

tions in the study of chemical dynamics by infrared fluorescence are excellent, and several major new directions are already off the drawing board and into the laboratory.

The research described here is generously supported by grants

from the National Science Foundation, Department of Energy, Air Force Office of Scientific Research, Army Research Office, and the Petroleum Research Fund, administered by the American Chemical Society. It is a pleasure to acknowledge the collaboration of many outstanding students, postdoctoral associates, and colleagues.

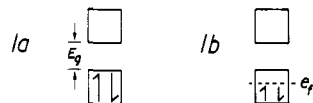
Structural and Electronic Properties of Linear Chain Compounds and Their Molecular Analogies

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Received May 19, 1982 (Revised Manuscript Received November 1, 1982)

The electronic structures of extended linear chain compounds are characterized by their energy bands, in contrast to the discrete energy levels in molecular systems. Energy bands are continuous regions of allowed energy values for an extended system, and are often indicated by rectangular blocks as shown in 1a and 1b.

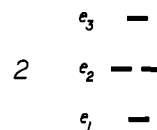


For an extended system of N repeat unit cells, where $N \rightarrow \infty$, any of its energy bands consists of N band orbital levels. Since each of those levels can accommodate two electrons, a given band is completely filled if each unit cell contributes two electrons to the band. The band orbitals of the highest occupied band may be either completely or partially filled as illustrated in 1a and 1b, respectively.

Many physical properties of an extended system are largely governed by the highest occupied and the lowest unoccupied bands, just as those of a molecule are influenced by the highest occupied and the lowest unoccupied molecular orbitals. The highest occupied band level at the absolute zero temperature is commonly referred to as the Fermi level e_f , while the energy gap between the highest occupied and the lowest unoccupied band levels is known as the band gap E_g . Thus, the band gap is nonzero in 1a but vanishes in 1b, so that the band structures 1a and 1b represent typical insulating (or semiconducting if E_g is small but nonzero) and metallic states, respectively.

One of the important quantities in describing the electronic structure of a molecule or an extended system is the so-called density of states. Consider, for example, a hypothetical molecule that has the allowed orbital

energy levels shown in 2, where the e_2 level is doubly



degenerate. Thus in 2, the number of allowed orbital levels (or density of states) with the energy e_2 is two, while that with the energy e_1 or e_3 is one. Of course, the density of states with the energy value other than the allowed energy levels is zero. Similarly, the density of states $n(e)$ in an extended system is the number of allowed band orbital levels having the energy value e per unit cell or per unit volume. In an extended system the density of states is generally a complicated function of energy, and its value at the Fermi level, $n(e_f)$, is important in describing the physical properties arising from a partially filled band.

A linear chain in a metallic state is susceptible to a structural distortion that introduces a band gap at the Fermi level.^{1a} This metal-insulator transition is known as a Peierls distortion, and is also called a $2k_f$ distortion. A nonlinear polyatomic molecule whose highest occupied level is degenerate but incompletely filled undergoes a structural distortion that lowers the molecular symmetry and thus removes the degeneracy. This phenomenon in molecules is called a Jahn-Teller distortion,^{1b} and is similar in nature to a Peierls distortion in extended linear chains.

A partially filled band results typically when a chain has an odd number of electrons per repeat unit cell. A chain with an even number of electrons per unit cell may also lead to a partially filled band when the chain structure has a special symmetry element² or when the chain is partially oxidized (reduced) by good electron acceptors (donors).³ From the viewpoint of one-electron

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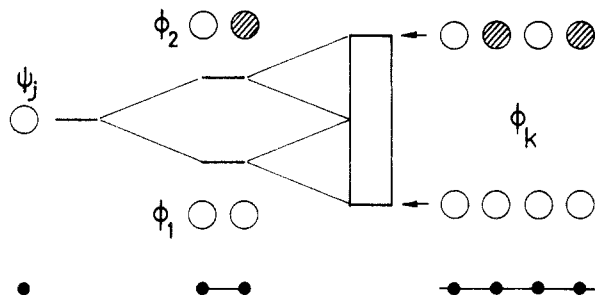
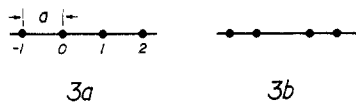


Figure 1. Formation of the band orbitals ϕ_k in terms of the orbital ψ_j of each lattice site as well as in terms of the molecular orbitals ϕ_1 and ϕ_2 of each dimeric unit (i.e., any two neighboring lattice sites).

tron theory that neglects electron–electron repulsion, any extended chain with a partially filled band is predicted to be metallic. However, such a material may become insulating even in the absence of a Peierls distortion, since a band gap can be introduced by electron–electron repulsion alone.⁴ This kind of insulating state is brought about so as to reduce the extent of electron–electron repulsion arising from orbital double occupancy⁵ and can be either magnetic or non-magnetic. Therefore, in understanding the chemical and physical problems associated with extended linear chain compounds, it is essential to recognize how electron–electron repulsion governs the occupancy of their band orbitals and how the resulting electronic states affect the structural and physical properties. These questions are briefly examined in the following discussion by drawing analogies between extended linear chains and discrete molecular systems in their structural and electronic phenomena.

