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Analytical estimate of effective charge and ground-state energies of two to five electron sequences up to atomic number 20 utilizing the variational method

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Abstract

Background The variational method, a quantum mechanical approach, estimates effective charge distributions and ground-state energy by minimizing the Hamiltonian's expectation value using trial wave functions with adjustable parameters. This method provides valuable insights into system behavior and is widely used in theoretical chemistry and physics. This paper aims to investigate ground-state energies and isoelectronic sequences using the variational method, introducing a novel approach for analyzing multi-electron systems. This technique allows for determining effective charge values and ground-state energies for 2–5 electrons sequence up to $Z \leq 20$. Hydrogenic wave functions are used as a trial wave function to calculate effective charge in 1 s, 2 s, and 2p states. Two varying parameters were used to calculate an approximate wave function for the system. These values are then used in non-relativistic Hamiltonian with electron–electron interaction terms to calculate the ground-state energy of an atom.

Result The results align with the reported experimental values, showing a marginal 1% error.

Conclusion A Python algorithm is established based on the variational principle. It was found that, based on a few selected parameters in scripting the program, a very promising result was obtained. Furthermore, adding more variational parameters can minimize the difference between experimental and theoretical values, and this technique can be extended to elements with higher atomic numbers.

Keywords Shielding effect, Electron–electron interaction, Trial wave function, Variational parameter, Quantum, Approximation method

1 Background

Various theoretical methods [1–14] are used to solve multi-electron systems. In 1959, Kinoshita et al. [15] improved the ground-state energy of the Helium atom by using a variational method. In 1966, Kotchoubey et al.

[16] calculated the energy and wave function of the lowest state of the Beryllium atom by developing and using an algorithm on the IBM 7090/94 computer systems. In 1976, Bunge et al. [17] yielded the ground-state energy of Beryllium by testing new configuration-interaction (CI) ideas. In 1978, Sucher estimated any atom's ground-state energy using the atomic shell model [18]. In 1981, Pearson et al. [19] estimated the energies for several two- and three-electron atoms in both ground and excited states using a simple and semiclassical model. In 1982, Kregar et al. [20] calculated the energies of atoms and ions up to Neon by an elementary approach. In 1984, Crandall

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et al. [21] calculated classical electron trajectories and a complete set of Eigenfunctions of the Hamiltonian for the class of "Helium-like" atomic model. In the same year, Kregar et al. [22] evaluated the effective charges for individual electrons using a simple algorithm. In 1986, Parker et al. [23] Calculated energies of inner electrons in atoms by assuming a Coulombic potential experienced by each electron. In 1989, Anno et al. discussed the Relativistic effect on the total electronic energy of an atom for obtaining the non-relativistic total energy [24]. In 1991, Davidson et al. [25] calculated the improved non-relativistic stationary nucleus correlation energies of the ground-state atomic ions from 3 to 10 electrons and Z up to 20. In 1993, Chakravorty et al. [26] estimated the non-relativistic correlation energies and relativistic corrections to ionization potentials for atomic ions with 11 to 18 electrons. In 2004, Rodrigues et al. [27] obtained binding energies for the Lithium (3 electrons) to the Dubnium (105 electrons) isoelectronic series using Dirac–Fock approximation. In 2021, Khan et al. [28] calculated ground-state energy and effective charges for 1 s and 2 s for the Beryllium atom using the variational method. This paper studies ground-state energies and isoelectronic sequences based on the variational method. For this purpose, a method is proposed to investigate a multi-electron system. This work explores the shape resonance behavior in two-electron atoms below the critical nuclear charge (CNC). It follows the resonance trajectory from critical nuclear charge (Z_c) to very tiny nuclear charges using complex-scaling and Hylleraas configuration–interaction basis functions [29]. The Deep post Hartree–Fock (DeePHF) method is a machine learning-based approach for accurate and transferable ground-state energy models in electronic structure problems, with reduced computational cost and linear scaling [30]. The research presents PauliNet, a deep quantum Monte Carlo (QMC) technique that computes electrical excited states via deep neural networks. For molecules with up to a few dozen electrons, it produces almost precise ground-state solutions and solves the Schrödinger equation [31]. A new algorithm has been developed to reduce computational expenses by ensuring that the cost of estimating ground-state energy increases linearly with the number of accuracy bits, thus reducing the need for an exponentially increasing number of gates for each circuit [32]. In this method, an approximation is given to estimate analytically the effective charge in a multi-electron system for which the Schrodinger equation could not be solved exactly. For instance, using this approach, the boron atom has been selected to calculate effective charges for 1 s and 2 s orbit and ground-state energies. Hamiltonian has been calculated for unperturbed and perturbed systems. We assume the nuclear charge is not shielded by the

electrons in an unperturbed system, neglecting the effect of electron–electron interaction. In a perturbed system, we assume a shielding effect of the nuclear charge by the electrons to improve the acquired results for the unperturbed system.

