Electronic structure of correlated electron systems

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Influence of polarizability on the crystal structure

- Ionic compounds are often cubic to maximize the Madelung energy i.e. negative charged ions surrounded by positive ones and visa versa
- Strongly polarizable ions could contribute with dipole –monopole interactions provided that they are asymmetrically coordinated as in layered compounds like TiS2 or MoS2
- They consist of a highly charged positive cation layer sandwiched between two polarizable anion layers.

	R _M (A)	F	C1	Br	I
Ba2+	1.36	C1	C1,C23	C23	C23
Pb2+	1.18	C1	C23	C23	C6*
Sr2+	1.16	C1	C1	C53	-
	1.00	C1	C35	C35	C6*
	0.95	C1	C19*	C19*	C6*
	0.82	C4	C19*	C6*	C6*
2+	0.79	-	C6*	C6* 🥌	C6*
re2+	0.77	C4	C19*	C19*	C6*
$2n^{2+}$	0.75	C4	C19*	C19*	C6*
L02+	0.74	C4	C19*	C19*	C6*
^{Mg} 2+	0.72	C4	C19*	C6*	C6*
וא	0.70	C4	C19*	C19*	C19*
	R _M (A)	0	S	Se	Te
Th_{4+}^{4+}	1.00	C1	C23	C23	-
Zr	0.72	C1	C6*	C6*	C6+
Hf₄+	0.71	C1	C6*	C6*	C6*
Sn ₄₊	0.69	C5	C6*	📕 C6*	-
Pt ₄₊	0.63	C6*	C6*	C6*	C6*
Ti	0.61	C4	C6*	C6*	C6*

These form layered Structures because of The large polarizability Of the anions

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> In the ionic model the lattice energy is given by $E = -NAZ^2 e^{2} / R + NBR^{-n}$.

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This kind of polarization reduction of U will however bring with it a large repulsive interaction Between same charge particles on i and i+,-1 i.e. a second nearest neighbor interaction

$$H_{\text{int}} = (U - 2zP)\sum_{i} n_{i\uparrow}n_{i\downarrow} + 2P\sum_{l,i}n_{l}n_{l+2a_{i}}$$

So the reduction of the Hubbard U in a polarizable medium like this introduces a strong Next nn repulsive interaction. This changes our model!!

For a different geometry actually the intersite interaction can also be strongly reduced perhaps even Attractive (Fe Pnictides)

> Jeroen van den Brink Thesis U of Groningen 1997 Van den Brink et al PRL 75, 4658 (1995) J. van den Brink et al EPL 50, 447 (2000)

In general we have to include the fields produced by other induced dipoles

- Consider again the interaction between two poiint charges one at r=0 and the other at r=R both on an atomic site.
- The electrostatic potential energy is given by

$$V(R) = \frac{e^2}{R} - \frac{1}{2} \sum_{i} \vec{d}_i \bullet \vec{p}_i = \frac{e^2}{R} - 2E_p(R)$$

 Where d_i is the field due to the two charges at r-0 and r=R and p is the net induced dipole moment at site i.

$$p_i^{\mu} = \alpha_i d_i^{\mu} + \sum_{\gamma} \sum_{j, j \neq i} M_{ij}^{\mu\gamma} p_j^{\gamma}$$
, with $\mu, \gamma = x, y, z$.

The elements of the matrix representing the dipole dipole interaction are given by

$$M_{ij}^{\mu\gamma} = \alpha_i (3l_{ij}^{\mu} \ l_{ij}^{\gamma} \ |l_{ij}|^{-5} - |l_{ij}|^{-3} \ \delta_{\mu\gamma}),$$

where $l_{ij} = l_i - l_j$ is the vector connecting the two dipoles. The solution c_i this set of equations gives the exact effective potential for the electrons.

For a 3D system the equations above reduce to the well know Clausius-Mossotti (C.-M.) result when the summations are replaced by integrations:



FIG. 5. The effective Coulomb interaction on different organic molecules. The carbon polarizability is 0.56 Å³. The full line represents the bare Coulomb repulsion. The dashed lines are guides for the eye.

Note short range interactions are reduced " screened " and intermediate range interactions are enhanced or antiscreened -quite opposite to conventional wisdom in solid state physics

Jeroen van den Brink Thesis U of Groningen 1997



FIG. 1. The polarization energy $2E_p$ as a function of separation between the electrons in one dimension. The lattice spacing is taken to be unity. The dashed line represents $2RE_p$ for $\alpha = 0.15$. Negative values of E_p represent screening and positive values anti-screening.

