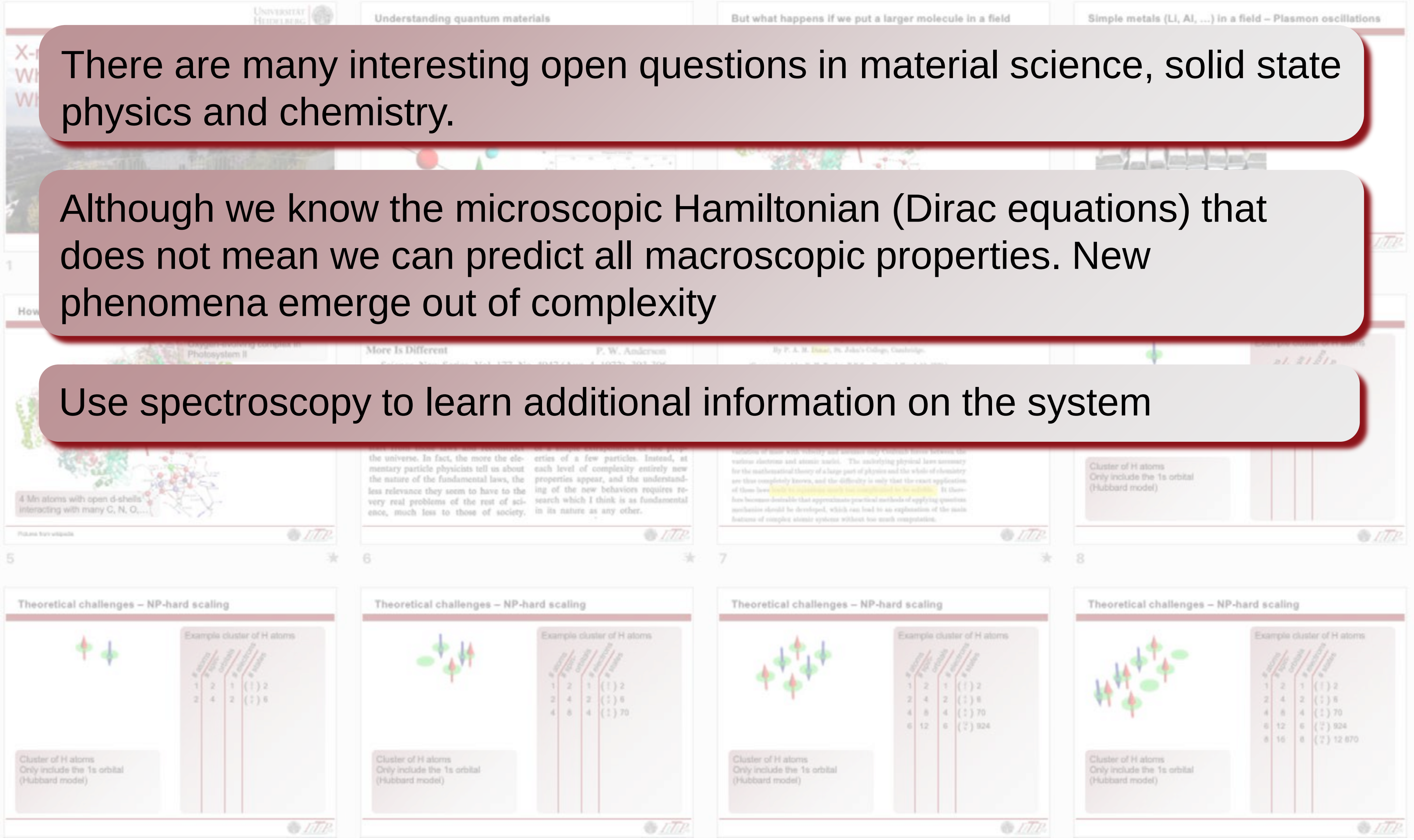
Quanty workshop in Heidelberg

7-11 October 2019

www.Quanty.org/workshop

X-ray core level spectroscopy:
What do we learn?
Which level of theory do we need?

Why IXS

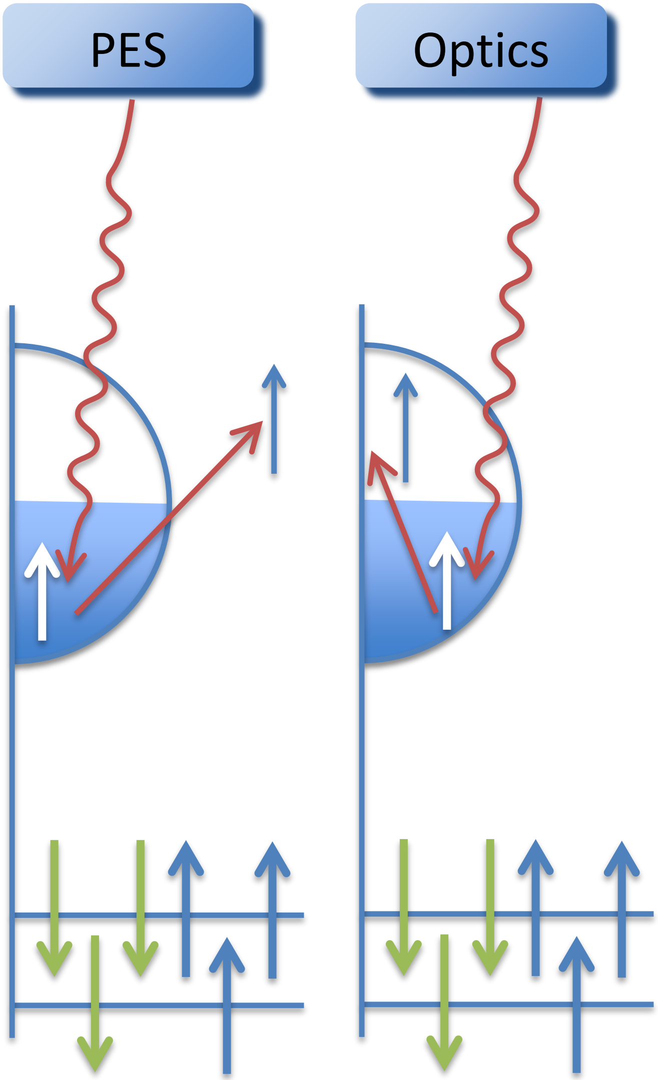


There are many interesting open questions in material science, solid state physics and chemistry.

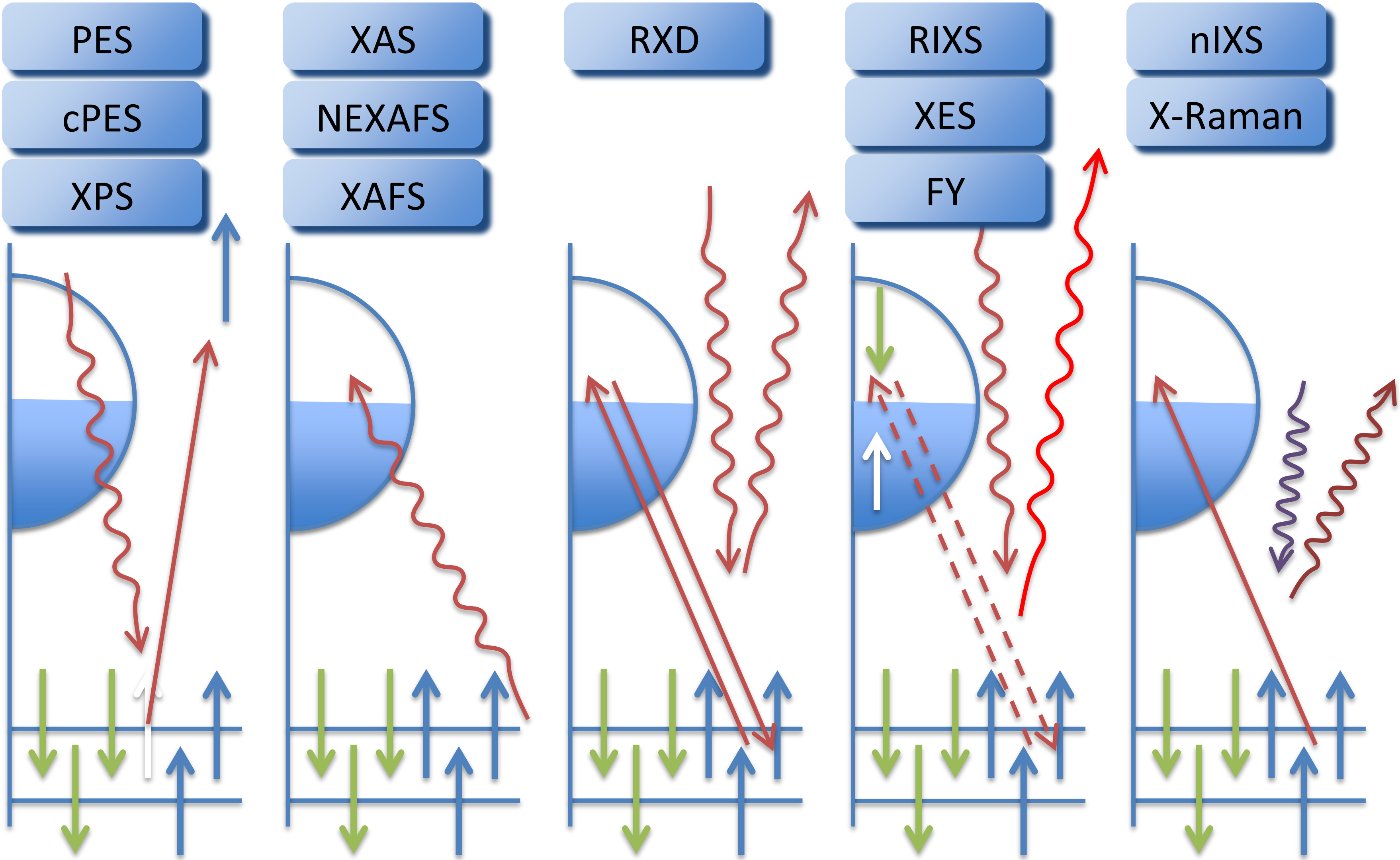
Although we know the microscopic Hamiltonian (Dirac equations) that does not mean we can predict all macroscopic properties. New phenomena emerge out of complexity

Use spectroscopy to learn additional information on the system

Many different spectroscopy types ... IXS conference



Many different spectroscopy types ... IXS conference



Time dependent perturbation theory

Fermi's golden rule

$$I = \sum_f \left| \langle f | T | i \rangle \right|^2 \delta(\omega + E_i - E_f)$$

Green's function – spectral representation (energy domain)

$$I = -\frac{1}{\pi} \mathrm{Im} \left\langle i \left| T^\dagger \frac{1}{\omega - H + \mathrm{i}\frac{\Gamma}{2}} T \right| i \right\rangle$$

Green's function – (time domain)

$$I = -Re \int_0^\infty e^{\mathrm{i}\omega t} \langle i | e^{\mathrm{i}Ht} T^\dagger e^{-\mathrm{i}Ht} T | i \rangle \, dt$$

Real-space Green’s function theory

~~Golden rule via Wave Functions~~

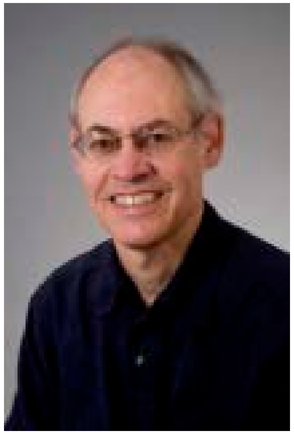
$$\xcancel{\mu(E) \sim \Sigma_f |\langle i|\hat{\epsilon}\cdot\mathbf{r}|f\rangle|^2 \delta(E - E_f)}$$

$\cancel{\Psi}$

Paradigm shift

Golden rule via Green’s Functions $\mathbf{G} = 1/(E - h - \Sigma)$

$$\boxed{\mu(E) \sim -\tfrac{1}{\pi}\mathrm{Im}\,\langle \mathrm{i}|\,\hat{\epsilon}\cdot\mathbf{r}'\,\mathrm{G}(\mathbf{r}',\mathbf{r},\mathrm{E})\,\hat{\epsilon}\cdot\mathbf{r}\,|\mathrm{i}\rangle}$$



No sums over final states !

Time dependent perturbation theory

Fermi's golden rule

$$\cancel{I = \sum_f \left| \langle f | T | i \rangle \right|^2 \delta(\omega + E_i - E_f)}$$

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$$I = -\frac{1}{\pi} \mathrm{Im} \left\langle i \left| T^\dagger \frac{1}{\omega - H + \mathrm{i}\frac{\Gamma}{2}} T \right| i \right\rangle$$

Green's function – (time domain)

$$I = -Re \int_0^\infty e^{\mathrm{i}\omega t} \langle i | e^{\mathrm{i}Ht} T^\dagger e^{-\mathrm{i}Ht} T | i \rangle \, dt$$

Time dependent perturbation theory

Green's function – (time domain)

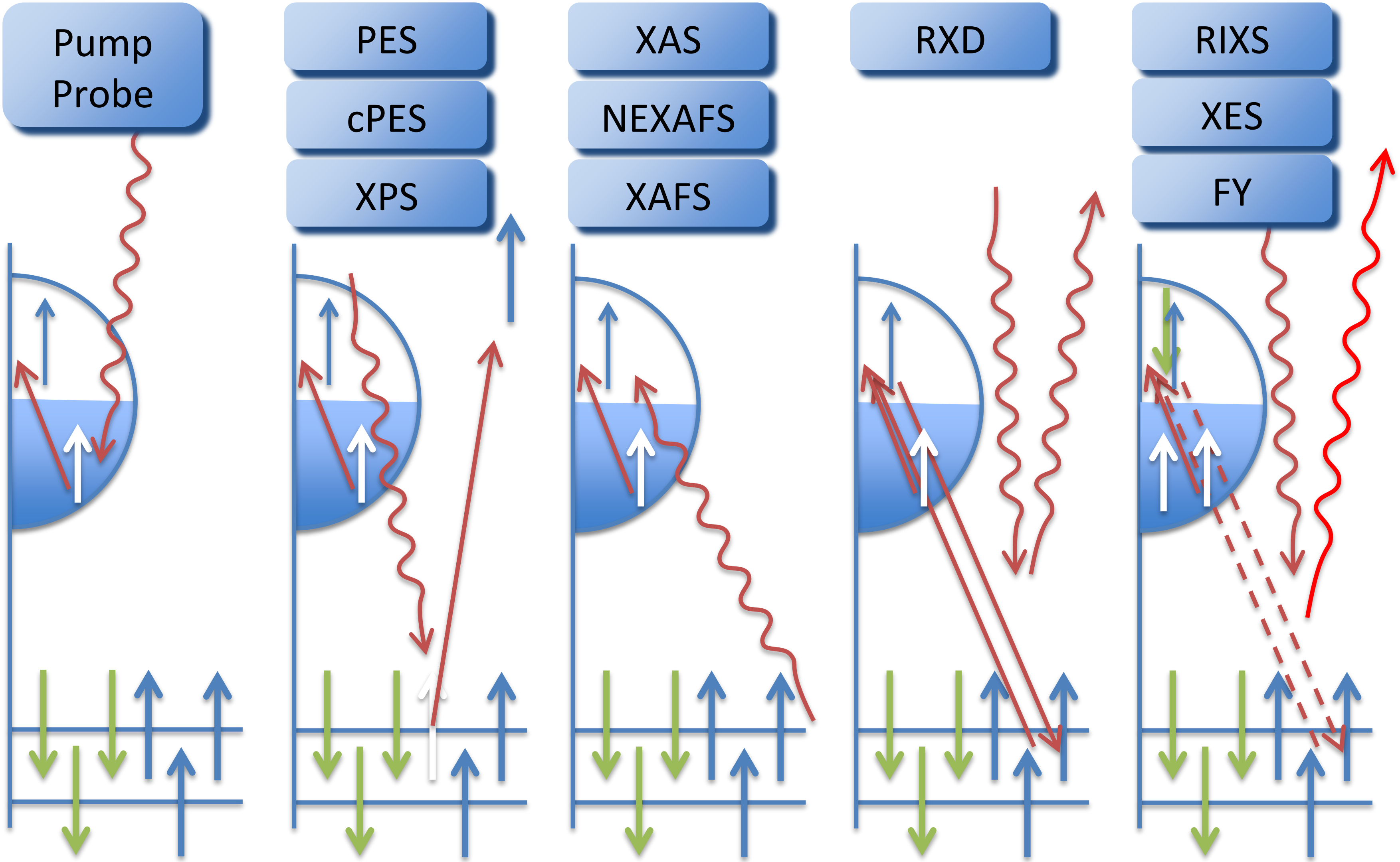
$$I = -Re\int_0^\infty e^{\mathrm{i}\omega t}\left\langle i\left|e^{\mathrm{i}Ht}\,T^\dagger\,e^{-\mathrm{i}Ht}\,T\right|i\right\rangle dt$$

$$I = -Re\int_0^\infty e^{\mathrm{i}\omega t}\left\langle i\left|T^\dagger(t)\,T(t=0)\right|i\right\rangle dt$$

At time *t*=0 an excitation is created
In spectroscopy one probes if at time *t* the excitation is still at the same place, or if it moved away.

Spectroscopy, including inelastic x-ray scattering probes the dynamics of the system

Time dependent spectroscopy



Pump
Probe

PES
cPES
XPS

XAS
NEXAFS
XAFS

RXD

RIXS
XES
FY

Nth order correlation functions in ω and *t* domain

Linear response in time and frequency domain

$$I_{spec} = -\mathrm{Im}\left\langle i \left| T^\dagger \frac{1}{\omega - H} T \right| i \right\rangle$$

$$I_{spec} = \mathrm{Re}\int_0^\infty e^{\imath\omega t}\left\langle i \middle| T^\dagger(t) T(t=0) \middle| i \right\rangle$$

Nth order response in time and frequency domain

$$I_{spec} = -\mathrm{Im}\left\langle i \left| T^\dagger \frac{1}{\omega_1 - H} T^\dagger \frac{1}{\omega_1 + \omega_2 - H} T \frac{1}{\omega_1 - H} T \right| i \right\rangle$$

$$I_{spec} = \mathrm{Re}\int_0^\infty e^{\imath\omega_2(t_2 - t_1)} e^{\imath\omega_1 t_3}\left\langle i \middle| T^\dagger(t_3) T^\dagger(t_2) T(t_1) T(t_0 = 0) \middle| i \right\rangle$$

Spectroscopy and IXS

Many types of spectroscopy. But the theoretical challenge to describe these is for all types very similar

$$I_{spec} = -\mathrm{Im}\left\langle i \left| T^{\dagger} \frac{1}{\omega - H} T \right| i \right\rangle$$

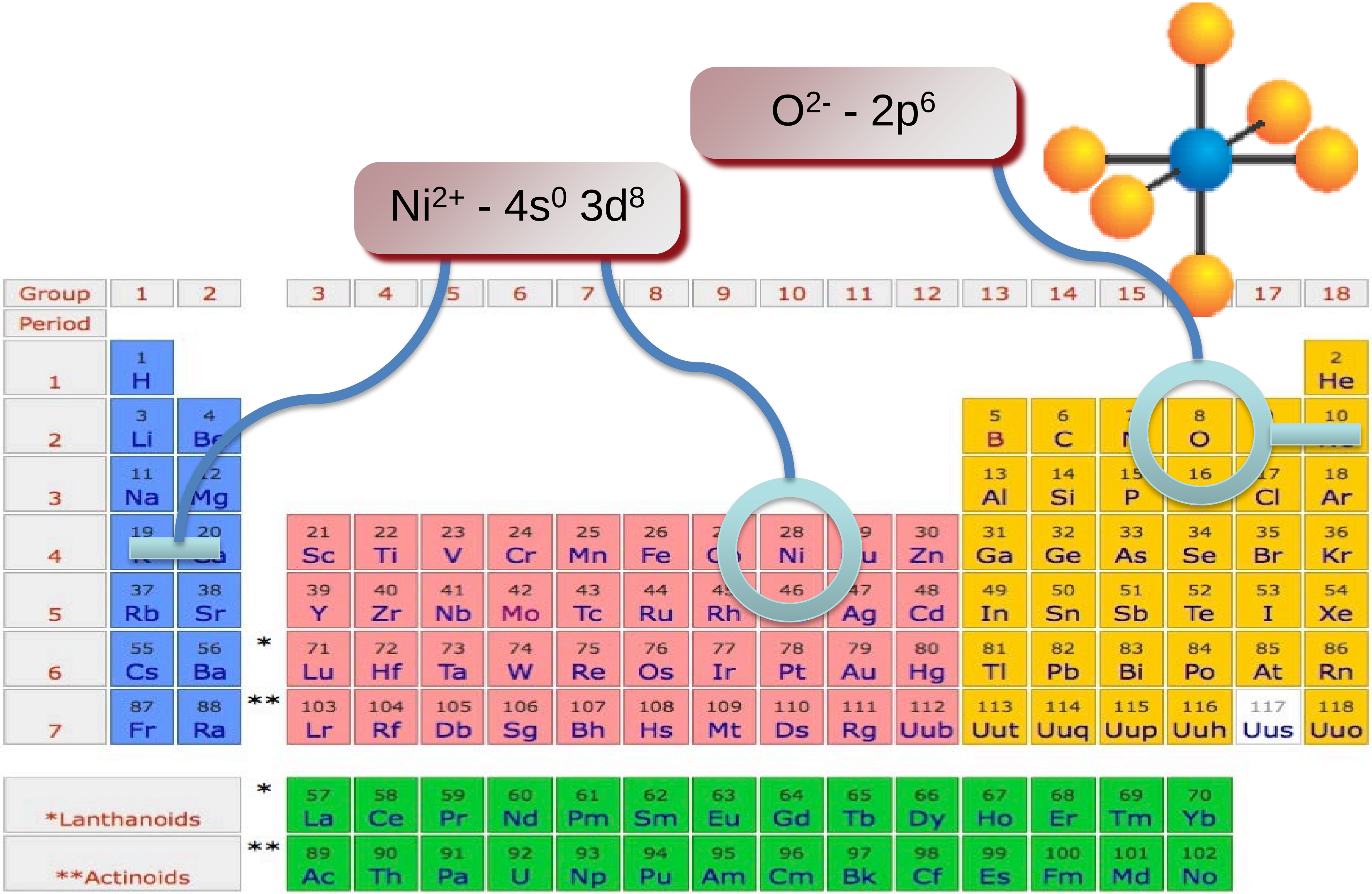
The interaction between matter and light is very well understood so the Operator T is not really a problem for all different spectroscopies

