5.04 Principles of Inorganic Chemistry II
Fall 2008

The LCAO method for cyclic systems provides a convenient starting point for the development of the electronic structure of solids.

At very large N, as the circumference of the circle approaches ∞, the cyclic problem converges to a linear one,
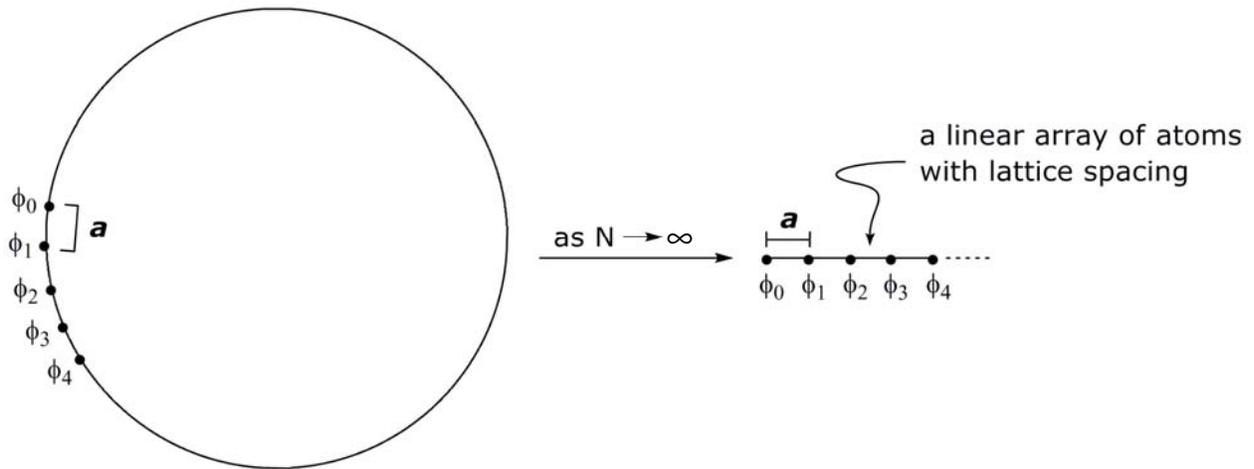
Qualitatively, from a MO energy level perspective,

MO's   **band**

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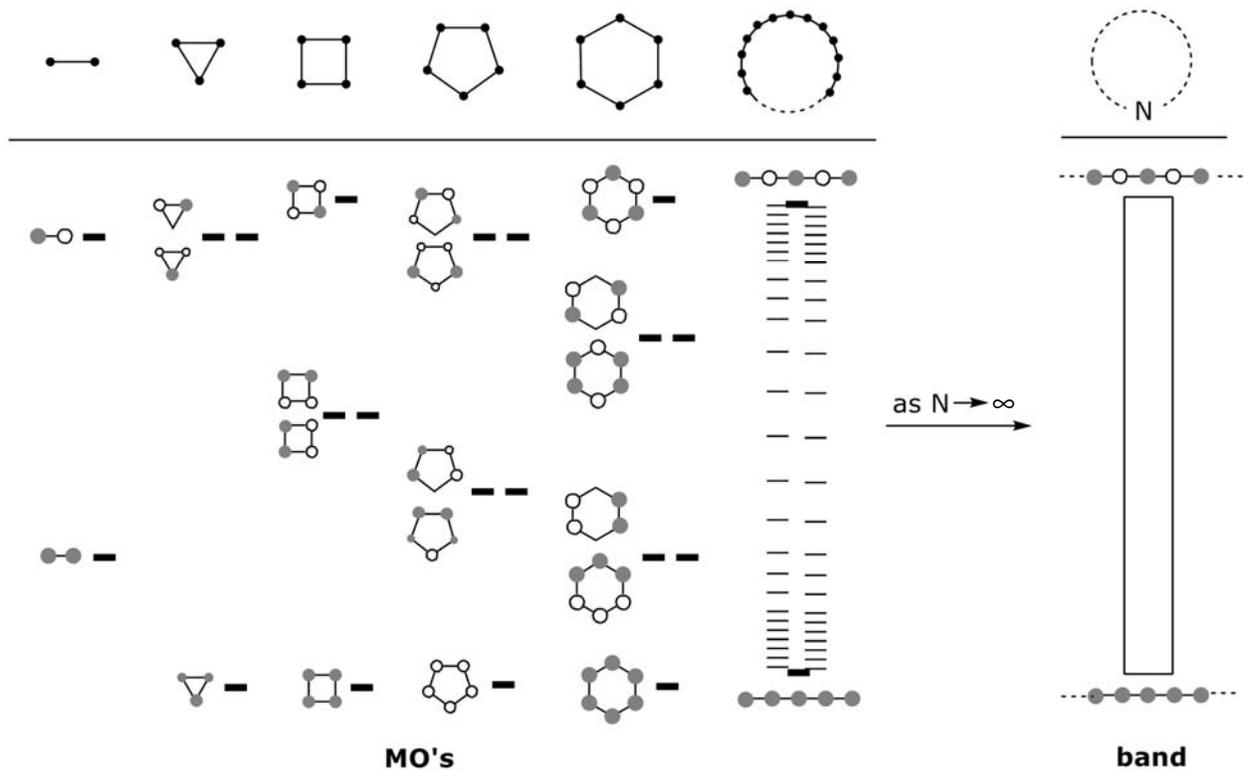
More quantitatively, in moving from cyclic to linear systems, instead of describing orbital (atom) positions angularly, the position of an atom is described by m*a*, where m is the number of the atom in the array and *a* is the distance between atoms. Thus, the θ of the N-cyclic derivation becomes m*a*,

