

## A brief review of Hartree-Fock Self-Consistent Field Approximation and Application of its Variants on Atoms with $Z= 1-20$ and Few Heavy Atoms

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**Abstract-** Ground state energies of various lighter atoms and few heavy atoms are calculated using Hartree-Fock method's several variants. Obtained results were compared with previous theoretical and numerical computations for the ground state energies of investigated atoms. It is found upon comparison that the energy differences are lying between  $15\mu$  Hartree to  $0.35$  Hartree for RHF, UHF, ROHF methods (non-relativistic) while  $79\mu$  Hartree to  $252$  Hartree for DHF method. Furthermore, differences of DHF energies and NIST data are also calculated and are found in range  $15\mu$  Hartree to  $10.6$  Hartree. The results suggested that Hartree-Fock method with its underlying approximation is suitable in estimating ground state energies and relativistic effects turn out to be important in case of heavier atoms.

**Index Terms-** Correlation effects, Hartree-Fock method, open and closed shell systems, Self-consistent fields.

### I. INTRODUCTION

The foundation of the Hartree-Fock theory was put forward in 1927, just after the discovery of the Schrodinger equation in 1926. DR Hartree introduced a mathematical technique, now called the self-consistent field method (SCF), to compute approximate wave functions and energies for atoms, molecules and ions [1]. These are called ab initio methods and use the Schrodinger equation to solve the many-body problem. The solution of the Schrodinger equation provides energy and wave function which describe the state of the system. In 1928 J.A. Gaunt and J.C. Slater [2] suggested that Hartree-Fock method can be more effective, if variational principle is applied to an ansatz as a product of single-particle function. V. A. Fock [3] and Slater independently noticed that the wavefunction for fermions used by Hartree was not anti-symmetric which was an essential condition for identical particles. Later on, in 1935 Hartree modified his method which fulfils the condition of anti-symmetry and now known as Hartree-Fock method (HF). HF method is an effective tool which can be used to calculate the ionization energies, excitation energies, electron expectation values, bond energies and distances of molecules. Further pioneering work presented by Sambe and Felton and Heijisen et al in [4-6]. Although the method is very useful for the estimation of ground state energies of atoms but it does not incorporate the correlation effects that arises due to electron-electron interaction. Correlation energies also contribute to the total energy and neglecting these

terms specially for the case of heavy atoms would affects the energy accuracy. There are other methods that provide better energy accuracy than Hartree-Fock method but required more computational cost. Few of them are; variational method, perturbative method density functional theory and related work can be found in [7-10]. In 2009, Hylleraas algorithm was used by Koki to calculate the ground state energy of helium atom [11]. In order to obtain more and more accurate ground state energies, another very efficient method has been in use now days, known as Quantum Monte-Carlo method. In 2010, the method was used by Doma and El-Gamal to estimate ground state energy of helium [12]. Using two basis sets along with density functional theory (DFT), Feng Wang et al 2012 calculated the wavefunctions of bound electrons. They included the electron correlation energies in their model. Quantum Monte-Carlo CASINO-Code have been used for computing the exact ground state or low-lying state conditions for two-electron atoms and found more suitable for the purpose. These methods are comparatively less complex than perturbative methods and are quite easy to use [13].

### II. MATERIAL AND METHODS

#### 1. Hartree-Fock Method

The Hartree-Fock (HF) method is widely used in quantum chemistry for approximate electronic structure calculations. The HF method is a mathematical framework used to find out the wavefunction and energy of a multi-electron system in a ground state. The equation of motion cannot be solved analytically for systems in which two or more than two particles interact with each other because an analytical solution for the Schrodinger equation exists only for a single electron atom. The problem that quantum mechanics is facing in dealing with the interacting electrons is related to their indistinguishable nature. A single Slater determinant can describe the state of the electrons and energy can be minimized by varying single-electron orbitals. The solution of the variationally obtained N-spin orbitals that are coupled together would provide HF wavefunction and energy of multi-electron system.

