From Materials to Models: Deriving Insight from Bands

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One-electron theory
Periodic system of the elements
Earthly matter is made of atoms, and atoms are (almost) round. The electronic structure of an atom can therefore be constructed from \textbf{atomic orbitals}:

$$
\varphi_i(\varepsilon_{nl}, r) Y_{lm}(\hat{\mathbf{r}}) \chi_\sigma(s),
$$

which are the solutions of Schrödinger’s equation for one electron in the spherically symmetric, selfconsistent potential, \(v(r)\), from the attractive protons in the nucleus and the repulsive other electrons in the atomic shells. \(\chi_\sigma(s)\) are the spin functions which are the eigenfunctions of \(\hat{s}_z\), \(Y_{lm}(\hat{\mathbf{r}})\) are the spherical Harmonics which are eigenfunctions of \(\hat{l}^2\) and \(\hat{l}_z\), and the radial functions satisfy the \textbf{radial Schrödinger equation}:

$$
-\left[ r \varphi_i(\varepsilon_{nl}, r) \right]'' = [\varepsilon_{nl} - v_i(r)] r \varphi_i(\varepsilon_{nl}, r),
$$

with \(v_i(r) = v(r) + l(l + 1)/r^2\).

The solutions are numbered in order of increasing one-electron \textbf{energy}, \(\varepsilon_{nl}\), by the \textbf{principal quantum number}, \(n\), which takes the values \(l + 1, l + 2, \ldots\), because with this convention, the energy levels for a Coulomb potential, \(-\frac{2Z}{r}\), are independent of \(l\) and given by Bohr’s 1913-formula (before quantum mechanics):

$$
\varepsilon_{nl} = -\left(\frac{Z}{n}\right)^2
$$

The radial functions decay at large distances as \(\exp(-\frac{Z}{n}r)\) and the \textbf{number of nodes} in the radial function is \(n - l - 1\).
For a neutral atom with \( Z \) protons in the nucleus and \( Z \) electrons in the shells, the effective charge, \( Z_{\text{eff}}(r) = -rv(r)/2 \), decreases from \( Z \) towards 1 as \( r \) increases from 0 to \( \infty \) due to the screening by the other electrons. As a consequence, the \( 2(2l+1) \)-degeneracy of the attractive Coulomb potential is lifted and the perturbation by the repulsive centrifugal potential, \( l(l+1)/r^2 \), will cause the one-electron energies for the same \( n \) to increase with \( l \):

\[
\varepsilon_{ns} < \varepsilon_{np} < \varepsilon_{nd} < \ldots
\]

Whereas the order of the \( s \)- and \( p \)-energies is always such that:

\[
\varepsilon_{ns} < \varepsilon_{np} < \varepsilon_{(n+1)s},
\]

the order of the \( d \)-energies is such that:

\[
\varepsilon_{(n+1)s} < \varepsilon_{nd} \quad \text{if the } nd\text{-shell is empty}
\]

\[
\varepsilon_{np} < \varepsilon_{nd} < \varepsilon_{(n+1)s} \quad \text{if the } nd\text{-shell is full}.
\]

Analogously, for the \( f \)-energies. If we now occupy the orbitals, of which there are \( 2(2l+1) \) per \( nl \)-subshell, with \( Z \) electrons in order of increasing energy, we recover the \textbf{Periodic Table}:
One step to the right adds one positively charged proton (and a neutron) to the nucleus and this attracts one more negatively charged electron to the atomic shell.

The letters s, p, d, ... signify electrons having orbital angular momentum 0, 1, 2, ... in units \( \hbar \); the number to the left of the letter denotes the principal quantum number of one orbit, and the superscript to the right denotes the number of electrons in the orbit.

### Periodic Table, with the Outer Electron Configurations of Neutral Atoms in Their Ground States

The notation used to describe the electronic configuration of atoms and ions is discussed in all textbooks of introductory atomic physics. The letters s, p, d, ... signify electrons having orbital angular momentum 0, 1, 2, ... in units \( \hbar \); the number to the left of the letter denotes the principal quantum number of one orbit, and the superscript to the right denotes the number of electrons in the orbit.

- **Z** atomic number
- **n** number of protons in the nucleus
- **nl** configuration of outer shells in the ground state of the neutral atom

<table>
<thead>
<tr>
<th>Periodic Table, with the Outer Electron Configurations of Neutral Atoms in Their Ground States</th>
<th>( Z )</th>
<th>( n )</th>
<th>( nl^x )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(^3)</td>
<td>Be(^4)</td>
<td>Sc(^{21})</td>
<td>Ti(^{22})</td>
</tr>
<tr>
<td>Na(^{11})</td>
<td>Mg(^{12})</td>
<td>Al(^{13})</td>
<td>Si(^{14})</td>
</tr>
<tr>
<td>K(^{19})</td>
<td>Ca(^{20})</td>
<td>Sc(^{21})</td>
<td>Ti(^{22})</td>
</tr>
<tr>
<td>Rb(^{37})</td>
<td>Sr(^{38})</td>
<td>Y(^{39})</td>
<td>Zr(^{40})</td>
</tr>
<tr>
<td>Cs(^{55})</td>
<td>Ba(^{56})</td>
<td>La(^{57})</td>
<td>Hf(^{72})</td>
</tr>
<tr>
<td>Fr(^{87})</td>
<td>Ra(^{88})</td>
<td>Ac(^{89})</td>
<td>Ce(^{58})</td>
</tr>
<tr>
<td>Th(^{90})</td>
<td>Pa(^{91})</td>
<td>U(^{92})</td>
<td>Np(^{93})</td>
</tr>
</tbody>
</table>
As $Z$ increases $v(r) = -\frac{2Z_{\text{eff}}(r)}{r}$ deepens and counteracts $\frac{l(l+1)}{r^2}$ such that bound states occur if $Z \geq 5$ (B), 21 (Sc), and 58 (Ce), for $l=1, 2,$ and 3, respectively. This leads to the insertion of the $p$-, $d$-, and $f$-series, whereby the length of the period (number of one-electron states in the $n$-shell) becomes $2(l_{\text{max}} + 1)^2$.

