

Energetics of isolated d-~~atom~~ atom

Textbook (old fashioned) J.C. Slater, Quantum Theory of Atomic Structure

* Here: neglect spin orbit coupling *

$$H_{Atom} = \sum_{i \in \sigma} -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{r_i} + \frac{1}{2} \sum_{\substack{i, j \\ \sigma, \sigma'}} \frac{e^2}{|r_i - r_j|}$$

N el atom: N-body problem. No exact soln.

- convenient dimensionless units $\vec{r} = a_B \vec{x}$ a_B : Bohr radius
Energy: Rydberg: $\frac{e^2}{2a_B} = 13.6 eV$

$$H_{Atom} [Ry] = - \sum_i \nabla_i^2 - \frac{2Z}{x_i} + \sum_{\substack{i, j \\ \sigma, \sigma'}} \frac{1}{|\vec{x}_i - \vec{x}_j|}$$

- Conserved quantities: $N, \vec{L}_{TOT}, \vec{S}_{TOT} \Rightarrow E(N, L, S)$
in principle, this is all you can say. Just go of best algorithm to solve H

- Density functional theory -

← Hohenberg-Kohn-Sham: \exists functional $\Phi(\rho(r))$ of electron density s.t. g.s. of H atom minimizes has ρ minimizing Φ , and $\Phi(\rho(r)) \rightarrow E_{gs}$.

• Procedure: auxiliary schr eqn

$$H_{KS}: \left[-\nabla^2 - \frac{2Z}{x} + 2 \int d^3x' \frac{\rho(x')}{|x-x'|} \right] \psi_n(x) + \int d^3x' V_{xc}(x, x') \psi_n(x) = E_n \psi_n(x')$$

Find N lowest eigenvalues

$$E = \sum_{i=1}^N E_i$$

Mean potential from all e^- . Int of e^- w/ itself

Issue: form of "exchange-correlation" pot $V_{xc}(x, x')$
No theory - various appx forms. Basic work-horse, CMP + quantum chemistry

- Fundamental ambiguity: SIC (self-interaction correction) direct coulomb term here includes int of e- w/ itself. Many forms of V_{xc} do also. Need to correct.

• Not problematic: solid w/ 10²³ e- in extended states
Problematic: atoms, TMO where d-orb. relatively localized

Alternative approach (high degree of acc, cumbersome)
- Hartree Fock + "CI" (configuration interaction)

Here: HF [physical intuition; notation, connect to literature]

(1) Choose complete set of orthonormal orbitals $\phi_i^\sigma(r)$

def N-ptcl state $\Psi(r_1, \sigma_1, \dots) = \text{Antisym} [\phi_{i_1}^{\sigma_1}(r_1) \dots \phi_{i_N}^{\sigma_N}(r_N)]$

$\Psi = d_{N\sigma_N}^\dagger \dots d_{i\sigma_i}^\dagger |0\rangle$ say $d_{j\sigma_j}^\dagger$ creates electron into state $j, \text{spin } \sigma_j$.

Matrix elt of H bet. 2 ~~sets~~ N ptcl. det's.

$$\hat{H} = \sum_{j\sigma} T_{jj} d_{j\sigma}^\dagger d_{j\sigma} + \sum_{ijkl} U_{ijkl} d_{i\sigma_1}^\dagger d_{j\sigma_2}^\dagger d_{k\sigma_2} d_{l\sigma_1}$$

$$T_{ij} = \int d^3\vec{x} \phi_i^*(\vec{x}) \left[-\nabla^2 - \frac{Z}{|\vec{x}|} \right] \phi_j(\vec{x})$$

$$U_{ijkl} = \int d^3\vec{x} d^3\vec{y} \phi_i^*(\vec{x}) \phi_j^*(\vec{y}) \phi_k(\vec{y}) \phi_l(\vec{x}) / |\vec{x} - \vec{y}|$$

Note: values of mat. elt. T_{ij}, U_{ijkl} dep. of on choice of basis ϕ .