To derive the HF equation, a self-consistent final field is required, which is calculated from the charge distribution with the assumed field. Because of this; the HF method is also known

as self-consistent field method (SCF). Hartree-Fock method is more often used to derive the solution of Schrodinger equation for atoms, molecules, nanostructures and solids.

For methods that describe the many-electron system for atoms and molecules more precisely, the HF solution is the crucial starting point for them.

There are some special cases of HF method:

- The restricted closed shell Hartree-Fock method (RHF), where atom is a system in which all orbitals are doubly occupied.
- The restricted open shell Hartree-Fock method (ROHF), where some of the electrons are not paired.
- Unrestricted Hartree-Fock method (UHF), where electrons can occupy any shell irrespective of Aufbau principle.
- Relativistic Hartree-Fock method or Dirac Hartree-Fock method (DHF), where relativistic effects are taken into account.

The Hartree-Fock method is a variational wavefunction based approach that relies on independent particle approximation. The model gives the final wavefunction without including correlation effects in it. The resulting wavefunction given by the model is assumed to be the best wavefunction within the independent particle approximation. In the case of many-electron atoms, the Coulomb repulsion between electrons plays a crucial role in changing the coulomb nuclear potential through shielding. Thus, by modifying the coulomb potential appropriately, large coulomb repulsion effects can be added remains within the domain of single-particle state.

The wavefunction and the Hamiltonian for n electron systems in HF approximation are expressed as

$$|\Psi\rangle = \frac{1}{\sqrt{N!}} \det \begin{vmatrix} |\varphi_1(1)\rangle & |\varphi_1(2)\rangle & \cdots & |\varphi_1(N)\rangle \\ |\varphi_2(1)\rangle & |\varphi_2(2)\rangle & \cdots & |\varphi_2(N)\rangle \\ \vdots & \vdots & \ddots & \vdots \\ |\varphi_N(1)\rangle & |\varphi_N(2)\rangle & \cdots & |\varphi_N(N)\rangle \end{vmatrix} \quad (1)$$

$i = 1, 2, \dots, N$

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_{i=1}^n \nabla_i^2 - \sum_{i=1}^n \frac{Ze^2}{r_i} + \sum_{i=1}^n \sum_{j=i+1}^n \frac{e^2}{r_{ij}} \quad (2)$$

After the application of Born-Oppenheimer approximation, the Schrödinger equation for atoms can be written as

$$\left( -\frac{\hbar^2}{2m} \sum_{i=1}^n \nabla_i^2 - \sum_{i=1}^n \frac{Ze^2}{r_i} + \frac{1}{2} \sum_{i=1}^{n-1} \sum_{j=i+1}^n \frac{e^2}{r_{ij}} \right) \Psi = E\Psi \quad (3)$$

Hartree-Fock method is classified into open and closed shell systems based on system's atomic configuration. Moreover, open shell system can be dealt with by one of two Hartree-Fock method, restricted (ROHF) and unrestricted (UHF) method. Correspondingly, restricted Hartree-Fock deals closed shell systems. In case of heavy atoms, the relativistic effects are included using relativistic Hartree-Fock method.

### 1.1. Restricted Hartree-Fock (RHF) or closed-shell systems

A SCF method for an atom is devised in manner that it gives a single determinant of one-electron functions. The variation in average energy is taken place regarding quantum numbers  $n$ ,  $l$ ,  $s$ ,  $m_l$  and  $m_s$ , but only those orbitals are varied independently that have unlike  $n$  and  $l$  labels. This is called RHF method. The method is restricted in a way that the radial dependence is same for those orbitals that have similar  $n$  and  $l$  values but different  $m_l$  and  $m_s$  values [14]. This method is usually adopted for closed shell atoms but could be used for open shell atoms as well. One of the examples for restricted open-shell Hartree-Fock theory (ROHF) is given in [15], although open-shell calculations have been a case of UHF type. It is more convenient to use ROHF method than UHF because UHF method is suitable only for specified open-shell orbitals having state of maximum multiplicity. Only for this case UHF wavefunction can estimate an appropriate spin eigen-function while those states which have smaller multiplicity are spoiled due to unnecessary spin components.

