Physics of Transition Metal Oxides

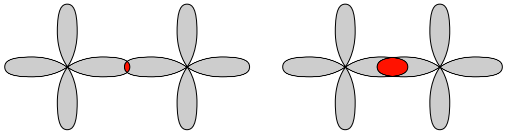
Lecture 3

Conduction electrons in oxides

In the last lecture, we finished with an overview of the tight-binding band description of solids. This model applies to oxides, because we can handle materials where localized states are important.

An important parameter of the tight-binding model is the the overlap integaral

$$t_i = -\int \phi^*(\mathbf{r})(V - V_0)\phi(\mathbf{r} + \mathbf{a}_i)d^3\mathbf{r}$$



Small overlap	Large overlap
Narrow bands	Wide bands
Large effective mass	Small effective mass
Hard to hop to next site	Easy to hop to next site
Low conductivity	High conductivity

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As overlap increases between orbitals at neighboring sites, the bands get wider.

Singleton01, p.35

The tight-binding model gave us a general form for the dispersion relation:

$$E(\mathbf{k}) = E_\phi - B - 2t_x \cos(k_x a) - 2t_y \cos(k_y b) - 2t_z \cos(k_z c),$$

or in one dimension

$$E(k) = E_0 - 2t \cos(ka).$$

Note that a series expansion of the cosine function gives us

$$\cos(ka) \approx 1 - \frac{(ka)^2}{2}.$$

For small ka, we thus have

$$E(k) \approx E_0 - 2t + ta^2k^2,$$

i.e. close to the bottom of a band we have an approximately parabolic behavior.

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Cox92, p67

Let us look again at the RuO_2 band diagram. This time we are more interested what happens at small k, i.e. close to the Γ point.

Comparing free-electron model and tight-binding model:

- both bands are qualitatively similar
- both bands have minima and maxima at the center or edge of the Brillouin zone.
- same k-space periodicity
- tops and bottoms of the bands are approximately parabolic, proportional to $(\mathbf{k}-\mathbf{k}_0)^2$.

Some comments regarding the tight-binding model

The Bloch wavefunction looked like this:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}}\phi(\mathbf{r}-\mathbf{T}),$$

where $\psi(\mathbf{r})$ is an atomic wavefunction. The wavefunctions are indexed with $\mathbf{k}$, but this $\mathbf{k}$ is a *crystal momentum*, not the *electron momentum* $\mathbf{p}=\hbar\mathbf{k}$, because ψ is not an eigenfunction of the momentum operator $\mathbf{p}=(\hbar/i)\nabla$. Looking at a single component in the $\sum_{\mathbf{T}}$

$$\frac{\hbar}{i}\nabla\psi_{\mathbf{k},\mathbf{T}}(\mathbf{r}) = \frac{\hbar}{i}\nabla\left(e^{i\mathbf{k}\cdot\mathbf{r}}\phi_{\mathbf{k}}(\mathbf{r})\right) = \hbar\mathbf{k}\psi_{\mathbf{k},\mathbf{T}} + e^{i\mathbf{k}\cdot\mathbf{r}}\frac{\hbar}{i}\nabla\phi_{\mathbf{k}}(\mathbf{r}) \neq \mathbf{p}\psi_{\mathbf{k},\mathbf{T}}.$$

In optics we have a group velocity of a wavepacket $v = d\omega/dk$. Bloch functions (for a free electron at least) describe an electron as a superposition of plane waves. The concept of a group velocity is therefore applicable to electrons as well

$$\mathbf{v} = \frac{1}{\hbar}\nabla_{\mathbf{k}}E,$$

where $\nabla_{\mathbf{k}} = (\partial E/\partial k_x, \partial E/\partial k_y, \partial E/\partial k_z)$ is a 3-dimensional derivative in $\mathbf{k}$-space.

