THEORETICAL INVESTIGATION USING DFT FOR ESTIMATING THE OPTIMAL BASIS SETS FOR SOME PESTICIDES

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Abstract. This paper concerns with the theoretical investigation for finding the optimal basis sets of density functional theory (DFT) for some commonly used pesticides, as these basis sets are crucial for accurately predicting the properties of molecules in addition to calculation time was. The evaluation of the performance of different basis sets for predicting the molecular properties of some pesticides including atrazine, simazine, propazine, diuron and monuron was explored. The determination of the best basis set was estimated with respect to the calculations of their geometries, size, functional groups and electronic structures. The optimal basis set was verified by the combination between the reaching of global minimum energy with the operation speed since the time of calculation is consider as expensive in theoretical studies. The results show that the DFT with 4-31G basis set was the accurate and much cheaper method for estimating the properties of pesticides and no need to use larger basis set. It was concluded that the presented work could provide a helpful guidance for researchers who concerning with the design and optimization of basis sets in studying pesticides and other related molecules.
Keywords: *computational chemistry, density functional theory, basis sets, pesticides, quantum chemistry*

Introduction

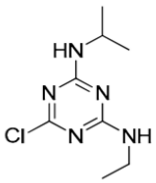
Pesticides are considered as important chemical substances that employed in order to protect humans from harmful pests include insects, weeds, fungi, and rodents. Indeed, the pesticides could play a vital role in modern agriculture, particularly in helping to protect crops and increase yields. On the other side, the widespread use of pesticides has also raised concerns about their potential negative impacts on human health and the environment. Consequently, there is a growing need for a better understanding of the mechanisms of action, fate, and impacts of pesticides. The last issue is quite important for the increasing demand for food, fuel, fiber, and the emergence of new pests and diseases (Meryem et al., 2021; Vlahović et al., 2017; Bonmatin et al., 2015; Liu et al., 2015; Krieger, 2001). On the other hand, in silico studies are considered as great and powerful tools in this field of study, since pesticides have a toxic effect on Homo sapiens rather than pets. So, it will be safe and wise to study the pesticides by in silico first in order to get a better understanding on their effects before using the traditional in vivo and in vitro methods (Shayma'a and Khalil, 2022). In silico studies can be performed by the quantum mechanical methods including semi-empirical, ab-initio, and density functional theory (DFT) methods. The last method (DFT) can be regarded as relatively the best method that could be employed for in silico treatments due to its apparent accuracy in contrast with other related methods (Khalil, 2020; Koch and Holthausen, 2001). In other words, DFT has emerged as a powerful tool for the theoretical investigation of molecular properties. Moreover, the DFT approach is enable the calculations of electronic structures and properties of molecules, including their energies, geometries, and spectra (Khalil and Abdulrahman, 2022; Lipkowitz and Boyd,

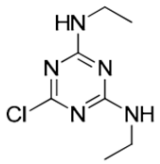
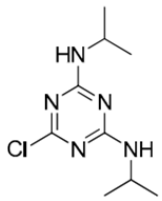
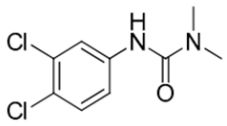
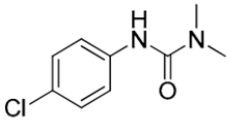
1996). It has been used in the study of pesticides to gain insights into their electronic and geometric structures, which can aid in the design of safer and more effective pesticides (Liu et al., 2015; Cramer, 2013; Bartók et al., 2010).

In general, the basis set is used to represent the wave function of a molecule or an atom which considered as an essential function for the approximation of Schrödinger equation (Chai et al., 2020). There are various types of basis sets, each with different advantages and disadvantages. Some common types of basis sets include Gaussian basis sets, Slater-type orbitals (STO), and plane wave basis sets (Leszczynski, 2012: Ramachandran et al., 2008). Gaussian basis sets are the most commonly used, and they are flexible and computationally efficient. STOs, on the other hand, are closer to the true solutions of the Schrödinger equation, but they require more computation resources. The choice of a basis set affects the accuracy of a quantum chemical calculation. The accuracy of theoretical calculations are increasing with the increase in the size of the basis set functions wither using DFT or ab-initio methods. In other words, the increase in the basis set means there is more electrons are taken under account with less approximation. But, there a problem is appeared due to increasing the basis set is the process time which even could make technical problems in the computer. Therefore, a balance between the accuracy and the time consumed must be taken under account in order to find the best results in a shorter time. Thus, a study that could evaluate a number of various basis sets that compared to the global minimum with the time consumed is very interesting. Such works will be carried out in the hope of providing valuable insights to the typical basis sets which suit the pesticides, and then can be used to enhance the accuracy of future DFT studies on such type of compounds (Rokhina and Suri, 2012). In recent years, there has been growing interest in developing more accurate and efficient basis sets for DFT calculations (Mardirossian and Head-Gordon, 2017; Grimme et al., 2015; Cramer, 2013; Tirado-Rives and Jorgensen, 2008; Khalil and Abdulrahman, 2022). One approach is the use of basis sets that are optimized for specific types of chemical systems or properties, such as basis sets optimized for transition metal complexes or basis sets optimized for non-covalent interactions. In addition to the choice of basis set, the choice of exchange-correlation functional can also affect the accuracy of a DFT calculation. It is important to carefully select both the basis set and the exchange-correlation functional in order to obtain reliable results.

