we would be interested in the second order correction $E_n^{(2)}$.

- The second order correction $E_n^{(2)}$ is given by

$$E_n^{(2)} = \sum_{i \neq n} \frac{\left| \left\langle \psi_n^{(0)} \middle| \hat{H}^{(1)} \middle| \psi_n^{(0)} \right\rangle \right|^2}{E_n^{(0)} - E_i^{(0)}} \tag{2.28}$$

Since $\hat{H}^{(1)}$ is small and it occurs in two factors,the second order correction is smaller than the first order correction. Here too we see that leveles closest to the *n*th level make the greatest contribution. The levels higher than the *n* make a positive contribution (push the energy up) while those levels lower than *n* makes a negative contribution(push the energy down).

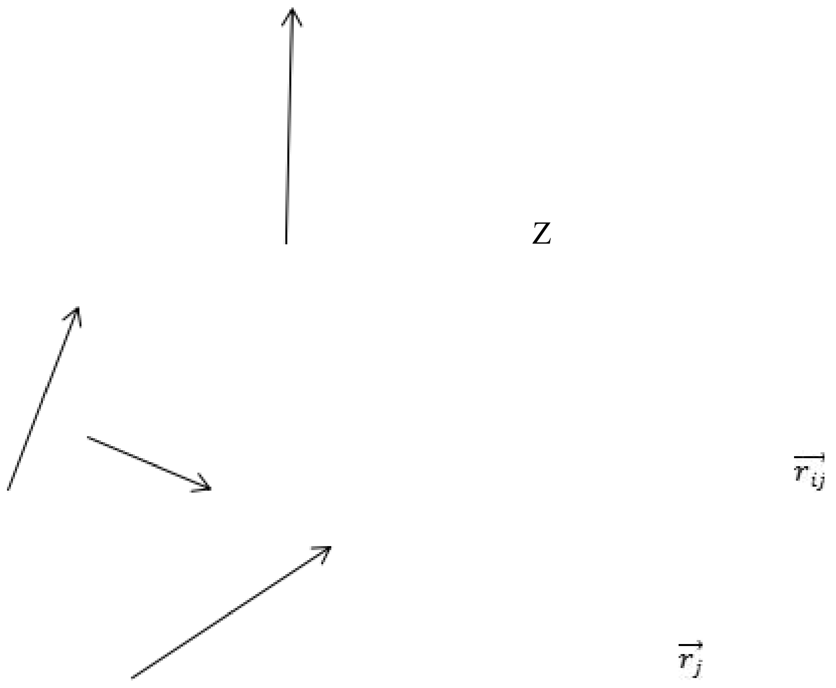
2.4. Hamiltonian of Multi-Electron Ions and Atoms

If we consider an ion with N electrons and Z protons in the nucleus; for a neutral multi-electron atom, *Z* = *N*. Again, because the nucleus is much heavier than the electrons. We assume it to be stationary at the origin of a spherical coordinate system, as shown in Figure 2.1. Including only the kinetic energy of the electrons and the potential energy due to the electrostatic interactions among the electrons and between the electrons and the nucleus, the Hamiltonian of the electrons in the ion for the orbital part of the motion only is

$$\hat{H} = \sum_{i=1}^{N}\left[-\frac{\hbar^2}{2m}\nabla_i^2 - \frac{Ze^2}{r_i}\right] + \sum_{i>j}^{N}\frac{e^2}{r_{ij}} \qquad (2.29)$$

Where, $r_{ij} = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}$, this faction in the last term of eq. (2.29) makes it impossible to solve the equation without approximations.

The form of the summation sign in the last term is to ensure that the electrostatic interaction between each pair of electrons is counted only once.



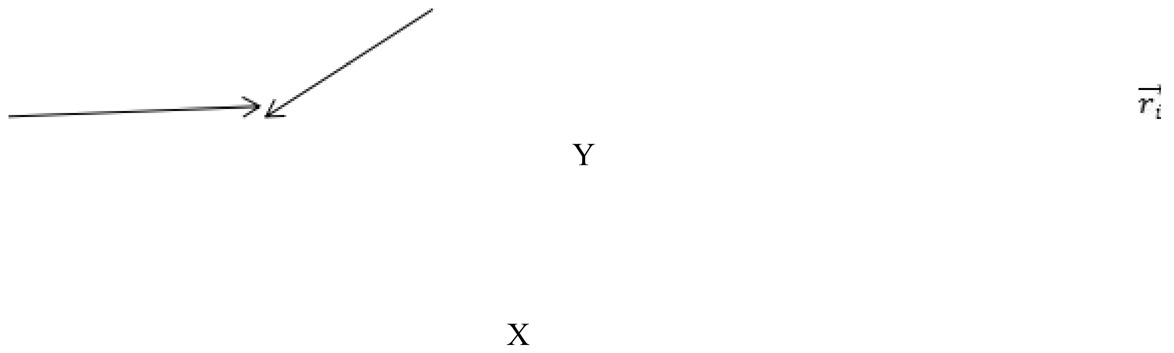


Figure 1. Coordinate system used for the model for the multi-electron ion or atom. The nucleus is assumed stationary at the origin (0, 0, 0).

The standard approximation procedure is to assume that each electron is moving primarily in a spherically symmetric potential V(r), due to the nucleus and the average potential of all the other electrons:

$$\widehat{\mathrm{H}} = \sum_{i=1}^{N}\left[-\frac{\hbar^2}{2m}\nabla_i^2 + V(r_i)\right] + \Delta V_{es}, \qquad (2.30)$$

Where

$$\Delta V_{es} = \left\{\sum_{i>j=1}^{N}\frac{e^2}{r_{ij}} - \sum_{i=1}^{N}\left[\frac{Ze^2}{r_i} + V(r_i)\right]\right\} \approx 0$$

is considered a negligibly small perturbation in a first order approximation or

$$\widehat{\mathrm{H}} \cong \left\{\sum_{i=1}^{N}\left[-\frac{\hbar^2}{2m}\nabla_i^2 + V(r_i)\right]\right\} \qquad (2.31)$$

Thus, the time-independent Schrodinger equation for the multi-electron ion or atom to be solved approximately is:

$$\left\{\sum_{i=1}^{N}\left[-\frac{h^2}{2m}\nabla_i^2 + V(r_i)\right]\right\}\Psi_{\{E\}_n}(\overrightarrow{r_1},\overrightarrow{r_2},\cdots,\vec{r}_{N-1},\vec{r}_N) = \{E\}_n\Psi_{\{E\}_n}(\overrightarrow{r_1},\overrightarrow{r_2},\cdots,\vec{r}_{N-1},\vec{r}_N). \quad (2.32)$$

2.5. The Centeral Field Approximation

The Central Field Approximation has been a very useful approach to solve the Hamiltonian of many electron atoms. The idea here is to assume that in addtion to its attraction to the nucleus, each electron experiences an average potential due to the other electrons. This potential is assumed to be spherically symmetric. The description of multi-electron atoms therefore usually starts with the central field approximation in which we re-write the Hamiltonian of eq. (2.30) in the form:

$$\hat{\mathrm{H}} = \sum_{i=1}^{N}\left(-\frac{h^2}{2m}\nabla_i^2 + V_{cent}(r_i)\right) + V_{res}, \qquad (2.33)$$

Where, V_{cent} is the central field and V_{res} is the residual electrostatic interaction.