2 Methodology

Due to an increase in the number of electrons in many electron systems, many additional terms are included in Hamiltonian, such as electron–electron interaction, spin–orbit interaction, and relativistic correction. One can write a modified Hamiltonian for the N electron system as:

$$H = H_o + H_{ee} + H_r + H_D + H_{SO} \quad (1)$$

where, H_{ee} denotes electron–electron interaction, H_r denotes relativistic correction, H_D denotes Darwin's term, and H_{SO} denotes spin–orbit interaction. These terms may be considered a perturbation to a system's total energy. In atomic systems, the effects of spin–orbit interaction and electron–electron repulsion are major perturbations, with their relative significance fluctuating according to the atomic number Z. For lighter elements (low Z), the effect of electron–electron repulsion is the main effect. In contrast, in heavier elements, the spin–orbit interaction becomes more important. Due to these interactions, it isn't easy to calculate the exact theoretical solution in many electron systems. Different approximation methods have been developed to obtain an approximate solution of an atom. For a system in which electrostatic repulsion between electrons is stronger than other interactions, the Hamiltonian can be written as a sum of core Hamiltonian and electron–electron interaction:

$$H = H_o + H_{ee} = \sum_i^N \left[\frac{p^2}{2m} - \frac{kZe^2}{r_i} \right] + \sum_{i \neq j} \frac{ke^2}{r_{ij}} \quad (2)$$

The spatial solution of Eq. (2) is an eigenfunction of the Hamiltonian with Eigenvalue E. Due to the second term in the equation, the separation of variable technique is not applicable to solving Eq. (2); therefore, an approximation method is generally used to find the solution of Hamiltonian [33–38]. An improved variational method based on variational parameters resolves these issues. These parameters are further used to analytically evaluate the effective charge of many states and the ground-state energy of the system. The theory used in this work is the same as in [28]. We reported effective charge and ground-state energies for two, three, four, and five electron sequences for atomic numbers up to $Z=20$. However, we used boron as

an example to show the calculation. The methodology used is summarized in Fig. 1.

2.1 Calculation for Boron

To calculate the ground-state energy of an atom, the variation method is one the most common techniques used in atomic physics; this method requires a trial wave function and then calculating the expected energy of that trial wave function as a function of the parameters that describe the wave function. A good choice of trial wave function form is essential for the success of the variational method. To calculate the ground-state energy of Boron, the trail wave functions of boron for different states, i.e., 1 s,2 s,2px is given below:

$$\Psi_{100} = \left(\frac{Z_{eff1}}{a_0}\right)^{\frac{3}{2}} \frac{1}{(\pi)^{\frac{1}{2}}} e^{-\frac{Z_{eff1}r}{a_0}} \tag{3}$$

$$\Psi_{200} = \left(\frac{Z_{eff2}}{a_0}\right)^{\frac{3}{2}} \frac{1}{(32\pi)^{\frac{1}{2}}} \left(2 - \frac{Z_{eff2}r}{a_0}\right) e^{-\frac{Z_{eff2}r}{2a_0}} \tag{4}$$

$$\Psi_{21-1} = \left(\frac{Z_{eff2}}{a_0}\right)^{\frac{3}{2}} \frac{1}{(64\pi)^{\frac{1}{2}}} \left(\frac{Z_{eff2}r}{a_0}\right) \sin\theta e^{-\frac{Z_{eff2}r}{2a_0}} e^{-i\theta} \tag{5}$$

2.2 Expected Unperturbed energy calculation for all electrons

The following equation calculates the unperturbed Hamiltonian:

$$\widehat{H}_o = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 - \sum_i \frac{Ze^2}{4\pi \epsilon_o r_i} \tag{6}$$

