Indian Journal of Pure & Applied Physics
Vol. 64, February 2026, pp. 148-157
DOI: 10.56042/ijpap.v64i2.22608

A Machine Learning-Driven Methodology for the Precise Determination of the Ground State Energy of Helium Atom

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Received: 11th August 2025; accepted: 12th January 2026

Here the ground state energy of helium atom is investigated and also a Machine Learning (ML) model is constructed using Gaussian Process Regression (GPR) algorithm for the same. The parameters free perturbative method in matrix representation approach is used,in which the approximation is improved by adding higher order *p*-orbital states. The error is reduced to be 1.93%.This allows us to confirm that the accuracy of the energy value will converge with respect to adding higher order states of *p*-orbital, *d*-orbital, etc. Since here prediction belongs to regression model, Gaussian Process Regression (GPR) is chosen. With small dataset we extend this work for ML energy prediction model using GPR technique which is used to inter or extrapolate the ground state energy value.Cross validation is also done using R^2 evaluation metric.

Keywords: Ground state energy, Helium atom, Perturbation method, Gaussian process regression, Artificial intelligence, Machine learning

1 Introduction

Helium (He) atom is a two-electron system which is a classic problem andit is a model system for the evaluation of ground state energy of many electrons system. From Hylleraas period *i.e.* 1929 to till 2021[1–3], so many methods and approximations were used to find the energy values of He atom. Quantum mechanical methods such as variational method[4,5], perturbation method[6-10], Finite element method[11-14] etc., were used for energy evaluation. Factors like relativistic corrections, non-relativistic corrections[15], and number of parameters usedwere also played an important role in the approximation of ground state energy value of the He atom. The calculated energy values of He atom by using those methods are given in Table 1.

Among all methods, a well-known method namely variational method is a more suitable method for the accurate quantum mechanical treatment of the ground state of He, because of its dependence on appropriate choices for the wave functions. After Hylleraas pioneering work in 1929, many studies have been devoted to solve Schrödinger equation of He atom as accurately as possible and accuracy is found upto 40 digits[16-26]. Next, the simplest approach, Perturbative method was carried out by Unsoldin 1926 by factorizing the wave functions in terms of spherical coordinates and the error was found to be 17 %[27]. In standard text book Perturbation theory calculations on He atom are large and the error is estimated around 15.45%[28]. In the last decade, Masse and Walker established the Perturbative method using matrix mechanics and found energy value of He atom for $1s^2$ state numerically. Later, theyhave used same approach and included 3 to 25 basis states in their energy calculations. Even though the variational method produces a high precision ground state energy value, the number of parameters used in them make the problem tedious. But this Perturbative Matrix representation method isan impactful simplest and parameters free energy evaluation technique. Masse and Walker used 7 basis states that is with one ground state(1s1s) and six excited states (1s2s,2s1s,1s3s,3s1s,1s4s,4s1s) of *s*-orbitals as basis sets for energy evaluation and the error percentage for ground state energy value of He atom is 2.14 %. To make convergence in their energy value towards the experimental,were carried out.They have used the same 1*sns* states as basis sets but they increased the number of basis sets as with one ground state (1s1s) and 24 excited states (1s2s,2s1s,…,13s1s) and their idea worked well, notable accuracy was obtained. They attained the error percentage as 2.02 %.

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Table 1 — Calculated ground state energy of He (in a.u.) using various methods

Methods	Ground state energy
Variational method (six parameters)	-2.90324
Variational method (eight parameters)	-2.903745
Variational method (10 parameters)	-2.903603
Variational method (14 parameters)	-2.903690
Variational method (18 parameters)	-2.903716
Variational method (25 parameters)	-2.903723
Variational method (39 Parameter)	-2.9037225
Variational method (20 parameters)	-2.9037179
Variational methods (Logarithmic, 246 terms)	-2.9037244
Perturbation Theory (hyper spherical coordinates,196 basis functions)	-2.90373
Correlated Variational method (8066 basis functions)	-2.903724 upto 63 digits
Finite element method (7497 terms)	-2.90324
Variational methods (correlated wavefunctions,4648 terms)	-2.903724 upto 16 digits
Variational method (Kinoshita Type expansion, 100 terms)	-2.90372
Heisenberg Model	-2.9039
Variational Method (22000 basis functions)	–2.90372upto 35 digits
Perturbation method (7 basis functions)	-2.84138
Perturbation method (25 basis functions)	-2.84464
Perturbative method (via Green's expansion)	-2.83475
Exp.	*-2.90338*

In order to reduce the error further, in the present study the same perturbative method with matrix representation is used. The number of basis sets are increased by including the excited states of p-orbitals in their calculation and the improvement in the accuracy of ground state energyis investigated. Using this computation results, energy prediction machine learning (ML) model is modelledin Gaussian Process Regression (GPR) framework. There are vast applications of ML in quantum chemistry such as studiesof structures of molecules and materials based on the quantum mechanics of electronic structure[29], prediction of Helmholtz harmonic free energies of molecular crystal[30], solving the Schrödinger equation, construction of interatomic potentials[31] and etc. Further developments were achieved by combining general properties of ML methods, mostly Neural Network and Gaussian Process Regression. Apart from those ML works, but not yet done, the forecasting of the ground state energy of He atom is done using GPR model whichis relevant to our computational work. In addition, the model is cross validated by R^2 score metrics.