The central field approximation works in the limit where

$$\left|\sum_{i=1}^{N} V_{cent}(r_i)\right| \gg |V_{res}| \qquad (2.34)$$

In this case, we can treat V_{res} as a perturbation and, we then have to solve a Schrodinger equation in the form:

$$\left[\sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m}\nabla_i^2 + V_{cent}(r_i)\right)\right]\psi = E\psi. \tag{2.35}$$

This is not as bad as it looks. By writing

$$\psi = \psi_1(r_1)\psi_2(r_2)\cdots\psi_N(r_N) \quad , \tag{2.36}$$

We end up with N separate Schrodinger equations of the form:

$$\left(-\frac{\hbar^2}{2m}\nabla_i^2 + V_{cent}(r_i)\right)\psi_i(r_i) = E_i\,\psi_i(r_i) \tag{2.37}$$

With

$$E = E_1 + E_2 + \cdots E_N \,, \tag{2.38}$$

This is much more tractable. We might need a computer to solve any one of the single particle wave Schrodinger equations of the type given in eq. 2.11, but at least it is possible in principle. Furthermore, the fact that the potentials that appear in eq. 2.11 only depend on the radial co-ordinate r_i (i.e. no dependence on the angles θ_i and ϕ_i) means that every electron is in a well-defined orbital angular momentum state, and that the separation of variables.

2.6. Alkali Spectra

The absorption spectra of alkali vapors (Such as lithium, sodium) appear quite similar in many respects to the absorption spectrum of H atom. They are only displaced to a considerable extent, toward longer wave lengths. These spectra also consist of a series of lines with regularly decreasing separation and decreasing intensity.

It cannot, however, be represented by a formula completely analogous to the Bohr formula. On the other hand, since the lines converge to a limit, we must be able to represent them as differences between two terms.

Rydberg formula,

$$V = T_{ps} - \frac{R}{(m+p)^2} \qquad \textit{where } m = 2,3 \tag{2.39}$$

p is a constant, known as Quantum Defect. T_{ps} is known as series limit. This series is known as Principal series. Other series, in addition to this, may be observed for the alkalis. They are diffuse series (T_{DS}), sharp series (T_{SS}) ,and Bergmann series (T_{BS}).

Sharp series

$$V = T_{SS} - \frac{R}{(m+s)^2} \qquad \textit{where } m = 2,3 \tag{2.40}$$

Diffuse series

$$V = T_{DS} - \frac{R}{(m+d)^2} \qquad \textit{where } m = 3,4 \tag{2.41}$$

Bergmann series

$$V = T_{BS} - \frac{R}{(m+f)^2} \qquad \textit{where } m = 4,5 \tag{2.42}$$

Selection rules: $\Delta n = 0,1,2,3$ and s, d, f is a constant known as Quatum Defect.

$\Delta l = \pm 1$

As a specific example, we consider the alkali metals such as lithium, sodium and potassium, which come from group I of the periodic table. They have one valence electron outside filled inner shells. They are therefore approximately one-electron systems, and can be understood by introducing a phenomenological number called the quantum defect to describe the energies.

Let us consider the sodium atom. The optical spectra are determined by excitations of the outermost 3s electron. The energy of each (*n, l*) term of the valence electron is given by:

$$E_{n,l} = -\frac{R}{(n-\delta(l))^2} \tag{2.43}$$

Where $n \geq 3$, $\delta(l)$ is the quantum defect.

The quantum defect $\delta(l)$ was introduced empirically to account for the optical spectra. In principle it should depend on both *n* and *l*, but it was found experimentally to depend mainly on *l* as given in the following table.

(*source* : reference data on atomic physics and atomic process by Boris.M.smirnov,2008)

Table 1. Values of quantum defect for the alkali atoms

l	Li	Na	K	Rb	Cs
s	0.40	1.35	2.19	3.13	4.06
p	0.04	0.85	1.71	2.66	3.59
d	0.00	0.01	0.25	1.34	2.46
f	0.00	0.00	0.00	0.01	0.02

The dependence of the quantum defect on l can be understood with reference to the figure where the radial probability densities for the 3s and 3p orbitals of a hydrogenic atom with $Z = 1$ are plotted with respect to normalized radial distance.

An individual electron in sodium atom experiences an electrostatic potential due to the Coulomb repulsion from all the other electrons in the atom. Ten out of eleven electrons are in closed sub-shells, which have spherically-symmetric charge clouds. The off-radial forces from electrons in these closed shells cancel because of the spherical symmetry.

3. MATHIMATICAL METHODOLOGY

In this section, I briefly present the mathematical techniques relevant in the development of this work.

3.1. The Schrodinger Equation of Hydrogen atoms in Spherical Coordinates

We separated time and position to arrive at the time independent Schrodinger equation which is

$$\mathcal{H}|E_i\rangle = E_i|E_i\rangle \tag{3.1}$$

Where E_i are eigen values and $|E_i\rangle$ are energy eigen states. We developed a one dimensional position space representation of the time independent Schrodinger equation, changing the notation such that $E_i \longrightarrow E$ and $|E_i\rangle \longrightarrow \psi$. In three dimensions the Schrodinger equation generalizes to

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi = E\psi \tag{3.2}$$

Where ∇^2 is the Laplacian operator. Using the Laplacian in spherical coordinates, the Schrodinger equation becomes

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\psi+V(r)\psi=E\psi \tag{3.3}$$

In spherical coordinates, $\psi = \psi(r,\theta,\varphi)$ and the plan is to look for a variables separable solution such that $\psi(r,\theta,\varphi) = R(r)Y(\theta,\varphi)$. We will in fact find such solutions where $Y(\theta,\varphi)$ are the spherical harmonic functions and $R(r)$ is expressible in terms of associated Laguerre functions.

Before we do that, interfacing with the arguments of linear algebra may partially explain why we are proceeding in this direction.

3.1.1. Complete Set of Commuting Observables for Hydrogen

Though we will return to equation (3.3), the Laplacian can be expressed

$$\nabla^2 = \frac{\partial^2}{\partial r^2} \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2}\left(\frac{\partial^2}{\partial \theta^2} + \frac{1}{tan\theta}\frac{\partial}{\partial \theta} + \frac{1}{sin^2\theta} \frac{\partial^2}{\partial \phi^2}\right) \tag{3.4}$$

The terms in parenthesis are equal to $-\frac{\mathcal{L}^2}{\hbar^2}$, so assuming spherical symmetry, the Laplacian can be written

$$\nabla^2 = \frac{\partial^2}{\partial r^2} \frac{2}{r} \frac{\partial}{\partial r} - \frac{\mathcal{L}^2}{r^2\hbar^2} \tag{3.5}$$

and the Schrodinger equation becomes

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} \frac{2}{r} \frac{\partial}{\partial r} - \frac{\mathcal{L}^2}{r^2\hbar^2}\right) + V(r)\right]\psi = E\psi \tag{3.6}$$

