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Comparative Quantum Computational Study Using HF and DFT Methods in Conjunction with Different Sizes of Basis Sets

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ABSTRACT

A quantum chemical study was conducted for a Schiff base derivative synthesized through the utilization of the B3LYP of density functional theory and Hartree–Fock (HF) methods in conjunction with basis sets of different sizes, including 3-21g, 3-21+g, 3-21+g*, 3-21+g**, and 6-31+g(d,p). This work aimed to test the computational efficiency and reliability of different procedures for the optimization and investigation of Schiff base derivatives. Various optimization parameters, such as the maximum force and displacement and their RMS values, were studied for all steps of optimizations. In addition, a frontier molecular orbital study was performed using all the basis sets to determine the gap energy and other electronic parameters for the most stable conformation of the investigated Schiff base molecule. The use of large-sized basis sets can result in a huge difference as in the case of 6-31+g(d,p), whereas no difference can be noticed between 3-21+g and 3-21+g*, specifically when HF method was used.

Introduction

Density functional theory (DFT) and Hartree–Fock (HF) methods have similar objectives in computational quantum theory, which provides a description of quantum state systems, such as molecules and atoms, that possess numerous electrons. Both methods obey the Born–Oppenheimer approximation [1]. The HF method describes the wavefunction of many electron systems in the form of the Slater determinant of wavefunctions of single electrons [2]. The problem with this assumption is that the general wavefunction of most electrons cannot behave as unified determinant. Moreover, electronic correlations are incompletely fused in HF techniques, which considerably elevates subsequent energies [3]. This issue can be avoided using DFT, which is computationally stronger because it depends on electronic density. This method is built on the theorems of Hohenberg–Kohn, with one of them stating that ground-state energy depends extremely on electronic density [4].

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The HF hypothesis excepts the independence of electron transfer in the potential mean field by overlooking the electron correlations [1]. On the other

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hand, the DFT method incorporates electron correlations and neglects the mean field. Moreover, DFT is very effective for quantum calculation in the ground state, with less difficulties encountered in the methodology in comparison with the HF method, which is computationally more demanding [2]. The HF method can be used to estimate the data on orbitals for use in very efficient and accurate strategies, that is, the commonly called post-HF methods such as the strategy of interaction configuration methods [3]. Nevertheless, the insufficient wavefunctions of the HF method for genuinely depicted atoms and particles are caused by the neglect of the Coulombic interactions of electrons (electron correlation) [4].

In regard to describing orbitals at subatomic levels, extended functions called basis sets determine the combination of coefficients [2]. Some of the basis sets focus on describing particles, and others deal with solitary pairs and bonds. Slater type orbitals (STOs) are one of the first basis sets utilized in early quantum theory emergence; they show some resemblance with hydrogen eigenfunctions [5] as described in Equation (1):

$$Snlm\zeta(r,v,\varphi) = Nrn - 1e - \zeta rYlm(\vartheta,\varphi) \qquad (1)$$

where N represents the normalized factor, and Ylm stands for the spherical harmonics [6]. STOs can be directly translated from the physical perspective, which makes them ideal candidates for describing MOs. Computationally, numerical determination of STOs need the integrals of the self-consistent field (SCF) method, which slows down the calculation speed [7]. Unique numerical approaches have been developed, and they allow STOs to be more productive when applied in SCF calculations. For more exact description, several functions, such as the basis set of two-fold zeta (Equation 2) in the HF method (where each orbital is independently treated), can be used to describe each orbital [8].

$$\phi 2s(r) = \phi 2sSTO(r,\xi 1) + d\phi 2sSTO(r,\xi 2) \qquad (2)$$

Two STOs function as a total representation of 2s orbitals, where d is a constant that estimates the tendency of STO toward the other orbital, and ξ depends on the orbital size. The basis sets of quadruple and triple zeta behave in a similar manner for double zeta that use extra Slater conditions, which increase the accuracy and demand more calculation time [9]. Other expanded basis sets, such as correlation consistent, diffuse, polarized, and split-valance sets, were developed. These extended sets can describe more than the basic orbital characteristics in minimal sets [2]. Although the use of double-zeta basis sets gives us a good tool for independent treatment of orbitals, it remains computationally expensive [10]. Therefore, the researchers used double zeta to treat the valance orbitals through solitary STO depiction because of the unnecessary calculation of inner shell electrons. This strategy includes split-valence premise sets, such as the 3-21g and 6-31g sets used in this study [11]. This work aimed to comparatively analyze the outcomes of B3LYP DFT and HF methods using different basis sets for the optimization and investigation of a recently synthesized Schiff base derivative from the conformations and energetic perspectives. The studied molecule was synthesized and characterized by Saleem et al. [12].

