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Research article

Semi-classical model and assessment of the two-electron atomic system energy in s orbitals

Jorge Andrés Ramos-Grez [*, a], **Vicente Bañados-BaySchmith** [a] **and Joaquín Meyer-Larraín** [b]

[a] Pontificia Universidad Católica de Chile, School of Engineering, Av. Vicuña
Mackenna 4860, Macul, 7820436, Santiago, Chile

[b] Pontificia Universidad Católica de Chile, Institute of Physics, Av. Vicuña Mackenna
4860, Macul, 7820436, Santiago, Chile

E-mail: jramos@uc.cl

Abstract. For physics and engineering undergraduate students, the semi-classical model formulation is a convenient approach to understanding electron behavior, which in turn facilitates the comprehension of more elaborate quantum mechanical formulations. In this line of thought, a two-electron atom semi-classical model was developed for the ground-state energy and excited states of He and ions. The two electrons are in a state occupying the same s orbital; thus, the average position distance was worked out from the classical orbital radius. Utilizing the Coulombic repulsion force between the electrons and the virial theorem, a relationship is established. Numerical results against optical spectroscopy yield an average energy relative error $< 0.23\%$. When compared against ab initio calculations, the average energy relative error is $< 2.15\%$. Exact energy values of the system for helium using ICI, QD Monte Carlo, variational and CCSD methods assessed the model. These latter results comparison can serve the purpose of illustrating to the undergraduate student that semi-classical models, although not entirely accurate, can still provide a close agreement with the scientific fundamentals to comprehend the physics behind electrons' behavior.

Keywords. Average distance between two points on a circumference, virial theorem, electron repulsive force, repulsive energy, s orbitals.

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1. Introduction

In 1912, Bohr's model for the hydrogen-like atoms (i.e., single electron system) was a breakthrough in its time; however, soon it followed that it was highly algebraically complicated to model the energy states (*eigenvalues*) of polyelectronic atoms semi-classically. In part, the electrostatic repulsion between the electrons (i.e., correlation terms) made it difficult to find closed-form exact analytical solutions to the associated Schrödinger Wave Equation (SWE). One such basic system was the helium atom with any of its s orbitals containing two electrons, be it at ground ($n = 1$) or an excited state ($n > 1$). However, from 1927 to 1929, several researchers such as Kellner [1], Slater [2], Unsöld [3], Hartree [4], Hylleraas [5] pursued this work and proposed several mathematical forms to solve the two-electron atom energy ground state problem, i.e. He

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[*] Corresponding author

atom and its isoelectronic ions. Regarding the estimation of the first ionization potential of helium, on one hand, Unsöld, applying perturbation on the Hamiltonian, obtained a low value of 20.30 eV, while by adding more terms, Kellner's solution improved to 23.75 eV. A much proximate value to Lyman's experimental result of 24.47 eV was obtained by Slater using a determinant to express the two-electron wavefunction, while Hyllerass added a correlation term to the wavefunction explicitly, achieving in both cases 24.35 eV. On the other hand, Hartree's self-consistent field method returned 24.85 eV, which overestimated the experimental values. Interesting to note is what Esposito and Naddea (2012) [6] mentioned about Italian physicist Majorana, who by 1930 had obtained 20.31 eV and later 22.95 eV for the same atomic system. Moreover, it is of scientific interest to continue looking for models and closed-form expressions for the energy eigenvalues of systems with more than one electron. To achieve this objective, one strategy has been based on a semi-classical interpretation of the dynamic behavior of such systems. Comparison of these semi-classical results against results obtained experimentally (e.g. optical spectra) or with those from other techniques such as: self-consistency and perturbation theory [1,3], variational schemes (e.g. Hartree–Fock and/or Density-Functional Theory implementations) [7]; and more recently, Iterative Complement Interaction (ICI) [8], Quantum Diffusion Monte Carlo (QDMC) [9] and Coupled Cluster with Singles and Doubles (CCSD) methods [10], using parametrized wave functions and their expansions together with energy minimization considerations, has been the benchmark to assess the effectiveness and certainty of the former semi-classical methods. As mentioned, Hylleraas [5] included in the wave function an explicit correlation term. When solving SWE using this trial wave function, after several iterations, he finally obtained an ionization potential of 24.58 eV for helium, close to the experimental value of 24.59 eV measured previously by Hertzberg [11]. Thus, this validates quantum mechanics since the small error was due to the neglect of relativity and nuclear motion in the calculations. Hylleraas' method of explicit correlation was later used for solving the two-electron H_2 molecule. Nonetheless, its generalization to polyelectronic atoms proved to be difficult. This, being one of the reasons for numerical computational schemes to emerge to solve and assess these complex atom systems from first principles and concepts from the then recently discovered Matrix Quantum Mechanics theory.

1.1. *Work related to semi-classical physics*

Leopold and Percival (1980) [12] proposed a semi-classical equivalent of the Hylleraas variational method for He applied to a two-electron atom, indicating that the failure of the old quantum theory to obtain an accurate energy is explained as an omission of zero-point motion through half-integer quantum numbers and the lack of a variational method to obtain an adequate model, and not to any intrinsic fault of the theory. Later on, Van der Merwe (1984) [13] studied the excitations of two-electron atoms based on the collective coordinate method. Wintgen et al. (1994) [14] reported progress in the semi-classical description of two-electron atoms, demonstrating that the regular and chaotic motion coexist, and must receive separate treatment. Tanner et al. (2000) [15], summarized the problems of the two-electron theory, between ground state and complete fragmentation, and the progress in measuring the spectra of two-electron atoms. Afterward, Kiselyov (2004) [16] considered a He atom as a three-particle edifice, and described the electrons with Euler's angles, using an adiabatic approach that solved the equation for an inter-electron angle. Kolganova et al. (1998) [17] previously worked out the three-body configuration space problem with hard-core potentials. Bucher and Rise (2007) [18] later showed that the energy eigenvalues estimation failure does not originate, under the orbits concept per se; instead, it was caused by the wrong choice of orbital trajectories. By choosing a semi-classical electron oscillator, Bucher et al. were able to calculate the energy states using perturbation and variational methods, suggesting that the results are promising for the application of semi-classical mechanics of two-electron atoms, including planetary atoms. Finally, studies of confined helium atoms by Wen-Fang (2007) [19] used the adiabatic hyperspherical approach method to study the helium atom spherical-parabolic potential. Afterward, regarding the energy levels of He atom, Salas and Arce (2017) [20] utilized the potential energy surface of the atomic structure and the Coulombic correlation, introducing a factorization of the internal eigenfunction, and an inter-parametric distance between the two electrons. Employing the ground state of He as a prototype, it was shown that the nonadiabatic potential energy surface affords a molecular-like interpretation of the structure of the atom. One interesting result suggests that in the case of the helium atom, when both electrons are on the same side of the orbital trajectory, the system is fully stable, but when they are on opposite sides, the behavior of the system tends to be chaotic (due to the classical three-body problem nature, i.e., one nucleus and two electrons). Further describing modern semi-classical concepts and their application to two-electron atoms, estimating a double excited state, obtained by both regular and chaotic two-electron dynamics semi-classical calculations. They further concluded that treating the motion of two electrons as synchronous permits a reduction to a one-electron problem, and when considering average electron-electron distances, combined with screening effects, the parallel and crossed Coulomb oscillations emulate quantum-mechanical symmetry constraints. The latter yields similar ground-state and excited-state energy levels of the He double spectrum.