With increasing $l$, the radial potential-well becomes more narrow and with it, the region where $\varepsilon_{nl} > v_l(r)$, i.e. which is classically-allowed. This increased localization of the orbitals with higher $l$ leads to their decreased chemical activity and, hence, the very similar chemical properties of the rare earths and actinides which are exclusively associated with their outer $s$-, $p$-, and possibly $d$-electrons.

When, in the process of filling the $nl$-subshell, we move from one element to the next, the added $nl$-electron will partly screen out the added proton. Specifically, the increase of $Z_{\text{eff}}(r)$ is 1 for $r$ in the region near the nucleus which is classically forbidden [$v_l(r) > \varepsilon_{nl}$] for an $nl$-electron, trails off in the classically-allowed region, and vanishes outside. Hence, $\varepsilon_{nl}$ will fall a bit, and $\varphi_l(\varepsilon_{nl})$ will contract.

When the filling of the $nl$-subshell is completed and we start to fill into the next, $n'l'$-subshell, the increase of $Z_{\text{eff}}(r)$ by unity does not start to trail off before $r$ reaches the region allowed for an $n'l'$-electron. If $n' \geq n$, this is outside the region of an $nl$-electron and $\varepsilon_{nl}$ will therefore drop sharply and $\varphi_l(\varepsilon_{nl})$ contract rapidly, the $nl$-shell thereby start to become part of the core.
One-electron energies (schematic)

Cs metal:
Cs Cs Cs Cs Cs Cs
Cs Cs Cs
Cs Cs Cs
Cs Cs Cs
Cs Cs Cs
Cs Cs Cs

V transition metal:
V V V V V V V V V
V V V V V
V V V V V
V V V V V

V2O3 transition metal oxide:
V3+O2−V3+
O2−V3+O2−

covalent-ionic

closely packed metallic bond

Rocksalt:
NaCl = Na+Cl−
an ionic solid

In the solid the orbitals (atomic wavefunctions) overlap, and this causes the levels to broaden into bands:

Diamond or graphite: CC covalently bonded solid, hybridization gap.

Cs 6s1 Cs 6s1

Cl 3s2 3p5

V 3d3 4s2 V 3d3 4s2

Na 3s1

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Cl 3s2 3p5

V 3d3 4s2 V 3d3 4s2
Many-electron wavefunctions and energies of atoms: The configurations given in the Periodic Table specify the occupations of the open $nl$-subshells. Due to the $2(2l+1)$-fold $m$- and $\sigma$-degeneracy of such a shell, several Slater determinants corresponding to the various possible occupancies of $m$ and $\sigma$ may be formed for this configuration. Since the Hamiltonian is invariant to all rotations, the proper linear combinations of Slater determinants are those which correspond to definite values of $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$, and $\hat{S}_z$, and the energy of such an $L$-$S$ term, designated $^{2S+1}L$, is independent of $M_L$ and $M_S$. The terms differ in energy by intra-atomic Coulomb energies, i.e. eVs. The $(2L+1)(2S+1)$-fold degeneracy of a term will be lifted by the SO coupling, in the presence of which $L$, $S$, $J$, and $M_J$, rather than $L$, $S$, $M_L$, and $M_S$, are good quantum numbers. Here $J$ is the quantum number for the length of $\hat{J} \equiv \hat{L} + \hat{S}$. An atomic level is thus designated by the symbol $^{2S+1}L_{2J+1}$, and the levels of a given term form its multiplet structure.

For a given configuration the state of the lowest total energy usually follows from the three Hund rules: First, choose the maximum value of $S$ consistent with the Pauli principle, then the maximum value of $L$, and finally the minimum value, $|L - S|$, of $J$ if the shell is less than half full, and the maximum value, $|L + S|$, of $J$ if the shell is more than half full.
From atoms to solids
Elemental metals
Close-packed elemental solids
Matching-method of Wigner and Seitz (1934)

Approximating the WS-cells with WS spheres and neglecting \( l,l' \) hybridization leads to the WS rules for elemental, cp solids:
Elastic scattering from a single atom:

\[ \lambda = \frac{2\pi}{\kappa} = \frac{2\pi}{\sqrt{E}} \]

\[ \varphi_l(\varepsilon, r) = j_{lm}(\kappa r) - \tan \eta_l(\varepsilon) n_l(\kappa r) \]

\[ \chi_l(\varepsilon, r) = \begin{cases} \cot \eta_l(\varepsilon) [\varphi_l(\varepsilon, r) - j_{lm}(\kappa r)] & \text{for } r < s \\ -n_l(\kappa r) & \text{for } s < r \end{cases} \]
Tail cancellation has much better $l$-convergence than matching at WS-cell boundary.
Atomic Spheres Approximation (1973): $\kappa \equiv 0$

\[ \sum_{RL} \left[ S_{R' L', RL} - \delta_{R' L', RL} \cot \eta_{RL}(\varepsilon) \right] v_{RL} = 0 \]
The bare structure matrix is given by:
\[ S_{l'm'} = (-)^{l+m+1} \frac{1}{2} \frac{(2l + 1)(2l' + 1)}{(l + m)! (l - m)! (l' + m)! (l' - m)!} \left( \frac{w}{d} \right)^{l+l'+1} \]