Calculating the ground-state $|i\rangle$ is in general a challenge

Calculating the propagator $\frac{1}{\omega - H}$ is in general a challenge

Use different levels of theory – approximating the extend of the solid or the Coulomb interaction

Which level of theory do we need – NiO as an example



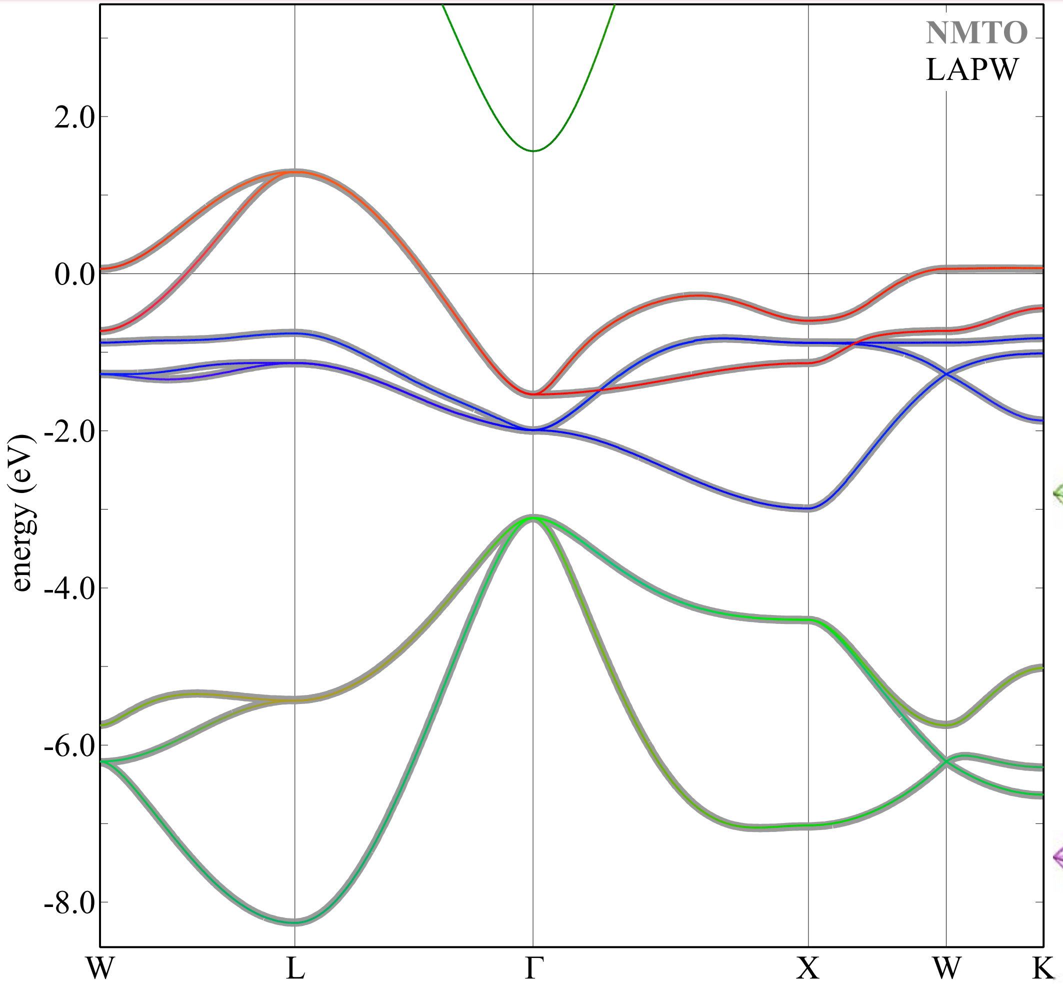
O^{2-} - $2p^6$

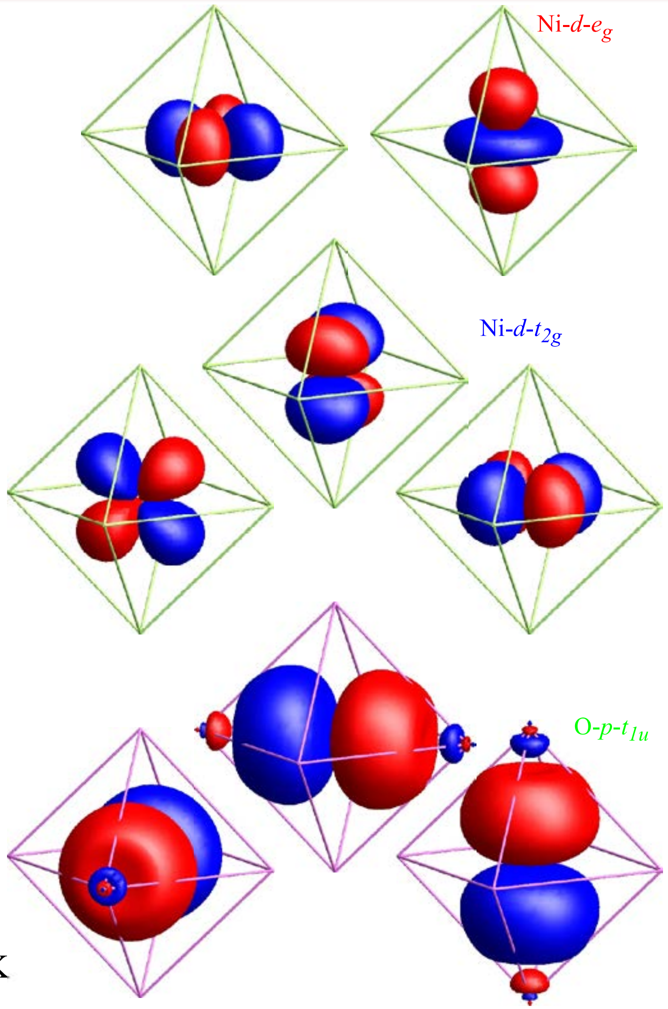
Ni^{2+} - $4s^0$ $3d^8$

Group	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15		17	18
Period																			
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
*Lanthanoids			*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
**Actinoids			**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

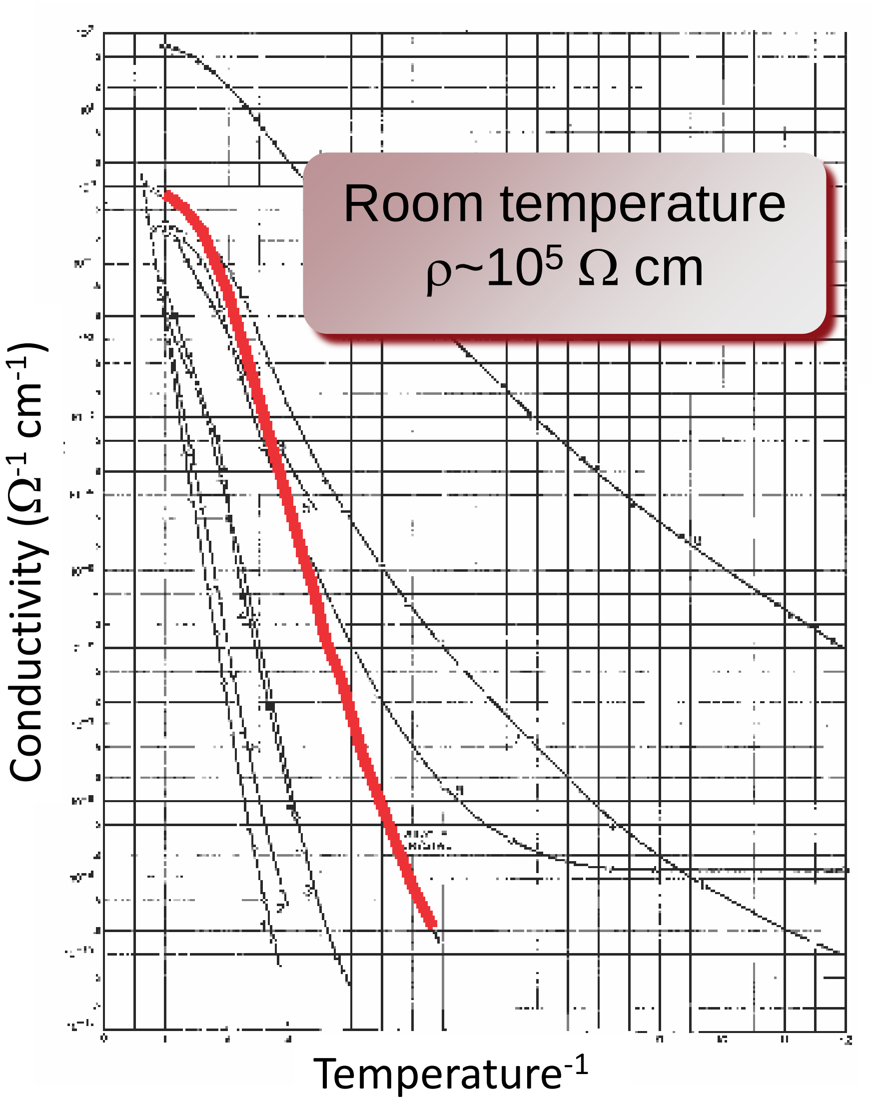
Electronic states of NiO on a mean-field level

Energy momentum (dispersion) relation and electronic eigenstates (orbitals)





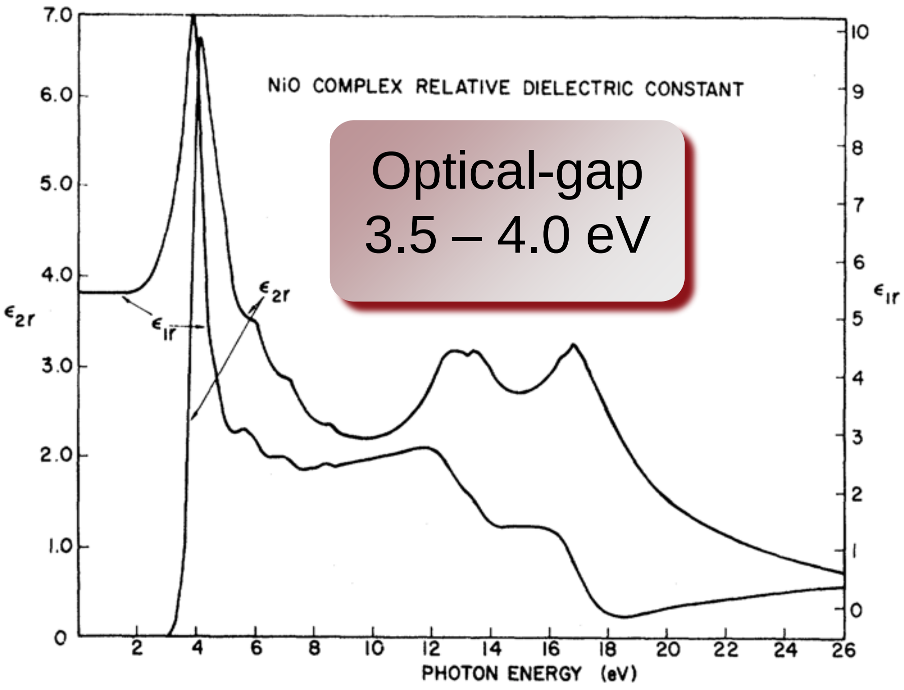
On a mean-field level NiO is a metal, in reality an insulator



Room temperature
ρ~10^5 Ω cm

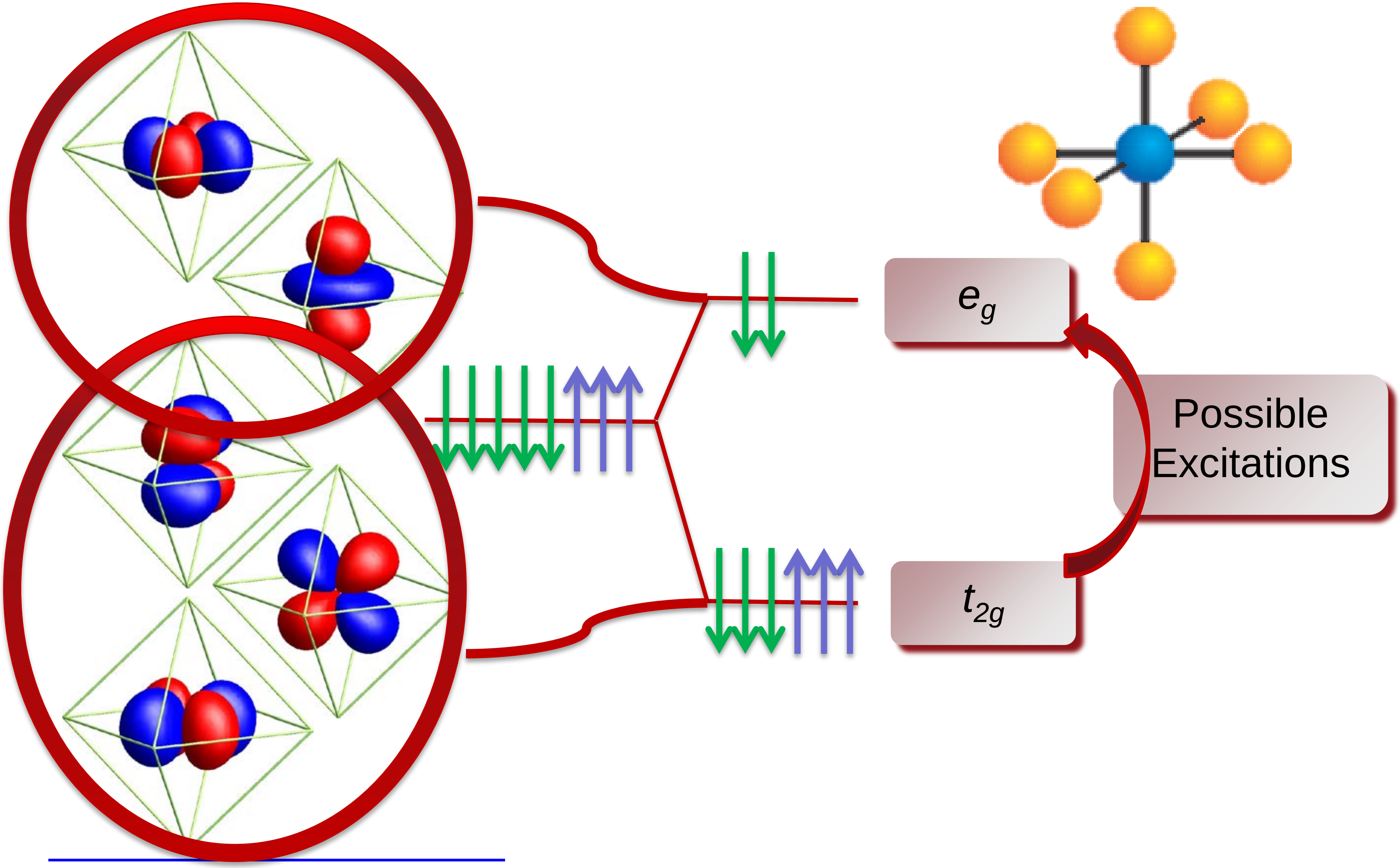
F. J. Morin, Phys. Rev. **93**, 1199 (1954)

R. Newman and R. M. Chrenko,
Phys. Rev **114** 1507 (1959)



Optical-gap
3.5 – 4.0 eV

After localization of d electrons one can make d-d excitations



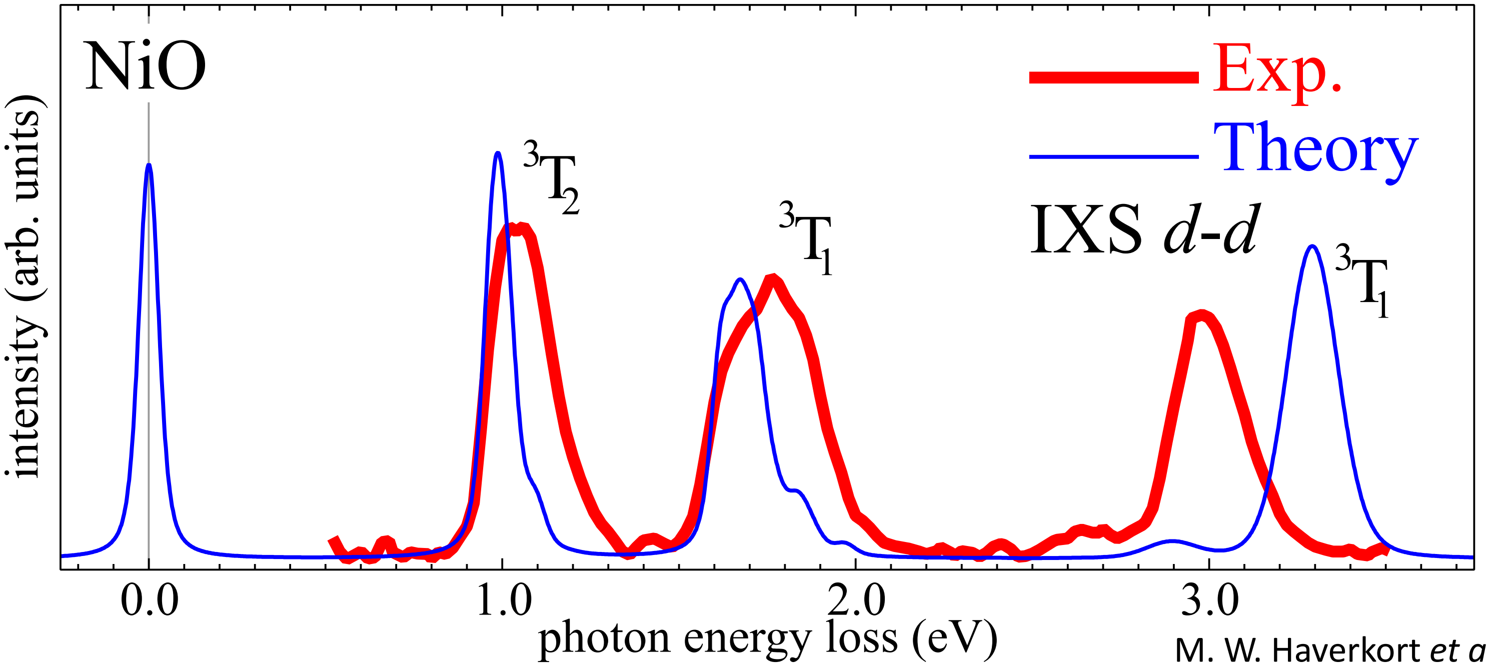
e_g

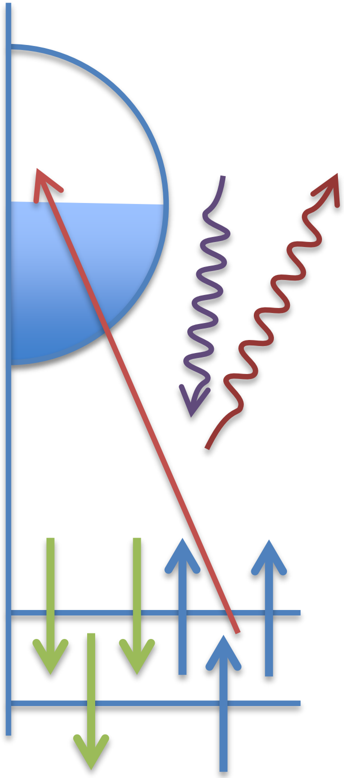
Possible Excitations

t_{2g}

nIXS d-d excitations NiO 3 peaks instead of 1

Experiment:
R. Verbeni, *et al.* J. Synchrotron Rad. **16**, 469 (2009).

