Physics of Transition Metal Oxides

Lecture 2

The electronic structure of oxides

What we covered in the last lecture:

1. A chemical approach to oxides, assigning oxidation states

2. Thermodynamic stability

3. Crystal structures

4. A brief classification based on the oxidation state discussion

   (a) d^0 insulators

   (b) Other closed-shell insulators

   (c) d^n impurities

   (d) Magnetic insulators

   (e) etc.

Models of electronic structure:

In order to understand how oxides behave, why some are insulators, other semiconductors, metals or superconductors, we need to have a model for their electronic structure.

No single model covers all cases.

In the previous lecture we looked at assigning oxidation states to individual atoms in a lattice. We saw that this is not always a simple process. The whole idea of having integral charges for each atom is a characteristic of an *ionic model.*

An extension of the ionic model is the *cluster model* which looks at the properties of a small group of atoms around a site.

These models work well for non-metallic crystals.

Metallic oxides:

Metallic systems are usually described using band theory, which looks at wavefunctions of electrons in a periodic lattice. In this model we have some electrons that are (more or less) localized and others that are free to move in the lattice.

Various extensions are also possible to bring the localized ionic models and delocalized band models closer to each other by adding electron-electron interactions, interactions of band electrons with lattice vibrations, influences of defects and lattice disorder, etc. These could be called intermediate models.
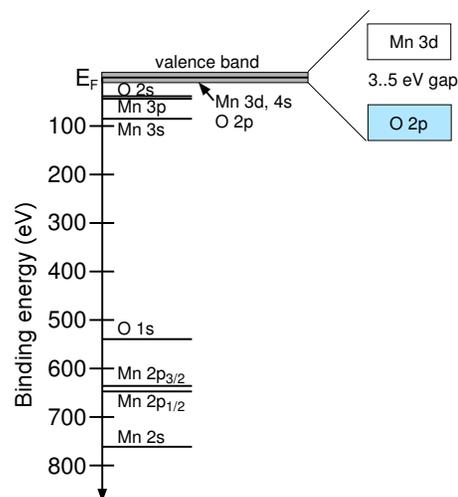
Ionic model:

The ionic model tells us that d^0 elements are special. We can expect them to be insulators with a filled valence band made up of oxygen $2p$ levels (Oxygen 2- has a closed $2p^6$ shell). The conduction band is made of the transition metal d orbitals and is completely empty.

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Crystal field theory:

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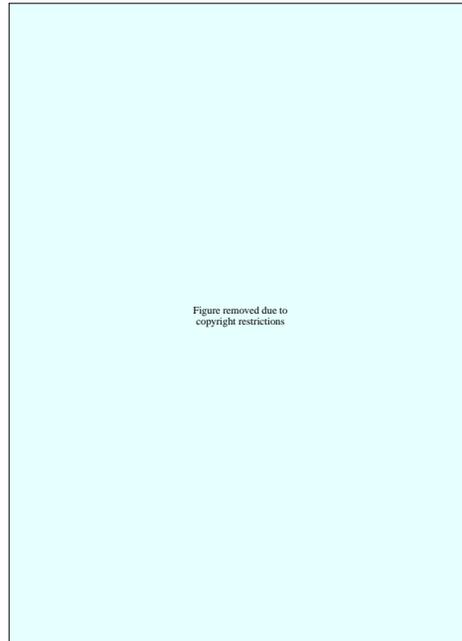
The problem with the ionic model is that ions are not free in a crystal. We always have an electrostatic interaction between an ion and other ions in a lattice. This influence is taken into account by the *crystal field theory*, which regards neighboring ions as negative point charges. A more advanced treatment that replaces point charges with orbitals and handles the overlap of electron clouds id the *ligand field theory*.

