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Continuous Energy Values of 3-Amino-4Nitraminofurazan Molecule by Modern Optimization Techniques

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Abstract

The conformational energy values of 3-amino-4-nitraminofurazan ($C_2N_4O_3H_2$) molecule changing with two torsion angles were firstly calculated using density functional theory (DFT) with Lee-Young-Parr correlation functional and 6-31 G(d) basis set on Gaussian Program. And then, these obtained discrete data were made continuous by using Fuzzy Logic Modelling (FLM) and Artificial Neural Network (ANN). This allowed us to make predictions about the untested data and, to obtain the optimized energy value depending on two torsion angles with reasonable computational cost, great efficiency and high accuracy. The obtained results were compared with the DFT results by using regression analysis.

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INTRODUCTION

Fuzzy Logic Modelling (FLM) is one of the important modern modelling techniques improved by Lotfi Zadeh in 1965 to cope with uncertainty that usually occurs in real practices (Lotfi Zadeh, 1965). In 1974, Mamdani had carried Zadeh's theory to the practice then the linguistic approach and fuzzy inference accomplishedly started to be applied to real life problems . Fuzzy logic suggests a corollary morphology which makes easier to implement very similar human reasoning capabilities to knowledge-based systems and, is a mathematical tool to eliminate the qualms relevant to human mental processes, for instance, cogitation and reasoning. The FLM approach has been commonly used in engineering, biology, physics and etc. (Sahiner et al., 2013; 2014; 2013) (Ruusunen & Leiviska, 2004) (Suganthi et al., 2015).

Another important modelling technique is Artificial Neural Network (ANN). The ANN or NN network is electrical equivalent of biological neural networks. Essentially, the processing fundamentals of a neural network resemble to neurons in the brain. These are originated from the whole of simple computational elements regulated on layers. It is estimated that the first work on ANN have started in 1943 by McCulloch and Pitts, who developed a cell model and defined artificial neurons (Neuralware, 1993). It has been played a decisive role in many areas of study for instance; automatic control, expert systems, data classification, time series prediction and a variety of engineering applications (Tumac, 2016).

Density Functional Theory (DFT) is a way to acquire all the ground-state features of molecules. The DFT method is a theory of electronic structure found upon the electron density distribution $\rho(r)$ in place of the electron wave function $\Psi(r)$. It has been used in a common way almost 30 years by physicists who were concerning with the electronic structure of molecules, solids, surfaces, etc. That has been more famous during last years with theoretical or computational chemists (Jones, 2015). One of its most commonly used versions is B3LYP which stands for Becke, 3-parameter Lee–Yang–Parr. DFT has one important deficiency in terms of computational costs. To fill this deficiency, one important way can be to consider the modern mathematical modelling techniques.3-Amino-4-nitraminofurazan molecule used in this study is an α-amino acid. The molecule crystallizes in the orthorhombic space group with a cell volume of 938.26 $Å^3$. Its density at 173°K is 1.842 $g \cdot cm^{-3}$ (Klapotke et al., 2015). The molecule is planar, only the nitro moiety is slightly tilted against the furazan plane by a torsion angle of O2–N3–C1–C2 = 4.4°. Short hydrogen bonding is observed between the amino and nitro groups. A deeper knowledge about the molecule can be reached in the literature (Klapotke et al., 2015).

In this study the conformational energy values of the title molecule depending on two torsion angles at DFT(B3LYP)/6-31 G(d) were made continuous by using both FLM and ANN. The minimum energy value of the molecule was determined by estimating the energy values at uncalculated torsion angles. This present approach gives a new point of view to solve molecular structure problems.

RESULT AND DISCUSSION

Density functional theory (DFT)

Gaussian is a software program of computational chemistry introduced by John Pople (Gaussian70: Written by John Pople's group at Carnegie-Mellon University in the 1970s. John Pople was awarded by Nobel prize in 1998 for his advancement of computational methods in quantum chemistry) (Reveles & koster, 2004; Hehre et al., 1972; 1970). It has been developed until today (Young, 2001). DFT is a way of approaching to the electronic structure of molecules. It means that all the ground-state assets of a system are functions of the charge density on the Gaussian program. The electron density is the core variable in place of the wave function. This decreases the computational obstacle of treating electron-electron interaction terms. This method assembles the capacity to integrate exchange-correlation impacts of electrons with rational costs and high correctness (Kohn,1965; Parr & yang, 1989; Gross & Dreizler, 1990; Koch et al., 2001; Fiolhais et al., 2003; Sholl, 2009).The exact exchange energy functional is signed from the point of the Kohn–Sham orbitals, and thus it is termed an implicit density functional. B3LYP is the most widely used version, that represents Becke, 3-parameter, Lee-Yang-Parr.