Assuming spherical symmetry, which we will have because a Coulomb potential will be used for $V(r)$. Without the radial variable, we have a complete set of commuting observables for the angular momentum operators in $\mathcal{L}^2$ and $\mathcal{L}_z$. Including the radial variable, we need a minimum of one more operator, if that operator commutes with both $\mathcal{L}^2$ and $\mathcal{L}_z$. The total energy operator, the Hamiltonian, may be a reasonable candidate. What is the Hamiltonian here? It is the group of terms within the square brackets. Compare equations (3.1) and (3.6) if you have difficulty visualizing that. In fact,

$$[\mathcal{H}, \mathcal{L}^2] = 0 \qquad \text{and} \qquad [\mathcal{H}, \mathcal{L}_z] = 0 \tag{3.7}$$

So the Hamiltonian is a suitable choice. The complete set of commuting observables for the hydrogen atom is $\mathcal{H}, \mathcal{L}^2$ and $\mathcal{L}_z$. We have all the eigenvalue/eigenvector equations, because the time independent Schrodinger equation is the eigenvalue/eigenvector equation for the Hamiltonian operator, i.e., the the eigenvalue/eigenvector equations are

$$\mathcal{H}|\psi\rangle = E_n|\psi\rangle, \tag{3.8}$$

$$\mathcal{L}^2 \,|\psi\rangle = l(l+1)h^2|\psi\rangle, \tag{3.9}$$

$$\mathcal{L}_z|\psi\rangle = m\hbar|\psi\rangle, \tag{3.10}$$

Where we subscripted the energy eigen value with an *n* because that is the symbol conventionally used for the energy quantum number (per the particle in a box and SHO). Then the solution to the problem is the eigen state which satisfies all three, denoted $|n, l, m\rangle$ in abstract Hilbert space.

The representation in position space in spherical coordinates is

$$\langle r, \theta, \phi|n, l, m\rangle = \psi_{nlm}(r, \theta, \phi). \tag{3.11}$$

3.2. Separating Radial and Angular Dependence

In this and the following sections, we illustrate how the angular momentum and magnetic moment quantum numbers enter the symbology from a calculus based argument. In writing equation (3.3), we have used a representation, so are no longer in abstract Hilbert space. One of the consequences of the process of representation is the topological arguments of linear algebra are obscured. They are still there, simply obscured because the special functions we use are orthogonal, so can be made orthonormal, and complete, just as bras and kets in a dual space are orthonormal and complete. The primary reason to proceed in terms of a position space representation is to attain a position space description. One of the by-products of this chapter may be to convince you that working in the generality of Hilbert space in Dirac notation can be considerably more efficient. we rely on connections between the two to establish the meanings of of *l* and *m.* They have the same meanings within these calculus based discussions.

As noted, we assume a variables separable solution to equation (3.3) of the form

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi) \tag{3.12}$$

An often asked question is “How do you know you can assume that?" You do not know. You assume it, and if it works, you have found a solution. If it does not work, you need to attempt other methods or techniques. Here, it will work. Using equation (3.12), equation (3.3) can be written

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)R(r)Y(\theta,\phi) + \frac{1}{r^2\sin\theta}\,\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)R(r)Y(\theta,\phi) + \frac{1}{r^2 sin^2\theta}\frac{\partial^2}{\partial\phi^2}R(r)Y(\theta,\phi) - \frac{2m}{\hbar^2}[V(r)-E]R(r)Y(\theta,\phi) = 0 \tag{3.13}$$

$$\Longrightarrow \quad Y(\theta,\phi)\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)R(r) + R(r)\frac{1}{r^2\sin\theta}\,\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)Y(\theta,\phi) + R(r)\frac{1}{r^2 sin^2\theta}\frac{\partial^2}{\partial\phi^2}R(r)Y(\theta,\phi) - \frac{2m}{\hbar^2}[V(r)-E]R(r)Y(\theta,\phi) = 0$$

(3.14)

Dividing the equation by $R(r)Y(\theta,\phi)$, multiplying by r^2, and rearranging terms, this becomes

$$\left\{\frac{1}{R(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)R(r)-\frac{2mr^2}{\hbar^2}[V(r)-E]\right\}+\left[\frac{1}{Y(\theta,\phi)\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)Y(\theta,\phi)+\frac{1}{Y(\theta,\phi)\sin^2\theta}\frac{\partial^2}{\partial\phi^2}Y(\theta,\phi)\right]=0 \tag{3.15}$$

The two terms in the curly braces depend only on *r*, and the two terms in the square brackets depend only upon angles. With the exception of a trivial solution, the only way the sum of the groups can be zero is if each group is equal to the same constant. The constant chosen is known as the separation constant. Normally, an arbitrary separation constant, like *K*, is selected and then you solve for *K* later. We are instead going to stand on the shoulders of some of the physicists and mathematicians of the previous 300 years, and make the enlightened choice of *l*(*l*+1) as the separation constant. It should become clear *l* is the angular momentum quantum number. Then

$$\frac{1}{R(r)}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)R(r)-\frac{2mr^2}{\hbar^2}[V(r)-E]=l(l+1) \tag{3.16}$$

Which we call the radial equation, and

$$\frac{1}{Y(\theta,\phi)\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)Y(\theta,\phi)+\frac{1}{Y(\theta,\phi)\sin^2\theta}\frac{\partial^2}{\partial\phi^2}Y(\theta,\phi)=-l(l+1) \tag{3.17}$$

Which we call the angular equation. Notice the signs on the right side are opposite so they do, in fact, sum to zero.

3.2.1. The Angular Equation

The solutions to equation (3.17) are the spherical harmonic functions, and the *l* used in the separation constant is, in fact, the same used as the index *l* in the spherical harmonics $Y_{l,m}(\theta,\phi)$. In fact, it is the angular momentum quantum number. But where is the index *m*?

How is the magnetic moment quantum number introduced? To answer these questions, remember the spherical harmonics are also separable, i.e. $Y_{l,m}(\theta,\phi) = f_{l,m}(\theta)g_m(\phi)$. We will use such a solution in the angular equation, without the indices until we see where they originate. Using the solution Y$(\theta,\phi) = f(\theta)g(\phi)$ in equation (3.17),

$$\frac{1}{f(\theta)g(\phi)\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)f(\theta)g(\phi)+\frac{1}{f(\theta)g(\phi)sin^2\theta}\frac{\partial^2}{\partial\phi^2}f(\theta)g(\phi)=-l(l+1) \quad (3.18)$$

$$\Rightarrow\frac{1}{f(\theta)\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)f(\theta)+\frac{1}{g(\phi)sin^2\theta}\frac{\partial^2}{\partial\phi^2}g(\phi)=-l(l+1) \quad (3.19)$$

Multiplying the equation by $sin^2\theta$ and rearranging,

$$\frac{\sin\theta}{f(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)f(\theta)+l(l+1)sin^2\theta+\frac{1}{g(\phi)}\frac{\partial^2}{\partial\phi^2}g(\phi)=0 \quad (3.20)$$

The first two terms depend only on θ, and the last term depends only on ϕ. Again, the only

Non-trivial solution such that the sum is zero is if the groups of terms each dependent on a single variable is equal to the same constant. Again using an enlightened choice, we pick m^2 as the separation constant, so

$$\frac{\sin\theta}{f(\theta)}\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\right)f(\theta)+l(l+1)sin^2\theta=m^2 \quad (3.21)$$

$$\frac{1}{g(\phi)}\frac{d^2}{d\phi^2}g(\phi)=-m^2 \quad (3.22)$$

and that is how the magnetic moment quantum number is introduced. Again, (3.21) and (3.22) need to sum to zero so the separation constant has opposite signs on the right side in the two equations.