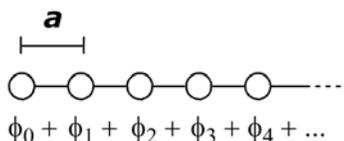$$\psi_j = \sum_m e^{ij\theta}\phi_m \qquad\Longrightarrow\qquad \psi_k = \sum_m e^{ik(ma)}\phi_m$$

$$E_j = \alpha + 2\beta\cos\frac{2\pi j}{N} \qquad\Longrightarrow\qquad E_k = \alpha + 2\beta\cos\frac{2\pi ja}{Na} \quad\longleftarrow \text{multiplied by } a/a$$

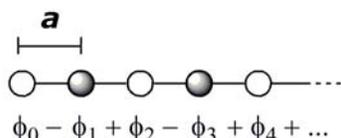$$= \alpha + 2\beta\cos ka$$

$$\text{where } k = \frac{2\pi j}{Na}$$

A few words about k. It is:

- ◆ a measure of the number of nodes
- ◆ an index of wavefunction and accordingly symmetry of wavefunction
- ◆ a "quantum number" for a given ψ_k
- ◆ a measure of length, related to wavelength λ^{-1}
- ◆ from DeBroglie's relation, $\lambda = \dfrac{h}{p}$, therefore k is also a wave vector that measures momentum

Returning to the foregoing discussion, note that k parametrically depends on *a*. Since *a* is a lattice parameter of the unit cell, there are as many k's as there are unit cells in the crystal. In the linear case, the unit cell is the distance between adjacent atoms: there are n atoms ∴ n unit cells or in other terms – there are as many k's as atoms in the 1-D chain.

Let's determine the energy values of limits, k = 0 and $k = \dfrac{\pi}{a}$:

$$at\ k = 0:\ \ \psi_0 = \sum_m e^{i0(ma)}\phi_m = \sum_m \phi_m$$

$$\phi_0 + \phi_1 + \phi_2 + \phi_3 + \phi_4 + \ldots$$

$$at\ k = \frac{\pi}{a}:\ \ \psi_{\frac{\pi}{a}} = \sum_n e^{i\left(\frac{\pi}{a}\right)(ma)}\phi_m = \sum_m e^{im\pi}\phi_m = \sum_m (-1)^m\phi_m$$

$$\phi_0 - \phi_1 + \phi_2 - \phi_3 + \phi_4 + \ldots$$

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The energies for these band structures at the limits of k are:

$$E_0 = \alpha + 2\beta\cos(0)a = \alpha + 2\beta$$

$$E_{\frac{\pi}{a}} = \alpha + 2\beta\cos(\frac{\pi}{a})a = \alpha - 2\beta$$

Note that k is quantized; so there are a finite number of values between $\alpha+2\beta$ and $\alpha-2\beta$ but for a very large number ($\sim 10^{23}$ atoms) between the limits of k. Thus, the energy is a continuous and smoothly varying function between these limits.
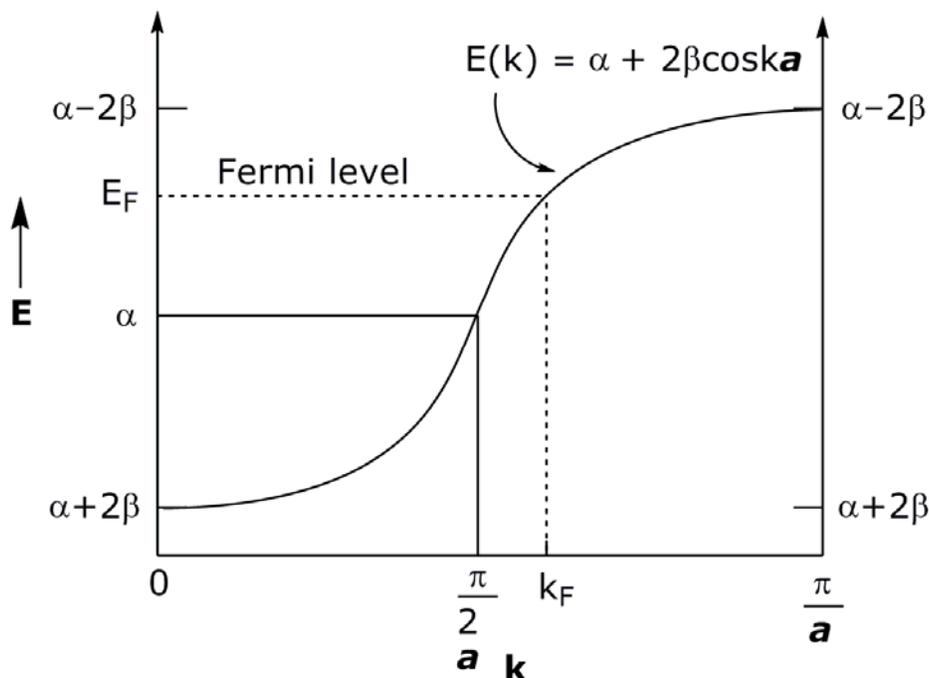

The range $-\frac{\pi}{a} \leq k \leq \frac{\pi}{a}$ or $|k| \leq \frac{\pi}{a}$ is unique because the function repeats itself outside these limits. This unique range of k values is called the **Brillouin** zone. The first Brillouin zone is plotted above from 0 to $\frac{\pi}{a}$ (symmetric reflection from $-\frac{\pi}{a}$ to 0).

With a given number of e⁻s in the solid, the levels will be filled to a certain energy called the **Fermi level**, which corresponds to a certain value of k (= k_F). In the above example, there are more electrons than there are orbitals, so $k_F > \frac{k}{2a}$. If each atomic orbital contributed 1e⁻ to the system, then E_F would occur for $k_F = \frac{\pi}{2a}$.

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The symmetry of the individual atomic orbitals determines much about band structure. Consider p-orbitals overlapping in a linear array (vs the 1s orbitals of the above treatment). Analyzing limiting forms:
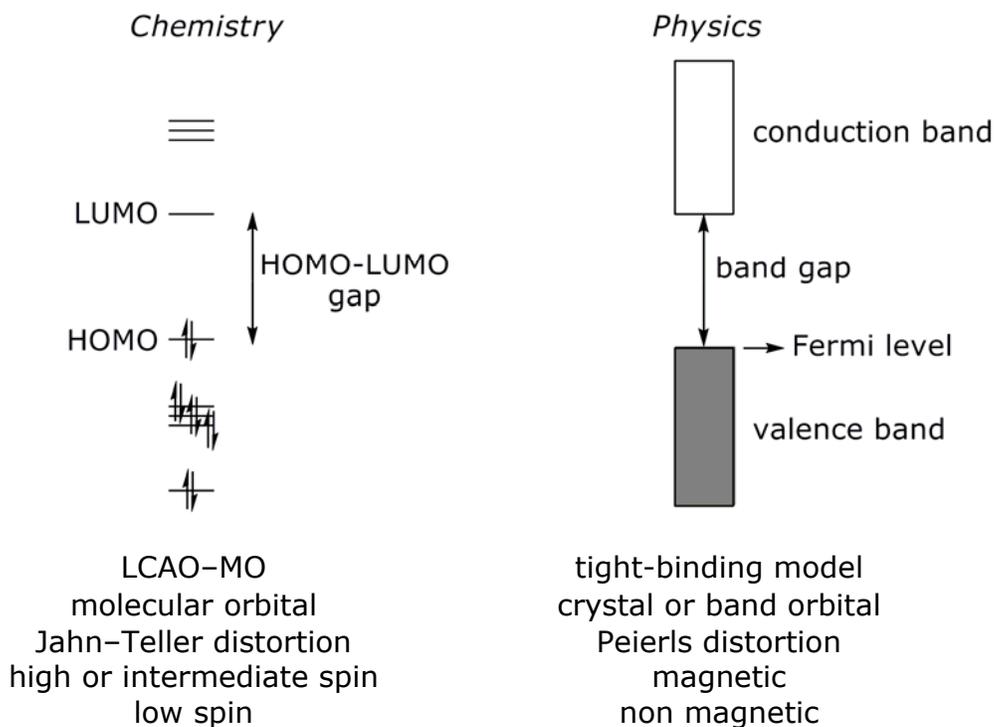
at $k = 0$: $\psi_0 = \phi_1 + \phi_2 + \phi_3 + \phi_4 + ...$