Effective coulomb interaction in low dimensions

- In low dimensions the exact results for a lattice of polarizable atoms results in a flattening out of the R dependence of the coulomb interactions.
- Recall that if there was no R dependence then mean field theory is exact!!
- This type of screening results in a strong decrease of electron correlations and also a break down of the Hubbard model

Now for a quantum mechanical model including non uniform polarizability

Meinders et al PRB 52, 2484 (1995) Van den Brink et al PRL 75, 4658 (1995) I will do this with an example recently worked out for the structure of the Fe pnictide superconductors

arXiv:08110214v Electronic polarons and bipolarons in Fe-based superconductors Mona Berciu et al

The New superconductors LaOFeAs as an example



Figure 1. Crystal structures of LaFeAsO (left) and BaFe₂As₂ (right)

The FeAs layer with Fe tetrahedrally coordinated by As



Both Fe and As layers are squares but relatively rotated by 45 degrees. i.e. the As are above and alternatively below the centers of the Fe squares

The model includes

- The nearest and next nearest neighbor hoping between the Fe centers in an assumed single band
- The on site coulomb repulsion of two electrons or holes on Fe
- The possible excitation of an As electron from occupied 4p to unoccupied 5s as a model for the polarizability
- An effective coupling of the As 4p and 5s due to a charge on Fe described by g

$$\mathcal{H}_{\rm Fe} = -\sum_{i,j,\sigma} \left(t_{ij} c_{i,\sigma}^{\dagger} c_{j,\sigma} + h.c. \right) + U_H \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$

$$\mathcal{H}_{As} = \Omega \sum_{i,\lambda,\sigma} p_{i,\lambda,\sigma}^{\dagger} p_{i,\lambda,\sigma}$$
, 5-10 eV i.e. high energy

$$\mathcal{H}_{\text{int}} = g \sum_{i,\sigma} \hat{n}_i \left[s_{i,\sigma}^{\dagger} \left(-\sin\theta p_{i,2,\sigma} + \cos\theta p_{i,3,\sigma} \right) \right. \\ \left. + s_{i-y,\sigma}^{\dagger} \left(-\sin\theta p_{i-y,1,\sigma} + \cos\theta p_{i-y,3,\sigma} \right) \right. \\ \left. + s_{i-x-y,\sigma}^{\dagger} \left(\sin\theta p_{i-x-y,2,\sigma} + \cos\theta p_{i-x-y,3,\sigma} \right) \right. \\ \left. + s_{i-x,\sigma}^{\dagger} \left(\sin\theta p_{i-x,1,\sigma} + \cos\theta p_{i-x,3,\sigma} \right) + h.c. \right] (3)$$



Because Omega is a high energy we can use perturbation theory in t as the smallest We assume only one particle so that U is not active The electronic Polaron eigen energies are given by

$$E_P(\vec{k}) = 4(\Omega - \sqrt{\Omega^2 + 4g^2}) + \epsilon_{\text{eff}}(\vec{k}).$$

$$\epsilon_{\text{eff}}(\vec{k}) = -2t_{\text{eff}} \left[\cos(k_x a) + \cos(k_y a) \right] - 4t'_{\text{eff}} \cos(k_x a) \cos(k_y a)$$

We use the know electronic polarizability of As to determine g For small g i.e. in the linear regime. g=2.5 eV for α = 10 cubic A

The Motion of a single quasi particle These move like electronic polarons



i.e. the overlap integral of the polarization clouds



FIG. 3: (a) $t_{\rm eff}/t$ and (b) $t'_{\rm eff}/t'$ vs. Ω , for a polarizability $\alpha_p = 7,10$ and $12\mathring{A}^3$. The dots show the values used here.