when the \( z \)-axis is turned from the first to the second orbital, and \( d \) is the distance. This simple expression yields bare canonical hopping integrals such as
\[ S_{dd}(\sigma, \pi, \delta) = (-6, 4, -1) \times 10^5 \left( \frac{w}{d} \right)^5, \]
which are useful for rough estimates, in particular for \( p, d, \) and \( f \) orbitals. To turn the \( z \)-axis in an arbitrary direction, the Slater-Koster scheme may be used. For the hopping integrals involving \( d \) orbitals, the canonical values were used in W.A. Harrison's Periodic Table, which however for the \( s \) and \( p \) orbitals used free-electron-like scaling, \( S \propto d^{-2} \).

The structure matrix is independent of the energy, the potential, and the scale of the lattice.

\[ \sum_L [S_{L'L}(k) - \delta_{LL'} \cot \eta_L (\varepsilon)] v_L = 0 \]
For elemental, closely-packed crystals, the \( l=l' \) diagonal blocks of the Bloch-summed structure constants may be diagonalized to form canonical bands.
Screening $\Rightarrow$ Ab initio TB-LMTO-ASA (1984):

$$n_{RL'}^{\alpha}(r - R') \equiv \sum_{RL} n_L(r - R) \left[ \delta_{RL,RL'} + \tan \alpha_l S_{RL,RL'}^{\alpha} \right]$$

$$j_l^{\alpha}(r) \equiv j_l(r) - \tan \alpha_l n_l(r)$$

$$(S^{\alpha})^{-1}_{RL,RL'} = (S^{-1})_{RL,RL'} - \delta_{RL,RL'} \tan \alpha_l,$$

$$\tan \eta_l^{\alpha}(\varepsilon) \equiv \tan \eta_l(\varepsilon) - \tan \alpha_l$$

$$\sum_{RL} \left[ S_{RL',RL}^{\alpha} - \delta_{RL',RL} \cot \eta_{RL}^{\alpha}(\varepsilon) \right] v_{RL} = 0$$

$a$: hard-sphere radius
$\alpha$: hard-sphere phase shift

Superposition of Neumann fcts to form screened Neumann fcts

screened Bessel fct

screened structure matrix
$\eta$: phase shift
$\eta^\alpha$: phase shift in hard-sphere medium

Tail-cancellation condition

This localization enables treatment of disorder, Wannier orbitals,…
Linear muffin-tin orbital (LMTO)

\[ \chi_{RL}(r_R) = \phi_{RL}(r_R) + \sum_{R'L'} \phi_{R'L'}(r_{R'}) \left( H_{R'L',RL} - \varepsilon_{\nu} \delta_{R'R} \delta_{L'L} \right) \]

\[ H_{R'l'm',Rlm}(k) = \sqrt{\Delta_{R'l'}} S_{R'l'm',Rlm}(k) \sqrt{\Delta_{Rl'}} + C_{R'l'l'm'} \delta_{R'R} \delta_{l'l} \delta_{m'm} \]
Screened canonical bands

\[ H = C + \sqrt{\Delta} S (1-\gamma S)^{-1} \sqrt{\Delta} \]

\[ S_{ss\sigma} = -2 \left( \frac{s}{R} \right), \quad S_{sp\sigma} = 2 \sqrt{3} \left( \frac{s}{R} \right)^2, \ldots \]

Hybridization between s, p, and d screened canonical bands

The screened canonical s-, p- and d-bands for the b.o.c. structure.

Fig. 13. – Unhybridized energy bands corresponding to the screening given by \( Q_s = 0.435, Q_p = 0.0907 \) and \( Q_d = 0.0025 \) (a) and hybridized energy bands (b) of b.o.c. vanadium.
Positions of band edges of the elemental metals
The cohesive properties (at $T=0$) can be computed from the (DFT) total-energy. But this provides little insight, because it is expressed in terms of largely cancelling quantities: the selfconsistently calculated Coulomb energies of the electron-electron and proton-proton repulsions, and of the electron-proton attraction, plus the kinetic energy of the electrons. However, the cohesive properties only involve total-energy differences and these are given to first order by the difference of the one-electron energies calculated for frozen one-electron potentials (i.e. the difference of kinetic energies avoids double counting of e-e interactions), plus the difference of Madelung energies. This so-called force theorem was originally proved within the LDA but with appropriate definitions it holds in general, but only to 1st order.
TYPES OF VIRTUAL DISPLACEMENTS:

Freeze the self-consistent sphere potentials $U_A^e(r)$ and $U_B^e(r) \rightarrow$ move them to structure II and insert in $E[\text{m}^3]$

$\Delta \varepsilon = \Delta \sum_{k} \varepsilon_k^e$ = change in sum of one electron energies

$+ \sum_{R \neq R'} \sum_{q_{R' \rightarrow R}} \left[ \nabla^2 - 1 \right] q_{R' \rightarrow R} \text{ change of itadecay energy for fixed charge transfer}$

$+ \sum_{R \neq R'} \sum_{q_{R' \rightarrow R}} \left[ \Delta \eta_R (q) u_R (1 - q^{1/2}) \Delta q_R (q) \right] \text{ self-interaction of } \Delta q_R (q)$