2 Methods

2.1 Perturbative Theory

According to Perturbative theory Hamiltonian representing the total energy of the known system is,

$$H = H^0 + H' \qquad \ldots (1)$$

where, H^0 is the unperturbed Hamiltonian, H' is the perturbed Hamiltonian. First order correction to the energy is an expectation value of perturbed Hamiltonian over the corresponding unperturbed states of the system and is given by,

$$E_n^{(1)} = \langle n|H'|n\rangle \qquad \ldots (2)$$

Finally, the total energy of the system is,

$$E = E^0 + E_n^{(1)} \qquad \ldots (3)$$

2.2 Perturbative Method for He Atom

On the basis of Perturbative method, the total Hamiltonian of the He atom is written as,

$$H = H^0 + V \qquad \ldots (4)$$

The known Hamiltonian of He atom is,

$$H^0 = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} \qquad \ldots (5)$$

H^0 is the Hamiltonian for two non-interacting electrons moving outside an alpha particle nucleus. Here an electrostatic repulsion between two electrons is taken as perturbed term as

$$V = \frac{1}{|r_1 - r_2|} = \frac{1}{r_{12}} \qquad \ldots (6)$$

The Orbital approximation states that each electron in a many electrons system occupies its own one electron function (wave function). According to this approximation wave function of two electrons in a He atom can be written as the product of two He$^+$ wave functions as,

$$|\psi_p\rangle = |\phi_1\phi_2\rangle = |n_1 l_1 n_2 l_2\rangle \qquad \ldots (7)$$

where n_n and l_n is principal and angular momentum quantum number of n^{th} state. Elaborately general view of the wave function of He atomis explained below.

Since the excited states of He consists of one electron in the hydrogenic ground state, and other in an excited state, then the wave function can be denoted by using their corresponding states as,

$$\psi_{100}\psi_{nlm}$$

Spatial function is either symmetric or antisymmetric depending on the electron's distribution in each state[32]. So, the combined form of total wave function on the basis of electrons occupation in their energy states is,

$$\psi(r_1, r_2) = \frac{1}{\sqrt{2}}\psi_{100}(r_1)\psi_{nlm}(r_2) \pm \psi_{100}(r_2)\psi_{nlm}(r_1) \qquad \ldots (8)$$

This equation is used to derive Coulomb and Exchange integral term for an energy state

In spherical coordinates, wave function is

$$\psi(r_1, r_2) = \phi_1\phi_2 = \{[P_{n_1l_1}(r_1)Y_{l_1m_1}(\theta_1, \varphi_1) * P_{n_2l_2}(r_2)Y_{l_2m_2}(\theta_2, \varphi_2)]\} \qquad \ldots (9)$$

where $Y_{lm}(\theta, \varphi)$ is angular part of the wave function and is derived as,

$$Y_{lm}(\theta, \varphi) = \varepsilon\sqrt{\frac{2l+1(l-|m|)!}{4\pi(l+|m|)!}}P_l^m(cos\theta)e^{im\varphi} \qquad \ldots (10)$$

$Y_{lm}(\theta, \varphi)$ is the standard spherical harmonic. Then $P_{nl}(r)$ is the radial part of wavefunction and given as,

$$P_{nl}(r) = \sqrt{\frac{2(n-l-1)!}{n^2(n+l)!}}\left(\frac{4r}{n}\right)^{l+1} e^{-2r/n}L_{n-l-1}^{2l+1}(4r/n) \qquad \ldots (11)$$

$P_{nl}(r)$ is the radial wave function.

2.2.1 Energy Calculation

The energy of the He atom for unperturbed states,

$$E_{n_1n_2}^0 = -\frac{2}{n_1^2} - \frac{2}{n_2^2} \qquad \ldots (12)$$

Here, the perturbed term of He atom is Coulomb interaction between the two electrons and is termed as $\frac{1}{|r_1-r_2|} = \frac{1}{r_{12}}$. This $\frac{1}{r_{12}}$ perturbed term is expanded in spherical harmonics as

$$\frac{1}{r_{12}} = \sum_{lm}\frac{4\pi}{2l+1}\frac{r_<^l}{r_>^{l+1}}(-1)^m Y_{l,-m}(\Omega_1)Y_{l,m}(\Omega_2) = \frac{1}{r_>} + (l > 0\ terms) \qquad \ldots (13)$$