The effective polaron mass is simply t/teff =2.2 this is light compared to conventional lattice polaron masses

Closer to real systems

- We use mainly 3d transition metal compounds as examples
- More than only spin and charge play a role here
- Orbital degrees of freedom in partly occupied d orbitals interact with spin and charge degrees of freedom
- We have to deal with multi band systems

Interplay between spin, charge, lattice and orbital degrees of freedom

- In the large U limit where polarity fluctuations are strongly suppressed in the low energy scale physics THE PHYSICS OF ATOMS AND IONS IN LOWER THAN SPHERICAL SYMMETRY PLAYS AN IMPORTANT ROLE
- We now deal with crystal and ligand field splittings, Hund's rule coupling, spin orbit coupling, superexchange interactions, and the role of orbital degeneracy

Some typical coordinations of TM ions

Octahedral coordination Red=TM ion White =Anion like O2-



Tetrahedral coordination Red = TM White =anion like O2-



As in NiO

As in LiFeAs

Free atom d wave function $\varphi_d(freeion) = R_{n,l}(r)Y_l^m(\theta,\phi) = R_{n,l}(r)p_l(\cos\theta)e^{im\phi}$

For d states I=-2; m=-2,-1,0,1,2; and for 3d n=3

With spin orbit coupling j=l+s or j=l-s s=spin =1/2 Spin Orbit $H = \lambda \vec{l} \cdot \vec{s}$ $\lambda \sim 40$ -100 meV for 3d and about 3 times larger for 4d For 3d's the orbital angular momentum is often quenched because $\lambda <<$ crystal field Real d orbitals in Octahedral coordination eg's have lobes pointing to anion forming sigma bonds and the t2g's have lobes pointing between the anions with pi bonds

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Two kinds of d orbitals generally used

$$d_{xy}, d_{xz}, d_{yz} \rightarrow t_{2g}$$
$$d_{x^2 - y^2}, d_{3z^2 - r^2} \rightarrow e_g$$

$$d_{xy} = \frac{1}{i\sqrt{2}} ([2,2] - [2,-2])$$

$$d_{3z^2 - r^2} = [2,0]$$

$$d_{x^2 - y^2} = \frac{1}{\sqrt{2}} ([2,-2] + [2,2])$$

$$d_{xz} = \frac{1}{i\sqrt{2}} ([2,1] - [2,-1])$$

All have 0 z component Of angular momentum

In cubic symmetry the two eg's and 3 t2gs are 2 and 3 fold degenerate respectively. The spin orbit coupling does not mix the eg orbitals to first order but it does mix the t2g's which then get split into a doublet and a singlet in cubic symmetry

Crystal and ligand field splitting

Many of the interesting transition metal compounds are quite ionic in nature consisting of negative anions like O (formally2-) and positive TM ions. Part of the cohesive energy is due to Madelung potentials produced by such an ionic lattice. Recall that O2- is closed shell with 6 2p electrons quite strongly bound to the O.

Expanding the potential produced by surrounding ions close to a central TM ion produced a different potential for the eg and t2g orbitals resulting in an energy splitting. The point charge contribution is:

$$V = \sum_{n,m} A_n^m r^n P_n^{|m|}(\cos \theta) e^{im\phi}$$
 The resulting energy shift of the d orbitals is;

 $\Delta E = \left\langle d_i \left| V \right| d_i \right\rangle$ In first order perturbation theory and the di are the eg and t2g wave functions defined above. Only terms with m=0,4 and n=4 will contribute

In cubic symmetry this splits the eg and t2g states by typically 0.5 to 1 eV with in Octahedral coordination the t2g energy lower than the eg energy

There is another larger contribution from covalency or the virtual hoping between the O 2p orbitals and the TM d orbitals. Since the eg orbitals are directed to O these hoping integrals will be larger than those for the t2g orbitals



Often about 1-2eV In Oxides

Density functional band theory provides good reliable values for the total crystal and Ligand field splitting even though the band structure may be incorrect.



Note the rather broad Cl 2p bands And the very narrow Ni 3d bands Split into eg and t2g. Note also the Crystal field spliting of about 1.5eV. Note also that DFT (LDA) predicts a metal for NiCl2 while it is a pale yellow magnetic insulator. Note also the large gap between Cl 2p band and the Ni 4s,4p bands With the 3d's in the gap. This is a typical case for TM compounds

Model one electron parameters



Hoping integrals

 Good estimates of the hoping integrals can be obtained from a tight binding fit to DFT band structure calculations. This even though one may be in a high U limit. More general multiband model Hamiltonian one often neglects direct Tm-Tm hoping because of large interatomic distances Intervened often by anions. Effective d band widths appear via Indirect hoping via anions

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Upp is often neglected because of effectively full or nearly full anion p bands. This approximation breaks down if the density of holes in the anion valence band becomes large as can happen in for example overdoped High Tc cuprates

Two new complications

- d(n) multiplets determined by Slater atomic integrals or Racah parameters A,B,C for d electrons. These determine Hund's rules and magnetic moments
- d-O(2p) hybridization (d-p hoping int.) and the O(2p)-O(2p) hoping (O 2p band width) determine crystal field splitting, superexchange, super transferred hyperfine fields etc.

