Multiplet Analysis

B. Delley

Paul Scherrer Institute, CMT,
Villigen PSI, Switzerland

Talk at Zuoz Summer School 2015 Aug. 19.

outline

- intro, quantum mechanics perspective of materials

- background on electronic structure

- A) orbital theories

- B) wavefunctions and multiplets

- set of examples

- conclusion

Quantum Mechanics: Particles - Waves

Planck 1900
$\hbar$ light corpuscle

de Broglie 1924
particle wave duality

Heisenberg 1927
$\sigma_{\boldsymbol{x}}, \sigma_{\boldsymbol{P}} \geq \hbar/2$

Schrödinger 1926
wave equation

Scope for this talk: electrons (nuclei) interacting with
photons [XAS,RIXS,XMCD] (neutrons,muons)

QM scale is important for useful materials:
- semiconductors: point defects
- atomic scale processes in chemical reactions
- atomic scale at the very edge: surface, interface, cracks

Quantum Mechanics: Schrödinger Equation

stationary form wave equation for a single particle:

$$\epsilon_k \Psi_k(\mathbf{r}) = \Big(\frac{-\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \Big) \Psi_k(\mathbf{r})$$

$\epsilon_k \ \Psi_k(\mathbf{r})$, a wave function in 3d, orbital

Many electrons: eigenvalue problem involving coupled partial differential equations in 3 coordinates.

General problem with N particles involves $3N$ coupled equations.

$$E_k \Psi_k(\mathbf{r_1}...\mathbf{r_n}) = \sum_i \Big(\frac{-\hbar^2}{2m} \nabla_i^2 + V(\mathbf{r_i}) + \frac{1}{2} \sum_j \frac{e^2}{|\mathbf{r_i} - \mathbf{r_j}|} \Big) \Psi_k(\mathbf{r_1}...\mathbf{r_n})$$

$E_k \ \Psi_k(\mathbf{r_1}...\mathbf{r_n})$ a many-particle wave function, can be expanded as sum of determinants involving orbitals

"The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to

Dirac 1928 equations much too complicated to be soluble."

Branches of Electronic Structure Theory

a) orbital theories: from back of envelope to first principles density functional theory (DFT), band-structure theory.

b) wavefunction theories: for finite size systems, often limited wf expansion, quantum chemistry, MULTIPLET.

c) model hamiltonians: great variety, strict simplification to specific interest like coupling to a particular type of collective mode.

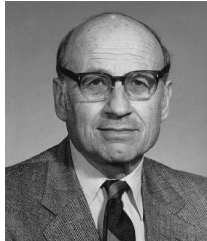a+b) may have minor extensions inspired by model hamiltonians. example LDA+U

from Schrödinger back to single-electron eqn: orbitals

John Slater 1900-1976
HF, LDA, books
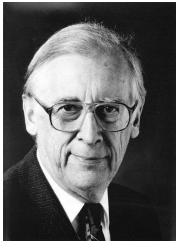
John Pople 1925-2004
NP 1998
UHF (+ Nesbet 1954)
GAUSSIAN

Walter Kohn *1923
NP 1998
1964/65 DFT

orbitals arise by factoring the wavefunction, and –
orbitals arise from single determinant form of approximate QM wavefunction

Further theories range from more crudely described orbitals (example Hückel: just
coefficients) to more elaborate theories involving more than one determinant as
approximate QM wavefunction.

QM and density functional theory

theorem Hohenberg Kohn 1964: the quantum mechanical ground state is a universal functional of the density.

$$E_{gs} = F[\rho] + \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$$

approximations are: Thomas-Fermi-Weizsäcker functionals.

theorem Kohn Sham 1965: define density and kinetic energy in terms of orbitals !

$$E_{gs} = \sum_i \frac{-\hbar^2}{2m}(\nabla\phi_i(\mathbf{r}))^2 + U_{elst}[\rho] + E_{xc}[\rho] + \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$$

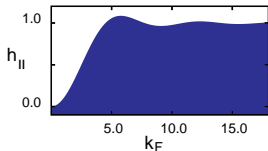with approximations: KS, then LDA, GGA, hybrid-GGA, meta-GGA ...

electrons in the field of classical nuclei (Born Oppenheimer)
electrons in the field of all other electrons (Orbitals)

minimization ot total energy $E_t = E + U_{\mathrm{stat}}$ yields:

$$\left(T + \hat{V}_{\mathrm{xc}} + V_{\mathrm{stat}}(\mathbf{r}) \right) \psi_j(\mathbf{x}_1) = \epsilon_j \psi_j(\mathbf{x}_1)$$