Note: Exact G.S. - superpos of many det
HF: choose l , optimize ϕ . CI: correct this.

$$E_{HF} = \sum_{i\sigma} T_{ii} + \sum_{i\sigma, j\sigma'} U_{ijji} - U_{ijij} \delta_{\sigma_i, \sigma_j}$$

\nwarrow sum over occ. orb
 \swarrow direct Coulomb ("Hartree")
 \swarrow exchange

- Choose occ. orb to min E_{HF} . \Rightarrow optimized over normalized ϕ 's: \Rightarrow min $E_{HF} - \sum_{i\sigma} \epsilon_{i\sigma} \left[\int d^3x |\phi_{i\sigma}(x)|^2 - 1 \right]$

\nwarrow Lagrange multipliers.

$$\frac{\delta E_{HF}}{\delta \phi_i} = 0 \Rightarrow \epsilon_{i\sigma} \phi_{i\sigma}(x) = \left[-\nabla^2 - \frac{Ze}{|x|} \right] \phi_{i\sigma}(x)$$

Hartree: Coulomb field of other e^-

$$+ \sum_{j \neq i} \int d^3y \frac{|\phi_{j\sigma'}(y)|^2}{|\vec{x} - \vec{y}|} \phi_{i\sigma}$$

Exchange

$$+ \sum_{j \neq i} \int d^3y \frac{\phi_{j\sigma'}^*(y) \phi_{j\sigma'}(x) \phi_{i\sigma}(y)}{|\vec{x} - \vec{y}|}$$

\Rightarrow These are N coupled nonlinear eqns.

General statement "Koopmans Theorem": Lagrange multiplier $\epsilon_{i\sigma}$ is energy to remove electron from orbital $i\sigma$ keeping everything else fixed [in real life, everything else never stays fixed]

Convenient choice of basis: eigenfunctions of L^2, L_z

$$\phi_i(\vec{x}) = v_p(|x|) Y_{LM}(\hat{x})$$

$$\hat{L}^2 Y_{LM} = L(L+1) Y_{LM}$$

$$L_z Y_{LM} = m Y_{LM}$$

$$\sum_{m=-L}^L Y_{LM}^*(\vec{x}) Y_{LM}(\vec{y}) = (P_L(\hat{x} \cdot \hat{y})) \frac{2L+1}{4\pi}$$

$$P_L(1) = 1$$

$$\int d^2\hat{x} |Y_{LM}(\hat{x})|^2 = 1$$

Shell: set of $(2L+1)$ orbitals, same n , same U_n^L .

Filled shell: when all $(2L+1)$ orbs are occupied.

Nb has meaning only within HF picture (but this is not so far from reality)

HF ~~matrix~~ ^{energy} elts in ∞ new basis

$$V_{\text{direct}} = \sum_{nn'} \sum_{\substack{LL' \\ mm'}} \int d^3x d^3y \frac{|U_n^L(x)|^2 |U_{n'}^{L'}(y)|^2 |Y_{Lm}(x)|^2 |Y_{L'm'}(y)|^2}{|\vec{x} - \vec{y}|}$$

For Suppose one of n, n' (say n') com to filled shell.

Sum over m' , $Y_{L'm'} \rightarrow \frac{2L'+1}{4\pi} \Rightarrow$

$$V_{\text{direct}}^{\text{at least 1 filled}} = \sum_{\substack{nL \\ m}} \sum_{\substack{n'L' \\ m'}}^{\text{filled}} \frac{(2L'+1)}{4\pi} \int x^2 dx y^2 dy d^3x \\ \times \int d^3x d^3y \frac{|U_n^L(x)|^2 |U_{n'}^{L'}(y)|^2 |Y_{Lm}(x)|^2}{|\vec{x} - \vec{y}|}$$

But then $\int d^3y \frac{1}{|\vec{x} - \vec{y}|}$ is indep of direction of x

\Rightarrow orthonormality of $Y_{Lm} \Rightarrow$

$$V_{\text{dir}}^{\text{filled}} = \sum_{\substack{nL \\ m}} \sum_{\substack{n'L' \\ m'}}^{\text{filled}} (2L'+1) \int d^3x d^3y \frac{|U_n^L(x)|^2 |U_{n'}^{L'}(y)|^2}{|\vec{x} - \vec{y}|}$$

occ orbitals in shell L'

\Rightarrow Direct interaction between filled shell + ^{part filled} other shell indep of which orbitals are occ in part filled
Dep only on mean charge dens

