Cumhuriyet Sci. J., 45(4) (2024) 604-608
DOI: https://doi.org/10.17776/csj.1510611

Cumhuriyet Science Journal

| csj.cumhuriyet.edu.tr | Founded: 2002 ISSN: 2587-2680 e-ISSN: 2587-246X Publisher: Sivas Cumhuriyet University

Employing Virial Coefficients for Optimal Solutions in Variational Calculations

Mahmut Özgür Sezer [1,a,*]

[1] *Department of Physics, Science Faculty, Selcuk University, Konya, Türkiye.*
**Corresponding author*

Research Article

History
Received: 04/07/2024
Accepted: 03/09/2024

ABSTRACT

In this study, virial coefficients for one and two-electron hydrogen and helium-like quantum dot structures confined in an infinite potential well were calculated. The virial coefficients were determined based on the dot radius using the Quantum Genetic Algorithm (QGA) method. Calculations were performed using Fernandez's expression; however, due to calculation errors in confined systems, this equivalent expression was found unsuitable as a direct stopping criterion. Instead, virial coefficients were calculated using the ⟨T⟩/⟨V⟩ relationship, and the results were plotted. The fitting function obtained for the virial coefficients is proposed as an effective cutoff criterion for electronic structure calculations of quantum dot systems.

Keywords: Quantum Genetic Algorithm (QGA), Variational calculations, Virial coefficients, Quantum dots.

[a] *msezer@selcuk.edu.tr* *https://orcid.org/0000-0002-8415-8440*

Introduction

There are many studies on quantum structures confined to various confining potentials for a long time [1-3]. Specifically, it is possible to calculate a various physical parameters including the optical properties of the dot structures, the states both with and without the influence of external electric and magnetic fields , and the transitions between these states [4-5]. Most of the calculations made have been used methods based on energy minimization and the calculations involve many iterations [6]. However, in order to ensure that precise and reliable results are obtained in iterative calculations, a termination criterion is needed to know where to stop the iteration. It is possible to reach the solution of such problems with the help of the virial Theorem, which was first formulated in classical mechanics and later found applications in quantum mechanics. The virial coefficient obtained from the virial theorem can be used as a cut off parameter in calculations based on the minimization of energy for any quantum system in a bound state.

The virial theorem, a fundamental concept in theoretical physics and astrophysics, plays a crucial role in understanding the dynamics of many-particle systems. Lord Rayleigh, a prominent physicist, published a generalized version of the virial theorem concerning gas pressure [7]. This theorem establishes an equality between the average total kinetic and potential energies of systems with many particles, providing insight into the energy transformations and formation processes of complex systems [8-11].

Cottrell and Paterson derived a version of the virial theorem in quantum mechanics, specifically for a particle system confined within a box. [12].

$$2\bar{T} - \overline{\sum_j \boldsymbol{r}_j . \nabla_j V} + \alpha \frac{\partial E}{\partial \alpha} = 0$$

Parker's formulation of the tensor form of the virial theorem [13] is regarded as a pioneering application of this theorem. Moreover, the virial theorem facilitates intricate calculations in statistical mechanics, such as those involving the proportionality theorem and temperature calculations based on average total kinetic energy. In astrophysics, it assists in determining the internal temperature, mass, radius, and stability of stars. Additionally, it provides insights into systems that exhibit temperature independence and are not in thermal equilibrium.

In 1964, William G. Hoover and Francis H. Ree presented a comprehensive combinatorial approach to star integrals, enabling the precise calculation of the first five virial coefficients for gases composed of rigid parallel squares and cubes with attractive forces [14].

A trial wave function uniformly expands all its coordinate vectors from a specific origin by a certain scale factor, aiming to better align with the actual spatial domain occupied by the system. By treating the scale factor as a variable parameter, the variational principle can be used to derive the virial theorem. In equilibrium or with fixed nuclei, the virial theorem has demonstrated its applicability for any normalized trial function through an appropriate choice of the scale factor. Therefore, satisfying the virial theorem is necessary but not sufficient to confirm that a wave function is an exact solution to the Schrödinger equation. By considering the first derivative of energy with respect to any parameter, a general form of the Hellmann-Feynman theorem is obtained. Using Ritz's variational method to solve the Schrödinger equation allows one to derive not only the energy for each state but also its derivative with respect to the scale factor. While scale factors can be independently varied for

states with different symmetry types, scaling becomes more complex for states sharing the same symmetry.