$$\widehat{H}_o = 2\widehat{H}_1 + 2\widehat{H}_2 + \widehat{H}_3 \tag{7}$$

$$E_o = 2E_1 + 2E_2 + E_3 \tag{8}$$

Here,

$$E_1 = \langle \Psi_{100} | \widehat{H}_1 | \Psi_{100} \rangle \tag{9}$$

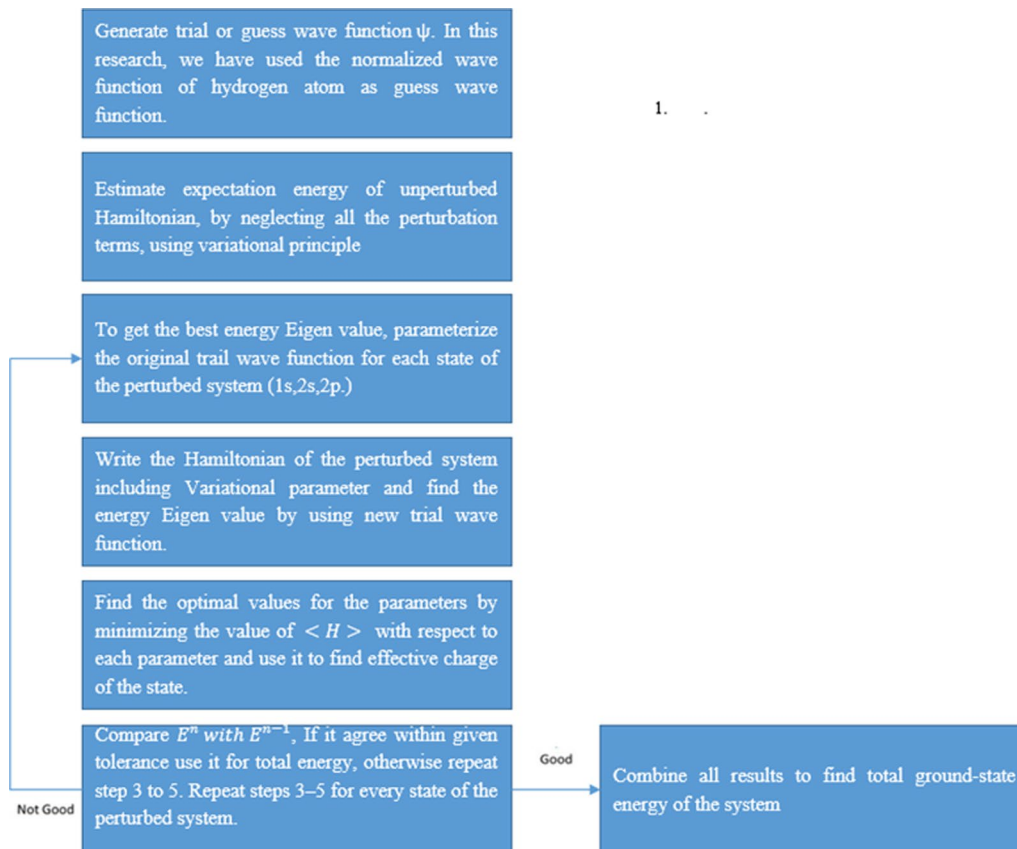


Fig. 1 Simplified algorithmic flowchart of the used methodology

$$E_1 = \left\langle \Psi_{100} \left| -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{Z_{\text{eff1}} e^2}{4\pi \epsilon_0 r_1} \right| \Psi_{100} \right\rangle \tag{10}$$

$$E_1 = \frac{0.5Z_{\text{eff1}}^2 \hbar^2}{a_0^2 m} - \frac{0.79577Z_{\text{eff1}}^2 e^2}{a_0 \epsilon_0} \tag{11}$$

$$E_2 = \left\langle \Psi_{200} \left| \hat{H}_2 \right| \Psi_{200} \right\rangle \tag{12}$$

$$E_2 = \left\langle \Psi_{200} \left| -\frac{\hbar^2}{2m} \nabla_2^2 - \frac{Z_{\text{eff2}} e^2}{4\pi \epsilon_0 r_2} \right| \Psi_{200} \right\rangle \tag{13}$$

$$E_2 = \frac{0.125Z_{\text{eff2}}^2 \hbar^2}{a_0^2 m} - \frac{0.01989Z_{\text{eff2}}^2 e^2}{a_0 \epsilon_0} \tag{14}$$

$$E_3 = \left\langle \Psi_{211} \left| \hat{H}_3 \right| \Psi_{211} \right\rangle \tag{15}$$

$$E_3 = \left\langle \Psi_{211} \left| -\frac{\hbar^2}{2m} \nabla_3^2 - \frac{Z_{\text{eff2}} e^2}{4\pi \epsilon_0 r_3} \right| \Psi_{211} \right\rangle \tag{16}$$

$$E_3 = \frac{0.104167Z_{\text{eff2}}^2 \hbar^2}{a_0^2 m} - \frac{0.0199Z_{\text{eff2}}^2 e^2}{a_0 \epsilon_0} \tag{17}$$

Put values of E_1, E_2, E_3 in Eq. (8):

$$E = \frac{Z_{\text{eff1}}^2 \hbar^2}{a_0^2 m} - \frac{1.59154Z_{\text{eff1}}^2 e^2}{a_0 \epsilon_0} + \frac{0.354167Z_{\text{eff2}}^2 \hbar^2}{a_0^2 m} - \frac{0.05968Z_{\text{eff2}}^2 e^2}{a_0 \epsilon_0} \tag{18}$$

2.3 Ground-state energy estimation for perturbed system

For the Perturbed System, to improve our results, we replaced Z_{eff1} with $Z - \alpha_1 - \alpha$ and Z_{eff2} by $Z - \alpha_2 - \beta/7.5$ in trail wave function where $\alpha_1 = 0$ for $1s^2$ and $\alpha_2 = 2$ for $2s^2$. The Hamiltonian of the perturbed system is given by Eq. (19):

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 - \sum_i \frac{Ze^2}{4\pi \epsilon_0 r_i} + \sum_{i \neq j} \frac{e^2}{4\pi \epsilon_0 r_{ij}} = \hat{H}_o + \hat{H}' \tag{19}$$

Ground Perturbed Energy for $1s^2$:

$$E = 2E_1 + V(r_{12}) \tag{20}$$

Ground Perturbed Energy for $2s^2$:

$$E = 2E_2 + V(r_{34}) + V(r_{13}) + V(r_{14}) + V(r_{23}) + V(r_{24}) \tag{21}$$

Since, $V(r_{13}) = V(r_{14}) = V(r_{23}) = V(r_{24})$. So,

$$E = 2E_2 + V(r_{34}) + 4V(r_{13}) \tag{22}$$

Ground Perturbed Energy for $2px$:

$$E = E_3 + V(r_{35}) + V(r_{45}) \tag{23}$$

Here, $V(r_{35}) = V(r_{45})$. So,

$$E = E_3 + 2V(r_{35}) \tag{24}$$

So, the total Hamiltonian:

$$\begin{aligned} \hat{H} = & 2\hat{H}_1 + 2\hat{H}_2 \\ & + \hat{H}_3 + \frac{e^2}{4\pi \epsilon_0 r_{12}} \\ & + \frac{e^2}{4\pi \epsilon_0 r_{34}} \\ & + \frac{4e^2}{4\pi \epsilon_0 r_{13}} \\ & + \frac{2e^2}{4\pi \epsilon_0 r_{35}} \end{aligned} \tag{25}$$