NOTE: This is the highest energy orbital with N nodes

at $k = \dfrac{\pi}{a}$: $\psi_{\frac{\pi}{a}} = \phi_1 - \phi_2 + \phi_3 - \phi_4 + ...$
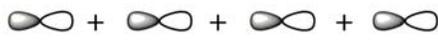
NOTE: Lowest energy orbital with N nodes

$$E(k) = \alpha - 2\beta \cos ka$$
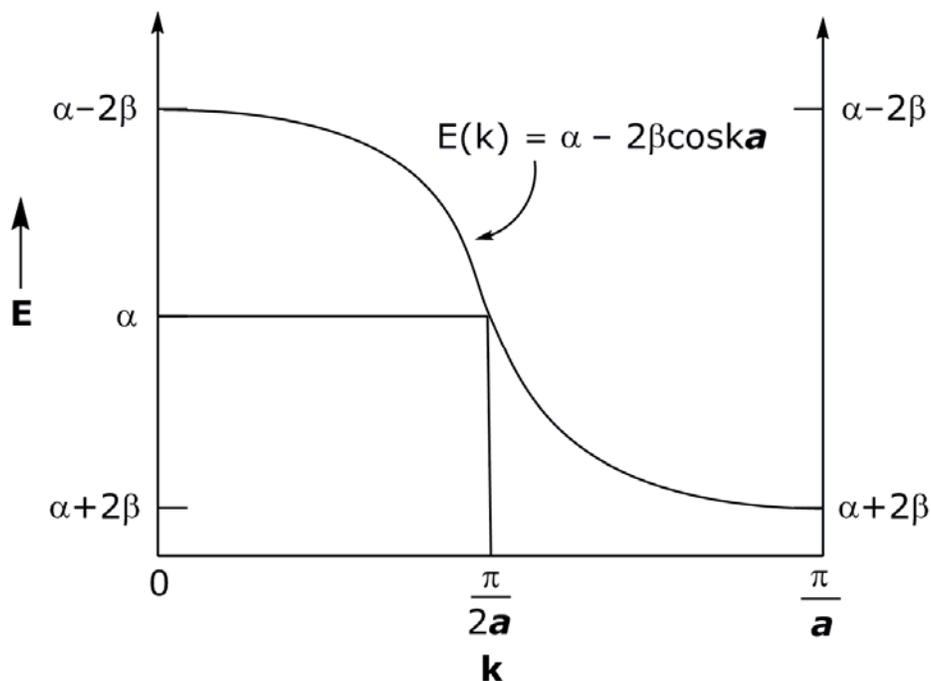
The energy band is opposite of that for the sσ orbital LCAO because the (+) LCAO for a pσ orbital is antibonding.

Thus, molecules are easily related to solids via Hückel theory. Not surprisingly, there is a language of chemistry describing the electronic structure of molecules that is related to the language of physics describing the electronic structure of solids. Below are some of the terms that chemists and physicists use to describe similar phenomena in molecules and solids:

Chemistry	Physics

$\equiv$

LUMO ——

HOMO $\pm$

conduction band

band gap

Fermi level

valence band

LCAO–MO	tight-binding model
molecular orbital	crystal or band orbital
Jahn–Teller distortion	Peierls distortion
high or intermediate spin	magnetic
low spin	non magnetic

Band Width or Dispersion

What determines the width or dispersion of a band? As for the HOMO-LUMO gap in a molecule, the overlap of neighboring orbitals determines the energy dispersion of a band – the greater the overlap, the greater the dispersion. Note how the band dispersion of a linear chain of H atoms varies as the 1s orbitals of the H atoms are spaced 1, 2, 3 Å apart (E of an isolated H atom is −13.6 eV):

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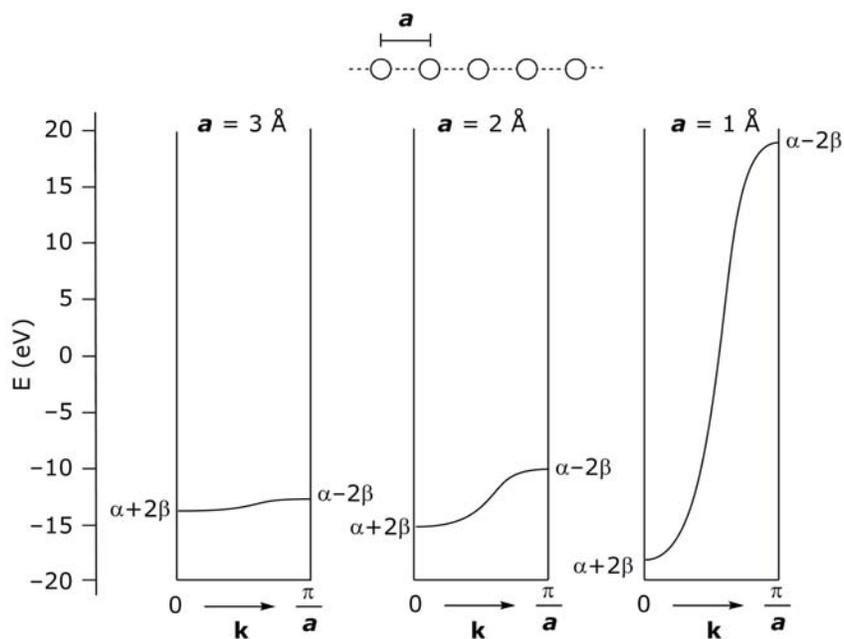
Density of States