For 1*sns* states of s-orbital, after substituting the n and l values as n=1, l=0then the corresponding $\frac{1}{r_{12}}$ term is found as,

$$\frac{1}{r_{12}} = \begin{cases} \frac{1}{r_1}\ if\ r_1 > r_2 \\ \frac{1}{r_2}\ if\ r_1 < r_2 \end{cases} \qquad \ldots (14)$$

But in the case of 1*snp* states,since *l=1 and m=0,*±1exchange degeneracy occurs. So, these states have separate expressions for Coulomb energy and exchange energy. In *1snp* states, *1s* is spherically symmetric, so*l=0* contributes significantly for Coulomb integration evaluation. Therefore, for coulomb integration $\frac{1}{r_{12}}$,

$$\frac{1}{r_{12}} = \begin{cases} \frac{1}{r_1}\ if\ r_1 > r_2 \\ \frac{1}{r_2}\ if\ r_1 < r_2 \end{cases} \qquad \ldots (15)$$

Due to theswapping of positions of electrons in both *1s* and *np*states (overlapping of orbitals)gives *l=1*. So, for the exchange integration perturbed term becomes as,

$$\frac{1}{r_{12}} = \begin{cases} \frac{r_2}{r_1^2}\ if\ r_1 > r_2 \\ \frac{r_1}{r_2^2}\ if\ r_1 < r_2 \end{cases} \qquad \ldots (16)$$

As per the definition of *J* and *K*, it can be written as,

$$J = \iint \psi_{100}^*(r_1)\psi_{nlm}^*(r_2)\frac{1}{r_{12}}\psi_{100}(r_1)\psi_{nlm}(r_2)d\tau_1 d\tau_2 \qquad \ldots (17)$$

$$K = \iint \psi_{100}^*(r_1)\psi_{nlm}^*(r_2)\frac{1}{r_{12}}\psi_{100}(r_2)\psi_{nlm}(r_1)d\tau_1 d\tau_2 \qquad \ldots (18)$$

Here *J* is the coulomb energy arises due to the coulomb interaction of the electrons and *K* is the exchange energy arises due to the exchange of electrons between the energy states[14]. In the case of 1*sns* states both *J* and *K* are same since $l = 0$. But $l = 1$ for *p*-orbital, so *J* and *K* are different for 1*snp* states. Coulomb integral or Coulomb energy fully depends on its radial function and the expression of it is similar for all types of states (1sns,1snp,1snd, etc..,). Since exchange integration is a quantum mechanical phenomenon and depends on both spin and spatial function, the perturbed term will be tuned as per the value of angular quantum number *l* for every orbital[33]. Then using the wave function expression of Eq. (11) as well as the results of $\frac{1}{r_{12}}$ term of the Eqs (14),(15) and (16), *J* and *K* will be derived for 1*snp* states as,

$$J = \left\{\int_0^\infty \frac{P_{n1}(r_2)}{r_2}\int_0^{r_2} P_{10}(r_1)dr_1dr_2 + \int_0^\infty P_{n1}(r_2)\int_{r_2}^\infty \frac{P_{10}(r_1)}{r_1}dr_1dr_2\right\} \qquad \ldots (19)$$

$$K = \left\{\frac{2}{3}\int_0^\infty P_{10}(r_2)\frac{P_{n1}(r_2)}{r_2}\int_{r_2}^\infty \frac{P_{10}(r_1)P_{n1}(r_1)}{r_1^4}dr_1dr_2\right\} \qquad \ldots (20)$$

The total energy of the perturbed system $E = E^0 + J + K$corresponds to singlet state with symmetric spatial function and antisymmetric spin configuration, they are called parahelium while $E = E^0 + J - K$ requires antisymmetric spatial function and symmetric spin configuration and corresponds to triplet state, they are called orthohelium. The ground state is necessarily parahelium; the excited states come in both forms. As mentioned earlier, J, the coulomb energy is a classical part which is equivalent to classical electrostatic interaction between two charge distributions whereas K, the exchange energy is quantum mechanical corrections to the Coulomb integral.

The power of matrix mechanics in Perturbative method is, perturbed term or Coulomb potential between the two electrons of each state are combined to form a matrix. This perturbed matrix term is used to find the ground state energy value. The mechanism for energy eigenvalue calculation is discussedbelow:
The Hamiltonian of a system in matrix notation is,

$$H = \sum_{p,q} H_{pq} \left|\psi_p\right\rangle\left\langle\psi_q\right| \qquad \ldots (21)$$

and matrix form,

$$H = \begin{bmatrix} H_{11} & H_{12} \ldots & H_{1q} \\ H_{21} & H_{22} \ldots & H_{2q} \\ \ldots & \ldots & \ldots . \\ H_{p1} & H_{p2} \cdots & H_{pq} \end{bmatrix} \qquad \ldots (22)$$