This brings us to the notion of an effective mass

Take a band electron and apply a force. The force will do work in time δt

$$\delta E = f v\,\delta t$$

In k-space the energy change is

$$\delta E = \frac{\mathrm{d}E}{\mathrm{d}k}\delta k = \hbar v\,\delta k.$$

Putting these together gives us

$$\hbar\frac{\mathrm{d}k}{\mathrm{d}t} = f.$$

In three dimensions this becomes

$$\hbar\frac{\mathrm{d}\mathbf{k}}{\mathrm{d}t} = \mathbf{f},$$

where $\mathbf{k}$ and $\mathbf{f}$ are vectors. It shows that $\hbar\frac{\mathrm{d}\mathbf{k}}{\mathrm{d}t}$ is equal to the external force acting on an electron.

From the last page,

$$\delta E = \frac{\mathrm{d}E}{\mathrm{d}k}\delta k = \hbar v\,\delta k.$$

This allows us to calculate the rate of change of an electron's velocity

$$\frac{\mathrm{d}v}{\mathrm{d}t} = \frac{1}{\hbar}\frac{\mathrm{d}^2E}{\mathrm{d}k\mathrm{d}t} = \frac{1}{\hbar}\frac{\mathrm{d}^2E}{\mathrm{d}k^2}\frac{\mathrm{d}k}{\mathrm{d}t}.$$

Combining this with the force from above,

$$\frac{\mathrm{d}v}{\mathrm{d}t} = \frac{1}{\hbar}\frac{\mathrm{d}^2E}{\mathrm{d}k^2}\frac{f}{\hbar}$$

Rearranging gives us

$$\frac{\hbar^2}{\frac{\mathrm{d}^2E}{\mathrm{d}k^2}} = m^*\frac{\mathrm{d}v}{\mathrm{d}t} = f.$$

$$m^* \frac{\mathrm{d}v}{\mathrm{d}t} = f,$$

where m^* is the *effective mass*, defined by

$$m^* = \frac{\hbar^2}{\frac{\mathrm{d}^2 E}{\mathrm{d}k^2}}.$$

Since we have second derivatives of energy, it is clear that in 3-dimensional space m^* is actually a 3 × 3 tensor. Effective mass allows us to think of an electron in simple mechanical terms of 'force = (mass × acceleration)'.

The effective mass is energy-dependent. If bands are nearly empty or nearly full, we can use a parabolic approximation for the dispersion curve close to a band bottom or top.

$$E(\mathbf{k}) \approx E_0 + \frac{\hbar^2}{2m^*}(\mathbf{k} - \mathbf{k}_0)^2,$$

which reduces a tight-binding description of a band electron to a form that is similar to the free-electron case. The mass m^* can be either positive or negative.

Effective mass conclusions:

- Light electrons form wide bands with a low density of states
- Heavy electrons form narrow bands with a high density of states

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1:Cu($4s^1$) s-electron conduction band,
2:Sc($3d^1$) d-electron conduction band

Singleton01, p.44,48

After a brief theory section, back to oxides:

Heavy electrons in narrow bands can be easily scattered by lattice defects or impurities. Electrons may also get trapped at such places, resulting in a metal-to-insulator transition.

We can also correlate the effective mass with conductivity, borrowing from the free-electron model

$$\sigma = \frac{ne^2\tau}{m^*},$$

where n is the number of free carriers with charge e per unit volume, and τ is the relaxation time, the interval between scattering events.

The Drude model also gives a prediction for the dielectric function

$$\epsilon(\omega) = \epsilon(\infty)\left[1 - \frac{\Omega_p^2}{\omega^2 + i\omega/\tau}\right],$$

where $\epsilon(\infty)$ is the high-frequency dielectric constant related to core electronic polarizability and Ω_p is the plasma frequency

$$\Omega_p^2 = \frac{ne^2}{\epsilon(\infty)\epsilon_0 m^*}.$$

The Fermi level:

Again, we look at the example of RuO$_2$, a metallic material.

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Cox92 p.74

It is often easier to visualize the shape of the Fermi surface as a 3-D plot, rather than the sections that are usually drawn in band diagrams.

Also remember that practically all interesting (at least for materials science) physics goes on in the vicinity of the Fermi level (or surface).

How the energy levels fill up:

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The Fermi level comes, of course, from the Fermi-Dirac statistics

$$f(E) = \frac{1}{\exp[(E-\mu)/k_B T] + 1},$$

where the chemical potential μ is very nearly the Fermi energy,

$$\mu \approx E_F = k_B T_F,$$

and can be expressed as a Fermi temperature, typically around 10^5K.