In a closed-shell treatment, each orbital is doubly occupied and wavefunction is a single Slater determinant based on an anti-symmetrized product of single-electron orbitals. The Hartree-Fock equations can be obtained through Variation method for a closed-shell atomic system.

$$\Psi = (\varphi_1\alpha)(\varphi_1\beta) \dots \dots (\varphi_n\alpha)(\varphi_n\beta)$$

$$\Psi = [(2n)!]^{-\frac{1}{2}} \begin{vmatrix} (\varphi_1\alpha)^1 & (\varphi_1\beta)^1 & \cdots & (\varphi_n\alpha)^1 & (\varphi_n\beta)^1 \\ (\varphi_1\alpha)^2 & (\varphi_1\beta)^2 & \cdots & (\varphi_n\alpha)^2 & (\varphi_n\beta)^2 \\ \vdots & \vdots & \cdots & \vdots & \vdots \\ (\varphi_1\alpha)^{2n} & (\varphi_1\beta)^{2n} & \cdots & (\varphi_n\alpha)^{2n} & (\varphi_n\beta)^{2n} \end{vmatrix} \quad (4)$$

When wavefunction  $\Psi$  is expressed in terms of a single Slater determinant in which each spatial orbital is doubly occupied then energy expectation value can be written as

$$\langle \Psi | \hat{H} | \Psi \rangle = \int \dots \int \Psi^* H \Psi d\tau_1 \dots d\tau_{2n} \quad (5)$$

If eq. (2) is used in eq. (5) then sum of integrals over the orbitals results the expectation value

$$\langle \Psi | \hat{H} | \Psi \rangle = 2 \sum_i H_i + \sum_i \sum_j (2J_{ij} - K_{ij}) = E \quad (6)$$

The factors of 2 in eq. (6) appear in dealing with a closed-shell system having  $2n$  electrons,  $n$  electron have spin up and remaining  $n$  have spin down and  $\frac{1}{\sqrt{2n!}}$  in eq. (4) is the normalization constant for closed-shell case. The first term on the right side of eq. (6) is the energy without electron-electron repulsion whereas  $J_{ij}$  and  $K_{ij}$  are coulomb and exchange integrals.

$$J_{ij} = \iint \Psi_i^*(1) \Psi_j^*(2) \frac{1}{r_{12}} \Psi_j(2) \Psi_i(1) d\tau_1 d\tau_2 \quad (7)$$

$$K_{ij} = \iint \Psi_i^*(1)\Psi_j^*(2) \frac{1}{r_{12}} \Psi_i(2)\Psi_j(1) d\tau_1 d\tau_2 \quad (8)$$

It is needed to find orbitals which result minimum energy. Eqs. (7 and 8) are the coulomb integrals which express the potential energy. This energy appears due to the interaction between electron 1 and 2 with electron distribution  $|\Psi_j(2)|^2$ . The effective potentials are calculated via these coulomb integrals for an electron moving under the influence of other electrons.

The Hartree-Fock equation is developed for those orbitals that result the minimum expectation value and following equation must be satisfied

$$F\Psi = \epsilon\Psi \quad (9)$$

$$F = H + \sum_i (2J_i - K_i) \quad (10)$$

where  $F$  is the Hartree-Fock Hamiltonian and  $\epsilon$  is a Hermitian matrix of Lagrangian multipliers, which appear accompany by orthonormality restrictions. Hamiltonian operator  $F$  with respect to the set of orbitals  $\Psi$  is established in a manner that, it remains consistent after  $\Psi$  experiences a transformation. Therefore, the set,  $\Psi'$  fulfills

$$F\Psi' = \epsilon'\Psi' \quad (11)$$

$$\epsilon' = U^* \epsilon U \quad (12)$$

Consequently,  $\Psi$  is selected such that  $\epsilon$  becomes diagonal, thus all the orbitals satisfy

$$F\Psi_i = \epsilon_i\Psi_i \quad (13)$$

Eq. (13) is a pseudo-eigenvalue problem, and  $F$  is an operator described through the solution of eq. (13). The above equation is known as Hartree-Fock equation. The sum of one-electron integrals,  $H_i$  and orbital energies,  $\Psi_i$ , gives the system's total energy.

$$E = \sum_i (H_i + \epsilon_i) \quad (14)$$

Where  $-\epsilon_i$  is the orbital energy almost equivalent to the ionization energy needed to eliminate an electron occupying in  $\Psi_i$ , which is a real explanation of orbital energies.