The total energy of the system is,

$$E_{total} = \frac{Na}{2\pi} \int_{-k_F}^{k_F} 2E(k)dk = \frac{2Na}{\pi} \int_0^{k_F} E(k)dk$$

normalization constant

or in other words, it is the area under the curve to k_F. Another useful quantity is the number of orbitals between $E(k) + dE(k)$, called the **density of states** (DOS). For a 1-D system,

DOS

$$n(E(k)) \propto \left(\frac{\partial E(k)}{\partial k} \right)^{-1}$$

inversely proportional to slope of E(k) curve at given k. Since slope at $k = 0$ and $k = \pi/a$ approaches 0, $n(E(k))$ is large
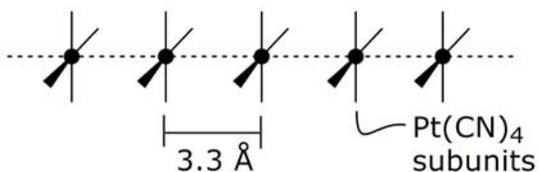
A plot of the above equations is,
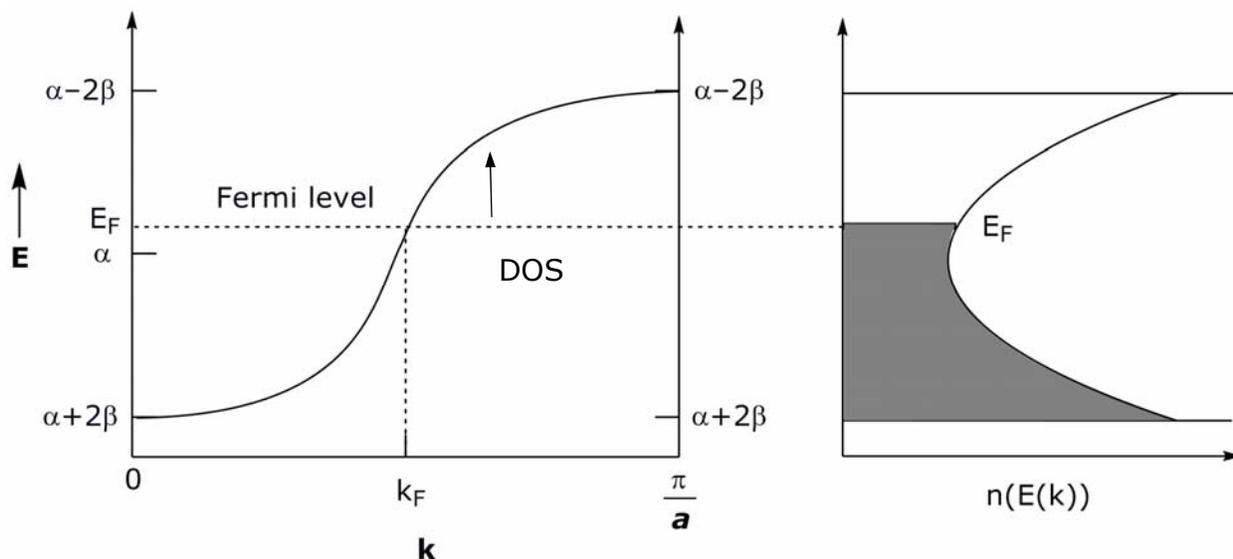
In the above DOS diagram, no energy gap separates the filled and empty bands, i.e. there is a continuous density of states – this property is characteristic of a metal. If an energy gap between filled and empty orbitals is present and it can be thermally surmounted, then it is **semiconductor**; an energy gap that cannot be surmounted is an **insulator**.
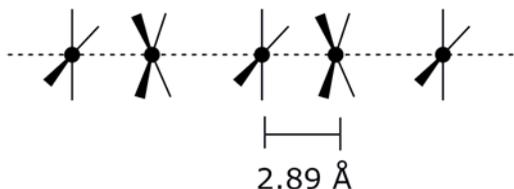
A 1-D Example

Arguably the best known 1-D system in inorganic chemistry is $K_2Pt(CN)_4$ and its partially oxidized compound (e.g. $K_2Pt(CN)_4Br_{0.3}$).