Exchange

E-5

$$U^{ex} = \sum_{nL} \sum_{m \rightarrow m'} \int d^3x d^3y \frac{U_{nL}^*(x) U_{nL}(y) U_{n'L'}^*(y) U_{n'L'}(x)}{|\vec{x} - \vec{y}|}$$

$$\times \sum_{m m'} Y_{Lm}^*(\vec{x}) Y_{Lm}(\vec{y}) Y_{L'm'}^*(\vec{y}) Y_{L'm'}(\vec{x})$$

For filled shell: $\sum_{m'=-L'}^{L'} Y_{L'm'}^*(\vec{y}) Y_{L'm'}(\vec{x}) = \frac{2L'+1}{4\pi} P_L(\vec{x} \cdot \vec{y})$

$$\Rightarrow U_{\text{filled}}^{ex} = \sum_{nL} \sum_{n'L'} \frac{2L'+1}{4\pi} \sum_m \int x^2 dx y^2 dy U_{nL}^*(x) U_{nL}(y) U_{n'L'}^*(y) U_{n'L'}(x)$$

$$\times \int d^2\vec{x} d^2\vec{y} \frac{Y_{Lm}^*(\vec{x}) Y_{Lm}(\vec{y}) P_L(\vec{x} \cdot \vec{y})}{|\vec{x} - \vec{y}|}$$

- everything in this eq is invariant under simul. rotations of \vec{x}, \vec{y} exc.

$$\boxed{\sum_m Y_{Lm}^*(\vec{x}) Y_{Lm}(\vec{y})} \Rightarrow \text{must pull out rotationally invariant part of this term}$$

: same as if sum over all m
+ mult by $M/2L+1$

$$\Rightarrow U_{\text{filled}}^{ex} = \sum_{nL} \sum_{n'L'} \frac{(2L'+1)M_L}{(4\pi)^2} \int d^3x d^3y U U U U$$

$$\times \frac{P_{L'}(\vec{x} \cdot \vec{y}) P_L(\vec{x} \cdot \vec{y})}{|\vec{x} - \vec{y}|}$$

Summary: Int bet. filled, part filled shells indep. of everything but "sphericalized charge density" in each shell:

\Rightarrow Cant give L or S dependence

* Widely made assumption - useful for thinking purposes but not highly accurate.

modification of filled shell wave functions due to interaction w/ part filled shell is negligible \Rightarrow int between part filled (d) + filled shells is linear in # of d-electrons

$$\Rightarrow E_{HF}^{Approx} [Filled\ Shell, N_d, L, S] = E_0 + N_d \epsilon_d + d-d\ int [L, S, \bar{n}]$$

ϵ_d involves int w/ filled shells

Probably safer: assume also contrib to nonlinear dep. of E on N_d from these ints
Get by ~~LDA~~ DFT or..

Now look at E_{dd} in detail. Dep on N_d , + on "configuration" (L, S values)

- Many states:

$N_d = 1$	10 states	$[5P, 5D]$
$N_d = 2$	30 triplet	$[5 \times 4/2 \times 3]$
	15 singlet	$5 + 5 \times 4/2$

↑ same orb ↘ diff orb

For given N_d . Classify states by total S_z , total L_z

$\therefore [H, L] = [H, S] = 0$, write H in this basis \Rightarrow nearly diagonal.

\Rightarrow Applied group theory problem of Slater, Racah

Consider interactions within same shell:

$$U_{LL}^{direct} = 2 \sum_{\substack{mm' \\ \sigma\sigma'}} \int_0^\infty x^2 dx \int_0^x y^2 dy |U_L(x)|^2 |U_L(y)|^2 \\ \times \int d^2\hat{x} d^2\hat{y} \frac{|Y_{Lm}(\hat{x})|^2 |Y_{Lm'}(\hat{y})|^2}{|\hat{x} - \hat{y}|}$$

$$U_{LL}^{exch} = 2 \sum_{\substack{mm' \\ \sigma\sigma'}} \delta_{\sigma\sigma'} \int_0^\infty x^2 dx \int_0^x y^2 dy |U_L(x)|^2 |U_L(y)|^2 \\ \times \int d^2\hat{x} d^2\hat{y} \frac{Y_{Lm}^*(\hat{x}) Y_{Lm}(\hat{y}) Y_{Lm'}^*(\hat{y}) Y_{Lm'}(\hat{x})}{|\hat{x} - \hat{y}|}$$