The resulting final field of given charge distribution must be self-consistent with the assumed initial field and that's why the method is known as SCF method.

## 1.2. Unrestricted Hartree-Fock (UHF) or open-shell systems

The orbitals that have similar  $n, l, m_l$  values but different  $m_s$  values, the equation of orbitals varies with respect to  $m_s$  values. This is termed UHF method and it is recommended to reader to see [14, 16] for further understanding. The open shell analysis is somewhat different from closed shell. The wavefunctions for open-shell possess the following specifications:

The total wavefunction resulting from the sum of all anti-symmetric products, that contain a closed-shell core  $\Psi_c$ , and a partially filled open shell chosen from a set  $\Psi_0$ . The complete set of orbitals  $\Psi$  is described by

$$\Psi = (\Psi_c, \Psi_0) \quad (15)$$

and assumed to be orthonormal, such that the two sets  $\Psi_c$  and  $\Psi_0$  are orthonormal and mutually orthogonal. The expression for the total energy can be written as

$$E = 2 \sum_k H_k + \sum_k (2J_{kl} - K_{kl}) + f [2 \sum_m H_m + f \sum_{mn} (2aJ_{mn} - bK_{mn}) + 2 \sum_{km} (2J_{km} - K_{km})] \quad (16)$$

where  $a, b$  and  $f$  are numerical constants. The first and second term serve as closed shell energy, the last term is the sum of open shell energy and the interaction energy of closed and open shell. Where  $f$  is a fractional occupation number of the open-shell, which is calculated by taking the ratio of number of occupied open-shell spin orbitals to the number of available open-shell spin orbitals;  $0 < f < 1$ . By using the same technique described above the full coulomb operator and exchange operator can be found for closed shell systems [17].

## 1.3. Dirac Hartree-Fock method

In order to calculate ground state energies and wavefunction of simple atoms non-relativistic methods are efficient but cannot be used for complex atoms. If spin orbit interactions and Darwin terms are included to Hamiltonian as small perturbations, then these methods can be extended for complex systems.

For heavier atoms these terms cannot be treated as small perturbations because relativistic effects are in greater magnitude and Dirac's relativistic Hamiltonian structure is appropriate for this purpose [18, 19].

Dirac Hamiltonian for an electron is,

$$\mathbf{H} = ic\boldsymbol{\alpha} \cdot \nabla - \beta c^2 - \mathbf{V}(\mathbf{r}) \quad (17)$$

$$\Psi = \begin{pmatrix} \frac{i}{r} \chi_{-k,m} Q(r) \\ \frac{1}{r} \chi_{k,m} P(r) \end{pmatrix} \quad (18)$$

$$\chi_{k,m} = \sum_{s=\pm\frac{1}{2}} C(l\frac{1}{2}; m-s, s) Y_l^{m-s} \phi_{\frac{1}{2}}^s \quad (19)$$

Here,  $\chi_{k,m}$  and  $\phi_{\frac{1}{2}}^s$  are the angular and spin parts of the spinor,  $C$  denotes Clebsch-Gordan coefficients and  $Y_l^{m-s}$  are spherical harmonics. The Dirac equations for a single electron atom can be obtained by minimizing the expectation value of Hamiltonian. Hence two equations for orbitals obtain,

$$\frac{dP}{dr} + \frac{k}{r} P + \left(2c + \frac{V-\epsilon}{c}\right) Q = 0 \quad (20)$$

$$\frac{dQ}{dr} - \frac{k}{r} Q - \left(\frac{V-\epsilon}{c}\right) P = 0 \quad (21)$$

where  $V$  represents the one electron potential and  $\varepsilon$  results from setting undetermined multiplier  $\lambda$  equals to  $-c^2 + \varepsilon$ . For a many electrons system, Grant has been used the following Hamiltonian

