Valence instability in a dimer of two-orbital system: possible charge separation due to ‘negative $U$’ effect

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Abstract

A novel mechanism of charge separation in a dimer of two-orbital molecular system is proposed. The effective electron–electron repulsive energy in the dimer, $U_{\text{eff}}$, has been estimated by means of valence-bond (VB) model calculations for the ground state of the dimer. It has been found that the HOMO–LUMO interplay leads to negative $U_{\text{eff}}$ in the strong dimerization condition, indicating spontaneous separation of charges on dimers ($2 \text{dimer}^- \rightarrow \text{dimer}^0 + \text{dimer}^2$). Possible relevance to experimental features in some [Pd(dmit)$_2$] salts (dmit = 1,3-dithiol-2-thione-4,5-dithiolate) is discussed.

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1. Introduction

In most molecular conductors based on organic $\pi$-donors or acceptors, the single-molecular orbital (MO) picture is retained for the conduction carriers. Only the highest occupied MO (HOMO) of donors or the lowest unoccupied MO (LUMO) of acceptors contributes to intermolecular charge transfer (CT) in these systems. The recent discovery of a single-component molecular metal based on a Ni-ditholate complex [1] shows a breakthrough of this single-MO limitation. In this case, both HOMO and LUMO contribute to the conduction bands [1,2]. Anion radical salts of a Pd-dithiolate complex, [Pd(dmit)$_2$], have a unique electronic structure with HOMO–LUMO interplay. In most [Pd(dmit)$_2$] salts, the molecules are strongly coupled to form dimers [Pd(dmit)$_2$]$_2^+$ having one unpaired electron on each. The unpaired electron occupies the anti-bonding combination of HOMO’s of the monomers, not the combinations of LUMO’s (Fig. 1). This HOMO–LUMO interchange by dimerization occurs when the sum of intradimer HOMO–HOMO and LUMO–LUMO

$\text{transfer energies ($t$)} > \text{monomer HOMO–LUMO level spacing, } \Delta$. This situation, established by experimental and theoretical studies [3–9], implies a potential role of the double-MO (two-level) configuration. However, the dimer-based single-MO picture still holds in their band structures [10,11], as justified by the perturbation theory [12]. In this Letter, we show that the HOMO–LUMO interplay in the [Pd(dmit)$_2$] dimer exhibits valence instability assisted by structural distortion, leading to a novel mechanism of charge separation. The charge separation, which is usually driven by inter-site electrostatic repulsions in the single-MO conductors, is an object of intense research because of their crucial role in the electronic properties and functionality [13–15]. The present mechanism should be distinguished from the conventional ones, because it is due to local quantum resonance.

2. Results and discussion

2.1. Effective on-site repulsion $U_{\text{eff}}$ of dimeric single-MO systems

In correlating electron systems, the on-site repulsion between electrons plays a significant role. It was found
that the effective repulsive energy between the correlating carriers in a dimeric system is given as

\[ U_{\text{eff}} = 2|t| + |U - (16t^2 + U^2)^{1/2}|/2 \approx 2|t| - 4t^2/U \]

by calculating the energy cost for pairing of carriers on one dimer site as

\[ 2D_2^+ \rightarrow D_2^0 + D_2^+ \]

where the HOMO’s with the Coulomb repulsive energy \( U \), resonate with each other by the CT \( t \), in a donor dimer \( D_2 \) [16,17]. The physical behavior of dimeric \( \pi \)-donor salts has been successfully explained thus in terms of the competition between the bandwidth and strength of dimerization \( t \) [17]. However, \( U_{\text{eff}} \approx 2|t| - 4t^2/U \) is a poor estimation of the cost for \( |t|/U > 0.2 \). To account for the behavior of correlating electrons in the strongly dimerized [Pd(dmit)\(_2\)] salts [11], we estimate here the effective on-site repulsive energy \( U_{\text{eff}} \) of the [Pd(dmit)\(_2\)] dimer, taking account of strong dimerization together with the HOMO–LUMO interplay.