Note: radial parts same for both, ~~angular parts~~ direct + exch
∴ deal w/ same shell

Consider angular int. $x > y \Rightarrow \frac{1}{|\hat{x} - \hat{y}|} = \sum_K \frac{y^K}{x^{K+1}} P_K(\hat{x} \cdot \hat{y})$
 $= \sum_K \frac{y^K}{x^{K+1}} \sum_{m=-K}^K \frac{4\pi}{2K+1} Y_{Km}^*(\hat{x}) Y_{Km}(\hat{y})$

⇒ direct: need term in $[Y_{Lm}^*(x) Y_{Lm}(x)] Y_{K m_H}^*(x)$
which transforms as singlet under rot. of x

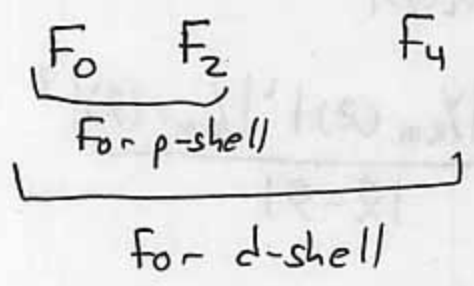
- what K can I get to by adding Y_L and adjoint Y_L^*

Answer: $2L, 2L-2, \dots, 0$

• Exch: $Y_{Lm}^*(\hat{x}) Y_{Lm'}(\hat{x}) Y_{K m_H}^*$; similar.

⇒ All Coulomb matrix elts are of

⇒ need radial integrals



consistency w/ Slater def.

$$F_k^L = 4 \int_0^\infty x^2 dx \int_0^x y^2 dy \frac{|U_L(x)|^2 |U_L(y)|^2}{x^{k+1}}$$

$$= 4 \int_0^\infty x^4 dx |U_L(x)|^2 \int_0^1 z^{k+1} dz U_L(zx)$$

Recall F has dimension of energy

Recall: must use optimized radial wave fns.

* Slater defines: E_{av} : energy of sphericalized charge dist: what you would get if you avg above expr. for E over all m_1, m_2

"center of gravity of multiplet"

For p: $E_{av} = F_0' - \frac{2}{25} F_2'$ \times # of distinct pairs

d: $E_{av} = F_0^2 - \frac{2}{63} F_2^2 - \frac{2}{63} F_4^2$

* Slater gives: energies ~~as~~ for all configurations in terms of E_{av} + F's.

You should think: E_{av} : not so well known (int w/ filled shells etc). Rest of energy: effect of pairwise d-d interactions. Form, presence of pairs F_0, F_2, F_4 follows from group theory. Values: HF estimates

Note empirical: higher ~~cent~~ ^{energy states}: energy ests less good. CI more imp't as go up.

Note Values of parms depend on HF wave functions which depend on ionization state. (or, empirically dep. on ionization state)
 HF estimates: Typically, 20-50% above empirical estimates

Some examples

Some #s: Fe [HF] $3p^6 3d^8$ configs. $F_0^{3d3d} = 1.4 \text{ Ry}$

1 Ratio: $F_2/F_4 \approx 0.65$. V. small variation

$F_2 = 0.6 \text{ Ry}$
 $F_4 = -0.4 \text{ Ry}$

Typical rule of thumb (will see indications later)
 F_0 & E_{av} strongly (factor of 2 or more) changed by solid state effects ("screening")
 F_2, F_4 ~~rather~~ (more precisely, multiplet splittings at fixed N)
 much less affected

Some examples (many more in Slater's book)