Mo(BCC-FCC) = $-35.4 + 0 + 0.63 = -35.4(\text{ mJ})$

Mo(FCC-BCC) = $+35.49 + 0 + 0.65 = 36.14(\text{ mJ})$
Itinerant magnetism in transition metals
The generalization of DFT to a spin-DFT was a first step in "helping" the density functional through symmetry breaking, to treat exchange and correlation more accurately than in the LDA, which merely uses the xc-energy density, $\epsilon_{xc}(\rho)$, calculated for the homogeneous electron gas as a function of its density. In its local approximation (LSD), spin-DFT uses $\epsilon_{xc}(\rho_\uparrow, \rho_\downarrow)$ for a homogeneous electron gas subject to a homogeneous magnetic field which creates a density and a spin density:

$$\rho = \rho_\uparrow + \rho_\downarrow \quad \text{and} \quad m = \rho_\uparrow - \rho_\downarrow.$$ 

The corresponding xc-potential is diagonal in spin and equals

$$\frac{\partial [\rho \epsilon_{xc}(\rho_\uparrow, \rho_\downarrow)]}{\partial \rho_\sigma} = \mu_{xc,\sigma}(\rho_\uparrow, \rho_\downarrow).$$

Expansion around the non spin-polarized values, $\rho_\uparrow = \rho_\downarrow = \rho/2$, i.e. in powers of $m$, yields:

$$\epsilon_{xc}(\rho_\uparrow, \rho_\downarrow) = \epsilon_{xc}(\rho) + \epsilon''_{xc}(\rho)m^2/4 + o(m^3),$$

and, hence, for the exchange-correlation potential:

$$\mu_{xc,\uparrow}(\rho, m) = \mu_{xc}(\rho) \pm m \rho \epsilon''_{xc}(\rho)/2 + o(m).$$

Here, $\mu_{xc}$ and $\epsilon''_{xc}(\rho)$ are both negative, so that increasing $m = \rho_\uparrow - \rho_\downarrow$ lowers the potential seen by a $\uparrow$-electron and rises it for a $\downarrow$-electron, i.e. exchange tends to align the spins. This leads to Hund’s 1st rule for degenerate levels (an open shell) in atoms and since the Pauli principle prevents multiple occupation, level-separation works against spin-polarization.
For a para- or ferromagnet (without SO coupling) in the presence of a uniform magnetic field, which provides the Zeeman splitting $\pm \mu_B H$, the band-structure problem decouples into separate Schrödinger equations, one for each direction of spin. By filling the states to a common Fermi level and solving selfconsistently, the zero-temperature spin-magnetizations, $m = \langle m(r) \rangle$, the uniform susceptibilities, $\frac{dm}{dH}$, and magnetic contributions to the cohesive properties may be computed. This was done in the mid-70ies using the ASA and the results were interpreted in terms of Stoner theory with the exchange constant, $I$, obtained from the Stoner equation: $C_{d\downarrow} - C_{d\uparrow} = mI + 2\mu_B H$, using the computed magnetization and splitting of the centers of the $d$-bands. Gunnarsson used the spin-splitting of the xc-potential to order $m$ and treated it by 1st-order perturbation theory on top of the paramagnetic bands. Hence, the band-splitting is:

$$\varepsilon_{f\downarrow}(k) - \varepsilon_{f\uparrow}(k) = \langle \psi_{jk}(r) | -\rho(r)\varepsilon_{xc}(\rho(r))m(r) | \psi_{jk}(r) \rangle + 2\mu_B H \approx mI + 2\mu_B H.$$ 

In the last approximation, the $j|k$-dependence of $I$ was neglected. Janak evaluated $I$ from essentially the same expression with the expectation value taken as the average over the paramagnetic Fermi surface as is appropriate when subsequently filling the exchange-split bands to a common Fermi level in order to get, first, the magnetization and, then, the splitting, $m/N(\varepsilon_F)$, by dividing $m$ by the paramagnetic DOS per spin. Equating this splitting with the approximation yields Stoner's expression for the exchange-enhanced spin-susceptibility:

$$\chi \equiv \mu_B m/H = 2\mu_B^2 N(\varepsilon_F)[1 - IN(\varepsilon_F)]^{-1}.$$
The values of $I$ obtained for Fe, Ni, Rh, Ir, Pd, and Pt from LSD ASA calculations of $C_{d\downarrow} - C_{d\uparrow}$ and from the approximation agree within a few percent. The dominating trend that $I$ decreases with increasing $Z$ and, hence, with increasing $\rho_s$ is due to $\varepsilon_{xc}$ being dominated by $\varepsilon_x \propto \rho^{1/3}$, so that the kernel is behaves like $-\rho\varepsilon''_x \propto \rho^{-2/3} \propto r_s^2$, which decreases with $\rho$. For understanding that in a given series, $I$ rises again until it drops sharply at the noble metals, one uses the ASA and expands $\psi_{jk}(r)$ on the FS in partial waves. Since only partial waves with the same $l$ contribute:

$$I \sim s \int_0^1 \left[ \frac{r_s(r)}{r} \right]^2 \left[ \alpha(r\varphi_{sp}(\varepsilon_F, r))^2 + (1 - \alpha)(r\varphi_d(\varepsilon_F, r))^2 \right]^2 d(r/s).$$

This form with $\alpha=0$ is the one discussed by Gunnarsson for the transition metals. He showed that the factor $\left[ \frac{r_s(r)}{r} \right]^2$, apart from its general decrease with $Z$, for $Z$ given and $r$ increasing, increases outside the last core $np$-shell, i.e. for $r \gtrsim 0.3s$, and peaks for $r \sim 0.8s$. This peaking is the combined result of the general increase of $r_s(r)$ with $r$ and the filling of the $nd$-shell, whose charge-density peaks for $r \lesssim 0.5s$. One factor $(r\varphi_d(\varepsilon_F, r))^2$ comes from $|\psi_{jk}(r)|^2$ and the other from $m(r)/m$. The product, $(r\varphi_d(\varepsilon_F, r))^4$, is very strongly peaked at a value $r \lesssim 0.5s$, which moves towards the edge of the core $np$-shell as the Fermi level moves towards the top, $A_d$, of the $d$-band where $(r\varphi_d(A_d, r))^4$ vanishes smoothly for $r$ approaching $s$. 