And total Energy:

$$E = 2E_1 + 2E_2 + E_3 + V(r_{12}) + V(r_{34}) + 4V(r_{13}) + 2V(r_{35}) \tag{26}$$

$$E_1 = \left\langle \Psi_{100} \left| \hat{H}_1 \right| \Psi_{100} \right\rangle \tag{27}$$

$$E_1 = \left(\frac{\alpha}{a_0} \right)^6 \frac{1}{\pi^2} \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \int_0^\infty e^{-\alpha \left(\frac{r}{a_0} \right)} r^2 \left[-\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\alpha e^2}{4\pi \epsilon_0} \right] e^{-\frac{\alpha r}{a_0}} dr \tag{28}$$

$$E = 2E_1 + 2E_2 + E_3 + V(r_{12}) + V(r_{34}) + 4V(r_{13}) + 2V(r_{35}) \tag{29}$$

$$E_2 = \left\langle \Psi_{200}^* \left| \hat{H}_2 \right| \Psi_{200} \right\rangle \tag{30}$$

$$E_2 = \left(\frac{\beta}{2a_0} \right)^6 \frac{1}{(32\pi)^2} \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \int_0^\infty e^{-\frac{\beta r}{4a_0}} \left(2 - \frac{\beta r}{2a_0} \right)^2 \left[-\frac{\hbar^2}{2m} \nabla_2^2 - \frac{\beta e^2}{8\pi \epsilon_0} \right] e^{-\frac{\beta r}{4a_0}} \left(2 - \frac{\beta r}{2a_0} \right) dr \tag{31}$$

$$E_2 = \frac{0.03125\beta^2\hbar^2}{a_o^2m} - \frac{0.004974\beta^2e^2}{a_o \in_o} \tag{32}$$

$$E_3 = \langle \Psi_{211} | \hat{H}_3 | \Psi_{211} \rangle \tag{33}$$

$$E_3 = \left(\frac{\beta}{2a_o}\right)^6 \frac{1}{(64\pi)^2} \int_0^{2\pi} d\theta \int_0^\pi \sin^2\theta \int_0^\infty e^{-\frac{\beta r}{4a_o}} \left(\frac{\beta r}{2a_o}\right)^2 \left[-\frac{\hbar^2}{2m} \nabla_3^2 - \frac{\beta e^2}{8\pi \in_o}\right] e^{-\frac{\beta r}{4a_o}} \left(\frac{\beta r}{2a_o}\right) \sin\theta dr d\theta \tag{34}$$

$$E_3 = \frac{0.026\beta^2\hbar^2}{a_o^2m} - \frac{0.0049736\beta^2e^2}{a_o \in_o} \tag{35}$$

2.4 Electron–electron interactions

$$V(r_{12}) = \frac{e^2}{4\pi \in_o} \left(\frac{\alpha}{a_o}\right)^6 \frac{1}{\pi^2} \int_0^\infty e^{-2\alpha\left(\frac{r_1}{a_o}\right)} r_1^2 \int_0^\infty e^{-2\alpha\left(\frac{r_2}{a_o}\right)} r_2^2 \int_0^\pi \frac{\sin\theta_2 d\theta_2}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2\cos\theta_2}} dr_2 dr_1 \tag{36}$$

$$\int_0^\pi \sin\theta_1 d\theta_1 \int_0^{2\pi} d\theta_2 \int_0^{2\pi} d\theta_1 \tag{37}$$

Using the following integral, simplify the equation:

$$\int x^n e^{-\frac{uvx}{w}} dx = -\frac{w}{uv} x^n e^{-\frac{uvx}{w}} - \sum_{i=1}^n \left[\prod_{l=1}^i (n+1-l) \right] \left(\frac{w}{uv}\right)^{i+1} x^{n-i} e^{-\frac{uvx}{w}} \tag{38}$$

$$\int_0^\infty x^n e^{-\frac{uvx}{w}} dx = \left(\frac{w}{uv}\right)^{n+1} \left[\prod_{l=1}^n (n+1-l) \right] \tag{39}$$

$$\int_0^r x^n e^{-\frac{uvx}{w}} x^n e^{-\frac{uvx}{w}} dx = -\frac{w}{uv} r^n e^{-\frac{uvr}{w}} + \left(\frac{w}{uv}\right)^{n+1} \left[\prod_{l=1}^n (n+1-l) \right] \tag{40}$$

$$- \sum_{i=1}^n \left[\prod_{l=1}^i (n+1-l) \right] \left(\frac{w}{uv}\right)^{i+1} r^{n-i} e^{-\frac{uvr}{w}}$$

$$\int_r^\infty x^n e^{-\frac{uvx}{w}} dx = \frac{w}{uv} r^n e^{-\frac{uvr}{w}} + \sum_{i=1}^n \left[\prod_{l=1}^i (n+1-l) \right] \left(\frac{w}{uv}\right)^{i+1} r^{n-i} e^{-\frac{uvr}{w}} \tag{41}$$

$$V(r_{12}) = \frac{e^2}{\pi \in_o} \left(\frac{\alpha}{a_o}\right)^3 \int_0^\infty e^{-2\alpha\left(\frac{r_1}{a_o}\right)} r_1^2 \left[-0.079577e^{-\frac{2\alpha r_1}{a_o}} \left(\frac{\alpha}{a_o}\right)^1 + \frac{0.079577}{r_1} - \frac{0.079577e^{-\frac{2\alpha r_1}{a_o}}}{r_1} \right] dr_1 \int_0^\pi \sin\theta_1 d\theta_1 \int_0^{2\pi} d\theta_1 \tag{42}$$

$$V(r_{12}) = \frac{0.0497359\alpha e^2}{a_o \in_o} \tag{43}$$

Similarly, using the same integral.