Nature of Energy Band

Let us consider the formation of an energy band based upon a regular chain 3a with repeat distance a .



In this chain of N sites (i.e., unit cells), the position of a j th site is given by $R_j = ja$. For simplicity of discussion, it is assumed that each lattice site j is represented by one orbital, ψ_j , and that these site orbitals ψ_j are orthonormal, $\langle \psi_i | \psi_j \rangle = \delta_{ij}$. Figure 1 shows schematically how the band orbitals ϕ_k of a chain are related to the molecular orbitals (ϕ_1 and ϕ_2) of a dimer and to the site orbitals ψ_j .⁶ The lowest (highest) level of the

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(5) (a) Whangbo, M.-H. *J. Chem. Phys.* **1981**, *75*, 4983. (b) Whangbo, M.-H. *Ibid.* **1980**, *73*, 3854. (c) Whangbo, M.-H.; Foahee, M. J.; Hoffmann, R. *Inorg. Chem.* **1980**, *19*, 1723. (d) Whangbo, M.-H.; *Ibid.* **1980**, *19*, 1728. (e) Whangbo, M.-H. *J. Chem. Phys.* **1979**, *70*, 4963. (f) Whangbo, M.-H., in ref 3d, p 127.

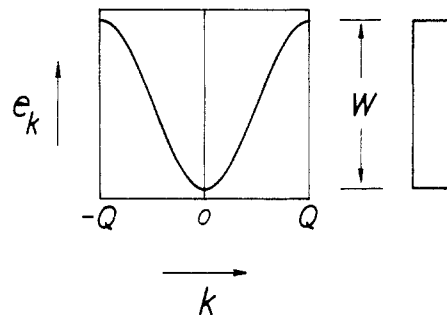
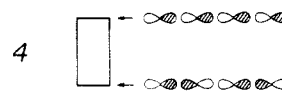


Figure 2. Variation of the band orbital energy e_k as a function of wave vector k , where $Q = \pi/a$.

band represents the maximum bonding (antibonding) interaction that results when the orbitals ψ_j combine in phase (out of phase) between all nearest-neighbor sites.^{2a,5f} To be precise, the band orbitals ϕ_k are written as

$$\phi_k = (1/N^{1/2}) \sum_j e^{ikR_j} \psi_j \quad (1)$$

where the band orbital index k , the wave vector, is related to the crystal momentum $\hbar k$. Note that the orbital coefficient e^{ikR_j} is equal to 1 at $k = 0$ and $(-1)^j$ at $k = \pm Q$ (here $Q = \pi/a$). Thus, the bottom and the top of the band occur at $k = 0$ and $k = \pm Q$, respectively. Unlike the case just described, the nodal properties of site orbitals may be such that the interaction between adjacent ones is antibonding. Then the bottom and the top of the resulting band would occur at $k = \pm Q$ and 0, respectively, as expected from 4, which shows a band



constructed from p-type site orbitals aligned along the chain direction.

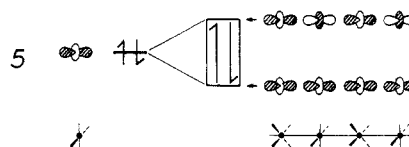
The band orbitals ϕ_k may be given as eigenfunctions of the core Hamiltonian (i.e., the kinetic plus the nuclear–electron attraction energies).^{5a,b} Then the band orbital energies e_k are given as

$$e_k = \langle \phi_k | H | \phi_k \rangle \simeq \bar{e} + 2t \cos(ka) \quad (2)$$

where the mean band energy \bar{e} is the Coulomb integral $\bar{e} = \langle \psi_j | H | \psi_j \rangle$ and the transfer energy t is the resonance integral $t = \langle \psi_j | H | \psi_{j+1} \rangle$. The dependence of the band orbital energy e_k on wave vector k is plotted in Figure 2, which together with eq 2 shows that the width of the band is given by $W = -4t$ (note that $t < 0$).

Partially Filled Band and Structural Distortion

When each site orbital ψ_j of the chain 3a is doubly occupied, the resulting band becomes completely filled. As an example, consider the highest occupied band (i.e., the d_{z^2} band) of a $[\text{Pt}(\text{CN})_4]^{2-}$ chain^{7a} depicted in 5,

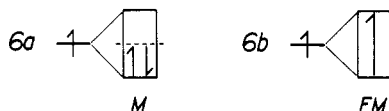


where the z -axis is taken along the chain. In this chain, square-planar $\text{Pt}(\text{CN})_4^{2-}$ units are stacked face to face

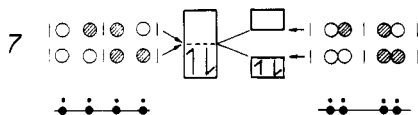
(6) Each site orbital ψ_j is represented as an s-type atomic orbital in Figure 1. In general, ψ_j may refer to any group orbital of the unit cell j that leads to a particular band under consideration.