1.2. *Work on two-electron systems*

Already in 1958, Pekeris [21] expanded the wave function of the original scheme of Hylleraas into a triple orthogonal set in three perimetric coordinates, obtaining a nonrelativistic energy value for helium accurate to within $0.01\,\mathrm{cm}^{-1}$, $0.40\,\mathrm{cm}^{-1}$ lower than the value computed by Kinoshita [22]. An ionization potential for helium of $198\,310.67\,\mathrm{cm}^{-1}$ against Herzberg's value of $198\,310.82 \pm 0.15\,\mathrm{cm}^{-1}$ was also achieved. Obtaining an energy of $-2.903\,724$ au within 0.5 microHartree of the exact value. Bunge et al. (1993) [23] used Roothaan–Hartree–Fock orbitals expressed in a Slater-type basis to report energy values for the ground states of He through Xe. Energy accuracy ranged between 8 and 10 significant figures, reducing it by 21 and 2770 times the energy errors of the previous compilation with a He energy of $2.8616\,7999\,5$ au. Umigar et al. (1993) [9] used the Diffusion Monte Carlo algorithm with very small time-step errors to obtain an energy of $-2.9037\,2460$ au. Kolganova et al. (1997) [24] did experimental work on the energy scattering of a He atom off a He dimer. Schwartz (2006) [7] did extensive variational computations reported for the ground state energy of the non-relativistic two-electron atom. Several different sets of basis functions were systematically explored, starting with 3091 terms, achieving the previous best calculation by Korobov [25]. Morton et al. (2006) [26] worked on the energy levels for the stable isotopes of atomic helium. Nakashima and Nakatsuji (2007) [8] solved the SWE for the helium atom and its isoelectronic ions with the free iterative complement interaction (ICI) method, followed by the variational principle. For helium, the calculated energy was correct to over 40-digit accuracy, $-2.9037\,2437\,7034\,1195\,9831\,1159\,2451\,9440\,4$ au.

1.3. *Regarding this proposed research work*

There is no doubt about the ubiquity and power of numerical methods today, particularly those based on Hartree–Fock and density-functional theories, used to solve complex atomic and molecular systems. However, the latter pose high requirements in computing power and often lose insight into the actual physics involved in the solution process, as it may appear cumbersome from a mathematical description to the undergraduate student's point of view. In that regard, semi-classical methods offer more physical and mathematical insight into the actual solving process, aiding the understanding of the physical phenomena involved at the atomic level from a more tangible point of view. In our present work, we developed an analytically and algebraically two-electron atom non-relativistic semi-classical model for the ground state energy ($n = 1$) and excited states ($n > 1$) of He and other atom ions. As it is known, s orbitals are symmetrical to the angular coordinates (i.e., their l quantum number is zero). Thus, a circular orbit for the two electrons bound to the nucleus can be considered under a semi-classical perspective. The model assumes the two electrons are in an energy state occupying the same orbital s; thus, the average distance between any of their two simultaneous positions was geometrically worked out as a function of the classical orbital radius r, i.e., $\overline{r} = \frac{4}{\pi} r$. Additionally, the repulsive force between the two electrons adds a radial component to the net force acting on each electron, altering their linear momentum, which in turn affects their de Broglie's wavelength and thus the orbital average radius, when obtained from Bohr's angular momentum quantum condition, rendering it larger, $\overline{r}' > \overline{r}$; much, in the same manner, a self-consistency electric repulsive charge field would radially expand when an additional charge is introduced. Utilizing the virial theorem (J. B. Goodenough, personal communication, August, 2003), a relationship between the kinetic energy of the two electrons and the total potential energy of the system, including the electronic correlation, allows us to obtain the closed-form expression for the energy of the system.

2. Theoretical framework

The semi-classical Hamiltonian for a two-electron system (e_1, e_2) orbiting the nucleus of atomic number Z, as illustrated in Figure 1, is a function of the principal quantum number of the s orbital n and the atomic number Z of the nucleus, and it corresponds to:

$$H(n,Z) = H(n)_{K_1} + H(n)_{K_2} - \frac{e_1^2 Z}{4\pi\epsilon_0} r(n)_1^{-1} - \frac{e_2^2 Z}{4\pi\epsilon_0} r(n)_2^{-1} + \frac{e_1 e_2}{4\pi\epsilon_0} \| r_2 - r_1 \|_n^{-1}. \tag{1}$$

The electrostatic attraction and repulsion terms correspond to those of a Coulombic potential. The term $H(n)_K$ corresponds to the kinetic energy of the electron in the n energy level. Further, by considering both electrons indistinguishable from each other, the terms of their linear momentum and radial distance in the s orbit can be made the same, thus the kinetic energies of both electrons 1 and 2 are equal in magnitude.