Fig. 1. shows the molecular structure of 3-amino-4-nitraminofurozan optimized by using a

spin-unrestricted DFT(B3LYP) method with 6-31 G(d) basis set, together with the atoms as numbered. Whole computations performed on a personal computer were made by using Gaussian 09 Rev. D.01 (Frisch et al., 2009) and Gauss-View molecular visualization programs (Frish et al., 2001). In the computations, firstly the molecular structure was scanned around eight possible torsion angles as 360o at increments of 20o by using the DFT-6-31 G(d) method. These Potential Energy Surface (PES) graphs showed the minimum-energy structures of the molecule. From these one dimensional PES graphs, it was seen that the lowest energy structures of the molecule were obtained for the two torsion angles of ($C_1C_2N_4H_{11}$) and ($C_2C_1N_3O_9$). These torsion angles were taken to obtain the two dimensional PES graph of the molecule which will be used as input data for FLM and ANN. The two dimensional PES graph is shown in Fig. 2. As seen from the fig the global optimized structure of the molecule comes out at the torsion angles of $C_1C_2N_4H_{11}$= 347^o and $C_2C_1N_3O_9$= 357^o and the energy of -521.891 Hartree/particle. (After this, the integer value being -521 in the energy values will be taken as zero to obstruct the complexity.)

Fuzzy logic modelling (FLM)

Fuzzy logic technique is a modern modelling technique. The concept "fuzzy logic" emerged from Zadeh's common article published in 1965 (Lotfi zadeh, 1965). "Fuzzy logic" starts with the definition of "fuzzy sets". Unlike conventional sets, a fuzzy set allows partial membership of an element to a cluster in the interval [0, 1]. A fuzzy set A in X is composed of its membership function, X is not empty. For the function

$$\mu A: X \rightarrow [0, 1],$$

μA(x) is commented as the degree of membership of x in fuzzy set A for each x ∈ X. The general structure of the fuzzy system is illustrated in Fig. 3. The fig shows that the system has four

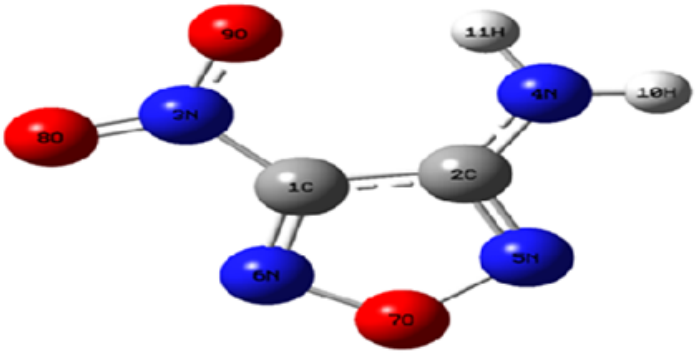

Fig. 1. Optimized structure of 3-amino-4-nitramino-furozan molecule.

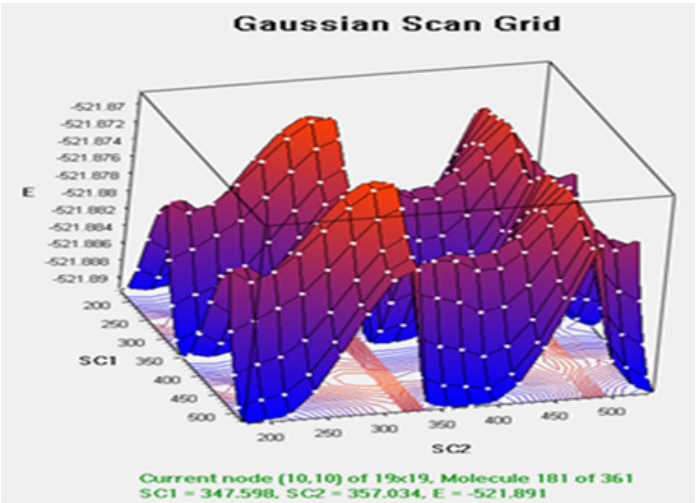

Fig. 2. Two dimensional PES graph of 3-amino-4-nitraminofurozan molecule. E= Energy, SC1= C1C2N4H11 and SC2=C2C1N3O9 torsion angles.