to form linear chains of platinum atoms.⁷ Upon partial oxidation of this chain, electron removal occurs from the top portion of the d_{z^2} band so that a partially oxidized $[\text{Pt}(\text{CN})_4]^{(2+\delta)-}$ chain becomes metallic.^{7a} The bonding between platinum atoms is strengthened by the partial oxidation, since the orbitals near the top of the d_{z^2} band are strongly antibonding between platinum atoms. As a consequence, the internuclear Pt–Pt distance in a $[\text{Pt}(\text{CN})_4]^{(2+\delta)-}$ chain becomes shorter as the extent of the partial oxidation δ increases.^{3b,7}

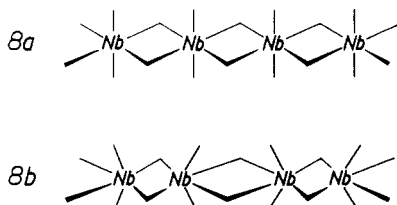
With one electron per site in 3a, the bottom half of its band orbitals may become doubly occupied as in 6a.



According to Figure 2, the Fermi wave vector k_f (i.e., the wave vector that leads to the Fermi level e_f) of 6a is $\pm Q/2$. Thus, the band orbitals ϕ_k in the region $-Q/2 \leq k \leq Q/2$ are doubly occupied in 6a. This half-filled band is split into two by the pairing-distortion 3a \rightarrow 3b as illustrated in 7.^{5f} Because of the concomitant



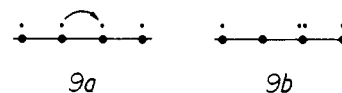
band gap introduction, the occupied band levels of 3b are lowered in energy with respect to those of 3a. Thus a regular chain with a half-filled metallic band is susceptible to a pairing distortion. For instance, consider a linear chain NbX_4 (X = halogen) that contains formal Nb^{4+} (d^1) ions. The ideal NbX_4 chain 8a is made up



of NbX_6 octahedra sharing their opposite edges. The observed structure 8b is derived from 8a by the pairing distortion of niobium atoms along the chain.⁸ The Peierls distortion expected from a half-filled metallic band is the pairing distortion (or the lattice dimerization) just described, and those from one-third- and one-quarter-filled metallic bands are lattice trimerization and tetramerization, respectively.

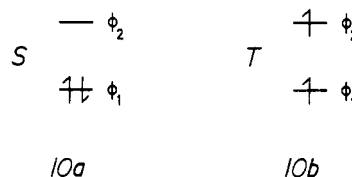
Electron Localization and Orbital Occupancy

As observed from magnetic insulators, a regular chain with a partially filled band may become insulating due simply to electron–electron repulsion.⁴ The electrons in such materials are often called localized electrons. Let us explore the meaning of electron localization in terms of the diagram 9, which shows an electron hop-



ping from one lattice site to another in a regular chain with one electron per site. If τ is the mean time of stay for an electron at a given site,⁹ τ would be infinite for a localized electron. Since a hopping electron may assume any energy value within the band of 9a, the uncertainty in energy is equal to W . Thus, according to the uncertainty principle, $\tau \simeq \hbar/W$ so that $\tau \rightarrow \infty$ as $W \rightarrow 0$. That is, electron localization occurs from a chain with a very narrow band. What makes electron hopping energetically unfavorable in such a case is the on-site repulsion brought about by having two electrons on a lattice site as in 9b.⁴

Localized insulating states can be accommodated within the framework of band orbital picture once it is recognized how electron–electron repulsion affects orbital occupancy.⁵ The electron–electron repulsion terms of importance are the on-site repulsion $U = (\psi_j\psi_j|\psi_j\psi_j)$ and the nearest-neighbor intersite repulsion $V = (\psi_j\psi_j|\psi_{j+1}\psi_{j+1})$. Let us first consider the relative stability of the singlet and the triplet states of a dimer (i.e., any two neighboring sites of a chain) shown in 10a and 10b,



respectively, where $\phi_1 = (\psi_j + \psi_{j+1})/2^{1/2}$ and $\phi_2 = (\psi_j - \psi_{j+1})/2^{1/2}$. The singlet state 10a has the lower lying orbital doubly occupied, which is favored in terms of orbital energy but opposed in terms of electron–electron repulsion. The opposite is the case with the triplet state 10b in which orbital double occupancy is avoided. Thus, when $e_2 - e_1 < U/2$, the triplet state becomes more stable than the singlet state.^{5e,f} Because of the relationship that $e_2 - e_1 = -2t = W/2$, the relative stability of those two states can be written as

$$E_T < E_S \quad (3)$$

if $W < U$. An extreme case of eq 3 occurs when the orbitals ϕ_1 and ϕ_2 are degenerate so that $e_1 - e_2 = W = 0$. Then the triplet state is more stable than the singlet state since U is nonzero. This is, of course, an example of Hund's rule.