Fernandez et al. [15,16] conducted research on applying the virial theorem to confined systems. These studies propose modifications to the formulation of the virial theorem, taking into account its relationship with boundary conditions. Mukhopadhyay and Bhattacharya [17] derived the accurate modified form of the virial theorem for bounded systems. Demir and colleagues [18] computed the virial coefficients for He and Li atoms confined within infinite spherical potentials, as defined for free atoms.

In this study, virial coefficients were calculated for H and He type quantum dot structures with one and two electrons confined to infinite potential. It has been suggested that virial coefficients can be used as a cut-off criterion to stop the iteration in electronic structure calculations of quantum dots performed with variational methods.

Theory

Where H is the time-independent Hamiltonian and ψ is state function of the system, the Schrödinder equation of the system is as follows,

$$\hat{H}\psi = E\psi. \quad (1)$$

If the operatör $\hat{A}$ is a linear and time-independent operator as below,

$$\hat{A} = \sum_i \hat{q}_i\hat{p}_i = -i\hbar \sum_i q_i \frac{\partial}{\partial q_i}, \quad (2)$$

Where the sum is over on 3n coordinates of n particles and then

$$\int \psi[\hat{H}, \hat{A}]\psi d\tau = 0 \quad (3)$$

can be written and, is known as hypervirial theorem [19]. The commutation of $\hat{A}$ ve $\hat{H}$ is,

$$\left[\hat{H}, \sum_i \hat{q}_i\hat{p}_i\right] = i\hbar \sum_i q_i \frac{\partial \hat{V}}{\partial q_i} - 2i\hbar\hat{T} = 0. \quad (4)$$

Here, $\hat{T}$ and $\hat{V}$ are kinetic and potential energy operators, respectiveliy and,

$$\left\langle \sum_i q_i \frac{\partial \hat{V}}{dq_i} \right\rangle = 2\langle T \rangle \quad (5)$$

is written. Where bra-ket represents to quantum mechanical averages.This equation is known as the quantum mechanical virial theorem for bound states. If there is a confining potential surrounding system and R is the dot Radius then Eq. 5 is written as follows [20].

$$\left\langle \sum_i q_i \frac{\partial \hat{V}}{dq_i} \right\rangle = 2\langle T \rangle + r\frac{\partial E}{\partial r_0} \quad (6)$$

Materials and Methods

For one electron system with an impurity confined infinite potential, Hamiltonian in given Eq.1 can be written as follow,

$$\hat{H} = -\frac{\hbar^2}{2m^*}\nabla^2 - \frac{Ze^2}{\varepsilon r} + V_c(\vec{r}) \quad (7)$$

where Z is the impurity charge, m^* is the effective mass and ε is the dielectric constant of the medium. The confining potential V_c is,

$$V_c(\vec{r}) = \begin{cases} 0, & r < R \\ \infty, & r \geq R \end{cases} \quad (8)$$

If Hamiltonien in Eq.7 is submitted in Eq.1 the energy and state function of the system can be computed from Schrödinger equations. In this case, state function of the system is one-electron wave fuction $\emptyset_{nlm}$. where nlm is the quantum numbers of the state function, this function can be written as linear combination of Slater-type orbital as follows,

$$\phi_p = \sum_{k=1}^{\sigma} c_{pk}\chi_k(\zeta_k, \vec{r}) \quad (9)$$

Where $k \rightarrow nlm$, σ is size of the basis set, c_{pk} is the expansion coefficients and ζ_k is screening constant. Unnormalized complex STOs $\chi_k(\zeta_k, \vec{r})$ are as follows

$$\chi_k(\zeta_k, \vec{r}) = r^{n-1}e^{-\zeta r}Y_{\ell m}(\theta, \varphi) \quad (10)$$

Hamiltonian of the two-electron system confined to infinite spherical potential (V_c) can be written as,

$$\hat{H} = -\sum_{i=1}^{2}\left(\frac{\hbar^2}{2m^*}\nabla_i^2 - \frac{Ze^2}{\varepsilon r_i}\right) + \frac{Ze^2}{\varepsilon|\vec{r}_1 - \vec{r}_2|} + V_c(\vec{r}_1, \vec{r}_2)\,. \quad (11)$$

where,

$$V_c(\vec{r}_1, \vec{r}_2) = \begin{cases} 0, & \vec{r}_1, \vec{r}_2 < R \\ \infty, & \vec{r}_1, \vec{r}_2 \geq R \end{cases}.$$