2.1. *Average distance between the electrons*

The expected value of the distance between the two electrons orbiting the 1s orbital represented by a circular trajectory, as shown in Figure 1, would be given by the integral

$$\overline{r} = \int_{-\frac{\pi}{2}}^{+\frac{\pi}{2}} r\sqrt{2 - 2\cos(\theta)}\, d\theta = \frac{4}{\pi} r. \tag{2}$$

The angle θ that sustains the average distance between the two electrons is also illustrated in Figure 1 and can be computed as [27]

$$\theta^* = 2\sin\left(\frac{\overline{r}}{2r}\right)^{-1} = 2\sin\left(\frac{2}{\pi}\right)^{-1} \tag{3}$$

If we now consider the average distance, $\overline{r}$, between the two electrons to be given by the average distance between any two points in a circumference of radius r, then Eq. 1 reduces to

$$\overline{H}(n,Z) = 2\overline{H(n)}_K - 2\frac{e^2 Z}{4\pi\epsilon_0} r^{-1} + \frac{e^2}{4\pi\epsilon_0}\frac{\pi}{4} r^{-1} = 2\overline{H(n)}_K - \frac{e^2}{4\pi\epsilon_0}\left(2Z - \frac{\pi}{4}\right) r^{-1}. \tag{4}$$

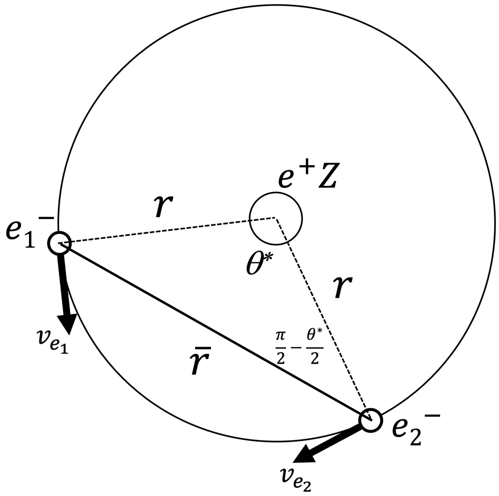


Figure 1. Semi-classical model of two-electron orbiting a 1s orbital of radius r around a nucleus of Z protons. The average separation distance between the two electrons $\bar{r}$ corresponds to $\frac{4}{\pi}r$. Electrons 1 and 2 move in opposite directions to comply with the zero total orbital momentum of the s orbital.

Because we have expressed the repulsion term as a function of an average electron distance within the orbit, we have then renamed the Hamiltonian as $\overline{H}$. The repulsion energy term is associated with a respective repulsion force along the line of sight of both electrons.

Now invoking the virial theorem, which states that the total kinetic energy of the system corresponds to minus half of the net potential energy of the system, analytically we obtain

$$2\overline{H}_K = -\frac{1}{2}\left(-\frac{e^2}{4\pi\epsilon_0}\left(2Z-\frac{\pi}{4}\right)\right)r^{-1} = \frac{e^2}{8\pi\epsilon_0}\left(2Z-\frac{\pi}{4}\right)r^{-1} = -\frac{1}{2}H_P. \tag{5}$$

Finally, we can substitute back the latter expression (Eq. 5) into Eq. 4 to obtain a compact expression for $\overline{H}$:

$$\overline{H}(n,Z) = -\frac{e^2}{8\pi\epsilon_0}\left(2Z-\frac{\pi}{4}\right)r(n).^{-1} \tag{6}$$

2.2. *Free body diagram of the orbiting electron*

The total repulsive Coulombic energy between two electrons in motion (e.g. equal charge and mass) separated a certain distance $\bar{r}$ must be divided equally due to symmetry. This suggests that the repulsive Coulombic force, where the repulsive external work or energy comes from, must also be divided equally in magnitude between the two moving charges. Thus, the expression for the repulsive force acting on either electron is

$$F_{\text{repulsive}} = \frac{1}{2}\left(\frac{e^2}{4\pi\epsilon_0}\frac{1}{\bar{r}^2}\right). \tag{7}$$

The repulsive force between the two electrons can be projected radially and tangentially along the electron's inertia or Coulombic force directions. The repulsive force radial component acts by pulling the electron outwards into a larger orbital radius, $r' > r$. Much in the same way, a self-consistent field of negative charges would be experienced under the repulsion of an added

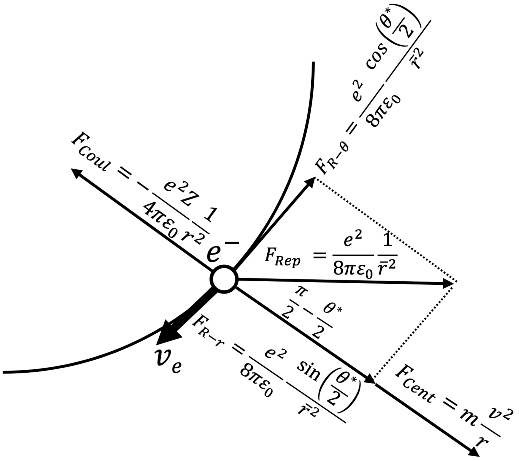


Figure 2. Free body diagram of the forces acting on one of the two electrons orbiting the 1s orbital.

extra electron. Applying Newton's second law to any of the two electrons (1 or 2), as illustrated in Figure 2, we obtain an expression for the resulting force acting upon the electron mass:

$$\vec{F}_e = \frac{p^2}{m_e r}\hat{r} + m_e a_\theta \hat{\theta} = \left(\frac{e^2 Z}{4\pi\epsilon_0} r^{-2} - \frac{e^2}{8\pi\epsilon_0}\frac{\pi^2}{16} r^{-2}\sin\left(\frac{\theta^*}{2}\right)\right)\hat{r} + \frac{e^2}{8\pi\epsilon_0}\frac{\pi^2}{16} r^{-2}\cos\left(\frac{\theta^*}{2}\right)\hat{\theta}. \tag{8}$$