$$H = \sum_k \left[ i\alpha(k)c^2 - \frac{Z}{r} \right] + \sum(\text{pairs } k, n)g(k, n) \quad (22)$$

where  $k$  runs over all electrons and  $g(k, n)$  represents two electron operator. Using the Racah's tensor operator method Grant wrote the following energy expression

$$E_T = \sum_A N_A I(A) + \sum_A [N_A(N_A - 1)/2] \times \{F^0(A, A) - \sum_{k>0} [(2j_A + 1)/(4j_A) \Gamma_{j_A k j_A} \cdot F^k(A, A)]\} + \sum(AB \text{ pairs}) N_A N_B \times \{F^0(A, B) - \sum_k \left(\frac{1}{2}\right) \Gamma_{j_A k j_B} G^k(A, B)\} \quad (23)$$

Where  $F^k$  and  $G^k$  are Slater integrals which represents the contribution to the total energy due to electrostatic interaction between A and B pair of electrons. A detail mathematical treatment can be seen from [20].

### III. RESULTS AND DISCUSSION

The energies for  $Z=1-23$  and for charge numbers 37, 38, 55, 56 are calculated from RHF, UHF, ROHF and DHF method and computed results are summarized in Table.1. For atoms (H-Ne)

ano-rc basis functions are used, and ccpvdz for (Na-Ar), aug-pc-4 for (K), ccptvz for (Ca), aug-cc-pvdz for (Sc), adzp for (Ti, V), dzp for (Rb, Sr), ugbs for (Cs, Ba) as an initial guess for the true Hartree-Fock calculation. Further description of these basis is given in Table.2. The computations are accomplished through a python code in company with python package PySCF and this is done on Linux system. More often, energies of molecules are calculated using python package PySCF but here atomic calculations are performed by the help of this package. All energies are measured in Hartree and are compared with existing [21, 22] calculated values and NIST [23] data. The difference of energies of all above mentioned methods from NIST data and Bunge are found for all aforementioned atoms. It is observed in Table.3 that the energy differences resulting from DHF method are much smaller than other methods, meaning that energies obtained from DHF method are in good agreement with NIST data. As, discussed in section1, the relativistic effects are important for atoms that have atomic number greater than 30 and must be taken into account in the wavefunctions. The RHF, ROHF and UHF methods do not account for relativistic effects and treat inter-electronic interactions in an average manner thus the energy differences for Rb, Sr, Cs and Ba atoms are considerably larger than from DHF.

Table.1. Ground state energies of Atoms  $Z=1-23, 37, 38, 55, 56$  in Hartree

Elements	Present results				Bunge 1993	NIST
	RHF	ROHF	UHF	DHF		
H	0.49(12)	0.499983742	0.499983742	0.499990378	N/A	0.49973329
He	2.861626(60)	2.861626(60)	2.861626(60)	2.8617(20)	2.861679993	2.90338609
Li	7.432(32)	7.432(40)	7.432(33)	7.433(30)	7.432726924	7.47797942
Be	14.5728(34)	14.5728(23)	14.5728(23)	14.575(22)	14.57302313	14.66844319
B	24.52(70)	24.52(70)	24.53(71)	24.54(70)	24.52906069	24.65809532
C	37.60(51)	37.60(44)	37.66(65)	37.65(42)	37.6886189	37.85578863
N	54.26(55)	54.26(50)	54.26(60)	54.33(14)	54.40093415	54.61162877
O	74.68(18)	74.68(20)	74.77(35)	74.87(13)	74.8093984	75.10984381
F	99.399(83)	99.399(83)	99.40(14)	99.49(26)	99.40934928	99.80712495
Ne	128.525(60)	128.525(60)	128.525(60)	128.67(90)	128.547098	129.0524585
Na	161.853(23)	161.853(23)	161.853(24)	162.0(13)	161.8589113	162.432
Mg	199.6082(12)	199.6082(12)	199.6082(12)	199.9(21)	199.6146361	200.3227769
Al	241.870(90)	241.870(90)	241.87(11)	242.3(15)	241.876707	242.7274558
Si	288.786(96)	288.786(96)	288.786(96)	289.4(34)	288.8543622	289.8981547
P	340.615(90)	340.615(90)	340.618(91)	341.4(13)	340.7187806	341.981871
S	397.413(43)	397.413(43)	397.413(43)	398.6(70)	397.5048955	399.0866474
Cl	459.467(20)	459.467(20)	459.471(60)	460.9(41)	459.4820719	461.4392275
Ar	526.7998(60)	526.7998(60)	526.7998(60)	528.6(0.10)	526.8175122	529.219683
K	599.157(20)	599.157(20)	599.157(20)	601.4(0.10)	599.1647831	602.02745
Ca	676.7579(15)	676.7579(15)	676.7579(15)	679.6(0.12)	676.7581817	680.23001