Oxygen p-shell $[1s^2 2p^2 2p^{4p}]$

$N_p = 1$ $L=1$ $S=1/2$ $9 \times (3 \text{ orb}, 3 \text{ spin})$ ϵ_p^1

$N_p = 2$ 3P $[L=1, S=1]$ $E_{av}^{(2)} - \frac{3}{25} F_2$ $9 \times$

1D $[L=2, S=0]$ $E_{av}^{(2)} + \frac{3}{25} F_2$ $5 \times$

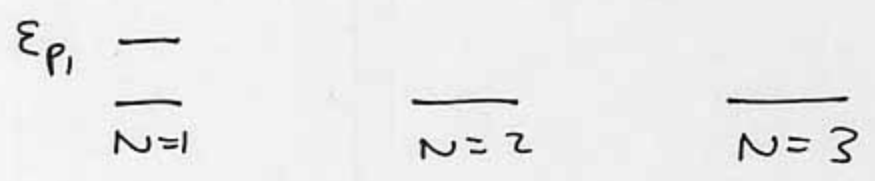
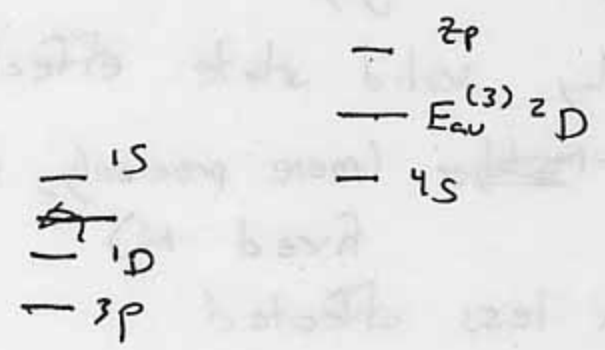
1S $[L=0, S=0]$ $E_{av}^{(2)} + \frac{12}{25} F_2$ $1 \times$

$N_p = 3$ 4S $[L=0, S=3/2]$ $E_{av}^{(3)} - \frac{9}{25} F_2$ $4 \times$

2D $[L=2, S=1/2]$ E_{av} $1 \times$

2P $[L=1, S=1/2]$ $E_{av} + \frac{6}{25} F_2$ $6 \times$

Pictures



Relation to simple notations

Hunds Coupling: $N_p = 2$: Triplet lowest: $\frac{6}{25} F_2$ to 1st orb
 $N_p = 3$ $3/2$ lowest $\frac{9}{25} F_2$

U : extra energy to charge: 2 defs: avg ϵ_i of lowest

1 2 (E-10)

$$U: E^{N_p=2} + E^{N_p=0} - 2 E^{N_p=1}$$

$$= \begin{bmatrix} E_{av}^{(2)} \\ E_{av} \end{bmatrix} - 2 \epsilon_p' \begin{pmatrix} -\frac{3}{25} F_2 \\ +\frac{3}{25} F_2 \\ +\frac{13}{25} F_2 \end{pmatrix}$$

$$\Rightarrow \begin{matrix} 1 & 2 & 3 \\ E^{N_p=3} & + E^{N_p=1} & - 2 E^{N_p=2} \end{matrix} \Rightarrow \begin{matrix} 2 \\ 3 \end{matrix} E_{av} \quad [3 \text{ pairs vs } 2 \times 1]$$

HF: $E_{av}^{(2)} = 2 \epsilon_p' + F_0' - \frac{2}{25} F_2'$ - all F's $\sim R^4 / \text{several}$

Next point: hole picture: quantum #s for removed e^- from filled shell same as g #s for adding to empty. If measure all energies from filled shell ϵ_f , formulas exactly same.

d electrons

$N_d = 1$	$^2 D [L=2, s=1/2]$	E_d'
$N_d = 2$	$^3 F [L=3, s=1]$	$E_{av}^d - \frac{58}{441} F_2 + \frac{5}{441} F_4$
	$^3 P [L=1, s=1]$	$E^{dov} + \frac{77}{441} F_2 - \frac{70}{441} F_4$
	$^1 G [L=4, s=0]$	$E^{dcv} + \frac{50}{441} F_2 + \frac{15}{441} F_4$
	$^1 D [L=2, s=0]$	$E^{dcv} + \frac{-13}{441} F_2 + \frac{50}{441} F_4$
	$^1 S [L=0, s=0]$	$E^{dcv} + \frac{140}{441} F_2 + \frac{140}{441} F_4$

$$E_{dcv} = F_0^2 - \frac{2}{63} F_2^2 - \frac{2}{63} F_4^2$$

Again Hund's coupling: Lowest $N_d=2$: $S=1$ $L=3$

Some #s

Ti $4s^0 3d^n$

	d^1	d^2	d^3	
E^{cv}	3.5	1.6	0.7	[Ry]
F^2	-	0.45	0.35	[Ry]