The d-d coulomb interaction terms contain density -density like integrals, spin dependent exchange integrals and off diagonal coulomb integrals i.e. Where n,n' m,m' are all different. The monopole like coulomb integrals determine the average coulomb interaction between d electrons and basically are what we often call the Hubbard U. This monopole integral is strongly reduced In polarizable surroundings as we discussed above. Other integrals contribute to the multiplet structure dependent on exactly which orbitals and spin states are occupied. There are three relevant coulomb integrals called the Slater integrals;

- F^0 = monopole integral
- F^2 = dipole like integral
- F^4 = quadrupole integral

For TM compounds one often uses Racah Parameters A,B,C with ;

$$A = F_0 - 49F_4;; B = F_2 - 5F_4;; C = 35F_4$$

Where in another convention ; $F_2 = \frac{1}{49}F^2;; F_4 = \frac{1}{448}F^4;; F_0 = F^0$

The B and C Racah parameters are close to the free ion values and can be carried over From tabulated gas phase spectroscopy data. "Moores tables" They are hardly reduced in A polarizable medium since they do not involve changing the number of electrons on an ion.

Reduction of coulomb and exchange in solids

- Recall that U or F0 is strongly reduced in the solid. This is the monopole coulomb integral describing the reduction of interaction of two charges on the same atom
- However the other integrals F2 and F4 and G's do not involve changes of charge but simply changes of the orbital occupations of the electrons so these are not or hardly reduced in solids. The surroundings does not care much if locally the spin is 1 or zero.
- This makes the multiplet structure all the more important!!!!! It can in fact exceed U itself

TABLE 4-5. COULOMB INTEGRALS (J) AND EXCHANGE INTEGRALS (K) OF THE SET $t_{2g}(xz,yz,xy)$ AND $e_g(x^2 - y^2, z^2)$ (Ref. 19) $J(z^2,z^2) = J(x^2 - y^2, x^2 - y^2) = J(xy,xy) = J(xz,xz) = J(yz,yz)$ $= F_0 + 4F_2 + 36F_4$ $J(x^2 - y^2, xz) = J(x^2 - y^2, yz) = J(xy,yz) = J(xy,xz)$ $= J(xz,yz) = F_0 - 2F_2 - 4F_4$ $J(z^2,xz) = J(z^2,yz) = F_0 + 2F_2 - 24F_4$ $J(z^2,xy) = J(z^2,x^2 - y^2) = F_0 - 4F_2 + 6F_4$ $J(x^2 - y^2, xy) = F_0 + 4F_2 - 34F_4$ $K(xy,yz) = K(xy,xz) = K(xz,yz) = K(x^2 - y^2, xz) = K(x^2 - y^2, yz)$ $= 3F_2 + 20F_4$ $K(z^2, x^2 - y^2) = K(z^2,xy) = 4F_2 + 15F_4$ $K(x^2 - y^2, xy) = 35F_4$

TABLE 4-6. VALUES OF THE MATRIX ELEMENTS $(ab|1/r_{12}|cd)$ DIFFERENT FROM ZERO

a	Ь	. C	d	$(ab 1/r_{12} cd)$
$(xz) (yz) (xz) (yz) (z^2) (z^2) (z^2) (x^2 - y^2) (x^2 - y^2) (x^2 - y^2)$	(z ²) (z ²) (xz) (yz) (xy) (xy) (xy) (xz) (xy) (xy)	(xz) (yz) (z^2) (xz) (yz) (xy) (xz) (yz)	$ \begin{vmatrix} (x^2 - y^2) \\ (yz) \\ (xz) \\ (yz) \\ (yz) \\ (yz) \\ (xz) \end{vmatrix} $	$\begin{array}{r} -2 \sqrt{3} F_2 + 10 \sqrt{3} F_4 \\ 2 \sqrt{3} F_2 - 10 \sqrt{3} F_4 \\ \sqrt{3} F_2 - 5 \sqrt{3} F_4 \\ - \sqrt{3} F_2 + 5 \sqrt{3} F_4 \\ \sqrt{3} F_2 - 5 \sqrt{3} F_4 \\ \sqrt{3} F_2 - 5 \sqrt{3} F_4 \\ \sqrt{3} F_2 - 5 \sqrt{3} F_4 \\ 2 \sqrt{3} F_2 - 10 \sqrt{3} F_4 \\ 3F_2 - 15F_4 \\ - 3F_2 + 15F_4 \end{array}$

. . . .