![Graph showing the relationship between $I$ and $r$ for different bands](image)
Slater-Pauling curve

FeCo bcc

NiCu

NiFe fcc + CoNi

NiFe bcc

FeCr

BCC

FCC

N(m) ≡ m / Δ = 1 / I

1 / I

m / 2

m / 2

E_F

Δ = m I

E

N(E)

b.c.c. Fe

1 / I

N(m)

m

m_{max}

m_0

\bar{N}(m)

-15

-10

-5

0

5

10

0.0

0.2

0.4

0.6

0.8

1.0

1.2

1.4

0.0

0.2

0.4

0.6

0.8

1.0

1.2

1.4

n_d

BCC

FCC

e_g

t_{2g}

n_d

N_{states per atom}

N_{states per atom}
The image depicts a Slater-Pauling curve with a graph on the right showing the relationship between the number of d-electrons and the number of Bohr magnetons per atom. The curve is labeled with various points and materials, including FeCo bcc, NiCu, NiFe fcc, and CoNi. The left side of the image contains a diagram illustrating the energy levels and the relationship between the number of electrons and the energy levels. The equation $N(m) \equiv m / \Delta = 1 / I$ is also shown. The graph on the right includes data points for different materials and their respective positions on the curve. The vertical axis represents the Bohr magnetons per atom, and the horizontal axis represents the number of d-electrons.
Compression

Canonical bands:

\[ H_{\ell'\ell''m',Rlm}(k) = \sqrt{\Delta_{R'\ell'} S_{R'\ell''m',Rlm}(k)} \sqrt{\Delta_{Rl}} + C_{R'\ell'} \delta_{R'R} \delta_{\ell'\ell} \delta_{m'm}. \]

\[ \Delta_d \propto s^{-5} \]

For \( N(m) \) on canonical (structure-constant) scale:

\[ N(m) \equiv \frac{m}{\Delta} = \frac{\Delta_d}{l} \propto s^{-5}/l \]
On exhibit at the entrance to the mineralogical museum in Copenhagen is a 20 tons iron-nickel meteorite found in Greenland. It consists of a bcc and an fcc phase with a common orientation throughout the entire meteorite, which therefore seems to have been a single crystal in the mother asteroid. The fcc phase (taenite) has been found to be an simple, ordered FeNi alloy consisting of alternating (100) layers of Fe and Ni, which disorders by heating to 750 K for 50 hours. This demonstrates that the meteorite has not — since its formation in the the parent planet— been reheated to a temperature above 730 K for longer than 50 hours. Attempting to get "insight" to the properties of the Earth’s inner core, we (1978) performed an LSD calculation for taenite. Most remarkable: The FM magnetization stays robustly above $2 \mu_B$ for pressures up to 5 Mbar (causing a 15% compression of $s$). Using, instead, the rigid-band picture and $\bar{N}(7.7, m)$, $m$ would drop significantly already at a 20% reduction of $\Delta_d/I$, i.e. at a mere 4% reduction of $s$. So apparently, taenite is special. We were fascinated by the thought that the earth’s core could be a ferromagnet, but 40 years ago we did not know how to treat fluctuations at high $T$. 

![Graphs showing paramagnetic and ferromagnetic FeNi phases](image-url)
**Wannier functions and orbitals (WOs)**

Since it makes the chemistry and physics intelligible and because DMFT requires a small basis set of correlated single-particle orbitals, it has become customary to project out of the Rydbergs-wide DFT Band structure a set (or sets) of so-called *maximally localized* Wannier functions, which span for instance the O \(2p\) and the TM \(d\)-bands, and, hence, have the TM \(sp\)-orbitals folded down into the tails of mainly the O \(2p\) orbitals, or merely the \(e_g\)-band with the tails of the O \(2p\)- as well as those of the \(sp\)- and \(t_{2g}\)-orbitals on the TM neighbors folded in.

We prefer to generate such Wannier orbitals *directly*, as symmetrically orthonormalized, minimal basis sets of NMTOs. These are like linear MTOs (LMTOs), which use a linear \(\left\{ \varphi(r), \dot\varphi(r) \right\}\)-expansion of the energy dependence of the partial waves. If the downfolding is massive and the range of the MTOs therefore long, and their energy dependence strong, the expansion needs to be of higher than linear order, hence of order \(N>1\).
Current material-specific many-body theory

Pick low-energy LDA bands
(by projection onto WOs or using NMTOs)
for specific many-body treatment
such as representation by a Hubbard Hamiltonian
and solution in the
dynamical mean-field approximation (DMFT)
or beyond.
Multiplet ligand-field theory using Wannier orbitals

Physical Review B 85, 165113 (2012)
M. W. Haverkort, M. Zwierzycki, and O. K. Andersen
Transition-metal oxides

Metal-insulator transition in $\text{V}_2\text{O}_3$

... and very many other earlier and later papers by other authors.
Wannier orbital Conduction band Hubbard model at 1/2 filling and T=2000K LDA+DMFT

U = 2.1 eV

U = 3.0 eV

T. Saha-Dasgupta and OKA 2002
But most correlated materials, such as $V_2O_3$, have more than one band at the Fermi level.