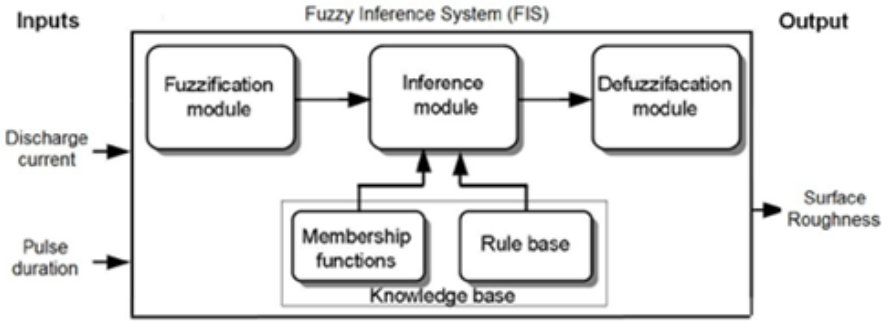

Fig. 3. The fuzzy logic modelling process.

core components: fuzzification, fuzzy rule base, defuzzification and fuzzy output engine.

Fuzzification transforms each piece of input data to degrees of membership by a lookup in some membership functions. Evidently the main idea in FLM is the allowance of partial belongings of any object to various subsets of a universal set in place of fitting to a single set entirely. Partial belonging to a set can be defined numerically by a membership function that takes values from 0 to 1 inclusive. Intuition, inference, rank ordering, angular fuzzy sets, neural networks, genetic algorithms, and inductive reasoning can be one of several methods to allocate membership values or functions to fuzzy variables (Lotfi zadeh, 1975) Fuzzy membership functions have different forms, like triangular, trapezoidal, z-shaped, gaussian, sigmoidal and s-shaped.

In this study, we have chosen to use triangular and trapezoidal membership functions in order to obtain fit results (Fig. 4). Fig. 5. illustrates the FLM model construction. The general form of a

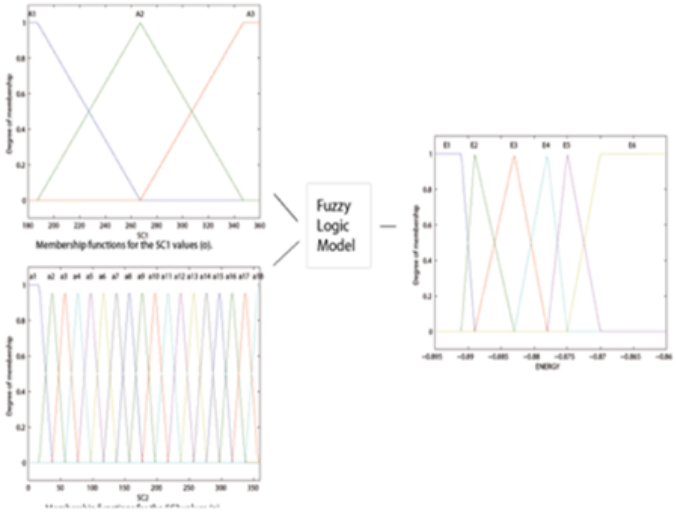

Fig. 4. Membership functions of input and output parameters used for fuzzy modelling.

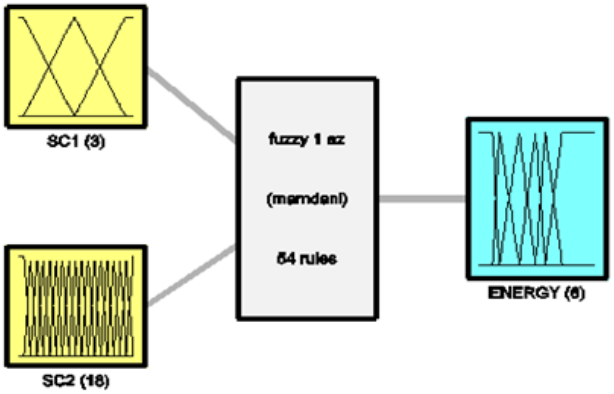

Fig. 5. General structure of fuzzy inference system.

