

**Hartree-Fock Computations of the Ionization Energies and the Effective  
Nuclear Charges of the First Ten Elements of the Periodic Table**

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*Abstract*

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*We present the Hartree-Fock computations of the effective nuclear charges, the first and the second ionization energies of the first ten elements of the periodic table. Our results are in fair agreement with those obtained from experiment.*

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**Keywords:** Hartree-Fock, first ionization energy, second ionization energy, effective nuclear charge.

## 1.0 Introduction

The most common type of an *ab initio* electronic structure approach is called the Hartree-Fock (HF) method, in which the electron-electron repulsion is taken into account in an averaged way (mean field approximation). This is a variational calculation; therefore the obtained approximate energies, expressed in terms of the system's wave function, are always equal to or greater than the exact energy, and tend to a limiting value called the Hartree-Fock limit. Many types of calculations begin with a HF calculation and subsequently correct for the omitted electronic correlation [1].

In computational physics and chemistry, the Hartree-Fock (HF) or Self-Consistent field (SCF) method is a method of approximation for the determination of the wave function and the energy of a quantum many-body system in a stationary state. In this approximation, each electron is described by a separate single-particle wave function that solves a Schrödinger-like equation [2].

The Hartree-Fock method often assumes that the exact,  $N$ -body wave function of the system can be approximated by a single Slater determinant (in the case where the particles are fermions) or by a single permanent (in the case of bosons)  $N$  spin-orbitals. By invoking the variational method, one can derive a set of  $N$ -coupled equations for the  $N$  spin-orbitals. A solution of these equations yields the Hartree-Fock wave function and energy of the system.

The Hartree-Fock method finds its typical application in the solution of the Schrödinger equation for atoms, molecules, nanostructures and solids but it has also found widespread use in nuclear physics. In atomic structure theory, calculations may be for a spectrum with many excited energy levels and consequently the Hartree-Fock method for atoms assumes the wavefunction is a single configuration state function with well-defined quantum numbers and that the energy level is not necessarily the ground state. Initially, both the Hartree method and the Hartree-Fock method were applied exclusively to atoms, where the spherical symmetry of the system allowed one to greatly simplify the problem. These approximate methods were (and are) often used together with the central field approximation, to impose that electrons in the same shell have the same radial part, and to restrict the variational solution to be a spin Eigen function. Even so, solutions by hand, of the Hartree-Fock equations for a medium sized atom were laborious; small molecules required computational resources far beyond what was available before 1950 [3].

## 2.0 Theoretical Analysis

In quantum mechanics an atom can be viewed as a many-particle system. While the wave function for a single particle system is a function of only the coordinates of that particular particle and time,  $\Psi(\mathbf{r}, t)$ , a many-particle system will depend on the coordinates of all the particles.

The Born-Oppenheimer Hamiltonian for  $N$  electrons moving about a heavy nucleus can be written as

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$$\hat{H} = \sum_{i=1}^N \frac{\hat{P}_i^2}{2m} - \sum_i \frac{Ze^2}{\vec{r}_i} + \sum_{i<j}^N \frac{e^2}{\vec{r}_{ij}} \tag{1}$$

Here, ( $r_i$ ) is the location/position of electrons,  $m$ ,  $-e$ , electron mass and charge respectively and  $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$ , the separation between electrons  $i$  and  $j$ .

The three sum of equation (1) embody

- a. the electron kinetic energy (the first term),
- b. the electron-nucleus attraction (the second term), and
- c. the electron-electron coulomb repulsion (the third term).

For the accuracy of the self consistent field, other approximations were neglected such as the spin-orbit interaction, hyperfine interaction, recoil motion of nucleus and relativity.

The self-consistent field methods are based on the Rayleigh-Ritz variational principle, which states that the ground state Eigen function of the Hamiltonian,  $\Psi(x_1, x_2, \dots, x_N)$ , is the wave function that minimizes the expectation value of H,

$$E = \langle \Psi | H | \Psi \rangle \tag{2}$$

subject to the constraints that  $\Psi$  obey the Pauli principle (i.e., that it be anti-symmetric under the interchange of any two of the  $x$ 's) and that it be normalized to unity:

$$\int |\Psi|^2 d^N x = 1 \tag{3}$$

where  $d^N x$  is the integration over all the spatial coordinates and summation over all of the spin coordinates of the  $N$  electrons. Also, this minimum value of  $E$  represents the ground state energy [2].