Each matrix element H_{pq} is the Hamiltonian for pq^{th} state and for He atom it is given as,

$$H = E^o_{n_1 n_2}\delta_{pq} + \left\langle n_1 l_1 n_2 l_2 \left| \frac{1}{r_{12}} \right| n_3 l_3 n_4 l_4 \right\rangle = -\frac{2}{n_1^2} - \frac{2}{n_2^2} + \iint \begin{matrix} d^3r_1 d^3r_2 P_{n_1 l_1}(r_1) Y_{l_1 m_1}(\theta_1, \varphi_1) P_{n_2 l_2}(r_2) Y_{l_2 m_2} \\ (\theta_2, \varphi_2) \frac{1}{r_{12}} P_{n_3 l_3}(r_1) Y_{l_3 m_3}(\theta_1, \varphi_1) P_{n_4 l_4}(r_2) \end{matrix} Y_{l_4 m_4}(\theta_2, \varphi_2) \qquad \ldots (23)$$

The angular part$(Y_{lm}(\theta, \varphi))$ is same for all spherically symmetric potentialswhere only the radial part is affected by its actual shape. For *s*-orbital since angular quantum number $l = 0$, all *1sns* states would have $Y_{lm}(\theta, \varphi)$ value as 1.The second term in the above equation is either a Coulomb integral or exchange integral.

Then from the Schrodinger equation,
$H\psi = E\psi$
$(H - EI)\psi = 0$ ('I'is the unit matrix)

Since $\psi \neq 0$, then $(H - EI) = 0$. So, the matrix $(H - EI)$ must be singular, which means its determinant is zero:

$$|H - EI| = \begin{vmatrix} H_{11} - E & H_{12} \ldots & H_{1q} \\ H_{21} & H_{22} - E \ldots & H_{2q} \\ \ldots & \ldots & \ldots . \\ H_{p1} & H_{p2} \cdots & H_{pq} \end{vmatrix} = 0 \qquad \ldots (24)$$

This H matrix is formed by evaluating J and K of each state. This J and K are computed numerically for 31 number of basis setsusing by PYTHON program. The Eq. (24) is similar to Cayley Hamilton characteristic equation and as said before, using this equation the energy eigenvalue of E of each state will be calculated.

The determinant term for n=7 is,

$$|H - EI| = \begin{vmatrix} -2.75 - E_1 & 0.1787 & 0.1787 & 0.0774 & 0.0774 & 0.0414 & 0.0414 \\ 0.1787 & -2.08 - E_2 & 0.0439 & 0.0042 & -0.0285 & 0.003 & -0.0021 \\ 0.1787 & 0.0439 & -2.08 - E_3 & -0.0285 & 0.0042 & -0.0021 & 0.003 \\ 0.0774 & 0.0042 & -0.0285 & -2.01 - E_4 & 0.0658 & 0.0175 & 0.0242 \\ 0.0774 & -0.0285 & 0.0042 & 0.0658 & -2.01 - E_5 & 0.0242 & 0.0175 \\ 0.0414 & 0.003 & -0.0021 & 0.0175 & 0.0242 & -2 - E_6 & 0.0191 \\ 0.0414 & -0.0021 & 0.003 & 0.0242 & 0.0175 & 0.0191 & -2 - E_7 \end{vmatrix} = 0$$

This calculation is done by PYTHON program. The PYTHON code is given in supporting information file.From determination eigenvalues of E_1, E_2, E_3, E_4, E_5, E_6 and E_7 are calculated and their corresponding eigenvectors also found. E_1 is ground state energy value where other energies E_2, E_3, E_4, E_5, $E_6$and E_7 are singlet and triplet states of *1s2s,1s2p,1s3p* respectively.

2.3.Gaussian Process Regression

GPR comes under supervised learning. It is a powerful approach because it permits automatically for well-defined quantification of the uncertainties.GPR is a statistical modeling and generates group of functions based on the priori assumptions of mean and kernel. That prior distribution is modified by the reference dataset and it provides a posterior distribution of the functions. The mean of these functions is the GPR prediction. Usually in addition to the function values, it calculates the variance values which indicates the uncertainties of the result(function values). Hence many literatures offer deep explanation of GPR modeland its applications[34], also that much of content is not needed here, but the important terms related to the constructed model are explained.

2.3.1 Kernels

A kernel is also known as a covariance function of two inputs, and specifies the "similarity" between two objects[35]. It is important to select the appropriate kernels wisely to construct the priori. Refinement of the statistical hyperparameters like variance σ is required because it assures the high performance of the model. This is done by specifying a prior(based on chosen kernel) and then refining the hyperparameters iteratively based on training set in order to generate posterior. There are many kernel types based upon their usage and few of them are Radial Basis Function(RBF), Rational quadratic Kernel, Periodic kernel, Linear kernel, Polynomial kernel. Among them we have chosen RBF. Mathematically the RBF kernel between two data points x and x′ is defined as,

$$K(x,x') = \exp\left(-\frac{\|x-x'\|^2}{2\sigma^2}\right) \qquad \dots (25)$$

where $|x-x'|$ is the distance between the two scalars(univariate GPR, since one feature is used), σ is the parameter of kernel length.