$$V(r_{34}) = \left\langle \Psi_{200} \Psi_{200} \left| \frac{e^2}{4\pi \in_o r_{12}} \right| \Psi_{200} \Psi_{200} \right\rangle \tag{44}$$

$$V(r_{34}) = \frac{0.005984\beta e^2}{a_o \epsilon_o} \tag{45}$$

$$V(r_{13}) = \frac{\langle \Psi_{200}\Psi_{100} | \frac{e^2}{4\pi\epsilon_o r_{13}} | \Psi_{200}\Psi_{100} \rangle}{\langle \Psi_{200}\Psi_{100} | \Psi_{200}\Psi_{100} \rangle} \tag{46}$$

$$V(r_{13}) = \frac{e^2}{\pi \epsilon_o} \left(\frac{5.707538}{a_o} \right)^3 \int_0^\infty e^{-\frac{11.415076r_1}{a_o}} r_1^2 \left[-0.0012434r_1^2 e^{-\frac{\beta r_1}{2a_o}} \left(\frac{\beta}{a_o} \right)^3 - 0.0049736r_1 e^{-\frac{\beta r_1}{2a_o}} \left(\frac{\beta}{a_o} \right)^2 - 0.02984e^{-\frac{\beta r_1}{2a_o}} \left(\frac{\beta}{a_o} \right)^1 + \frac{0.0795775}{r_1} - \frac{0.0795775e^{-\frac{\beta r_1}{2a_o}}}{r_1} \right] dr_1 \int_0^\pi \sin\theta_1 d\theta_1 \int_0^{2\pi} d\phi_1 \tag{47}$$

$$V(r_{13}) = \frac{12.5664e^2}{\epsilon_o} \left[-\frac{0.002375\beta}{(0.0438\beta + 1)^3 a_o} - \frac{0.000104\beta^2}{(0.0438\beta + 1)^4 a_o} - \frac{0.0000091122\beta^3}{(0.0438\beta + 1)^5 a_o} + \frac{0.0361434}{a_o} - \frac{0.0361434}{(0.0438\beta + 1)^2 a_o} \right] \tag{48}$$

$$V(r_{35}) = \frac{\langle \Psi_{211}\Psi_{200} | \frac{e^2}{4\pi\epsilon_o r_{35}} | \Psi_{211}\Psi_{200} \rangle}{\langle \Psi_{211}\Psi_{200} | \Psi_{211}\Psi_{200} \rangle} \tag{49}$$

$$V(r_{35}) = \frac{e^2}{32\pi \epsilon_o} \left(\frac{\beta}{2a_o} \right)^3 \int_0^\infty e^{-\frac{\beta r_1}{2a_o}} r_1^2 \left(2 - \frac{\beta r_1}{2a_o} \right)^2 \left[\frac{0.95493e^{-\frac{\beta r_1}{2a_o}}}{r_1^2} \left(\frac{a_o}{\beta} \right)^1 - \frac{1.90986}{r_1^3} \left(\frac{a_o}{\beta} \right)^2 + \frac{1.90986e^{-\frac{\beta r_1}{2a_o}}}{r_1^3} \left(\frac{a_o}{\beta} \right)^2 + 0.009947e^{-\frac{\beta r_1}{2a_o}} \left(\frac{\beta}{a_o} \right)^1 + \frac{0.079577}{r_1} + \frac{0.159155e^{-\frac{\beta r_1}{2a_o}}}{r_1} \right] dr_1 \int_0^\pi \sin\theta_1 d\theta_1 \int_0^{2\pi} d\phi_1 \tag{50}$$

$$V(r_{35}) = \frac{0.005854\beta e^2}{a_o \epsilon_o} \tag{51}$$

2.5 Optimal values

To calculate the optimal values, put values. $E_1, E_2, E_3, V_{12}, V_{34}, V_{35}, V_{13}$ in Eq. (26) and find the minima concerning α and β .

$$\frac{\partial E}{\partial \alpha} = \frac{2\alpha^2}{a_h^2 m} + \frac{0.049735e^2}{a_o \epsilon_o} - \frac{0.3183\alpha e^2}{a_o \epsilon_o} \tag{52}$$

$$\alpha = 0.29246217 \tag{53}$$

$$Z_{eff1} = Z - \alpha_1 - \alpha \tag{54}$$

$$Z_{eff1} = 4.70753783 \tag{55}$$

$$\frac{\partial E}{\partial \beta} = \frac{\partial}{\partial \beta} \left(\frac{\alpha^2 \hbar^2}{a_o^2 m} - \frac{0.159154\alpha^2 e^2}{a_o \epsilon_o} + \frac{0.0885\beta^2 \hbar^2}{a_o^2 m} - \frac{0.0149216\beta^2 e^2}{a_o \epsilon_o} + \frac{0.0497359\alpha e^2}{a_o \epsilon_o} + \frac{0.017692\beta e^2}{a_o \epsilon_o} + \frac{50.2656e^2}{\epsilon_o} \left[-\frac{0.002375\beta}{(0.0438\beta + 1)^3 a_o} - \frac{0.000104\beta^2}{(0.0438\beta + 1)^4 a_o} - \frac{0.0000091122\beta^3}{(0.0438\beta + 1)^5 a_o} + \frac{0.0361434}{a_o} - \frac{0.0361434}{(0.0438\beta + 1)^2 a_o} \right] \right) \tag{56}$$

Table 1 The values of the best parameters of the trial wave function for Boron

Atomic no.	Element symbol	Z_{eff1}	Z_{eff2}	Ground-state energy (au)
5	BI	4.70753783	2.55658043	-24.64356486

$$\beta = 3.325646775 \tag{57}$$

$$Z_{eff2} = Z - \alpha_2 - \left(\frac{\beta}{7.5}\right) \tag{58}$$

$$Z_{eff2} = 2.55658043 \tag{59}$$

By putting the value of Z_{eff1} and Z_{eff2} in Eq. (18), we have calculated the ground-state energy value:

$$E = -670.9809eV = -24.64356486au \tag{60}$$

Parameters that produced the good energy eigenvalues of boron (Br I) are reported in Table 1.