Blundell01, p.46

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Coordination types:

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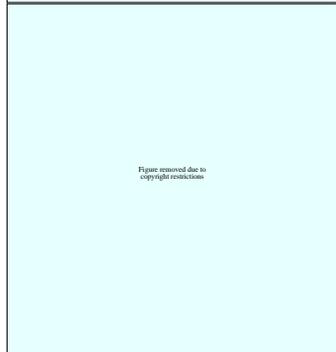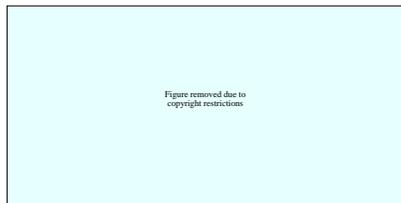
We shall look at octahedral symmetry (typical for a transition metal). The crystal field arises due to the negatively charged electrons at the corners of an octahedron or a tetrahedron.

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Octahedral sites:
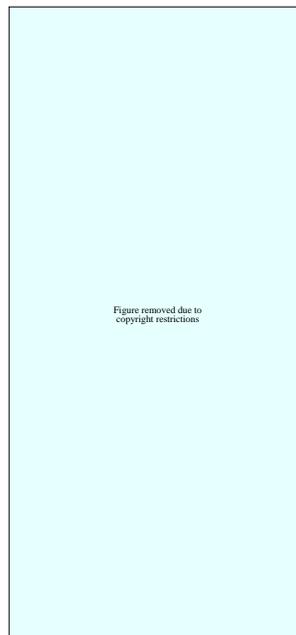
Look how the e_g and t_{2g} orbitals line up with the neighboring oxygens.

The d_{xy} orbital has less overlap with the O2_p orbitals (nodes in the x, y directions) and thus has a lower electrostatic energy than the $d_{x^2-y^2}$ orbital, which has lobes in the xy directions.

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Tetrahedral sites:

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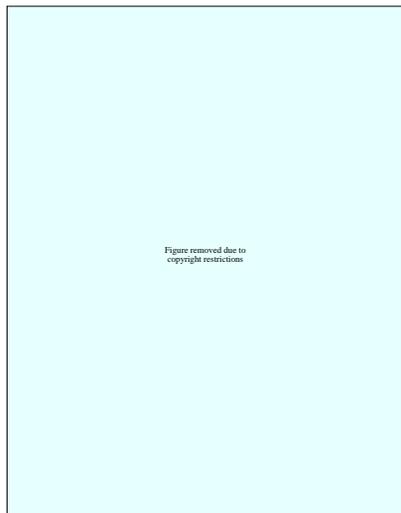
In a tetrahedral symmetry the situation is quite different. The orbitals that point along the x and y axes now avoid the neighboring oxygens and therefore have *lower* energy. This means that the e_g levels are now lower in energy than the t_{2g} levels.

Blundell01, p.47

Filling electronic levels:

Why is all this important?

We have to look at how the levels fill up. This was already briefly discussed last time.

The key here is to follow Hund's rules (these apply only to a ground state and assume that there is only a single incomplete shell):

1. The electronic wavefunction should *maximize* S (the total spin). This reduces Coulomb repulsion between electrons by separating them as much as possible. Remember that two electrons with parallel spins cannot share an orbital.

2. *Maximize* L

3. This rule deals with spin-orbit coupling. This is not always the main contributor (crystal field may be larger). So this is less important for transition metals.

Low spin and high spin:

If all d orbitals were degenerate (as in a free ion), we would always have a *high spin* state. This example for Fe^{2+} shows why crystal field theory is useful in predicting the presence of *low spin* states in some d electron configurations.

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As explained last time, this also explains why we may have insulators with a narrow gap for partly-filled d orbital configurations.

Magnetic moment:

As mentioned above, Hund's third rule, which says that the total angular momentum J is $J = |L - S|$ for less than half-filled shells and $J = L + S$ if a shell is more than half filled.