triangular MF can be stated as:

$\mu(x,a,b,c)=\max(\min((x-a)/(b-a),(c-x)/(c-b)),0)$.

where, x is a vector and, a,b and c are scalar parameters. A trapezoidal membership function can be stated mainly as:

$\mu(x, a, b, c, d)=\max(\min((x-a)/(b-a),1,(d-x)/(d-c)),0)$.

where, d is also a scalar parameter.

Fuzzy rules cover all probable fuzzy relations of inputs and outputs. There is an expression of above mentioned rules in If–Then format. Fuzzy approach does not contain any mathematical equations and model parameters. The fuzzy inference procedure involves all the uncertainties, nonlinear relationships and model complications in the form of If-Then statements. Mamdani and Takagi-Sugeno systems are two types of inference systems (Mamdani, 1974; Sugeno & Takagi, 1983; 1985) We have formed the Mamani- type fuzzy rules, connecting input variables to the output variable and, summarized a chance selection in some of rules in the following form:

- If (Angle1 is A1) and (Angle2 is a10) then (Energy is E1)
- If (Angle1 is A2) and (Angle2 is a10) then (Energy is E4)
- If (Angle1 is A3) and (Angle2 is a10) then (Energy is E1)
- If (Angle1 is A1) and (Angle2 is a15) then (Energy is E5)
- If (Angle1 is A2) and (Angle2 is a15) then (Energy is E6)
- If (Angle1 is A3) and (Angle2 is a15) then (Energy is E5) .

All the fuzzy rules are considered by fuzzy inference engine in the fuzzy rule base and learned how to convert a set of inputs to matching outputs. We can examine two basic kinds of inference operators: minimization (min) and product (prod). Generally, both methods work efficiently. We have implemented the prod method because of better performance. Defuzzification is a process of generating a measurable outcome in fuzzy logic for given fuzzy sets and matching membership degrees. It is characteristically required in fuzzy control systems. The rules convert several variables into a fuzzy result defined by means of membership in fuzzy sets. In this stage we have different types of defuzzifications such as centroid, bisector, smallest of a maximum, middle of a maximum and largest of a maximum. In this paper we have applied centroid method for the discrete case which is given by the formula

$$real\ output=\int \mu_A(x)xdx/\int \mu_A(x)dx,$$

where,
$\int \mu_A(x)dx\neq 0$

for all μ_A. More detailed information can be got from (Mamdani, 1974; Sugeno & Takagi, 1983; 1985).

There are inputs and outputs in a fuzzy inference system. Our inputs in this study are SC1 ($=C_1C_2N_4H_{11}$) as the first input and, SC2($=C_2C_1N_3O_9$) as the second input variables, respectively. Our output is the energy value of the molecule changing with respect to SC1 and SC2. In the all FLM process, we use Matlab (R2011A) Fuzzy Logic Toolbox. By using FLM approach we have obtained a basic way for the estimation of the global minimum energy value of the molecule. Firstly, FLM is used to build a Mamdani model for the estimation of the energy of the molecule based on different torsion angles. The constructed membership functions for the inputs (SC1, SC2) and output (Energy) are shown in Fig. 4.respectively. The first angle value is increased by a step of 20^o starting with 187^o and ending with 347^o while the second angle value is again increased by step of 20^o starting with 17^o and ending with 357^o. So, we have three fuzzy numbers for the first torsion angle and, eighteen for the second torsion angle. The first angle values (A1, A2, A3) and the second angle values (a1, a2, …, a18) are considered as the input data and, the energy values of the molecule (E1, E2, ..., E6) are considered as the output data in our model.