The additional term is the coulomb interaction between electrons. ψ is the state function of the system and is constructed from the Slater determinant (ground state) or the appropriate combination of these determinants (excited states) and it can be given for ground states as follows,

$$\psi(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}\left(\emptyset_{1s}(\vec{r}_1)\emptyset_{1s}(\vec{r}_2)\right)[\alpha(1)\beta(2) - \alpha(2)\beta(1)] \quad (12)$$

Where $\emptyset_{1s}(\vec{r}_1)$ is one electron orbital and is given Eq. 9, $\alpha(i)\ ve\ \beta(i)$ are electron spin up and down functions. For the system confined to the infinite spherical potential considered, with the approach of Fermandez [16], virial coefficients were calculated using the expression

$$2E - < V \geq -r_0\frac{\partial E}{\partial r_o} = \frac{r_0}{2}\left|\frac{d\psi(\vec{r}_1, \vec{r}_2)}{dr}\right|^2 \quad (13)$$

The wave function of the system is constructed from Slater determinants, which are generated from single-electron spin orbitals. Since single-electron spin orbitals are constructed as linear combinations of Slater-type orbitals in determining the electronic structure of atomic systems, the same approach can be applied to confined systems, often referred to as artificial atoms. In this study, a linear combination of STOs with different screening parameters for s (or p, d) type atomic orbitals was selected to construct one-electron atomic orbitals. To preserve the orthogonality of the orbitals, the same set of screening parameters was used for all spatial orbitals with the same angular momentum. To accurately calculate the expected energy value, five basis sets (σ = 5) were used, and the QGA procedure was combined with the HFR

methods to minimize the total energy over the STOs. This approach allowed for both the accurate representation of wave function behavior and the optimization of energy calculations.

The Genetic Algorithm (GA) can be defined as a search and numerical optimization technique in which individuals that adapt well to the environment survive, while those that do not adapt are eliminated [21-24]. The Quantum Genetic Algorithm (QGA) consists of three main processes: reproduction (or copying), crossover, and mutation. In the reproduction process, the survival probabilities of individuals are calculated. Individuals with a high probability of survival are passed on to the next generation, while those with a lower probability are eliminated. The crossover process is similar to the natural crossover mechanism in biology and is carried out on individuals obtained during the reproduction stage. The genetic information of two randomly selected individuals is exchanged by cutting at a specific point. The information on the left of the cut in one individual is swapped with the information on the right of the cut in the other, and vice versa. This allows both individuals to carry each other's genetic information. The mutation process is applied to escape local minima and is performed on a randomly selected individual. In the application of crossover and mutation processes, a probability of execution is determined. The crossover probability is chosen to be high in order to increase diversity within the population, while the mutation probability is kept low to avoid incorrect solutions. If the probability is set too high, convergence becomes difficult, and randomness increases. The initial population was composed of 100 randomly selected individuals who were solutions of the Schrödinger equation. Each individual in the initial population was evaluated, and then the QGA method was executed based on these energy values.

Achieving the desired precision in calculating physical quantities using the variational method often requires extensive iterations. However, to effectively manage computation time, establishing a stopping criterion is essential. Although its application in atomic and molecular systems differs, the virial coefficient can serve as a viable stopping parameter for determining the electronic structure of bonded systems, even considering their distinct states compared to free atoms and molecules. Virial ratio can be written as

$$\frac{\langle T\rangle}{\langle V\rangle} = -\frac{1}{2} \tag{14}$$

When determining the electronic structure of confined systems, the ratio approaches a certain value at large dot radii, but significantly different values can be obtained due to the confinement effect at small dot radii.

Results and Discussion

The virial coefficients for one and two-electron confined systems were calculated using Equation 13 derived by Fernandez. Virial coefficients were determined using the system energy and wave functions calculated with the quantum genetic algorithm. Since the errors that occur in calculations in confined systems depend on the dot radius, it was not appropriate to use Fernandez's equivalent expression as a direct stopping criterion. Considering that in finite systems errors in calculations depend on the dot radius, it was not considered appropriate to use Fernandez's equivalent expression as a direct stopping criterion. Virial coefficients in the system were calculated from ⟨T⟩/⟨V⟩. The graph of the values found is drawn depending on the dot radius and can be seen in Fig.1.