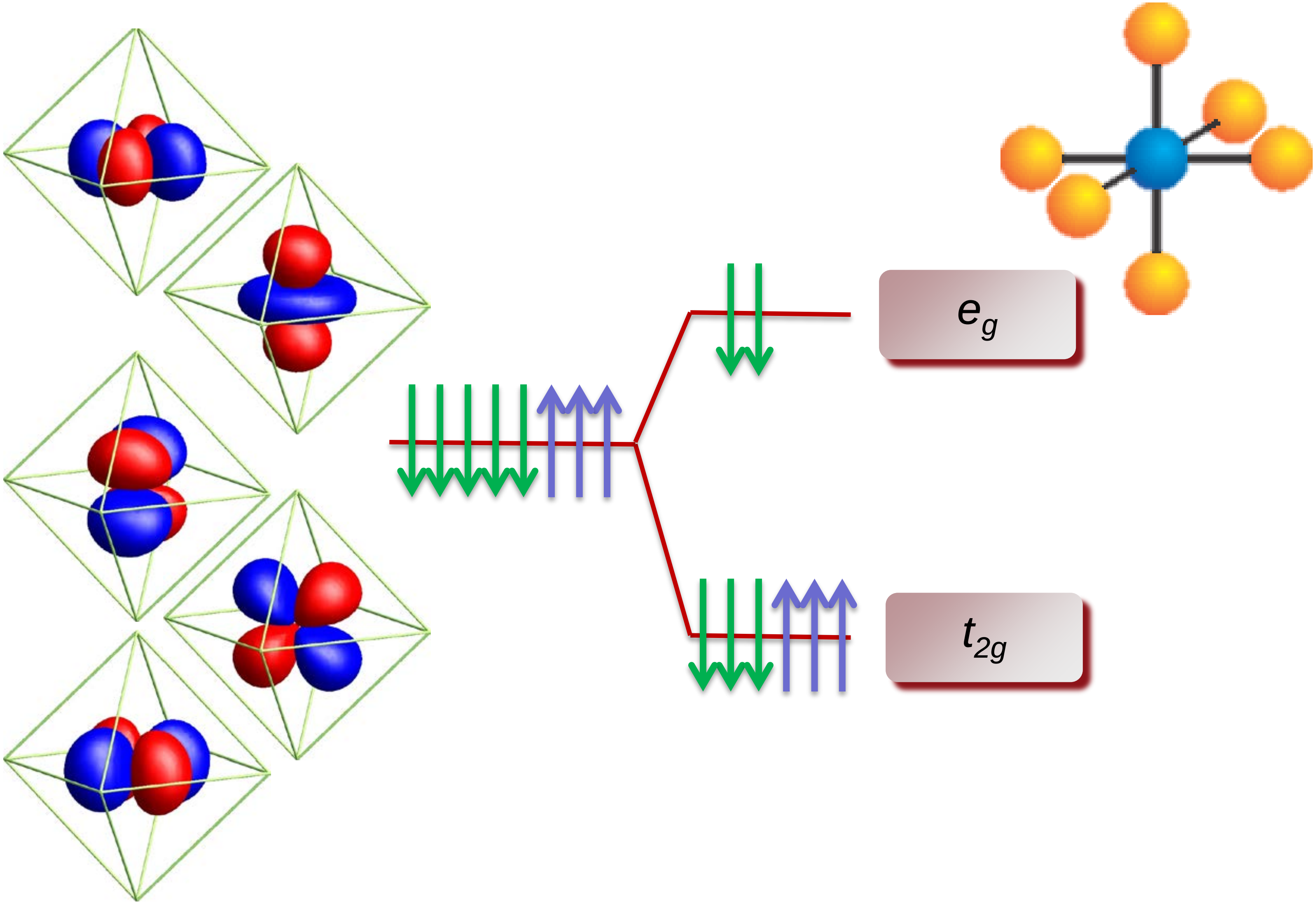




M. W. Haverkort *et al.* PRB **85**, 165113 (2012)

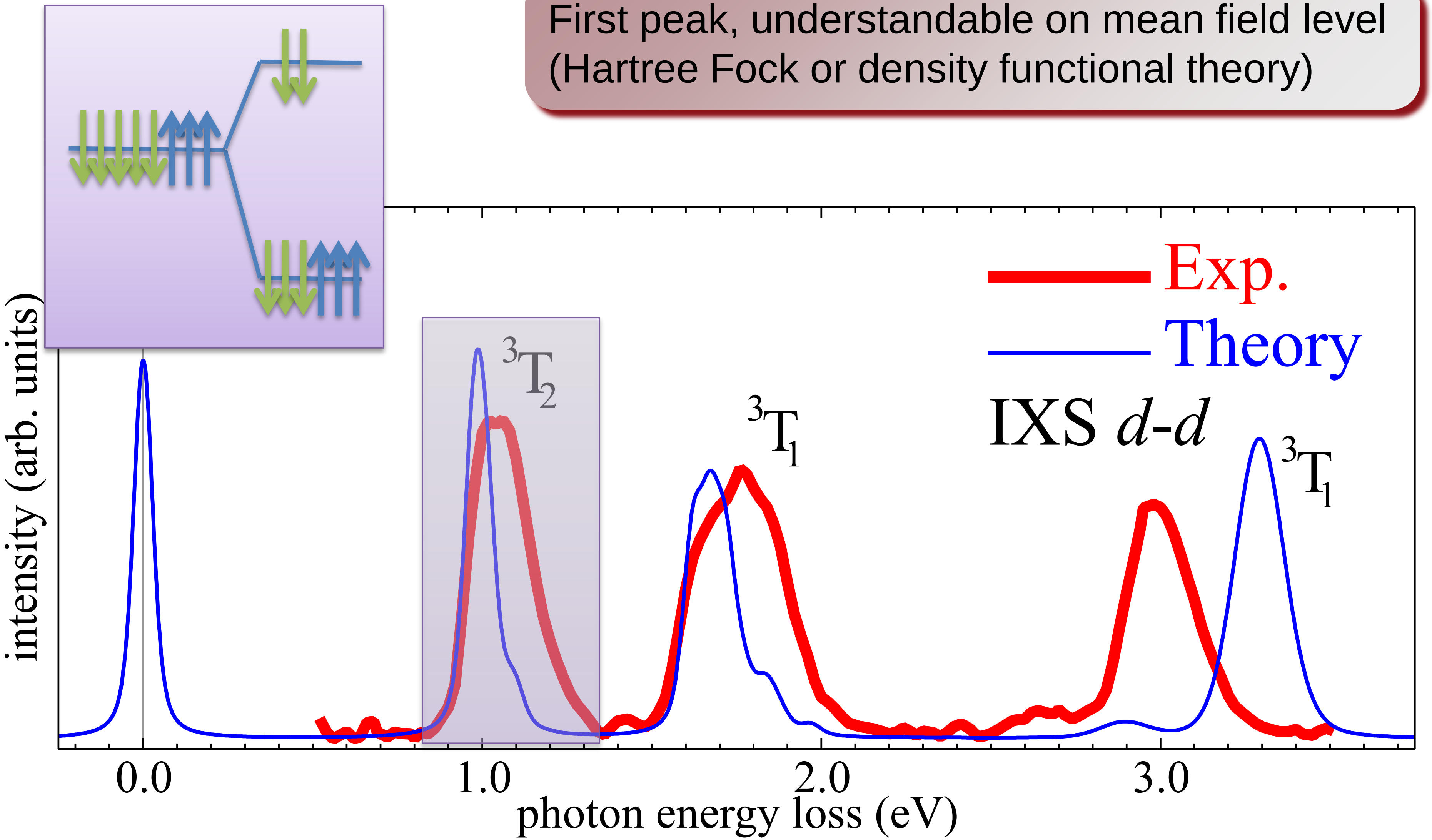
PRL **99,** 257401 (2007)

Orbital energy level diagram



First peak, excitation from t_{2g} to e_g

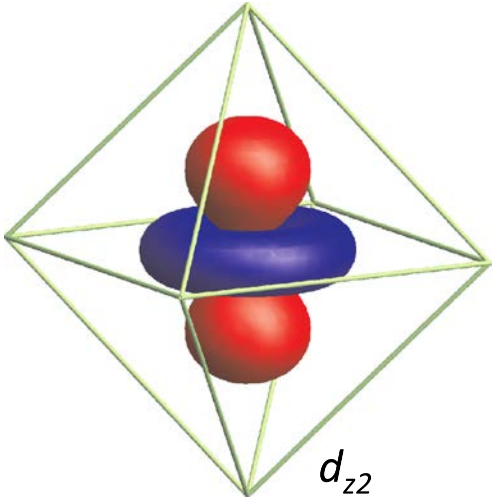
First peak, understandable on mean field level
(Hartree Fock or density functional theory)



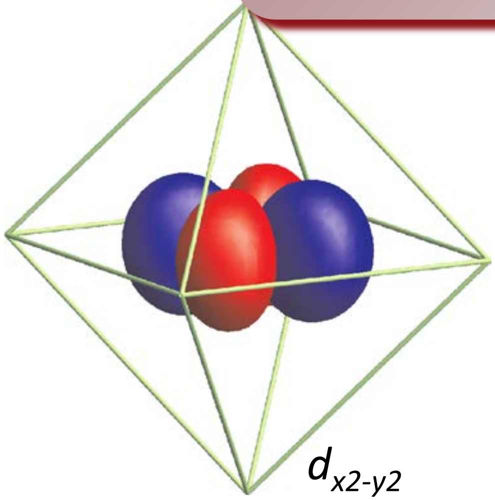
Third peak – Coulomb repulsion

$$\int \psi_1^*(r_1)\psi_2^*(r_2)\frac{1}{|r_1 - r_2|}\psi_1(r_1)\psi_2(r_2)$$

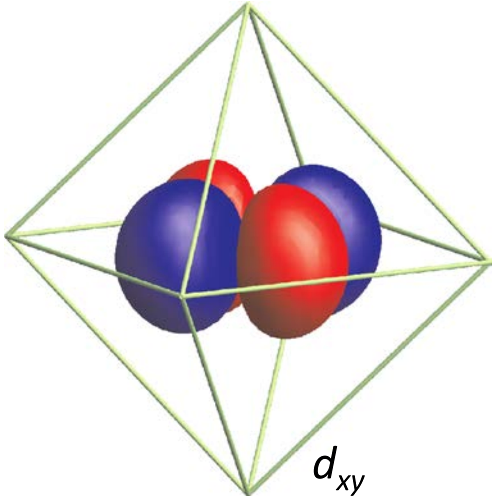
Coulomb repulsion is smaller when electrons are farther apart



d_{z2}



$d_{x2\text{-}y2}$

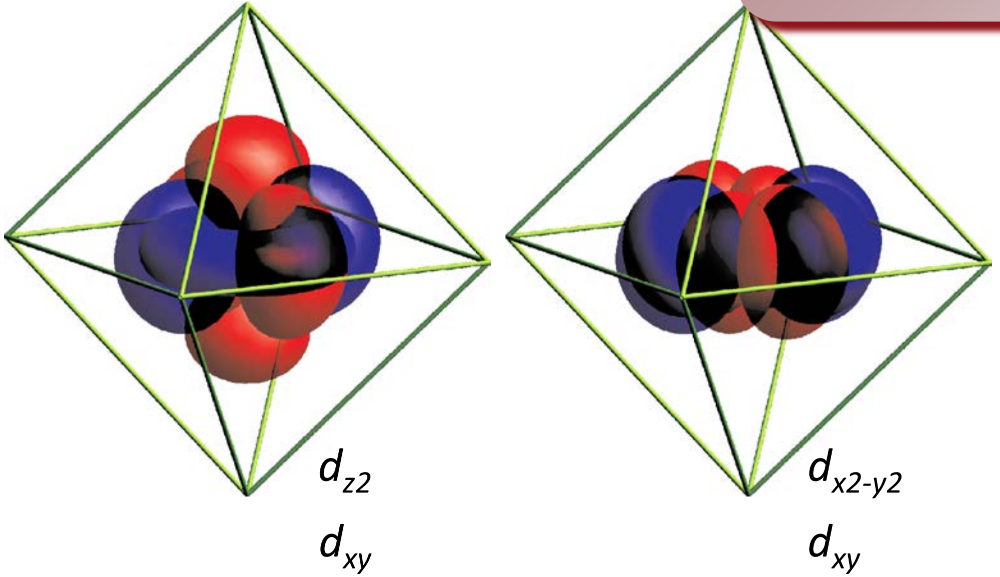


d_{xy}

Third peak – Coulomb repulsion

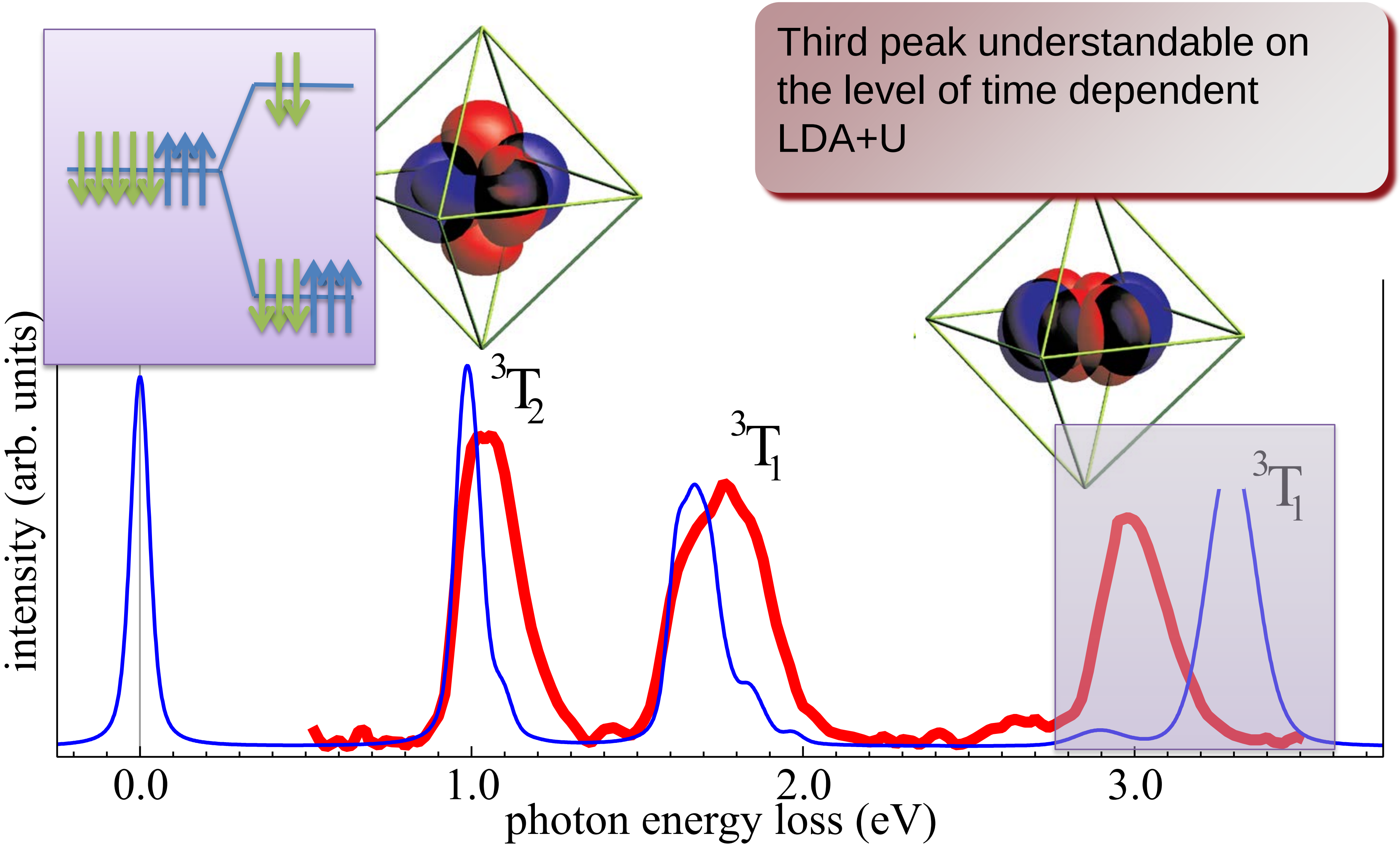
$$\int \psi_1^*(r_1)\psi_2^*(r_2)\frac{1}{|r_1 - r_2|}\psi_1(r_1)\psi_2(r_2)$$

Coulomb repulsion is smaller when electrons are farther apart



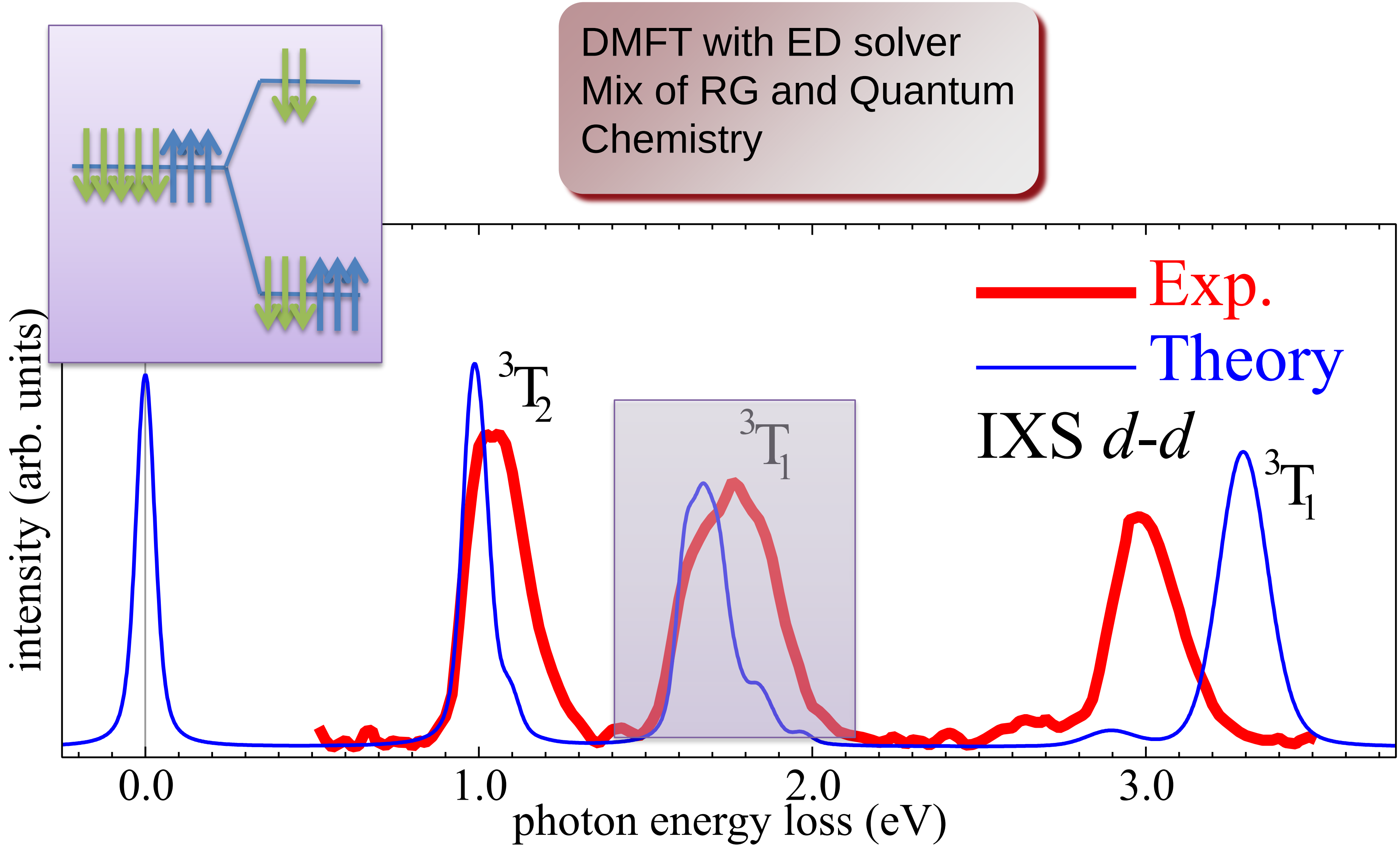
First peak, excitation from t_{2g} to e_g

Third peak understandable on the level of time dependent LDA+U



Second peak, double excitation from t_{2g} to e_g

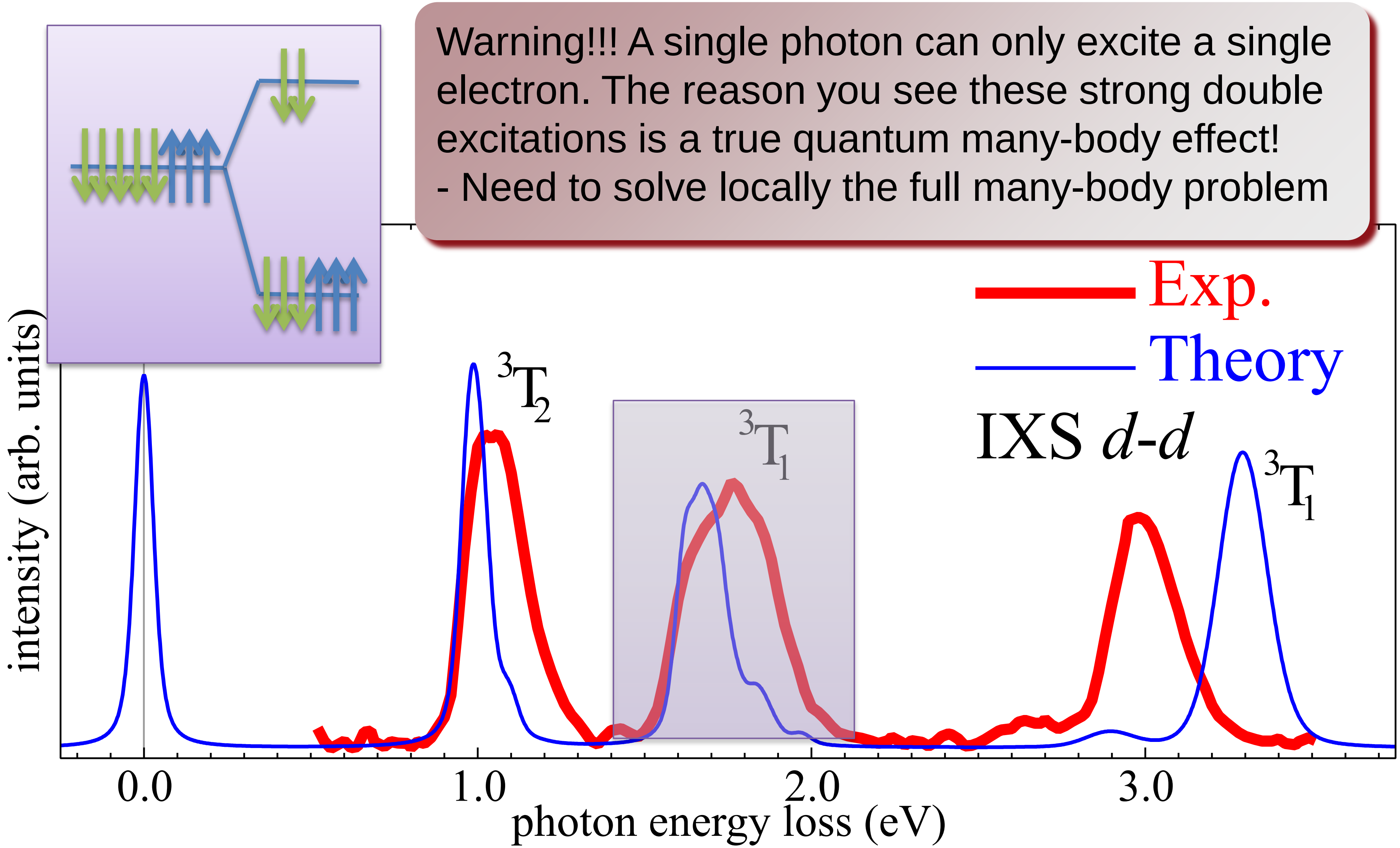
DMFT with ED solver
Mix of RG and Quantum Chemistry



Second peak, double excitation from t_{2g} to e_g

Warning!!! A single photon can only excite a single electron. The reason you see these strong double excitations is a true quantum many-body effect!