<b>Sc</b>	759.7(17)	759.7(17)	759.7(17)	763.3(71)	759.7357123	763.94497
<b>Ti</b>	848.2(0.11)	848.2(0.11)	848.3(93)	852.8(45)	848.4059907	853.35608
<b>V</b>	942.75(15)	942.75(21)	942.75(12)	948.1(43)	942.8843308	948.86758
<b>Rb</b>	2938.058(64)	2938.058(64)	2938.058(50)	2978(2)	2938.357453	2978.5328
<b>Sr</b>	3131.192(53)	3131.192(53)	3131.192(53)	3177(2)	3131.545686	3176.6117
<b>Cs</b>	7553.9(16)	7553.9(16)	7553.9(16)	7787(5)	7553.933658	7777.2597
<b>Ba</b>	7883.5(19)	7883.5(19)	7883.5(19)	8135(7)	7883.543827	8125.27581

Table. 2. Basis sets and their description

Basis Type	Description
ano-rc	Natural atomic orbitals relativistic correlated semi-core orbitals basis sets
ccpvdz	Correlation-consistent polarized valence-only double Zeta basis sets
aug-pc-4	Augmented polarization-consistent basis sets
ccpvtz	Correlation-consistent polarized valence triple Zeta basis functions
aug-cc-pvdz	Augmented correlation-consistent polarized valence-only double Zeta basis sets
adzp	Augmented double Zeta basis functions
dzp	Double Zeta polarized basis sets
ugbs	Universal Gaussian basis sets

Table.3. Difference of Energies in Hartree

Elements	Difference of energies from Bunge				Difference of DHF from NIST
	RHF	UHF	ROHF	DHF	
<b>H</b>	N/A	N/A	N/A	N/A	0.000257088
<b>He</b>	5.32982E-05	5.32982E-05	5.32982E-05	7.97227E-05	5.32982E-05
<b>Li</b>	3.97991E-05	1.5818E-05	3.97991E-05	0.000794195	1.5818E-05
<b>Be</b>	0.000165181	0.000165181	0.000165181	0.002728726	0.000165181
<b>B</b>	0.000430958	0.003572035	0.000430958	0.01240447	0.003572035
<b>C</b>	0.085722539	0.018836986	0.085722539	0.032972623	0.018836986
<b>N</b>	0.139764189	0.135257573	0.139764189	0.070109527	0.135257573
<b>O</b>	0.124135172	0.032456415	0.124135172	0.061039111	0.032456415
<b>F</b>	0.009497516	0.004617388	0.009497516	0.088088675	0.004617388
<b>Ne</b>	0.021520809	0.021520809	0.021520809	0.131421496	0.021520809
<b>Na</b>	0.005884657	0.005854606	0.005884657	0.21141322	0.005854606
<b>Mg</b>	0.006339071	0.006339071	0.006339071	0.311072037	0.006339071
<b>Al</b>	0.006573576	0.003197411	0.006573576	0.447788707	0.003197411
<b>Si</b>	0.067454527	0.067454527	0.067454527	0.579466482	0.067454527
<b>P</b>	0.103761322	0.099973671	0.103761322	0.755416804	0.099973671
<b>S</b>	0.091773775	0.091773775	0.091773775	1.095116282	0.091773775
<b>Cl</b>	0.014891313	0.010928414	0.014891313	1.419988608	0.010928414
<b>Ar</b>	0.01764689	0.01764689	0.01764689	1.815009042	0.01764689