Consider now an alternative to the metallic state 6a. The ferromagnetic (FM) insulating state 6b of a half-filled band has every band orbital singly occupied, and hence removes the electron–electron repulsion arising from the orbital double occupancy in 6a. The relative stability of the metallic and the FM states is given by^{5e,f}

$$E_{\text{FM}} < E_{\text{M}} \quad (4)$$

if $W < (\pi/4)U$. This expression is similar not only to the electron localization condition determined by using many-body theory¹⁰ but also to its molecular counterpart (eq 3) concerning the relative stability of the low-spin and high-spin states of a dimer. From the viewpoint of total electronic energy in which all electron–electron repulsion terms but U and V are neglected, the

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(8) (a) Whangbo, M.-H.; Foeshee, M. J. *Inorg. Chem.* 1981, 20, 113. (b) Taylor, D. R.; Calabrese, J. C.; Larsen, E. M. *Ibid.* 1977, 16, 721. (c) Blight, D. G. Kerpert, D. L. *Phys. Rev. Lett.* 1971, 27, 504. (d) Kerpert, D. L.; Marshall, R. E. *J. Less-Common Met.* 1974, 34, 153.

(9) Krüger, E. *Phys. Status Solidi B* 1978, 85, 261.

(10) Hubbard, J. *Proc. R. Soc. London, Ser. A* 1964, 277, 237.

FM state **6b** is equivalent to any localized state that has each site orbital ψ_j of **3a** singly occupied either with up-spin or with down-spin.¹¹

Charge and Spin-Density Alternation

Besides the FM state, electron–electron repulsion could lead to a number of other electronic states for a regular chain with a half-filled band. It is convenient to regard these states as derived from the metallic state when its occupied orbitals ϕ_k ($-k_f \leq k \leq k_f$, where $k_f = Q/2$) are modified by mixing with the unoccupied orbitals ϕ_{k+2k_f} .^{5a} Namely, new band orbitals may be defined as

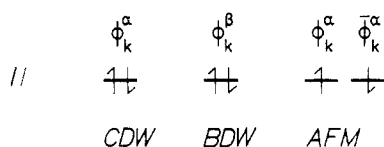
$$\phi_k^\alpha = M_\alpha(\phi_k + \alpha_k \phi_{k+2k_f})$$

$$\bar{\phi}_{-k}^\alpha = M_\alpha(\phi_k - \alpha_k \phi_{k+2k_f})$$

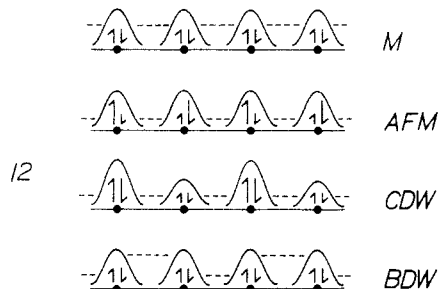
$$\phi_k^\beta = M_\beta(\phi_k + i\beta_k \phi_{k+2k_f})$$

where M_α and M_β are the normalization constants and the mixing coefficients α_k and β_k are even and odd functions of k , respectively. The electron densities resulting from the orbitals ϕ_k^α , $\bar{\phi}_{-k}^\alpha$, and ϕ_k^β are respectively given by $(\phi_k^\alpha)^* \phi_k^\alpha$, $(\bar{\phi}_{-k}^\alpha)^* \bar{\phi}_{-k}^\alpha$, and $(\phi_k^\beta)^* \phi_k^\beta$, each of which consists of the terms associated with on-site densities ψ_j^2 and those associated with nearest-neighbor intersite densities $\psi_j \psi_{j+1}$. An essential consequence of the orbital mixing defined in eq 5 is electron density alternation. It is on-site densities ψ_j^2 that alternate in magnitude in $(\phi_k^\alpha)^* \phi_k^\alpha$ and $(\bar{\phi}_{-k}^\alpha)^* \bar{\phi}_{-k}^\alpha$, but intersite densities $\psi_j \psi_{j+1}$ in $(\phi_k^\beta)^* \phi_k^\beta$. The band orbital densities $(\phi_k^\alpha)^* \phi_k^\alpha$ and $(\bar{\phi}_{-k}^\alpha)^* \bar{\phi}_{-k}^\alpha$ differ only in that the sites of density accumulation (depletion) in the former coincide with those of density depletion (accumulation) in the latter.

Thus, when the modified orbitals of eq 5 are occupied as indicated in 11 for all k in the region $-k_f \leq k \leq k_f$,^{5a}



there occur charge density wave (CDW, or diagonal CDW^{12a}), bond density wave (BDW, or off-diagonal CDW¹²), and antiferromagnetic (AFM, or spin density wave) states. The characteristic charge and spin density distributions in the AFM, CDW, and BDW states are compared with those of the metallic (M) state in 12. In



(11) The energy difference between any two different spin arrangements of a magnetic insulator is small, which is described in terms of spin Hamiltonians.