The objective of the presented research is concerned with the exploring the most suitable basis sets for selected five pesticides using DFT calculations. These including three from triazine class (atrazine, simazine and propazine) and two from arylurea class (diuron and monuron) as their chemical structures shown in *Table 1*.

Table 1. *The pesticides names, structure and class that used in the study*.

Pesticide name	Chemical structure	Class
Atrazine		Triazines

Simazine		Triazines
Porpazine		Triazines
Diuran		Arylurea
Monuron		Arylurea

Materials and Methods

In general, the theoretical investigations can be made through the following two main steps. The first or initial step is carried out by two dimensional drawing the chemical structure of the compounds using suitable program. Then, the two dimensional structure of selected compounds transferred to the related three dimensional software for optimization and properties calculation purposes. Thus, the chemical structures of the selected pesticides (*Table 1*) were drawn, using two dimensional ChemDraw Ultra versions 19.0. Then, the built up two dimensional molecular structures of these pesticides were transferred to the related ChemBio3D Ultra software for theoretical calculations. The theoretical treatments where initiated with energy minimization using computational chemistry program Gaussian 09W (G09) for structure optimization in order to reach the global minimum of each molecule. From the computational chemistry point of view (Khalil, 2020), the best results that one could get from the energy minimization task must be started using molecular mechanics MM2 for reaching the root of the mean of squared components (RMS) gradient in less than 0.418 kJ/mol. Then the optimization was continued using semi-empirical methods started with Austin Model number 1 (AM1), followed by the more advanced Parameterized Model number 3 (PM3) in order to decrease the later HF and DFT optimizations time. Next step was to deploy HF-STO3 and perform energy minimization. Finally, the energy minimization task was supported using DFT treatments with exchange-correlation B3LYP at DFT STO3G, DFT 32-1G, DFT 4-31G, 6-311G and 6-311G basis sets until reaching the minimum RMS gradient of 0.418 kJ/mol in each basis set (Khalil and Hamed, 2015; Khalil and Zarari, 2015; Khalil and Al-hakam, 2014). All the theoretical calculations were carried out using a personal computer (PC) with a Pentium i7

processor (CPU 2.30 GHz), random-access memory (RAM) of 6 GB and a Windows 10 operating system.

Results and Discussion

According to the literatures, the global minimum of chemical structure optimization could be obtained in systematic manner from light to heavy theoretical treatments (Khalil, 2020). Such treatments are not limited to quantum mechanical methods, as must be started using molecular mechanics ways. The last methods such as MM2 and MMFF94 (Merck Molecular Force Field 94) are only employ the laws of classical physics according to Newton's and Hook's models (Khalil, 2020). Thus, the essential task of getting the global minimum could be reached when one starts with using molecular mechanics and then followed by semi-empirical, ab-initio and DFT calculations. In a similar manner, the energy minimization treatments using the last two methods should start with small basis sets and then gradually increased to larger.

On the other hand, the approach of quantitative structure-activity relationship (QSAR) can be considered as a vital tool for researchers, particularly for its significant assistance in reducing the issue of trial and error. Additionally, utilizing QSAR to evaluate the biological activities of molecules as termed in silico may be considered as comparable to that of experimental in vivo and in vitro methods. Additionally, utilizing QSAR to evaluate the biological activities of unknown molecules as termed in silico may be considered as comparable to that of experimental in vivo and in vitro methods. In comparison, the method of in silico has a significant advantages from hazards, cost and time consumed point of view (Shayma'a and Khalil, 2022). Therefore, any work that could support the treatment of in silico can be considered as very interesting particularly for finding the optimal basis sets of pesticides as the presented work.