Next chosen White kernel which is used to define noise variance at the priori is defined as,

$$k(x_i,x_j) = \sigma^2\delta_{ij}$$

where σ^2 is the noise variance which is uncorrelated. δ_{ij} is Kronecker delta and it has value of 1 if x_i and x_j are equal otherwise it values as 0. Since it adds noise along the diagonal of kernel matrix ($K(x,x')$), the uncertainties areproduced in the result of the model.

2.3.2 Fitting and Smoothness

Then fitting of data is also an important thing that depends on kernel length. If the length is less than 1.0, model treats small changes even noise as highly significant, which cause overfitting of dataset with model. Its results in the corresponding model are fit very well only for training data, but it would perform poorly for unknown or test data. At the same time, increasing length scale may cause underfitting. Due to the insufficientinput data, it may occur. The underfitting of the model will have poor performance even for training data. So, chosen length scale should be moderated one.

Smoothness is also a one of the important factors to construct a good prediction model.It refers to how gradually or abruptly the prediction values changes as the input data changes. This also controlled by hyperparameter associated with the kernel or covariance function. So obviously this factor too influences the fitting of data.

2.3.3 Validation of the Model

After the model has been fitted, it must be validated before it can be broadly applied. For validation we have used R^2 score which is also known as the coefficient of determination. This metric is used to evaluate the performance of a regression model. It gives how well our model predict the output. The possible values of it were in the range of 0 to 1 which based on the fitting of data such as perfect fit, excellent fit, good fit, poor fit and worst fit.

3 Results and Discussion

This study, from n=3 to$n$ = 31 (n is the number of basis sets)ground state energy is calculated using PYTHON program. The calculated results are given in Table 2. On comparing with Pingak et al. study, here for n=7 the error percentage is reduced to 1.93 % from 2.02 %. As the number of basis sets increases from 7, the abrupt change is happened in energy value at n=15 which produce the error percentage as 1.85%.Plotted a graph for number of basis sets versus computed ground state energy value and shown in Fig. 1. It shows that a sudden fall occurred in the energy value from the basis states n=7 to n=15, which means that increasing of basis states from 7 to 15 cause a significant approximation occurred in ground state energy value. The accuracy between themis in the range of 10^{-3} that is 0.002 a.u. So, the statement given by Masse and Walker as “Even so, it is not necessary to diagonalize a large matrix, because to a reasonably good approximation the He wave functions turn out to be combinations of only three or four basis state” is not matched with our result (They may be mentioned only for s-orbital). Because here the combinations of seven basis states are used for diagonalization of Hamiltonian matrix for good approximations. Furtherly increased the number of basis sets upto30 to approximate low-lying energy of He atom and for n=30 the calculated ground state energy value is -2.8499a.u. But now the approximationis in 10^{-4} decimal range. Since energy gap between first state and nth state is given by $E_n = -\frac{13.6\,Z^2}{n^2}$, in which energy gap is proportional to the inverse square of n. So quietly as we for higher order states, energy gap will be reduced and it becomes continuum states which are almost overlapped. This is the reason for less impact on result for n=16 to 30 basis states. It is shown in Fig. 1 as a nearly flat line variation. It means increasing the basis sets above 15 states cause a

Table 2 — The calculated ground state energy of He atom (in a.u.) by considering various number of basis states

S. No.	No. of basis states	Present work (Inclusion of 1*sns* and 1*snp* states)	Earlier study (Inclusion of 1*sns* states alone)
1	3	-2.83043779328682	
2	4	-2.83801277520875	
3	5	-2.84435503165054	
4	6	-2.84584372753520	
5	7	-2.84726622146033	-2.84138 -2.84138
6	8	-2.84783902272248	
7	9	-2.84840126462961	
8	10	-2.84868392805869	
9	11	-2.84896394278265	
10	12	-2.84912452336860	
11	13	-2.84928423642790	
12	14	-2.84938429341464	
13	15	-2.84948401074990	-2.84406
14	16	-2.84955059719784	
15	17	-2.84961703243700	
16	18	-2.84966359110016	
17	19	-2.84971007557896	
18	20	-2.84974391136929	
19	21	-2.84977770788508	
20	22	-2.84980307165935	
21	23	-2.84982841332052	
22	24	-2.84984791662383	
23	25	-2.84986740689860	
24	26	-2.84988080487515	
25	27	-2.84989611758069	
26	28	-2.84990837226435	
27	29	-2.84992061793878	
28	30	-2.84993058021703	
29	31	-2.84994049796152	