Low-energy multiband Hubbard Hamiltonian

$$\hat{H} = \sum_{im\sigma, i'm'\sigma'} \delta_{\sigma,\sigma'} h_{im,i'm'} c_{im\sigma}^\dagger c_{i'm'\sigma'} + \frac{1}{2} \delta_{i,i'} \sum_{imm'\sigma\sigma'} U_{imm'} \hat{n}_{im\sigma} \hat{n}_{i'm'\sigma'} - d.c.$$

$h_{im,i'm'}$ is the LDA one-electron part. For the two-electron, on-d-site term, we use:

$$\frac{1}{2} \sum_{m=1}^{\infty} \sum_{m'=1}^{\infty} \sum_{\sigma} \sum_{\sigma'} U_{imm'} \hat{n}_{im\sigma} \hat{n}_{i'm'\sigma'} \approx$$

$$U_i \sum_m \hat{n}_{im\uparrow} \hat{n}_{im\downarrow} +$$

$$(U_i - 2J_i) \sum_m \sum_{m' \neq m} \hat{n}_{im\uparrow} \hat{n}_{im'\downarrow} +$$

$$(U_i - 3J_i) \sum_m \sum_{m' > m} \left( \hat{n}_{im\uparrow} \hat{n}_{im'\uparrow} + \hat{n}_{im\downarrow} \hat{n}_{im'\downarrow} \right)$$

for two electrons in

same orbital
different orbitals and spins

same spin
MOTT TRANSITION IN Cr-DOPED V$_2$O$_3$

D. B. McWhan, T. M. Rice, and J. P. Remeika

LDA+U: Ezhov, Anisimov, Khomskii, Sawatzky 1999
Fig. 2. An illustration of the 'umbrella-like' distortion of the oxygen octahedra in V$_2$O$_3$ due to the Cr$^{3+}$ substitution and the expansion in the vanadium–vanadium distance across the shared octahedral face.
LDA band structure of V$_2$O$_3$ projected onto various orbital characters:

Blow up energy scale and split the panels:

Pick various sub-bands by generating the corresponding minimal $N$MTO basis set:

For the low-energy Hamiltonian we just need the $t_{2g}$ set
\((V_{1-x}M_x)_2O_3\)

**V\textsubscript{2}O\textsubscript{3}

3d \((t_{2g})^2\)

Minimal Coulomb repulsion = \(U - 3J = 4.25 - 3 \times 0.7 \text{ eV}\)

\(a_{1g} - e_g^\pi\) crystal-field splitting = 0.3 eV

\(c_{g,2}^\pi\)

\(e_{g,1}^\pi\)
LDA $t_{2g}$ NMTO Wannier Hamiltonian

\begin{align*}
(a_{1g}^{(1)} | H | e_{g_{22}}^{2(2)}) &= -0.25 \text{ eV} \\
(a_{1g}^{(4)} | H | a_{1g}^{(1)}) &= -0.49 \text{ eV}
\end{align*}

\begin{align*}
(a_{1g}^{(1)} | H | e_{g_{22}}^{2(2)}) &= -0.25 \text{ eV} \\
(a_{1g}^{(4)} | H | a_{1g}^{(1)}) &= -0.49 \text{ eV}
\end{align*}

U > W \rightarrow \text{ single occ}

LDA+DMFT

$$
\mathcal{H}_{t_{2g}} = \mathcal{H}_{LDA}^{t_{2g}} + \sum_R U_R
$$

$$
-G^{-1}(k,\omega)_{ij} = H_{ij}^{LDA} (k)
$$

$$
H_{ij}^{QP} (k) = Z_i^{1/2} \left\{ H_{ij}^{LDA} (k)ight. 
$$

Crystal-field enhanced and mass-renormalized QP bands

390 K
Comparison with PES (Mo et al. PRL 2004):

FIG. 4: (Color online) Left-hand side: Intensity plot of the k-resolved spectral function $A(k,\omega)$ calculated by LDA+DMFT for $U=4.2$ eV, $J=0.7$ eV and $T \sim 390$ K. The total and orbitally resolved spectral functions are shown on the right-hand side. Solid (red) line represents the total spectral function, dashed (green) and dot-dashed (blue) lines are for the $e_g^+$ and $a_{1g}$ orbitals respectively.
$e_g$ electrons are "localized" and only coherent below $\sim 250$K

$\alpha_{ig}$ electrons are "itinerant" and coherent below $\sim 400$K

More important for the temperature dependence of the conductivity is, however, that internal structural parameters of V$_2$O$_3$ change with temperature, as we shall see later.
LDA $t_{2g}$ NMTO Wannier Hamiltonian

\[
(a_{1g}^{(1)} | H | e_{g^2}^{(2)}) = -0.25 \text{ eV}
\]

\[
(a_{1g}^{(4)} | H | a_{1g}^{(1)}) = -0.49 \text{ eV}
\]

\[
(a_{1g}^{(4)} | H | a_{1g}^{(1)}) = -0.41
\]