Materials and Methods

Calculations were carried out utilizing the HF and DFT methods. The optimization and FMO of the Schiff base structure were achieved using the 3-21g, 3-21+g, and 3-21+g* basis sets of HF method and 3-21g, 3-21+g*, and 6-31+g(d,p) of the B3LYP hybrid function of the DFT method using Gaussian 09 computational software. Koopmans' theorem was applied to carry out the electronic properties of the Schiff base and obtain the FMO [1]. The electron affinity (E_A) and ionization potential (I_P) were calculated depending on the highest-occupied molecular orbital–lowest-unoccupied molecular orbital (HOMO-LUMO) values. Other parameters, including softness (r), hardness (χ), electrochemical potential (μ), electronegativity (η), and energy gap (ΔE), were obtained based on these values as stated in Equations (3) to (6) [11].

$$\mu = -\frac{1}{2}(I_P + E_A) \qquad (3)$$

$$\eta = -\frac{1}{2}(E_{HOMO} + E_{LUMO}) \qquad (4)$$

$$\chi = -\frac{1}{2}(E_{HOMO} - E_{LUMO}) \qquad (5)$$

$$\Delta E = (E_{LUMO} - E_{HOMO}) \qquad (6)$$

Reactivity parameters were also determined: net electrophilicity ($\omega^{\pm}$), electronic donating power (ω^{-}), electronic withdrawing power (ω^{+}), and electrophilicity index (ω) [13] (Equations (7) to (10)) [14].

$$\omega = \frac{\mu^2}{2\chi} \qquad (7)$$

$$\omega^{-} = \frac{(3I_P + 3E_A)^2}{16(I_P - E_A)} \qquad (8)$$

$$\omega^{+} = \frac{(I_P + 3E_A)^2}{16(I_P - E_A)} \qquad (9)$$

$$\omega^{\pm} = \omega^{+} - (-\omega^{-}) \qquad (10)$$

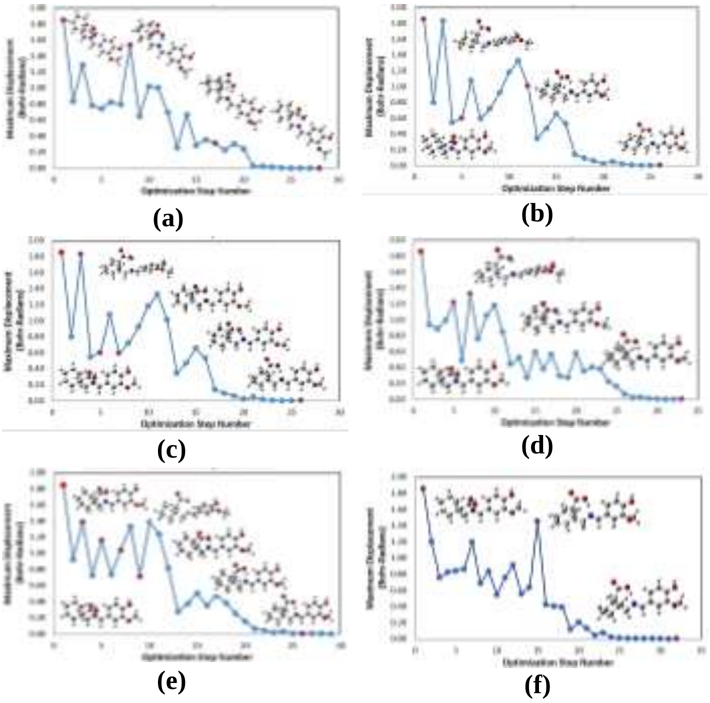
Results and Discussion

For every selected basis set of DFT and HF method optimization, the total energy (Hartree), maximum internal displacement (Bohr radians), and maximum internal force (Hartree/Bohr radians) were obtained for each optimization step of the studied molecule. A total of 26–33 optimization steps were needed to reach the lowest energy structure depending on the basis sets of the used methods. For all basis sets, the energy decrement is important in the first steps, and it then slowed down to the minimal values, which is supported by the values of RMS grad norm in Figure 2. The patterns of maximum displacement (Figure 1) and maximum force (Figure 3) gave more information regarding the optimized structures and the means of achieving minimal energy. The values of optimization parameters (Table 1) indicate that upgrading HF/3-21+g to HF/3-21+g* basis set had no effect on the optimization process, and the latter is computationally more expensive. Moreover, DFT/6-31+g(d,p) provides more reliable values, with more stable structures and relatively lower values of maximum force and maximum displacement. Figure 4 shows the most stable structure of the studied molecule optimized using DFT/6-31+g(d,p) basis set; it is expected to be the most suitable size of basis set for such a molecular system.