- Need to solve locally the full many-body problem



Quanty – www.quanty.org – a flexible script language

Ground-state by
Quantum chemistry (CI (S,D,T,…), RAS, …)
Renormalization group / Matrix product states
Or combinations of these with basis set truncations

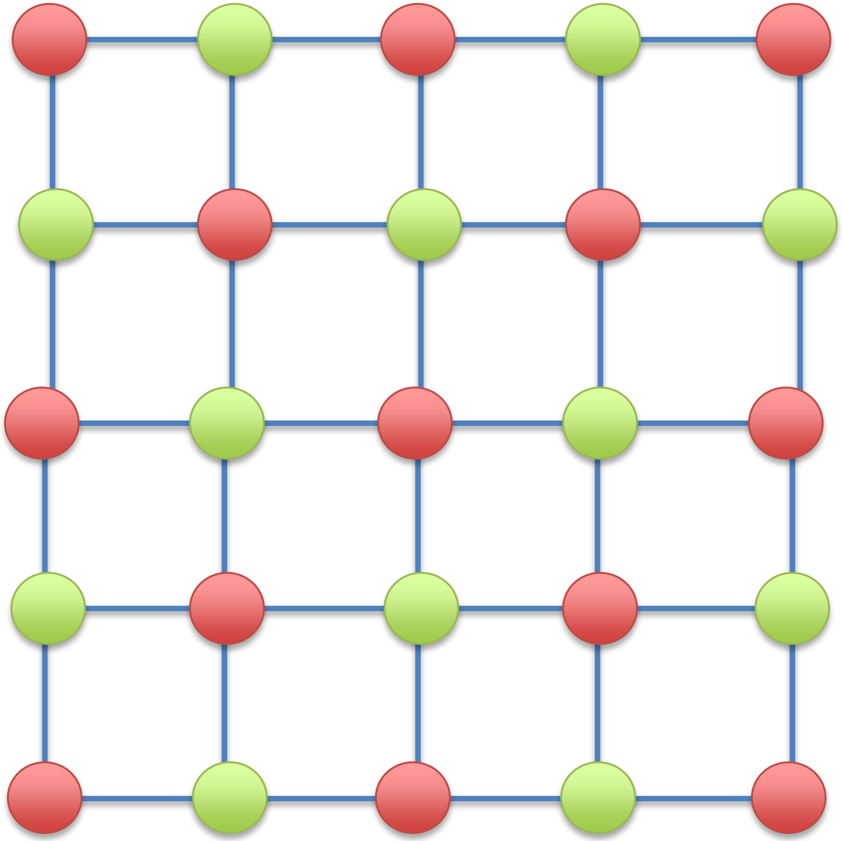
Mix ideas from quantum chemistry and renormalization group theory
PRB **85**, 165113 (2012) – PRB **90**, 085102 (2014).

Spectroscopy using Green’s functions.
Any order of response for any operator
Diagrammatic expansions
Self energy of excited states due to decay of quasi particles

Multiplet crystal field theory

Some history –
theory developed in 1930^{+}

Crystal with many atoms
(for example NiO)

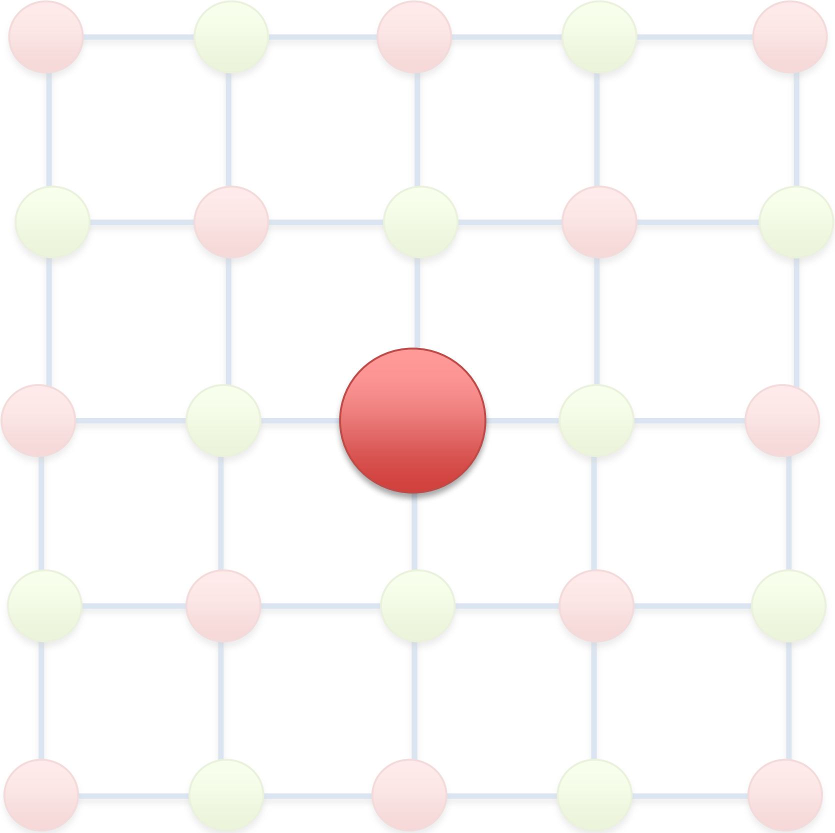


Multiplet crystal field theory

Some history –
theory developed in 1950$^+$

Crystal with many atoms
(for example NiO)

Approximate a solid by a single atom with an additional effective field to mimic the effect of the solid

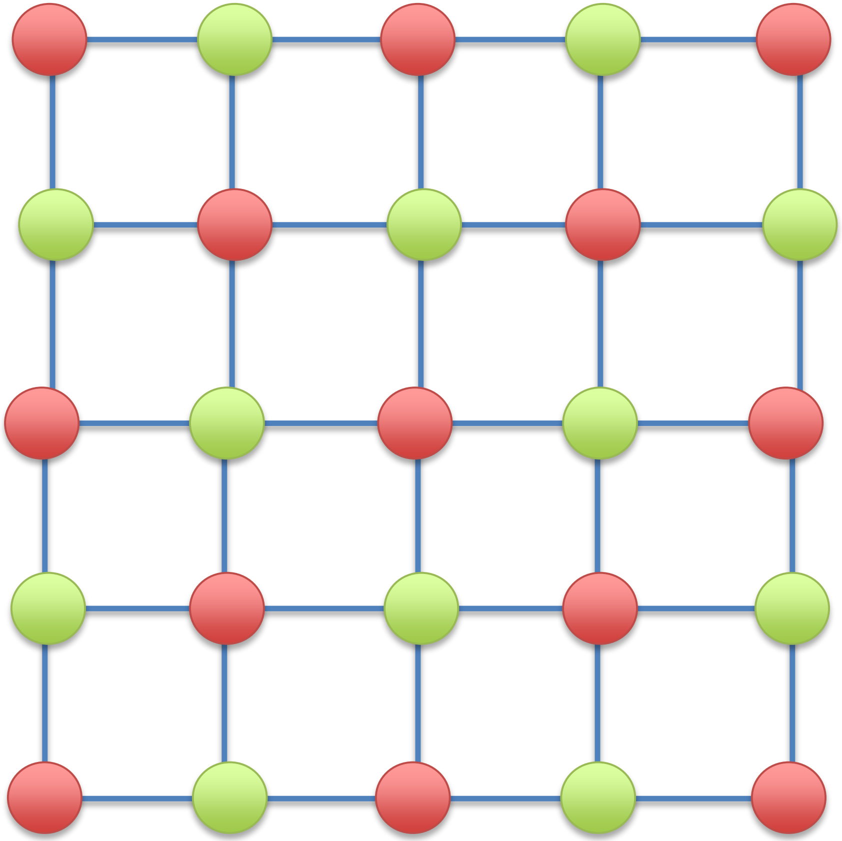


All local multiplets included and correct crystal symmetry. Works for strongly correlated insulators and low energy excitations that do not lead to charge fluctuations. (Magnetic excitations – orbital excitations.) Also works for XAS on strongly correlated insulators on excitonic edges.

Multiplet ligand field theory

Add covalence explicitly, but short range.

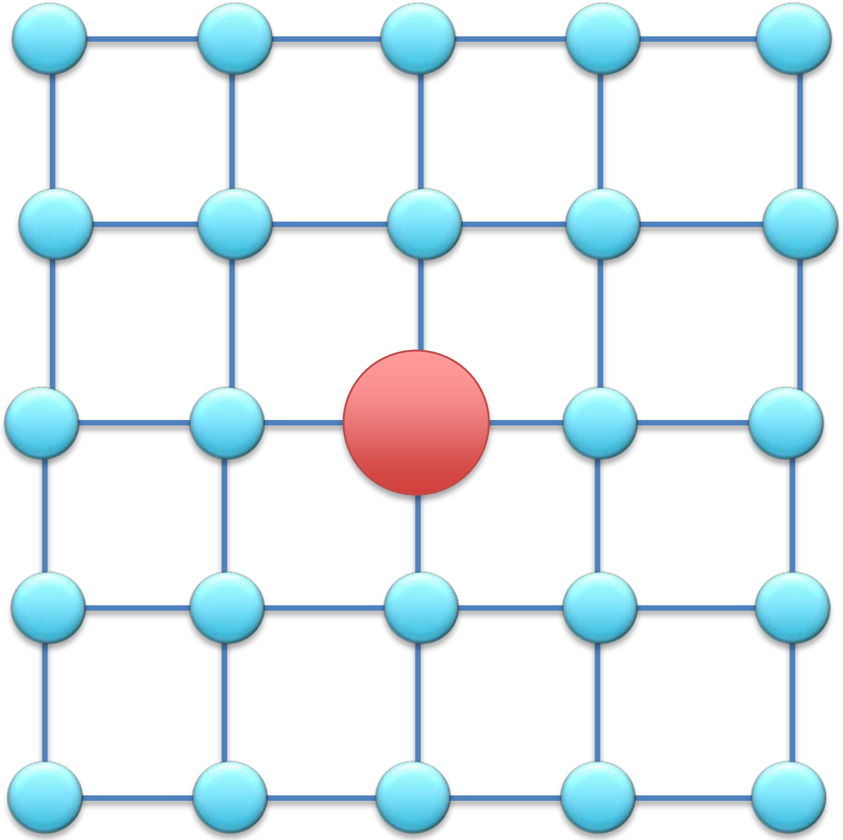
Crystal with many atoms (for example NiO)



Multiplet ligand field theory

Add covalence explicitly, but short range.

Approximate a solid by a single atom interacting with a bath. Add all interactions on the local atom, take the bath in mean-field theory



Multiplet ligand field theory

Add covalence explicitly, but short range.

Approximate a solid by a single atom interacting with a bath. Add all interactions on the local atom, take the bath in mean-field theory

Approximate the bath by a single "site" (i.e. 5 orbitals for a d-shell)

Multiplet ligand field theory

Add covalence explicitly, but short range.

Approximate a solid by a single atom interacting with a bath. Add all interactions on the local atom, take the bath in mean-field theory

Approximate the bath by a single "site" (i.e. 5 orbitals for a d-shell)

Early days –
parameters from experiment

Multiplet ligand field theory

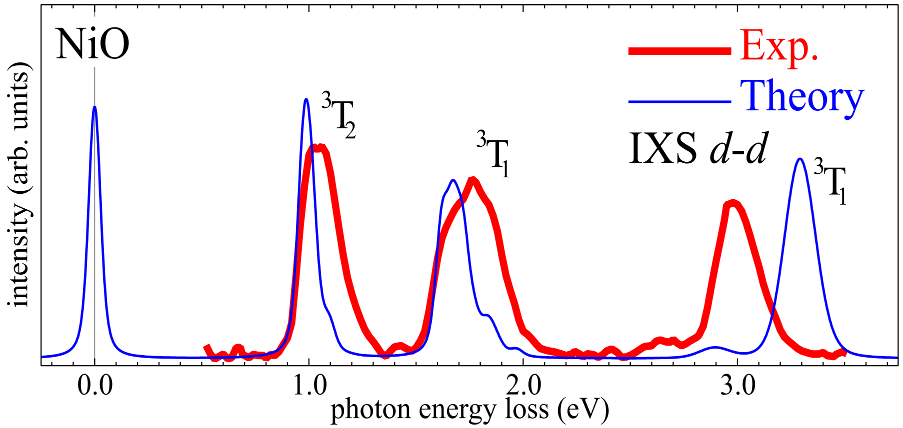
Add covalence explicitly, but short range.

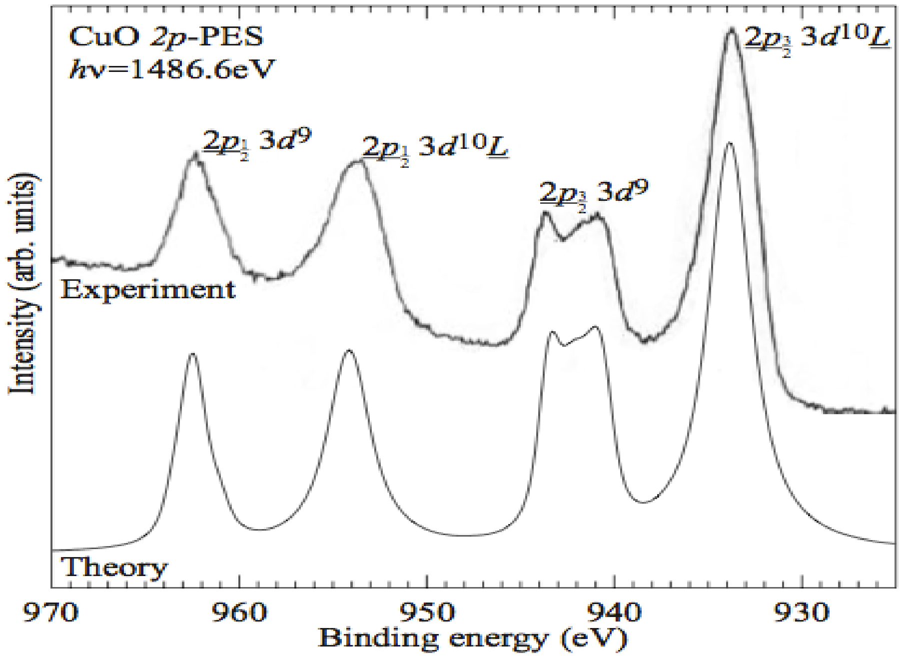
Approximate a solid by a single atom interacting with a bath. Add all interactions on the local atom, take the bath in mean-field theory

Approximate the bath by a single “site” (i.e. 5 orbitals for a d-shell)

Early days –
parameters from experiment

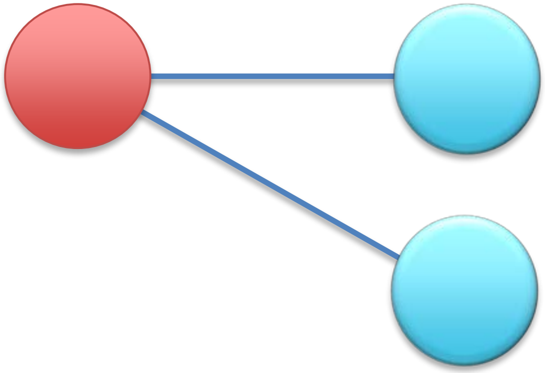
Nowadays –
parameters from theory (DFT)





Beyond – Multiplet ligand field theory

Add more than one ligand. Often needed to get good agreement between ab initio based theory and experiment

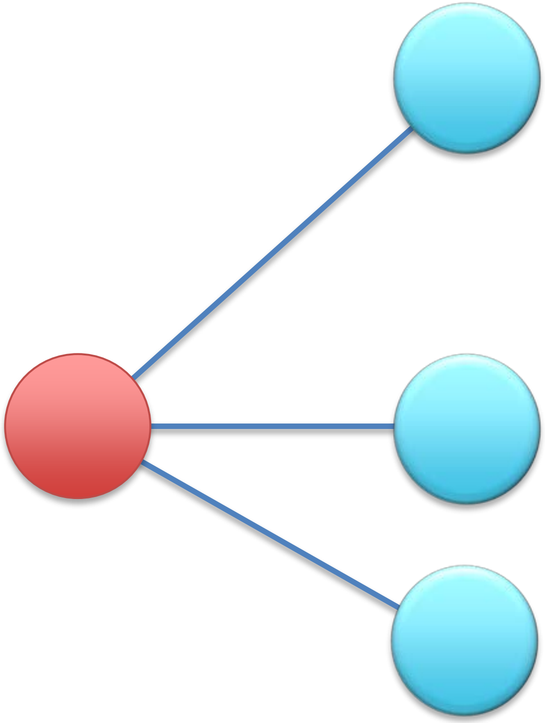


Beyond – Multiplet ligand field theory

Add more than one ligand. Often needed to get good agreement between ab initio based theory and experiment

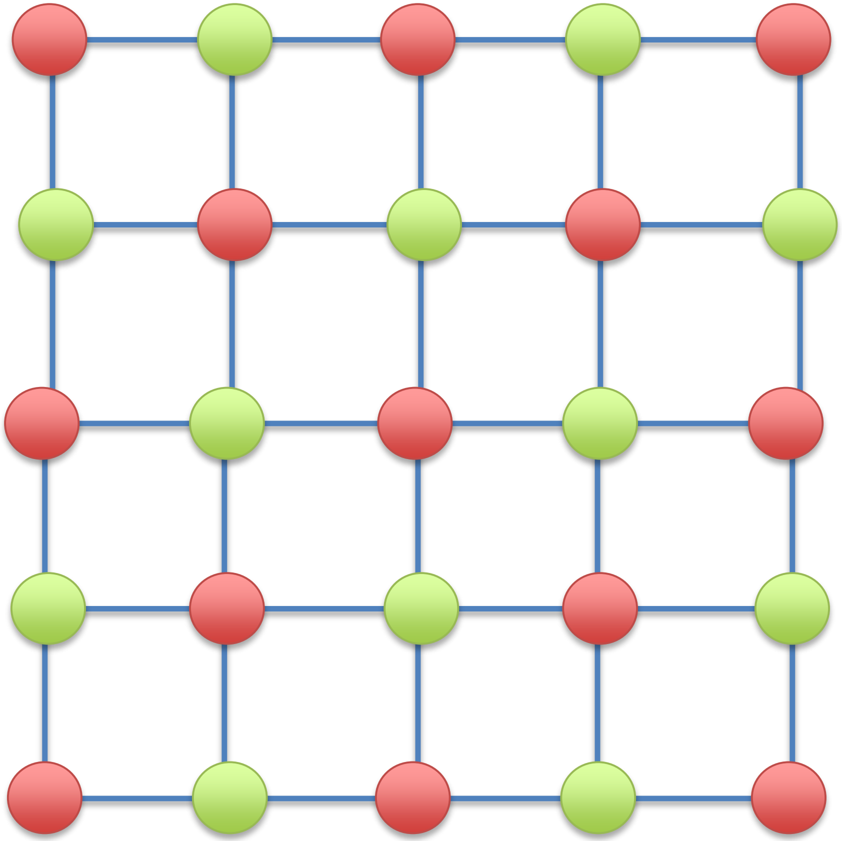
Add both occupied and unoccupied ligand orbitals (π-back bonding)

With renormalization group techniques Quanty can handle hundreds of ligand / bath orbitals



LDA + Multiplet ligand field theory

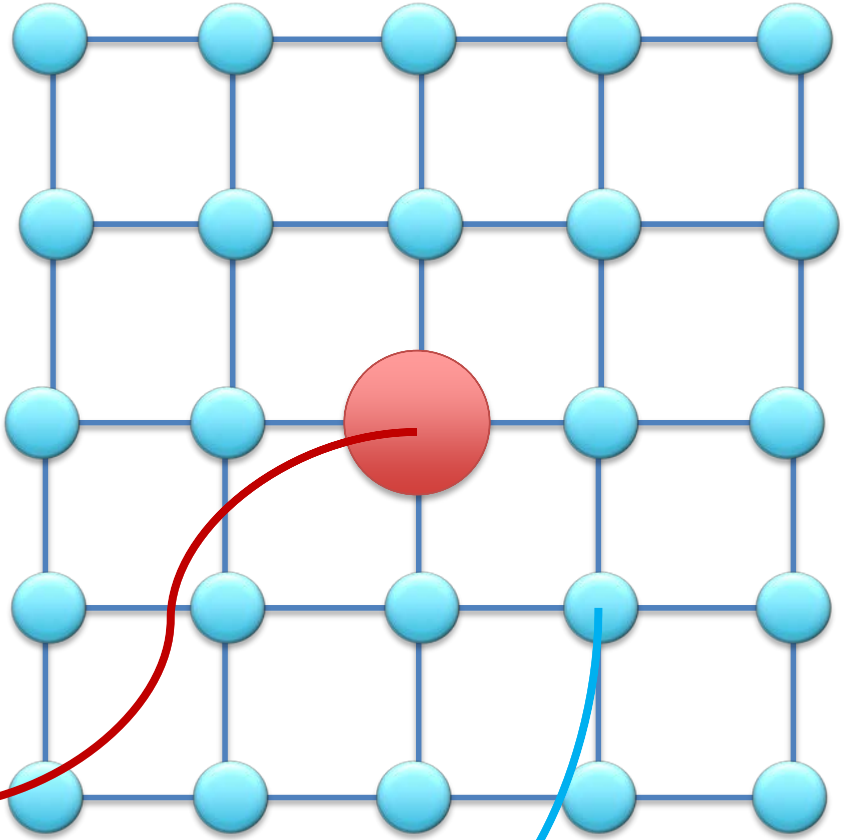
But how to deal with covalence to neighboring correlated open shell sites?