LDA+DMFT

Crystal-field splitting = 0.3 eV

Xtal-enhancement = 1.85 eV ~ 3J

$U > W \rightarrow$ single occ

$e_g^{\pi}$ crystal-field splitting = 0.3 eV

$e_g^{\pi}$

undo hybridization

390 K
U=4.2 eV, 0% Cr, T=390 K

U=4.2 eV, 3.8% Cr, T=580 K
Real structure

Ideal structure

\[ t = -0.49 \, \text{eV} \]

\[ t = -0.72 \, \text{eV} \]
Fig. 2. An illustration of the 'umbrella-like' distortion of the oxygen octahedra in V$_2$O$_3$ due to the Cr$^{+3}$ substitution and the expansion in the vanadium–vanadium distance across the shared octahedral face.
$V_2O_3 \ 3d \ (t_{2g})^2$

Hund's-rule coupling
Comparison with polarization dependent X-ray absorption, $S=1$ (Park et al. 2000)

From XAS by V 2$p$ interpreted via cluster calc.s Park et al. concluded that

$$\text{PM: } \frac{\left( e^{\pi}_{g}, a_{1g} \right)}{\left( e^{\pi}_{g}, e^{\pi}_{g} \right)} = \frac{1}{1} \quad \text{PI: } \frac{\left( e^{\pi}_{g}, a_{1g} \right)}{\left( e^{\pi}_{g}, e^{\pi}_{g} \right)} = \frac{2}{3}$$

I.e., the ratios between $V 3d\left(t_{2g}\right)$ occupations in the $V 3p$ core region are:

$$\text{PM: } \frac{n\left(a_{1g}\right)}{n\left(e^{\pi}_{g}\right)} = \frac{1}{3} \quad \text{PI: } \frac{n\left(a_{1g}\right)}{n\left(e^{\pi}_{g}\right)} = \frac{1}{4}$$

Our LDA Wannier-function + DMFT calc.s yield:

$$\begin{align*}
\text{PM: } & \quad \frac{n\left(a_{1g}\right)}{n\left(e^{\pi}_{g}\right)} = \frac{0.18 + 0.68 \times 0.22 + 0.07 \times 1.78}{0.32 + 0.77 \times 1.78 + 0.06 \times 0.22} = \frac{0.45}{1.70} = 0.26 \\
\text{PI: } & \quad \frac{n\left(a_{1g}\right)}{n\left(e^{\pi}_{g}\right)} = \frac{0.18 + 0.68 \times 0.10 + 0.07 \times 1.90}{0.32 + 0.77 \times 1.90 + 0.06 \times 0.10} = \frac{0.38}{1.79} = 0.21
\end{align*}$$
This metal-insulator transition in $V_2O_3$ is not, like in the case of a single band, e.g.:

- **Wannier orbital and LDA conduction band**
- **Hubbard model, LDA+DMFT**
  - Band 1/2 full
  - $T=2000K$
  - $U=2.1 \text{ eV}$
  - $U=3.0 \text{ eV}$

caused by disappearance of the quasi-particle peak and driven by $U$, but by removing a band overlap through changing a lattice distortion and thereby “completing” the lowest Hund’s-rule state with energy $U-3J$. 
Conclusion

The \((t_{2g})^2\) system \(V_2O_3\) is described by a Hubbard model derived from LDA \(t_{2g}\)-WOs with \(U=4.25\) and \(J=0.7\) eV. DMFT shows that the paramagnetic insulating state is basically the Hund’s rule \((e_{1g,\pi})^\uparrow (e_{2g,\pi})^\uparrow\) state with Coulomb repulsion \(U-3J\). In the metal, the trigonal (umbrella) distortion is slightly larger then in the insulator and causes the bottom of the \(a_{1g}\) band to overlap the top of the \(e_g\) \(\pi\) band. The \(a_{1g}\) electrons stay coherent to higher temperatures (~450K) than the \(e_g\) \(\pi\) electrons (~250K).
MOTT TRANSITION IN Cr-DOPED V$_2$O$_3$

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V 3d$^2$

Paramagnetic M and I corundum str

AFI monoclinic

LDA+U: Ezhov, Anisimov, Khomskii, Sawatzky 1999
Robinson, *Acta Cryst.* 1975:

\( V_2O_3 \) at 300K ~ Alpha  \( (V_{0.99}Cr_{0.01})_2O_3 \)  

\( V_2O_3 \) at 900K ~ Beta
A Microscopic View on the Mott transition in Cr-doped V$_2$O$_3$


Scanning PES

![Graphs showing PES intensity versus binding energy at different temperatures.](image-url)
Conclusion

The phase diagram of Cr-doped V$_2$O$_3$ has been explored from macro- to microscopic scales by combining InfraRed spectroscopy, Scanning PhotoEmission Microscopy and X-Ray Diffraction with LDA+DMFT calculations. With decreasing temperature, microscopic domains become metallic and coexist with an insulating background. This explains why the associated PM phase is a bad metal. Both domains are stabilized by Cr-induced strain fields. The tendency towards phase separation is associated with a thermodynamical instability, which is reduced by pressure.
**Force Theorem** (Pauli, Feynmann, a.o.)

Consider a general $N$-particle system (E&Nucl.) with

$$
\hat{H} \equiv \sum_{i=1}^{N} -\frac{\nabla^2_{i}}{2m_i} + w\left(\mathbf{r}_1, \ldots, \mathbf{r}_N\right) + \sum_{i=1}^{N} v_{\text{ext},i}(\mathbf{r}_i) \equiv \hat{t} + v
$$

in a stationary state, $\Phi\left(\mathbf{r}_1, \ldots, \mathbf{r}_N\right)$. $w$ is the interaction (e.g. $\sum_i \sum_j \frac{Z_i Z_j}{|\mathbf{r}_i - \mathbf{r}_j|}$) between the particles.