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Normal platinocyanide, $K_2Pt(CN)_4$:
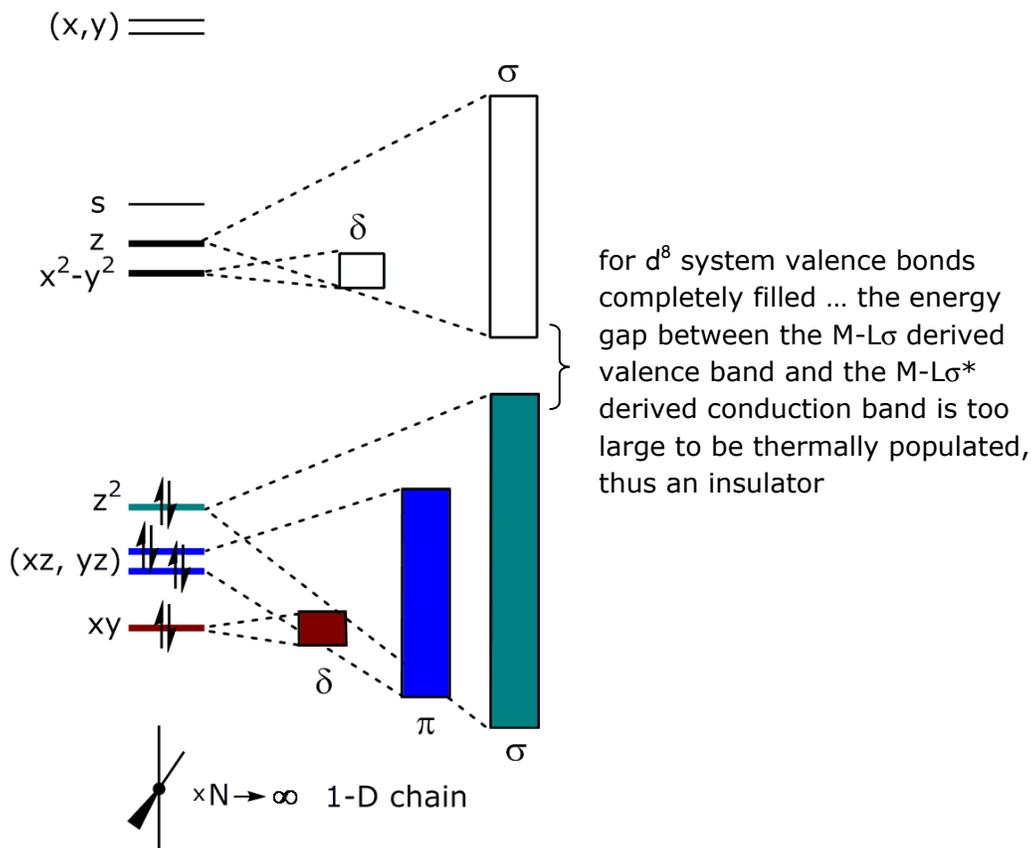
an insulator, pale yellow compound

$Pt(CN)_4$ subunits

3.3 Å

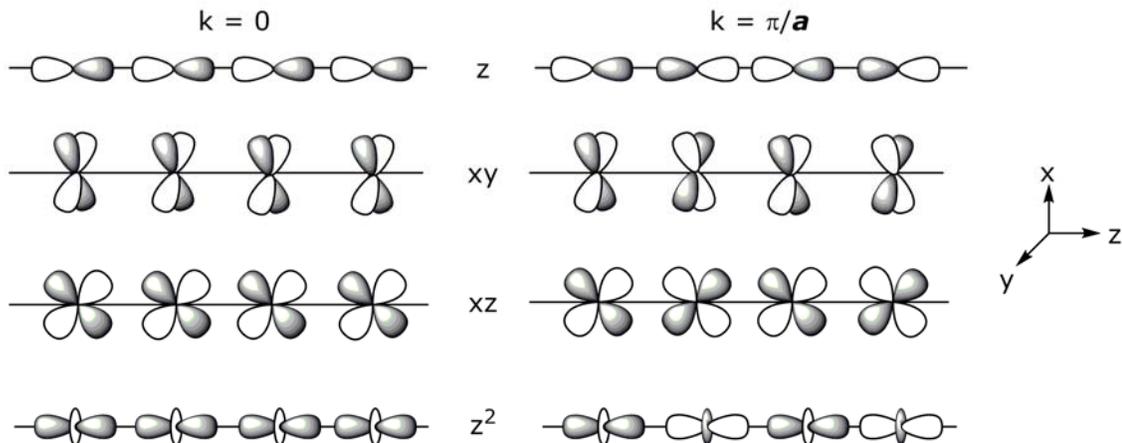Partially oxidized platinocyanide, $K_2Pt(CN)_4Br_{0.3} \bullet 3H_2O$:

along chain: a conductor (500-1000 Ω^{-1} cm^{-1}) a copper-colored with metallic luster