Electrons are fermions which obey Pauli's exclusion principle. This requires that the wave function  $\Psi$  of electrons should be anti-symmetric with respect to the interchange of coordinates  $x$  of any two electrons.

$$\Psi(x_1, x_2, \dots, x_N) = -\Psi(x_1, x_2, \dots, x_N) \tag{4}$$

Slater determinants satisfy this anti-symmetric condition through appropriate linear combination of Hartree products, which are the non-interaction electron wavefunctions.

For an  $N$ -electron system, the Slater determinant becomes,

$$\Psi(x_1, x_2, \dots, x_N) = (N!)^{-\frac{1}{2}} \det \psi_\alpha(x_j) \tag{5}$$

The physical interpretation of this wavefunction is that each electron moves independently in an orbital  $\psi_\alpha$  under the average influence of all other electrons [4].

It may be noted here that the Slater determinantal wavefunction can also be conveniently written as

$$\Psi^N = \frac{1}{\sqrt{N!}} \sum_{P-1}^{N!} (-1)^p P \{ \chi_i(x_1) \chi_j(x_2) \dots \chi_k(x_N) \} \tag{6}$$

where the summation is over all possible  $N!$ , number of permutations amongst the  $N$  completely identical electrons and  $p$  is the parity of the permutation  $P$  [5].

For orthonormality,

$$\int \psi_\alpha^*(x) \psi_{\alpha'}(x) dx = \delta_{\alpha\alpha'} \tag{7}$$

Since the Hamiltonian (1) does not involve the electron spin variables, the spins decouple from the space degree of freedom, so that each single-particle wavefunction can be written as a product of space and spin functions:

$$\psi_\alpha(x) = \chi_\alpha(\vec{r}) |\sigma_\alpha\rangle \tag{8}$$

where  $\sigma_\alpha = \pm 1/2$  is the spin projection of the orbital  $\alpha$ . The orthonormality constraint in (7) then takes the form

$$\delta_{\sigma_\alpha \sigma_{\alpha'}} \int \chi_\alpha^*(\vec{r}) \chi_{\alpha'}(\vec{r}) d^3 r = \delta_{\alpha\alpha'}, \tag{9}$$

So the orbitals can be orthogonal by either their spin or space dependence.

After some algebra, the energy,  $E$ , is given by

$$E = \sum_{\alpha=1}^N \left\langle \alpha \left| \frac{p^2}{2m} \right| \alpha \right\rangle + \int \left[ -\frac{Ze^2}{r} + \frac{1}{2} \Phi(\vec{r}) \right] \rho(\vec{r}) d^3 r - \frac{1}{2} \sum_{\alpha, \alpha'=1}^N \delta_{\sigma_\alpha \sigma_{\alpha'}} \left\langle \alpha \alpha' \left| \frac{e^2}{r_{ij}} \right| \alpha \alpha' \right\rangle \tag{10}$$

In this expression, the one-body matrix elements of the kinetic energy are

$$\left\langle \alpha \left| \frac{p^2}{2m} \right| \alpha \right\rangle = -\frac{\hbar^2}{2m} \int \chi_\alpha^*(\vec{r}) \nabla^2 \chi_\alpha(\vec{r}) d^3 r \tag{11}$$

The electron density is the sum of the single-particles densities,

$$\rho(\vec{r}) = \sum_{\alpha=1}^N |\chi_\alpha(\vec{r})|^2 \tag{12}$$

The electrostatic potential generated by the electrons is

$$\Phi(\vec{r}) = e^2 \int \frac{1}{\vec{r} - \vec{r}'} \rho(\vec{r}') d^3 r' \tag{13}$$

so that

$$\nabla^2 \Phi = -4\pi e^2 \rho(\vec{r}), \quad (14)$$

and the exchange matrix elements of the inter-electron repulsion are

$$\left\langle \alpha\alpha' \left| \frac{e^2}{r_{ij}} \right| \alpha'\alpha \right\rangle = e^2 \int \chi_\alpha^*(\vec{r}) \chi_{\alpha'}(\vec{r}') \frac{1}{|\vec{r} - \vec{r}'|} \chi_{\alpha'}(\vec{r}) \chi_\alpha(\vec{r}') d^3r d^3r' \quad (15)$$