3.2.2. The Azimuthal Angle Equation

The solution to the azimuthal angle equation, equation (3.22), is

$$g(\phi) = e^{im\phi} \Longrightarrow g_m(\phi) = e^{im\phi} \tag{3.23}$$

where the subscript *m* is added to $g(\phi)$ because it is now clear there are as many solutions as there are allowed values of *m*.

3.2.3. The Reduced Mass

Equation (3.3) describes a single particle in a central potential. The hydrogen atom is a two

body problem, and the potential is not central but is dependent upon the distance between the nucleus and the electron. Were we able to anchor the nucleus to a stationary location we could designate an origin, equation (3.3) would be an accurate description. This is not possible, but we can reach a similar end by picturing the center of mass being anchored to a fixed location. If we use the reduced mass in place of the electron mass,

$$\mu = \frac{m_p m_e}{m_p + m_e} \tag{3.24}$$

the radial coordinate *r* accurately describes the distance between the nucleus and the electron. The effect in equation (3.3) is cosmetic; where there was an *m* representing *me*, it is replaced by

μ. Because the proton is about 1836 times more massive than the electron, the reduced mass is nearly identically the electron mass. Many authors simply retain the electron mass. Since the center of mass is not actually anchored, a second set of coordinates is required to track the center of mass using this scheme.

3.2.4. Solution of the Radial Equation

The radial equation (3.16) using the reduced mass and the Coulomb potential, $V(r) = \frac{-e^2}{r}$, is

$$\frac{1}{R(r)}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)R(r) - \frac{2\mu r^2}{\hbar^2}\left[\frac{-e^2}{r} - E\right] - l(l+1) = 0 \tag{3.25}$$

$$\Rightarrow \frac{d}{dr}\left(r^2\frac{d}{dr}\right)R(r) - \frac{2\mu r^2}{\hbar^2}\left[\frac{-e^2}{r} - E\right]R(r) - l(l+1)R(r) = 0 \tag{3.26}$$

$$\Rightarrow \frac{d}{dr}\left(r^2\frac{d}{dr}\right)R(r) + \left[\frac{2\mu r^2}{\hbar^2}\frac{e^2}{r} + \frac{2\mu r^2}{\hbar^2}E - l(l+1)\right]R(r) = 0 \tag{3.27}$$

The plan is to get (3.27) into a form comparable to equation $y_j^{k''}(x) + \left(-\frac{1}{4} + \frac{2j+k+1}{2x} - \frac{k^2-1}{4x^2}\right)y_j^k(x) = 0$, and we already know the solutions are $y_j^k(x) = e^{-x/2}x^{(k+1)/2}L_j^k(x)$. We will be able to glean additional information by comparing the equations term by term. The energy levels of the hydrogen atom and the meaning of the indices of the associated Laguerre polynomials, which will be quantum numbers for the hydrogen atom, will come from the comparison of individual terms.

We will make three substitutions to get the last equation $\mathcal{Y}_j^{k''}(x)+\left(-\frac{1}{4}+\frac{2j+k+1}{2x}-\frac{k^2-1}{4x^2}\right)\mathcal{Y}_j^k(x)=0$

The first is

$$\mathcal{Y}(r)=rR(r)\Rightarrow R(r)=\frac{\mathcal{Y}(r)}{r} \tag{3.28}$$

Making this substitution in the first term and evaluating the derivatives

$$\frac{d}{dr}\left(r^2\frac{d}{dr}\right)R(r)=\frac{d}{dr}\left(r^2\frac{d}{dr}\right)(r^{-1})\mathcal{Y}(r)$$

$$=\frac{d}{dr}r^2\left[(-r^{-2})\mathcal{Y}(r)+(r^{-1})\frac{d\mathcal{Y}(r)}{dr}\right]$$

$$=\frac{d}{dr}\left[-\mathcal{Y}(r)+r\frac{d\mathcal{Y}(r)}{dr^2}\right]$$

$$=-\frac{d\mathcal{Y}(r)}{dr}+\frac{d\mathcal{Y}(r)}{dr}+r\frac{d^2\mathcal{Y}(r)}{dr^2}$$

$$=r\frac{d^2\mathcal{Y}(r)}{dr^2}. \tag{3.29}$$

The substitution serves to eliminate the first derivative. We would have both a first and second derivative if we had evaluated the first term using R(r). With this and the substitution of equation (3.28), equation (3.27) becomes

$$r\frac{d^2\mathcal{Y}(r)}{dr^2}+\left[\frac{2\mu re^2}{\hbar^2}+\frac{2\mu r^2}{\hbar^2}E-l(l+1)\right]\frac{\mathcal{Y}(r)}{r}=0 \tag{3.30}$$

$$\Rightarrow\frac{d^2\mathcal{Y}(r)}{dr^2}+\left[\frac{2\mu e^2}{\hbar^2 r}+\frac{2\mu E}{\hbar^2}-\frac{l(l+1)}{r^2}\right]\mathcal{Y}(r)=0 \tag{3.31}$$

The second substitution is essentially to simplify the notation, and is

$$\left(\frac{\epsilon}{2}\right)^2 = -\frac{2\mu E}{\hbar^2}$$

Where the negative sign on the right indicates we are looking for bound states, states such that $E < 0$, so including the negative sign here lets us have an ϵ which is real. The last equation becomes

$$\frac{d^2\mathcal{Y}(r)}{dr^2} + \left[\frac{2\mu e^2}{r\hbar^2} - \frac{\epsilon^2}{4} - \frac{l(l+1)}{r^2}\right]\mathcal{Y}(r) = 0 \tag{3.32}$$

The third substitution is a change of variables, and notice it relates radial distance and energy

through equation $\left(\frac{\epsilon}{2}\right)^2 = -\frac{2\mu E}{\hbar^2}$,

$$x = r\epsilon \Rightarrow r = \frac{x}{\epsilon},$$

$$\Rightarrow dr = \frac{dx}{\epsilon} \Rightarrow \frac{d^2\mathcal{Y}(r)}{dr^2} = \frac{d}{dr}\frac{d\mathcal{Y}(r)}{dr} = \epsilon\frac{d}{dx}\epsilon\frac{d\mathcal{Y}(r)}{dx} = \epsilon^2\frac{d^2\mathcal{Y}(x)}{dx^2}, \tag{3.33}$$

so our radial equation becomes

$$\epsilon^2\frac{d^2\mathcal{Y}(x)}{dx^2} + \left[\frac{2\mu e^2\epsilon}{x\hbar^2} - \frac{\epsilon^2}{4} - \epsilon^2\frac{l(l+1)}{x^2}\right]\mathcal{Y}(r) = 0$$

$$\Rightarrow \frac{d^2\mathcal{Y}(x)}{dx^2} + \left[-\frac{1}{4} + \frac{2\mu e^2}{\hbar^2\epsilon x} - \frac{l(l+1)}{x^2}\right]\mathcal{Y}(r) = 0, \tag{3.34}$$

and equation (3.34) is equation $\mathcal{Y}_j^{k''}(x) + \left(-\frac{1}{4} + \frac{2j+k+1}{2x} - \frac{k^2-1}{4x^2}\right)\mathcal{Y}_j^k(x) = 0$, where

$$l(l+1) = \frac{k^2-1}{4}, \tag{3.35}$$

And

$$\frac{2\mu e^2}{\hbar^2 \epsilon} = \frac{2j+k+1}{2}, \tag{3.36}$$

the solutions are,

$$y_j^k(x) = e^{-x/2} x^{(k+1)/2} L_j^k(x). \tag{3.37}$$

3.2.5. Eigen energies from the Solution of the Radial Equation

Equation (3.35) tells us $k = 2l + 1$.