LDA + Multiplet ligand field theory

But how to deal with covalence to neighboring correlated open shell sites?

Replace the full coulomb interaction on all sites, but one by a potential. Set this potential such that the local charge density (matrix) is the same at the impurity and the mean-field approximated sites



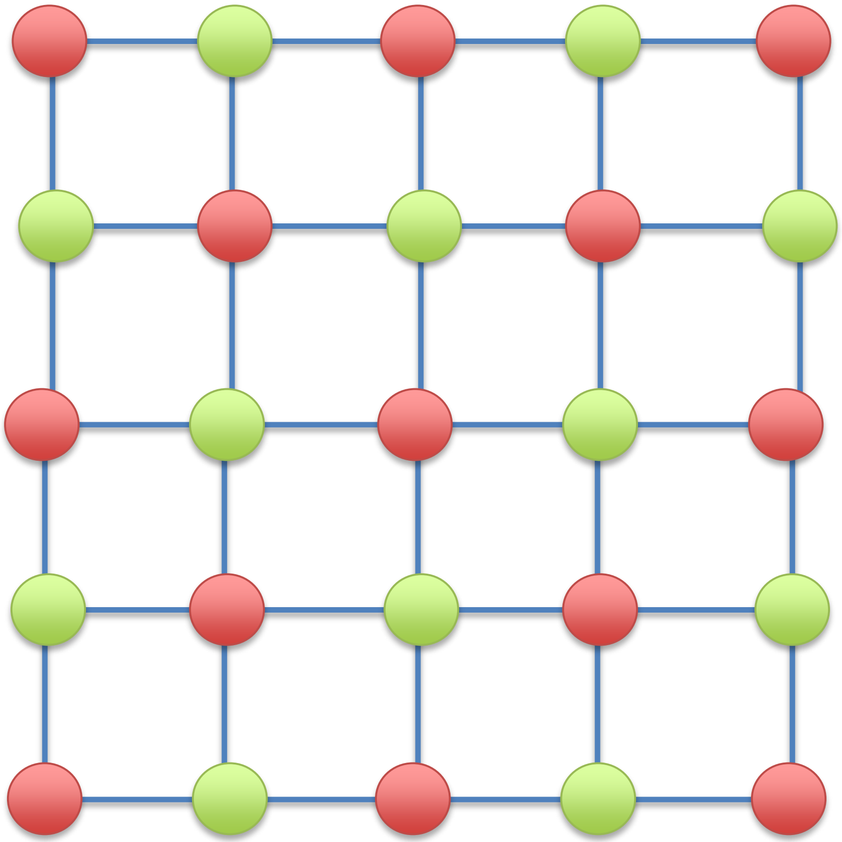
$$\left\langle \psi_0 \left| a^{\dagger}_{n,l,m,\sigma,i=0} a_{n,l,m,\sigma,i=0} \right| \psi_0 \right\rangle$$

$$\left\langle \psi_0 \left| a^{\dagger}_{n,l,m,\sigma,i=\infty} a_{n,l,m,\sigma,i=\infty} \right| \psi_0 \right\rangle$$

Dynamical Mean-Field Theory

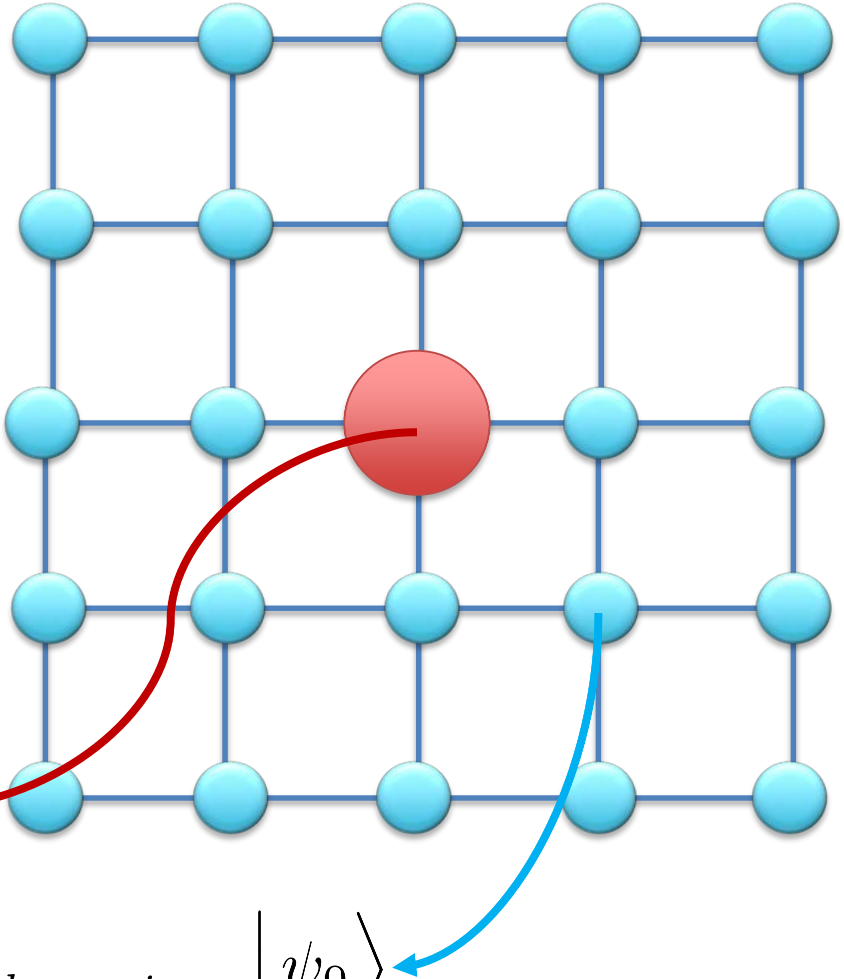
Dynamical Mean-Field Theory

In LDA+MLFT we approximated the solid by a single atom interacting with a bath (set of ligand orbitals) such that the one particle density at the impurity and mean-field approximated neighbors are equivalent



Dynamical Mean-Field Theory

In LDA+MLFT we approximated the solid by a single atom interacting with a bath (set of ligand orbitals) such that the one particle density at the impurity and mean-field approximated neighbors are equivalent

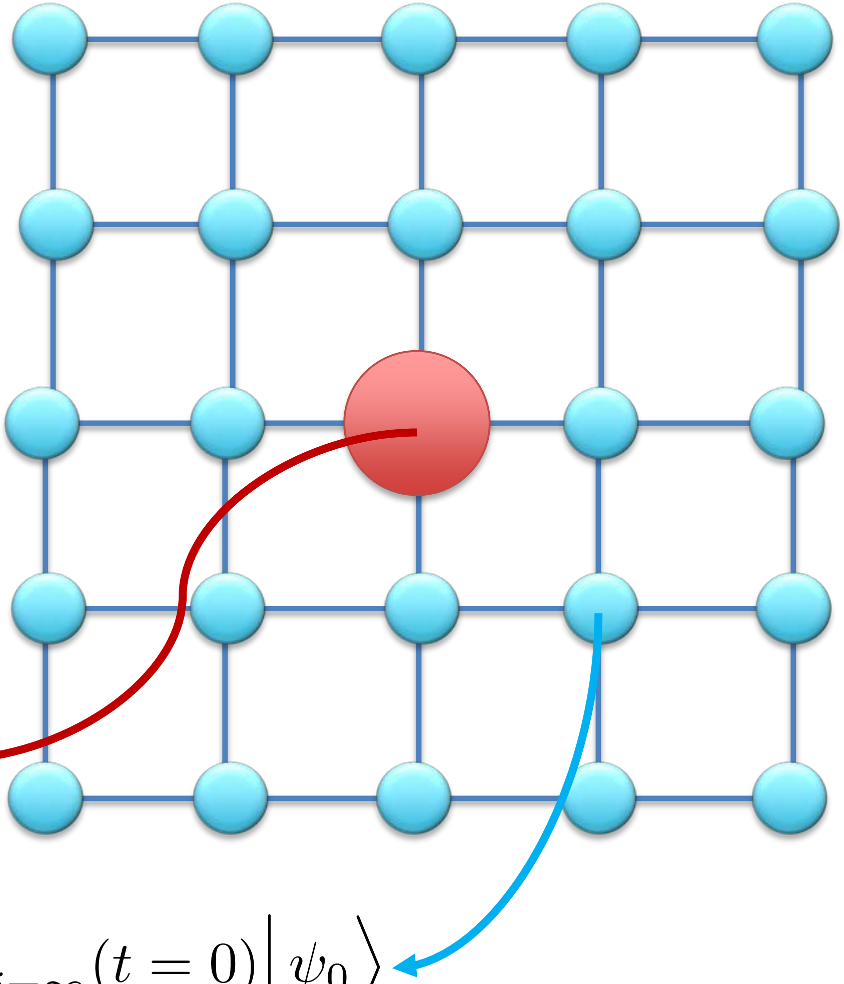


$$\left\langle \psi_0 \left| a^\dagger_{n,l,m,\sigma,i=0} a_{n,l,m,\sigma,i=0} \right| \psi_0 \right\rangle$$

$$\left\langle \psi_0 \left| a^\dagger_{n,l,m,\sigma,i=\infty} a_{n,l,m,\sigma,i=\infty} \right| \psi_0 \right\rangle$$

Dynamical Mean-Field Theory

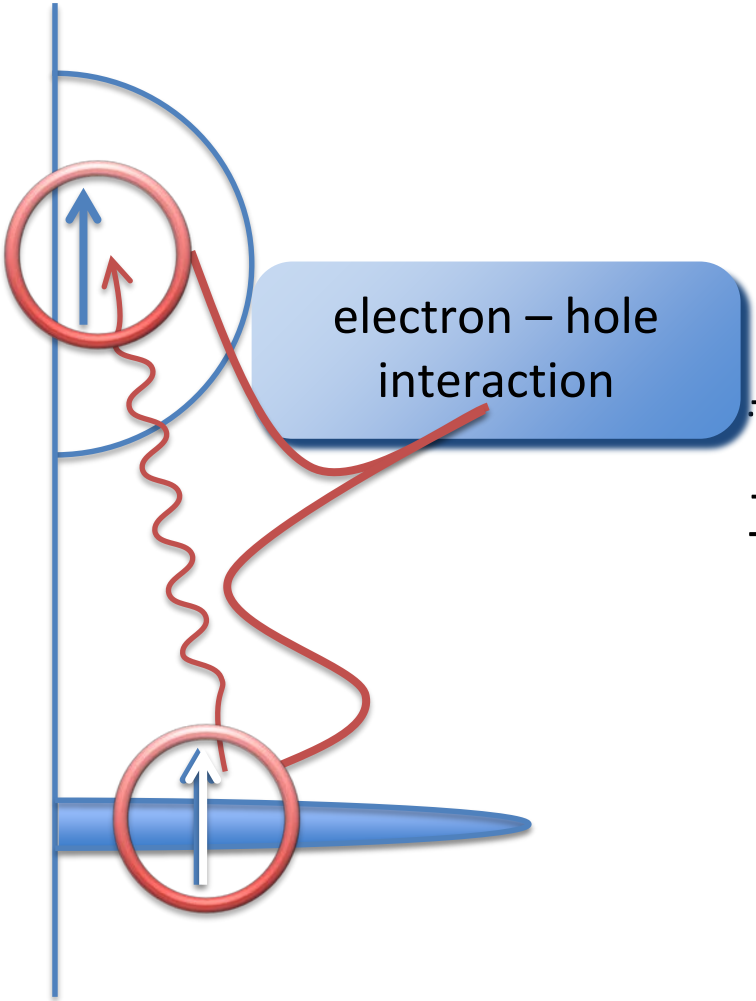
In DMFT we make the one particle Green's function between the impurity and bath self consistent

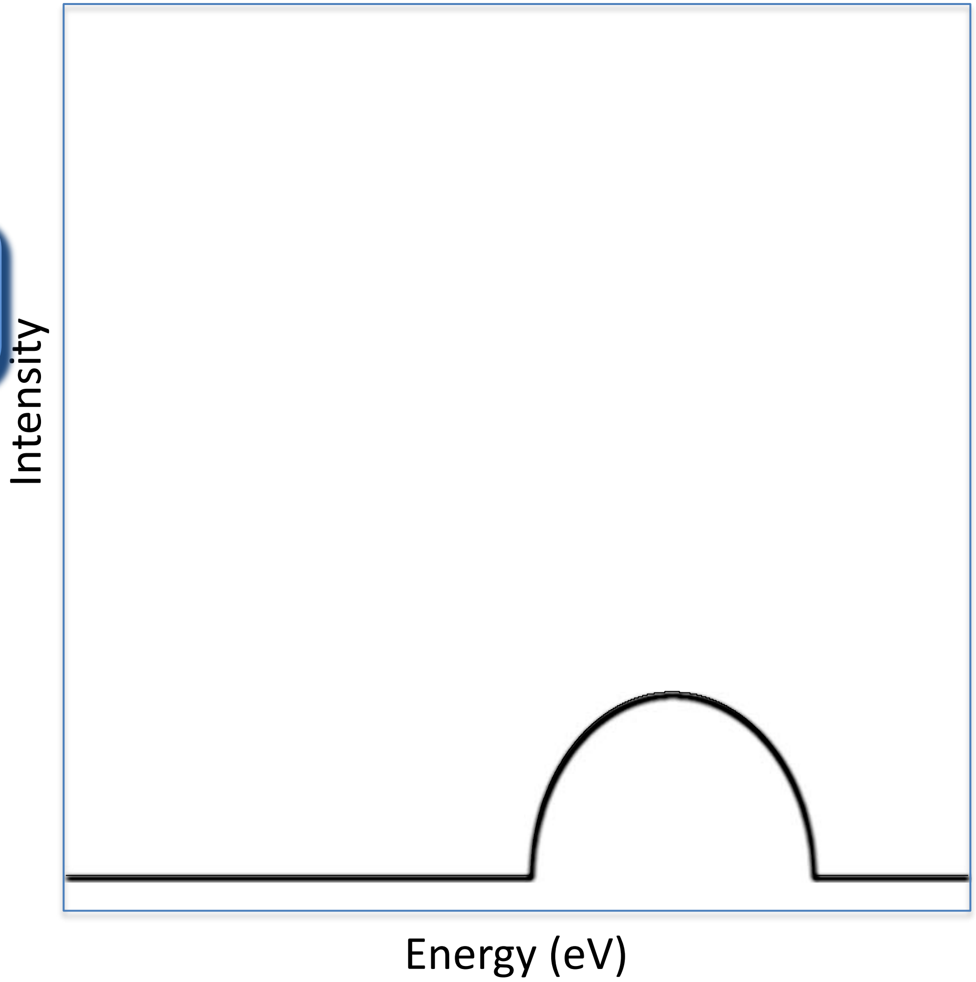


$$\left\langle \psi_0 \left| a^\dagger_{n,l,m,\sigma,i=0}(t) a_{n,l,m,\sigma,i=0}(0) \right| \psi_0 \right\rangle$$

$$\left\langle \psi_0 \left| a^\dagger_{n,l,m,\sigma,i=\infty}(t) a_{n,l,m,\sigma,i=\infty}(t=0) \right| \psi_0 \right\rangle$$

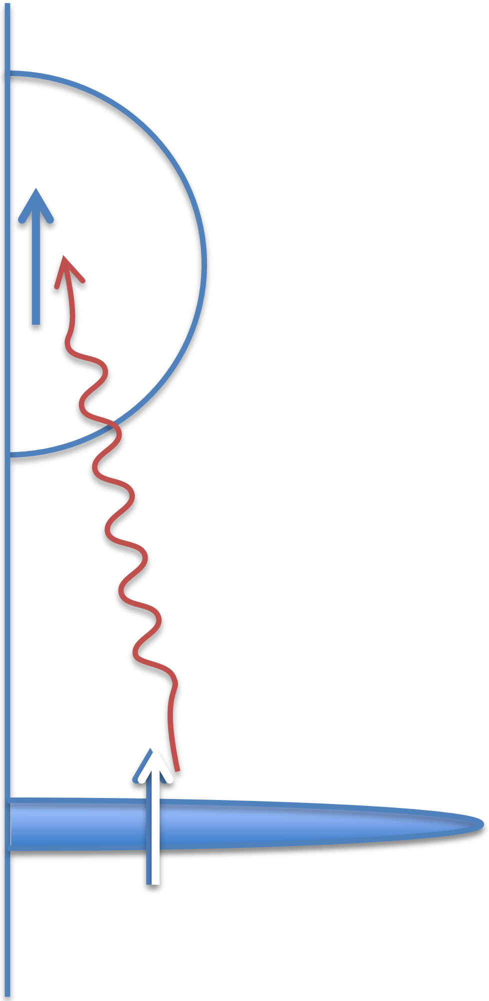
Example – bands excitations, resonances and excitons

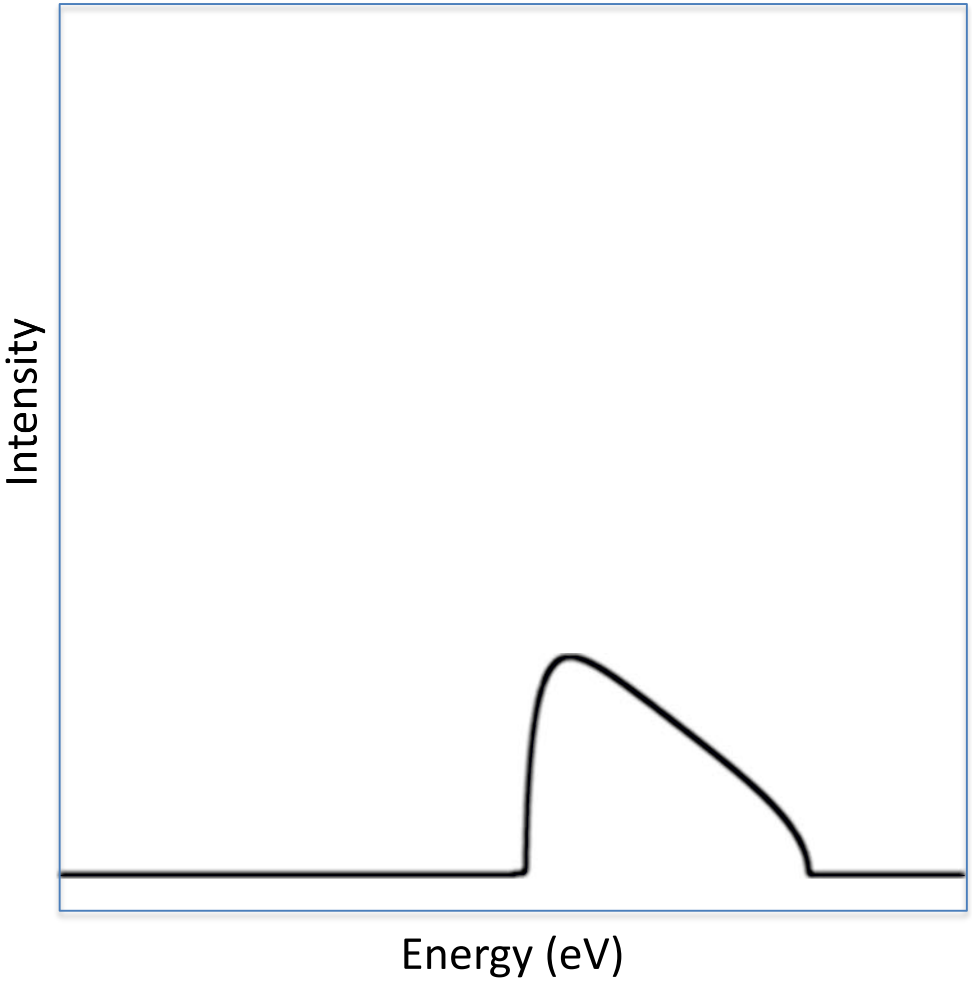

electron – hole interaction



M.W.Haverkort et al. EPL, 108 57004(2014)

