Correl 18. Lecture 2.

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From Materials to Models: Deriving Insight from Bands



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 **atomic orbitals**:

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

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 **radial Schrödinger** equation:

$$-[r\varphi_l(\varepsilon_{nl},r)]'' = [\varepsilon_{nl} - v_l(r)]r\varphi_l(\varepsilon_{nl},r),$$

with $v_l(r) \equiv v(r) + l(l+1)/r^2.$

The solutions are numbered in order of increasing one-electron **energy**, ε_{nl} , by the **principal quantum number**, *n*, which takes the values l + 1, l + 2,..., 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 **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, $Z_{\text{eff}}(r) \equiv -rv(r)/2$, decreases from Z towards 1 as r increases from 0 to ∞ 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:

 $\varepsilon_{ns} < \varepsilon_{np} < \varepsilon_{nd} < \dots$

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:

 $\varepsilon_{(n+1)s} < \varepsilon_{nd}$ if the *nd*-shell is empty

 $\varepsilon_{np} < \varepsilon_{nd} < \varepsilon_{(n+1)s}$ if the *nd*-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 **Periodic Table**:

Li ³ 2s Na ¹¹ 3s	Be ⁴ 2s ² Mg ¹² 3s ²	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, \ldots signify electrons having orbital angular momentum 0, 1, 2, in units A ; 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.														C ⁶ 2s ² Si ¹ 3s ²	2p ²	N ⁷ 2s ² 2p ³ P ¹⁵ 3s ² 3p ³	0 ⁸ 2s ² 2p ⁴ S ¹⁶ 3s ² 3p ⁴	F ⁹ 2s ² 2p ⁵ Cl ¹⁷ 3s ² 3p ⁰	Ne ¹⁰ 2s ² 2p Ar ¹⁸ 3s ² 3p	Z atomic number =
K ¹⁹	Ca ²⁰	Sc ²¹	TIP	22	1 23	Cr ²	*	n ²⁵	Fe ²⁶	Co27	Ni2	⁸ Cu	29 Z	n ³⁰	Ga ³¹	Ge	32	As ³³	Se ³⁴	Br ³⁵	Kr ³⁶	protons in the
45	4s ²	3d 4s ²	3d 4s ²	2 3	3d ³ 1s ²	3d ⁵ 4s	3d 4s	15 2	3d ⁶ 4s ²	3d ¹ 4s ²	3d ⁸ 4s ²	3d 4s	0 30 4s	∤ 10 ,2	4s ² 4p	4s2	4p ²	4s ² 4p ³	4s24p4	4s ² 4p ¹	5 4s ² 4p	nucleus
Rb ³⁷	Sr ³⁸	Y 39	Zr	40	Vb 41	Mo	42 To	43	Ru ⁴⁴	Rh ⁴⁵	Pd	6 Ag	47 C	d ⁴⁸	In ⁴⁹	Sn	50	Sb51	Te ⁵²	153	Xe ⁵⁴	=
55	5s ²	4d 5s ²	4d 5s ⁵	2 4	4d4 58	4d ⁵ 58	4d 5s	76	4d ⁷ 5s	4d ⁸ 5s	4d1 -	o 4d 5s	10 44 5s	/10 2	5s ² 5p	5s ²	5p ²	5s ² 5p ³	5s ² 5p ⁴	5s ² 5p	5 5s ² 5p	number of electrons in
Cs ⁵⁵	Ba ⁵⁶	La ⁵⁷	Hf 4f	72 1 14	Fa ⁷³	W7	R	e ⁷⁵	Os ⁷⁶	lr ⁷⁷	Pt7	⁸ Au	79 H	g ⁸⁰	TI ⁸¹	Pb	82	Bi ^{s3}	Po ⁸⁴	At ⁸⁵	Rn ⁸⁶	the neutral atom
68	6s ²	5d 6s ²	5d 6s	2 1	$5d^3$ $5s^2$	5d ⁴ 6s ²	50 68	15 2	5d ⁶ 6s ²	5d ⁹	5d ⁹ 6s	5d 6s	10 50 61	110 5 ²	6s ² 6p	6s2	6p ²	6s ² 6p ³	6s ² 6p ⁴	6s ² 6p	5 6s ² 6p	5 6
Fr ⁸⁷	Ra ⁸⁸	Ac ⁸⁹		_		_		-	-			-	1	-	-						-	
7s	7s ²	6d 7s ²		Ce ⁵ 4 <i>f</i> ²	8 P 4)	r 59 F ³	Nd ⁶⁰ 4f*	Pn 4f	n ⁶¹ Si 5 4/	m ⁶² E	u ⁶³	Gd ⁶⁴ 4f ⁷ 5d	Tb ⁶⁵ 4f ⁸ 5d	Dy 4f	10 4j	0 ⁶⁷ f11	Er ⁶ 4f ¹	⁸ Tn ² 4f ¹	3 4f	570 Li	u71 (14 1 ←	nı configuration of
			1	6s ² Th ⁹ - 6d ² 7s ²	$6s^2$ $6s$ Th ⁹⁰ P - $5j$ $6d^2$ $6c$ $7s^2$ $7s$	² 6s a ⁹¹ U ² 5/ 1 6c ² 7x	6s ² U ⁹² 5f ³ 6d 7s ²	² 6s ¹² N ³ 5f ² 7s	2 6s ² p ⁹³ Pu 5f ⁰ 2 7c ²	6s ³ 1 ⁹⁴ Ar 5 <i>f</i> 2 7 c	s ² m ⁹⁵ f ⁷ s ²	6s ² Cm ⁹⁶ 5f ⁷ 6d 7s ²	6s ² Bk ⁹⁷	6s Cl	2 6. 198 E	s ⁹⁹	99 Fn	6s 1 ¹⁰⁰ M	d ¹⁰¹	é 6s [:] Lv	w ¹⁰³	outer shells in the ground state of the neutral atom

