

Evaluation of the Electronic Structure Resulting from ab-initio Calculations on Simple Molecules Using the Molecular Orbital Theory

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Abstract: Hartree Fock (HF) and Density Functional Theory (DFT) have been commonly used to model chemical problems. This study uses the Molecular Orbital Theory (MOT) to evaluate the electronic structure of five diatomic molecules generated by HF and DFT calculations. The evaluation provides an explanation of how the orbitals of a molecule come to be and how this affects the calculation of the physical quantities of the molecule. The evaluation is obtained after comparing the orbital wave functions calculated by MOT, HF, and DFT. This study found that the nature of the Highest Occupied Molecular Orbital (HOMO) of a molecule is determined by the valence orbital properties of the constituent atoms. This HOMO property greatly influences the precision of calculating the molecular electric dipole moment. This shows the importance of understanding the orbital properties of a molecule formed from the HF and DFT calculations.

Keywords: Electronic structure; Molecular Orbital Theory; ab-initio; Hartree Fock; Density Functional Theory.

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Introduction

The rapid advancement of computer hardware and software has created adequate access to quantum mechanical modeling of chemical problems. A theoretical model is defined by the theoretical method and basis set. A theoretical method is an approach used to solve the many-body Schrödinger equation. The basis set is a mathematical description of the orbital wave function. Calculations with a theoretical model of a system will produce the total electronic energy of the system.

Total electronic energy is commonly used to analyze two main problems in chemistry: structure and reactivity. The stability of the conformer structure can be analyzed from the negativity of the total electronic energy of the structure (Madinah, et al., 2020). The

reactivity can be analyzed from the difference in the total electronic energy of the initial, final, and transition state (Susanti, et al., 2020). Total electronic energy itself is obtained from various theoretical methods. Two of them are Hartree Fock (HF) and Density Functional Theory (DFT).

Molecular Orbital Theory (MOT) analyzes these problems based on the electronic structure of the system being studied. The electronic structure is expressed by the orbital wave function and orbital energies. The stability of the conformer structure can be analyzed from the difference between the Highest Occupied Molecular Orbital (HOMO) energy and the Lowest Unoccupied Molecular Orbital (LUMO) energy. Reactivity can be seen from the difference between the HOMO and LUMO energies of the reacting molecules (Anh, 2007). Adequate analysis requires a thorough

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understanding of the properties of these orbitals. This study uses MOT to evaluate the orbital properties generated by the HF and DFT calculations.

Method

This study models the bonds between atoms in a molecule with the interaction between the valence orbital of these atoms. The molecules of the calculated object are grouped according to the similarity of the angular part of the interacting orbital wave function. Group A consists of molecules formed by the interaction of two *s* orbitals, namely HLi, HBe, and HNa. Group B consists of molecules formed by the interaction of *s* and *p* orbitals, namely HO and HF.

There are two quantities that are studied of these molecules. These two quantities are the orbital wave function and dipole moment. These two quantities correspond to the stable geometry of the molecule. For the MOT calculation, the stable geometries of the molecules are obtained from experimental data. The bond lengths between the atoms of the HLi, HBe, HO, HF, and HNa molecules in Å are 1.5949, 1.3431, 0.96966, 0.9169, and 1.8873, respectively (Haynes, 2016). For HF and DFT calculations, this geometry is obtained through optimization calculations.

The MOT calculation is done using Mathematica (Wolfram Research, 2020) software with the following routine. First, defining the interacting orbitals. The orbital wave function is defined by the Slater Type Orbital.

$$\chi = N_{n\zeta} r^{n-1} \exp(-\zeta r) Y_l^m(\theta, \phi) \quad (1)$$

where *n*, *l*, *m* are quantum numbers, ζ is the orbital exponent, and $N_{n\zeta}$ is the normalized constant. Orbital energy is defined by the first ionization potential of the atoms of the molecule (based on Koopman's theorem (Ramachandran, 2008). The first orbital exponents and ionization potentials of the atoms are shown in Table 1. Second, interacting with the orbitals.