Table 1: Optimization parameters of the most stable structures of the studied basis sets.

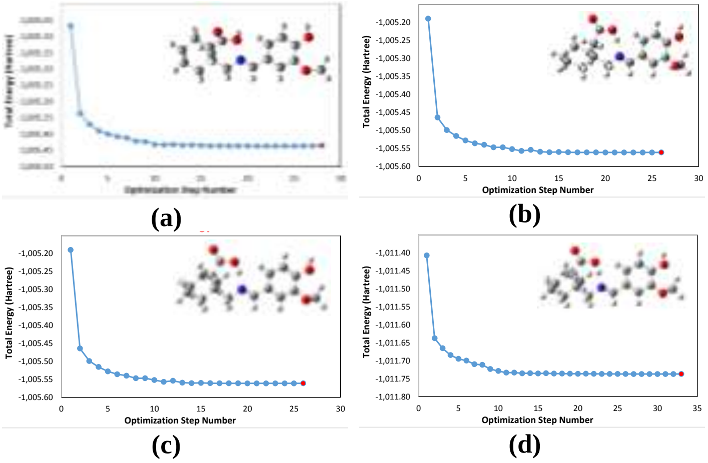
Method	**Basis set**	**Total Energy (H)**	**Maximum Force (H/B-R)**	**Maximum displacement (B-R)**
HF	3-21g	-1005.435	0.000021	0.000904
	3-21+g	-1005.560	0.000052	0.001378
	3-21+g*	-1005.560	0.000052	0.001378
DFT	3-21g	-1011.736	0.000042	0.000870
	3-21+g*	-1011.884	0.000035	0.001686
	6-31+g(d,p)	-1017.379	0.000007	0.000315

* H= Hartrees, B-R= Bohr-Radians.

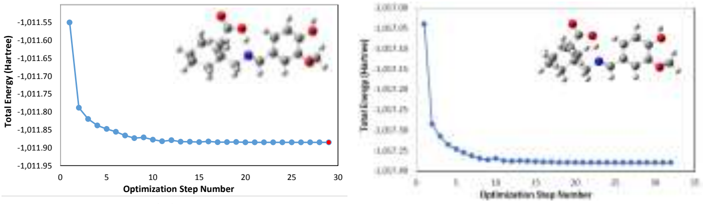


(a) (b) (c) (d) (e) (f)

Figure 1: Max. internal displacement with optimization steps based on (a) HF/3-21g, (b) HF/3-21+g, (c) HF/3-21+g*, (d) DFT/3-21g, (e) DFT/3-21+g*, and (f) DFT/6-31+g(d,p).

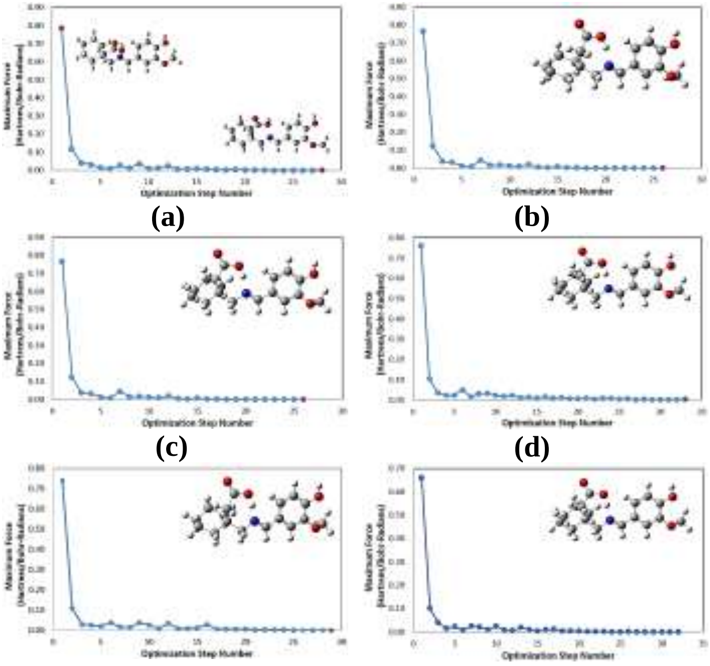


(a) (b) (c) (d)



(e) **(f)**

Figure 2: Changes in the total energy with steps of optimization based on (a) HF/3-21g, (b) HF/3-21+g, (c) HF/3-21+g*, (d) DFT/3-21g, (e) DFT/3-21+g*, and (f) DFT/6-31+g(d,p).