Cosine directors are obtained by trigonometry from Figure 1, and result in

$$\sin\left(\frac{\theta^*}{2}\right) = \frac{2}{\pi}, \tag{9}$$

$$\cos\left(\frac{\theta^*}{2}\right) = \sqrt{1 - \frac{4}{\pi^2}}, \tag{10}$$

and replacing them in Eq. 8 and canceling out terms, we obtain

$$\vec{F}_e = \frac{p^2}{m_e r}\hat{r} + m_e a_\theta \hat{\theta} = \frac{e^2}{8\pi\epsilon_0}\left(2Z - \frac{\pi^2}{16}\frac{2}{\pi}\right) r^{-2}\hat{r} + \frac{e^2 \pi}{128\epsilon_0}\sqrt{1 - \frac{4}{\pi^2}}\, r^{-2}\hat{\theta}. \tag{11}$$

Separating terms according to each unit vector, two expressions are isolated:

$$F_r = \frac{p^2}{m_e r} = \frac{e^2}{8\pi\epsilon_0}\left(2Z - \frac{\pi}{8}\right)\frac{1}{r^2}, \tag{12}$$

$$F_\theta = m_e a_\theta = \frac{e^2}{128\epsilon_0}\sqrt{\pi^2 - 4}\,\frac{1}{r^2}. \tag{13}$$

From Eq. 12 we can isolate the magnitude of the linear momentum in the radial direction, thus

$$p = \sqrt{\frac{m_e e^2}{8\pi\epsilon_0}\left(2Z - \frac{\pi}{8}\right)\frac{1}{r}}. \tag{14}$$

2.3. *De Broglie's mass wavelength and Bohr's quantum condition*

From Eq. 14, the corresponding de Broglie wavelength of the electron particle would then take the following expression:

$$\lambda = h\left(\sqrt{\frac{m_e e^2}{8\pi\epsilon_0}\left(2Z - \frac{\pi}{8}\right)r^{-1}}\right)^{-1}. \tag{15}$$

Now we can combine de Broglie's wavelength with Bohr's angular momentum quantization condition to obtain

$$2\pi r(n) = nh\left(\sqrt{\frac{m_e e^2}{8\pi\epsilon_0}\left(2Z - \frac{\pi}{8}\right)r(n)^{-1}}\right)^{-1}. \tag{16}$$

From where we can isolate the radial orbit as a function of the principal quantum number n:

$$r(n) = \frac{2n^2 h^2 \epsilon_0}{\pi m_e e^2}\left(2Z - \frac{\pi}{8}\right)^{-1}. \tag{17}$$

Finally, substituting the latter relationship back into Eq. 6, one gets the expression for the average value of the total average Hamiltonian as a function of n and Z quantum parameters:

$$\overline{H}(n, Z) = -\frac{e^4 m_e}{4n^2 h^2 \epsilon_0^2}\left(Z^2 - 3Z\frac{\pi}{16} + \frac{\pi^2}{128}\right). \tag{18}$$

The algebraic expression presented here for the energy of the two-electron system was developed using the virial theorem to obtain the system's kinetic energy, rather than using the linear momentum, which was obtained directly from the force analysis of any of the two electrons. Moreover, the correlation term was based on the average distance between the two electrons orbiting the same orbital circular trajectory, e.g. s orbital family. However, the linear momentum was used to obtain de Broglie's electron wavelength, and then the orbital radius was quantized using Bohr's angular momentum condition. This combination rendered an expression modulated by two binomial terms, providing a quadratic polynomial expression on Z.

3. Ab initio computation by HF-DFT

Quantum ESPRESSO (QE) software was used to find the energy of various atom ions with different excitation configurations, specifically using the `ld1.x` command.

This command is a QE tool used to generate pseudopotentials from atomistic calculations. It solves the Schrödinger equation for an atom in its reference configuration, denoted by the input script file, and thus delivers the total energy of this system.

In our case, the input script file generates a PBE (Perdew–Burke–Ernzerhof) type exchange and correlation functional calculation, in which a "PAW" (Projector Augmented-Wave) type pseudopotential is created with certain chosen parameters, such as the atom's atomic number, the specific electronic configuration of the electrons in the system, and the minimum operating parameters of the software. The program generates the specified pseudopotential and provides details of the calculations performed. Specifically, it reports the kinetic energy, the local configuration energy (e.g., potential energy), the Hartree potential energy (e.g., repulsive energy), and the exchange-correlation energy (e.g., due to magnetic spins permutation). Together, these components sum to give the ion system's total electronic energy.

4. Numerical experiments

Validation of the obtained analytical results from the average repulsion distance between two electrons for 19 ions ranging from atomic number Z, 2 (He) to 20 (Ca^{18+}) was done against values of the corresponding ionization potentials obtained from [28]. The semi-classical model was implemented, and numerical results were obtained using MathCAD 14 software. MS Excel was used to obtain correlation values and average, and RMS errors from the data.

Moreover, an energy comparison was carried out between the results of the semi-classical proposed model, including the average repulsion distance between two electrons of the same 19 ions, with results obtained from HF-DFT computation using QE software. This is for energy levels corresponding to the principal quantum number $n = 1$, 2 and 3, while the quantum numbers l and m_l are both maintained equal to zero.

These results allowed us to obtain the absolute energy error in eV, between the developed semi-classical two-electron model, the experimental results, and the QE ab initio computational results. This is simply as

$$\Delta H(Z,n) = \left|H(Z,n)_{\mathrm{SC}} - H(Z,n)_{\mathrm{Experiment,QE}}\right|, \tag{19}$$

while the energy relative error was calculated in terms of

$$\%\Delta H(Z,n) = \frac{\Delta H(Z,n)}{\left|H(Z,n)_{\mathrm{SC}}\right|}. \tag{20}$$

Additionally, ab initio energies obtained by QE of the two-electron ion systems were decomposed into their kinetic, potential, exchange-correlation and Hartree energy components and compared with the semi-classical obtained magnitudes, for $n = 1$, 2, and 3. These results are presented in tables and graphs, as shown in the following section.

Table 1. Values of two-electron atom (ion) energy eigenvalues from semi-classical, ab initio and empirical results.