Table 1. The first ionization potential and the exponential orbital of the atoms of the molecule

Molecule	IP (eV) (Haynes, 2016)	ζ (Ghosh & Biswas, 2002)
H	13.598443	1
Li	5.391719	0.65
Be	9.32270	0.975
O	13.61805	2.275
F	17.4228	2.6
Na	5.139074	0.7333

The interaction between orbital wave functions is represented by the overlap integral

$$S_{12} = \int \chi_1^*(\vec{r}) \chi_2(\vec{r} - \vec{R}) d\vec{r}^3 \quad (2)$$

where \vec{R} is the position vector of orbital 2. The relation between the overlap integral and the orbital energy is expressed by the interaction energy obtained by the Wolberg Hemholds Approximation.

$$H_{12} = \frac{1}{2} K (H_{11} + H_{22}) S_{12} \quad (3)$$

where *K* is the equilibrium constant (for intermolecular bonds the value is 1.75), *H*₁₁ and *H*₂₂ are the energy of orbital 1 and 2, respectively. Third, solve the Secular equation in Equation (3) to obtain the wave function and molecular orbital energies. The molecular orbital (OM) wave function is expressed as a linear combination of the atomic orbital (OA) wave function. Each OA contributes to the OM expressed by the OM expansion coefficient. Routine calculations are carried out for HNa molecules (representing group A) and HF molecules (representing group B).

$$\begin{aligned} (H_{11} - e_i S_{11}) c_{1i} + (H_{12} - e_i S_{12}) c_{2i} &= 0 \\ (H_{21} - e_i S_{21}) c_{1i} + (H_{22} - e_i S_{22}) c_{2i} &= 0 \end{aligned} \quad (3)$$

HF and DFT calculations (with functional exchange-correlation B3LYP) were performed using Gaussian 16 software.(Frisch, et al., 2016) The calculation routines are as follows.(Rusydi, et al., 2020) First, optimization calculations to obtain the ground spin state for each molecule. This calculation is done by trying several possible spin states. The spin state which provides the lowest total electronic energy is the ground spin state of the molecule. Second, optimization calculations to obtain an orbital wave function that corresponds to the stable geometry of the molecule. Both the first and second routines were carried out on a 3-21G basis set. Third, optimization calculations to obtain the dipole moment of each molecule. This calculation is done with three variations of the base set: 3-21G, 6-31G, and 6-31G (d, p).

Result and Discussion

Orbital interactions

The MOT calculations for the HNa and HF molecules (Figure 1) yielded two and four OM, respectively. The two molecules have one OM bonding and one OM antibonding each. The other two OMs in the HF molecule are nonbonding. OM bonding and antibonding have something in common, namely, they are composed of the OA contribution of the two atoms. This distinguishes the two from nonbonding OM which is only composed of OA of one atom.

Of the three OA 2p of F atoms, namely 2p_x, 2p_y, and 2p_z, interacting with OA 1s of the H atom is 2p_z. During the MOT calculation, H and F atoms are placed

on the z-axis. This causes only integral overlap between $1s_H$ and $2p_{zF}$ which is not worth 0. Convolution between $1s_H$ and $2p_{xF}$ positive phase and convolution between $1s_H$ and $2p_{xF}$ negative phase cancel each other out. This also applies to convolutions between $1s_H$ and $2p_{yF}$. As a result, the integral overlap of these orbitals is 0. These two F atomic orbitals do not interact with the H atomic orbital and form a nonbonding OM on the HF molecule.

The interacting OA phase determines the nature of the OM formed. OM bonding is always produced by

the interaction of two in-phase orbitals whereas OM antibonding is the opposite. In the HNa molecule, in which the interacting AO is two s orbitals, the phases are shown by the same sign of the OM expansion coefficient. In the HF molecule, the OM expansion coefficient sign does not indicate whether the two OAs are in phase or not. The s and p orbital interactions are in a phase when the two similar phases are facing each other. If the two like phases are separated by opposite sex phases, the s and p orbitals are not in phase.