In this study, virial coefficients of unconfined Hydrogen and Helium atoms were used as a stopping criterion in the electronic structure calculations of Hydrogen and Helium-like quantum dot structures confined by an infinite potential well. The graph of the obtained virial coefficients as a function of dot radius was plotted, and a fitting function was defined for this purpose, as shown in Figure 1

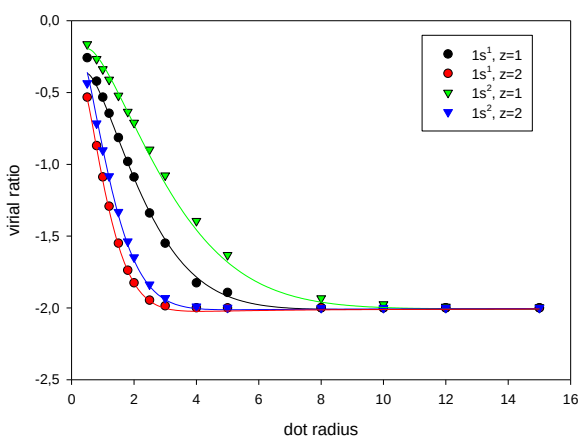

Figure 1. The curves of the virial coefficients calculated for one and two electron systems were drawn according to the dot radius. The continuous lines show the fit functions.

The best fit function representing data shown in Figure 1 was found as follows.

$$V_{fit} = -2 + a.exp(-b.R^{3/2}) + c/R. \tag{15}$$

Here V_{fit} refers to virial ratios and R represents of dot radius. a, b and c are parameters and also absolute error values were found by fit programme of each parameter are given in Table 1.

Table 1. Parameters of fit function given in Eq. (15)

Level, impurity	a	b	c	Δa	Δb	Δc	r^2
1s1, z=1	2.0396	0.2661	-0.1112	0.0937	0.0097	0.0511	0.99
1s1, z=2	2.2283	0.8045	-0.1090	0.0647	0.0143	0.0265	0.99
1s2, z=1	2.0992	0.1639	-0.0876	0.0698	0.0060	0.0431	0.99
1s2, z=2	2.2358	0.6374	-0.0714	0.1080	0.0168	0.0470	0.99
1s1, z=1	2.0396	0.2661	-0.1112	0.0937	0.0097	0.0511	0.99
1s1, z=2	2.2283	0.8045	-0.1090	0.0647	0.0143	0.0265	0.99

Using absolute error of parameters a, b and c absolute error of V_{fit} given in Eq.15 is given as follows,

$$\Delta V_{fit} = \sqrt{\left(\left(\frac{\partial(V_{fit})}{\partial a}\Delta a\right)^2 + \left(\frac{\partial(V_{fit})}{\partial b}\Delta b\right)^2 + \left(\frac{\partial(V_{fit})}{\partial c}\Delta c\right)^2\right)} \quad (16)$$

Table 2. As an example, the table of virial coefficients calculated with the help of the Fernandez equation and the curve fitting method for the case of $1s^1$, z=2.

R	V_{cal}	V_{fit}	$\lvert V_{cal}-V_{fit} \rvert$	ΔV
1s1, z=1	2.0396	0.2661	-0.1112	0.0937
1s1, z=2	2.2283	0.8045	-0.1090	0.0647
1s2, z=1	2.0992	0.1639	-0.0876	0.0698
1s2, z=2	2.2358	0.6374	-0.0714	0.1080
1s1, z=1	2.0396	0.2661	-0.1112	0.0937
1s1, z=2	2.2283	0.8045	-0.1090	0.0647

The iteration process was stopped when the difference between the virial coefficient calculated from the iteration and the one obtained from the fit function was smaller than ΔVfit. Values for several different dot radii are presented in Table 2. As can be seen in Table 2, when the 4th and 5th columns are compared, it is observed that Vcal - Vfit consistently remains smaller than ΔVfit. This indicates that while the absolute error is relatively large for small dot radii, it significantly decreases for larger dot radii. Therefore, it was concluded that these results provide a robust and reliable criterion for stopping the iteration process, ensuring the accuracy and precision of the calculations. In summary, this approach not only enhances the reliability of the method but also contributes to the overall efficiency and accuracy of the computational process. Therefore, it is deemed appropriate to consider the use of virial coefficients as a stopping criterion in iterative calculations performed with variational methods as a strategic approach that can both enhance the speed and ensure the accuracy of the computations.

Conflict of interest

There is no conflict of interest among the authors.