We are going to take what appears to be a slight diversion to evaluate a particular set of factors in equation (3.36), $\hbar^2/\mu e^2$, which recurs repeatedly. Going back to the old quantum theory, this is called the Bohr radius, that is

$$a_0 = \frac{\hbar^2}{\mu e^2} = 0.529 \text{ A}. \tag{3.38}$$

We want to express lengths in terms of the Bohr radius because it is a natural length for the hydrogen atom.

Equation (3.36) gives us the eigen energies of the hydrogen atom, but requires some development. Since $k = 2l + 1$,

$$\frac{2j+k+1}{2}=\frac{2j+(2l+)+1}{2}=j+l+1. \qquad (3.39)$$

From the associated Laguerre polynomials, the indices j and k are non-negative. The sum $j + l + 1$ can, therefore, assume any integer values of 1 or greater. We are going to rename it n, or

$$n = j + l + 1. \qquad (3.40)$$

The new integer index n is known as the principal quantum number. Using the principal quantum number, it follows that the eigen energies of the hydrogen atom are

$$E_n = -\frac{\hbar^2}{2\mu a_0^2 n^2} = -\frac{13.6eV}{n^2}, \qquad (3.41)$$

Where the quantity 13.6 eV is called the Rydberg, usually denoted R or Ry. The ground state energy is E_o = -13.6 eV. when n = 1. It is often convenient to express excited state energies in terms of the ground state energy.

4. RESULTS AND DISCUSSION

4.1. The Schrödinger Equation for Two-electron Atoms para and ortho States.

Let us consider an atom(or ion) consisting of a nucleus of charge *Ze* and mass M and two electrons of mass *m*. As in the case of one-electron atoms,we shall begin our treatment by neglecting all but the coulomb interactions between the particles,and by writing down the schrodinger equation for the spatial part of the wave function describing the relative motion. The separation of the centre of mass motion is some what more complicated than for the case of one-electron atoms, since we are dealing with a three-body problem.

The schrodinger equation for the spatial part ψ (r_1, r_2) of the wave function describing the relative motion is for a two-electron system.

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2_{r1}-\frac{\hbar^2}{2\mu}\nabla^2_{r2}-\frac{\hbar^2}{M}\nabla_{r1}.\nabla_{r1}-\frac{ze^2}{(4\pi\epsilon_0)r_1}-\frac{ze^2}{(4\pi\epsilon_0)r_2}+\frac{e^2}{(4\pi\epsilon_0)r_{12}}\right]\psi(r_1,r_2)$$
$$=E\psi(r_1,r_2) \qquad (4.1)$$

Where μ=mM/(m+M) is the reduced mass of an electron with respect to the nucleus and $r_{12}=|r_1-r_2|$.

We shall first consider the case of an ínfinitely heavy'nucleus (M=∞) so that (i) $\mu=m$ and (ii) the 'mass polarisation'term $(-\frac{\hbar^2}{M})\nabla_{r1}.\nabla_{r1}$ can be omitted. We shall work in atomic units (a.u.), in which the Hamiltonian is

$$H=-\frac{1}{2}\nabla^2_{r_1}-\frac{1}{2}\nabla^2_{r_2}-\frac{Z}{r_1}-\frac{Z}{r_2}+\frac{Z}{r_{12}} \qquad (4.2)$$

And the schrodinger equation for $\psi(r_1, r_2)$ becomes

$$\left[-\frac{1}{2}\nabla_{r1}^2 - \frac{1}{2}\nabla_{r2}^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{Z}{r_{12}}\right]\psi(r_1, r_2) = E\psi(r_1, r_2) \qquad (4.3)$$

This equation is unchanged when the coordinates of two electrons are interchanged. Thus, if we denote by p_{12} a permutation operator that interchanges the spatial coordinates of the two electrons, the wave functions

$$\psi(r_2, r_1) = p_{12}\psi(r_1, r_2) \qquad (4.4)$$

And $\psi(r_2, r_1)$ satisfy the same schrodinger equation. Moreover, both functions $\psi(r_1, r_2)$ and $\psi(r_2, r_1)$ must be continuous, uniform and bounded. If $\psi(r_1, r_2)$ corresponds to a non-degenerate eigen value, $\psi(r_1, r_2)$ and $\psi(r_2, r_1)$ can only differ by a multiplicative factor λ,

$$\psi(r_2, r_1) = p_{12}\psi(r_1, r_2) = \lambda\psi(r_1, r_2) \qquad (4.5)$$

Applying the permutation operator p_{12} twice, we must obtain $\psi(r_1, r_2)$ again.

Thus

$$\begin{aligned} \mathrm{P}_{12}^2\psi(r_1, r_2) &= \lambda p_{12}\psi(r_1, r_2) \\ &= \lambda^2\psi(r_1, r_2) \\ &= \psi(r_1, r_2) \qquad (4.6) \end{aligned}$$

So that $\lambda^2 = 1$, $\lambda = \pm 1$ and

$$\psi(r_2, r_1) = \pm\,\psi(r_1, r_2) \qquad (4.7)$$

Wave functions which satisfay (4.7) with the pluse sign (that is,whose spatial part remains unchanged upon permutating the spatial part remains unchanged upon permutating the spatial coordinates of the two electrons) are said to be space-symmetric and will be denoted by $\psi_+(r_1, r_2)$ on the other hand, wave functions satisfying (4.7) with the minus sign (that is, whose spatial part changes sign on interchanging spatial coordinates of the two electrons) are said to be space-anti symmetric and will be written $\psi_-(r_1, r_2)$.

For degenerate eigen values the eigen functions of (4.3) can always be chosen so (4.7) holds. Thus the eigen functions of a two-electron atoms can be classified as being either space-symmetric or space-anti symmetric. The states described by space-symmetric wave functions are colled para states; those corresponding to space-anti-symmetric wave functions are known as ortho states.