### 2.2. Evaluation of energies and \( U_{\text{eff}} \) of dimers with HOMO–LUMO interplay

The model Hamiltonian to describe the [Pd(dmit)\(_2\)]\(_2\) system is expressed in an extended Hubbard form in terms of the electrons in LUMO and holes in HOMO,

\[ H = H_{\text{CT}} + H_{\text{Coulomb}}. \]

\[ H_{\text{CT}} = \sum_{\sigma = \alpha, \beta} \sum_{n=1,2} (\epsilon^0_{\alpha n} n_{\alpha n} - \epsilon^0_{\beta n} n_{\beta n}) + t_{LL}(c^\dagger_{1L, \alpha} c_{2L, \beta}) + (c^\dagger_{2L, \alpha} c_{1L, \beta}) + t_{HH}(c^\dagger_{1H, \alpha} c_{2H, \beta} + c^\dagger_{2H, \alpha} c_{1H, \beta}), \]

where, for instance, \( c^\dagger_{1 \alpha, \alpha} \) and \( c_{2 \alpha, \alpha} \) denote creation of a spin-\( \alpha \) (up) electron in the LUMO of monomer 1 and annihilation of a spin-\( \beta \) (down) hole in the HOMO of monomer 2, respectively, and \( n_{\alpha} = c^\dagger_{\alpha} c_{\alpha} \) is the number operator. The reference state (the vacuum of the electron and hole) is \( 2[Pd(dmit)]^0 \) with fully occupied HOMO and vacant LUMO. The diagonal terms in the CT Hamiltonian \( H_{\text{CT}} \) stand for the one-particle orbital energies. We henceforth write \( \epsilon^0_{\alpha} = 0 \) (chemical potential of a virtual external electron) and \( \epsilon^0_{\beta} = -A \), using the HOMO–LUMO separation, \( A = \epsilon^0_{\alpha} - \epsilon^0_{\beta} \). The optical experiments [4,5] and intermolecular overlap calculations [5–7,10] of the [Pd(dmit)\(_2\)] salts indicated that \( |t_{LL}| \approx |t_{HH}| = t \) and the HOMO–LUMO CT is negligible due to the symmetry difference between the HOMO and LUMO. The parameter \( U \) denotes the repulsion of two carriers within an MO, \( U' \) the intramolecular electron–hole attraction, and \( V \) the intermolecular Coulomb interaction between the net charges (Fig. 1). The spin dependence of \( U' \) and \( V \) is averaged out for the low-spin states concerned. The orbital dependence of \( U \) and \( V \) is also neglected, because both HOMO and LUMO are well delocalized similarly over the whole molecule. For this reason, we set \( U' = U \) in what follows, though, strictly speaking, \( U' < U \) [9]. In this electron–hole (e–h) picture, the optical HOMO–LUMO excitation energy corresponds to the e–h pair creation energy, \( \Delta' = \Delta - U' \). The experimental estimation, \( \Delta' = 0.8–0.9 \) eV, has been inferred from the optical spectrum of a [Pd(dmit)\(_2\)]\(^-\) solution [4,5].

Following these simplifications, the eigenvalues of \( H \) are obtained as \( E(N_e, N_h) \) for low-lying low-spin levels of the model, such as specified by the numbers of electrons and holes, \((N_e, N_h)\), by the VB calculations (Appendix A). The results are

\[ E(2,0) = (u - X)/2 + V \quad (\text{spin}, S = 0), \]

\[ E(1,1) = (u - X)/2 + \Delta' \quad (S = 0), \]

\[ E(1,0) = -|t| \quad (S = 1/2), \]

\[ E(2,1) = -|t| + u - 2|t|(|t| + u) + u^2 + \Delta' \quad (S = 1/2), \]

\[ E(2,0) = (u - X)/2 + V \quad (S = 0), \]

\[ E(0,0) = 0 \quad (S = 0), \]

\[ E(1,1) = (u - X)/2 + \Delta' \quad (S = 0), \]

\[ E(1,0) = -|t| \quad (S = 1/2), \]

\[ E(0,0) = 0 \quad (S = 0), \]

\[ E(2,1) = -|t| + u - 2|t|(|t| + u) + u^2 + \Delta' \quad (S = 1/2), \]

\[ E(1,1) = (u - X)/2 + \Delta' \quad (S = 0), \]

\[ E(1,0) = -|t| \quad (S = 1/2), \]

\[ E(0,0) = 0 \quad (S = 0), \]

\[ E(2,1) = -|t| + u - 2|t|(|t| + u) + u^2 + \Delta' \quad (S = 1/2), \]
\[ E(2, 2) = (u - Y)/2 + 2\Delta' + 4r^2(1 - u/Y)/(7u + Y) \]  
\[ (S = 0), \]  
where \( u = U - V, \)  
\[ X = (16r^2 + u^2)^{1/2} \]  
and  
\[ Y = (48r^2 + u^2)^{1/2}. \]  