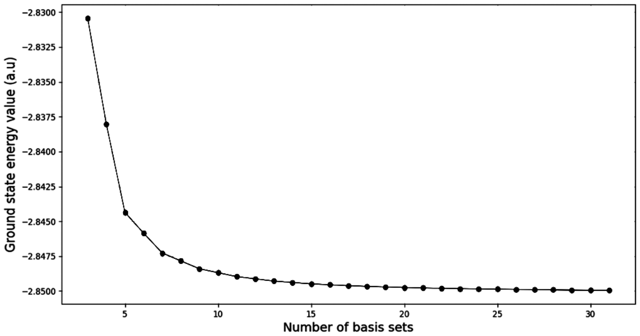

Fig. 1 — Calculated Ground state energy of He atom

negligible effect in energy value approximation. So, this may be hidden truth of Masse and walker's statement. Finally, all indicates that the inclusion of higher order states of *p*-orbital improves the ground state energy value of He atom. So, when the Coulomb interactions between two electrons in the ground state and excited states of p-orbitals are combined with Coulomb potentials between two electrons ground and excited states of s-orbital as a perturbed term, then this idea enhances the accuracy of energy values of He atom. Here, the quantum concept of the probability of existence of electrons in the higher order *np* states is behind it. Generally, we know that the occurrence of electrons in an atom is mystery. So, its existence is always expressed by Born's statistical interpretation of the wavefunction. Simply, electrons spread out in the space anywhere around the nucleus of the atom. That space is the orbitals such as *s,p,d,f* etc.., Since during the excitation of He atom one electron always present in ground state while other occupy any other excited states. This is the key point of our work. Because position of one electron is fixed and another one has the choice of any excited states of s or p or d or f orbitals. In the previous work Masse & Walker and Pingak *et al.*, have used excited states of s orbital alone. Here,we include the existence probability of another electron in higher order states of orbitals of p, which means extending electron 'space'(electron's cloud) from s orbital top orbital for our calculations. Thus, the extended 'space' which havetheexcited states of s and p give their contribution in the approximation of ground state energy value of He atom through their existence.

Initially three basis sets having a ground state and first 2 excited states of *p*-orbitals (*1s2p, 2p1s*) alone that is *1s1s,1s2p,2p1s* for the same computation but it calculates ground state energy as -2.8304 a.u. which cause 2.51 error percentage. The reason for this controversy is the electronic structure of an atom. According to Aufbau's principle the lowest energy orbitals are filled before electrons are placed in highest energy orbitals[36]. In He atom 2*s* state is the first excited state. Therefore, the probability of existence of second electron in excited *s* states must be included. Another fact is, 2*s* state is a metastable state[37] that is long lived excited state while 2*p* state has low life time, because 2*s* →1*s* transition is not possible and 2*p* →1*s* transition is allowed. Thus, the probability of finding another electron is more in first excited state of s orbital that is 2s. So, the basis states 1s2s and 2s1s should be added for approximating the ground state energy value. Then the results are fed into an energy prediction ML model constructed using Gaussian Process Regression technique. Here, the number of basis sets are the features while their corresponding ground state energy are the labels. As we discussed about the importance of kernel. Further, the accuracy of the calculated ground state energy is heavily influenced by the selection of basis orbitals. When calculations are limited to *s*-orbital excited states, the error tends to be larger; however, incorporating *p*-orbital states greatly improves convergence and lowers the error to less than 2 %. This illustrates that contributions from higher angular momentum improve the representation of electron correlation and the spatial versatility of the wave function.

The machine learning model was built using a dataset derived from the computed ground state energies obtained through the perturbative matrix method for various numbers of basis states, specifically from n = 3 to n = 31. The input feature corresponds to the number of basis states, while the target labels are the associated ground state energy values. Before training the model, duplicate entries were eliminated, and the input feature was normalized to enhance numerical stability. Additionally, the dataset was examined for consistency in convergence to ensure that the trends observed were physically meaningful. Next, a ML model for forecasting the ground state energy value of He atom for different number of basis sets is constructed using Gaussian Process Regression Technique. Choosing a Kernel and its length is a challengeable one, because the accuracy of data prediction depends on them. In the present work, Radial Basis Function kernel and White kernel are chosen. The length of RBF is fixed as 3 which means to correlate two basis set sizes within 3 units apart are strongly correlated. In white kernel, two parameters have to be defined one is noise level which is taken as10^{-3} (0.001) and another one noise level bound which is selected as lower limit10^{-6} (0.000001) and upper limit10^{-2} (0.01). Hence, noise is spread by 0.001 unit and the noise level bound instructs the model that it can adjust the noise variance anywhere from 10^{-6} to 10^{-2} in future prediction. Simply it is the optimization range of noise during training. For higher n values the corresponding ground state energy value may be approximated in the range of 10^{-5} to 10^{-6} so that the lower bound value is tuned as 10^{-6}. Finally, alpha parameter which is used to regularize the noise is selected as 10^{-8}. This tiny value is added to the diagonal of kernel matrix to make its inversion more stable and fits the noise tightly. A GPR graph is plotted for ground state energy with respect to the number of basis sets and shown in Fig. 2. Red dotted lines represented the actual training data and the blue line express the model prediction which is a smooth curve. Then broad blue stripe is the uncertainties of each data point and named as confidence level. Here, 28 data (n=3,4,5,…,31) is trained. Prediction line fitted well with training values. Fitting level is calculated using R^2 score as 98.56 %. More data can be added, but the variation in the output for higher n values is in the range of 10^{-9}, 10^{-10}, etc. So, it's not needed to predict approximated ground state energy value for higher number of basis sets, in which best