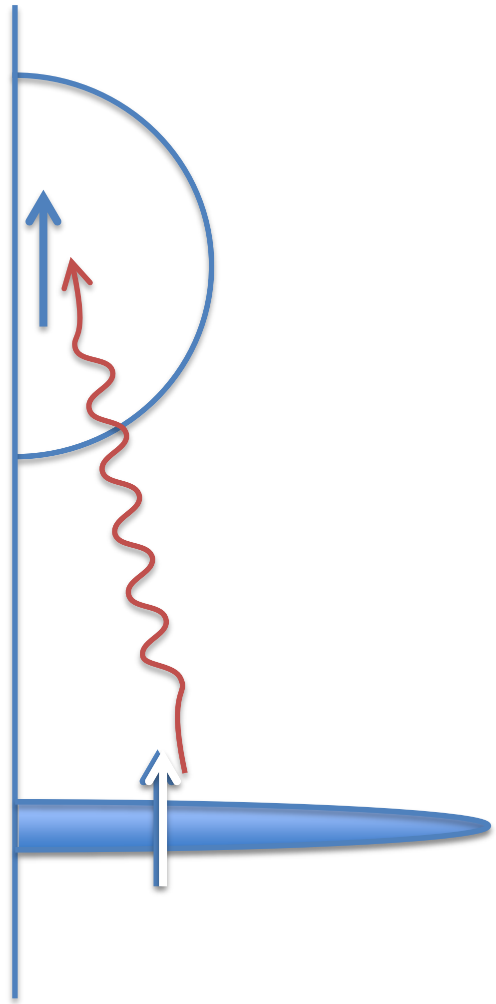
Example – bands excitations, resonances and excitons

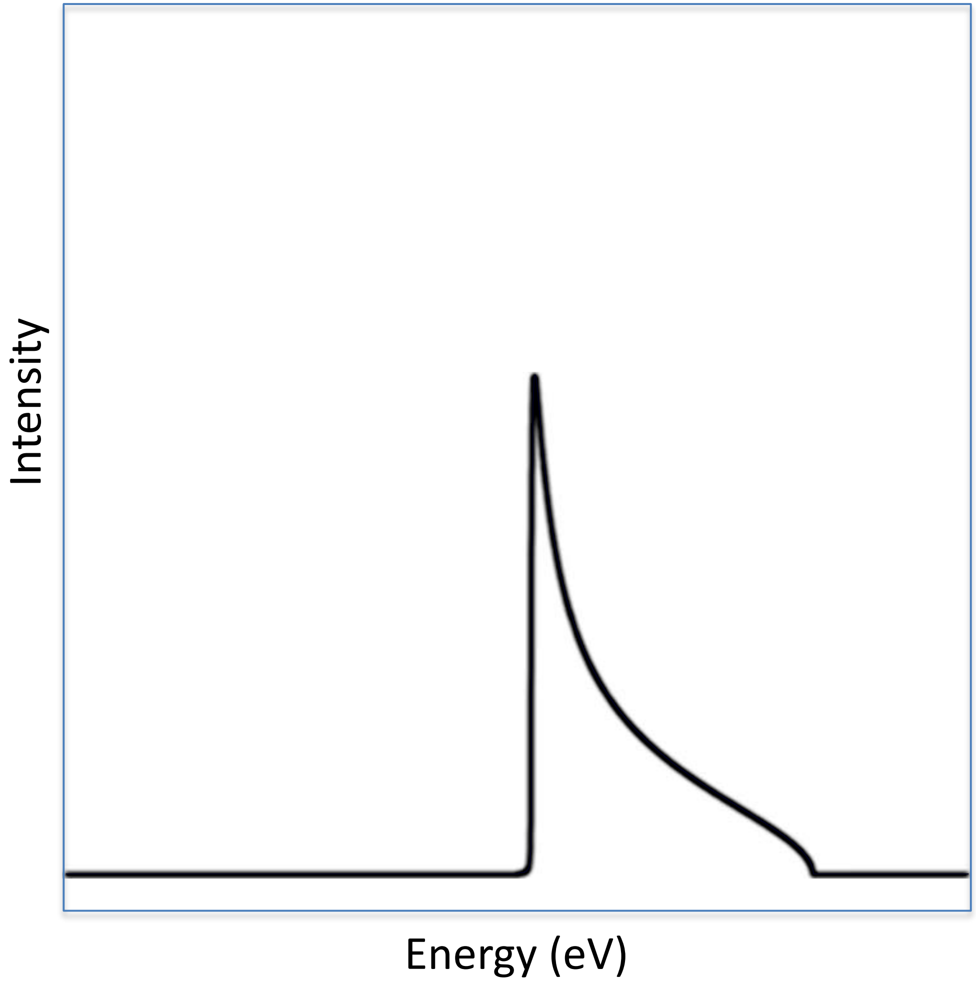




M.W.Haverkort et al. EPL, 108 57004(2014)

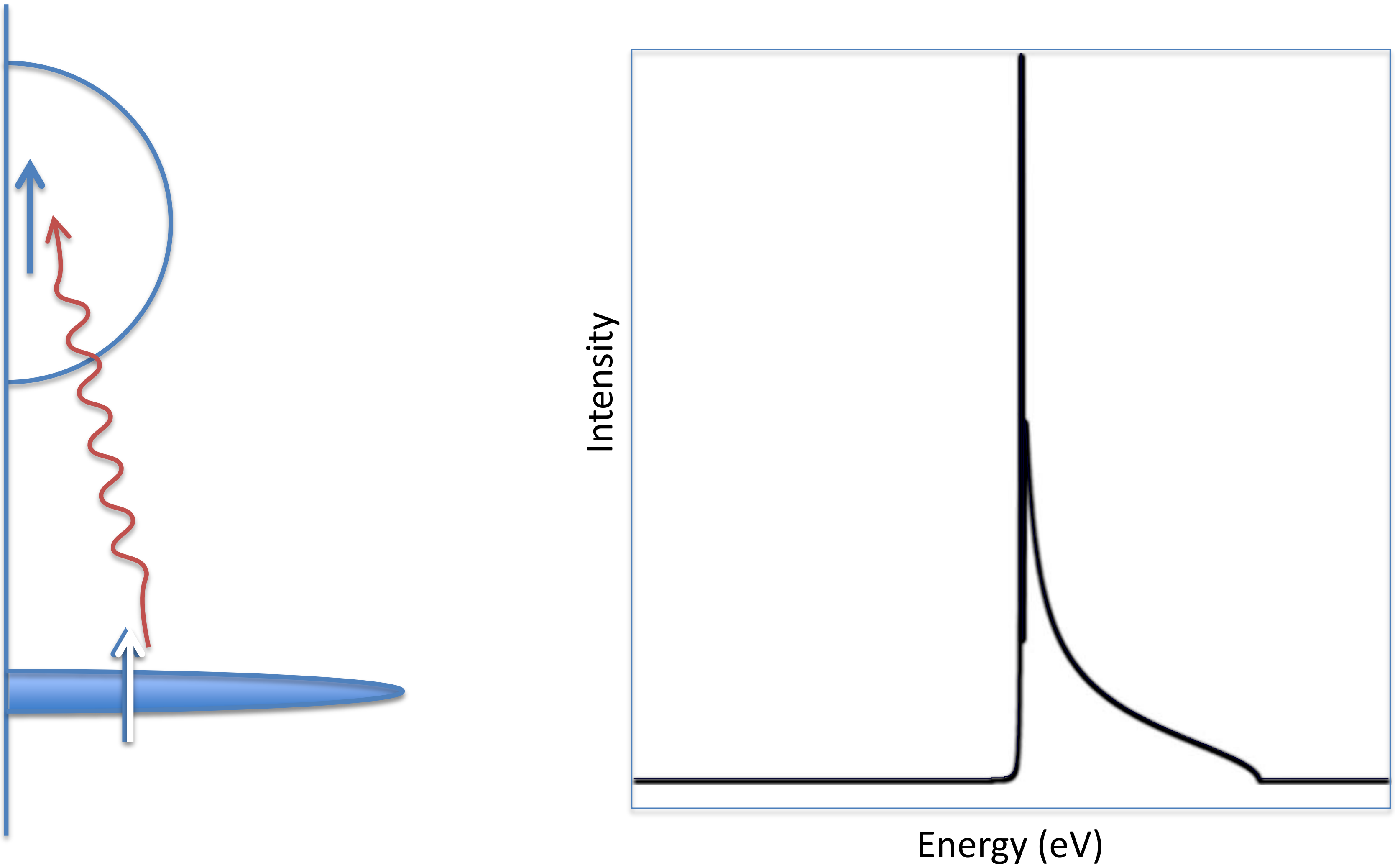
Example – bands excitations, resonances and excitons





M.W.Haverkort et al. EPL, 108 57004(2014)

Example – bands excitations, resonances and excitons



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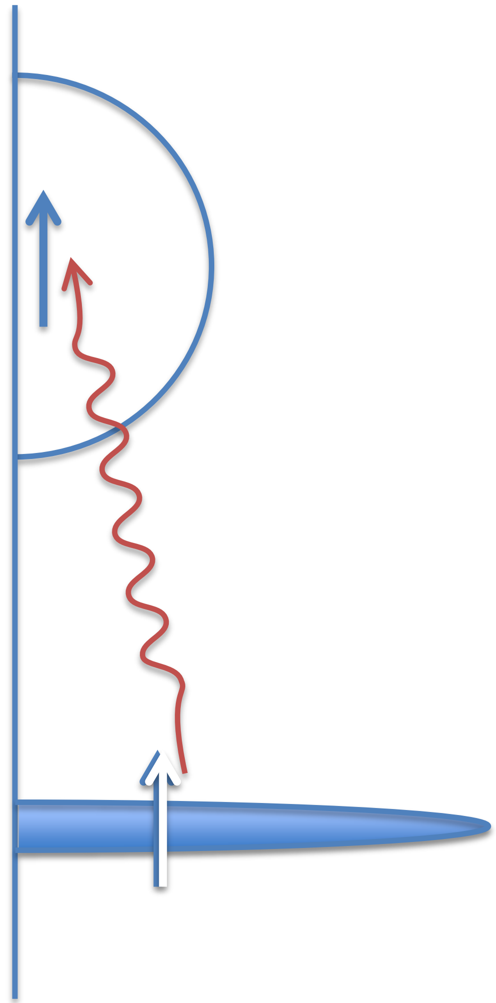

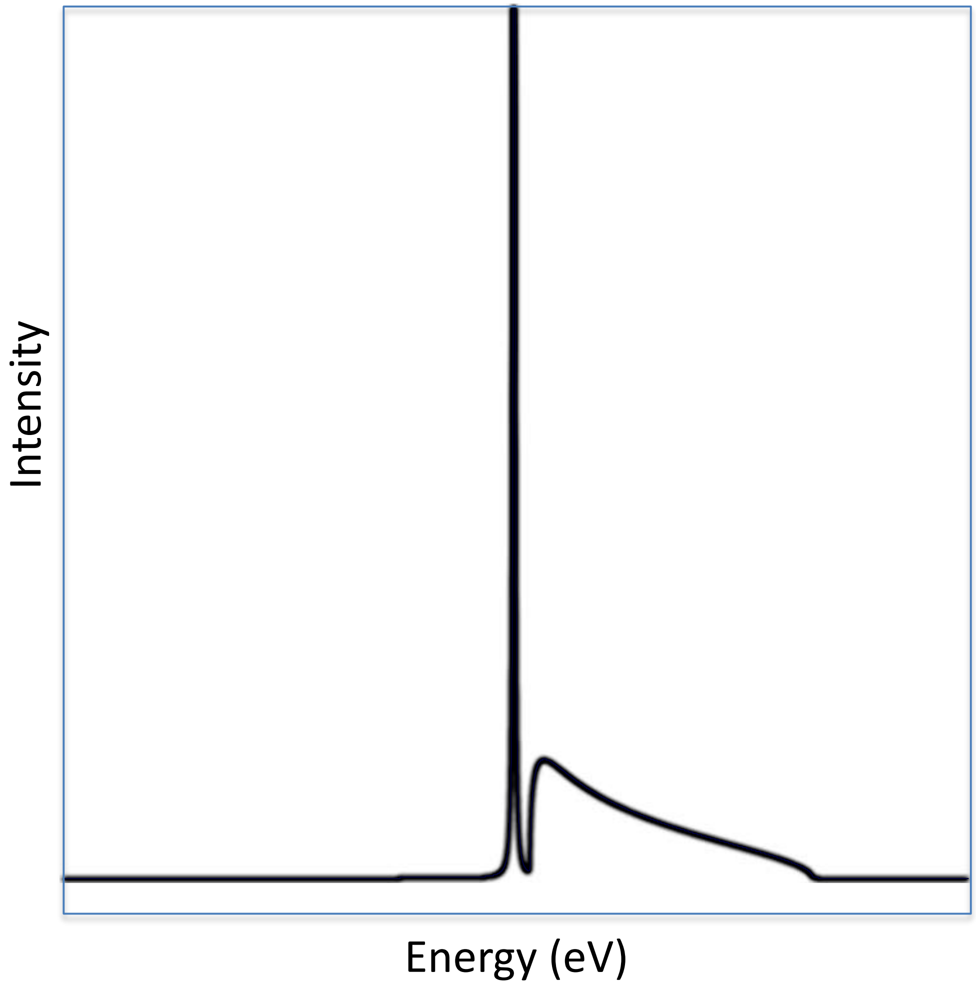

M.W.Haverkort et al. EPL, 108 57004(2014)

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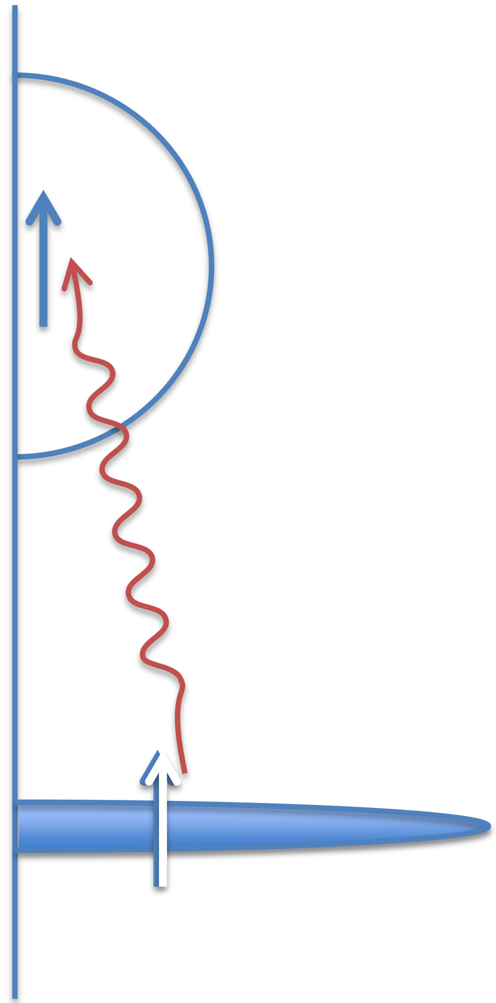

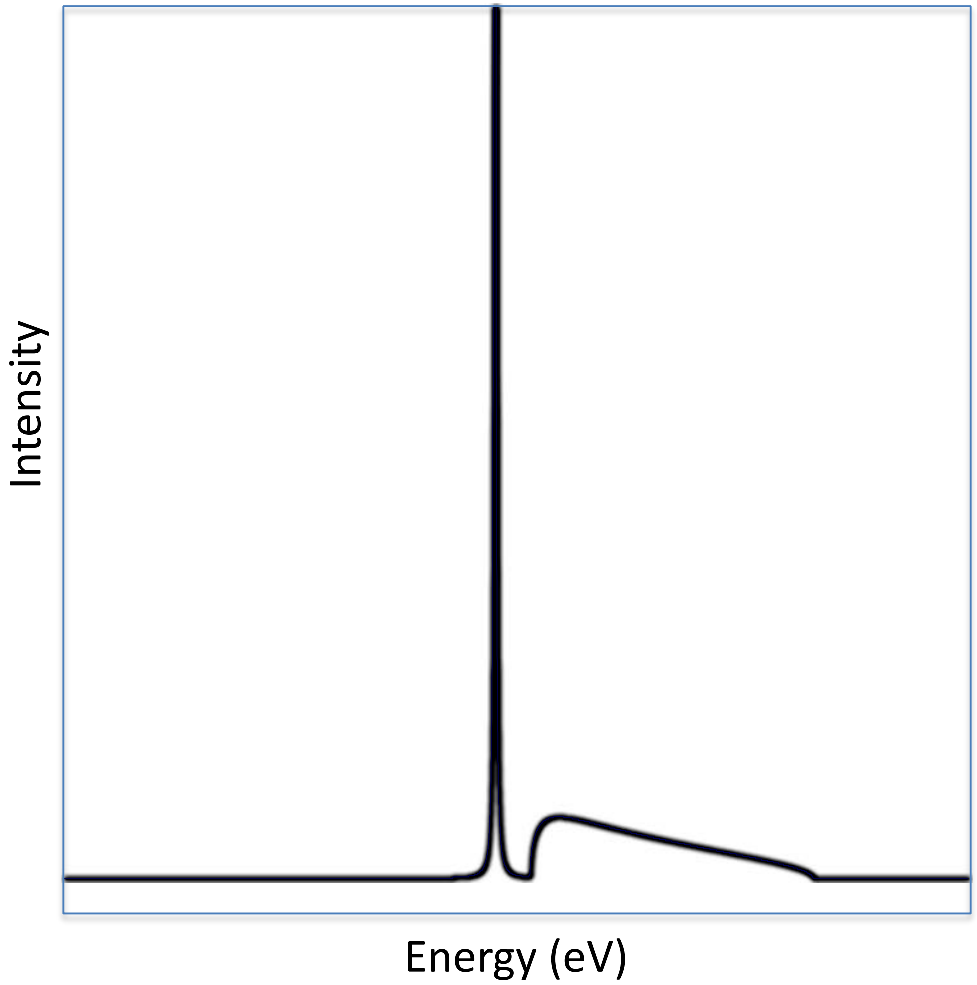

M.W.Haverkort et al. EPL, 108 57004(2014)