The ground state energies, \( E_n, \) for [Pd(dmit)\( _2 \)]\( ^{2-} \) (\( n = N_c - N_h = 0, 1, 2 \)) are obtained by choosing the lowest one, when \( \Delta', U, V \) and \( t \) are given. No experimental estimation of \( U \) and \( V \) is available for [Pd(dmit)\( _2 \)] in solid state media. The accepted values for the bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) salts are \( U \approx 1 \) eV and \( V \approx U/4 \) [13,14]. For [Pd(dmit)\( _2 \)], we assume \( U \) is slightly less than 1 eV, i.e., \( U \approx \Delta', \) and \( V \approx U/2 \) in what follows, taking account of the more extended \( \pi \)-orbitals and stronger dimerization as compared with the BEDT-TTF salts. Our attention is directed to the strong dimerization regime, \( |t| \sim U, \) since \( |t| = 0.7 \) eV has been inferred from the optical data on the [Pd(dmit)\( _2 \)] salts [4,5]. The energies given in Eqs. (6)–(11) are plotted versus \( |t|/U \) in Fig. 2, with \( \Delta' = U \) and \( V = U/2. \) Collapse of the single-MO picture appears as the crossovers near \( |t| \sim \Delta'/2 \) for \( n = 0 \) and 1, referring to the compensation of the cost for e–h pair creation by the CT energy gain. The ground states for \( |t| \sim \Delta'/2 \) are consistent with the MO theory [3–7]; the primarily active MO is the HOMO.

The effective repulsive energy within a dimer, \( U_{\text{eff}}, \) is the energy cost, \( E_2 + E_0 - 2E_1. \) It is plotted against \( |t|/U \) in Fig. 3. Unlike the single-MO case, \( U_{\text{eff}} \) is not a monotonic function of \( t; \) \( U_{\text{eff}} \) is almost constant for \( |t| > U/3, \) and slightly reduces as \( |t| \) exceeds \( U/2 = u. \) The high stability of \( E(2, 2), \) arising from the many resonating configurations (Fig. 2, inset), is crucial for this behavior. Screening of the hole charge by the LUMO electrons plays a key role in this HOMO–LUMO double-bonding in [Pd(dmit)\( _2 \)]\( ^{2-} \).

### 2.3. Effect of structural distortion on \( U_{\text{eff}} \)

Stronger dimerization is expected for [Pd(dmit)\( _2 \)]\( ^{2-} \) because of the absence of net molecular charge, while [Pd(dmit)\( _2 \)]\( ^{2-} \) is loosened by the electrostatic repulsion. To see this effect, we estimate \( U_{\text{eff}}, \) using \( |t| \) and \( V \) decreasing with \( n. \) This distortion causes a remarkable effect. For example, the choice of \( t_0/t = V_0/V = 1.25 \) for \( E_0 \) and \( t_2/t = V_2/V = 0.8 \) for \( E_2 \) provides abrupt decrease in \( U_{\text{eff}} \) due to the crossovers and negative \( U_{\text{eff}} \) for \( |t| > U \) (Fig. 3). The negative \( U_{\text{eff}}, \) caused by the stability of the double-bonded [Pd(dmit)\( _2 \)]\( ^{2-} \) overwhelming the electron pairing cost in [Pd(dmit)\( _2 \)]\( ^{2-} \), means that the uniform charge distribution ([Pd(dmit)\( _2 \)]\( ^{2-} \)) is unstable against the charge separation.

\[ 2\text{[Pd(dmit)\( _2 \)]} \rightarrow \text{[Pd(dmit)\( _2 \)]} + \text{[Pd(dmit)\( _2 \)]}, \]  
 accompanined by the energy gain due to the enhanced dimerization in [Pd(dmit)\( _2 \)]\( ^{2-} \). Note that no such effect is operative in a neutral dimer in a single-MO system. If this type of distortion is permitted in the crystal, the system can undergo a spontaneous charge disproportionation, or condensation of Jahn–Teller bipolarons. The resultant ordering of the charge in the crystal should then be prescribed by the interdimer Coulomb repulsion, which is not taken account of in the present scheme, so as to minimize the long-range electrostatic energy, as was described by Seo [13] and Mori [14,15].

Let us now briefly look at some experimental facts informative of the proposed valence instability. A metal-to-insulator transition, involving commensurate and incommensurate structural distortions, was found at 56.5 K in Cs[Pd(dmit)\( _2 \)] [5]. The incommensurate one was related to the charge–density-wave appearing below 60 K due to the nesting of the Fermi surface [5]. On the other hand, the commensurate distortion, as well as the splitting in the near-infrared spectrum [5], suggests...
the formation of nonequivalent dimers with different valences. Recently, another case deserving our attention has been found; sufficiently pure samples of (C₂H₅)₂(CH₃)₂Sb[Pd(dmit)₂]₂ exhibit a phase transition from a paramagnetic insulator to a non-magnetic state as temperature passes down by 70 K. This transition is accompanied by formation of nonequivalent dimers similar to those assumed in Fig. 3. Further investigations of these phase transitions are now underway to elucidate the mechanism.