(e) **(f)**

Figure 3: Max. internal force with steps of optimization based on (a) HF/3-21g, (b) HF/3-21+g, (c) HF/3-21+g*, (d) DFT/3-21g, (e) DFT/3-21+g*, and (f) DFT/6-31+g(d,p).

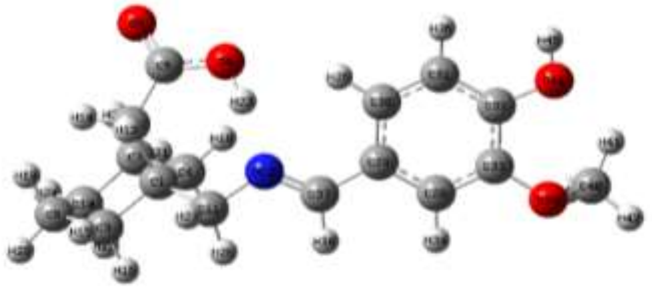
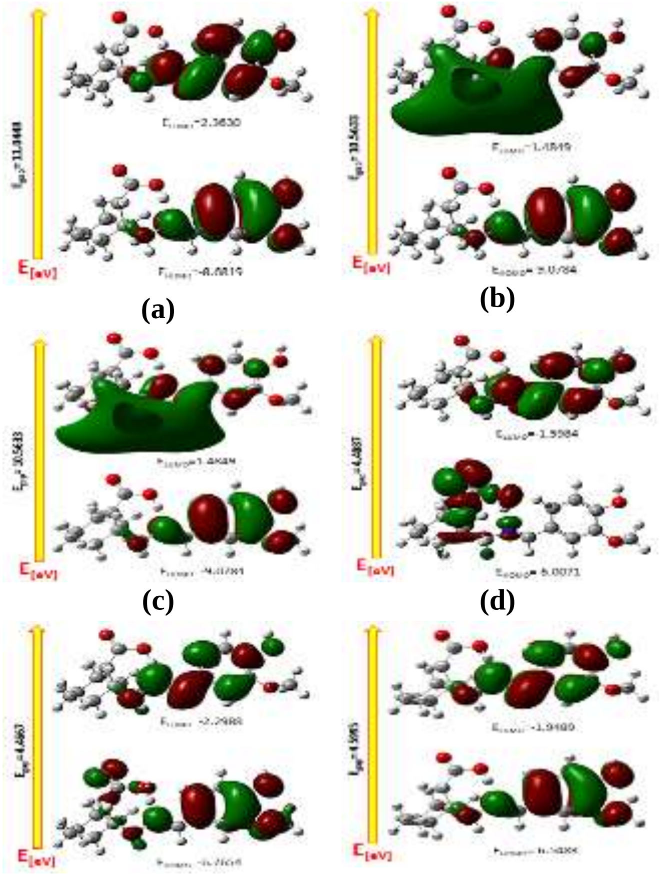


Figure 4: Optimized structure of the studied molecule with the lowest energy based on DFT-B3YLP/6-31+g(d,p).

The energy of FMO, which represents the LUMO–HOMO, are important in determining the reactivity of drugs when interacting with specific receptors [15]. HOMO energy can be used to determine the linkage between the electronic configuration of drugs and their activity [16]. Most phenomena related to electronic structures can be determined from studying FMO energies, including photoexcitation, magnetism, charge transfer processes, and molecular and kinetic electronics [17]. Figure 5 depicts the HOMO-LUMO of the lowest energy structures of the investigated molecule based on the studied basis sets.



(e) **(f)**

Figure 5: Visualization of FMO structures with the corresponding energies in eV based on (a) HF/3-21g, (b) HF/3-21+g, (c) HF/3-21+g*, (d) DFT/3-21g, (e) DFT/3-21+g*, and (f) DFT/6-31+g(d,p).

FMO energies usually define the capability of a molecule to receive and donate electrons. Vital roles can be played by molecular orbitals, including ultraviolet-visible spectra [18], quantum chemistry [19], luminescence [20], photochemical reactions [21], optical and electronic properties [22], and pharmaceutical studies [23-25]. On the other hand, the chemical stability and molecular kinetics can be predicted by the values of HOMO–LUMO energy gap [26], where high values imply a low chemical reactivity with a high kinetic stability [27] because of the difficulty of elevating an electron to a LUMO lying relatively high above a HOMO with low energy [28]. Table 2 lists the FMO energy values and the energy gap calculated using different basis sets of DFT and HF methods. In the DFT methods, the gap energy values increased with the increase in the accuracy of the basis sets from 4.4087 eV in 3-21g to 4.5995 eV in 6-31+g(d,p).