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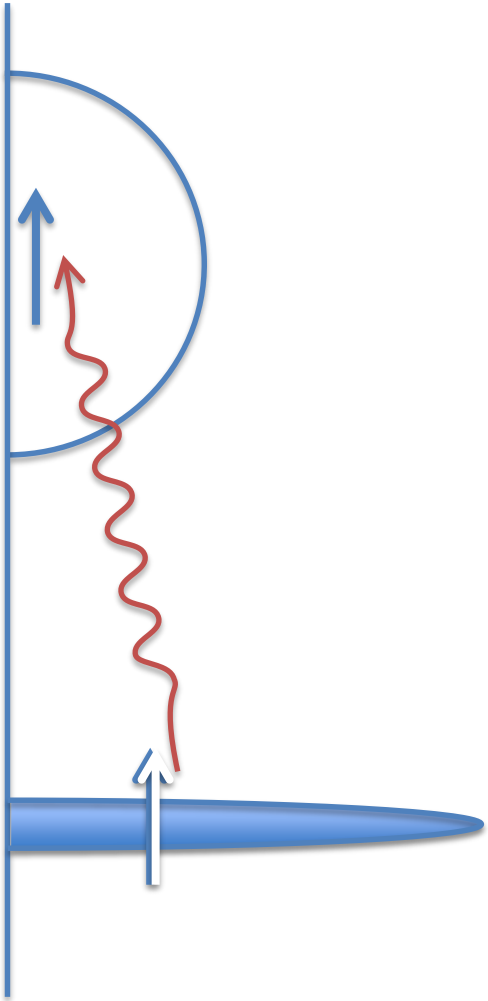
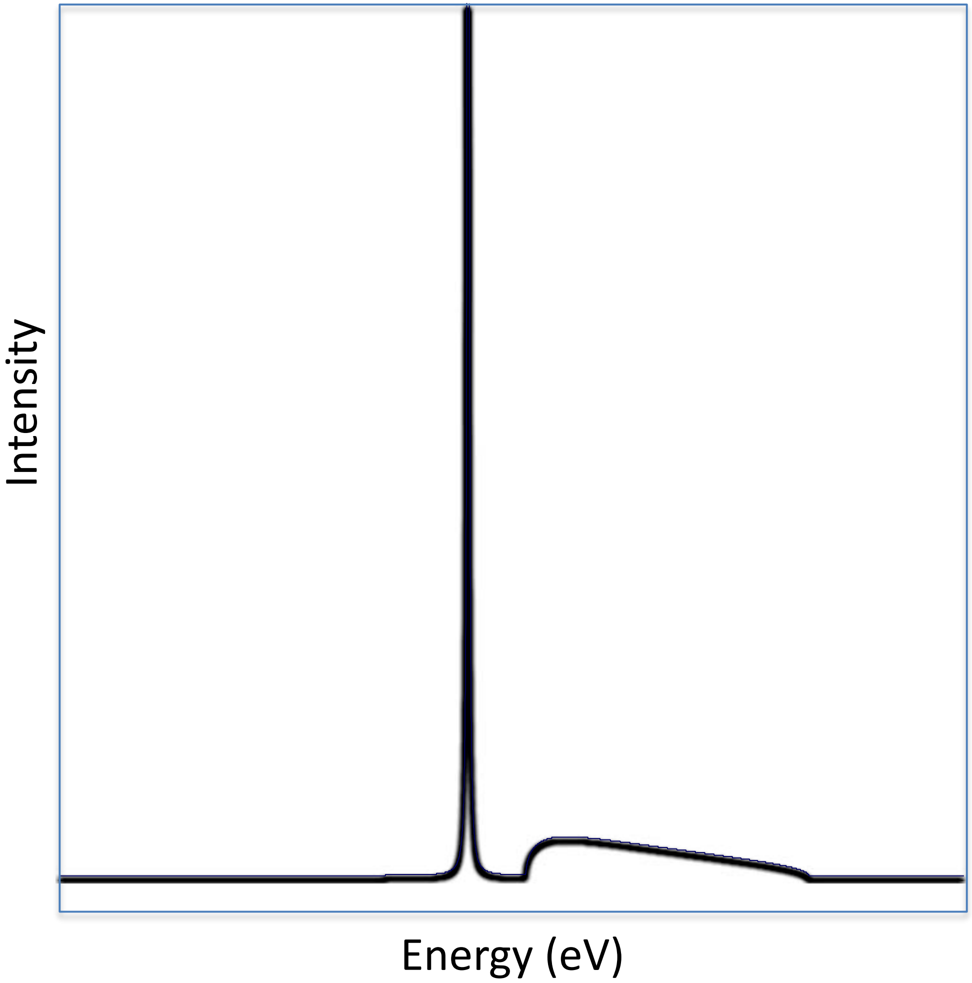
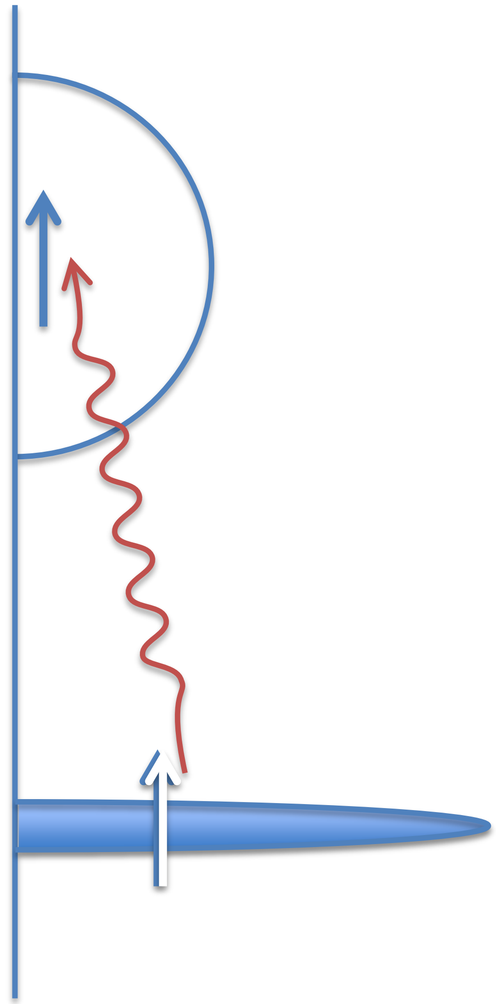
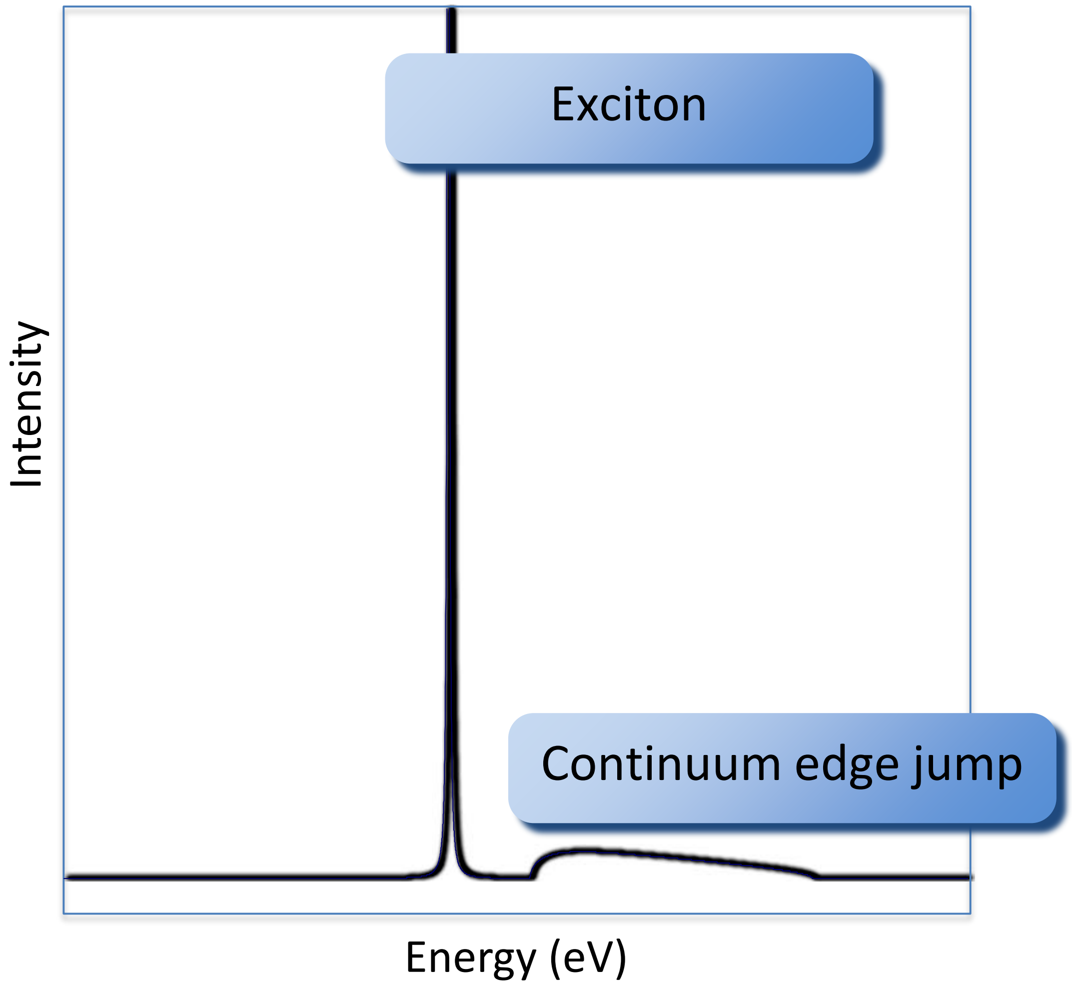




M.W.Haverkort et al. EPL, 108 57004(2014)

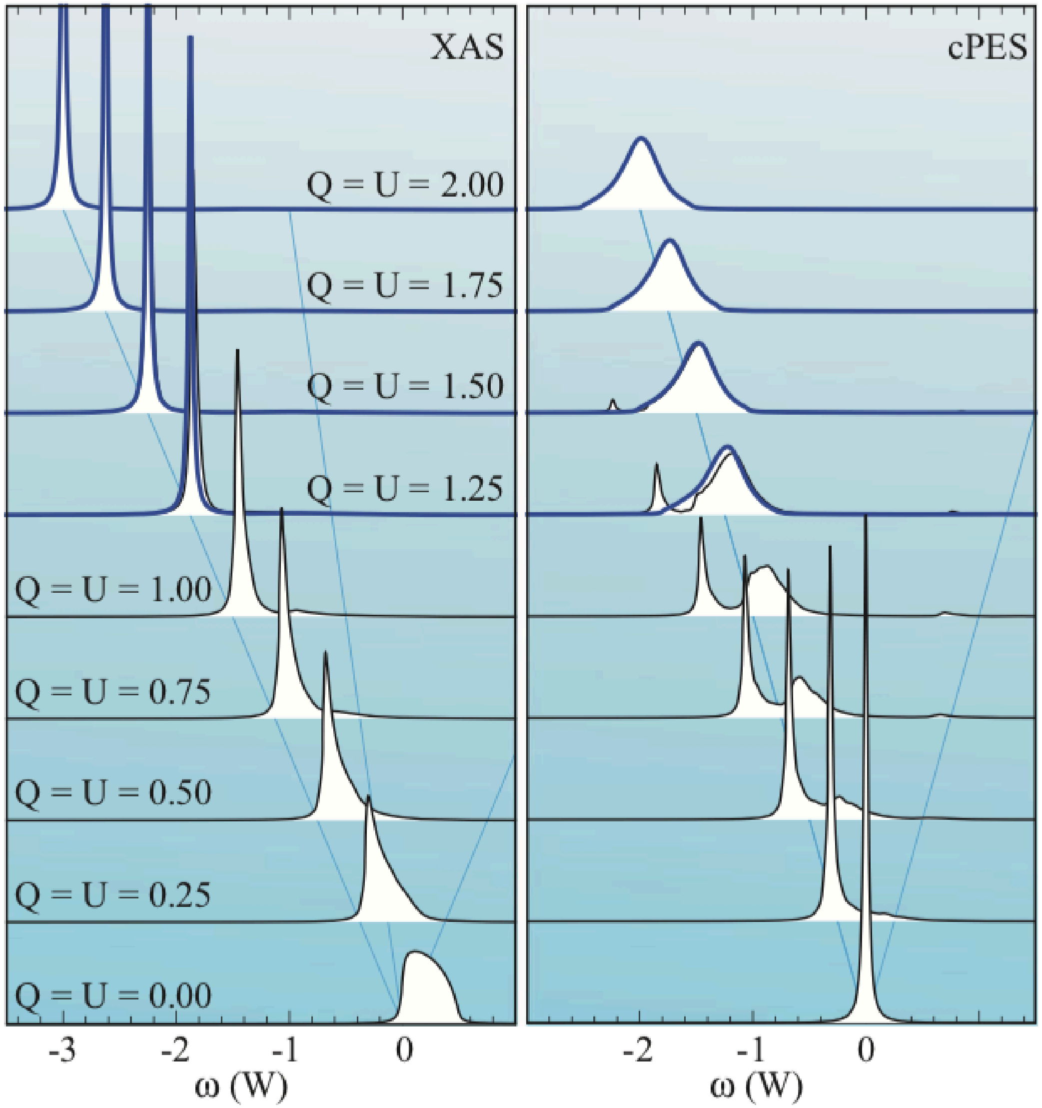
Example – bands excitations, resonances and excitons





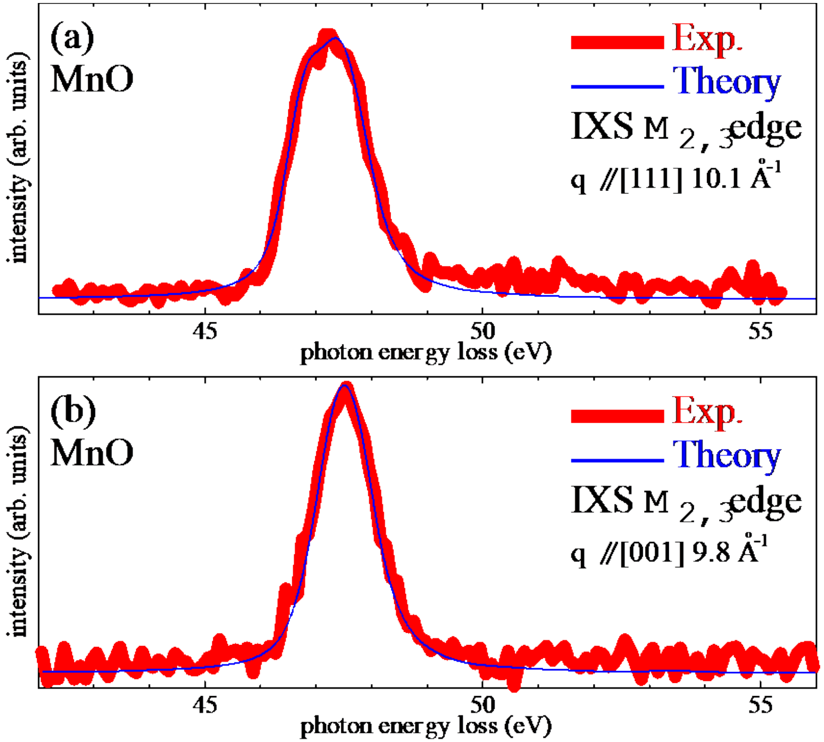
M.W.Haverkort et al. EPL, 108 57004(2014)

XAS and XPS on an DMFT level

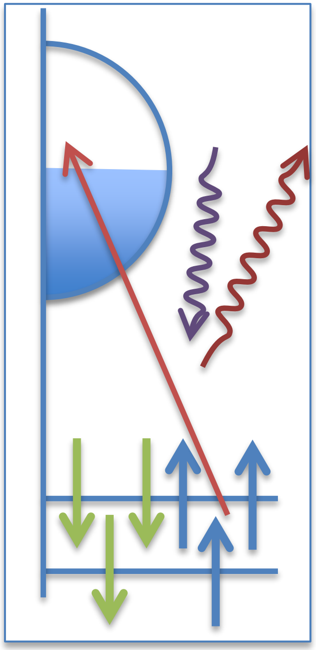


M.W.Haverkort et al. EPL, 108 57004(2014)

nIXS in MnO – M_{23} edge *3p* to *3d* – giant resonances -



Excitons are well described using a local model (**LDA+MLFT**)



J. of Phys.: Conf. Ser. **190** 012047 (2009)
J. of Phys.: Conf. Ser. **712** 012001 (2016)

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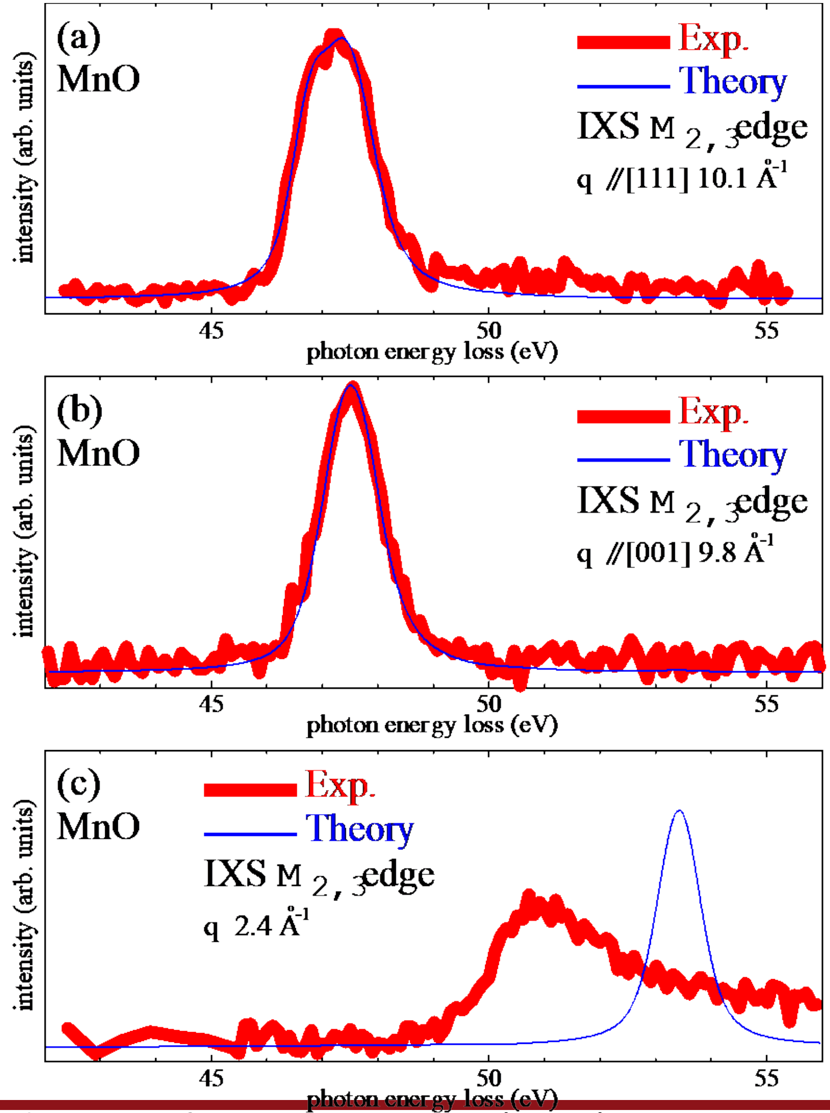

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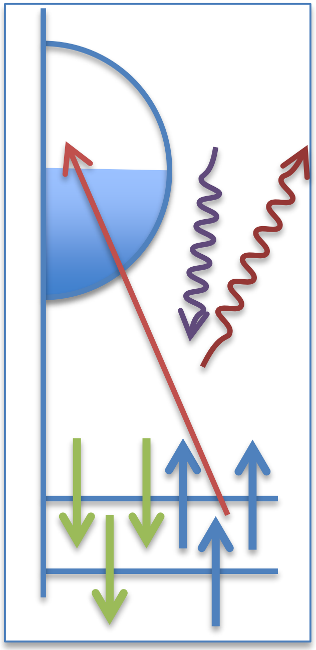

Resonances (multiplets above the continuum edge) are not well described using a local model

J. of Phys.: Conf. Ser. **190** 012047 (2009)
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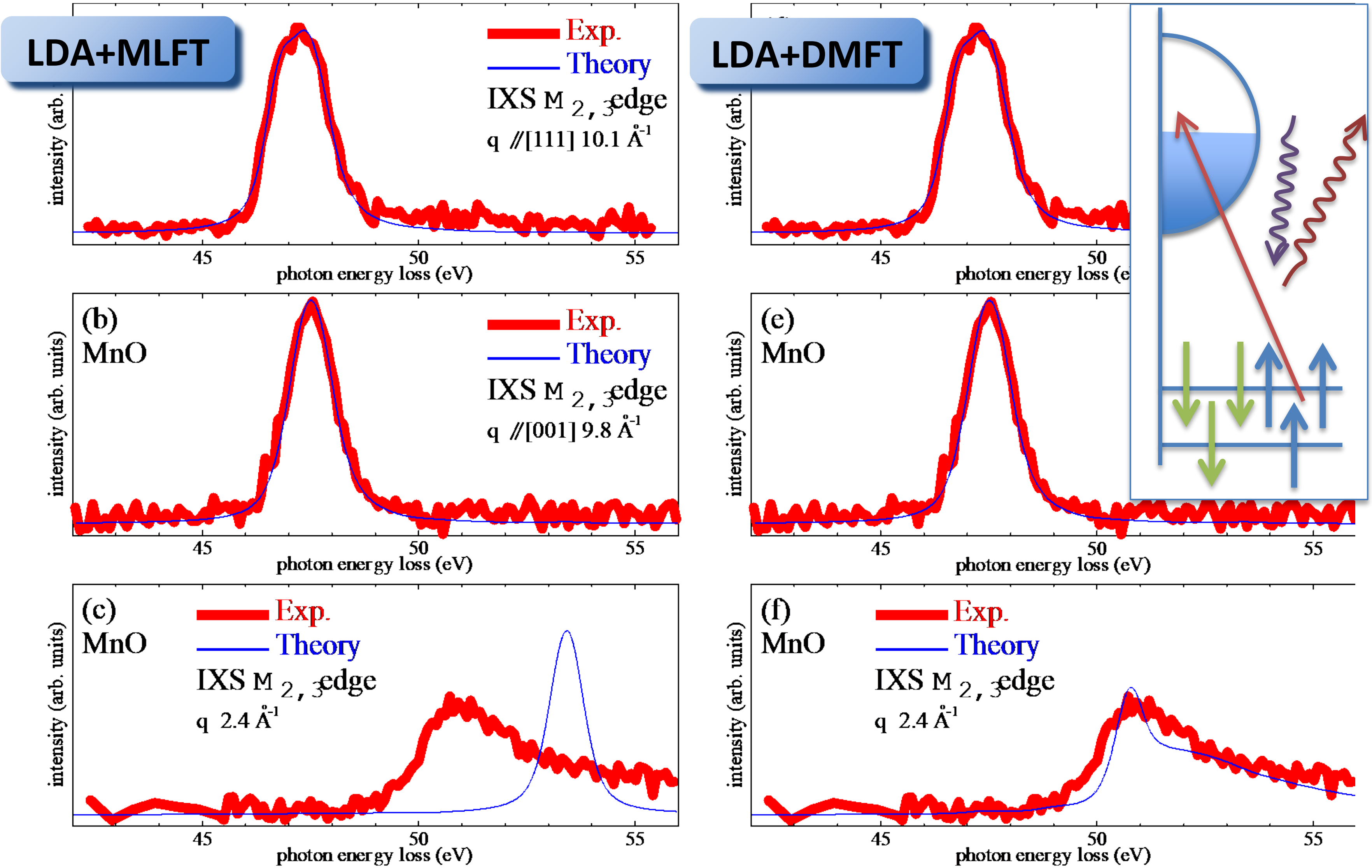
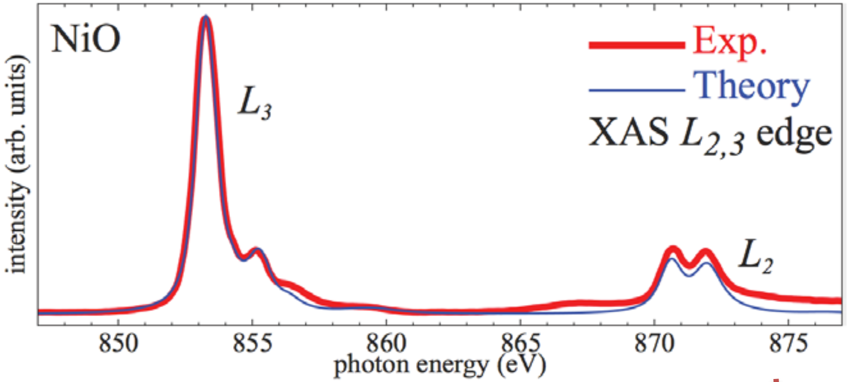
nIXS in MnO – M_{23} edge *3p* to *3d* – giant resonances