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If we look (in one dimension) how a free-electron band fills up to the fermi level

$$E_F = \frac{\hbar\, k_F^2}{2m}$$

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The density of states is

$$D(E) = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E} = D(E_F)\sqrt{\frac{E}{E_F}}.$$

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The density of states at the Fermi level is

$$D(E_F) = \frac{3n}{2k_B T_F} = \frac{m\, k_F}{\hbar^2 \pi^2}.$$

In some cases we don't care about the *shape* of the Fermi surface but only about the *density of states* at the Fermi level.

One example is electronic specific heat, defined as a change in internal energy U brought about by a change in temperature

$$C = \left(\frac{dU}{dT}\right)_V.$$

This would be normally measured as the amount of heat needed to change the temperature of a sample by an amount dT

$$dQ = C\, dT.$$

The electronic contribution to specific heat of a material is only important at low temperatures (at high temperatures, lattice vibrations, phonon contribution dominates).

The specific heat has a general (approximate) form $C_{el} = \gamma T$, where the Sommerfeld constant, γ, is

$$\gamma = \frac{\pi^2}{3} k_B^2\, D(E_F),$$

where T is the absolute temperature and k_B is the Boltzmann constant, $D(E_F)$ is the density of states at the Fermi level.

The electronic specific heat thus depends only on the density of states at the Fermi level, not the shape of the Fermi surface.

$$\gamma = \frac{\pi^2}{3} k_B^2\, D(E_F),$$

For a free-electron system, the density of states at the Fermi level was

$$D(E_F) = \frac{3n}{2k_B\, T_F}.$$

We now replace the electron density with N_A In a free-electron case the Sommerfeld factor is

$$\gamma_0 = \frac{\pi^2 R}{2T_F},$$

where $R = N_A k_B$ is the gas constant. In a more general case we would use the effective mass in the density-of-states expression, $D(E_F) = \frac{m^* k_F}{\hbar^2 \pi^2}$. This allows us to write the Sommerfeld constant as

$$\gamma = \frac{m^*}{m}\gamma_0.$$

This shows (again) the importance of the effective mass. In terms of specific heat, this can be seen nicely by comparing the data of 'normal' materials with *heavy fermion* systems, such as $CeCu_2Si_2$ or UBe_{13} or UPt_3.

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Uranium and cerium have a suitable $5f$ or $4f$ configuration to produce a very sharp hybridized band at the Fermi level.

Typical metals have a γ of around 1-7, various oxides are in the range 5-15, heavy fermion systems show 200-500

Another parameter that depends only on the density of states at the Fermi level is the Pauli paramagnetic susceptibility.

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Blundell01 p.143

Each electronic level is occupied by two electrons with opposite spin direction. Putting a system like this in a magnetic field will change the energies of the electrons, depending on their spin directions, creating two subbands, separated by $2\mu_B B$. The number of electrons with spin up (or down) is in unit volume

$$n_\uparrow = \frac{1}{2} D(E_F)\mu_B B,$$
$$n_\downarrow = \frac{1}{2} D(E_F)\mu_B B.$$

This gives a magnetization

$$M = \mu_B(n_\uparrow - n_\downarrow) = D(E_F)\mu_B^2 B.$$

The magnetic susceptibility is

$$\chi_P = \frac{M}{H} \approx \frac{\mu_0 M}{B} = \mu_0 \mu_B^2 D(E_F)$$

For localized spins susceptibility is

$$\chi = \frac{n\mu_0\mu_B}{k_B T}$$

We saw here that some parameters depend only on the density of states (electronic specific heat, Pauli paramagnetism). Others depend on the shape of the Fermi surface. These include conductivity and plasma frequency.

We looked at comparisons of the tight-binding model and the free-electron model. Convenient free-electron equations can often be used if the effective mass of the carriers is modified suitably.

We now continue by looking at how band models cover the gap between localized states and free metallic electrons.

Stoner enhancement

Some materials are ferromagnetic due to *band ferromagnetism*, also known as *itinerant ferromagnetism*.