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.



As Z increases $v(r) = -\frac{2Z_{eff}(r)}{r}$ deepens and counteracts $+\frac{l(l+1)}{r^2}$ such that bound states occur if $Z \ge 5$ (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 $2(l_{max} + 1)^2$.

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, ε_{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 $n' \ge n$, this is outside the region of an *nl*-electron and ε_{nl} will therefore drop sharply and $\varphi_l(\varepsilon_{nl})$ contract rapidly, the *nl*-shell thereby start to become part of the core.



 V_2O_3

metal

oxide:

ionic



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 σ -degeneracy of such a shell, several Slater determinants corresponding to the various possible occupancies of *m* and σ 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 $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$. 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:



$$arphi_{l}(arepsilon,r)=j_{lm}\left(\kappa r
ight)- an\eta_{l}\left(arepsilon
ight)\,n_{l}\left(\kappa r
ight)$$

energydependent MTO $\chi_l(\varepsilon, r) = \begin{cases} \cot \eta_l(\varepsilon) [\varphi_l(\varepsilon, r) - j_{lm}(\kappa r)] & \text{for } r < s \\ -n_l(\kappa r) & \text{for } s < r \end{cases}$



Tail cancellation

has much better *l*-convergence than matching at WS-cell boundary

Atomic Spheres Approximation (1973): $\kappa \equiv 0$

r - tange (E) + - 1 $\varphi_{\ell}(\varepsilon, i)$ a-1-1 ASA: $\sum_{RL} \left[S_{R'L',RL} - \delta_{R'L',RL} \cot \eta_{Rl} \left(\varepsilon \right) \right] v_{RL} = 0$

The bare structure matrix is given by:

$$S_{ll'm} = (-)^{l'+m+1} 2 \left(l+l'\right)! \times \left[\frac{(2l+1)(2l'+1)}{(l+m)!(l-m)!(l'+m)!(l'-m)!}\right]^{\frac{1}{2}} \left(\frac{w}{d}\right)^{l+l'+1}$$

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

$$S_{dd(\sigma,\pi,\delta)} = (-6, 4, -1) 10 (w/d)^5$$
,

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.

$$\sum_{L} \left[S_{L'L} \left(\mathbf{k} \right) - \delta_{L'L} \cot \eta_l \left(\varepsilon \right) \right] v_L = \mathbf{0}$$

For elemental, closely-packed crystals, the *I=I*' diagonal blocks of the Bloch-summed structure constants may be diagonalized to form canonical bands.