(12) (a) Paldus, J.; Cizek, J. *Phys. Rev. A* **1970**, *2*, 2268. (b) Kertész, M. *Phys. Status Solidi B* **1975**, *69*, K141. (c) Kertész, M.; Koller, J.; Azman, A. *J. Chem. Phys.* **1977**, *67*, 1180. (d) Fukutome, H. *Prog. Theor. Phys.* **1968**, *40*, 998, 1227. (e) Ooshika, Y. *J. Phys. Soc. Jpn.* **1957**, *12*, 1246.

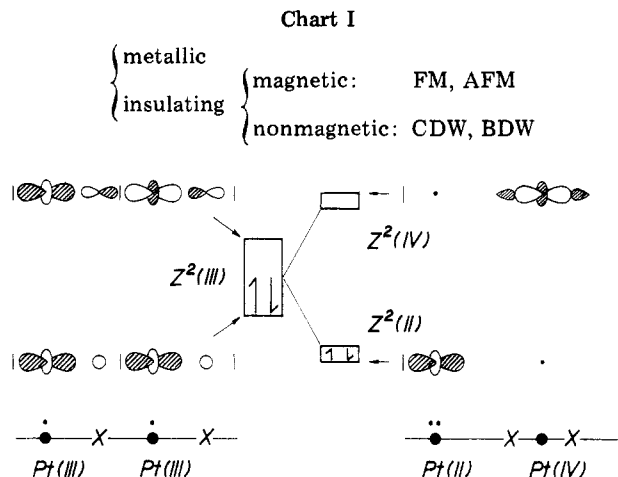


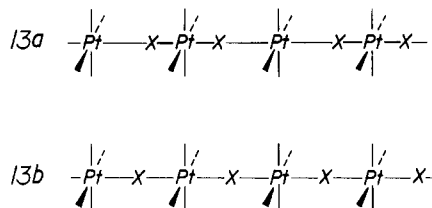
Figure 3. Correlation between the d_{z^2} band of a $[\text{Pt}^{\text{III}}\text{L}_4\text{X}]$ chain and that of a $[\text{Pt}^{\text{II}}\text{L}_4\text{Pt}^{\text{IV}}\text{L}_4\text{X}_2]$ chain, where the z -axis taken along the chain direction, and the label z^2 refers to d_{z^2} .

each electronic state of **12**, the magnitude of the up-spin (down-spin) electron density on a lattice site is represented by the length of the upward (downward) arrow, while the magnitude of the bond order between any to neighboring sites is indicated by the height of the dashed line. Thus, the AFM state exhibits spin density alternation, and the CDW state charge density alternation. The bond orders of the BDW state alternate in magnitude, but those of other states are uniform. Note that the essential difference between the CDW and BDW states lies in whether the density alternation refers to on-site or intersite electron density.

In the metallic state the symmetry of the density distribution is identical to that of the chain lattice. This is not the case with the CDW, BDW, or AFM state, in which either spin or charge density distribution has lower symmetry than does the chain lattice. Occurrence of such a phenomenon, often described as the Hartree–Fock instability,¹³ is due to electron–electron repulsion. With respect to the metallic state **6a** in which all the orbitals ϕ_k in the region $-k_f \leq k \leq k_f$ are doubly occupied, it amounts to reducing the extent of orbital double occupancy (and hence the extent of electron–electron repulsion) to fill the modified orbitals of eq 5 as shown in 11. When an AFM, CDW, or BDW character is created on top of the metallic state as depicted in 11 (i.e., $\alpha_k \neq 0$ and $\beta_k \neq 0$ in eq 5), a band gap is introduced in the resulting state. The magnitudes of the band gaps in the AFM, CDW, and BDW states are, like the energy lowering factors favoring the formation of those states, proportional to the electron repulsion terms U , $(4V - U)$, and V , respectively.^{5a} Thus, the AFM state reduces on-site Coulomb interactions as in the FM state, and the CDW state reduces nearest-neighbor Coulomb interactions while increasing on-site Coulomb interactions at the same time. The BDW state enhances nearest-neighbor exchange interactions, which originate from intersite electron densities $\psi_j \psi_{j+1}$.^{5a,12}

(13) (a) Thouless, D. J. “The Quantum Mechanics of Many Body Systems”; Academic Press: New York, 1961. (b) Löwdin, P.-O. “Quantum Theory of Atoms, Molecules and Solid State”; Löwdin, P.-O., Ed.; Academic Press: New York, 1966; p 601. (c) Cizek, J.; Paldus, J. *J. Chem. Phys.* **1967**, *47*, 3976. (d) Hirao, K.; Nakatsuji, H. *J. Chem. Phys.* **1978**, *69*, 4535, 4548. (e) Böhm, M. *Ber. Bunsenges. Phys. Chem.* **1981**, *85*, 755. (f) Fukutome, H. *Prog. Theor. Phys.* **1972**, *47*, 1156. (g) Ostlund, N. S. *J. Chem. Phys.* **1972**, *57*, 2994.