Z	H_{n_1}	$\mathbf{QE}_{n_1}$	$\sum \mathbf{I}_{e_1,e_2}$	$\mathbf{Err(eV)}_{\sum \mathbf{I}_i}$	$\mathbf{Err(\%)}_{\sum \mathbf{I}_i}$	$\mathbf{Err(eV)}_{\mathbf{QE}}$	$\mathbf{Err(\%)}_{\mathbf{QE}}$
2	−78.8861	−78.7213	−79.003	0.1169	0.1482	0.1648	0.2088
3	−198.9142	−197.4671	−198.089	0.8252	0.4148	1.4471	0.7275
4	−373.3650	−370.6088	−371.606	1.7590	0.4711	2.7562	0.7382
5	−602.2387	−598.1621	−599.585	2.6537	0.4406	4.0766	0.6769
6	−885.5351	−880.1327	−882.058	3.4771	0.3927	5.4031	0.6101
7	−1223.2543	−1216.5231	−1219.086	4.1683	0.3408	6.7312	0.5503
8	−1615.3962	−1607.3344	−1610.702	4.6942	0.2906	8.0618	0.4991
9	−2061.9609	−2052.5673	−2056.975	4.9859	0.2418	9.3936	0.4556
10	−2562.9484	−2552.2223	−2557.961	4.9874	0.1946	10.7251	0.4185
11	−3118.3587	−3106.2996	−3113.750	4.6087	0.1478	12.0591	0.3867
12	−3728.1917	−3714.7993	−3724.415	3.7767	0.1013	13.3924	0.3592
13	−4392.4476	−4377.7215	−4390.063	2.3847	0.0543	14.7261	0.3353
14	−5111.1261	−5095.0663	−5110.784	0.3421	0.0067	16.0598	0.3142
15	−5884.2275	−5866.8338	−5886.705	2.4775	0.0421	17.3937	0.2956
16	−6711.7516	−6693.0240	−6717.962	6.2104	0.0925	18.7276	0.2790
17	−7593.6985	−7573.6369	−7605.338	10.9195	0.1438	20.0616	0.2642
18	−8530.0682	−8508.6726	−8546.892	16.8238	0.1972	21.3956	0.2508
19	−9520.8606	−9543.6890	−9544.886	24.0254	0.2523	22.8284	0.2398
20	−10566.076	−10598.1315	−10598.783	32.7072	0.3095	32.0557	0.3034

5. Results and discussion

5.1. *Semi-classical vs. experimental and QE ab initio energies*

Table 1 illustrates the two-electron systems (atoms or ions) ground state energies from He to Ca^{18+} from evaluation of Eq. 18 and comparison with the corresponding energy sum of the two ionization potentials of the last two electrons in the ion system. The energy difference in eV between the semi-classical model and the empirical data [28] increases for Z values greater than 2 up to $Z = 10$, to then decrease monotonically up to $Z = 14$, to further increase above zero up to $Z = 20$. The energy error in eV of the semi-classical model compared to ab initio calculations increases from $Z = 2$ up to 18, suddenly jumping at $Z = 19$ and 20. The RMS value energy error concerning experimental values is 10.9149 eV, while for ab initio values, it corresponds to 14.9224 eV.

For ground state energy, comparing the numerical results of the semi-classical model against experimental results from optical spectroscopy yields an average energy relative error less than 0.23 % for principal quantum number, $n = 1$, and atomic number Z up to 20. This value is considerably low when compared to other analytical approximations, such as perturbation theory, variational analysis using hydrogen-like wave functions or Monte Carlo simulations. Such as the early work of Ivanova and Safronova (1975) [29], where they used perturbation theory to calculate the atomic energy levels. Followed by the work of Beli'c et al. (1994) [30] on variational calculations, or the work of Joslin et al. (1992) [31] in which they studied two-electron atoms using the quantum Monte Carlo method.

Furthermore, the trend in energy relative error between the semi-classical model and the aforementioned experimental values and the QE ab initio computations increases from Z values up to 5 and then decreases monotonically. However, for the experimental values, from $Z = 14$, the energy relative error trend increases again, reaching the same energy relative error values when considering the QE ab initio values. The RMS energy relative error concerning experimental values corresponds to 0.2641 %, while to QE ab initio values it accounts for 0.4484 %.

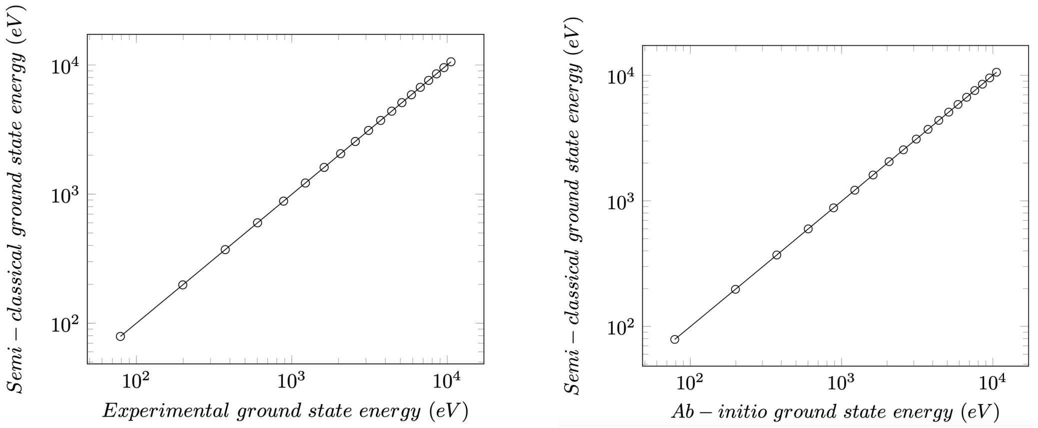
Table 2. Values of two-electron atom (ion) energy eigenvalues for n = 2 and 3 from semi-classical and ab initio models.