- The bare canonical s., p- and d-bands for the f.c.c. structure.

Screening \Rightarrow Ab initio TB-LMTO-ASA (1984):

ma

a: hard-sphere radius α: hard-sphere phase shift

Superposition of Neumann fcts to form screened Neumann fcts

screened Bessel fct

$$n_{R'L'}^{lpha}\left(\mathbf{r}-\mathbf{R}'
ight)\equiv\sum_{RL}n_{L}\left(\mathbf{r}-\mathbf{R}
ight)\left[\delta_{RL,R'L'}+ anlpha_{l}S_{RL,R'L'}^{lpha}
ight]$$

 $j_{l}^{\alpha}\left(r\right)\equiv j_{l}\left(r\right)-\tan\alpha_{l}n_{l}\left(r\right)$

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

$$an\eta_{l}^{lpha}\left(arepsilon
ight)\equiv an\eta_{l}\left(arepsilon
ight)- anlpha_{l}$$

$$\sum_{RL} \left[S^{\alpha}_{R'L',RL} - \delta_{R'L',RL} \cot \eta^{\alpha}_{Rl} \left(\varepsilon \right) \right] v_{RL} = 0$$

screened structure matrix η: phase shift η^α: phase shift in hard-sphere medium Tail-cancellation condition

This localization enables treatment of disorder, Wannier orbitals,...



$$\chi_{RL}(\mathbf{r}_{R}) = \phi_{RL}(\mathbf{r}_{R}) + \sum_{R'L'} \dot{\phi}_{R'L'}(\mathbf{r}_{R'}) \left(H_{R'L',RL} - \varepsilon_{\nu} \delta_{R'R} \delta_{L'L} \right)$$

 $H_{R'l'm',Rlm}^{\gamma}(\mathbf{k}) = \sqrt{\Delta_{R'l'}} S_{R'l'm',Rlm}^{\gamma}(\mathbf{k}) \sqrt{\Delta_{Rl}} + C_{R'l'} \delta_{R'R} \delta_{l'l} \delta_{m'm}.$

Screened canonical bands



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

S1'm'; 1m(k) $H = C + \sqrt{\Delta} S (1 - \gamma S)^{-1} \sqrt{\Delta}$ $S_{ss\sigma} = -2(s/R), S_{sp\sigma} = 2\sqrt{3}(s/R)^2,...$

Hybridization between s, p, and d screened canonical bands



Fig. 13. – Unhybridized energy bands corresponding to the screening given by $Q_s = 0.435$, $Q_p = 0.0907$ and $Q_s = 0.0095$ (a)) and hybridized energy bands (b)) of b.e.e. 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.











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:

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

The corresponding xc-potential is diagonal in spin and equals $\partial [\rho \epsilon_{xc}(\rho_{\uparrow}, \rho_{\downarrow})] / \partial \rho_{\sigma} \equiv \mu_{xc\sigma}(\rho_{\uparrow}, \rho_{\downarrow})$. 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:

$$\mu_{xc} \uparrow (\rho, m) = \mu_{xc}(\rho) \pm m\rho \epsilon_{xc}^{\prime\prime}(\rho)/2 + o(m).$$

Here, μ_{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 occcupation, 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 $\pm \mu_B \mathcal{H}$, 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, $m = \langle m(\mathbf{r}) \rangle$, the uniform susceptibilities, 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: $C_{d\downarrow} - C_{d\uparrow} = mI + 2\mu_B \mathcal{H}$, 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:

 $\varepsilon_{j\downarrow}(\mathbf{k}) - \varepsilon_{j\uparrow}(\mathbf{k}) = \langle \psi_{j\mathbf{k}}(\mathbf{r}) | -\rho(\mathbf{r}) \epsilon_{xc}^{\prime\prime}(\rho(\mathbf{r})) m(\mathbf{r}) | \psi_{j\mathbf{k}}(\mathbf{r}) \rangle + 2\mu_B \mathcal{H} \approx mI + 2\mu_B \mathcal{H}.$

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 paramagnet tic DOS per spin. Equating this splitting with the approximation yields Stoner's expression for the exchange-enhanced spin-susceptibility:

 $\chi \equiv \mu_B m / \mathcal{H} = 2 \mu_B^2 N(\varepsilon_F) [1 - IN(\varepsilon_F)]^{-1}.$

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 ρ , is due to ϵ_{xc} being dominated by $\epsilon_x \propto \rho^{1/3}$, so that the kernel is behaves like $-\rho \epsilon_x'' \propto \rho^{-2/3} \propto r_s^2$, which decreases with ρ . For understanding that in a given series, *I* rises again until it drops sharply at the noble metals, one uses the ASA and expands $\psi_{jk}(\mathbf{r})$ on the FS in partial waves. Since only partial waves with the same *l* contribute:

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

This form with $\alpha = 0$ is the one discussed by Gunnarsson for the transition metals. He showed that the factor $[r_s(r)/r]^2$, apart from its general decrease with Z, for Z given and r increasing, increases outside the last core *np*-shell, i.e. for $r \ge 0.3s$, 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 $r \leq 0.5s$. One factor $(r\varphi_d(\varepsilon_F, r))^2$ comes from $|\psi_{j\mathbf{k}}(\mathbf{r})|^2$ and the other from $m(\mathbf{r})/m$. The product, $(r\varphi_d(\varepsilon_F, r))^4$, is very strongly peaked at a value $r \leq 0.5s$, 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.











Compression

Canonical bands:

$$H_{R'l'm',Rlm}^{\gamma}(\mathbf{k}) = \sqrt{\Delta_{R'l'}} S_{R'l'm',Rlm}^{\gamma}(\mathbf{k}) \sqrt{\Delta_{Rl}} + C_{R'l'} \delta_{R'R} \delta_{l'l} \delta_{m'm}$$

 $\Delta_d \varpropto s^{\text{-5}}$

For <u>*N(m)*</u> on canonical (structure-constant) scale:

$$\underline{N}(m) \equiv m / (\Delta / \Delta_d) = \Delta_d / I \propto s^{-5} / I$$



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 750K 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 $\overline{N}(7,7,m)$, m would drop significantly already at a 20% reduction of Δ_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.



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 O2p 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 $\{\varphi(r), \dot{\varphi}(r)\}$ -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,¹ M. Zwierzycki,² and O. K. Andersen¹



Transition-metal oxides

Metal-insulator transition in V_2O_3

PHYSICAL REVIEW B 76, 085127 (2007)

Enhanced crystal-field splitting and orbital-selective coherence induced by strong correlations in V₂O₃

Alexander I. Poteryaev,¹ Jan M. Tomczak,¹ Silke Biermann,¹ Antoine Georges,¹ Alexander I. Lichtenstein,² Alexey N. Rubtsov,³ Tanusri Saha-Dasgupta,⁴ and Ole K. Andersen⁵

Electronic structure of V₂O₂ : Wannier orbitals from LDA-NMTO calculations arXiv:0907.2841v1 [cond-mat.mtrl-sei] 16 Jul 2009

arxiv:0907.2841v1 [cond-mai.min-sci] 10.0012009

T. Saha-Dasgupta,^{1,2} O. K. Andersen,¹ J. Nuss,¹ A. I. Poteryaev,^{3,4} A. Georges,³ and A. I. Lichtenstein,⁵

PRL 104, 047401 (2010)

PHYSICAL REVIEW LETTERS

week ending 29 JANUARY 2010 Oldin Hit. RCI al nationena (1990)

Inequivalent Routes across the Mott Transition in V2O3 Explored by X-Ray Absorption

E. Rodolakis, ^{1,2} P. Hansmann, ^{3,4} J.-P. Rueff, ^{2,5} A. Toschi, ³ M. W. Haverkort, ⁴ G. Sangiovanni, ³ A. Tanaka,⁶ T. Saha-Dasgupta,⁷ O. K. Andersen, ⁴ K. Held, ³ M. Sikora,⁸ I. Alliot,^{8,9} J.-P. Itié, ² F. Baudelet, ² P. Wzietek, ⁶ P. Metcalf, ¹⁰ and M. Marsi¹

A microscopic view on the Mott transition in chromium-doped V_2O_3

S. Lupi, L. Baldassarre^{*}, B. Mansart^{*}, A. Perucchi^{*}, A. Barinov^{*}, P. Dudin^{*}, E. Papalazarau^{*}, F. Rodolakis^{*, I}, I. P. Rueff^{*}, J. P. Itie⁴, S. Ravy^{*}, D. Nicoletti[†], P. Postorino^{*}, P. Hansmann^{*}, N. Parragh^{*}, A. Toschi^{*}, T. Saha-Dasgupta^{*}, D. K. Andersen^{*}, G. Sangiovanni[†], K. Held^{*}, & M. Marsi[†]

... and very many other earlier and later papers by other authors.

