Abstract

Density functional theory (DFT) and Time-dependent density function (TD-DFT) theory provide good results ~~to elucidate~~ for elucidating the structure and electronic transition of various molecules. We apply these two methods to study the HOMO and LUMO of three series of benzene derivatives including C_6H_5-XH_3, C_6H_5-YH_2 and C_6H_5-ZH for elements from Group 14, 15 and 16. Hückel theory shows that DFT and TD-DFT differ in their evaluations of π-bonding resonance integrals. The HOMO-LUMO gap of benzene derivatives display red shifts in all theories. In Hückel theory, the red shift of a benzene derivative is caused by either an increase of HOMO or a decrease of LUMO level[1], which is inconsistent with DFT and TD-DFT where both energy levels change. A locally modified Hückel theory fits the HOMO and LUMO energies of C_6H_5-ZH derivatives well. The difficulties ~~to use~~ in using Hückel theory to fit other series suggest that global π-bonding modifications are needed.

1. Introduction

Computational quantum chemistry has become a standard numerical tool ~~for~~ in chemical research. ~~Besides molecular geometry predictions,~~In addition to predicting molecular geometries, quantum calculations generate molecular orbitals ~~like~~ such as the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital). The energies of HOMO and LUMO ~~energies~~ are important intrinsic properties of molecules that are relevant to their photophysics, photochemistry, reactivity, stability, acidity, basicity, ~~etc~~. among others.

A variety of quantum chemistry methods have been developed over the past decades. Density functional theory (DFT) developed by Kohn and Sham is one of the widely studied and tested methods, which takes electron-electron correlation into account in the calculation. Consequently, DFT results in more accurate molecular structures and ground electronic states ~~like~~ such as the HOMO state (highest occupied molecular orbital) as ~~opposed to~~ compare to the Hatree Fock method.

Despite the advancement of DFT in studies of molecular structures, its predictions of the higher energy unoccupied molecular orbitals, such as LUMO (lowest unoccupied molecular orbital), need to

be cross-examined. To address such ~~an~~ this issue, time-dependent density functional theory (TD-DFT) was developed[2]. TD-DFT stresses on electronic transitions and can calculate the UV-VIS spectroscopy of a molecule. Therefore, TD-DFT produces more reliable unoccupied molecular orbitals, including LUMO.

In this work, we first intend to apply DFT and TD-DFT to investigate three series of benzene derivatives: (1) $C_6H_5XH_3$ with X = carbon, silicon or geranium; (2) $C_6H_5YH_2$ with Y = nitrogen, phosphorus or arsenic; (3) $C_6H_5ZH_2$ with Z = oxygen, sulfur or selenium, as shown in Figure 1. These derivatives find applications in numerous industries, such as pharmaceutical drug designs, manufacture of polymers and plastic materials, industrial solvents, and pigments. In Organic Chemistry, the substituent group on benzene dictates the position of the second substituent group on a benzene ring. The above benzene derivatives are also ideal candidates that can be studied by using Hückel theory.

Hückel theory was developed to simplify the complex quantum chemistry calculations for the planar conjugated molecules. In Hückel theory, there are two fundamental quantities: Coulomb integral α, which is related to interactions between an electron and the nucleus prior to bond formation, and resonance integral β, which arises from quantum effects and is often viewed as hopping of an electron between two neighboring nuclei. ~~Coulomb integral is related to interactions between an electron and the nucleus prior to bond formation. Resonance integral arises from quantum effects and is often viewed as hopping of an electron between two neighboring nuclei.~~ The resonance integral accounts for the energy gain ~~of~~ associated with bond formation.

Some modifications of Hückel theory have been extended to investigate heterocyclic compounds and the benzene derivatives with single substituents. The schematic of the model is shown in Figure 1. In this work, we adapt Hückel theory to compare with the HOMO and LUMO energies and the HOMO-LUMO gaps calculated from DFT and TD-DFT for the derivatives in Figure 1. Our aims are to understand the fundamental difference between DFT and TD-DFT by using Hückel theory as well as the question regarding the possibility to apply Hückel theory to the results of DFT and TD-DFT.

Reference:

(1)Brutschy, B. (2000). *The Structure of Microsolvated Benzene Derivatives and the Role of Aromatic Substituents. Chemical Reviews, 100(11), 3891–3920.* doi:10.1021/cr990055n

(2)Laurent, A. D., & Jacquemin, D. (2013). *TD-DFT benchmarks: A review. International Journal of Quantum Chemistry, 113(17), 2019–2039.* doi:10.1002/qua.24438

In benzeneC_6H_6, each carbon atom has one (p) orbital that is perpendicular to the plane of the benzene ring, which is formed by the (sp^2) hybridization of carbon atoms. The three (sp^2) hybridized orbitals on each carbon form sigma bonds with adjacent carbon atoms and with hydrogen atoms. The π bonds result from the overlapping of the (p) orbitals on the carbon atoms.

The Coulomb integral(alpha) represents the energy of a π-electron at a given atomic orbital, corresponding to the energy of an electron occupying a specific p orbital in the absence of any interactions with other orbitals.

The resonance integral quantifies the overlap between adjacent π-orbitals, and measures the energy change that occurs when an electron hops between two adjacent atomic orbitals. The value of Beta is generally negative, indicating that the energy of the system decreases as π-electrons delocalize between adjacent p orbitals.

When constructing the Hückel matrix for a π-electron system, the values of alpha and beta are utilized as follows: the diagonal elements, alpha, correspond to the energy of each individual p orbital, while the off-diagonal elements, beta, correspond to the interactions between adjacent p orbitals.