Z	H_{n_2}	H_{n_3}	QE_{n_2}	QE_{n_3}	$\mathrm{Err(eV)}_2$	$\mathrm{Err(\%)}_2$	$\mathrm{Err(eV)}_3$	$\mathrm{Err(\%)}_3$
2	−19.7215	−8.7651	−20.9388	−9.7234	1.2173	6.1724	0.9583	10.9329
3	−49.7285	−22.1016	−51.3413	−23.4367	1.6128	3.2431	1.3351	6.0409
4	−93.3412	−41.4850	−95.3012	−43.1586	1.9599	2.0998	1.6736	4.0342
5	−150.5596	−66.9154	−152.8407	−68.9048	2.2810	1.5150	1.9894	2.9730
6	−221.3837	−98.3928	−223.9699	−100.6832	2.5862	1.1682	2.2904	2.3278
7	−305.8136	−135.9171	−308.6943	−138.4981	2.8807	0.8457	2.5810	1.8989
8	−403.8491	−179.4885	−407.0168	−182.3524	3.1677	0.7844	2.8639	1.5956
9	−515.4902	−229.1068	−518.9393	−232.2479	3.4491	0.6691	3.1411	1.3710
10	−640.7371	−284.7720	−644.4633	−288.1858	3.7262	0.5815	3.4138	0.1988
11	−779.5896	−346.4843	−783.5896	−350.1671	3.9999	0.5131	3.6828	1.0629
12	−932.0479	−414.2435	−936.3188	−418.1925	4.2709	0.4582	3.9490	0.9533
13	−1098.1119	−488.0497	−1102.6516	−492.2623	4.5397	0.4134	4.2126	0.8631
14	−1277.7815	−567.9029	−1282.5882	−572.3771	4.8067	0.3762	4.4742	0.7878
15	−1471.0569	−653.8031	−1476.1289	−658.5371	5.0710	0.3448	4.7340	0.7241
16	−1677.9379	−745.7502	−1683.2740	−750.7425	5.3361	0.3180	4.9923	0.6694
17	−1898.4246	−843.7443	−1904.0236	−848.9936	5.5990	0.2949	5.2493	0.6221
18	−2132.5170	−947.7854	−2138.3779	−953.2906	5.8609	0.2748	5.5052	0.5809
19	−2380.2152	1057.8734	−2400.7920	−1068.7899	20.5768	0.8645	10.9165	1.0319
20	−2641.5190	−1174.0084	−2665.6952	−1186.3679	24.1762	0.9152	12.3595	1.0582

Table 2 shows that for $n = 2$ and $n = 3$ the energy error in eV of the semi-classical model with respect to QE ab initio computation increases in both cases quadratically with an R^2 of 0.9997 for Z values greater than 2 up to $Z = 18$; however, then drastically increasing at $Z = 19$ and 20. For values of $n = 2$, the average energy error is 5.3560 eV, and for $n = 3$ is 4.0161 eV. For values of $n = 2$ and 3, this model's energy relative error concerning ab initio calculations decreases from $Z = 2$ up to 18, to slightly increase at $Z = 19$ and 20. For $n = 2$, a decreasing power trend shows an exponent of -1.3940 and R^2 of 0.9966 and for $n = 3$ a decreasing power trend shows an exponent -1.3220 and R^2 of 0.9983. The RMS energy relative error accounts for 1.7999 % for $n = 2$ and 3.2711 % for $n = 3$. When compared against ab initio calculations for values of n equal to 1, 2 and 3, the average energy relative error falls within 0.4165 %, 1.1501 %, and 2.1435 %, respectively.

Additionally, Figure 3(a) shows a high correlation between the semi-classical model results and the experimental results from [28]. The R^2 value of the associated linear regression is 0.9999 and the slope accounts for 1.0028. The same can be said for Figure 3(b), when the semi-classical model is compared against the QE ab initio results for $n = 1$. In this case, the R^2 value corresponds again to 0.9999 and the slope to 0.9994.

In Figure 4, the ground state energy ($n = 1$) and $n = 2$ and $n = 3$ values of both the semi-classical model and the QE ab initio are plotted against the atomic number Z in a semi-log plot. The trend for all n values shows decreasing increments and a close match fit between both data sets with an R^2 of 0.9999. For $n = 2$ an RMS energy error of 8.1747 eV is obtained, whereas for $n = 3$, the RMS energy error accounted for 5.1049 eV. Moreover, if the data sets are plotted against each other, a linear regression yields a slope of 1.0057 with R^2 of 0.9989 for $n = 2$, while a slope of 1.0086 for $n = 3$ has an R^2 of 0.9999.



(a) **(b)**

Figure 3. (a) Two-electron atom (ion) ground state energy: semi-classical vs. experimental; R^2 value of the associated linear regression is 0.9999 and the slope accounts for 1.0028. (b) Two-electron atom (ion) ground state energy: semi-classical vs. ab initio; R^2 value corresponds to 0.9999 and the slope accounts for 0.9994.

5.2. *QE ab initio energy components*

As shown in Table 3, ab initio energies of the two-electron ion systems were decomposed into their kinetic (positive), potential (negative), exchange-correlation (negative), and repulsive (positive) energy components for $n = 1$. When considering the same energy components but for

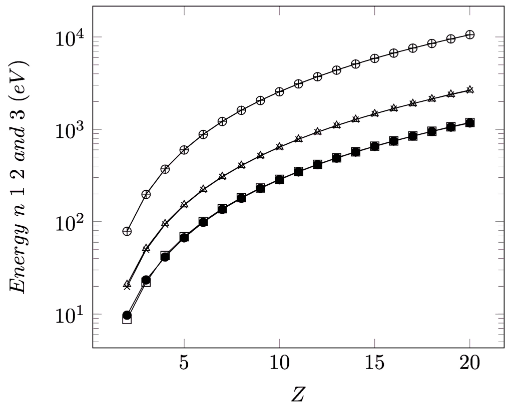


Figure 4. Two-electrons atom (ion) energy (eV) for $n = 1, 2$ and 3. Semi-classical & ab initio vs. atomic number of species. From ground state (+) & (∘), RMS energy error accounts for 14.9224 eV. For $n = 2$ (×) & (△) polynomial fit gives an R^2 of 0.9999 for both data sets, having an RMS energy error of 8.1747 eV. For $n = 3$ (∗) & (□) polynomial fit with an R^2 of 0.9999 for both data sets, having an RMS energy error of 5.1049 eV.

$n = 2$ and 3, a magnitude decrease with n number is observed, i.e. more circular and larger radius orbital trajectories, and an exponential behavior for the kinetic and potential, followed by linear behavior for the exchange-correlation and repulsive terms. The positive kinetic energy reduces with n and increases exponentially with Z values. The negative potential energy reduces with n and increases exponentially with Z value. The same is true for exchange energy, but it behaves linearly, negatively increasing with Z, becoming less negative with n. For the repulsive term, energy rises almost linearly with Z but decreases with n.

