

## ELG法による擬一次元金属錯体の高圧下I-M-I遷移の超効率的定量解析

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## Highly efficient analyses of I-M-I transition in quasi-1D metal complexes by elongation method

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The one-dimensional (1D)  $d^8$  transition metals systems,  $[M(\text{dmg})_2]$ ,  $M=\text{Ni}$ ,  $\text{Pd}$  and  $\text{Pt}$ ,  $\text{dmg}=\text{Bis}(\text{dimethylglyoximato})$ ] have attracted a lot of attentions for their interesting electrical and optical properties. For example, the  $\text{Pt}(\text{dmg})_2$  system (structure shown in Fig. 1(a)) based on molecular stacking units exhibits insulator-to-metal-to-insulator (IMI) transition [1] at high pressure with potential applications of pressure switch devices. For the further development of this kind of metals, we carefully examined the nature of this transition from the stand point of electronic structures .

The structure of  $\text{Pt}(\text{dmg})_2$ , is a  $d^8$ -square-planar complex with Pt-Pt distance of 3.26 Å in the direction of stack at normal pressure (shown in Fig. 1(b)). However, the distance of this metal bond (Pt-Pt) between two units will decrease when the pressure increases. Considering the stacking behaviors of the  $\text{Pt}(\text{dmg})_2$  system, we developed the elongation (ELG) method [2] including the relativistic effects by third order Douglas-Kroll (DK3) to theoretically simulate the chain stacking process for heavy metal included systems and examine the orbital energy gaps changes along with the increasing of unit size at different distance of metal bond. The different distance of metal bond represents the situation of  $\text{Pt}(\text{dmg})_2$  system at different pressure.

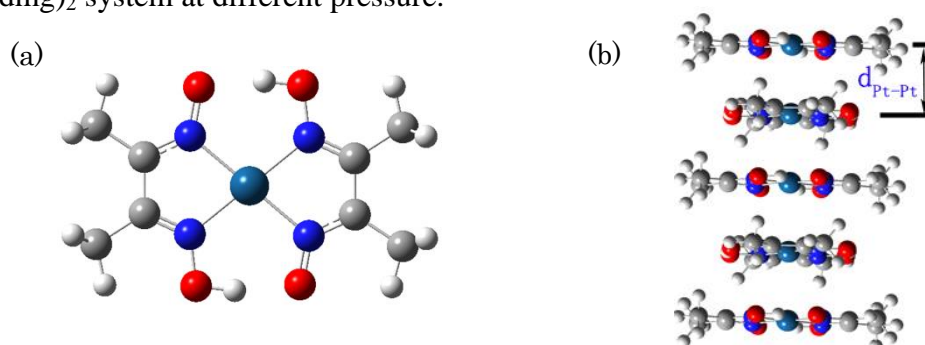


Fig. 1 The structure of  $\text{Pt}(\text{dmg})_2$ . (a). For one Unit, (b) For the stacking structure.

The orbital energy gaps of 16 units of  $\text{Pt}(\text{dmg})_2$  system, calculated by ELG with DK3 correction at mini basis set of HF level, become narrow as the chain elongates (shown in Fig. 2). Meanwhile, the orbital gap also decreases, if the distance of metal bond decreases. In other words, when the pressure increases, the electrical conductivity of  $\text{Pt}(\text{dmg})_2$  system is

enhanced because of the narrowing orbital energy gaps.

In order to more accurately investigate the details of this gap changes, 8 units of  $\text{Pt}(\text{dmg})_2$  are calculated by mPW1PW91 method with large basis set. The LanL2DZ basis set is employed to include the relativistic effect for metal atoms, and 6-31G(d,p) for the rest atoms.