The results that obtained for the basis sets investigations of the selected pesticides using theoretical methods in order to reach the global minimum are listed in Table 2. Interestingly, these show a systematic decrease in the global minimum with the increase in the advancement of the computational method. For example, the decrease in global minimum takes the following consequence:

MM2>AM1>PM3> HF-STO3> DFT –STO3G> DFT 32-1G> DFT 4-31G> DFT 6-31G> DFT 6-311G

The results of *Table 2* also show that the global minima of DFT 4-31G is enough for the calculations of pesticides as there is no sufficient decreasing in the global minima when increasing the basis set. In other words, there is a significant changes regarding energy value from MM2 method until (HF-STO3), after that the changes from (HF-STO3) to (DFT 32-1G) decreases to a lesser extent. Then, after upgrading the basis set to (DFT 4-31G) the energy started to decrease in a little mood again. But, there is no such reasonable change using more advanced basis sets (DFT 6-31G and DFT 6-311G), indicating that (DFT 4-31G) is the optimal basis set that used for the presented job as illustrated clearly in *Figure 1*. Such an important foundation is very useful in the task of theoretical calculations due to the substantial reduction in process period. In other words, there is a reduction of about the half of the expected time in contrast to that consumed using the advanced basis sets. Such a ratio of reduction in time will be

increased when using relatively larger compounds as the reduction in time may be more than 50%.

Table 2. *The global minimum energy values after each minimization process at different computational methods and related basis sets.*

Comp.	MM2 (a)	AM1 (a)	PM3 (a)	HF-STO3(b)	DFT STO-3G(b)	DFT 32-1G(b)	DFT 4-31G(b)	DFT 6-31G(b)	DFT 6-311G(b)
Atrazine	*	196.94	21	-2.71	*	*	-2.75	-2.75	-2.751
Propazine	50.7	180.37	-6.11	-2.81	-2.82	-2.84	-2.85	-2.85	-2.85
Simazine	46.53	214.01	*	-2.61	-2.62	-2.63	-2.64	-2.65	-2.65
Monuron	35.39	101.55	31.25	-2.48	-2.49	-2.51	-2.52	-2.52	-2.52
Diuron	19.31	-44.31	-121.42	-3.76	-3.78	*	-3/82	-3/82	-3.82

*Notes: a=kJ/mol; b=kJmol X 10^{6-}; *=no energy value can be estimated due to software technical problem.*

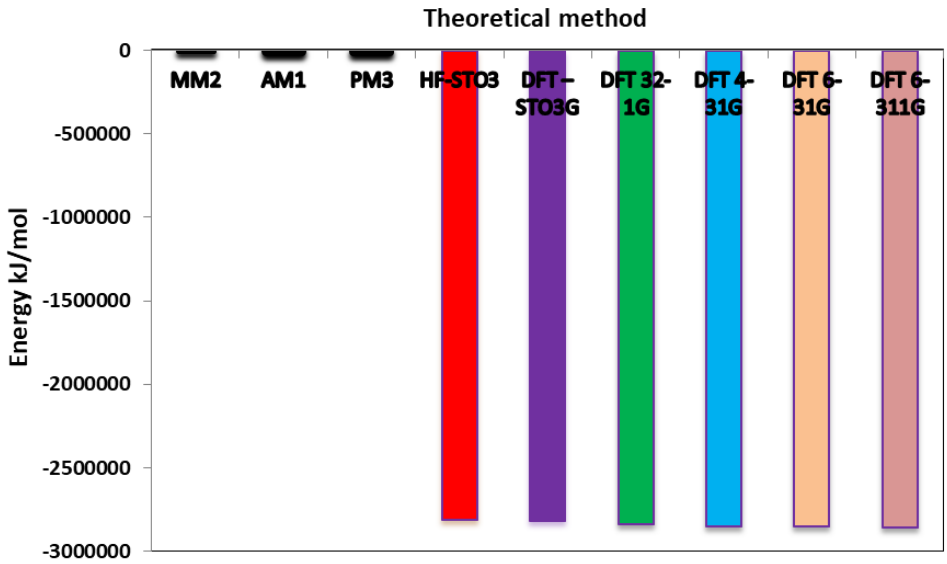


Figure 1. *Exhibit the effect of theoretical methods and the change of DFT basis set on the global minimum.*

Conclusion

On the basis of the presented results, one could conclude that the theoretical calculations using DFT method can be employed for determining the physical properties of pesticides in a similar manner to ordinary chemical substances. The results indicate that the use of DFT with 4-31G basis set is quite enough for reaching the global minimum of these chemical substances. Such achievement is quite important and helpful from theoretical point of view as making the theoretical treatments are much cheaper and more accurate. In other words, the period of time that could consumed for the minimization process using the suggested basis set of 4-31G is about half of that consumed for the larger basis sets with somewhat the same accuracy. Thus, the presented work may provide a useful guidance for theoretical scientists who interesting with the design and optimization of the basis sets functions especially in treating pesticides and other related compounds.

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Conflict of interest

The authors declare that there is no any conflict of interest regarding this research.

