First-principles study of molecular-based spin liquid materials: $X[\text{Pd(dmit)}_2]_2$ and $\kappa$-H/D$_3$(Cat-EDT-TTF/ST)$_2$

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We theoretically study two classes of quasi-two-dimensional molecular conductors, $\beta'$-$X[\text{Pd(dmit)}_2]_2$ and $\kappa$-H/D$_3$(Cat-EDT-TTF/ST)$_2$. In their Mott insulating phase with localized $S = 1/2$ spins, some members show quantum spin liquid (QSL) behavior, while others show various ground states including those under pressure. Therefore it is important to seek for a systematic view among different members.

The family of $\beta'$-$X[\text{Pd(dmit)}_2]_2$ ($X = \text{Et}_y\text{Me}_4-Z, y = 0, 1, 2, \text{Et} = \text{C}_2\text{H}_5, \text{Me} = \text{CH}_3, \text{and } Z = \text{P}, \text{As}, \text{and Sb}$), show various ground states depending on $X$ such as antiferromagnetic state, QSL, charge ordering states [1]. We performed a systematic study of their electronic structures by first-principles density functional theory (DFT) calculations [2]. The parameters of the effective dimer model are discussed in relation with the QSL state in $X = \text{EtMe}_3\text{Sb}$. We also show that the recent analysis using the tight-binding model where fragments of molecular orbital are taken as basis functions can analyze the multi-orbital nature of this system [3].

In $\kappa$-H$_3$(Cat-EDT-TTF)$_2$, every two $\text{H(Cat-EDT-TTF)}$ units share a hydrogen (H) atom with a short O-H-O hydrogen bond [4]. It shows a Mott insulating state and is considered as a QSL candidate; its selenophene analog, Cat-EDT-ST, and deuterated materials are also synthesized and show different properties [4]. We performed first-principles DFT calculations, and found a stable H-localized structure (different from the experimentally determined one), where charge disproportionation occurs between the two types of $\text{H(Cat-EDT-TTF)}$ units [5]. We compare relative stabilities between this H-localized state and experimentally-determined deutrium localized structure found in the deuterated sample [4].