Empirical #

↪ charge of size of HF orbital

Multiplet en [eV]

\bar{E} [eV]	3F	3P	1G	1D	1S
	21	22.2	22.6	22	25

⇒ E_{d^0} not avail. d^1, d^2, d^3 ⇒ $U = 13.6 eV \approx 1 Ry$
 $E_d \approx 2.8 Ry$

DP E_d : plausible: 3d sits $\sim 5 \text{ \AA}$ from nucleus · charge 3. Exchange, centrif barr. \approx compensate

Hunds effects: probably not so important. J_H : 1eV
 This state is $L=3$ but ligand field will mix up L's; ⇒ effect probably smaller

Mn: empirical E^{cv}

not avail

	d^6	d^5	d^4	
F_2	.5	.6	.7	[Ry]

d^5 Many States: mostly high spin

	6S	4G	4F	4D	4P	2I	2H ...	2S
	-5.24	-26/4	-0.03	-1.38	.18			

- 6S
- 4G
- 4F
- 4D

⇒ lowest | spin flip energy: -3eV

simple process $\approx 4eV$

Note here are v. far from filled shell

d^4	5D	3H	3G	$^3F^1$	$^3F^2$	3D	$^3P^1$	$^3P^2$	$^3F^2$	1T	$^1G^1$	$^1G^2$	1F	1d	3d	1s_1	1s_2
$E[eV]$	-3.7	-1.3	-0.7	2.	-0.14	.23	1.1	.5	-0.14	-0.1	2.5	1.3	1.8	5.1	-1.4	7.3	2.6

d^4 manifold: spread over ~ 10 eV.

Low states: high spin. 3H 3D 3G
 -1.3 -0.7 1.4 ... \Rightarrow Hund's en (if can go into low-lying states)

d^3	4F	4P	2H	2G	2F	$^2D^1$	$^2D^2$	$2P$
	-2.7	-0.4	0.1	-0.7	2.4	4	1.5	0.1

+ "U"

$\Rightarrow J \sim -2$

N_1	8d	6d	4d	2d
	0.6	0.7	0.8	

8d : just like d^2 - interp F_2 for holes

3F	3P	1G	1D	1S
-1.2	0.7	1.3	0.2	5

~ 1.5 eV Hund's en \rightarrow $^3F - ^1D$

Fundamental Question: how much of this multiplet stuff is important for behavior of actual solids

- "U": energy to change valence
 - "J": Hund's coupling - nature of low lying multiplets
- ? How changed by presence of other ions in solid?

U:

E12.5

Fundamental definition: ~~average of multi.~~
part of energy dep. only on N.

⇒ diff of average energies of multiplets $E = N\epsilon_d + \frac{N(N-1)U}{2}$

$$E_{N+1} + E_{N-1} - 2E_N = \frac{(N+1)N - 2N(N-1) + (N-1)(N-2)}{2} U = U$$

However: in most cases, multiplets are spread over too wide a range ⇒ center differences not useful 3

Typically ~ U ≈ 15-20 eV

- Better to consider energy differences between low-lying multiplets. ~~Typically smaller~~
- Better to do this case-by-case