Multiplet structure for free TM atoms rare Earths can be found in the reference

$$E(n, L, S, \lambda) = nI + \frac{1}{2}n(n-1)U_{ave} + U(n, L, S, \lambda)$$
$$U_{ave} = F^{0} + \frac{2}{63}(F^{2} + F^{4}) = F^{0} - \frac{2l}{4l+1}J(d, d)$$
$$J(d, d) = \frac{1}{14}(F^{2} + F^{4})$$

$$C(d,d) = \frac{1}{14} \left(\frac{9}{7}F^2 - \frac{5}{7}F^4\right)$$

 $E(n, Hund) = \alpha_I(n)I + \alpha_{F^0}(n)F^0 + \alpha_J(n)J + \alpha_C(n)C$ $U^{eff} = E(n+1, Hund) + E(n-1, Hund) - 2E(n, Hund)$

$$\alpha_{I}(n) = n;; \alpha_{F^{0}}(n) = \frac{n!}{2};; \alpha_{J}(n) = No - of - parallel - spin - pairs$$

VanderMarel etal PRB 37, 10674 (1988)

VanderMarel etal PRB 37, 10674 (1988)

Table 2.1. Parameters determining the energies of the Hund's Rule ground states in LS coupling for all d occupations and the expression for the d-d gap for those occupations.

state	αI	^α F ⁰	αJ	°c	U ^{eff}
d ⁰ (¹ S)	0	0	0	0	
d ¹ (² D)	1	0	0	0	(F ⁰ -J-C)
$d^{2}(^{3}F)$	2	1	-1	-1	F ⁰ -J+C
d ³ (⁴ F)	3	3	-3	- 1	F ⁰ −J+C
d ⁴ (⁵ D)	4	6	-6	0	F ⁰ -J-C
d ⁵ (⁶ S)	5	10	-10	0	F ⁰ +4J
d ⁶ (⁵ D)	6	15	-10	0	F ⁰ -J-C
$d^{7}(^{4}F)$	- 7	21	-11	- 1	F0-J+C
d ⁸ (³ F)	8	28	-13	-1	F ⁰ -J+C
d ⁹ (² D)	9	36	-16	0	F ⁰ -J-C
$d^{10}(^{1}S)$	10 .	45	-20	0	and the second sec

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Row Parameter		Hartree-Fock	Empirical	
3 <i>d</i>	F	15.31 + 1.50(Z - 21)	1.5 + 0.21(Z - 21)	
	J	0.81 + 0.080(Z - 21)	0.59 + 0.075(Z - 21)	
*	С	0.52J	0.51J	
4d	J	0.59 + 0.056(Z - 39)		
	С	0.50J		
5d	J	0.60 + 0.053(Z - 71)		
	С	0.52J		
4 <i>f</i>	F^{0}	23.8 + 0.93(Z - 57)	6.7 + 0.033(Z - 57)	
	J	0.90 + 0.036Z - 57)	0.69 + 0.014(Z - 57)	
	С	0.50J	0.45J	
51	J	0.66 + 0.035(Z - 89)	0.33 + 0.070(Z - 89	
	С	0.41 <i>J</i>	0.41 <i>J</i>	

TABLE IV. Interpolation formulas for F^0 , J, and C as a function of atomic number Z.

Hunds' rules First the Physics

- Maximize the total spin—spin parallel electrons must be in different spatial orbitals i.e. m values (Pauli) which reduces the Coulomb repulsion
- 2nd Rule then maximize the total orbital angular momentum L. This involves large m quantum numbers and lots of angular lobes and therefore electrons can avoid each other and lower Coulomb repulsion

Hunds' third rule

- < half filled shell J=L-S > half filled shell J=L+S
- Result of spin orbit coupling

$$\mathbf{H}_{so} = \sum_{j} \frac{1}{2m^2 c^2} (\nabla V(r_j) \times p_j) \bullet s_j$$

 Spin orbit results in magnetic anisotropy, g factors different from 2, orbital contribution to the magnetic moment, ---

A little more formal from Slater " Quantum theory of Atomic structure chapter 13 and appendix 20