5.3. *Semi-classical vs. QE ab initio energy components*

From Figure 5(a), the semi-classical vs. ab initio kinetic, potential, and repulsive energy components are plotted in log-log scale. As it is known, there is no semi-classical interpretation for the exchange-correlation energy, which in this case is obtained by the QE ab initio software modeling. However, by splitting its value between the potential energy and the repulsive energy components, a linear tendency of the three components (kinetic, potential and repulsive) resulted when compared against the semi-classical values, as observed in the latter figure. The splitting assignment of the exchange-correlation energy component was done by fitting a minimum error linear form with Z for both energy terms, this is:

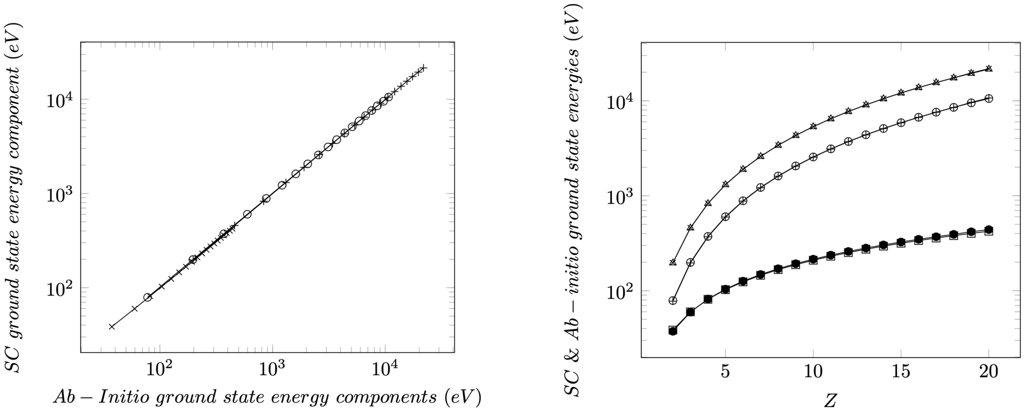
$$E_{\text{Potential}} = \frac{E_{\text{Exc}}}{2} + \Delta_{\text{Exc}} = \frac{E_{\text{Exc}}}{2} + \frac{7}{2}(Z-1), \tag{21}$$

$$E_{\text{Repulsive}} = \frac{E_{\text{Exc}}}{2} - \Delta_{\text{Exc}} = \frac{E_{\text{Exc}}}{2} - \frac{7}{2}(Z-1). \tag{22}$$

The R^2 value of the associated linear regression of all three energy components is 0.9999. For the kinetic, potential and repulsive energy components, the slope accounts for 0.9929, 0.9953 and 0.9586, respectively. Figure 5(b) shows high data coincidence between the semi-classical and the ab initio kinetic, potential and repulsive component energy values.

Table 3. Values of two-electron atom (ion) energy eigenvalues components (eV) for $n = 1$ from QE ab initio: (Kin) kinetic, (Pot) potential, (Rep) repulsive and (Exc) exchange-correlation energy components. Potential and repulsive energy terms with "*" appear corrected from the exchange-correlation energy component.

Z	**QE$_{\text{Kin}}$**	**QE$_{\text{Pot}}$**	**QE$_{\text{Rep}}$**	**QE$_{\text{Exc}}$**	$\frac{1}{2}$**QE$_{\text{Exc}}$**	**Δ_{Exc}**	**QE$_{\text{Pot*}}$**	**QE$_{\text{Rep*}}$**
2	77.7143	−183.1179	55.1503	−28.4679	−14.2340	3.5	−193.8518	37.4163
3	196.3358	−437.8175	89.2163	−45.2018	−22.6009	7.0	−453.4183	59.6155
4	369.4154	−801.3826	123.2482	−61.8897	−30.9449	10.5	−821.8274	81.8033
5	596.9321	−1273.8044	157.2712	−78.5611	−39.2805	14.0	−1299.0849	103.9907
6	878.8790	−1855.0781	191.2908	−95.2245	−47.6123	17.5	−1885.1903	126.1786
7	1215.2530	−2545.2011	225.3086	−111.8836	−55.94181	21.0	−2580.1429	148.3668
8	1606.0524	−3344.1721	259.3254	−128.5401	−64.2701	24.5	−3383.9422	170.5554
9	2051.2765	−4251.9904	293.3416	−145.1950	−72.5975	28	−4296.5879	192.7441
10	2550.9245	−5268.6554	327.3573	−161.8487	−80.924	31.5	−5318.0798	214.9330
11	3104.9963	−6394.1669	361.3728	−178.5017	−89.2509	35.0	−6448.4178	237.1219
12	3713.4915	−7628.5247	395.3880	−195.1541	−97.5771	38.5	−7687.6017	259.3109
13	4376.4101	−8971.7285	429.4030	−211.8061	−105.9031	42.0	−9035.6315	281.5000
14	5093.7518	−10423.7783	463.4180	−228.4578	−114.2289	45.5	−10492.5072	303.6891
15	5865.5167	−11984.6741	497.4328	−245.1092	−122.5546	49	−12058.2287	325.8782
16	6691.7046	−13654.4157	531.4475	−261.7605	−130.8802	52.5	−13732.7959	348.0673
17	7572.3155	−15433.0031	565.4622	−278.4116	−139.2058	56.0	−15516.2089	370.2564
18	8507.3494	−17320.4363	599.4769	−295.0626	−147.5313	59.5	−17408.4676	392.4456
19	9633.3725	−19500.8847	637.8924	−314.0692	−157.0346	63.0	−19594.9193	417.8578
20	10709.0880	−21648.7556	672.6590	−331.1229	−165.5615	66.5	−21747.8170	440.5976



(a) **(b)**

Figure 5. (a) Two-electron atom (ion) ground state energy: semi-classical vs. ab initio: kinetic (○), potential (+), repulsive (×) energy component. The R^2 value of the associated linear regression of all three energy components is 0.9999. For the potential, correlation, and kinetic components, the slope accounts for 0.9953, 0.9586, and 0.9929, respectively. (b) Two-electrons atom (ion) ground state energies: semi-classical vs. ab initio kinetic (+) & (○), potential (×) & (△), repulsive (∗) & (□) energy component. R^2 value of the associated linear regressions is 0.9999, and the slope accounts for 1.0028 among the two energy data sets for each energy component.