4.2. The Central-field Approximation for two- electron atom

We may improve our treatment by splitting the basic Hamiltonian (6.2) as

$$H = H_0 + H' \tag{4.8}$$

Where

$$H_0 = -\frac{1}{2}\nabla_{r_1}^2 + V(r_1) - \frac{1}{2}\nabla_{r_2}^2 + V(r_2) \tag{4.9}$$

Is the sum of the two individual Hamiltonians

$$h_i = -\frac{1}{2}\nabla_{r_i}^2 + V(r_i) \tag{4.10}$$

And

$$H' = \frac{1}{r_{12}} - \frac{Z}{r_1} - V(r_1) - \frac{Z}{r_2} - V(r_2) \tag{4.11}$$

In the above formulae *V*(r) is a central potential which should be chosen in such a way that the effect of the perturbation H' is small. Roughly speaking, the net effect of each electron on the motion of the other one is to screen some what the charge of the nucleus, so that a simple guess for *V*(r) is

$$V(r) =-\frac{Z-s}{r} =-\frac{Z_e}{r} \tag{4.12}$$

Where S is a 'screening constant'and the quantity $Z_e = Z - S$ may be considered as 'effective chargee'. Since the potential (4.12) is a coulomb interaction, the corresponding individual electron energies are given (in a.u) by

$$\mathrm{E}_{n_i} =-\frac{1}{2}\frac{(Z-S)^2}{n_i^2} =-\frac{1}{2}\frac{Z_e^2}{n_i^2} \tag{4.13}$$

And are independent of the quantum numbers $l_i \; and \; m_i$.

Neglecting the perturbation H', the total energy of the atom is just the sum of the individusal electron energies (4.13). in particular, the ground state energy E_o is then given approximately (in a.u) by

$$E_o \approx -(Z-S)^2 =-Z_e^2 \tag{4.14}$$

The corresponding spatial part of the ground state wave function being

$$\psi_0(r_1, r_2) =\frac{Z_e^3}{\pi} e^{-Z_e(r_1+r_2)} \tag{4.15}$$

Here we simply remark that the value of $Z_e = 1.70$ would make the approximate expression (4.14) agree with the experimental value $E_o =- 2.903 \; a.u$ of the ground state energy of helium. Since *Z*= 2 in this case, the corresponding screening constant is *S*=0.30. thus, for the ground state of helium, we see that in this simple, 'average shielding'approximation, the screening effect of each electron on the other one is equivalent to about one-third of the electronic charge.

A better choice for the central potential *V*(*r*) than the coulomb form (4.12) is provided by an expression of the same type, but in which the 'screening constant'*S* varies with the distance *r*.

Indeed, at a small distances $(r \rightarrow 0)$, the potential acting on an electron is essentially the coulomb attraction –*Z*/*r* of the nucleus, while for large *r* $(r \rightarrow \infty)$, this potential is just the coulomb field –(*Z*-1)/*r* due to a net charge (*Z*-1), namely the nuclear charge *Z* screened by the charge (-1) of the other electron. Thus we expect the quantity *S* in (4.12) to be infact an increasing function of *r*, which takes on the values *S*=0 at *r*=0 and *S*=1 at *r*=∞. Since a potential of the form (4.12) where *S* is a function of *r* is no longer a coulomb potential, the *l* degenerancy which is characteristic of the coulomb field is removed. Thus the individual electron energies E_{nl} (where we have dropped the subscript *i*) are still degenerate with respect to the quantum number *m*, but now depend on both quantum number *n* and *l*. The principal quantum number *n* is defined as in the case of hydrogenic atoms, the number of nodes of the radial function being $n_r = n - l - 1,$ with *n*= 1,2,... and *l*= 0,1,... n-1. Calling $U_{nlm}(r)$ an individual electron orbital, solution of the single particle equation

$$\left[-\frac{1}{2}\nabla_r^2 + V(r)\right] U_{nlm}(r) = E_{nl} U_{nlm}(r) \tag{4.16}$$

We see that $U_{nlm}(r)$ is just the product of a radial function and a spherical harmonic $Y_{lm}(\theta, \phi)$.

The Hamiltonian (4.9), interms of the individual electron orbital $U_{nlm}(r),$ our new zero-order spatial wave functions, which are the properly symmetrised eigen states of (4.9) are given by

$$\psi_0^0(r_1, r_2) = U_{100}(r_1) U_{100}(r_2) \tag{4.17}$$

For the state and by

$$\psi_{\pm}^0(r_1, r_2) = \frac{1}{\sqrt{2}}[U_{100}(r_1) U_{nml}(r_2) \pm U_{nml}(r_1) U_{100}(r_2)] \quad n \geq 2, \tag{4.18}$$

For the genuinely discrete exited states. We still neglect the perturbation H', the total energy of the atom is just

$$E_{1s,nl}^{(0)} = E_{1s} + E_{nl} \tag{4.19}$$

For example Magnesium atomic number of 12, and therefore has a nucleuse with a charge of +12e with electrons orbiting around it. The energies of the electrons in their shells are estimated using the Bohr formulae:

$$E_n =- \left(\frac{Z}{n}\right)^2 R_H, \tag{4.20}$$

Where, R_H = 13.6 eV is the Rydberg constant and Z is the atomic number.

The first two electrons go into the $n = 1$ shell. These electrons see the full nuclear charge of +12e. With $n = 1$ and Z = 12, we find $E_1 =- 12^2 R_H =- 1{,}958.4eV.$ the next eight electrons go into the $n = 2$ shell. These are presumed to orbit outside the $n = 1$ shell. The two inner electrons partly screen the nuclear charge, and the $n = 2$ electrons see an effective charge $Z_{eff} =+ 10e.$ therefore the energy is $E_2 =- \left(\frac{10}{2}\right)^2 R_H =- 340eV.$ finally, the outermost electron in the $n = 3$ shell orbits outside the filled $n = 1$ and $n = 2$ shells, and therefore sees $Z_{eff} = 2$. With $Z = 2$ and $n = 3$ we find $E_3 =- 6.04eV.$ we can 47evels47er this in the following table.

Shell	n	Z_{eff}	*Energy (eV)*
1s	*1*	*12*	*-1,958*
2s,2p	*2*	*10*	*-340*
3s	*3*	*2*	*-6.04*

Table energies of the principal atomic shells of Magnesium according to the Bohr model.

Thus for magnesium atom (Z = 12) from equation (4.19) and the above table the total energy $(E_T^0 =- 2304.4\ eV)$ the experimental values are $(E_0^{exp} =\ eV).$ As we should expect, our crude approximation gives an energy which is too low because we have neglected the repulsion term between the electrons, whose effect is clearly to raise the energy levels. This absence of electron-electron repulsion is a fundamental source of error in this approximation.

And the total orbital angular momentum quantum number is L=*l*. The para(+) and ortho(-) states (4.18) are still degenerate, but the degeneracy in *l* is removed. For a fixed value of *n* the (algebraic) value of E_{nl} is an increasing function of *l*. Indeed, electrons with a small value of *l* are more likely to penetrate at certain times the 48evels48eriz barrier'(which is proportional to $l(l+1)/r^2$) and hence to feel the fully unscreened attractive coulomb potential –Z/r of the nucleus. We therefore expect that the energy of the atom will be an increasing function of L (*l*). We note that in the central field approximation leading to (4.19) the energy of the atom is specified by the electron configuration, that is by the values of the quantum numbers *n* and *l* of the electrons. For the genuinely discrete states of two-electron atoms considered here, one remains in the ground state (that is, with *n*=1 and *l*=0) while the other, 48evels48er active'electron has the quantum numbers *n* and *l*. Following in convention used in spectroscopy the value of *n* and *l* are usually indicated by writing *n* as a number, and *l* as a letter, (i.e. s for *l*=0, p for *l*=1, d for *l*=2, etc.). if there are *k* electrons having the same values of *n* and *l*, this is denoted as $(nl)^k$. For example, in this notation the ground state (4.17) is 48evels48erized by the configuration $(1s)^2$ also written $1s^2$, the first excited states (4.18) by the configurations (1s)(2s) or 1s2s, (1s)(2p) or 1s2p, and so on.