If crystal-field effects are large, this is not always the case. The magnetic moment is given by

$$\mu_{eff,1} = \mu_B g_J \sqrt{J(J+1)},$$

where g_J is the Landé g factor, given by

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}.$$

We can compare experimental magnetic moments p_{exp} and the calculated value $p_1 = \mu_{eff,1}/\mu_B$. As shown in the following table the real values are closer to

$$\mu_{eff,2} = 2\mu_B \sqrt{S(S+1)},$$

i.e. L=0, always, and $J = S$, $g_J = 2$. The table shows $p_2 = \mu_{eff,2}/\mu_B$ values.

ion	shell	HS	LS	S	L	J	term	p_1	p_{exp}	p_2
Ti^{3+}, V^{4+}	$3d^1$	t_{2g}^1	-	$\frac{1}{2}$	2	$\frac{3}{2}$	$^2D_{3/2}$	1.55	1.70	1.73
V^{3+}	$3d^2$	t_{2g}^2	-	1	3	2	$^3F_2$	1.63	2.61	2.83
Cr^{3+}, V^{2+}	$3d^3$	t_{2g}^3	-	$\frac{3}{2}$	3	$\frac{3}{2}$	$^4F_{3/2}$	0.77	3.85	3.87
Mn^{3+}, Cr^{2+}	$3d^4$	$t_{2g}^3 e_g^1$	t_{2g}^4	2	2	0	$^5D_0$	0	4.82	4.90
Fe^{3+}, Mn^{2+}	$3d^5$	$t_{2g}^3 e_g^2$	t_{2g}^5	$\frac{5}{2}$	0	$\frac{5}{2}$	$^6S_{5/2}$	5.92	5.82	5.92
Fe^{2+}	$3d^6$	$t_{2g}^4 e_g^2$	t_{2g}^6	2	2	4	$^5D_4$	6.70	5.36	4.90
Co^{2+}	$3d^7$	$t_{2g}^5 e_g^2$	$t_{2g}^6 e_g^1$	$\frac{3}{2}$	3	$\frac{9}{2}$	$^4F_{9/2}$	6.63	4.90	3.87
Ni^{2+}	$3d^8$	$t_{2g}^6 e_g^2$	-	1	3	4	$^3F_4$	5.59	3.12	2.83
Cu^{2+}	$3d^9$	$t_{2g}^6 e_g^3$	-	$\frac{1}{2}$	2	$\frac{5}{2}$	$^2D_{5/2}$	3.55	1.83	1.73
Zn^{2+}	$3d^{10}$	$t_{2g}^6 e_g^4$	-	0	0	0	$^1S_0$	0	0	0

Blundell01, p.49

The experimental magnetic moment p_{exp} is often closer to p_2 than to p_1. This shows that in a number of cases the crystal field splitting is more important than spin-orbit coupling. This effect is known as *orbital quenching*

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Jahn-Teller distortions:

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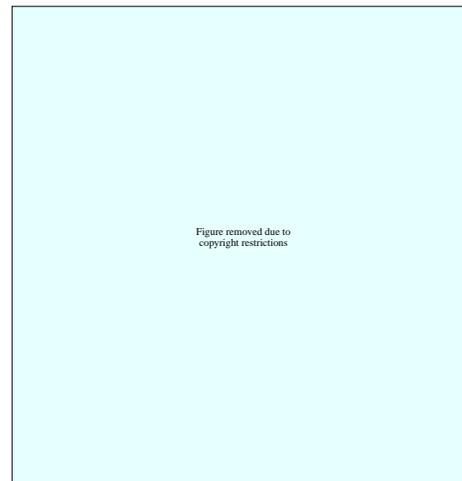
Blundell01, p.50

The *Jahn-Teller theorem* says that a non-linear molecule in an electronic state with orbital degeneracy will distort so as to remove this degeneracy.

This works because the added elastic energy is compensated by the reduced electronic energy. For example, Mn^{3+} does this due to the $3d^4$ configuration. It would not reduce the total energy of a Mn^{4+} ion ($3d^3$ configuration).

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Jahn-Teller distortions:

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Assume that the lattice distortion is quantified by Q. The distortion along a normal mode direction would be

$$E(Q) = \frac{1}{2}M\omega^2 Q^2,$$

where M is the mass of the ion and ω is the normal mode frequency. The elastic energy is at minimum at $Q = 0$ (no distortion). The orbital energy does not change if an orbital is empty or completely filled.