Figure 2 shows a 3D projection of ground-state energy in the z-axis within parameters Z_{eff1} and Z_{eff2} in the x-y plane; in this figure intensity of the color gradient from yellow to dark blue shows variation in ground energy from minimum to maximum, respectively, the gradient shows by increasing values of Z_{eff1} and Z_{eff2} we get approximate ground-state energy.

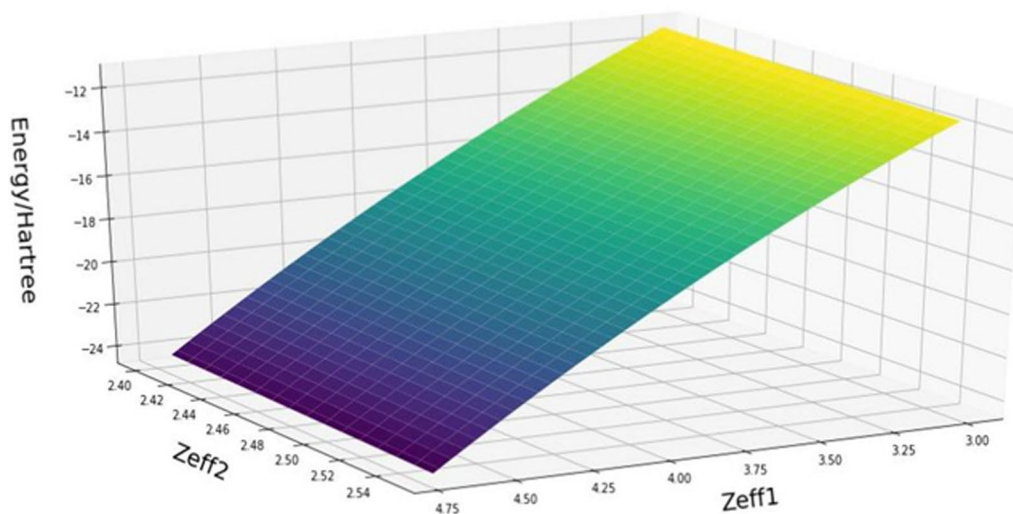


Fig. 2 The variation of the ground-state energy of the boron atom with respect to the variational parameters Z_{eff1} and Z_{eff2}

For confirmation, we compared the results of the analytical method suggested in this study with previously published experimental and theoretical data [39–42].

3 Result

From Fig. 3, it is observed that Z_{eff} greatly affects the atomic size of an atom, as the Z_{eff} decreases, the nuclear radius will grow because there is more screening of the electrons from the nucleus, as a result, the bonding energy between the nucleus and the electron decreases. Furthermore, it is also observed the screening effect is affected by the state of the atom, the value of Z_{eff2} less than Z_{eff1} . The electron close to the nucleus experiences the maximum charge of the nucleus which counterintuitively outer electrons cannot due to the shielding effect of the inner electron. The color gradient in the graph shows binding energy increases due to radius reduction.

4 Discussion

Trial wave functions (4), (5), and (6) are used to calculate ground-state energy eigenvalues for different sequence variational methods. These trial wave functions contain two variational parameters, namely. Z_{eff1} and Z_{eff2} . Our program helps us to vary the parameters successively in loops until the experimental eigenvalue reported in NIST [35] is obtained. Calculated variational parameters for