One electron wave function

 $\mathcal{U}_{n\ell m_{2}}(r, \theta, \phi) = (-1)^{(m_{2} + 1m_{2}l)/2} \frac{(2\ell+1)(\ell-1m_{2}l)!}{(\ell+1m_{2}l)!}$ × Rn (r) P (cos B) e im \$ $)d_{op} = \sum_{i} f_{i} + \sum_{i} (pairs i_{i}) q_{i}$ one electron = $-\nabla_{i}^{2} - \frac{22}{V_{i}}$ gin = 2 -> Multiplets -> Hundsme We need to calculate $\langle ij|g|rt
angle$

Where I, j, r, t label the quantum Numbers of the occupied states and we sum over all the occupied states in the total wave function

Two Types of Integral's Lijlglijt and Lijlgljit For 2 electrons in same shell $i_j|q|_{i_j} \ge \sum_{k=0}^{k} (l_i m_i: l_j m_i) F^k(n_i l_i: n_i l_j)$ F* = R'(ij:ij) - Pirect Coulomb <ijiqiji > = Sims ms.) > b* (kim; kim;) G(ni; h)

 $\frac{1}{V_{12}} = \sum_{k=1}^{\infty} \sum_{\substack{(k+1m) \\ (k+1m) \\ \vdots}}^{\infty} \frac{r_k^{k}}{r_k^{k+1}} P_k^{(cos \Theta_1)} P_k^{(m)} \frac{r_k^{m}}{r_k^{k+1}}$ $x \in \lim(\phi, -\phi_2)$ $\lambda i j | q | r Z 7 = \int (\psi_{i}^{*}(\hat{r}_{i}) \psi_{i}^{*}(\hat{r}_{i}) \frac{1}{|r_{i} - r_{i}|} \psi_{i}^{*}(\hat{r}_{i}) \psi_{i}^{*}(\hat{r}_{i})$ 12. 22. $s_{i}^{c} = s_{i}^{c}$ $s_{i}^{c} = s_{i}^{c}$ $= \sum_{k=0}^{\infty} \sum_{m_{2}-k}^{k} \frac{(k \cdot lm)!}{(k \cdot lm)!} (-1)^{m_{2}+lm_{2}} + m_{2} + m_{2} + m_{2} + lm_{2} +$ $\times \int \frac{(2l_i+1)(l_i-lm_i)!}{(l_i+(m_i-1)!} \times -\frac{2}{3} \times -\frac{2}{3}$ X S S R (ri) R(r.) R(r) R(r) 2r2 rizzdr, dr X P. (coso,) P. (coso,) P. (coso,) sind, d.O. $\begin{array}{c} X \int P_{e_{1}}(\cos \theta_{1}) P_{e_{1}}(\cos \theta_{2}) P_{e_{1}}(\cos \theta_{2}) \frac{\sin \theta_{1}}{2\pi} d\theta_{2} \\ \times \int e^{i(1-m_{e_{1}}+m_{e_{1}}+m)\theta_{1}} \frac{d\theta_{1}}{2\pi} \times \int e^{i(1-m_{e_{1}}+m_{e_{1}}+m_{e_{1}}+m_{e_{1}}+m_{e_{1}}+m_{e_{1}}+m_{e_{1}}+m_{e_{1}}+m_{e_{1}}+m_{e_{1}}+m_{e_{1}}+m_{e_{2}}+m_{e_{1}$

From orthogonahity Sp m = m - m = -m + m = m me + me = me + me (Conserv. 17) 6 we use Ck (lin; l'm') = (-1) (m+1m1+m'+1m1+(m-m')+1m-m'1)/2 $\times \int \frac{(k - lm - m'l)!}{(k + lm - m'l)!} \int \frac{(2l + l)(l - lml)!}{(l + lml)!} \int \frac{(2l' + l)(l' - lm'l)!}{(l' + lm'l)!}$ X 1 (Pe (a) P (a) P (a da Tabulated + Appendix 20 <injale IT = Sims, ins,) Sling, ins,) Sling, ing, + ing, me, + me, x Z c* (lime: l, mer) c* (ly me: ly me) Rig + () Highest possible value of k=ltl' i.e. litly or let.

Nultiplet structure of 3d TM free atoms

VanderMarel etal PRB 37, 10674 (1988)



Note the high energy scale Note also the lowest energy state for each case i.e. Hunds Rule;