3. Summary

It has been shown that the strong dimerization reduces the energy cost of carrier pairing on a [Pd(dmit)₂] dimer by forming a HOMO–LUMO double bond. This can cause the spontaneous charge separation, 2[Pd(dmit)₂]₀ → [Pd(dmit)₂]⁺ + [Pd(dmit)₂]⁻, with the aid of enhanced dimerization in [Pd(dmit)₂]⁺. This valence instability, which is not expected for the conventional single-MO systems, is a possible mechanism of the phase transitions observed in some [Pd(dmit)₂] salts.

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Appendix A

The diagonal terms of $H$ can be readily obtained just by counting the orbital energy terms of $H_{CT}$ and the classical Coulomb interactions $H_{Coulomb}$ for each electron–hole configuration. The HOMO–LUMO Hund coupling is neglected for the sufficiently large $\Delta$ assumed. The CT Hamiltonian $H_{CT}$ yields cross-terms describing the quantum resonance between the configurations. Neglect of the HOMO–LUMO CT, referring to the conservation of $N_e$ and $N_h$, enables us to treat electrons and holes separately. All the configurations are given by operating creation operators on the vacuum $|0\rangle$, from which symmetrized linear combinations of the equivalent configurations belonging to the same diagonal energy are built as bases in the sub-space of the low-lying low-spin states. The rules for the symmetrization are

(i) A bonding state $(c^\dagger_{1\alpha} - \text{sgn}(t) \ c^\dagger_{2\alpha} |0\rangle)/\sqrt{2}$ is formed from $c^\dagger_{1\alpha} |0\rangle$ and $c^\dagger_{2\alpha} |0\rangle$.

(ii) A spin-singlet state $(c^\dagger_{1\alpha} c^\dagger_{2\beta} - c^\dagger_{1\beta} c^\dagger_{2\alpha} |0\rangle)/\sqrt{2}$, from $c^\dagger_{1\alpha} c^\dagger_{2\beta} |0\rangle$ and $c^\dagger_{1\beta} c^\dagger_{2\alpha} |0\rangle$.

(iii) An ionic state $(c^\dagger_{1\alpha} c^\dagger_{2\beta} + c^\dagger_{2\alpha} c^\dagger_{1\beta} |0\rangle)/2|0\rangle$.

The anti-bonding combinations and the non-bonding spin-triplet states $((c^\dagger_{1\alpha} c^\dagger_{2\beta} + c^\dagger_{1\beta} c^\dagger_{2\alpha}) |0\rangle)/\sqrt{2} |0\rangle$, $c^\dagger_{1\alpha} c^\dagger_{2\beta} |0\rangle$ and $c^\dagger_{2\alpha} c^\dagger_{1\beta} |0\rangle$ are thus eliminated, because they are different in symmetry from the ground state and do not favor the stability. Taking account of all the preferred combinations and combining the electron and hole sub-spaces, we obtain symmetrized basis set for reduced effective Hamiltonian, $H(N_e, N_h)$, whose lowest eigenvalue is the ground state for the given $N_e$ and $N_h$ (Fig. 4). For example, the basis set for $H(2,1)$ is

\[ (c^\dagger_{1\alpha} c^\dagger_{2\beta} - c^\dagger_{1\beta} c^\dagger_{2\alpha}) (c^\dagger_{1\alpha} + c^\dagger_{2\beta}) |0\rangle /2, \]

\[ (c^\dagger_{1\alpha} c^\dagger_{2\beta} + c^\dagger_{1\beta} c^\dagger_{2\alpha}) (c^\dagger_{1\alpha} + c^\dagger_{2\beta}) |0\rangle /2, \]

\[ (c^\dagger_{1\alpha} c^\dagger_{2\beta} + c^\dagger_{1\beta} c^\dagger_{2\alpha}) (c^\dagger_{1\alpha} + c^\dagger_{2\beta}) |0\rangle /2. \]

The $H(2,2)$ matrix includes the fully ionized configuration, $[\text{Pd(dmit)}]^{2+} [\text{Pd(dmit)}]^{2-}$. Explicit inclusion of this yields too complicated form of eigenvalues. Instead, the second-order correction has been made for the perturbing cross terms between this configuration and the others, which leads to the third term of $E(2,2)$ in Eq. (11).

References