The orbital energy gap of 8 units of  $\text{Pt}(\text{dmg})_2$  will decrease as the pressure increases. However, when the distance is less than 2.6 Å, the energy gap becomes large again (shown in Fig. 3). This energy gaps changes are very similar to the experiment data. When the pressure of the system increases, the  $\text{Pt}(\text{dmg})_2$  system indicates the IMI transition. The orbital shape of the HOMO and LUMO is also compared as the metal bond changes for the distance of metal bond is equal to 2.3 Å, 2.6 Å, and 3.2 Å. The result shows that at normal pressure (3.2 Å) the transition is attributed to  $dz^2$  to  $dp_z$ . While when the pressure increases, the transition is changed to  $dp_z$  to  $dz^2$ , at the same time, because of the small energy gap, the material shows the metallic properties. When the pressure is increasing, the transition changes back again. However, the orbitals involving the transition become less. This change of orbital transition clearly explains the experiment phenomenon. Under the pressures, the orbital transition arises the IMI transition of  $\text{Pt}(\text{dmg})_2$  systems. This findings will also guide us for the further material design and properties improvement.

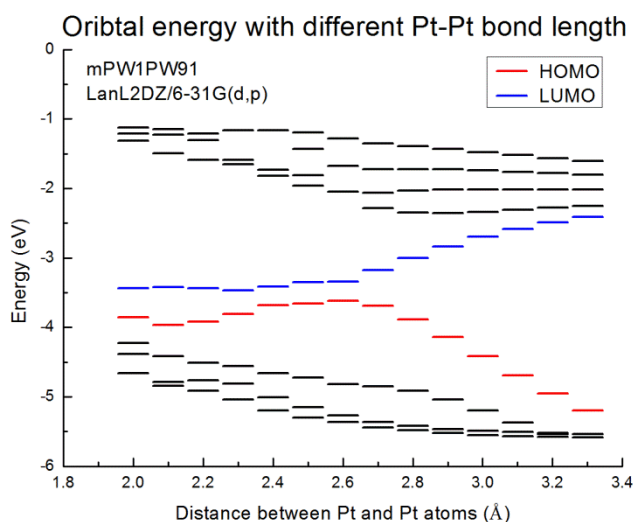


Fig. 3 The orbital energy gaps of 8 units of  $\text{Pt}(\text{dmg})_2$  system.

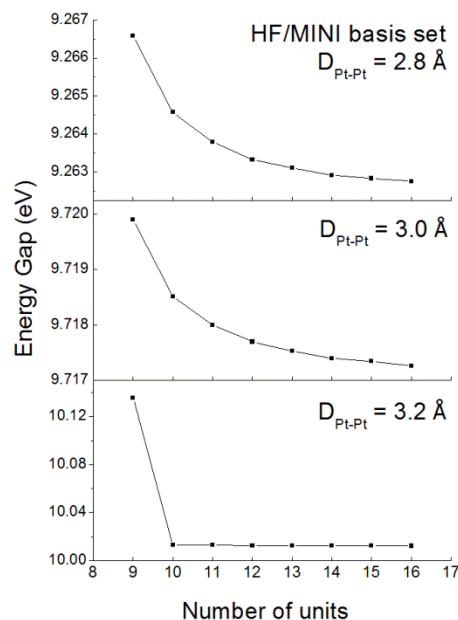


Fig. 2 The orbital energy gap changes by ELG method with DK3 approximation.

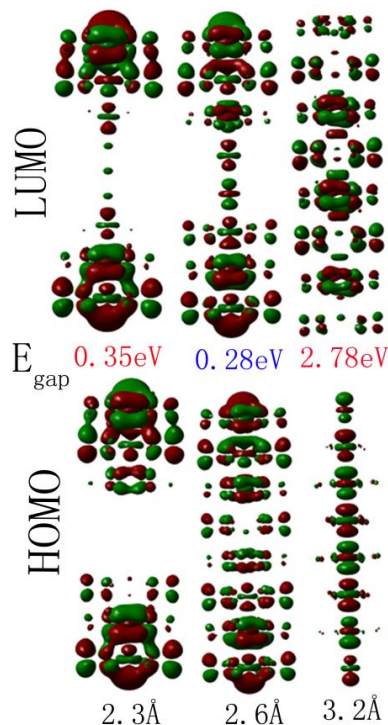


Fig. 4 The orbital shape of HOMO and LUMO.

[1] Takeda, K.; Shirotani, I.; Yakushi, K. *Chem. Mater.* **2000**, *12*, 912.

[2] Imamura, A.; Aoki, Y.; Maekawa, K. *J. Chem. Phys.* **1991**, *95*, 5419.