From our discussion of the wave functions of one-electron atoms it is also clear that for states of the excited electron corresponding to large values of *n* and *l* the orbitals $u_{nlm}(r)$ are concentrated at much larger values of *r* than the ground state orbital $u_{100}(r)$. We may then speak of an 48 evel'(1s) electron with spatial quantum numbers (1,0,0) which is moving in the unscreened coulomb field –*Z*/*r* of the nucleus, and an 48evel'electron, which moves in the fully screened potential –(*Z*-1)/*r*. For such states of large *n* and *l* the 'zero-order'energy levels are then given approximately (in a.u.) by

$$E_n^{(0)} = -\frac{1}{2}Z^2 - \frac{1}{2}\frac{(Z-1)^2}{n^2} \tag{4.20}$$

Apart from the addition constant $-Z^2/2$, we see that these energy 49evels are identical to those of a hydrogenic atom of nuclear charge Z-1.

From the above discussion it is clear that according to this approximation each electron moves independently of the other one in a net central potential *V*® which represents the attraction of the nucleus plus some average central repulsive potential due to the other electron.

4.3. Quantum Mechanical Calculation of the Schrödinger Equation of Alkali Metals.

Form of the potential energy,

$$V(r) =-\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}\left(1+\frac{b}{r}\right)$$

(4.21)

This form represents the potential energy requirement at large distance,

$$V(r) =-\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$$

(4.22)

and at small distance

$$V(r) =-\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$$

(4.23)

Since this is radial dependence and we need to solve only radial equation of the Schrödinger equation of hydrogen atom problem

$$V(r) = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}\left(1+\frac{b}{r}\right)$$

(4.24)

$$= \frac{c}{r}\left(1+\frac{b}{r}\right)$$

(4.25)

where, $c = -\frac{1}{4\pi\varepsilon_0}e^2$

Now, the Hamiltonian for one electron atom,

$$\widehat{\mathrm{H}} = -\frac{\hbar^2}{2\mu}\nabla^2 + V(r)$$

$$= -\frac{\hbar^2}{2\mu}\nabla^2 + \frac{c}{r}\left(1+\frac{b}{r}\right)$$

(4.26)

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi + \frac{c}{r}\left(1+\frac{b}{r}\right)\psi = E\psi$$

(4.27)

$$\nabla^2\psi + \frac{2\mu}{\hbar^2}\left[E - \frac{c}{r}\left(1+\frac{b}{r}\right)\right]\psi = 0$$

(4.28)

The radial equation:

$$\frac{d^2\chi}{dr^2} + \left[\frac{2\mu}{\hbar^2}E - \frac{2\mu}{\hbar^2}\frac{c}{r}\left(1+\frac{b}{r}\right) - \frac{\ell(\ell+1)}{r^2}\right] R(r) = 0 \qquad (4.29)$$

$$\frac{d^2\chi}{d^2} - \left[-\frac{2\mu}{\hbar^2}E + \frac{2\mu}{\hbar^2}\frac{c}{r} + \frac{2\mu}{\hbar^2}\frac{cb}{r^2} + \frac{\ell(\ell+1)}{r^2}\right] R(r) = 0 \qquad (4.30)$$

by taking

$$A = -\frac{2\mu}{\hbar^2}E \quad ; \qquad B = -\frac{2\mu c}{\hbar^2}$$

and substituting in equation (4.44)

$$\frac{d^2\chi}{dr^2} - \left[A - \frac{B}{r} + \frac{-Bb+\ell(\ell+1)}{r^2}\right]\chi = 0 \qquad (4.31)$$

let,

$$\ell^*(\ell^*+1) = -Bb + \ell(\ell+1) \qquad (4.32)$$

so,

$$\frac{d^2\chi}{dr^2} - \left[A - \frac{B}{r} + \frac{\ell^*(\ell^*+1)}{r^2}\right]\chi = 0 \qquad (4.33)$$

The Same radial equation as in hydrogen atom, solution with n^* where $n^* = \ell^* + p + 1$

$$E - \frac{R}{(n^*)^2} = -\frac{R}{(\ell^*+p+1)^2} \qquad (4.34)$$

$$n = \ell + p + 1$$

$n^* = \ell^* + p + 1 = \ell^* - \ell + n$

so,

this imples

$$n^* = n - (\ell - \ell^*) = n - \Delta\ell \qquad (4.35)$$

Now, from equation (4.46)

$$\ell^*(\ell^*+1) =- Bb + \ell(\ell+1)$$

$$\Rightarrow (\ell^2 - (\ell^*)^2) + (\ell - \ell^*) = Bb$$

$$\Rightarrow (\ell - \ell^*)(\ell + \ell^* + 1) = Bb$$

$$\Rightarrow \Delta\ell = \frac{Bb}{\ell+\ell^*+1} = \frac{Bb}{2\ell+1} \tag{4.36}$$

$$= \frac{\frac{B}{2}b}{\ell+\frac{1}{2}} = \frac{b \quad 1}{a_1 \; \ell+\frac{1}{2}}$$

$$E_{n,\ell} =- \frac{Rhc}{\left(n-\frac{b \quad 1}{a_1 \, \ell+\frac{1}{2}}\right)^2}$$

This energy expression is dependent on both *n* and *l.* From eqn. (4.48), (4.49) and (4.50)

$$E_{n,\ell} =- \frac{Rhc}{\left\{n-\frac{Bb}{2\ell+1}\right\}^2} \tag{4.37}$$

Now we know

$$E = hv$$

$$= \frac{c}{\lambda} \qquad \bar{v} = \frac{1}{\lambda}$$

$$E = \frac{hc}{\lambda} \Rightarrow \frac{1}{\lambda}(cm^{-1}) = \frac{E}{hc}$$

From the above steps

$$E_{n,\ell} =- \frac{R}{\left\{n - \frac{Bb}{2\ell+1}\right\}^2} \, cm^{-1} \tag{4.38}$$

Where, R = 109,728.7 cm^{-1} = 13.6 eV

4.4. Calculating the Ionization Energy of Alkali Metals.

Now from equ. (4.38) to calculate the ionization energy of alkali metal we use the following formula $E_{n,\ell} =-\frac{R}{\left\{n-\frac{Bb}{2\ell+1}\right\}^2} cm^{-1}$ where R= 13.6 eV and Bb is the the quantum defect.