Wannier orbital Conduction band (LDA)

Hubbard model at 1/2 filling and T=2000K LDA+DMFT











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

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

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

$$\begin{array}{l} \frac{1}{2} \sum\limits_{m=1}^{\sum} \sum\limits_{m'=1}^{\sum} \sum\limits_{\sigma \sigma'} U_{imm'} \, \hat{n}_{im\sigma} \, \hat{n}_{im'\sigma'} \approx \\ U_i \sum\limits_{m} \hat{n}_{im\uparrow} \, \hat{n}_{im\downarrow} + & \text{for two electrons in} \\ U_i \sum\limits_{m} \hat{n}_{im\uparrow} \, \hat{n}_{im\downarrow} + & \text{same orbital} \\ (U_i - 2J_i) \sum\limits_{m} \sum\limits_{m'\neq m} \hat{n}_{im\uparrow} \, \hat{n}_{im'\downarrow} + & \text{different orbitals and spins} \\ (U_i - 3J_i) \sum\limits_{m} \sum\limits_{m'>m} \left(\hat{n}_{im\uparrow} \, \hat{n}_{im'\uparrow} + \hat{n}_{im\downarrow} \, \hat{n}_{im'\downarrow} \right) & \text{same spin} \end{array}$$





LDA band structure of V₂O₃ projected onto various orbital characters:

Blow up energy scale and split the panels:

Pick various subbands by generating the corresponding minimal NMTO basis set:

For the low-energy Hamiltonian we just need the t_{2g} set







LDA+DMFT

$$\mathcal{H}_{t_{2g}} = \mathcal{H}_{t_{2g}}^{LDA} + \sum_{R} \mathcal{U}_{R}$$

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



Crystal-field enhanced and mass-renormalized

390 K









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

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

Real structure 8 6'

Ideal structure



 $t = -0.49 \ eV$

 $t = -0.72 \ eV$



 $V_2O_3 \ 3d \ (t_{2g})^2$



Hund's-rule coupling





Comparison with polarization dependent X-ray absorption, S=1 (Park et al 2000)

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

$$\mathsf{PM}: \quad \frac{\left(e_{g}^{\pi}, a_{1g}\right)}{\left(e_{g}^{\pi}, e_{g}^{\pi}\right)} = \frac{1}{1} \qquad \mathsf{PI}: \quad \frac{\left(e_{g}^{\pi}, a_{1g}\right)}{\left(e_{g}^{\pi}, e_{g}^{\pi}\right)} = \frac{2}{3}$$

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

$$\mathsf{PM}: \quad \frac{n\left(a_{1g}\right)}{n\left(e_{g}^{\pi}\right)} = \frac{1}{3} \qquad \mathsf{PI}: \quad \frac{n\left(a_{1g}\right)}{n\left(e_{g}^{\pi}\right)} = \frac{1}{4}$$

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

$$\mathsf{PM}: \quad \frac{n\left(a_{1g}\right)}{n\left(e_{g}^{\pi}\right)} = \frac{\begin{array}{c} \mathsf{n}(a_{1g}) \\ 0.18 + 0.68 \times 0.22 + 0.07 \times 1.78 \\ 0.32 + 0.77 \times 1.78 + 0.06 \times 0.22 \\ \mathsf{n}(e_{g}^{\pi}\mathsf{WO}) \times \mathsf{n}(e_{g}^{\pi}) \\ \mathsf{n}(a_{1g}\mathsf{WO}) \times \mathsf{n}(a_{1g}\mathsf{WO}) \times \mathsf{n}(a_{1g}) \\ \mathsf{PI}: \quad \frac{n\left(a_{1g}\right)}{n\left(e_{g}^{\pi}\right)} = \frac{0.18 + 0.68 \times 0.10 + 0.07 \times 1.90}{0.32 + 0.77 \times 1.90 + 0.06 \times 0.10} = \frac{0.38}{1.79} = \frac{1}{4.7}$$