The surface of the energy values of the mole-

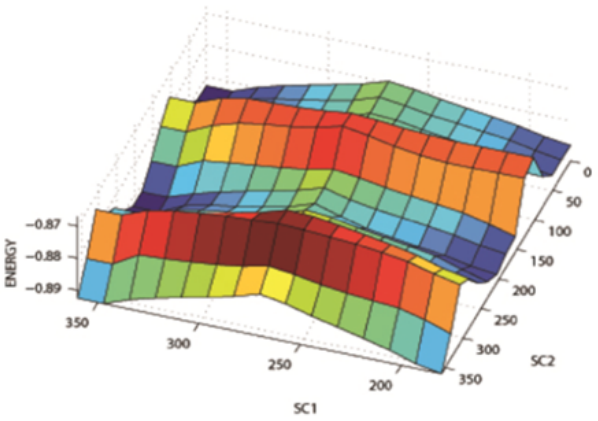

Fig. 6. Surfaces of fuzzy inference system defuzzified by centroid methods.

cule as function of both SC1 and SC2 obtained by using centroid methods in the defuzzification stage are represented in Fig. 6. By FLM we have modelled the relation between the input and output data. The fuzzy logic approach sets the continuous function between the input and output variables. If we want to know the best values of the inputs that give the global minimum value of the output, we have to make local searches around the local minimums that can be seen from the model surfaces. Because the number of the local minimums is finite, it is simple to find the global minimum energy of the molecule, truthfully. If we dissect the possible minimum energy values of the molecule, we could see that it is possible to find the deeper energy value as a global minimum of the molecule by making adjustments on the elements of the fuzzy inference system. The comparison of DFT and Mamdani type FLM predictions can be seen in Fig. 7. It shows a correlation value of 0.883.

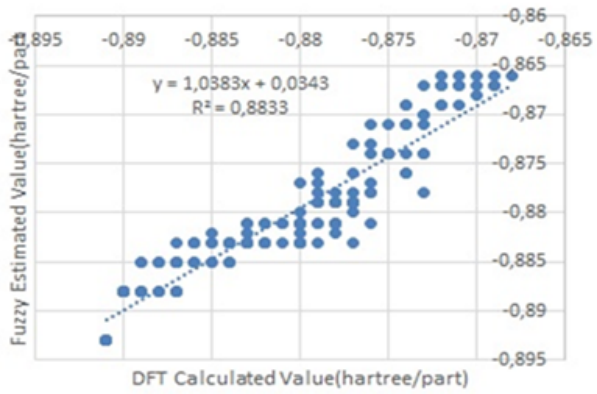

Fig. 7. Comparison of DFT and Mamdani type FLM predictions.

Artifical neural network (ANN)

ANNs are electrical equivalents of the biological neural nets. Biological nerve cells named neurons take signals from circumjacent neurons or receptors through dendrites and, operate the received electrical pulses at the cell body and hand in signals throughout a wide and massive nerve fibre, named an axon. The electrical model of a real biological neuron comprises of a linear activator, followed by a non-linear inhibiting function. The linear activation function produces the total of the weighted input excitation, whereas the non-linear inhibiting function starts an enterprise to capture the signal levels of the sum. The resulting signal, created by an electrical neuron, is

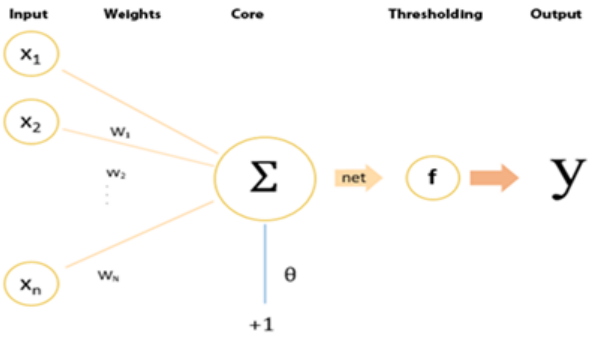

Fig. 8. The ANN modelling process.

hence limited. ANN is a collection of such electrical neurons linked in different topology (Fig. 8). ANN models can be classified with various criteria, for instance their learning ways (supervised versus unsupervised), architectures (feed forward versus recurrent), output types (binary versus continuous), node types (uniform versus hybrid), implementations (software versus hardware), connection weights (adjustable versus hard wired), operations (biologically motivated versus psychologically motivated), etc. (Tumac, 2016).