Calculating the orbital energy shift is complicated, but the distortion is always small, and we can use a Taylor series expansion of orbital energy vs. Q. As a rough approximation we only keep the linear term from the Taylor series, AQ or $-AQ$, corresponding to raising or lowering of a level.

This allows us to write the sum of electronic and elastic energy as

$$E(Q) = \pm AQ + \frac{1}{2}M\omega^2 Q^2.$$

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Jahn-Teller distortions:

$$E(Q) = \pm AQ + \frac{1}{2}M\omega^2 Q^2.$$

The minimum is at a point where the derivative of E is zero, i.e. $\partial E/\partial Q = 0$. This gives

$$Q_0 = \frac{A}{M\omega^2}$$

and a minimum energy

$$E_{min} = -A^2/2M\omega^2,$$

which is negative. If only this specific orbital is filled, the system can make a net energy saving by distorting. The strongest effect is usually seen in d^4 and d^9 configurations due to the partial filling of the e_g orbitals.

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Jahn-Teller distortions:

Interestingly this effect is not seen in low-spin d^7 configurations, such as Ni^{3+} in $LaNiO_3$. This material is metallic. Jahn-Teller distortion is characteristic of localized electrons and is not found in metallic lattices.

The Jahn-Teller distortions mostly involve e_g electrons. The effect of t_{2g} electrons is much weaker, showing that e_g electrons are normally much more important from the point of view of bonding with neighbors.

Jahn-Teller distortions can be *static* or *dynamic*. In the dynamic case the direction of the distortion can flip from one axis to another. Distortion can also hop from site to site. This can happen in materials that have a mixture of valence states, e.g. a mixture of Mn^{3+} and Mn^{4+}.

In some materials, such as $DyVO_3$, the Jahn-Teller distortion can be *cooperative*.

Charge transfer:

The crystal field discussion only applies to a single crystal site, i.e. we calculate the energies of electrons within a single atom. as a function of local bonding interactions.

Another important effect is *charge transfer*, i.e. excitations of electrons from one atom to another. We approach the charge transfer type description starting from the ionic picture presented earlier.

A simple example would be MgO. In the ionic picture, the highest energy filled orbital is the oxygen $2p$. The experimental band gap is 7.5 eV. The first empty level is magnesium $3s$.

The Madelung constant

This figure shows the components that need to be calculated to estimate the band gap of a material such as MgO.
First of all, a free O^{2-} ion does not exist. We need to put the ions into a crystal where they are subject to long-range electrostatic potentials. The *Madelung potential* is usually given as

$$V(0) = -\alpha_M \frac{e^2}{R},$$

where α_M is the *Madelung constant* for a particular lattice, $\pm e$ are the point charges in a lattice, and R is the nearest neighbor distance.

Cox92, p.48

It is clear that the Madelung constant is of major importance. Calculating it is not trivial due to the long range of electrostatic interactions.

The Madelung constant

For a simple ionic case, consider NaCl with Cl^- at origin:

Number and type of ions	representative position	distance from origin
$6Na^+$	R(1,0,0)	$R\sqrt{1}$
$12Cl^-$	R(1,1,0)	$R\sqrt{2}$
$8Na^+$	R(1,1,1)	$R\sqrt{3}$
$6Cl^-$	R(2,0,0)	$R\sqrt{4}$
$24Na^+$	R(2,1,0)	$R\sqrt{5}$
$24Cl^-$	R(2,1,1)	$R\sqrt{6}$
$12Cl^-$	R(2,2,0)	$R\sqrt{8}$
$24Na^+$	R(2,2,1)	$R\sqrt{9}$
$6Na^+$	R(3,0,0)	$R\sqrt{9}$
$24Cl^-$	R(3,1,0)	$R\sqrt{10}$
$24Na^+$	R(3,1,1)	$R\sqrt{11}$
$8Cl^-$	R(2,2,2)	$R\sqrt{12}$

This gives a series

$$V(0) = -\frac{e^2}{R}\left[\frac{6}{\sqrt{1}} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \frac{24}{\sqrt{5}} - \frac{24}{\sqrt{6}} - \frac{12}{\sqrt{8}} + \cdots\right]$$

$$= -\frac{e^2}{R}[6.000 - 8.486 + 4.619 - 3.000 + 10.733 - 9.798 - 4.243 + \cdots].$$

The Madelung constant

This series converges very slowly to a finite value of $\alpha_M = 1.7476$ for NaCl.

