Density Functional Theory Study of Dilute Transition Metal Phthalocyanines

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Organometallic (OM) crystals are studied in fields such as industrial pigments, molecular electronics, and photovoltaics. A particular class of OM crystals known as transition metal-phthalocyanines (TM-Pc), a molecular crystal composed of chains of planar OM molecules with a transition metal center and four coordinated pyrrole-aromatic rings joined by nitrogen atoms similar to porphyrin, is particularly useful. The structure resembles a dish rack pattern where the planar TM-Pcs of adjacent chains are oriented nearly perpendicular to each other. While TM-Pcs have been studied for decades due to their interesting optical properties and applications as dyes, there has been recent interest in understanding the magnetic properties with various transition metals.

Due to crystal arrangement, inter-chain interactions among TM-Pcs are relatively weak when compared to intra-chain interactions. This property allows the chains of TM-Pcs to be isolated and approximated as a pseudo 1D system. The electronic structure and spin exchange are computationally examined along chains of CuPc when they have been diluted with the metal-free variant, H$_2$Pc. Density functional theory is employed with the Hubbard U correction to account for electron correlation on the copper d-orbitals. Since the diluted systems are effectively 1D with narrow bands along their stacking axis, a 1D nearest-neighbor Heisenberg model is applied where the exchange coefficients are determined through the Broken Symmetry method. The effect of the Hubbard U and dilution on the electronic structure will be discussed.