The interpretation of the various terms of (10) is quite straight forward. The kinetic energy is the sum of the kinetic energies of single particle orbitals, while the electron-nucleus attraction and direct inter-electron repulsion are just what would be expected from a total charge of  $-Ne$  distributed in space with density  $\rho(\mathbf{r})$ . The final term in (10) is the exchange energy, which arises from the anti-symmetry of the trial wave function (5). It is a sum over all pairs of orbitals with the same spin projection; pairs of orbitals with different spin projections are “distinguishable” and therefore do not contribute to this term.

### Ionization Energy

Ionization energy can be defined as being the energy required to remove the outermost electron from a gaseous atom. A "gaseous atom" means an atom that is all by itself, not hooked up to others in a solid or a liquid. When enough energy is added to an atom, the outermost electron can use that energy to pull away from the nucleus completely, leaving behind a positively charged ion. The ionization energy is the exact quantity of energy that it takes to remove the outermost electron from the atom [6]. The first and second ionization energies are depicted by

$$1^{\text{st}} \text{ ionization energy: } X_{(g)} \rightarrow X_{(g)}^+ + e^- \quad (16)$$

$$2^{\text{nd}} \text{ ionization energy: } X_{(g)}^+ \rightarrow X_{(g)}^{2+} + e^- \quad (17)$$

The relationship between nuclear charge,  $Z$  and effective nuclear charge  $Z^*$  is given by

$$Z^* = Z - S \quad (18)$$

where  $S$  is the shielding.

### 3.0 Material and Methods

We used the FORTRAN code developed by Koonin and Meredith [2]. For a large atom with many electrons, the accurate solution of the Hartree-Fock equation is a considerable task. However, if we consider the ground state of systems with at most 10 electrons (requiring three shells: 1s, 2s and 2p), then the numerical work can be managed in a reasonable amount of time. A lattice of several hundred points with a radial step size of  $\leq 0.01 \text{ \AA}$  extending out to  $\approx 3 \text{ \AA}$  should be sufficient for most cases [2].

First, the code is compiled and installed in the computer system. The programme runs interactively. A menu choice is made to change physical parameters to the system of interest. The following are then inputted: the nuclear charge for the atomic system, number of electrons in the 1s state, number of electrons in the 2s state, number of electrons in the 2p state, radial step size in Angstrom, outer radius of the lattice in Angstrom and number of iterations.

Output is then set to be displayed on the screen and also saved in a file with a filename of our choice. The code is then run which displays output on the screen and also saves the result of the run in a file.

The ground state energy was first computed. Then energies of the ions ( $X^+$  and  $X^{2+}$ ) were computed. Subsequently, the effective nuclear charges, the first and second ionization energies were calculated for the first ten elements of the periodic table. The results were then analyzed using the graphing tool *Origin 5.0*.

### 4.0 Results and Discussion

Table 1: Ground state and ionization energies

Element (Atomic)	Ground State	Computed Values		Experimental values [12]	
		1st ionization (eV)	2nd ionization	1 <sup>st</sup> Ionization (eV)	2nd ionization
Hydrogen (1)	-8.400	8.400		13.5984	
Helium (2)	-77.638	31.415	46.223	24.5874	54.4176
Lithium (3)	-183.655	3.359	73.759	5.3917	75.6400
Beryllium (4)	-388.380	10.907	18.840	9.3227	18.2111
Boron (5)	-654.160	10.800	24.301	8.2980	25.1548
Carbon (6)	-1006.818	13.032	20.239	11.2603	24.3833
Nitrogen (7)	-1455.460	15.917	33.890	14.5341	29.6013
Oxygen (8)	-2008.563	16.091	40.556	13.6181	35.1211
Fluorine (9)	-2676.801	23.226	47.737	17.4228	34.9708
Neon (10)	-3470.442	31.097	56.995	21.5646	40.9630