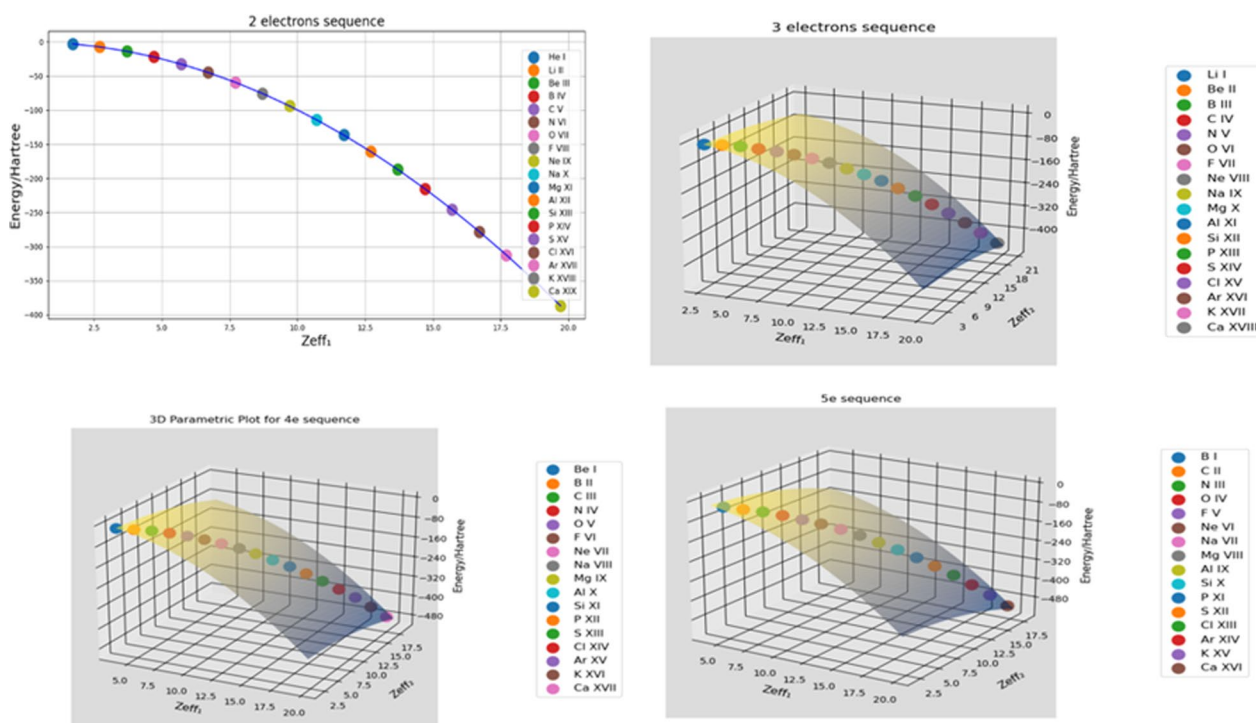


Fig. 3 Energy plotting of two, three, four, and five electron sequences with respect to variational parameters

Table 2 Comparison of the calculated results of ground-state energy of boron and beryllium atoms of sequence V and IV with reported experimental and theoretical values

Element	Parameter	Calculated values	Previously reported values	Percentage of error
B I	Calculated ground-state energy using effective charge	-24.64356486	-24.65807839 (35)	0.06
			-24.5290 (38)	0.46
Be I	Calculated ground-state energy using effective charge	-14.69746365	-14.66721 (36)	0.2
			-14.488 (37)	1.4
			-14.3423 (28)	2.4

boron are reported in Table 1, followed by Fig. 2, which shows the variation of ground-state energy of boron atoms concerning these parameters. Table 2 compares the calculated results of B I and Be I atoms of sequences V and IV with experimental and previously reported values. In Tables 3, 4, 5, and 6, various parameters for 2 electrons sequence up to $2 \leq Z \leq 20$, 3 electrons sequence up to $3 \leq Z \leq 20$, 4 electrons sequence up to $4 \leq Z \leq 20$, and 5 electrons sequence up to $5 \leq Z \leq 20$ respectively were obtained using the suggested methods and compares

them to values that were obtained experimentally [39]. For 2 electron sequences, only one parameter is involved because of single state (1 s) involvement, whereas other states are also involved in other sequences. In Fig. 3, the energy of different electron sequences concerning the variational parameters Z_{eff1} and Z_{eff2} is plotted, and it is observed that energy is affected by the shielding effect and atomic radius of the nucleus. Therefore, the different cations of the same element have different expected energy.

Table 3 Various parameters for 2 electrons sequence up to $2 \leq Z \leq 20$

Atomic no.	Element symbol	Z_{eff1}	Ground-state energy (au)	Nist data (au) [35]	Percentage of error
2	He I	1.70753783	-2.903307585	-2.903384126	0.003
3	Li II	2.70753783	-7.299640081	-7.279832599	0.3
4	Be III	3.70753783	-13.68748205	-13.65658337	0.2
5	B IV	4.70753783	-22.06683349	-22.03478841	0.1
6	C V	5.70753783	-32.4376944	-32.41595947	0.07
7	N VI	6.70753783	-44.80006478	-44.80156628	0.003
8	O VII	7.70753783	-59.15394463	-59.19344731	0.07
9	F VIII	8.70753783	-75.49933395	-75.59388265	0.1
10	Ne IX	9.70753783	-93.83623275	-94.00496995	0.2
11	Na X	10.70753783	-114.164641	-114.4313222	0.2
12	Mg XI	11.70753783	-136.4845587	-136.8716202	0.3
13	Al XII	12.70753783	-160.795986	-161.3337406	0.3
14	Si XIII	13.70753783	-187.0989226	-187.8196495	0.4
15	P XIV	14.70753783	-215.3933688	-216.333976	0.4
16	S XV	15.70753783	-245.6793244	-246.8806655	0.5
17	Cl XVI	16.70753783	-277.9567895	-279.4650351	0.5
18	Ar XVII	17.70753783	-312.2257641	-314.0922173	0.6
19	K XVIII	18.70753783	-348.4862481	-350.7691275	0.6
20	Ca XIX	19.70753783	-386.7382416	-389.4955923	0.7

Table 4 Various parameters for 3 electrons sequence up to $3 \leq Z \leq 20$

Atomic no.	Element symbol	Z_{eff1}	Z_{eff2}	Ground-state energy (au)	Nist data (au) [35]	Percentage of error
3	Li I	2.70753783	1.195188665	-7.477441542	-7.477974348	0.007
4	Be II	3.70753783	2.277260599	-14.33296958	-14.32583078	0.05
5	B III	4.70753783	3.364072635	-23.47545112	-23.42871141	0.2
6	C IV	5.70753783	4.455242132	-34.90830907	-34.78605097	0.3
7	N V	6.70753783	5.550417749	-48.63460887	-48.3989604	0.5
8	O VI	7.70753783	6.649281388	-64.65710055	-64.2692191	0.6
9	F VII	8.70753783	7.751547417	-82.97825949	-82.39936866	0.7
10	Ne VIII	9.70753783	8.856960472	-103.6003235	-102.7916177	0.8
11	Na IX	10.70753783	9.965292645	-126.5253251	-125.4508282	0.8
12	Mg X	11.70753783	11.07634052	-151.7551197	-150.3765921	0.9
13	Al XI	12.70753783	12.18992233	-179.291409	-177.577101	0.9
14	Si XII	13.70753783	13.30587529	-209.1357612	-207.0547803	1
15	P XIII	14.70753783	14.4240533	-241.2896278	-238.8150321	1
16	S XIV	15.70753783	15.54432481	-275.7543578	-272.8622295	1
17	Cl XV	16.70753783	16.66657107	-312.5312101	-309.2024731	1
18	Ar XVI	17.70753783	17.79068451	-351.6213632	-347.8418263	1
19	K XVII	18.70753783	18.91656741	-393.0259246	-388.7877861	1
20	Ca XVIII	19.70753783	20.04413074	-436.7459377	-432.0411977	1