This high value can be contributed to the high stability of the investigated molecule with a relatively less chemical reactivity.

lists the other parameters derived from HOMO-LUMO values. The high values of ω- compared with ω+ along with the elevated electronegativity imply that the studied molecule has a very promising potential to be used for most applications that require an electron-donating capability.

Table 2: Values of FMO energies and the energy gap of different basis sets under HF and DFT methods.

Method	Basis set	HOMO (eV)	LUMO (eV)	ΔE (eV)	IP (eV)	EA (eV)
HF	3-21g	-8.681	2.363	11.044	8.682	-2.363
	3-21+g	-9.078	1.484	10.563	9.078	-1.485
	3-21+g*	-9.078	1.484	10.563	9.078	-1.485
DFT	3-21g	-6.007	-1.598	4.408	6.007	1.598
	3-21+g*	-6.765	-2.298	4.466	6.765	2.299
	6-31+g(d,p)	-6.548	-1.948	4.599	6.548	1.949

Table 3: Electronic parameters derived from FMO energy values of different basis sets under HF and DFT methods.

Method	Basis set	μ	η	χ	ω	ω-	ω+	ω±
HF	3-21g	-3.159	3.159	5.522	0.904	3.174	0.014	3.188
	3-21+g	-3.797	3.797	5.282	1.365	3.923	0.126	4.050
	3-21+g*	-3.797	3.797	5.282	1.365	3.923	0.126	4.050
DFT	3-21g	-3.803	3.803	2.204	3.280	5.457	1.654	7.111
	3-21+g*	-4.532	4.532	2.233	4.598	7.144	2.611	9.755
	6-31+g(d,p)	-4.249	4.249	2.300	3.925	6.336	2.088	8.424

Conclusions

Using of basis sets of different sizes, the HF and DFT methods gave an idea about the accuracy and efficiency of describing organic molecules, such as Schiff base derivatives. Comparable results have been obtained from the use of the studied basis sets when adding diffuse functions with no noticeable changes with included polarization functions as is the case with similar data outcomes on the 3-21+g and 3-21+g*. Large basis sets, however, are more accurate for these types of molecules in terms of describing structural stability. The 6-31+g(d,p) basis set produced a more stable optimized structure (-5 Hartree) than smaller basis sets. In general, DFT has provided considerably lower energy gaps, which are reasonable. Although 6-31+g(d,p) is recommended in the literature, the other basis sets of DFT provide acceptable alternative that can reduce the time and CPU consumption when dealing with relatively larger organic molecules.

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Conflict of Interest

Authors disclaim any relevant conflict of interest.

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دراسة كيمياء كمومية مقارنة باستخدام طريقتي نظرية الكثافة الوظيفية وهارتري فوك وباحجام قواعد اساس مختلفة

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الخلاصة:

في هذا الدراسة، تم إجراء دراسة كيميائية كمومية لمشتق قاعدة شيف تم تحضيره مؤخرًا باستخدام نظرية الكثافة الوظيفية B3LYP وطرق هارتري–فوك بالتزامن مع أحجام مختلفة من مجموعات الأساس، بما في ذلك 3−21g، 3−21+g، 3−21 +g*، 3−21g+** و6−21+g(d,p) . الهدف من هذه الدراسة هو اختبار كفاءة الحوسبة وموثوقية الإجراءات المختلفة لتحسين ودراسة مشتقات قاعدة شيف طاقيًا. يتم دراسة عوامل التحسين المختلفة مثل القوة القصوى والانزياح بالإضافة إلى قيم RMS لجميع خطوات التحسين. بالإضافة إلى ذلك، إجراء دراسة للمدار الجزيئي الحدودي وفقاً لجميع مجموعات الأساس من أجل معرفة فجوة الطاقة والعوامل الإلكترونية الأخرى لأكثر تكوين ثباتًا لجزيء قاعدة شيف المدروس. يمكن أن يحدث فرق كبير عند استخدام مجموعات أساس ذات حجم كبير كما في 6−21+g(d,p) ، في حين لا يمكن ملاحظة أي فرق بين 3−21g+ و3−21+g*، خصوصًا مع طريقة هارتري–فوك.

الكلمات المفتاحية :نظرية الكثافة الوظيفية، هارتي–فوك، قواعد شف، فجوة الطاقة، قواعد الاساس، تحسين حوسبي.