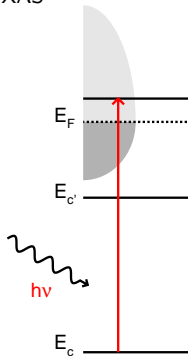

basic idea: Slater approximation, use dynamical
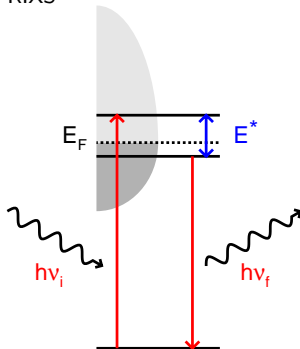exchange potential of homogeneous electron gas

Orbitals sketch: X-Ray Core Spectroscopies

x-ray absorption
XAS
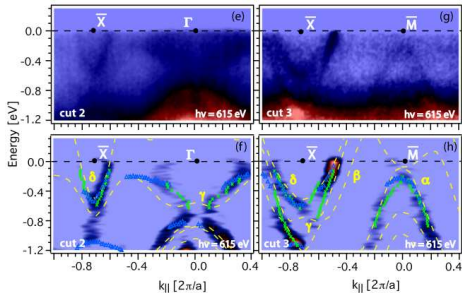
resonant inelastic x-ray scattering
RIXS

E_F

$E_{c'}$

$h\nu$

E_c

E_F

E^*

$h\nu_i$

$h\nu_f$

intra atomic e-e interaction leads to atomic multiplet spectra:
Moser et al PRB 53, 2518 (1984) XAS, EELS, XPS

DFT bandstructure and ARPES of LaRu₂P₂
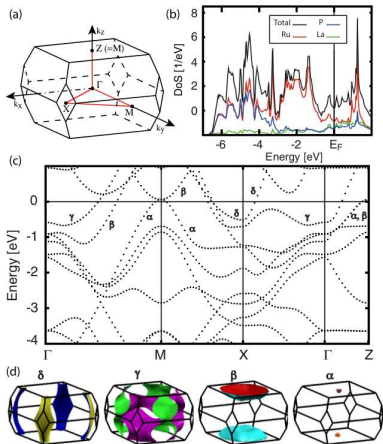
← DFT predictions.   ARPES results ↑

decisive early input for Phys. Rev. Lett. 2012 Razzoli et al.

EXAFS theory, an application of DFT

EXAFS (extended absortion fine structure) involves excitations high above the absorption edge. The final state electrons are well described by the mean field. The oscillations in absorption versus photon energy can be interpreted as coming from interference of the single electron wave with the multiply scattered waves. It can yield structural information. EXAFS codes are specialized DFT codes for such highly exited orbital waves. Example, FEFF code by Rehr et al.

Excitation Energies for the Ti^{4+} Ion: Atomic Multiplets

ground state configuration $3s^23p^63d^0$, excited states $3s^23p^53d^1$

KS	TDDFT-RPA	TDDFT-ALDA	MULT-AR	MULT-SO	exp
38.18	51.27	49.37	51.29	51.30	49.01
38.18	40.74	39.14	37.75	37.90	38.61
38.18	38.18	38.18	37.50	37.69	38.05
				37.59	38.34
38.18	38.18	38.18	37.50	37.41	38.36
				37.36	38.12
				34.91	36.05
38.18	38.18	36.89	34.67	34.68	35.84
				34.46	35.62
				33.21	34.38
38.18	38.18	36.15	33.09	32.93	34.14
				32.79	34.03

TDDFT: Excitations in Hilbertspace spanned by single excitations from ground state determinant of molecule.

Multiplet theory: Hilbertspace spanned by minimal basis set in atomic configuration. energies in [eV]. $K = 0$ between det. differing by more than a double excitation.

Wave-Functions: Atomic Multiplet Theory and Calculations

number of states spanned by open shells, example:

ground state configuration $3d^6$: dimension $\binom{10}{6} = 210$

XAS final state configuration $2p^5 3d^7$: dimension $\binom{5}{6}\binom{10}{7} = 720$

<div style="border:1px solid;">

Cowan, Thole:
HF scalar relativistic atom
SO + e-e jj blocked variation
xtal-field second variation
challenge: lower symmetries than C_{4v}
development now by Frank de Groot

</div>

<div style="border:1px solid;">

present approach:
DFT Dirac atom
e-e + xtal-field variation
challenge: large matrices
Uldry PRB 85 125133 2012

</div>

crystal environment breaks spherical symmetry
our preference: define crystal field by position and charge of neighbor ions

Moser Schneider Baer Delley al PRB 53, 2518 (1984)
Cowan Thole Sawatzky (1985)