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

 $U = 2.1 \text{ eV} \qquad U = 3.0 \text{ eV}$

T. Saha-Dasgupta and OKA 2002

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 $(t_{2\varrho})^2$ system V₂O₃ 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 $(e_{1,g}^{\pi})^{\uparrow} (e_{2,g}^{\pi})^{\uparrow}$ 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^{π} band. The a_{1g} electrons stay coherent to higher temperatures (~450K) than the e_g^{π} electrons (~250K).





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A Microscopic View on the Mott transition in Cr-doped V_2O_3

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Scanning PES



Conclusion

The phase diagram of Cr-doped V_2O_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.

The Materials Trend, PRL 87, 047003 (2001)



Force Theorem (Pauli, Feynmann, a.o.) Consider a general N-particle system (E&Nucl.) with

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

in a stationary state, $\Phi(\mathbf{r}_1, ..\mathbf{r}_N)$. 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 Ω is

$$\mathbf{F}_{ext;i}^{\Omega} \equiv \int dV_1 \int_{\Omega} dV_i \int dV_N \left| \boldsymbol{\Phi} \left(\mathbf{r}_1, \mathbf{r}_i, \mathbf{r}_N \right) \right|^2 \left[-\bar{\bigtriangledown}_i v_{ext,i} \left(\mathbf{r}_i \right) \right]$$

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

$$\mathbf{F}^{\Omega} \equiv -\sum_{i} \mathbf{F}^{\Omega}_{ext,i},$$

which together with the external one keeps the system in state Φ .

Use the variational principle with a trial function, $\bar{\Phi} \equiv \Phi + d\Phi$, obtained from Φ by translating it rigidly from region $\Omega - d\mathbf{u}$ to Ω :

$$d\Phi \equiv \Phi\left[\mathbf{r}_{1} - \theta^{\Omega}\left(\mathbf{r}_{1}\right) d\mathbf{u}, \dots \mathbf{r}_{N} - \theta^{\Omega}\left(\mathbf{r}_{N}\right) d\mathbf{u}\right] - \Phi\left(\mathbf{r}_{1}, \dots, \mathbf{r}_{N}\right)$$
$$= -\sum_{j} \theta^{\Omega}\left(\mathbf{r}_{j}\right) \vec{\bigtriangledown}_{j} \Phi\left(\mathbf{r}_{1}, \dots, \mathbf{r}_{j}, \dots, \mathbf{r}_{N}\right) \cdot d\mathbf{u}$$

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

$$\begin{aligned} \mathbf{0} &= \left\langle \mathbf{\Phi} \left| \hat{H} - E \right| d\mathbf{\Phi} \right\rangle = \int dV_{1} \dots \int dV_{N} \mathbf{\Phi}^{*} \left(\hat{H} - E \right) d\mathbf{H} \\ &+ \sum_{j}^{N} \frac{1}{2m_{j}} \int dV_{1} \dots \int_{\Sigma} \mathbf{dS}_{j} \cdot d\mathbf{f}_{j} \dots \int dV_{N} \end{aligned} \\ d\mathbf{f}_{j} &\equiv \mathbf{\Phi}^{*} \vec{\nabla}_{j} \left(-\vec{\nabla}_{j} \mathbf{\Phi} \cdot d\mathbf{u} \right) - \left(-\vec{\nabla}_{j} \mathbf{\Phi} \cdot d\mathbf{u} \right) \vec{\nabla}_{j} \mathbf{\Phi}^{*} \\ &= - \left[\mathbf{\Phi}^{*} \vec{\nabla}_{j} \vec{\nabla}_{j} \mathbf{\Phi} - \left(\vec{\nabla}_{j} \mathbf{\Phi}^{*} \right) \left(\vec{\nabla}_{j} \mathbf{\Phi}^{*} \right) \right] \cdot d\mathbf{u} \end{aligned} \\ \vec{\overline{\sigma}}_{kin,j} \left(\mathbf{r}_{j} \right) &\equiv \frac{1}{2m_{i}} \int dV_{1} \dots \int dV_{j-1} \int dV_{j+1} \dots \int dV_{N} \end{aligned}$$

$$\begin{aligned} & \sum_{j=1}^{2m_j} \int \sum_{j=1}^{N} \int \sum_{j=1}^{N-j-1} \int \sum_{j=1}^{N$$



