

Title: Difference between HOMO & LUMO, and Electron Density: Avoiding Common Misconceptions in Photocatalytic (DFT) Research in nanomaterials

Author: Zi-Jing Chiah

Abstract: This article explores the distinction between HOMO (Highest Occupied Molecular Orbital), LUMO (Lowest Unoccupied Molecular Orbital), and electron density in molecular and material sciences. While HOMO and LUMO describe specific energy levels relevant to electronic transitions, electron density represents the spatial distribution of all electrons in a system. The article addresses common misconceptions in research, particularly in density functional theory (DFT) studies, where shifts in HOMO/LUMO positions are often mistakenly equated with changes in electron density. Clear differentiation and complementary analyses are emphasized to ensure accurate interpretations in fields like photocatalysis and electronic materials.

In the field of molecular and material science, concepts such as the Highest Occupied Molecular Orbital (HOMO), Lowest Unoccupied Molecular Orbital (LUMO), and electron density are fundamental to understanding chemical and physical phenomena. HOMO and LUMO are energy-level descriptors that represent the frontier orbitals of a molecule, where the HOMO is the highest energy orbital occupied by electrons, and the LUMO is the lowest energy orbital available for occupation. These orbitals are critical for understanding chemical reactivity, charge transfer, and optical properties. On the other hand, electron density refers to the spatial distribution of electrons within a molecule or material, providing insight into where electrons are likely to be found in physical space. This property governs bonding characteristics, electrostatic potential, and charge localization.

Although both HOMO/LUMO and electron density are integral to describing a material's electronic structure, they are distinct in nature. HOMO and LUMO represent only a small part of the overall electronic structure, focusing specifically on the energy levels that are most relevant to electronic transitions or chemical reactivity. In contrast, electron density encompasses the full spatial distribution of all electrons in a system, including both occupied and unoccupied orbitals. For example, while shifts in the positions of HOMO and LUMO on the material's surface due to doping or surface functionalization indicate changes in the electronic structure, these shifts do not necessarily translate to changes in the electron density unless there is explicit charge redistribution. The position of HOMO and LUMO governs properties like the bandgap, while the electron density reflects the actual distribution of electrons that influence bonding and charge localization.

Despite their fundamental differences, there is a notable trend in the scientific literature where the two concepts are often conflated, particularly in computational studies such as density functional theory (DFT) applied to photocatalytic systems. HOMO and LUMO, while useful for predicting optical and electronic properties, represent just the frontier orbitals and cannot describe the entire electron density of a system. However, researchers sometimes mistakenly interpret shifts in HOMO/LUMO positions as evidence of changes in electron density or charge transfer, without performing explicit analyses to confirm this. For example, while doping a

photocatalyst might shift the positions of HOMO or LUMO levels on the material's surface and alter the bandgap, the actual redistribution of electron density—which governs charge transfer and reaction mechanisms—requires tools such as charge density difference maps, Bader charge analysis, or electron localization function (ELF) calculations. Without these additional analyses, conclusions about charge redistribution remain speculative and potentially misleading.

To avoid these conceptual mix-ups, it is essential for researchers to clearly differentiate between energy-level shifts (HOMO/LUMO) and real-space electron density changes. HOMO and LUMO provide critical insights into the reactivity and electronic transitions of a system, but they are only part of the overall picture. Incorporating complementary analyses, such as charge density difference plots or population analysis, can provide a more accurate understanding of electronic structure and reaction mechanisms. By addressing this common confusion, future studies can enhance the accuracy and reliability of predictions in fields like photocatalysis, electronic materials, and beyond.