Table 2: 1st and 2nd Effective Nuclear Charge  $Z^*$

Element	Effective nuclear charge $Z^*_1$	Effective nuclear charge $Z^*_2$
Hydrogen	.849	
Helium	1.844	
Lithium	2.937	2.844
Beryllium	3.538	3.689
Boron	4.390	4.531
Carbon	5.135	5.375
Nitrogen	5.877	6.130
Oxygen	6.614	6.872
Fluorine	7.351	7.611
Neon	8.084	8.347

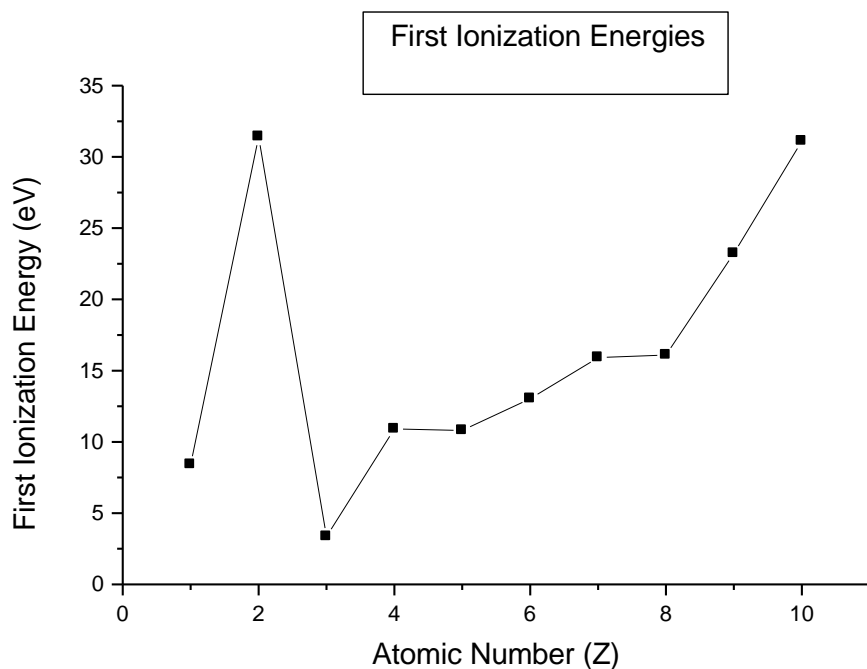


Figure 1: First ionization energy Vs. atomic number (Z)

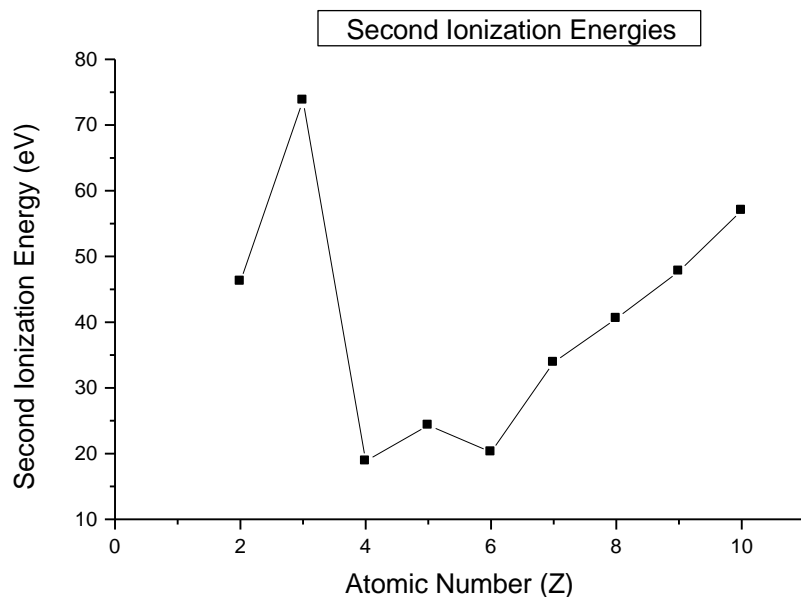


Figure 2: Second ionization energy Vs. atomic number (Z)