Integrating again over Ω and projecting onto $d\mathbf{u}$ yields:

The 1st-order density matrix,

$$n\left(\mathbf{r}_{1},\mathbf{r}_{1'}\right) \equiv N \int d\mathbf{r}_{2} \int d\mathbf{r}_{N} \Phi\left(\mathbf{r}_{1},.,\mathbf{r}_{N}\right)^{*} \Phi\left(\mathbf{r}_{1'},.,\mathbf{r}_{N}\right),$$

is Hermitean and may therefore be diagonalized:

$$n(\mathbf{r}_1, \mathbf{r}_{1'}) = \sum_{k}^{\infty} \psi_k^*(\mathbf{r}_1) \ n_k \psi_k(\mathbf{r}_{1'})$$

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

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

$$\vec{\overline{\sigma}}_{kin,i}(\mathbf{r}) = \frac{1}{2m_i} \sum_{k} n_{i,k} \left[\begin{array}{c} \psi_{i,k}^*(\mathbf{r}) \, \vec{\nabla} \vec{\nabla} \psi_{i,k}(\mathbf{r}) - \\ \left(\vec{\nabla} \psi_{i,k}(\mathbf{r}) \right)^* \left(\vec{\nabla} \psi_{i,k}(\mathbf{r}) \right) \end{array} \right]$$

The kinetic force,

$$\mathbf{F}_{kin}^{\Omega}\equiv\int_{\mathbf{\Sigma}}\mathbf{dS}\cdot\sum_{i}\overline{\overline{\sigma}}_{kin,i}\left(\mathbf{r}
ight),$$

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

on the nuclei. F_{ext}^{Ω} will therefore be independent of Ω as long as it contains the same nucleii.

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

$$\mathbf{F}_{kin}\left(\mathbf{r}\right) \equiv \bigtriangledown \cdot \sum_{i} \overline{\vec{\sigma}}_{kin,i}\left(\mathbf{r}\right)$$
$$= \sum_{i} \frac{1}{2m_{i}} \sum_{k} n_{i,k} \begin{bmatrix} \psi_{i,k}^{*}\left(\mathbf{r}\right) \overrightarrow{\bigtriangledown} \nabla^{2} \psi_{i,k}\left(\mathbf{r}\right) - \\ \left(\nabla^{2} \psi_{i,k}\left(\mathbf{r}\right)\right)^{*} \left(\overrightarrow{\bigtriangledown} \psi_{i,k}\left(\mathbf{r}\right)\right) \end{bmatrix}$$

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*

$$-\bigtriangledown^{2}\psi_{k}\left(\mathbf{r}
ight)=\left[arepsilon_{k}-v_{k}\left(\mathbf{r}
ight)
ight]\psi_{k}\left(\mathbf{r}
ight)$$

with a local, possibly state-dependent potential, $v_k(\mathbf{r})$, then

$$\begin{split} \mathbf{F}_{kin}\left(\mathbf{r}\right) &= \sum_{k} n_{k} \left[\begin{array}{c} \left[\varepsilon_{k} - v_{k}\left(\mathbf{r}\right) \right] \psi_{k}^{*}\left(\mathbf{r}\right) \vec{\bigtriangledown} \psi_{k}\left(\mathbf{r}\right) - \\ \psi_{k}\left(\mathbf{r}\right) \vec{\bigtriangledown} \left\{ \left[\varepsilon_{k} - v_{k}\left(\mathbf{r}\right) \right] \psi_{k}\left(\mathbf{r}\right) \right\} \end{array} \right] \\ &= \sum_{k} n_{k} \left| \psi_{k}\left(\mathbf{r}\right) \right|^{2} \vec{\bigtriangledown} v_{k}\left(\mathbf{r}\right) \end{split}$$

► We thus have the obvious result that the oneelectron potential is that effective, external potential whose force balances the kinetic force.