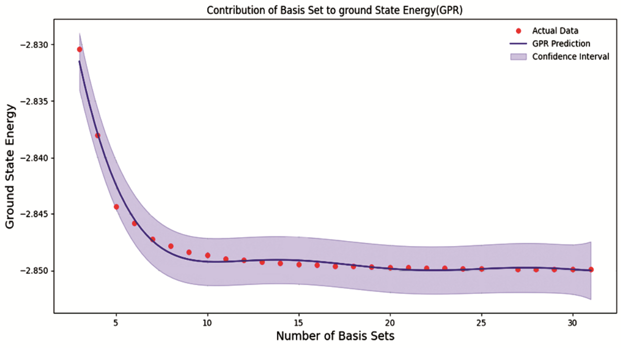

Fig. 2 — GPR Prediction

Table 3 — Total energy (in hartree) of He atom is calculated by various ab initio methods and basis sets

Methods	Basis set	Total Energy	ΔE^a
HF	STO-3G	-2.80778396	0.095596
	3-21G*	-2.83567987	0.0677
	6-31G(d)	-2.85516043	0.04822
	6-31G(d,p)	-2.85516043	0.04822
	6-311G(d)	-2.85989542	0.043485
	6-31++G(d,p)	-2.85565054	0.047729
	6-311++G(d,p)	-2.85998392	0.043396
MP2	STO-3G	-2.80778396	0.095596
	3-21G*	-2.84717649	0.056204
	6-31G(d)	-2.86636055	0.037019
	6-31G(d,p)	-2.88063745	0.022743
	6-311G(d)	-2.87641836	0.026962
	6-311G(d,p)	-2.88457791	0.018802
	6-31++G(d,p)	-2.88128435	0.022096
	6-311++G(d,p)	-2.88469621	0.018684
CCSD	3-21G*	-2.8505767	0.052803
	6-31G(d)	-2.87016214	0.033218
	6-31G(d,p)	-2.88736503	0.016015
	6-311G(d)	-2.87641836	0.026962
	6-311G(d,p)	-2.89057115	0.012809
	6-31++G(d,p)	-2.88805392	0.015326
	6-311++G(d,p)	-2.89070572	0.012674
Exp		*-2.90338*	

approximation is obtained in n=15. Even though this model is valuable for small range of data, it's our first step, base of our research building which comes successfully. In this study, Gaussian Process Regression (GPR) was chosen for its excellent performance with limited datasets and its capability to offer uncertainty assessments. In contrast, Neural Networks typically need larger datasets to prevent overfitting, while Support Vector Regression often requires meticulous kernel adjustment and fails to provide direct uncertainty data. For the current size of the dataset, GPR demonstrates greater stability and interpretability. When compared to conventional ab initio electronic structure calculations, the machine learning model drastically cuts computational expenses after training, allowing for swift predictions of energy trends without the need for repetitive diagonalizations of extensive Hamiltonian matrices.

In order to demonstrate higher basis functions are required to get the accurate ground state energy of He atom, calculations are performed using three model chemistries such as Hartree–Fock (HF), Møller–Plesset second-order perturbation theory (MP2), and coupled-cluster with single and double excitations (CCSD) in combination with Gaussian-type basis sets. The employed basis sets range from minimal (STO-3G) to large, polarized, and diffuse-augmented triple-zeta sets (6-311++G(d,p)). The computed values, together with the experimental reference (−2.90338 hartree), are given in Table 3.The energy difference between the calculated and experimental values is plotted and are given in Fig. 3. All these calculations are performed using Gaussian 09 program[38]. The trend across all methods shows that increasing the number and flexibility of basis functions leads to systematically lower (more negative) total energies, reflecting an improved approach to the complete basis set (CBS) limit. In the minimal STO-3G basis, each He 1s orbital is represented by a single contracted Gaussian combination of three primitive functions, which limits its ability to reproduce the exact radial form of the wavefunction[39]. As the basis is increased to split-valence forms such as 3-21G* and 6-31G(d), additional functions are introduced that allow separate radial flexibility for core and valence regions. The inclusion of polarization functions (d-type) enables angular distortion of the electron density in response to correlation effects, which is particularly beneficial at correlated levels of theory. It must be noted that the ground state energy notation used in Table 2 and Fig. 1 is a.u., but in Table 3 and Fig. 3, the ground state energy notation used is hartree. Both notations describe same unit. Gaussian09W program gives energy in hartree. Discussion with hartree unit is given in Table 3 and Fig. 3.