<b>K</b>	0.007493831	0.007411288	0.007493831	2.319814085	0.007411288
<b>Ca</b>	0.000244831	0.000244831	0.000244831	2.891467676	0.000244831
<b>Sc</b>	0.000649302	0.002326669	0.000649302	3.564389983	0.002326669
<b>Ti</b>	0.117214648	0.066419801	0.117214648	4.40295688	0.066419801
<b>V</b>	0.134304235	0.131812486	0.134304235	5.276644236	0.131812486
<b>Rb</b>	0.298949608	0.298870404	0.298949608	40.60494735	0.298870404
<b>Sr</b>	0.352842194	0.352842194	0.352842194	45.56642456	0.352842194
<b>Cs</b>	0.00081741	0.00081741	0.000707922	233.0899014	9.763859435
<b>Ba</b>	0.000667753	0.000667753	0.000667753	252.3857958	10.65381282

The relativistic effects exist in all atoms regardless of their atomic numbers; only magnitude of these effects has central importance for required precision. The magnitude of relativistic effects is small for those atoms which have small atomic number while it is larger for heavier atoms. This is the reason that errors in energies of H-V atoms using non-relativistic methods (RHF, UHF, ROHF) are not significant but are present in greater magnitude in Rb, Sr, Cs, and Ba atoms. This is due to the fact that as the charge number increases, the three most common relativistic effects are occurred: (i) the relativistic contraction and stabilization of s orbitals and also of p orbitals but to a smaller extent, (ii) the spin-orbit splitting of p, d, f,....etc., (iii) the relativistic expansion and destabilization of d and f orbitals. These facts could be understood by writing the following Bohr's expressions for inner 1s orbital in terms of relativistic approach

$$r = a_{rel} = \frac{n^2 4\pi\epsilon_0 \hbar^2}{m_{rel} Z e^2} \quad \text{and} \quad m_{rel} = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}} \quad (24)$$

By taking all constants ( $e, \hbar, m_0, 4\pi\epsilon_0$ ) equal to 1 then the velocity for 1s orbital is  $v_{1s} = Z$ , which means that the velocity being proportional to  $Z$  and core electrons move with a speed comparable

#### IV. CONCLUSION

To test the effectiveness of the Hartree-Fock method and its variants (RHF, UHF and DHF methods) in precession measurements, ground state energies of several atoms have been calculated. Upon comparing the obtained results with other theoretical results [21, 22] and NIST data [23] for same atoms, it is found that the results are good agreement with other results. The study discusses the importance of suitable choice of basis set, resulting in greater accuracy of estimated energies. Nevertheless, the energy accuracy can further be improved using larger basis sets and with the inclusion of relativistic effects in the basis functions or by applying post Hartree-Fock methods. This review concludes that Hartree-Fock method provides a good estimation of ground state energies of atoms but in terms of precession, more better methods are available than Hartree-Fock method.

to speed of light ( $c \cong 137.036$  a.u.), therefore relativistic mass in denominator of radial equation would shrink the core orbitals. This shrinking of orbitals (s, p) causes to increase the ionization potential and electron affinities which stabilize the orbitals. This relativistically shrank radial distribution of inner s and p orbitals screen the nucleus resulting the increase in d and f orbitals and destabilize the orbitals. Consequently, the ionization potential decreases for valence d and f orbitals. The difference in energies between ground states and excited states of atoms may be affected by the stabilization/destabilization of the orbitals. It is considered in non-relativistic case that speed of light is infinite as compare to speed of electron of all orbitals, thus there is no relativistic contraction of inner orbitals. So, energies of Rb, Sr, Cs and Ba atoms calculated by using the non-relativistic methods (RHF, UHF, ROHF) end up with large errors. Because these atoms have large atomic numbers so have large atomic mass therefore their inner orbitals (s,p) must be contracted relativistically and hence their total ground state energies would increase. The results for these atoms using the DHF method are much closer to NIST data, which means that this method is a better choice for the computation of heavier atoms

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