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Blundell01 p.146

Again, we look at what happens close to the Fermi level, assuming a metallic system. We take electrons with energies from $E_F - \delta E$ to E_F in the spin-down band, and flip their spins, placing them in the spin-up band with energies from E_F to $E_F + \delta E$. The number of electrons moved is $D(E_F)\delta E/2$ and they increase in energy by δE. The total energy change is $D(E_F)\delta E/2 \times \delta E$.

The total kinetic energy change is

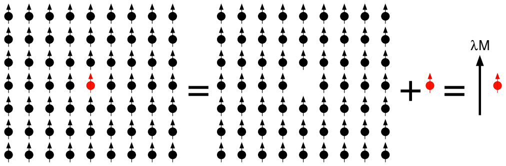
$$\triangle E_{KE} = \frac{1}{2} D(E_F)(\delta E)^2.$$

The process clearly costs energy and shouldn't happen (and normally doesn't).

In rare cases the *total* energy of a crystal could drop, due to molecular field effects, i.e. each electron sees the collective field generated by all the neighbors.

If it does happen, the number of up and down spins are

$$n_\uparrow = \frac{1}{2}(n + D(E_F)\delta E),$$
$$n_\downarrow = \frac{1}{2}(n - D(E_F)\delta E).$$



This gives a magnetization $M = \mu_B(n_\uparrow - n_\downarrow)$, assuming that each electron contributes 1 μ_B. The molecular field energy is

$$\Delta E_{PE} = -\int_0^M \mu_0(\lambda M')\,\mathrm{d}M' = \frac{1}{2}\mu_0\lambda M^2 = -\frac{1}{2}\mu_0\mu_B^2\lambda(n_\uparrow - n_\downarrow)^2$$

If we now write $U = \mu_0\mu_B^2\lambda$,

$$\Delta E_{PE} = -\frac{1}{2}U(D(E_F)\delta E)^2.$$

The total change of energy is

$$\Delta E = \Delta E_{KE} + \Delta E_{PE} = \frac{1}{2}D(E_F)(\delta E)^2[1 - U\,D(E_F)].$$

Spontaneous magnetization is possible if $\Delta E < 0$, which implies that

$$U\,D(E_F) \geq 1,$$

which is the *Stoner criterion*. The U describes exchange between two parallel-spin electrons (to Coulomb interactions). Spontaneous magnetization can occur if Coulomb interactions are strong and the density of states at the Fermi level is high.

Even if the Stoner criterion is not fulfilled and spontaneous magnetization does not occur, susceptibility may still be changed.

The total energy change for a system in an external field can be calculated if we note that an energy shift by δE results in a magnetization of $M = \mu_B(N_\uparrow - N_\downarrow) = 2\mu_B D(E_F)\delta E$,

$$\begin{aligned}\Delta E &= \frac{1}{2}D(E_F)(\delta E)^2(1 - U\,D(E_F)) - M\,B\\ &= \frac{M^2}{2\mu_B^2 D(E_F)}(1 - U\,D(E_F)) - M\,B.\end{aligned}$$

This is minimized when

$$\frac{M}{\mu_B^2 D(E_F)}(1 - U\,D(E_F)) - B = 0.$$

Magnetic susceptibility is thus

$$\chi = \frac{M}{H} \approx \frac{\mu_0 M}{B} = \frac{\mu_0\mu_B^2 D(E_F)}{1 - U\,D(E_F)} = \frac{\chi_P}{1 - U\,D(E_F)}.$$

χ is thus larger than χ_P by a factor $(1 - U\,D(E_F))^{-1}$. This is known as *Stoner enhancement*.

Stoner enhancement is a significant effect in magnetic oxides, because often the d bands are narrow, giving a high density of states $D(E_F)$ at the Fermi level. The overlap between d orbitals can be much larger in $3d$ oxides than between s or p orbitals in other non-transition elements, increasing the value of U.

Band magnetism is found in ferromagnetic elements, such as Fe, Co, and Ni. Also found in oxides, such as CrO_2.

Ferromagnetism is not always the most stable form of magnetic ordering. Various antiferromagnetic configurations are commonly found in oxides, such as MnO, CoO, FeO, Cr_2O_3, α-Fe_2O_3, $LaFeO_3$, $LaCrO_3$, $LaMnO_3$.