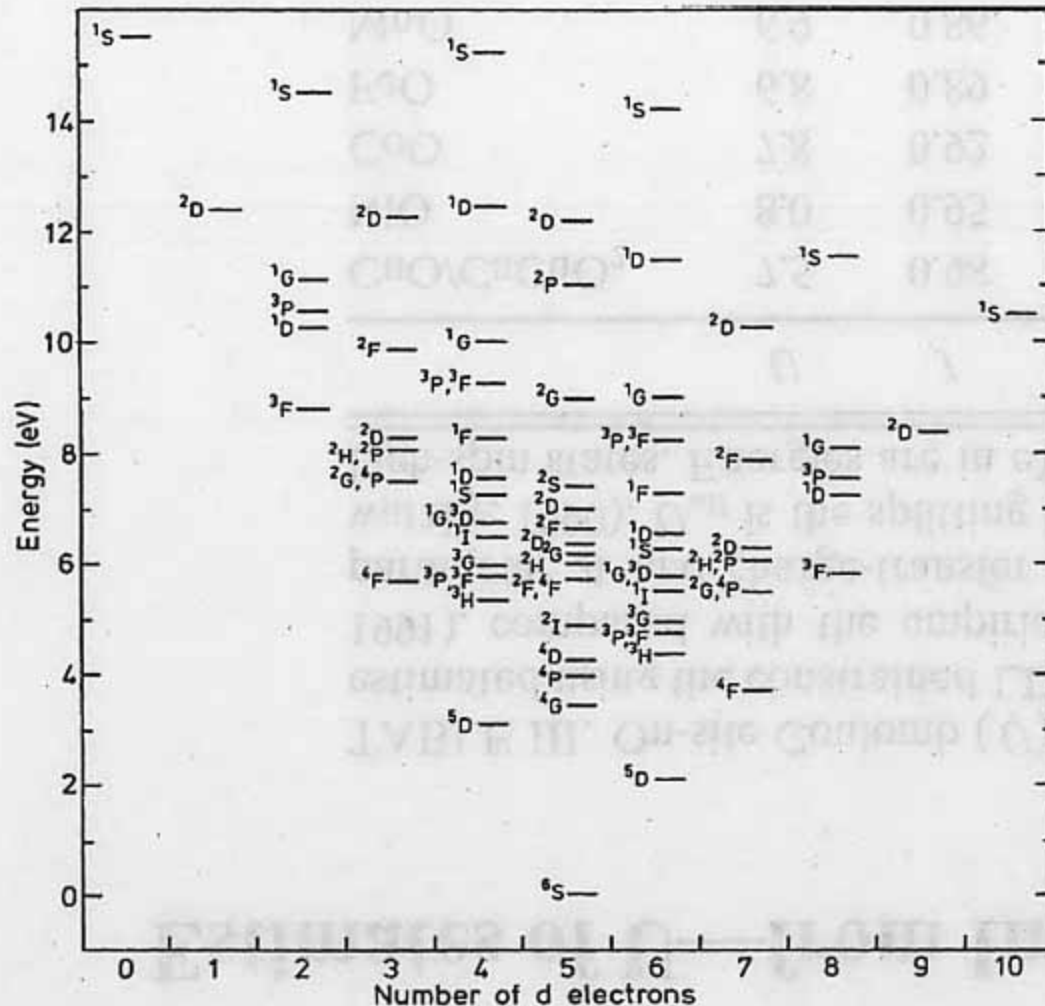
J: I prefer: energy difference between lowest energy (max spin) next lowest (max-1 spin).

then changed
of other
presence

energy to change values
of multiplets
couple - value of
multiplets

Mn energy levels—Ag host

E12.5



Energy levels for single Mn in Ag host.

S,D,..refer to orbital symmetry of many electron wave function; superscript numerals give value of $(2S_{tot}+1)$ Free-ion F2,F4 and adjusted U

Key points:

- High spin states strongly favored
- In solid environment 'U' not so big

From van der Marel, Westra, Sawatzky and Hillebrecht, PRB 31 1936 (1985).