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After considering the Madelung potential, we at least have the correct sign for the band gap, but it is much too large.

The next step is to consider polarization of the ions. This can be done using a *shell model* where a light electronic shell is connected to a heavy core with a spring constant. This brings dielectric constants, elastic constants, and vibrational data to the model. The details are not important here. In general the polarization effects reduce the binding energy of electrons in filled levels, i.e. the filled oxygen levels rise and the empty levels fall.

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Orbital overlap

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Finally, we have the broadening of atomic energy levels due to overlap between neighboring ions.
This broadening cannot be calculated based on the ionic model. The values are either derived from experiments or band-structure calculations.

This discussion shows the difficulty of calculating band gaps using the ionic model. MgO is a relatively good example. In case of TiO_2, for example, we have O^{2-} and Ti^{4+}. The larger charges mean that the final band gap of 3eV has to be obtained by subtracting terms that are 50 eV or larger. Ionic models can thus give only qualitative estimates.

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Impurity levels:

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One area where the ionic model does give useful numbers is the analysis of defects or impurities in oxides. The figure shows the energy levels of various impurities in sapphire Al_2O_3.
As a rule, ionization energies increase with atomic number. A jump between Mn and Fe is caused by the start of electron pairing beyond the d^5 configuration.

The ionic model is also useful for estimating the effects of polarization. Polarization happens on two scales:

- *purely electronic*. This is a fast process and determines the dielectric properties at optical frequencies.

- *atomic*. Much slower. Determines the static dielectric constant.

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Cluster model:

Cluster models attempt to obtain better accuracy than ionic models without doing a full band-structure calculation. The idea is to consider interactions between a metal atom and ligands (mostly oxygens). This is achieved by doing a molecular orbital calculation on a small cluster.

Molecular orbital calculation is another *independent electron* model. Electrons move in a potential field and inter-electron repulsion is handled in some average way. A popular technique is called *linear combination of atomic orbital* (LCAO) approximation. The basis is formed by atomic orbitals $\{\phi\}$. The molecular orbital has a form:

$$\Psi = \sum_i c_i \phi_i,$$

where coefficients c_i and the *orbital energy* are found by solving

$$\mathcal{H}c = \epsilon \mathcal{S}c.$$

$\mathcal{H}$ is the Hamiltonian and $\mathcal{S}$ describes the overlap of atomic orbitals.

If there are N atomic orbitals, there will also be N molecular orbitals. Many of them have equal energies, i.e. levels may be degenerate if the cluster has high symmetry.

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Cox92, p.55

This is a molecular orbital diagram of an octahedral metal cluster MO_6^{n-}.

Especially interesting are the levels with t_{2g} or e_g symmetry. The e_g set is a σ-type orbital with lobes pointing along the metal-oxygen bond. The t_{2g} set is π-type, with orbitals perpendicular to the M-O direction.

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Configuration interaction models:

Try to avoid calculating molecular orbitals. Instead, construct wavefunctions by mixing different configurations of atomic orbitals. For NiO, for example, the first approximation is $\Psi(d^8)$. Interaction between Ni and O is included by adding configurations $\Psi(d^9\underline{L})$ and $\Psi(d^{10}\underline{L}^2)$, where $\underline{L}$ represents a hole in the ligand (oxygen) orbitals. Overlap interactions between a metal and oxygens is done by combining many-electron states, rather than orbitals, as in MO theory. The NiO ground state would then be

$$\Psi_0 = \alpha\Psi(d^8) + \beta\Psi(d^9\underline{L}) + \gamma\Psi(d^{10}\underline{L}^2).$$

Cox92, p.62

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Configuration interaction model:

Finding the energies and mixing coefficients α, β, γ, etc. is done in a similar way as in MO calculation. Unknown parameters are the overlap integrals S_{mn}, unperturbed energies H_{nn} and the off-diagonal Hamiltonian elements H_{mn}. The overlap integrals may be omitted, off-diagonal elements taken from band-structure calculations, and diagonal elements fitted to experimental data.