Table 5 Various parameters for 4 electrons sequence up to $4 \leq Z \leq 20$

Atomic no.	Element symbol	Z_{eff1}	Z_{eff2}	Ground-state energy (au)	Nist data (au) [35]	Percentage of error
4	Be I	3.70753783	2.014236844	-14.69746365	-14.66843312	0.2
5	B II	4.70753783	3.018640441	-24.3352101	-24.3531327	0.07
6	C III	5.70753783	4.023250528	-36.46715156	-36.54589262	0.2
7	N IV	6.70753783	5.028051552	-51.09355893	-51.24605729	0.3
8	O V	7.70753783	6.0330293	-68.21467607	-68.45492762	0.4
9	F VI	8.70753783	7.038170886	-87.83072311	-88.17500257	0.4
10	Ne VII	9.70753783	8.043464682	-109.9418995	-110.4086782	0.4
11	Na VIII	10.70753783	9.048900217	-134.5483865	-135.1596992	0.4
12	Mg IX	11.70753783	10.05446807	-161.6503499	-162.429701	0.5
13	Al X	12.70753783	11.06015977	-191.2479417	-192.227136	0.5
14	Si XI	13.70753783	12.06596766	-223.3413021	-224.5574796	0.5
15	P XII	14.70753783	13.07188485	-257.9305606	-259.4173511	0.6
16	S XIII	15.70753783	14.07790508	-295.0158378	-296.8215236	0.6
17	Cl XIV	16.70753783	15.08402268	-334.5972457	-336.7727902	0.6
18	Ar XV	17.70753783	16.09023251	-376.6748895	-379.2785005	0.7
19	K XVI	18.70753783	17.09652984	-421.2488678	-424.347842	0.7
20	Ca XVII	19.70753783	18.1029104	-468.3192732	-471.9822847	0.8

Table 6 Various parameters for 5 electrons sequence up to $5 \leq Z \leq 20$

Atomic no.	Element symbol	Z_{eff1}	Z_{eff2}	Ground-state energy (au)	Nist data (au) [35]	Percentage of error
5	B I	4.70753783	2.55658043	-24.64356486	-24.65807839	0.06
6	C II	5.70753783	3.548716852	-37.40239339	-37.44195816	0.1
7	N III	6.70753783	4.542696842	-52.93544274	-52.98963518	0.1
8	O IV	7.70753783	5.538013099	-71.24483218	-71.29981956	0.08
9	F V	8.70753783	6.534311401	-92.33188266	-92.37359172	0.04
10	Ne VI	9.70753783	7.531342951	-116.1974311	-116.2126421	0.01
11	Na VII	10.70753783	8.528930702	-142.8420161	-142.8217445	0.01
12	Mg VIII	11.70753783	9.526946726	-172.2659892	-172.2024424	0.04
13	Al IX	12.70753783	10.52529714	-204.4695822	-204.3621223	0.05
14	Si X	13.70753783	11.523912	-239.4529495	-239.3081342	0.06
15	P XI	14.70753783	12.52273848	-277.2161939	-277.0364355	0.06
16	S XII	15.70753783	13.52173612	-317.7593841	-317.5628286	0.06
17	Cl XIII	16.70753783	14.52087359	-361.0825658	-360.8928257	0.05
18	Ar XIV	17.70753783	15.52012631	-407.1857688	-407.0315719	0.04
19	K XV	18.70753783	16.51947484	-456.0690122	-455.9889893	0.02
20	Ca XVI	19.70753783	17.51890363	-507.7323077	-507.7650781	0.006

5 Conclusion

In this research, a pattern has been generated using the **Variational Method** [28], which has been applied to 2 electrons, 3 electrons, 4 electrons, and 5 electrons sequences up to $Z \leq 20$ to calculate **ground energy states** and effective charges. In this study, the Hamiltonian is the energy operator for multi-electron systems, so

it has additional terms in the Hamiltonian of the hydrogen atom. The **Hydrogen-like wave functions** were used as **trial wavefunctions** in the variational method to find a suitable wave function to calculate the effective charges of the 1 s and 2 s states for atoms. The ground-state energies were calculated with the help of effective charge values used in the Hamiltonian. The **shielding**

effect contributes to the total energy of the atomic system. The calculated ground energies were found to be within 1%. Though the errors are small, this occurs due to approximation used in the variational principle. Adding more variational parameters can minimize the difference between experimental and theoretical values.

Acknowledgements

We thank to Professor Dr. Zaheer Uddin for their kind assistance and outstanding efforts.

Author contributions

Kousar Shaheen developed a Python program to carry out this work and extracted the results. Saba Javid worked on conclusions and rechecked the equations. Ahmed Ali Rajput set up the introduction and overall layout of the manuscript. Roohi Zafar contributed to the discussion of results and enhanced its readability.

Funding

There is no funding for this research work.

Availability of data and materials

Data used in this work are available in the respective table and can be obtained from NIST website.

Declarations

Ethics approval and consent to participate

There is no ethical issue in this research.

Consent for publication

Not applicable.

Competing interests

There is no conflict of interest among the authors.

Received: 19 May 2024 Accepted: 6 September 2024

Published online: 19 September 2024

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