References

[1] Özmen, A., Yakar, Y., Çakır, B., Atav, Ü., Computation of the oscillator strength and absorption coefficients for the intersubband transitions of the spherical quantum dot, *Opt. Commun*., (2009) 282, 3999.

[2] Çakır, B., Yakar, Y., Özmen, A., Sezer, M.Ö., Şahin, M., Linear and nonlinear optical absorption coefficients and binding energy of a spherical quantum dot, *Superlattices Microstruct*., (2010) 47, 556.

[3] Çakır, B., Yakar, Y., Özmen, A., Linear and nonlinear optical absorption coefficients of spherical quantum dot inside external magnetic field. *Physica B*, (2017) 510, 86-91.

[4] Rahimi, F., Ghaffary, T., Naimi, Y., Khajehazad, H., Effect of magnetic field on energy states and optical properties of quantum dots and quantum antidots, *Optical and Quantum Electronics*, (2021) 53 (47).

[5] Çakır, B., Yakar, Y., Özmen, A., Refractive index changes and absorption coefficients in a spherical quantum dot with parabolic potential, *Journal of luminescence*, (2012) 132, 10, 2659.

[6] Çakır, B., Özmen, A., Atav, Ü., Yüksel, H., Yakar, Y., Investigation of electronic structure of a quantum dot using Slater-type orbitals and Quantum Genetic Algorithm, *Int. J. Mod. Phys. C*, (2007)18, 61-72.

[7] Rayleigh, Lord, Scientific Papers (1905), Vol. 5: 1902-1910. Cambridge: University Press.

[8] Poincaré, H., *Lectures on Cosmological Theories*, (1911) Paris: Hermann.

[9] Zwicky, F. "Die Rotverschiebung von extragalaktischen Nebeln", Helvetica Physica Acta (1933) 6: 110–127.

[10] Ledoux, P., On the radial pulsation of gaseous stars, *Astrophysical Journal*, (1945) 102, 143–153.

[11] Kohn, W., Two applications of the variational method to quantum mechanics, *Physical Review*, (1947), 71(10), 635-636.

[12] Cottrell, T. L., & Paterson, S., The virial theorem in quantum mechanics, The London, Edinburgh, and Dublin *Philosophical Magazine and Journal of Science*, (1951) 42(327), 391-395.

[13] Parker, E. N., Tensor Virial Equations. *Physical Review*, (1954) 96(6), 1686–1689.

[14] Hoover, W. G., & Ree, F. H., Calculation of Virial Coefficients., *J. Chem. Phys.*, (1965) 43(2), 375-392.

[15] Fernandez F. M., Castro, E., Hypervirial theorems and enclosed quantum-mechanical systems, *Phy. Rev. A*, (1981) 24(5), 2344.

[16] Fernandez F. M., Castro, E., Virial theorem and boundary conditions for approximate wave functions, *Int. J. Quantum. Chem*., (1982) 11, 741.

[17] Mukhopadhyay, S., Bhattacharyya, K., Confined systems and the modified virial theorem from semiclassical considerations, *Int. J. Quantum Chem*., (2005) 101, 27.

[18] Demir, C., Yakar, Y., Çakır, B., Özmen, A., Excited state energies, orbital energies and virial coefficients in confined multi-electron systems, *J. Lumin*., 251, 119185, 2022.

[19] Hirschfelder, J. O., Classical and Quantum Mechanical Hypervirial Theorems, *J. Chem. Phys*., (1960) 33 (5), 1462-1466.

[20] Fernandez, F. M., Castro, E., The virial theorem for systems subjected to sectionally defined potentials, *J. Chem. Phys*., 75 (6), 2908, 1981.

[21] J. H. Holland, *Adaptation in Natural and Artificial Systems* (1975) University of Michigan Press, Ann Arbor, MI.

[22] Çakir, B., Özmen, A., & Yakar, Y., Investigation of electronic structure of a Quantum Dot using Slater-Type Orbitals and Quantum Genetic Algorithm, *Int. J. of Modern Physics C*, (2007) 8(1), 61-72.

[23] Çakır, B., Özmen, A., Atav, Ü., Yakar, Y., Yüksel, H., Calculation of electronic structure of a spherical quantum dot using a combination of quantum genetic algorithm and Hartree Fock Roothaan method, *Int. J. of Modern Physics C*, (2008) 19(4), 599-609.

[24] Demir, C., Yakar, Y., Çakır, B., Özmen, A., Energies of the ground and excited states of confined two-electron atom in finite potential well, *Physica B*, (2023) 662, 414967.