REFERENCES

[1] Bartók, A.P., Payne, M.C., Kondor, R., Csányi, G. (2010): Gaussian approximation potentials: The accuracy of quantum mechanics, without the electrons. – Physical Review Letters 104(13): 4p.

[2] Bonmatin, J.M., Giorio, C., Girolami, V., Goulson, D., Kreutzweiser, D.P., Krupke, C., Liess, M., Long, E., Marzaro, M., Mitchell, E.A., Noome, D.A. (2015): Environmental fate and exposure; neonicotinoids and fipronil. – Environmental Science and Pollution Research 22: 35-67.

[3] Chai, L., Ji, S., Zhang, S., Yu, H., Zhao, M., Ji, L. (2020): Biotransformation mechanism of pesticides by cytochrome P450: A DFT study on dieldrin. – Chemical Research in Toxicology 33(6): 1442-1448.

[4] Cramer, C.J. (2013): Essentials of computational chemistry: theories and models. – John Wiley & Sons 607p.

[5] Grimme, S., Brandenburg, J.G., Bannwarth, C., Hansen, A. (2015): Consistent structures and interactions by density functional theory with small atomic orbital basis sets. – The Journal of Chemical Physics 143(5): 20p.

[6] Khalil, R.A., Abdulrahman, S.A.H. (2022): NEWLY DEVELOPED STATISTICALLY INTENSIVE QSAR MODELS FOR BIOLOGICAL ACTIVITY OF ISATIN DERIVATIVES. – Studia Universitatis Babes-Bolyai, Chemia 67(1): 139-152.

[7] Khalil, R.A., Al-hakam, A.Z. (2014): Theoretical estimation of the critical packing parameter of amphiphilic self-assembled aggregates. – Applied Surface Science 318: 85-89.

[8] Khalil, R.A., Hamed, A.Y. (2015): Theoretical investigation using DFT for predicting the factors affecting the melting point of series of alkylammoniumformates ionic liquids. – Arab Journal of Physical Chemistry 2(2): 56-63.

[9] Khalil, R., Zarari, A.H. (2015): Theoretical investigations for the behavior of hydrotropes in aqueous solution. – Journal of the Turkish Chemical Society Section A: Chemistry 2(4): 42-52.

[10] Khalil, R.A. (2020): A simple approach to quantum chemistry. – Nova Science Publishers 133p.

[11] Lipkowitz, K.B., Boyd, D.B. (Eds.). (1996): Reviews in Computational Chemistry. – John Wiley & Sons, Inc. 419p.

[12] Koch, W., Holthausen, M.C. (2001): A chemist's guide to density functional theory. – Wiley 313p.

[13] Krieger, R. (Ed.). (2001): Handbook of pesticide toxicology: Principles and agents. – Academic Press 2000p.

[14] Leszczynski, J. (Ed.). (2012): Handbook of computational chemistry (Vol. 3). – Springer Science & Business Media 721p.

[15] Liu, Y., Pan, X., Li, J. (2015): A 1961–2010 record of fertilizer use, pesticide application and cereal yields: a review. – Agronomy for Sustainable Development 35: 83-93.

[16] Mardirossian, N., Head-Gordon, M. (2017): Thirty years of density functional theory in computational chemistry: an overview and extensive assessment of 200 density functionals. – Molecular Physics 115(19): 2315-2372.

[17] Meryem, G., Rabah, K., Fatiha, M., Leila, N., Aziz, B.A., Imane, D., Rachid, M. (2021): Computational investigation of vanillin@ βéta-cyclodextrin inclusion complex: Electronic and intermolecular analysis. – Journal of Molecular Liquids 321: 28p.
[18] Ramachandran, K.I., Deepa, G., Namboori, K. (2008): Computational chemistry and molecular modeling: principles and applications. – Springer Science & Business Media 397p.
[19] Rokhina, E.V., Suri, R.P. (2012): Application of density functional theory (DFT) to study the properties and degradation of natural estrogen hormones with chemical oxidizers. – Science of the Total Environment 417: 280-290.
[20] Shayma'a, H.A., Khalil, R.A. (2022): Developed QSPR Model for the Melting Points of Isatin Derivatives. – Turkish Computational and Theoretical Chemistry 6(1): 1-8.
[21] Tirado-Rives, J., Jorgensen, W.L. (2008): Performance of B3LYP density functional methods for a large set of organic molecules. – Journal of Chemical Theory and Computation 4(2): 297-306.
[22] Vlahović, F., Ivanović, S., Zlatar, M., Gruden, M. (2017): Density functional theory calculation of lipophilicity for organophosphate type pesticides. – Journal of the Serbian Chemical Society 82(12): 1369-1378.