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Blundell01 p.97

Band structure and *spin density waves*

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Look again at a basic $3d$ band diagram. Assume a d^1 configuration, i.e. a single electron in the d-band. This would put the Fermi level inside the d-band, resulting in a conductor.

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If we now have a short wavelength spin wave, i.e. antiferromagnetic arrangement on neighboring sites, this would effectively double the unit cell size from a to $2a$.

Remember from earlier discussion: the number of bands equals the number of electronic levels in the unit cell (in a purely atomic view).

The effect is that now the d band will split into two (two sites). The lower band can hold *two* electrons *per pair of metal atoms*. The lower band will thus be completely full, and we have a narrow-gap insulator.

Cox92 p.67,77

Peierls instability

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Singleton01 p.81

The *Peierls theorem* states that true one-dimensional metals can not exist.

In a one-dimensional lattice the system will always distort so that a gap opens at the Fermi level. This saves electronic energy by lowering the energy of electrons close to the Fermi level. In 1D, the electronic energy win is always larger than the elastic energy loss.

Such instability occurs in $NbSe_3$, a platinum chain compound $K_2[Pt(CN)_4]Br_{0.3}3H_2O$, and also in blue molybdenum bronze, $K_{0.3}MoO_3$.

This distortin is a *charge density wave*, very similar to a spin density wave described earlier.

Similar distortions do not have a big effect in 3-dimenisonal systems. Here are two examples of typical Fermi surface shapes:

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Cox92 p.81

Even if there is a periodic spin or charge distortion in the lattice (shown by dashed lines in k-space), only a small number of electrons would be affected. It is not possible to destroy the Fermi surface in all directions. A material would thus remain a metal even if a distortion occurs.

Distortions, such as spin waves can be *commensurate*, i.e. the period of the distortion is an integral multiple of the lattice constant. For a spin wave, this would give an antiferromagnetic configuration of spins

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Blundell01 p.160

Waves can also be *incommensurate*. This happens in Chromium metal, for example. Chromium has a BCC structure. A spin-density wave forms at $T_\mathrm{N} = 310$ K. The wave vector is $\mathbf{q} \approx 0.96(2\pi/a)$, close to a pure antiferromagnet. There is an increase in the electrical resistivity of Chromium just below T_N as the opening energy gaps destroy part of the Fermi surface.

Intermediate models between band theory and ionic or cluster theory: The **Hubbard model:**

In 'pure' band theory repulsion between electrons is handled by assuming the presence of an average effective potential. This works well for conduction electrons in metals.

Oxides often have rather narrow bands and the concentration of conduction electrons can be much lower than metals. *Electron correlations* become much more important.

The idea of Mott and Hubbard models is to ignore electron repulsion unless two electrons are *at the same atom*.

The important parameters are:

- The overlap integrals of the tight-binding model. These determine the electronic bandwidth W.
- Electron repulsion, parametrized by the *Hubbard* U.

We can see what the meanings of these two parameters are by looking at the case of NiO. The valence state of Ni in NiO is $2+$, giving a $3d^8$ electronic configuration. The partly-filled d band would indicate that NiO should be a *conductor*. In fact, NiO is an *insulator* with a gap of 4 eV. The gap arises due to correlations between the d electrons.

In NiO, the Ni sites redistribute electrons

$$\mathrm{Ni}^{2+} + \mathrm{Ni}^{2+} = \mathrm{Ni}^{+} + \mathrm{Ni}^{3+},$$

or in terms of electronic configuration

$$d^8 + d^8 = d^9 + d^7.$$

When analyzing the band structure, we first need to know how far on the energy scale are the d^9 and d^7 electronic configurations. This energy difference is the Hubbard U.

We must also remember that in a solid, the electronic bands have a certain width W. In insulators U is much larger than W.

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The two Hubbard bands would correspond to the $3d^9$ and $3d^7$ configurations. U itself is defined in the atomic limit, i.e. for a free ion in a gas phase! As ions are brought closer to each other, overlap between orbitals increases and we start to see an increase of badwidth.
For large U and small W we get a gap and an insulator.
For small U or large W we can get a conductor.