$\perp$ to chain: an insulator (0.05-0.01 Ω^{-1} cm^{-1}), a yellow compound

2.89 Å

Note: $d(Pt-Pt) = 2.78$ Å in Pt metal

To explain these disparate properties of the 1-D compounds, consider the molecular subunit $Pt(CN)_4{}^{2-}$:

(x,y)

σ

s

z

x^2-y^2

δ

for d^8 system valence bonds completely filled … the energy gap between the M-Lσ derived valence band and the M-Lσ* derived conduction band is too large to be thermally populated, thus an insulator

z^2

(xz, yz)

xy

δ

π

σ

$\times N \rightarrow \infty$ 1-D chain

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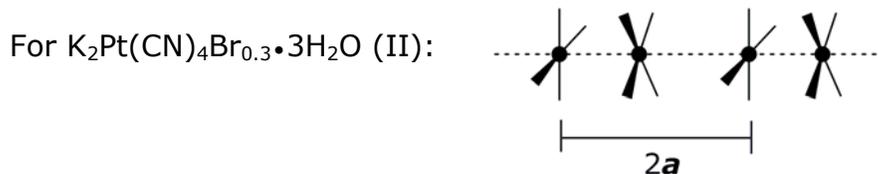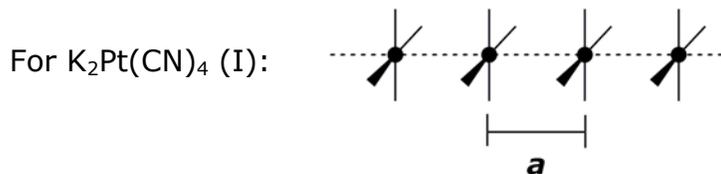The dispersion of the bands is due to the different overlaps of the dσ, dπ and dδ orbitals.