The **force** by the external potential on particle $i$ in region $\Omega$ is

$$
F_{\text{ext};i}^{\Omega} \equiv \int dV_1. \int_{\Omega} dV_i. \int dV_N |\Phi\left(\mathbf{r}_1, \ldots, \mathbf{r}_i, \ldots, \mathbf{r}_N\right)|^2 \left[-\nabla_i v_{\text{ext},i}(\mathbf{r}_i)\right]
$$

We shall derive an expression for the **internal** force,

$$
F^{\Omega} \equiv -\sum_i F_{\text{ext};i}^{\Omega},
$$

which together with the external one keeps the system in state $\Phi$. 

\[\text{Footnote: are my nails}\]
Use the variational principle with a trial function, $\tilde{\Phi} \equiv \Phi + d\Phi$, obtained from $\Phi$ by translating it rigidly from region $\Omega - du$ to $\Omega$:

$$d\Phi \equiv \Phi \left[ r_1 - \theta^\Omega (r_1) \, du, \ldots, r_N - \theta^\Omega (r_N) \, du \right] - \Phi (r_1, \ldots, r_N) = - \sum_j \theta^\Omega (r_j) \, \nabla_j \Phi (r_1, \ldots, r_j, \ldots, r_N) \cdot du$$

Since $\tilde{\Phi}$ is discontinuous when one of its arguments crosses the boundary of $\Omega$, the expectation value of the kinetic energy contains a surface integral:

$$0 = \langle \Phi \mid \hat{H} - E \mid d\Phi \rangle = \int dV_1 \cdots \int dV_N \Phi^* (\hat{H} - E) \, d\Phi$$

$$+ \sum_j \frac{1}{2m_j} \int dV_1 \cdots \int_{\Sigma} dS_j \cdot df_j \cdots \int dV_N$$

$$df_j \equiv \Phi^* \nabla_j (\nabla_j \Phi \cdot du) - (\nabla_j \Phi \cdot du) \nabla_j \Phi^* = - \left[ \Phi^* \nabla_j \nabla_j \Phi - (\nabla_j \Phi^*) (\nabla_j \Phi) \right] \cdot du$$

$$\frac{\sigma_{\text{kin},j} (r_j)}{2m_j} = \frac{1}{2m_j} \int dV_1 \cdots \int dV_{j-1} \int dV_{j+1} \cdots \int dV_N$$

$$\times \left[ \Phi^* \nabla_j \nabla_j \Phi - (\nabla_j \Phi^*) (\nabla_j \Phi) \right]$$

$$F_{\text{kin}}^\Omega = \int_{\Sigma} dS \cdot \sum_j \sigma_{\text{kin},j} (r_j)$$

Since

The sum

The latte

The outside

The mass

The he

particles inside $\Sigma$ cancels ($w$ is symmetric).
Integrating again over $\Omega$ and projecting onto $du$ yields:

$$n(r_1, r_2) = N \int dr_2 \int dr_N \Phi(r_1, \ldots, r_N) \Phi^*(r_1, \ldots, r_N).$$

The 1st-order density matrix,

$$n(r_1, r_2) = \sum_{k}^{\infty} \psi_k^*(r_1) n_k \psi_k(r_1),$$

is Hermitean and may therefore be diagonalized:

$$n(r_1, r_2) = \sum_{k}^{\infty} \psi_k^*(r_1) n_k \psi_k(r_1).$$

The eigenvalues, $n_k$, are the occupation numbers, and the eigenvectors, $\psi_k(r)$, are the set of orthonormal single-particle natural orbitals.

The kinetic-energy stress tensor field, $\overline{\sigma}_{kin,i}(r)$, for particle $i$ may now be expressed as:

$$\overline{\sigma}_{kin,i}(r) = \frac{1}{2m_i} \sum_k n_{i,k} \left[ \psi_{i,k}^*(r) \nabla^2 \psi_{i,k}(r) - \left( \nabla \psi_{i,k}(r) \right)^* \nabla \psi_{i,k}(r) \right]$$

The kinetic force,

$$F_{kin}^\Omega = \int_{\Sigma} dS \sum_i \overline{\sigma}_{kin,i}(r),$$

is thus expressed in terms of the values and two first derivatives of the single-particle orbitals at the surface of $\Omega$.

To find the net force on the electrons in $\Omega$, so the force is the one on the nuclei. $F_{ext}^\Omega$ will therefore be independent of $\Omega$ as long as it contains the same nuclei.

Using Green's theorem, we may define the kinetic force density:

$$F_{kin}(r) = \nabla \cdot \sum_i \overline{\sigma}_{kin,i}(r)$$

$$= \sum_i \frac{1}{2m_i} \sum_k n_{i,k} \left[ \psi_{i,k}^*(r) \nabla^2 \psi_{i,k}(r) - \left( \nabla \psi_{i,k}(r) \right)^* \nabla \psi_{i,k}(r) \right]$$

We now specialize to electrons and nuclei, and neglect the nuclear kinetic force. If the natural orbitals of the electrons satisfy a one-electron Schrödinger equation

$$-\nabla^2 \psi_k(r) = [\varepsilon_k - v_k(r)] \psi_k(r)$$

with a local, possibly state-dependent potential, $v_k(r)$, then

$$F_{kin}(r) = \sum_k n_k \left[ [\varepsilon_k - v_k(r)] \psi_k^*(r) \nabla \psi_k(r) - \psi_k(r) \nabla \left\{ [\varepsilon_k - v_k(r)] \psi_k(r) \right\} \right]$$

$$= \sum_k n_k |\psi_k(r)|^2 \nabla v_k(r)$$

We thus have the obvious result that the one-electron potential is that effective, external potential whose force balances the kinetic force.