We have applied a multi-layered feed forward neural network with a back propagation algorithm in this paper. Back propagation algorithm is a gradient descent technique to minimize the fault for a certain training pattern where it regulates the weights in a short period of time (Neuralware, 1993). The model established with two input parameters and one output parameters (Fig. 9.). We have used 114 experiment outcomes in the processes of ANN model: 81 of the experi-

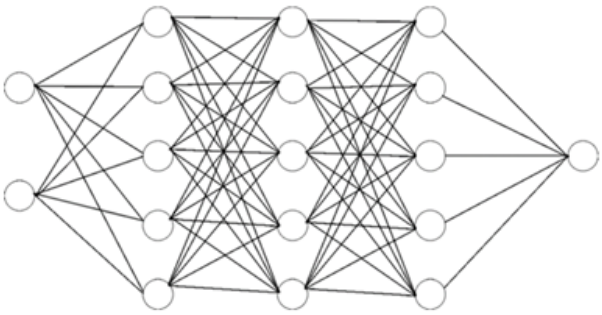

Fig. 9. The architecture neural network modelling.

ments for the training of the model, 33 for testing the trained model. In ANN, as can be seen from Fig. 9. three unit hidden layers were designated, and all of them were determined as with 5 cells. The transfer functions are tangent sigmoid and purelin in hidden and output layers. The transfer function tangent sigmoid is a hyperbolic function and purelin is a linear transfer function. Node types as hybrid and training algorithm as Levenberg-Marquart were chosen. Therefore, the model was trained by using 208 iterations. The trained model was only tested with the input values. The values of parameters:

- number of input layer units =2
- number of hidden layer =3
- number of the first hidden layer units = 5
- number of the second hidden layer units = 5
- number of the third hidden layer units = 5
- number of output layer units = 1
- learning rate (Mu) = 0.001
- mean squared error (mse) = 0.00028.

The correlation graph between DFT and ANN

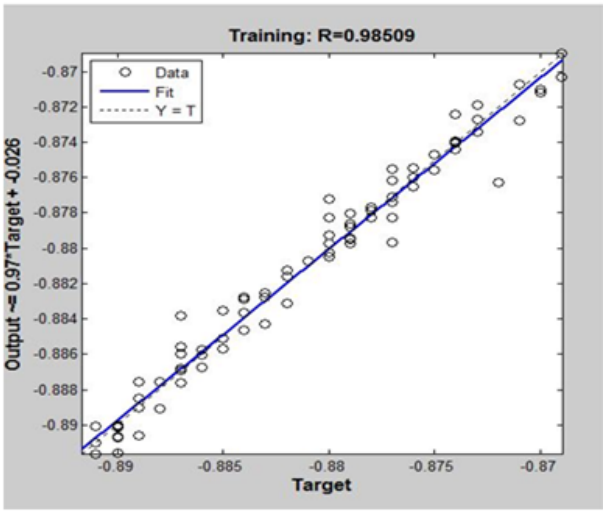

Fig. 10. Corelation graph between DFT and ANN predictions.

can be seen in Fig. 10. It shows a good agreement with a correlation value of 0.985.

In Table 1, for some SC1 and SC2 values the obtained FLM and ANN results are compared with the results obtained by DFT. As an example, for SC1=347o and SC2= 357 o the global energy values are obtained as -0.891, -0.893 and -0890 Hartree/part by DFT, FLM and ANN, respectively.

CONCLUSIONS

FLM and ANN were employed to make the energy values depending on two torsion angles continuous and to determine the global minimum energy value for the title molecule. The obtained results were compared with the results calculated by DFT. It was concluded that the FLM and ANN are 88% and 98% consistency rate according to

Table 1: The comparison of the energy values obtained by DFT with the predicted results by FLM and ANN.

Input Data		DFT	FLM	ANN
SC1	SC2			
207	177	-0.887	-0.885	-0.889
307	177	-0.887	-0.885	-0.887
227	197	-0.884	-0.885	-0.885
327	197	-0.889	-0.888	-0.891
247	217	-0.879	-0.881	-0.878
347	357	-0.891	-0.893	-0.890
347	217	-0.891	-0.893	-0.890
267	237	-0.875	-0.874	-0.874
287	257	-0.876	-0.878	-0.876
207	277	-0.876	-0.873	-0.876
307	277	-0.877	-0.873	-0.877

the values with DFT, respectively. Comparative observation showed that the FLM gives a higher error than ANN but, still both of them gives successful results for predicting in this kind of physical problems. So, we can state that ANN and FLM can also be reported as an alternative assistant approach for molecular energy measurements.

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