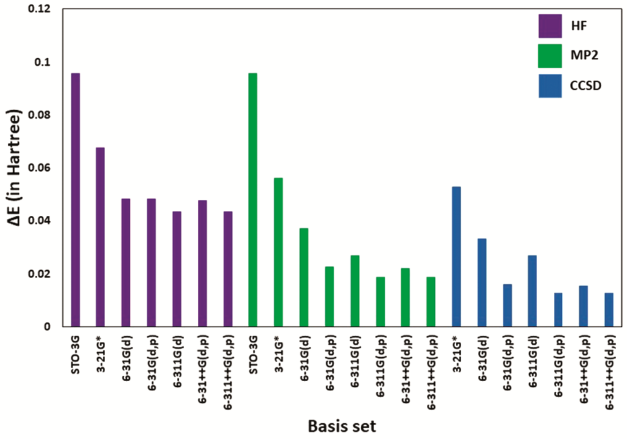

Fig. 3 — The energy difference (ΔE) between theoretical and experimental values calculated by various ab initio methods (HF, MP2, CCSD) and basis sets

In the context of He, the number of contracted basis functions increases systematically with basis set quality. The STO-3G minimal basis employs two contracted functions (one per electron spin) formed from three primitive Gaussians, offering only a crude representation of the 1s orbital. The 3-21G* set expands this to four contracted functions, with split-valence flexibility and an added d-type polarization function. The 6-31G(d) basis employs six primitives for the core orbital and split valence for the outer shell, yielding five contracted functions in total. Augmenting with d-polarization on He, as in 6-31G(d,p), increases angular flexibility without greatly changing the radial part. The triple-zeta 6-311G(d) and 6-311G(d,p) sets expand the valence space to three distinct radial components, resulting in seven contracted functions. The addition of diffuse s- and p-type functions, indicated by "+" and "++", further increases the number of functions by two to four, depending on the augmentation scheme. This systematic increase in basis size, from two to more than ten contracted functions for He correlates directly with the monotonic lowering of total energy, as the variational space available to the wavefunction becomes increasingly complete.

At the HF level, the total energy converges from −2.80778 hartree with STO-3G to −2.85998 hartree with 6-311++G(d,p), a gain of ~0.052 hartree. When electron correlation is introduced via MP2, the energies become more negative by ~0.020–0.026 hartree relative to HF for comparable basis sets, indicating recovery of a substantial portion of the correlation energy. CCSD further improves upon MP2 by ~0.003–0.005 hartree, consistent with its more complete inclusion of coupled excitations. The most negative theoretical result in this study, −2.89071 hartree at CCSD/6-311++G(d,p), lies within 0.0127 hartree of the experimental non-relativistic value, with the remaining deviation attributable to residual basis set incompleteness and omission of higher-order excitations. In summary, the data illustrate the critical role of basis functions in determining the accuracy of computed atomic energies. Both radial and angular flexibility, achieved through split-valence, polarization, and diffuse augmentation, are necessary to capture the electron correlation effects that dominate the difference between mean-field and experimental values. For the He atom, convergence toward the experimental limit is only achieved when high-level correlation methods are combined with triple-zeta quality, diffuse-augmented, polarized basis sets.

4 Conclusion

This study, the influence of *p*-orbitals in the approximation of ground state energy value of He atom is investigated using perturbative method in matrix approach and constructed the energy prediction ML model in GPR framework. Also, this have demonstrated that the addition of higher order states (1*snp*) in the approximation increases the accuracy of ground state energy of He. Adding more basis wave functions broadens the Hilbert space used to depict the electronic wavefunction, facilitating a more precise characterization of electron correlation and spatial arrangement. This enhanced representation improves the estimation of the ground state energy instead of suggesting a direct rise in the probability of electron existence. To improve the accuracy, further studies are required using higher order states of orbitals such as *d*-orbitals, *f*-orbitals, etc. However, by including*d* and *f* orbitals does not do any significant changes in approximation. Mild or negligible accuracy is obtained which means occupation or population of the electrons in excited states of *d* and *f* is small. In addition, the present study demonstrated the ML GPR model successfully predicts the ground state energy of He. The ML GPR model have good accuracy on predicting the ground state energy value for the corresponding n values.

The current approach can be applied to additional two-electron atoms and small molecular systems by properly defining the basis states and the perturbative Hamiltonian matrix. With the right adjustments, the integrated perturbative–machine learning framework could become a computationally efficient instrument for forecasting low-energy electronic characteristics of more intricate systems.

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