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The gas phase ionization energies are shown here for creating a d^{n+1}, d^{n-1} pair.
We see a peak close to a half-filled band, because in that case moving an electron away from a d^5 ion to another d^5 ion would require a spin flip, which costs extra energy.

Cox92 p.83,85

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Cox92 p.81

One of the biggest problems is estimating the real magnitude of U in a crystal. As we talked last week, we need to include the Madelung potential, polarization, possibly other corrections. Ionic calculations plus bandwidth estimates appear to give a very traditional band diagram for NiO, with O $2p$ lower in energy than the $3d$ levels.
Remeber the warnings regarding ionic models and quantitative results!

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Hüfner96 p.185

The Hubbard model replaces the complex d orbitals with a single electronic level, split into two subbands as discussed earlier. We can now have a situation where the lower sub-band is full and the upper sub-band is empty, giving a *Mott insulator*, i.e. overlap between neighboring sites is so small that conductivity drops abruptly to zero (*Mott transition*).

This model does not include hybridization effects between the metal and oxygen orbitals. This is very important in oxides!
In fact, in many cases electrons are not removed simply from the d-band of the metal, but mostly from the *oxygen*, i.e. there is significant charge transfer between the metal and the oxygen.
This charge transfer energy is characterized by Δ.

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Hüfner96 p.180

Let's look at a simple case of LiNbO$_3$. Here we have the Nb^{5+} configuration. The electronic levels of Nb are [Kr]$4d^4 5s^1$, i.e. the electronic state of Nb^{5+} is $4d^0$. Ion bombardment creates defects in the lattice, giving rise to Nb^{4+} ions with an electronic state of $4d^1$.
Photoelectron emission spectra show clearly the location of a narrow d-band within 1 eV of E_F and the broader O$2p$ band ≈ 6 eV below the Fermi level.

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Hüfner96 p.195,200

Careful analysis of the NiO photoelectron spectrum shows that the O$2p$ levels and a charge-transfer d^8L^{-1} state are in fact between the 'Hubbard' d^7 and d^9 levels. The gap is thus defined by the empty d^9 state and a charge-transfer d^8L^{-1} level, which shows that NiO is, in fact, a *charge-transfer insulator*, not a *Mott insulator*.

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Rao98 p.296

Insulating oxides are broadly divided into two groups:

- **(a)** Charge-transfer insulators, i.e. the gap is defined by an empty d-state and the oxygen $2p$ band.
- **(b)** Mott-Hubbard insulator, i.e. the gap is defined by split levels within the d-band. Oxygen $2p$ is lower in energy.

The parameters are:

- The on-site Coulomg repulsion $U_{dd} = E(d^{n+1}) + E(d^{n-1}) - 2E(d^n)$
- The charge transfer energy Δ between the ligand (oxygen) $2p$ and metal $3d$ levels. Δ is the energy related to the $d^n \rightarrow d^{n+1}L^1$ transition, where L^1 represents a hole in the ligand levels).

- Zaanen, Sawatzky, Allen compared these energies with the hybridization strength between the metal and the ligand (the transfer integrals from the tight-binding model).

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A: $U_{dd} \gg \Delta$, gap defined by a $d^n p^m \rightarrow d^{n+1}p^{m-1}$ transition. Band gap is defined mostly by Δ.
B: $\Delta \gg U_{dd}$, the lowest energy excitation is from a $d_i^n d_j^n$ state to a $d_i^{n+1} d_j^{n-1}$ state. Band gap defined mostly by U_{dd}.
C: $\Delta > U_{dd}$, but the O $2p$ band overlaps with the lower d-band, giving a half-filled band and metallic conductivity.
D: $\Delta \gg U_{dd}$, but U is very small, comparable to the band width W, The two d-bands overlap, leading to metallic conductivity.

Rao98 p.294

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Rao98 p.296

Another region is called a *covalent insulator*. In this case the upper d-band and the oxygen $2p$ bands overlap and would give a metal. The energy levels are slightly shifted due to the overlap between metal and oxygen orbitals, creating a narrow hybridization gap.

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