Atoms	Ground state atomic number	Electronic configuration	quantum defect(Bb)
Lithium	3	[He]2s	0.40

$$E_{2,0} =-\frac{R}{\left\{n-\frac{Bb}{2\ell+1}\right\}^2} cm^{-1} \tag{4.39}$$

$$=-\frac{13.6\ ev}{(2-\frac{0.40}{2(0)+1})^2}$$

$$=-\frac{13.6\ ev}{(1.6)^2}$$

= - 5.31 ev

Atoms	Ground state atomic number	Electronic configuration	quantum defect(Bb)
Sodium	11	[Ne]3s	1.35

$$E_{3,0} =-\frac{R}{\left\{n-\frac{Bb}{2\ell+1}\right\}^2} cm^{-1} \tag{4.40}$$

$$= -\frac{13.6\ ev}{(3-\frac{1.35}{2(0)+1})^2}$$

$$= -\frac{13.6\ ev}{(1.65)^2}$$

= - 4.99 ev

Atoms	Ground state atomic number	Electronic configuration	quantum defect(Bb)
Potassium	19	[Ar]4s	2.19

$$E_{4,0} = -\frac{R}{\left\{n-\frac{Bb}{2\ell+1}\right\}^2}\ cm^{-1} \tag{4.41}$$

$$= -\frac{13.6\ ev}{(4-\frac{2.19}{2(0)+1})^2}$$

$$= -\frac{13.6\ ev}{(1.81)^2}$$

= - 4.15 ev

Atoms	Ground state atomic number	Electronic configuration	quantum defect(Bb)
Rubidium	37	[Kr]5s	3.13

$$E_{5,0} = -\frac{R}{\left\{n-\frac{Bb}{2\ell+1}\right\}^2}\ cm^{-1} \tag{4.42}$$

$$= -\frac{13.6\ ev}{(5-\frac{3.13}{2(0)+1})^2}$$

$$= -\frac{13.6\ ev}{(1.87)^2}$$

$= -\ 3.89$ ev

Atoms	Ground state atomic number	Electronic configuration	quantum defect(Bb)
Ceseium	54	[Xe]6s	4.06

$$E_{6,0} = -\frac{R}{\left\{n - \frac{Bb}{2\ell+1}\right\}^2}\ cm^{-1} \qquad (4.43)$$

$$= -\frac{13.6\ ev}{(6 - \frac{4.06}{2(0)+1})^2}$$

$$= -\frac{13.6\ ev}{(1.96)^2}$$

$= -\ 3.54$ ev

4.5. Compare Calculated and Experimental Ionization Energy of Some Alkali metals.

The IE from Alkali quantum formula along with the experimental values is shown in the table. The table shows a semi-quantitative agreement between calculated and experiment. Since we can interpret ionization energies as a proof for the existence of electronic shells of atoms one can also imply that these shells are also retained in the Alkali quantum formula.

Table 2. Calculated and Experimental Ionization Energy of Alkali metals

Z (atomic number)	Element name	Ground state level	Electronic configration	Experimental IE(ev)	Calculated IE(ev)
3	Lithium	$^2S_{1/2}$	$1s^2\ 2s^1$	5.39	5.31
11	Sodium	$^2S_{1/2}$	$[Ne]3s^1$	5.14	4.99
19	Potassium	$^2S_{1/2}$	$[Ar]4s^1$	4.34	4.15
37	Rubidium	$^2S_{1/2}$	$[Kr]5s^1$	4.18	3.89
55	Cesium	$^2S_{1/2}$	$[Xe]6s^1$	3.89	3.54

From table 2 for Lithium n=2 and l=0, this leads to a prediction for ground state energy of $E_{2,0}$= -5.31 a.u, which with 1.5% of the experimentaly measured energy $E^{exp}_{2,0}$ = -5.39 a.u. for Sodium n=3 and l=0, this leads to a prediction for ground state energy of $E_{3,0}$ = -4.99 a.u, which with 2.9% of the experimentaly measured energy $E^{exp}_{3,0}$ = -5.14 a.u. for Potassium n=4 and l=0, this leads to a prediction for ground state energy of $E_{4,0}$ = -4.15 a.u, which with 4.4% of the experimentaly measured energy $E^{exp}_{4,0}$ = -4.34 a.u. for Rubidium n=5 and l=0, this leads to a prediction for ground state energy of $E_{5,0}$ = -3.89 a.u, which with 6.9% of the experimentaly measured energy $E^{exp}_{5,0}$ = -4.18 a.u. for Cesium n=6 and l=0, this leads to a prediction for ground state energy of $E_{6,0}$= -3.54 a.u, which with 8.99% of the experimentaly measured energy $E^{exp}_{2,0}$ = -3.89 a.u.

5. SUMMARY and CONCLUSIONS

In conclusion, based on centeral field approximation we are carried out a detailed study on many electron atoms. That is the hamiltonian of many electron atoms under centeral field approximation a large part of the electron-electron repulision can be included in to the central potential. The remaining part(the residual part) can be small to be treat as a perturbation.

In this centeral potential, the total wave function is a product of a single electron wave functions, each labeled by the set of quatum numbers (n, l, m_l, m_s). the total wave function of many electron atoms under centeral field approximation the sum of the wave function of a single electron.

It has been shown that since the hamiltonian of many electron atoms under centeral field approximation only depend on the radial part we can separate the radial part from the angular part using separation of variable technice. From this we have observe that the energy level of an atoms under centeral field approximation determaind by the quantum number n and l. So in order to determined the energy level of an atoms we can find the centeral potential.

It has been shown that the energy level of the alkalis are described by a simple formula involving the quantum defect. And it has been shown that the energy level of hydrogen-like atoms is determined similar to hydrogen atom.

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APPENDICES

Appendix A

A.1 Summary of quantum numbers

A hydrogen-like atomic orbital $\psi_{n\ell m}$ is uniquely identified by the values of the principal quantum number *n*, the azimuthal quantum number ℓ, and the magnetic quantum number *m*. These three quantum numbers are natural numbers, their definitions and ranges are:

$$H\psi_{n\ell m} = \frac{E_h}{2n^2}\psi_{n\ell m} \qquad n = 1, \cdots, \infty, \qquad \text{(principal quantum number)}$$

$$l^2\psi_{n\ell m} = \hbar^2\ell(\ell + 1)\psi_{n\ell m}, \qquad \ell = 0, \cdots, n - 1, \qquad \text{(azimuthal quantum number)}$$

$$l_z\psi_{n\ell m} = \hbar m\,\psi_{n\ell m}, \qquad m = -\ell, \cdots, \ell. \qquad \text{(magnetic quantum number)}$$

Here E_h is the atomic unit of energy, and $n \geq \ell + 1$.

A.2 Indication of ℓ by letters

It is very common to denote the orbitals of different angular momentum by different letters, 2s-, 3p-orbital, etc. For historical reasons $\ell = 0$ orbitals are designated by *s*(sharp), $\ell = 1$ by *p* (principal), $\ell = 2$ by *d* (diffuse). and $\ell = 3$ *f* (fundamental). For higher ℓ orbitals the alphabet is followed, while *j* orbitals are omitted. Thus we get the following association between letters and ℓ quantum numbers

s p d f g h i k

0 1 2 3 4 5 6 7

For instance, hydrogenic g-orbitals $(\ell = 4)$ start at principal quantum number $n = 5$, so that we can speak of 5g-, 6g-, etc. Orbitals, but a hydrogen-like 4g-orbital is not defined (i.e., does not appear as a solution of the hydrogen-like schrodinger equation).