Atom with Single Open Shell

example: V atomic orbital levels
relativistic DFT calculation for neutral atom:

n	ℓ	j	κ	occ.	eigenvalue (ev)
1	0	1/2	-1	2.00	-5349.033
2	0	1/2	-1	2.00	-600.364
2	1	1/2	1	2.00	-506.793
2	1	3/2	-2	4.00	-499.717
3	0	1/2	-1	2.00	-69.602
3	1	1/2	1	2.00	-44.311
3	1	3/2	-2	4.00	-43.473
3	2	3/2	2	3.00	-5.314
4	0	1/2	-1	2.00	-4.959
3	2	5/2	-3	0.00	-5.248

Note: the neutral atom is a fair approximation for the avg charge distr.
The formal charge hints at filling of localized shells:
V neutral atom: $3d^3\ 4s^2$, V^{3+} : $3d^2$

Hilbert space is spanned by determinants

Sketch of combinatorial possibilities for determinants for p^2 charactereized by occupancy of spin-orbitals m_σ, m_ℓ

1	1 - 1 - - -
2	1 - - - 1 -
3	- - 1 - 1 -
4	1 1 - - - -
5	1 - - 1 - -
6	- 1 1 - - -
7	- - 1 1 - -
8	- 1 - - 1 -
9	1 - - - - 1
10	- - - 1 1 -
11	- - 1 - - 1
12	- - - - 1 1
13	- 1 - 1 - -
14	- 1 - - - 1
15	- - - 1 - 1

15 for p^2, 45 for d^2 , for L^n : $n_h = (4L+2)!/((4L+2-n)!n!)$

Open Shell with e-e Interaction

Term energies for V^{3+} d^2:

n	ndeg	J	S	L	energy (eV)	symbol
1	21	4.0	1.0	3	0.000	^3F
2	5	2.0	0.0	2	1.287	^1D
3	9	2.0	1.0	1	1.575	^3P
4	9	4.0	0.0	4	2.022	^1G
5	1	0.0	0.0	0	4.977	^1S

Hund's rules for ground state:
1) maximum multiplicity, $= 2S + 1$
2) largest value of the total orbital angular momentum

V^{3+} with e-e Interaction and S-O coupling

n	ndeg	J	symbol$_J$	energy (eV)	exp energy
1	5	2	$^3F_2$	0.000	0
2	7	3	$^3F_3$	0.040	0.040
3	9	4	$^3F_4$	0.092	0.091
4	5	2	$^1D_2$	1.337	1.359
5	1	0	$^3P_0$	1.601	1.627
6	3	1	$^3P_1$	1.615	1.641
7	5	2	$^3P_2$	1.646	1.669
8	9	3	$^1G_4$	2.076	2.280
9	1	0	$^1S_0$	5.031	5.265

The L-S term symbols are a reminder of the states being perturbed by S-O. No strict reference to quantum numbers is implied.

Hund's rules for ground state:
3a) outermost subshell half-filled or less: lowest value of J
3b) outermost subshell more than half-filled: highest value of J

crystal field or hybridization can be of comparable strength as the open shell on-site e-e interaction.

all states may become formally 'fully symmetric'.
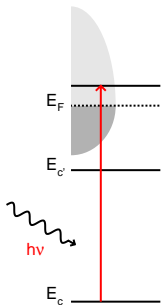
$I(\omega) \propto \sum_c |\langle \psi_c | \hat{\mathcal{O}} | \psi_0 \rangle|^2 \frac{\Gamma_c/\pi}{(\hbar\omega + E_0 - E_c)^2 + \Gamma_c^2}$

ψ_c, ψ_0 are wavefunctions. The matrix element eq for dipole transitions involves a dipole mtx elem between the active orbitals and also an overlap factor for the passive orbitals.

Note: Γ_c core hole limits spectral resolution, physically due to core hole decay, here just a parameter

a sample sketch of core hole determinants

core	valence
1 1 1 1 1 -	1 - 1 - 1 - - - - -
1 1 1 - 1 1	1 - 1 - 1 - - - - -
1 1 1 1 1 -	1 - 1 - - - 1 - - -
1 1 1 1 1 -	1 - 1 - - - - - 1 -
1 1 1 - 1 1	1 - 1 - - - 1 - - -

for V^{3+} $2p^6$ $3d^2$ groundstate has 720 excited states in the configuration.