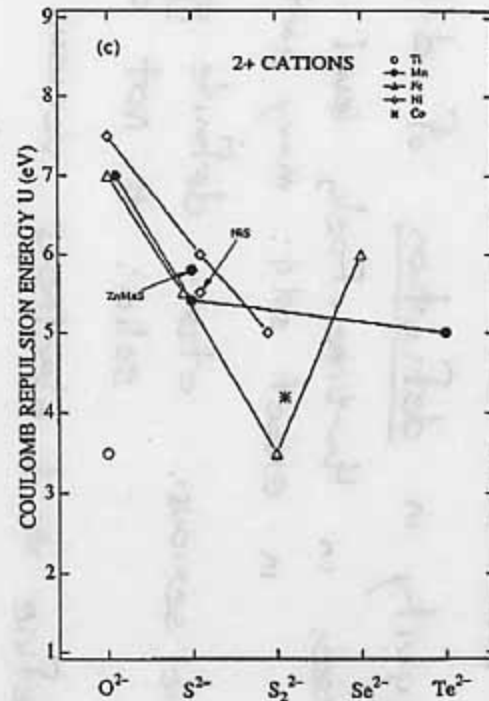
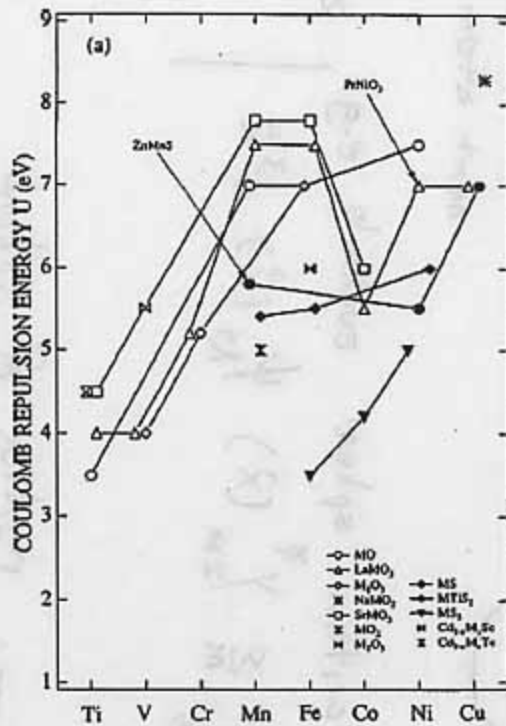
Fig. 2

Estimates of U —from Imada et al RMP

TABLE III. On-site Coulomb (U) and exchange (J) energies estimated using the constrained LDA method (Anisimov *et al.*, 1991), compared with the empirical estimates for the Racah parameter A and charge-transfer energy Δ (Zaanen and Sawatzky, 1990). U_{eff} is the splitting between the d^{n-1} and d^{n+1} high-spin states. Energies are in eV.

	U	J	U_{eff}	A	Δ
CuO/CaCuO ₂	7.5	0.98	6.5	4.0	4.0
NiO	8.0	0.95	7.1	(6.0)	(4.92)
CoO	7.8	0.92	6.9	5.02	5.53
FeO	6.8	0.89	5.9	4.46	6.21
MnO	6.9	0.86	10.3	5.43	8.23
VO	6.7	0.81	5.9	3.54	10.47
TiO	6.6	0.78	5.8	3.02	10.01

U estimated from photoemission xperiments (Imada et al RMP)



E12.5

~~Renormaliza~~

Solid state effects:

① Hybridization: electron in d orbital can go into other states on solid.

⇒ As saw in Anderson model, levels get width

⇒ ambiguity in definition of d-levels

[seen before: in Hartree-Fock, level unambiguous, in exact soln: many particle states]

Here more serious: atom: definite quantum #s N, L
solid: # not conserved.

To define # d electrons, various methods

Simplest: "atomic sphere approx"



Draw sphere, some radius, (half-way to next atom?)

Then within sphere evaluate e.g. 2

$$\sum_{\text{levels } N} \left| \int_0^{R_s} \sum_{\text{levels } N} \sum_m Y_{2m}^*(\vec{x}) \psi_N(\vec{x}) d^3x \right|^2$$
 Projected d charge

• Ambiguities: radius of sphere
Potential not sph & sym (sometimes approx. as)

• Difficult to vary charge by integer amounts
Typically: estimate "U" by putting making small variations

Specifically put, in sphere

$$\delta \mu \sum_{m0} |Y_{2m}\rangle \langle Y_{2m}|$$

chemical potential

to force density variation

Projector onto states m

- typically alternate from cell to cell (ch. neutrality)
 $\Downarrow \delta n$

\Rightarrow work out $\frac{\delta^2 E}{\delta n^2}$; get rid of $\frac{\delta^2 T}{\delta n^2}$

Interpret remainder as U . - Typ.

Note: - includes "relaxation" - are finding lowest energy configuration. Different result if don't let surrounding relax.

Typically: in $3d$ oxides: $U \sim 10$ eV
 Metals: U ~~is~~ ~ 1 eV

Big ? - How fast is relaxation?

If it can't happen as fast

as U^{-1} , then is it a reasonable thing to do?