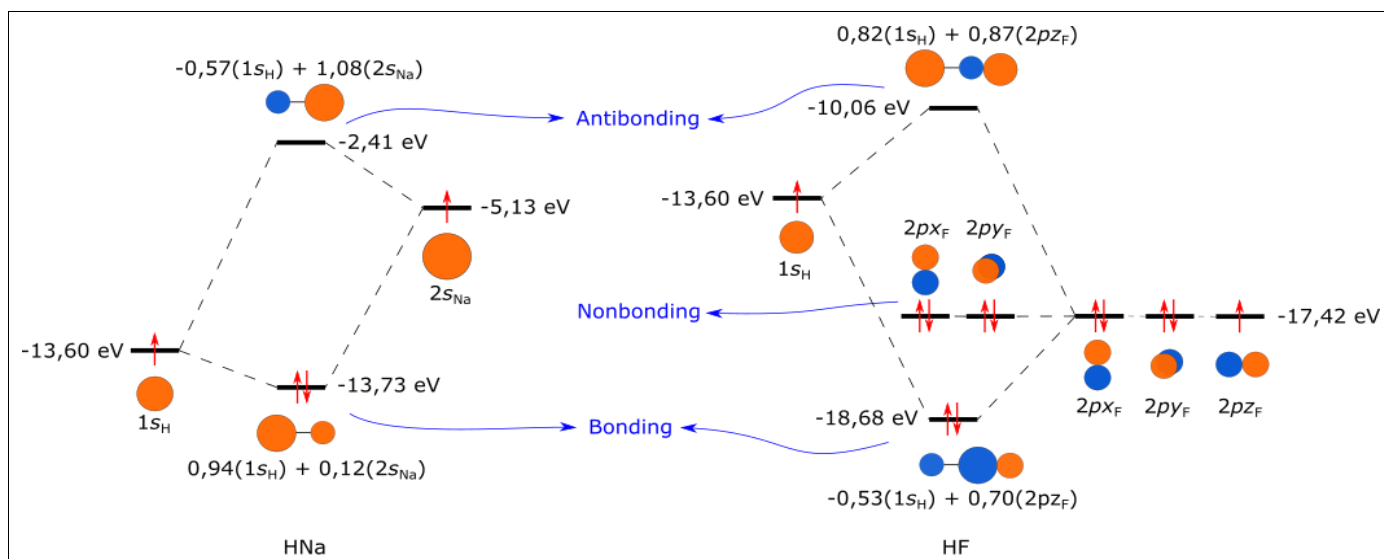


Figure 1. The results of the MOT calculation. The arrows represent the electrons filling the orbitals, while the lobes visualize the orbital shapes. The orange and blue lobes represent the positive and negative phases of the orbital wave function, respectively.

Table 2. Some of the outermost OM wave functions from the calculation on the basis of the 3-21G set. The displayed OM corresponds to the orbitals formed in the MOT calculation.

Molecule	Molecular orbitals	Contribution consultants				
		s_1	s_2	px_2	py_2	pz_2
<i>Hartree Fock</i>						
HNa	LUMO	-0.16	+0.16	0.00	0.00	+0.61
	HOMO	+0.75	+0.31	0.00	0.00	-0.12
HF	LUMO	+1.30	-0.62	0.00	0.00	+0.73
	HOMO	0.00	0.00	+1.16	0.00	0.00
	HOMO ⁻¹	0.00	0.00	0.00	+1.16	0.00
	HOMO ⁻²	-0.43	+0.31	0.00	0.00	+0.90
<i>Density Functional Theory</i>						
HNa	LUMO	-0.33	+0.71	0.00	0.00	+0.49
	HOMO	+0.73	+0.36	0.00	0.00	-0.08
HF	LUMO	+1.28	-0.57	0.00	0.00	+0.80
	HOMO	0.00	0.00	+1.16	0.00	0.00
	HOMO ⁻¹	0.00	0.00	0.00	+1.16	0.00
	HOMO ⁻²	-0.47	+0.36	0.00	0.00	+0.87

Information:

- LUMO : Lowest Unoccupied Molecular Orbital.
- HOMO : Highest Occupied Molecular Orbital.
- HOMO-n : Orbital with n energy levels below HOMO.

Index 1 represents the H atom, while index 2 represents the Na atom (in the HNa molecule) and the F atom (the HF molecule).

The arrangement of electrons in the OM calculated by the MOT shows an important difference between the HNa and HF molecules. HOMO HNa molecules are formed from the orbital interactions of the two constituent atoms while HOMO HF is not formed from the orbital interactions of the two constituent atoms. This also applies to the other molecules in group A and group B, respectively.

In contrast to MOT, the calculation of HF and DFT on the basis of the 3-21G set involves a lot of OA. The OA involved for each atom is as follows.