We summarize in Chart I the various band electronic states that may arise from a regular chain with a half-filled band. Both the FM and AFM states occur from a narrow band, while the metallic and BDW states occur from a wide band. Due to the increase in on-site Coulomb interactions, the CDW state cannot be realized unless $(U - 4V) < 0$ ^{5a,b,14} and/or unless its alternative electronic states are made unstable by a certain structural modification of the chain. For example, the mixed-valent $[\text{Pt}^{\text{III}}\text{L}_4\text{Pt}^{\text{IV}}\text{L}_4\text{X}_2]$ chain 13a is ob-



tained from the monovalent $[\text{Pt}^{\text{III}}\text{L}_4\text{X}]$ chain 13b that consists of $\text{Pt}^{\text{III}}\text{L}_4\text{X}_2$ octahedra sharing their opposite corners X.¹⁵ As shown in Figure 3, the highest occupied band of 13b (i.e., the d_{z^2} (III) band) is half-filled and has antibonding character between platinum and halogen atoms.^{8a} This antibonding combination in the d_{z^2} band is a consequence of the fact that the d orbitals of platinum are higher lying than the s and p orbitals of halogen. The pairing distortion of halogen atoms 13b \rightarrow 13a converts the antibonding orbitals of the $\text{Pt}^{\text{III}}\text{L}_4\text{X}-\text{Pt}^{\text{III}}$ centers in 13b into the d_{z^2} lone pair orbitals of the $\text{Pt}^{\text{II}}\text{L}_4$ units and the $\text{Pt}^{\text{IV}}-\text{X}$ antibonding of the $\text{Pt}^{\text{IV}}\text{L}_4\text{X}_2$ units. Because of the removal of the antibonding interactions, the d_{z^2} (II) band of 13a is lowered significantly relative to the d_{z^2} (III) band of 13b.^{8a} This orbital energy lowering must be far greater than what one expects from the simple introduction of a band gap as indicated in 7, in order to overcome the on-site repulsion from the Pt^{II} sites in 13a.^{15b}

The CDW (i.e., diagonal CDW) or the BDW (i.e., off-diagonal CDW) that arises from a half-filled band is commensurate in that the periodicity of the electron density distribution is an integral multiple of that of the chain lattice. An incommensurate CDW originates from a partially filled metallic band whose occupancy is not a simple fraction of the number of lattice sites such as $1/2$, $1/3$, and $1/4$.¹⁶ A commensurate CDW is locked into place because its sliding motion along the chain faces a large potential barrier. However, an incommensurate CDW, which consists of both diagonal and off-diagonal CDW characters, can easily slide along the chain unless pinned to the lattice by impurities.¹⁶

Pairing Distortion and BDW

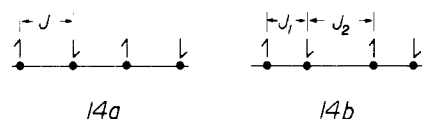
When formed on a regular chain with a half-filled band, a BDW makes the potentials acting on the two

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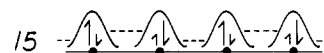
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sides of a lattice site unequal, thereby inducing a pairing distortion.^{5a,17} Therefore, it may be said that the Peierls distortion (i.e., the pairing distortion) in such a chain is driven by a BDW created on top of the metallic state. A pairing distortion is also found in linear AFM chain compounds that are comprised of ion radicals. This phenomenon is known as a spin-Peierls distortion.¹⁸ In contrast to a Peierls distortion that refers to a phase transition from a metallic to a non-magnetic insulating state, a spin-Peierls distortion alters an AFM state with a uniform spin-exchange parameter to another with two alternating parameters, 14a \rightarrow 14b. A spin-Peierls phenomenon is usually de-



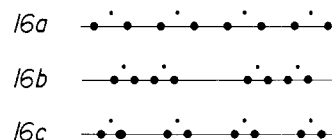
scribed in terms of the magnetic energy associated with spin Hamiltonians.¹⁸ Within the framework of electronic Hamiltonians, a spin-Peierls distortion can be considered to result when a BDW is introduced into an AFM state as depicted in 15.^{5a} As already mentioned,



the formation of a BDW is favorable in a wide band, but that of an AFM state in a narrow band. Therefore, the extent of a BDW that can be formed on top of an AFM state would be small. This explains why the magnitude of a spin-Peierls distortion is small compared with that of a Peierls distortion. Ultimately, no BDW is expected from a truly localized state, which occurs when $W = 0$.^{5a} This is consistent with the observation that nonzero spin-exchange parameter J is needed to predict a spin-Peierls distortion in the spin Hamiltonian analysis, because J is related to the band width as $J = W^2/4U$.^{16c,18a}