5.4. *Semi-classical vs. exact methods for Helium atom energy values*

Exact energy values of the two-electron system for the ground state of the helium atom using methods, such as Hy-Ci [32], full ICI [8], QD Monte Carlo [9], variational expansion [7] and CCSD [10] with a large basis set as a reference energy, were also consulted to assess our semi-classical model results for helium −2.8990 0665 7211 au. This to complement the Hartree–Fock-DFT computed values, as reference points, to assess our semiclassical model. Table 4 shows a chronological-based summary of 15 selected studies from the literature in which the energy of the ground state of He (1^1S, L = 0) was obtained using these methods and compared to our results. Our semi-classical model results compare well against Slater, Hylleraas and Ruiz 3p3p models, being more accurate than Unsöld, Kellner, Hartree, Bunge, Ruiz 1s'1s' and DFT-PBE-PAW models.

Table 4. Values of helium 1^1S energy eigenvalues from different methods vs. experimental value −2.9033 0694 au.

Method	**Reference**	**Year**	**$\mathrm{E_{He}}$ 1^1S (au)**	**Err %**
Hamiltonean perturbation	Unsöld [3]	1927	−2.7460 1014	5.28
Hamiltonean perturbation (extra terms)	Kellner [1]	1927	−2.8727 9526	0.91
Wave function determinant	Slater [2]	1927	−2.8948 4484	0.15
Self consistency field	Hartree [4]	1928	−2.9132 1949	0.49
Wave function explicit correlation	Hylleraas [5]	1929	−2.8948 4484	0.15
Expansion series (38 terms)	Kinoshita [22]	1957	−2.9037 2250	0.01
Wave function expansions	Pekeris [11]	1959	−2.9037 2438	0.01
Roothaan–Hartree–Fock	Bunge et al. [23]	1993	−2.8616 7999	1.44
Quantum diffusion Monte Carlo	Umrigar et al. [9]	1993	−2.9037 2460	0.01
Exact-DFT	Umrigar & Ganzo [33]	1994	−2.9037 2437 7034	0.01
Coupled cluster with singles and doubles	Koppler & Noga [10]	1995	−2.9037 0560	0.01
Extensive variational computation	Schwartz [7]	2006	−2.9037 2437 7034	0.01
Iterative complement interaction	Nakashima et al. [8]	2007	−2.9037 2437 7034	0.01
Hy-CI Slater orbitals 1s'1s'	Ruiz [32]	2015	−2.8762 1971 7792	0.94
Hy-CI Slater orbitals 3p3p	Ruiz [32]	2015	−2.8999 8445 0188	0.12
Hy-CI Slater orbitals 8d8d	Ruiz [32]	2015	−2.9027 0018 1175	0.02
Hylleras trial function expansion	Purwaningsih et al. [34]	2019	−2.9015 0171 0650	0.06
DFT-PBE-PAW	this work	2025	−2.8929 5465	0.36
Proposed semi-classical model	this work	2025	−2.8990 0665 7211	0.15

6. Conclusions

A semi-classical model is presented based on Bohr's angular momentum quantization with a correction for the correlation term in the total Hamiltonian based on the average distance the two electrons would have, were they orbiting simultaneously a given s orbital (semi-classical trajectory) in a given atom or ion.

This model further uses a combination of the virial theorem to obtain an expression for the total Hamiltonian and de Broglie's wavelength condition based on the linear momentum of the electron from Newton's second law, considering the attraction and repulsive forces acting on the electron to obtain the corrected orbital radius under the effect of the electrostatic repulsion.

The algebraic equation of this semi-classical closed-form model is modulated by the product of two binomials having a dependence on the atomic number: $\left(2Z-\frac{\pi}{4}\right)\left(2Z-\frac{\pi}{8}\right)$, rather than the single Z^2 dependence of Bohr's hydrogenous atom model.

The semi-classical model developed for a two-atom system, such as He or other atomic number ions, gives numerical results that are less than 1 % accurate, but higher (up to $Z = 14$)

than the corresponding sum of the ionic potentials of the last two electrons in the ionic system measured experimentally by spectroscopy analysis.

A high correlation between the semi-classical model results and the experimental results (from spectrographic measurements) for the ground energy gives an R^2 value of the associated linear regression and a slope almost equal to 1. The same can be observed when the semi-classical model results are compared against the QE ab initio results for $n = 1$. In this case, the R^2 value corresponds again to a value almost equal to 1.

The ground state ($n = 1$) and energy state values $n = 2$ and 3 of both the semi-classical model and the QE ab initio when plotted against the atomic number Z show decreasing increments and a close match polynomial fit of both data sets. RMS energy error decreases with n values: 14.9224, 8.1747, and 5.1049 eV, respectively. When data sets are plotted against each other, a linear regression yields a slope and R^2 values of almost 1.

For ground state, the energy relative error of the semi-classical model concerning the experimental values and the QE ab initio gives an RMS value (energy relative error) of 0.2641 % and 0.4484 %, respectively. For energy state values $n = 2$ and 3, this model's energy relative error concerning ab initio calculations decreases from $Z = 2$ up to 18, to slightly increase at $Z = 19$ and 20. The RMS energy relative error accounts for 1.7999 % for $n = 2$ and 3.2711 % for $n = 3$.

From a chronological-based summary of 15 studies from the literature in which the energy of the ground state of He (1^1S, L = 0) was obtained using these methods our semi-classical model results compare well against Slater, Hylleraas, and Ruiz 3p3p models, being more accurate than Unsöld, Kellner, Hartree, Bunge, Ruiz 1s'1s' and DFT-PBE-PAW models.

It is expected that the herewith developed semi-classical formulation of a two-electron atomic system energy in s orbitals may help achieve a simplified understanding for undergraduate students of physics and engineering to provide them with a further comprehension of the more elaborate quantum mechanical model of the electron behavior in their professional careers or graduate studies.

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Declaration of interests

The authors do not work for, advise, own shares in, or receive funds from any organization that could benefit from this article, and have declared no affiliations other than their research organizations.

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