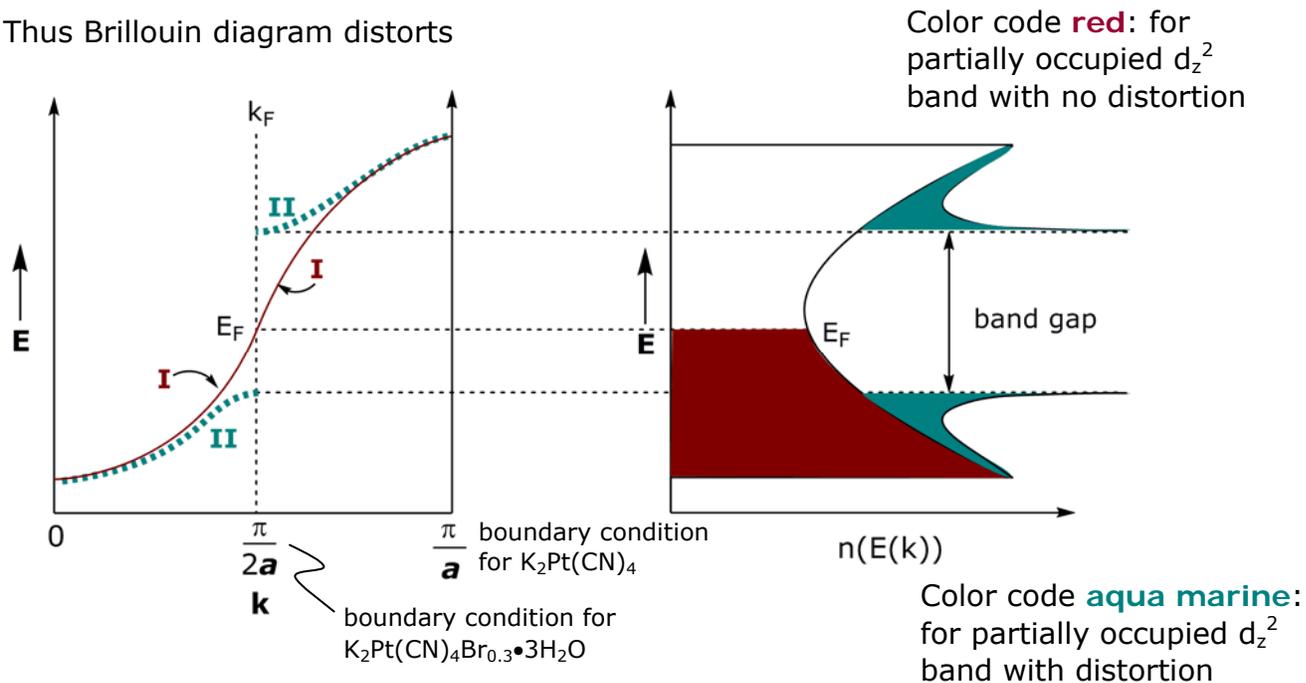Band structure (or first Brillouin zones) derived from the frontier MO's is:
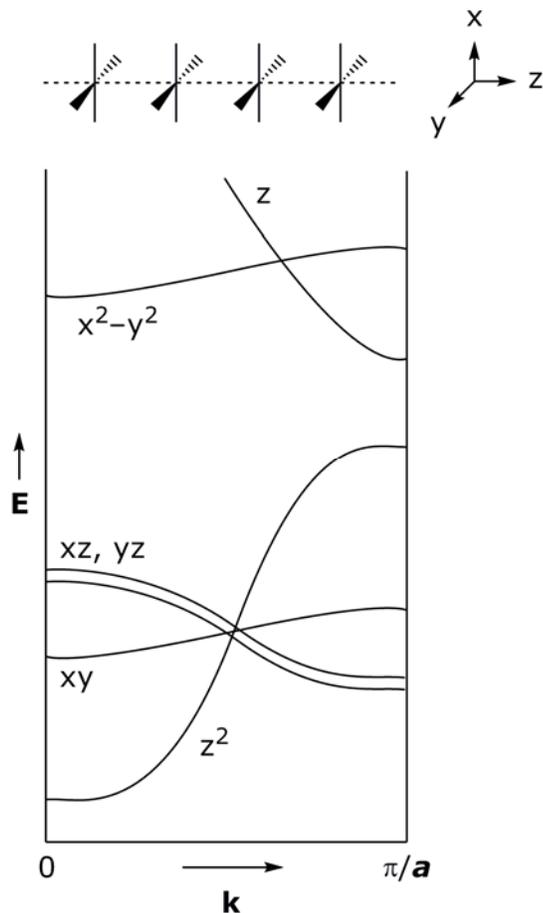
For partially oxidized system, the σ bond derived from d_{z^2} should be partially filled and thus metallic, but it is not, partially oxidized $K_2Pt(CN)_4Br_x$ is a semiconductor. To explain this anomaly, consider how the band structure is perturbed upon partial oxidation:
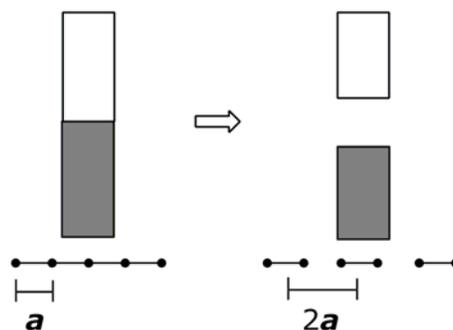
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Isolating on the d_{z^2} band in $K_2Pt(CN)_4$, the Pt atoms are evenly spaced with lattice dimension a (I). Upon oxidation, the Pt chain can distort to give a lattice dimension $2a$ (II). In the case of the $K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$ the distortion is a rotation of Pt subunits and formation of dimers within chain, thus the unit cell dimension is pinned to every other Pt atom.

For $K_2Pt(CN)_4$ (I):

For $K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$ (II):

Thus Brillouin diagram distorts

Color code **red**: for partially occupied d_z^2 band with no distortion

boundary condition for $K_2Pt(CN)_4$

boundary condition for $K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$

Color code **aqua marine**: for partially occupied d_z^2 band with distortion

or pictorially…

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The Brillouin diagram above is for a distorted $K_2Pt(CN)_4$ but filled d_{z^2} orbital. Hence both aqua marine bands are filled and the material that thus possesses the electronic structure shown below is insulating, despite the distortion
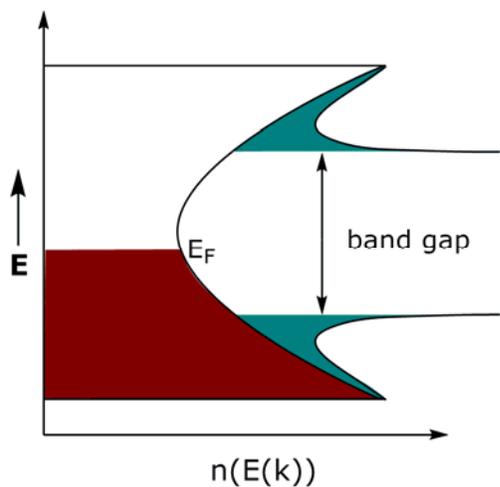
Upon partial oxidation of $K_2Pt(CN)_4$ to produce $K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$, the d_{z^2} band is now partially filled. Hence a conductive material results. The conductivity is along the Pt-Pt axis, explaining the electrical anisotropy of the material

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