$2k_f$ vs. $4k_f$ Distortion and Molecular Analogy

With one electron per every two sites, the regular chain 16a will have its band one-quarter filled. Thus,



if electron-electron repulsion is neglected, the Fermi wave vector is given by $k_f = \pm Q/4$ so that the appropriate Peierls distortion (or the $2k_f$ distortion) is a lattice tetramerization such as 16a \rightarrow 16b. Because of electron-electron repulsion, however, the chain 16a might undergo a lattice dimerization such as 16a \rightarrow 16c as if $k_f = \pm Q/2$. This kind of structural distortion is termed a $4k_f$ distortion.¹⁹ As an example, let us con-

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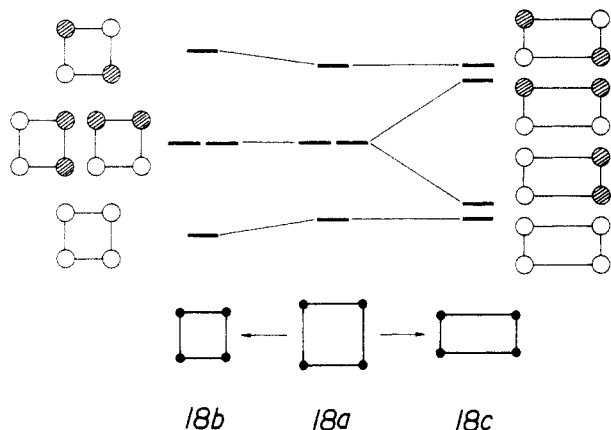
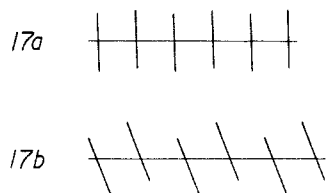


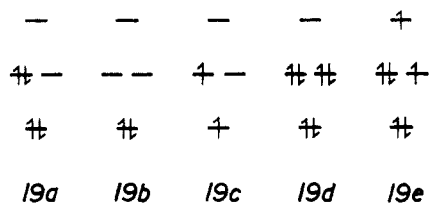
Figure 4. Correlation between the MO levels of the tetramers 18a, 18b, and 18c.

sider a salt of 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) with the methylethylmorpholinium cation (MEM⁺), i.e., MEM(TCNQ)₂.^{19e-g} With the formal oxidation of (TCNQ)₂⁻, the band made up the lowest unoccupied molecular orbitals of neutral TCNQ units becomes the highest occupied band of each TCNQ chain in MEM(TCNQ)₂, which is one-quarter filled. The TCNQ chains in MEM(TCNQ)₂ as viewed along the chain direction above and below ~335 K are schematically shown in 17a and 17b, respectively. The



TCNQ units are almost uniformly spaced in 17a, while they are dimerized in 17b. Below ~20 K the TCNQ chain 17b is known to undergo a dimerization along the chain direction, thereby leading to a tetramerized structure.^{19e-g}

The cause for the $4k_f$ distortion in a quarter-filled band may be accounted for in terms of its molecular analogy, i.e., the distortion from a square-planar tetramer 18a. Figure 4 shows how the MO levels of 18a vary as it undergoes a "dimerization", 18a → 18c, and a "tetramerization", 18a → 18b. The electronic states 19a–19e are obtained when the MO's of 18a are half-



quarter-, and three-quarters-filled. The MO correlation diagrams of Figure 4 allow us to examine which distortion, dimerization or tetramerization, would be preferred in 19a–19e. The half-filled configuration 19a is expected to follow a dimerization as in the case of the

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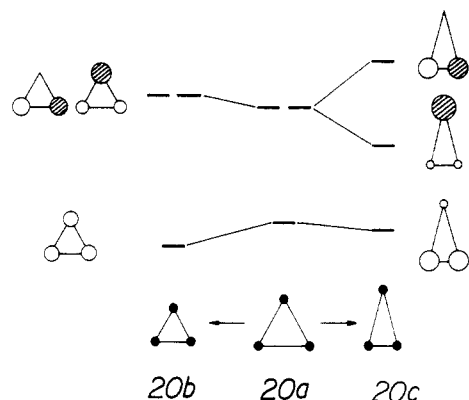
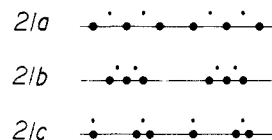


Figure 5. Correlation between the MO levels of the trimers 20a, 20b, and 20c.

Jahn–Teller distortion of cyclobutadiene,²⁰ while the quarter-filled configuration 19b would be stabilized by a tetramerization. When the interactions among the four sites of 18a are weak, the MO levels of 18a split only slightly so that the high-spin state 19c would be favored over the low-spin state 19b due to electron–electron repulsion. Consequently, the quarter-filled configuration 19c will induce a dimerization just as in the case of the half-filled configuration 19a.

The above discussion suggests that the $2k_f$ and the $4k_f$ distortions of a linear chain compound are the same in nature as the Jahn–Teller distortions that are associated with the low-spin and the high-spin states of a discrete molecule, respectively. The distortions from quarter-empty configurations are similar to those from quarter-filled configurations. That is, the states 19d and 19e are expected to undergo a tetramerization and a dimerization, respectively.