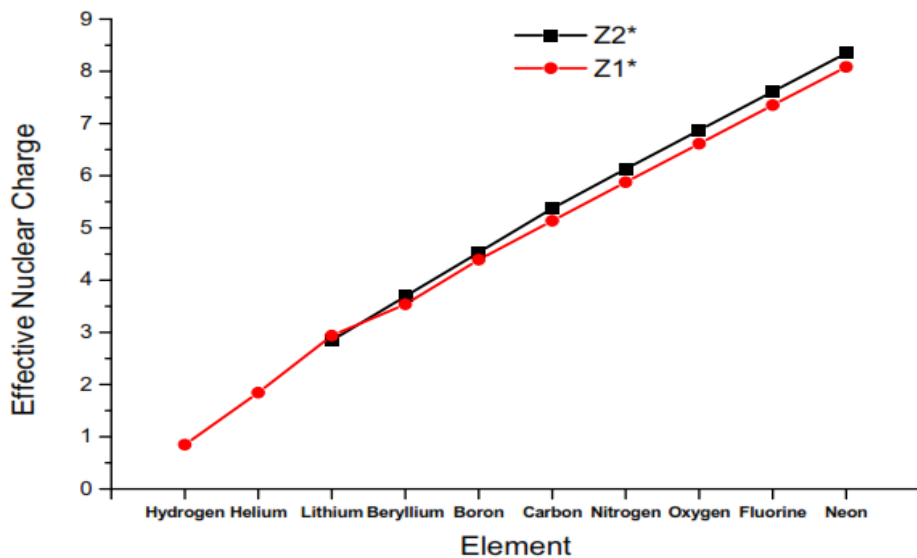


Figure 3: Effective nuclear charge Z\* vs. elements

Table 1 gives the computed ground state total energies and the values of the first and second ionization energies of the first ten elements of the periodic table.

From Table 1, the computed ground state energies are all negative. This means that the energies bind the electrons to the nucleus. In all the tables, the energies fall consistently from Hydrogen to Neon.

From Table 1, it can be observed that the first ionization energy of Helium is greater than that of hydrogen. This is in agreement with the results of Rioux and DeKock [7]. The electrons provide some screening for each other as mutual repulsion pushes them away from the nucleus. The outer electron of Lithium occupies a new shell screened by two electrons and the ionization is much less than that of Hydrogen or Helium. This is in good agreement with the results of Lang and Smith [8]. Similarly, the computed first ionization energy of Beryllium is higher than that of lithium but much lower than that of helium. The second ionization energies from helium to boron are higher and follow a similar pattern [9].

From Table 1, Figure 1 and Figure 2, the second ionization energies are more than the first ionization energies. This is so because at the second level, there are more protons than electrons holding the electrons down therefore more energy is required to pull out the second electron than the first [9]. The remarkable difference between the first and second ionization energies of lithium is due to the sudden breaking-in to an inner level, closer to the nucleus with less shielding [10].

Table 2 and Figure 3 show the computed effective nuclear charge for the first ten elements of the periodic table.  $Z_1^*$  shows a steady increase from Hydrogen to Neon. Going across the table, the effective nuclear charge increases because the electrons do not move farther away from the nucleus (they stay in the same orbital). However, the charge of the nucleus increases as more protons are present. Because of shielding, the effective nuclear charge is somewhat less than the nuclear charge [11]. From figure 3, it can be seen that as the nucleus becomes more positive, the effective nuclear charge,  $Z^*$ , increases.

The computed first and second ionization energies compare favourably with National Institute of Standards and Technology (NIST) experimental data as reported by [12].

## 5.0 Conclusion

The Hartree-Fock method was used to compute the effective nuclear charge, the first and the second ionization energies of the first ten elements of the periodic table. To a reasonable degree, there was a good agreement between the computed values with experimental values. A characteristic change between helium and lithium in the first ionization energy was observed. Also, a jump in energy between the first and second ionization energies for lithium was observed.

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