The main advantage is that excited states are also calculated and it is easier to analyze photoemission spectra. In general, CI technique is more useful for interpreting spectroscopic data. electron repulsion and polarization effects can be included by using experimental values for unperturbed energies.

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Band theory:

Band theory looks at free electrons in a periodic lattice.

- Works well for simple metals like alkalies.

- Not applicable to transition metals because d electrons can not be described as free electrons.

The solution is to use a tight binding model where localization is also considered. This is achieved by building the periodic wavefunctions in the lattice from individual localized atomic wavefunctions.

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The wavefunction

We start with the atomic wavefunctions $\phi_j(\mathbf{r})$, defined by

$$\mathcal{H}_{\text{at}}\phi_j(\mathbf{r}) = E_j\phi_j(\mathbf{r}),$$

where $\mathcal{H}_{\text{at}}$ is the Hamiltonian of a single atom.

There are several assumptions:

- close to each lattice point, the crystal Hamiltonian $\mathcal{H}$ can be approximated by $\mathcal{H}_{\text{at}}$

- the bound states are well localized, which means that if r is larger than the lattice constant, $\phi_j(\mathbf{r})$ should be very small

- $\phi_j(\mathbf{r})$ is a good approximation to a stationary state of a crystal, as is $\phi_j(\mathbf{r}+\mathbf{T})$, where $\mathbf{T}$ has the symmetry of the crystal.

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The Bloch functions

We can now build Bloch functions $\psi_{j,\mathbf{k}}$ of electrons in the crystal from linear combinations of the atomic wavefunctions

$$\psi_{j,\mathbf{k}} = \sum_{\mathbf{T}} a_{\mathbf{k},\mathbf{T}}\phi_j(\mathbf{r}+\mathbf{T}),$$

Where the sum over $\mathbf{T}$ runs over an infinite crystal. The possible values of $\mathbf{k}$, however, are limited to the Brillouin zone.

This function satisfies the requirements for a Bloch function, i.e.

$$\psi(\mathbf{r}+\mathbf{T}) = e^{i\mathbf{k}\cdot\mathbf{T}}\psi(\mathbf{r})$$

as we can see here

$$
\begin{aligned}
\psi(\mathbf{r}+\mathbf{T}) &= \sum_{\mathbf{T}'} e^{i\mathbf{k}\cdot\mathbf{T}'}\phi_j(\mathbf{r}+\mathbf{T}-\mathbf{T}') \\
&= e^{i\mathbf{k}\cdot\mathbf{T}}\left[\sum_{\mathbf{T}'} e^{i\mathbf{k}\cdot(\mathbf{T}'-\mathbf{T})}\phi_j(\mathbf{r}-(\mathbf{T}'-\mathbf{T}))\right] \\
&= e^{i\mathbf{k}\cdot\mathbf{T}}\left[\sum_{\overline{\mathbf{T}}} s^{i\mathbf{k}\cdot\overline{\mathbf{T}}}\phi_j(\mathbf{r}-\overline{\mathbf{T}})\right] \\
&= e^{i\mathbf{k}\cdot\mathbf{T}}\psi(\mathbf{r}).
\end{aligned}
$$

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We now have Bloch functions with a wave vector $\mathbf{k}$ that still display the atomic character of the levels.

The problem with this function is that the 'band' energies would simply be the *atomic energy levels*, E_n, regardless of the value of $\mathbf{k}$.

Here we have to make the first approximations:
We have to recognize that $\psi_j(\mathbf{r})$ is not exactly zero as we move away from an atom (although it should be small).