In a similar manner, the $2k_f$ and the $4k_f$ distortions from a chain with a third-filled (or a third-empty) band may be estimated in terms of the distortions expected from an equilateral triangle trimer 20a. The appropriate MO correlation diagrams for the distortions 20a → 20b and 20a → 20c, shown in Figure 5, suggest that a regular chain 21a with a third-filled band (i.e., two electrons per every three sites) would prefer the $4k_f$ distortion 21a → 21c^{19b} to the $2k_f$ distortion 21a → 21b



if the interactions among the lattice sites are weak in 20a.

The localized electrons in the quarter-filled $4k_f$ structure 16c and those in the third-filled $4k_f$ structure 21c may be antiferromagnetically oriented. Then the $4k_f$ → $2k_f$ distortions 16c → 16b and 21c → 21b can be regarded as the spin–Peierls distortions in the linear chains with quarter- and third-filled bands, respectively.

(20) The singlet configuration 19a of 18a is higher in energy than the triplet configuration of 18a that has each of the degenerate orbitals of 18a singly occupied by an up-spin electron. Another singlet configuration in 18a, which results when the two electrons in one of the degenerate orbitals of 19a are transferred to the other of the degenerate orbitals, may be referred to as 19a'. Then, a symmetry-adapted singlet state may be approximated by a linear combination of 19a and 19a'. In cyclobutadiene, the lowest energy singlet state of 18c that is derived from 19a of 18a upon dimerization is lower in energy than the lowest energy triplet state of 18c.^{1b}

Competition between Electron Localization and Superconductivity

The ability to carry an electrical current without resistance is referred to as superconductivity,^{16c,21} and the temperature at which a material becomes superconducting upon cooling is called the superconducting transition temperature, T_c . It is known that T_c is raised upon increasing the density of states at the Fermi level $n(e_f)$,^{3a,21} and a high transition temperature T_c is likely to occur from a nearly half-filled narrow band⁹ partly because the $n(e_f)$ value of such a band is generally large. As already pointed out, electrons in such a band are also susceptible to electron localization. Thus, competition between superconductivity and electron localization may occur, as observed from several organic salts of tetramethyltetraselenafulvalene (TMTSF) with inorganic ions X^- , i.e., (TMTSF)₂X.²² For instance, (TMTSF)₂PF₆ undergoes a spin density wave (SDW) transition near 12 K at ambient pressure.²³ However, an applied pressure of ~ 12 kbar is known to suppress the SDW transition and give rise to superconductivity at $T_c \approx 0.9$ K.²⁴ On the other hand, (TMTSF)₂ClO₄ becomes superconducting at $T_c \approx 1$ K without any

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applied pressure.²⁵ It is certainly a challenge to unravel the structural and electronic factors responsible for such delicate changes in the physical properties of (TMTSF)₂X.

Concluding Remarks

The electronic structure of a given system is characterized by its orbital occupancy, which is in turn governed by a balance between two opposing energy components. That is, the double occupancy of low-lying orbitals is promoted by orbital energy but opposed by electron-electron repulsion. Since this is true for any material, regardless of whether extended or discrete, it is only natural that similarities do exist between extended and discrete systems in their structural and electronic phenomena. Some of those similarities were identified and analyzed in this article. It should also be noted that common facets exist between molecular ring current and bulk superconductivity²⁶ and that a solid-state polymerization process, as to whether thermally or photochemically allowed, can be discussed in terms of the Woodward-Hoffmann rules.²⁷ Further investigation of such similarities between extended and discrete systems would help us to build true bridges of comprehension between chemistry and physics associated with solid-state materials.

This work was in part supported by the Camille and Henry Dreyfus Foundation through a Teacher-Scholar Award to the author. I would like to thank Prof. T. A. Albright, Prof. J. K. Burdett, Dr. F. J. DiSalvo, Dr. R. C. Haddon, Dr. T. Hughbanks, and Dr. J. M. Williams for their valuable comments on this work.

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Characterization of Chromia and Molybdena Catalysts by Oxygen Chemisorption

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Received June 24, 1982 (Revised Manuscript Received November 1, 1982)

This Account is concerned with the development of methods, based on the selective chemisorption of oxygen, to characterize the specific surface area of chromia and molybdena catalysts. Selective chemisorption techniques, especially for hydrogen and carbon monoxide, are well-known for the characterization of supported metal catalysts. Comparable methods for supported transition-metal oxide and sulfide catalysts have

been relatively neglected, and more study will be needed before we understand in detail what is being measured. The author's interest in this topic originated some 30 years ago in a more general context.

Two papers by Dowden aroused hopes, around 1950, that a unitary electronic theory of catalytic action would be successful.^{1,2} Dowden's approach was based on application of band theory (of electronic energy levels) to insulator, semiconductor, and metal catalysts.³ The author's first work on transition-metal oxide catalysts

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