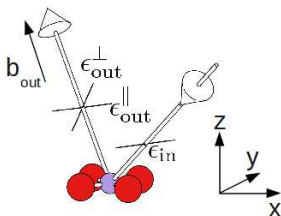for L_c L^n : $n_{h*} = 2(2L_c + 1)(4L + 2)!/((4L + 2 - n - 1)!(n + 1)!)$

RIXS

RIXS
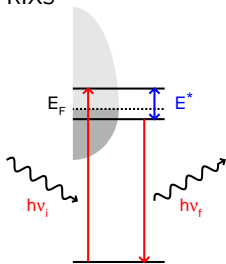
$$I(\Delta\omega, \omega) = \sum_f \left| \sum_c \frac{\langle \psi_f | \mathcal{O}'^\dagger | \psi_c \rangle \langle \psi_c | \mathcal{O} | \psi_0 \rangle}{E_i - E_0 - \hbar\omega_i - i\Gamma_c} \right|^2 \frac{\Gamma_f/\pi}{(E_f + E_0 - \hbar\Delta\omega)^2 + \Gamma_f^2}$$

Note: Γ_f limits spectral resolution

It is easy to specify such calculations

basic set of keywords:
new XAS
atom V
ground_state 2p6 3d2
core_hole_broad 0.3
scaler_coulomb 1.0
scaler_so_coupling 1.0
scaler_xtal_field 1.0
xtal_file ligands.dat
polar_in 0 0 1

specify:
for linear polarization:
polarization vector
for unpolarized detection:
beam direction
in same coordinate system as ion positions

XAS for cubic SrTiO$_3$

Ti^{4+} ground state configuration $2p^63d^0$
$\rightarrow 2p^53d^1$
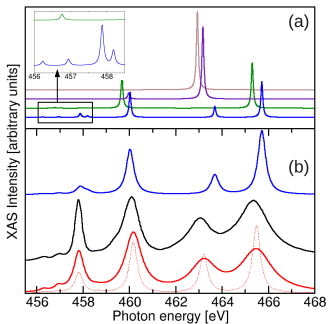
a) 'raw' theory
NR
NR+xtal
SO
SO+xtal
(incl Γ_c0, $\Delta\epsilon_c$)

b) semi-empirical comparison
raw
exp Schlappa et al 2008
$S_{coul} = 0.85$ $S_{xtal} = 1.3$ $S_{SO} = 0.93$
$\Gamma = 0.2 ... 0.8$ eV

RIXS monoclinic MnO
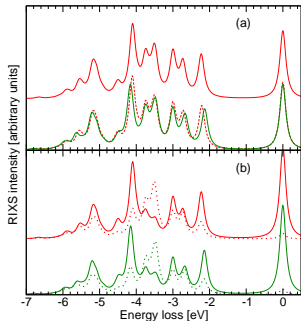
exp Ghiringelli et al 2009
Mn configuration $2p^6 3d^5$ at $+3.6eV$,
$\Gamma_f = 0.10eV$
cubic MnO
monoclinic
a) with polarization average on detector
comparison with cubic scaled
b) polarization dependence for
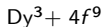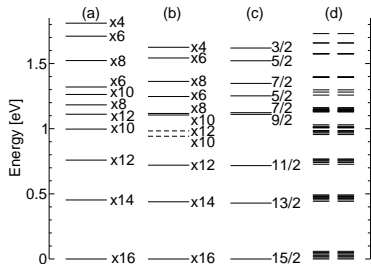$\epsilon_{out}^{\parallel}$ full line
$\epsilon_{out}^{\perp}$ dotted line

distortion of MnO_6 octahedra has smaller impact than polarization
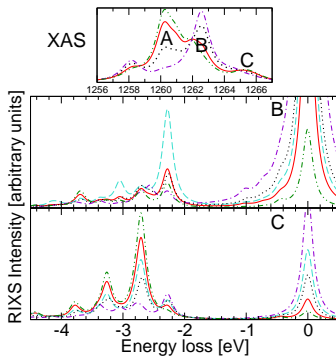
example with Rare Earth element

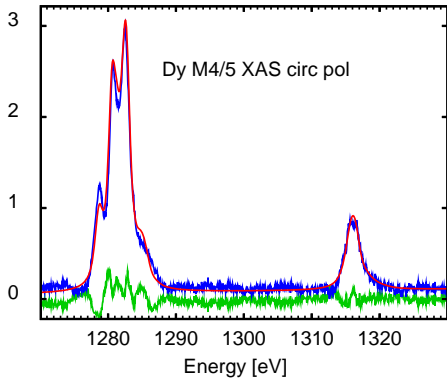Dy^{3+} $4f^9$
a) raw
b) $S_{coul} = 0.85$ $S_{SO} = 0.95$
c) exp NIST docu
d) Dy phtalocyanine: $S_{xtal} = 0.1$

predicted XAS and RIXS spectra for
Dy phthalocyanine

Dy M4/5 XAS circ pol

Conclusion

despite Dirac's somewhat pessimistic view:

- multiplet calculations for localized open shell atoms give a fair account of the near edge structure in XAS and other core spectroscopies.

- the multiX code makes such calculations accessible to anybody interested.

- such computations can help to establish the proper hypothesis on the state of a material.

- Systematic computation of crystal-field multiplets for x-ray core spectroscopies; A Uldry F Vernay B Delley,Phys. Rev. B 85, 125133 2012.

- Program Docu+Download: http://multiplets.web.psi.ch