We retain the basic form of the wavefunction and write it as

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

Note the change from ϕ_j to ϕ. The significance is that ϕ is not necessarily an *exact* atomic stationary-state wave function. Instead, it is a linear combination of (a small number) of atomic wave functions

$$\phi(\mathbf{r}) = \sum_n b_n\phi_n(\mathbf{r}).$$

A complete set of atomic levels should also include the ionized levels. We discard them here. That is the first major deviation from the free-electron model.

Due to the way that the crystal wavefunction is constructed, this method is also known as *linear combination of atomic orbitals*, or LCAO.

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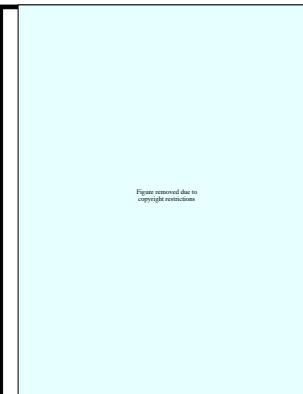
We look at a simple example with atoms arranged along Cartesian unit vectors: $\mathbf{a}_1 = a\mathbf{e}_1, \mathbf{a}_2 = b\mathbf{e}_2, \mathbf{a}_3 = c\mathbf{e}_3$.
The potentials involved in this calculation are:
- The actual crystal potential $V(\mathbf{r})$
- The potential associated with an isolated atom, $V_0(\mathbf{r})$

The crystal Hamiltonian is thus

$$\mathcal{H} = \mathcal{H}_{\text{at}} + \{V(\mathbf{r}) - V_0(\mathbf{r})\},$$

with $\mathcal{H}\psi_{\mathbf{k}}(\mathbf{r}) = E(\mathbf{k})\psi_{\mathbf{k}}(\mathbf{r})$.

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We now operate with this Hamiltonian on our Bloch functions

$$\mathcal{H}_{\text{at}} \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}} \phi(\mathbf{r}-\mathbf{T}) + \{V(\mathbf{r}) - V_0(\mathbf{R})\} \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}} \phi(\mathbf{r}-\mathbf{T}) = E(\mathbf{k}) \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}} \phi(\mathbf{r}-\mathbf{T}).$$

We wish to calculate $E(\mathbf{k})$. We therefore multiply by $\phi^*(\mathbf{r})$ from the left and integrate over all $\mathbf{r}$:

$$\int \phi^*(\mathbf{r}) \mathcal{H}_{\text{at}} \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}} \phi(\mathbf{r}-\mathbf{T}) d^3\mathbf{r} +$$

$$\int \phi^*(\mathbf{r}) \{V(\mathbf{r}) - V_0(\mathbf{r})\} \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}} \phi(\mathbf{r}-\mathbf{T}) d^3\mathbf{r}$$

$$= \int \phi^*(\mathbf{r}) E(\mathbf{k}) \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}} \phi(\mathbf{r}-\mathbf{T}) d^3\mathbf{r}$$

We now need to remember that our wavefunctions form an orthonormal basis,

$$\int \psi_m^*(\mathbf{r}) \psi_n(\mathbf{r}) d\mathbf{r} = \delta_{mn}$$

Using this, we can see that the first term gives E_ϕ; the integral with $\mathbf{T} = 0$ is far grater than all others due to the short range of $\phi(\mathbf{r})$. The third term gives $E(\mathbf{k})$ for the same reasons.

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The band structure is derived from the second term

$$\int \phi^*(\mathbf{r}) \{V(\mathbf{r}) - V_0(\mathbf{r})\} \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}} \phi(\mathbf{r}-\mathbf{T}) d^3\mathbf{r}$$

The value of this integral is nonzero only when $\mathbf{T} = 0$ (on-site) or close to the reference site, i.e. for our simple model $\mathbf{T} = \pm a\mathbf{e}_1, \pm b\mathbf{e}_2, \pm c\mathbf{e}_3$. We can now split the integral into four parts:

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

$$(e^{ik_x a} + e^{-ik_x a}) \int \phi^*(\mathbf{r})(V - V_0)\phi(\mathbf{r}+\mathbf{a}_1) d^3\mathbf{r} +$$

$$(e^{ik_y b} + e^{-ik_y b}) \int \phi^*(\mathbf{r})(V - V_0)\phi(\mathbf{r}+\mathbf{a}_2) d^3\mathbf{r} +$$

$$(e^{ik_z c} + e^{-ik_z c}) \int \phi^*(\mathbf{r})(V - V_0)\phi(\mathbf{r}+\mathbf{a}_3) d^3\mathbf{r}$$

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Or, written in a more concise way

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

with

$$B = -\int \phi^*(\mathbf{r})(V - V_0)\phi(\mathbf{r}) d^3\mathbf{r}$$

$$t_x = -\int \phi^*(\mathbf{r})(V - V_0)\phi(\mathbf{r}+\mathbf{a}_1) d^3\mathbf{r}$$

$$t_y = -\int \phi^*(\mathbf{r})(V - V_0)\phi(\mathbf{r}+\mathbf{a}_2) d^3\mathbf{r}$$

$$t_z = -\int \phi^*(\mathbf{r})(V - V_0)\phi(\mathbf{r}+\mathbf{a}_3) d^3\mathbf{r}$$

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The parameters t_x, t_y, and t_z are *transfer integrals*. These integrals shows how easy it is for an electron to hop from one lattice site to another one.

- The original N atoms with j doubly degenerate energy levels have become j $2N$-fold degenerate bands.

- The transfer integrals give a direct measure of the width of a band. Carriers close to the bottom of a band have an effective mass which is inversely proportional to the band width. Small transfer integrals mean that the bands are narrow, effective masses high, i.e. carriers are localized.

- The shape of the bands in k-space depends on the real-space crystal structure. If atomic distances are larger in one direction, then the bandwidth is narrower for carrier movement in that direction.

- The bands also carry the original atomic signatures.

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The energies of the bands can also be discussed from the point of view of chemical bonds between atoms. A bond would correspond to a particular linear combination of atomic orbitals with a specific symmetry.

Bonds can be

- *non-bonding*, i.e. there is no energy change related to a particular orbital configuration
- *bonding*, i.e. the energy of the combined orbital is lower, electron density at midpoint between two ions is lower
- *antibonding*, i.e. the combined orbit has higher energy, or larger electron density.

The effect of bonding/antibonding orbitals can be seen, for example in the case of Ge (and various binaries).

Cox92, p.65

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The energy shifts of bonding or antibonding orbitals also depends on the **k** (direction and velocity of a carrier). This can be seen in a band-structure diagram or *dispersion* curve. This figure applies to the one-dimensional lattice shown earlier.

In three dimensions we usually look at certain high-symmetry directions in the crystal and plot the band dispersions in a diagram labeled with high symmetry point labels. This example is for rutile-type RuO_2, calculated with the augmented plane wave method. Each unit cell contains two formula units. We thus have 10 bands of Ru $4d$ character and 12 O $2p$ levels.

Cox92, p.67

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It is often useful to plot the total *density of states*, which is obtained from the band diagram by integrating over **k**. The value in the plot is actually $N(E)dE$, i.e. the number of states per unit volume (or cell) in an energy interval E to $E + dE$.

The Ru d band is partially filled, which is why the Fermi level is within the d band (RuO_2 is metallic).

The lower plots show *partial densities of states*, contribution to the total DOS by oxygen $2p$ orbitals and ruthenium $4d$ levels.

The Ru levels can also be separated into t_{2g} and e_g levels, showing that the signature of atomic orbitals is still visible.

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The band structure can be directly measured by photoelectron spectroscopy. For comparison, we see the RuO_2 DOS and corresponding UPS and XPS spectra. For UPS, the light source is 21 eV and ionization cross-sections for O $2p$ and Ru $4d$ orbitals are similar. In XPS the Ru $4d$ electrons are much more easily ionized and the d spectrum dominates.

Cox92, p.71

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