- Atom H: 1s, 2s.
- Atom F: 1s, 2s, 2px, 2py, 2pz, 3s, 3px, 3py, 3pz.
- Atom Na: 1s, 2s, 2px, 2py, 2pz, 3s, 3px, 3py, 3pz, 4s, 4px, 4py, 4pz.

The orbitals are grouped according to the angular portion of their wave function. In the H atom, there is 1 AO group, namely s_1 , while on the Na and F atoms there are four AO groups, namely s_2 , px_2 , py_2 , and

pz_2 . Table 2 displays the resultant OA expansion coefficient for each group.

The first important result of the HF and DFT calculations, shown in Table 2, is the resultant largest contribution of each atom. In the LUMO and HOMO HNa molecules, the OA group that makes the largest contribution from the Na atom is the s orbital group. In the LUMO and HOMO-2 HF molecules, the OA group that makes the largest contribution from the F atom is the pz orbital group. This shows that the OA group that makes the dominant contribution to OM is a group with the same angular wave function as the valence orbital of the atoms making up the molecule.

HOMO and HOMO-1 HF molecules are only composed of one OA group. This can be understood by the overlap integrals that have been described in the MOT calculation results. The two orbitals are nonbonding orbitals.

The second important result is the resultant sign of the greatest contribution of each atom. In the HNa molecule, s_1 and s_2 are opposite to LUMO and the same to HOMO. In the HF molecule, s_1 and $2pz_2$ are the same for LUMO and opposite in HOMO-2. Referring to the MOT calculation, these results show that the LUMO orbitals of the HNa and HF molecules are antibonding, the HOMO of the HNa molecule is bonding, and the HOMO-2 of the HF molecule is bonding.

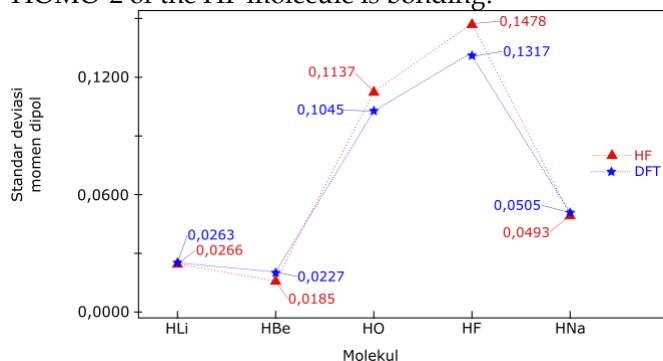


Figure 2. The standard deviation of the HF and DFT calculation results for the dipole moment of each molecule with the variation of the base set 3-21G, 6-31G, and 6-31G (d, p). Molecules are arranged from left to right according to the increase in the number of electrons.

Electric dipole moment

The standard deviation of the HF and DFT calculations, shown in Figure 2, represents the precision of the calculation with respect to changes in the basis set. The number of electrons in a molecule is proportional to the number of interacting orbitals. The trend in Figure 2 shows that there is no relationship between the number of orbitals of a molecule and the precision of calculating the molecular dipole moment.

The standard deviation of the calculated dipole moment of group A molecules is relatively lower than that of group B molecules. Standard deviation is

inversely proportional to precision. Therefore, the HF and DFT calculations of group A molecules are more precise than group B molecules.

Conclusion

This study has used the MOT to explain how the OM calculated from HF and DFT can become such. There are so many OAs that make up the OM in an HF or DFT calculation. The interaction of many OA can be understood by the interaction of the valence OA of the atoms of the molecule. The OA resultant of each atom that gives the largest contribution to OM comes from the OA group which has the same angular wave function as the valence OA of each atom. The phase of the resultant OA which gives the greatest contribution will determine the nature of the OM formed. This study found that the precision of HF and DFT calculations to the dipole moment of molecules in group A (HLi, HBe, and HNa) was higher than that of group B molecules (HO and HF). The standard deviation of the calculated dipole moment of group A molecules is less than 0.1000 while group B molecules are the opposite. This study suspects that this is due to the differences in the HOMO properties of the two molecules. The HOMO of group A molecules is formed from the interaction of the two constituent atoms while the HOMO of group B molecules is only formed from the contribution of the orbitals of one atom only.

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