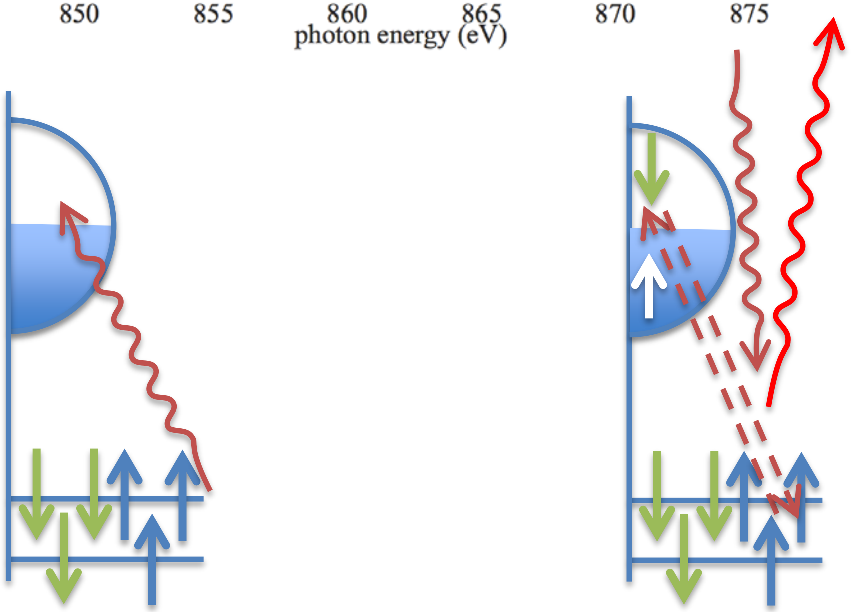


J. of Phys.: Conf. Ser. **190** 012047 (2009)
J. of Phys.: Conf. Ser. **712** 012001 (2016)

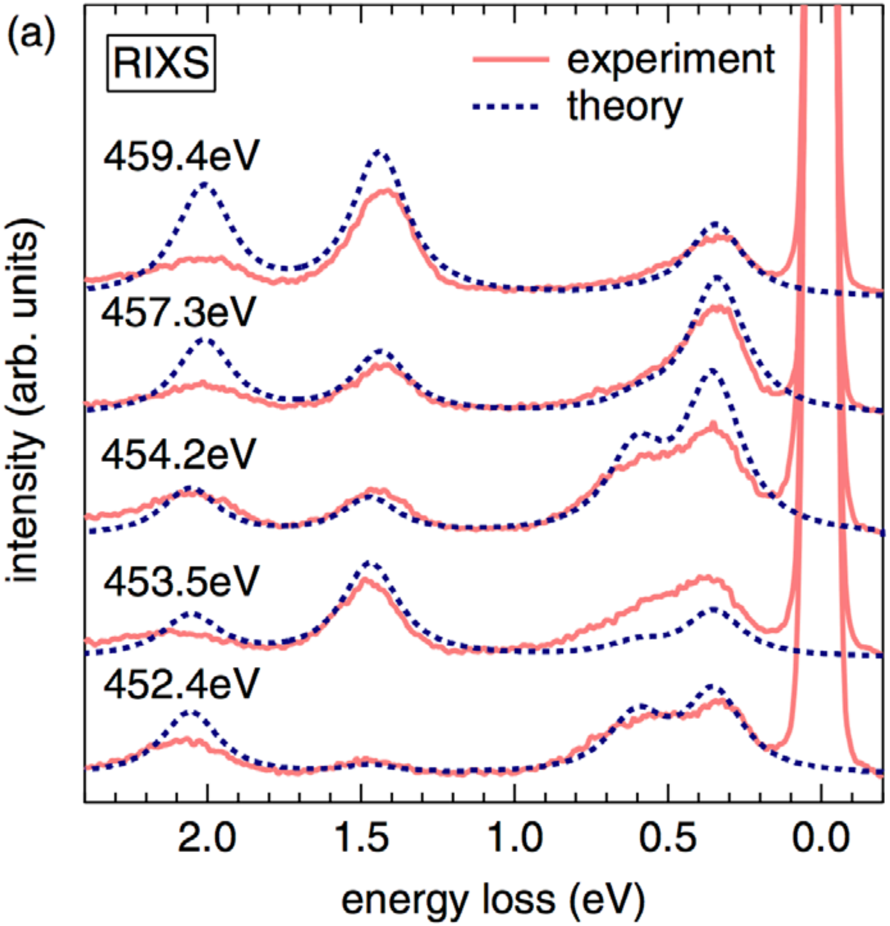
Core level spectroscopy of excitionic states LDA+DMFT

Ab initio calculation of spectra





Beyond linear response - RIXS

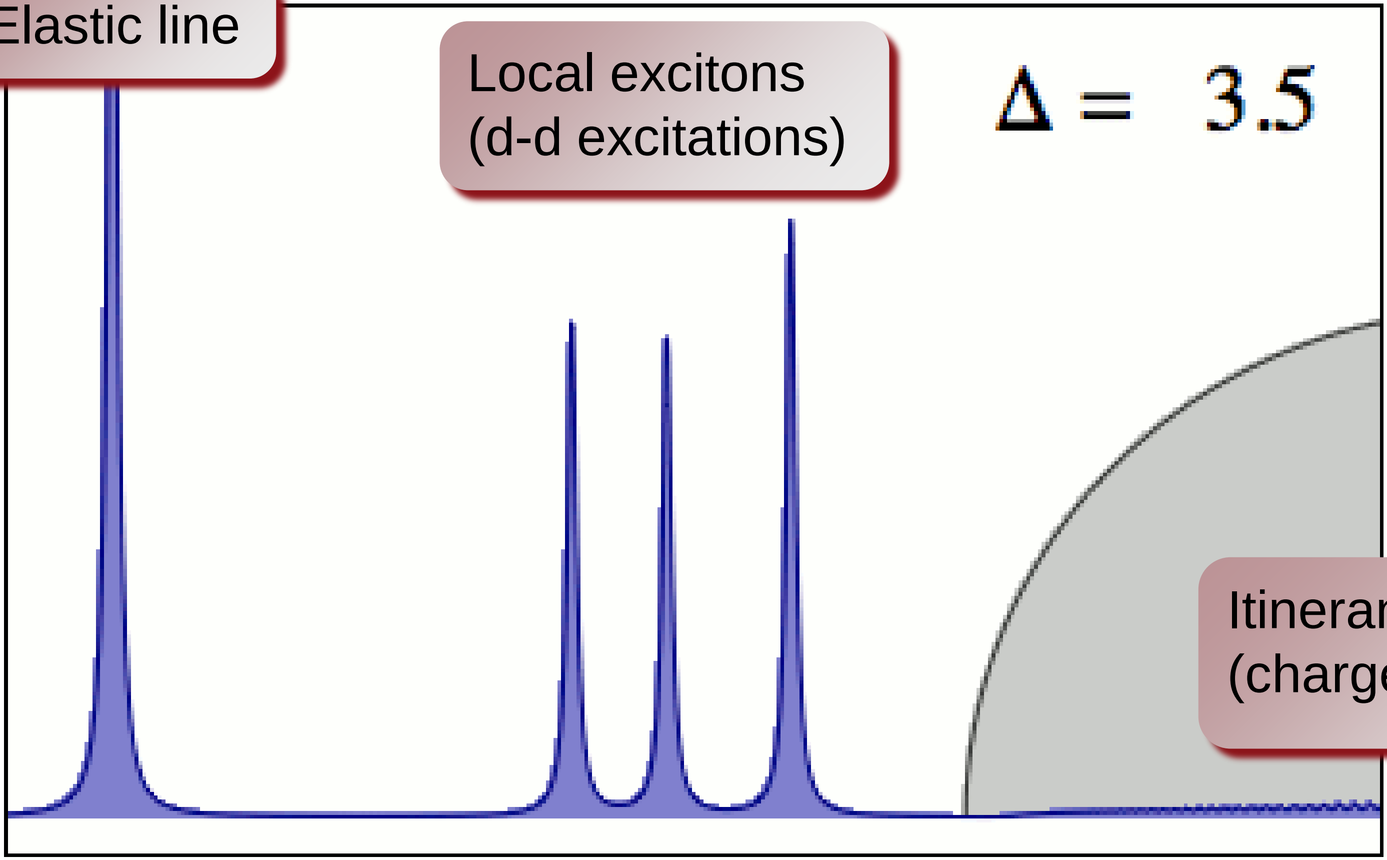


PRL **95,** 097203 (2005), PRL **107**, 107402 (2011)
PRB **85**, 165113 (2012), J. Phys.: Condens. Matter 24 255602 (2012)

Decay of localized into delocalized states – resonances

Interaction of localized with delocalized states

Example RIXS of Cuprates as function of charge transfer energy Δ



Elastic line

Local excitons (d-d excitations)

Itinerant excitations (charge-transfer)

Decay of localized into delocalized states – resonances

Interaction of localized with delocalized states

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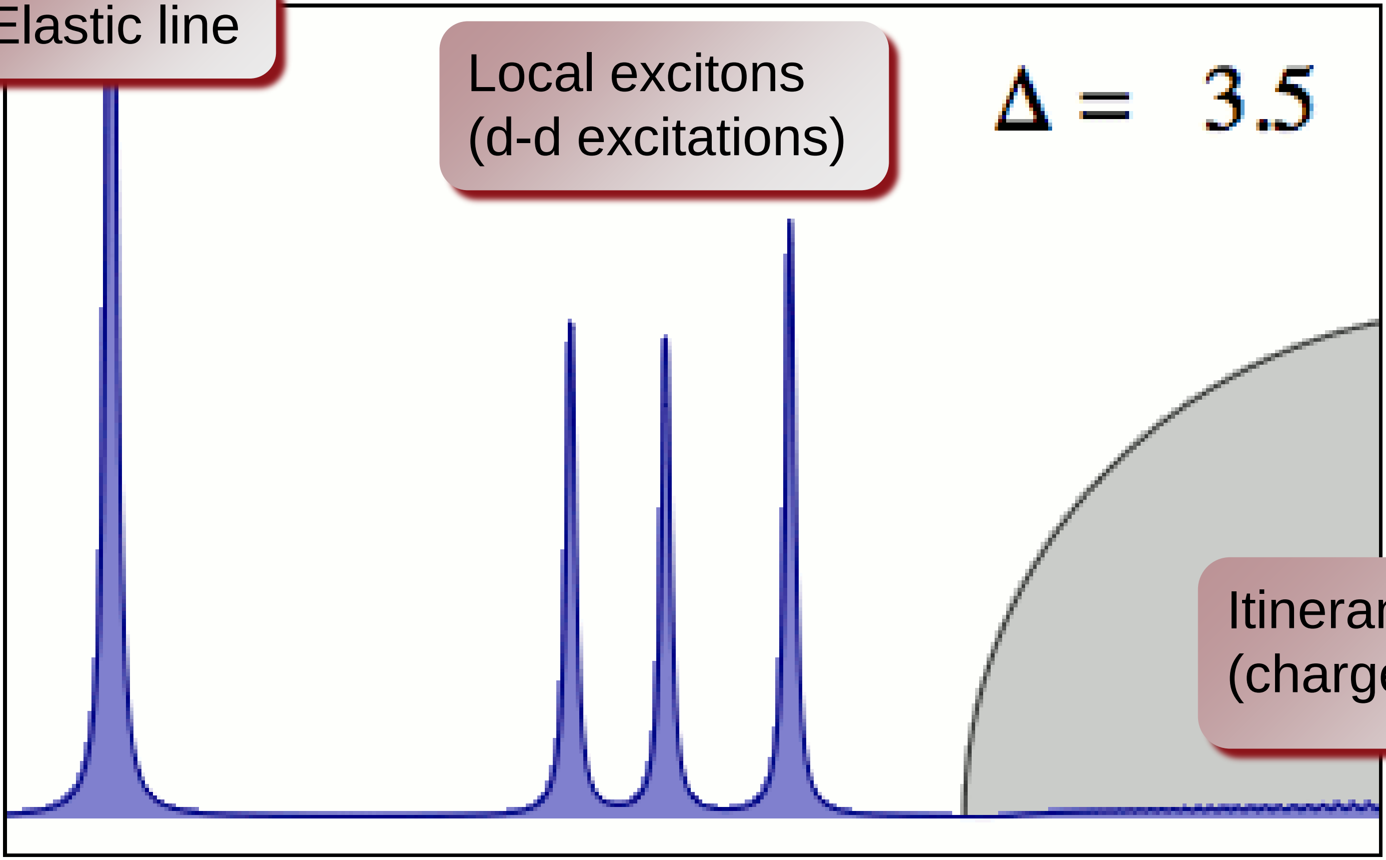

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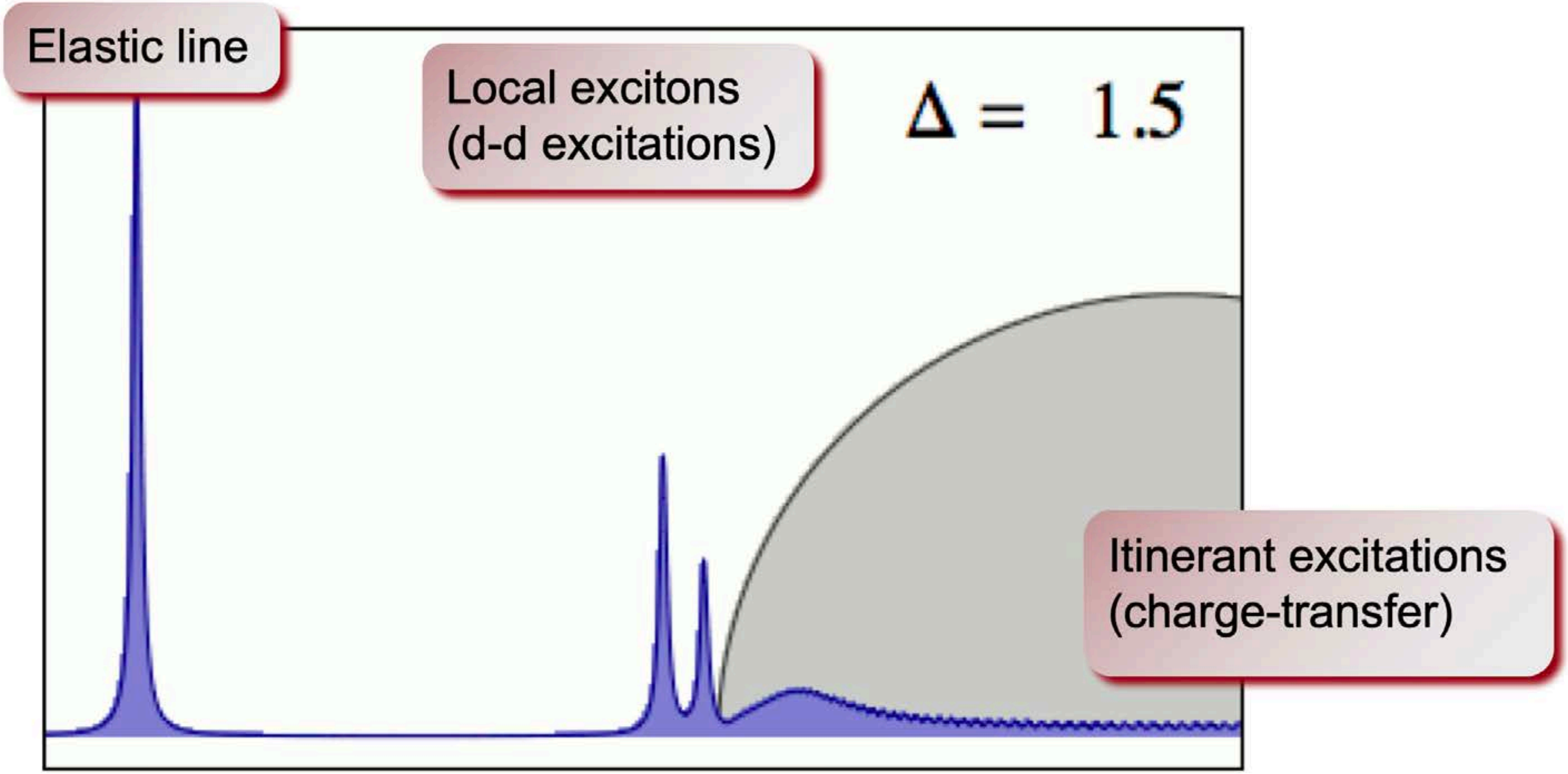


Self energy and line-width

The intensity measured in a spectroscopy experiment is given by

$$I = -\frac{1}{\pi}\mathrm{Im}\left\langle i \left| T^{\dagger} \frac{1}{\omega - H + \mathrm{i}\frac{\Gamma}{2}} T \right| i \right\rangle$$

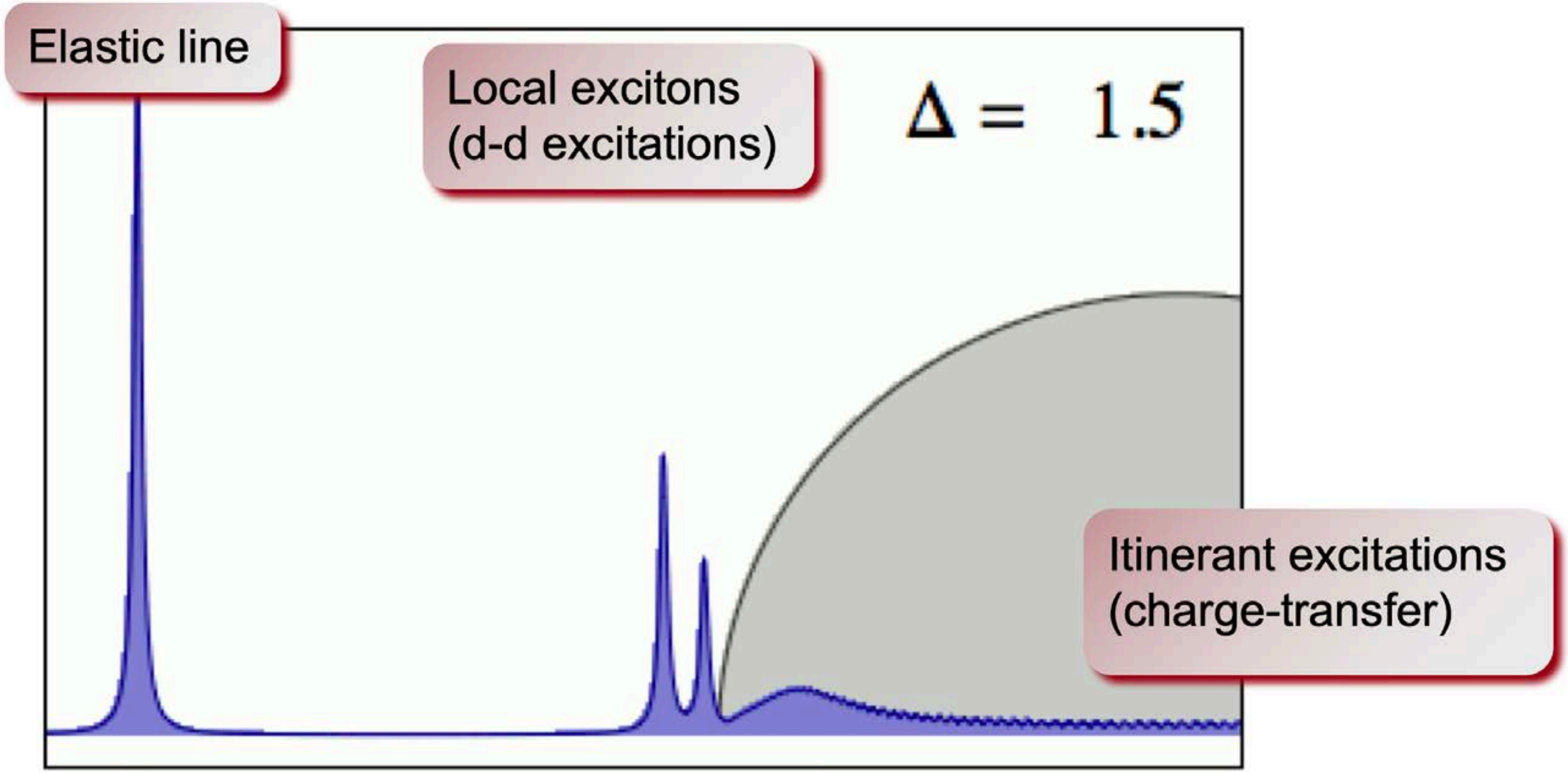
With Γ the line width of the peak, equal to the lifetime of the particle in the time domain

If H is the Hamiltonian of the universe, than Γ=0.

The lifetime of a propagator is due to Couplings not included into the Hamiltonian or due to states not included into the Hilbert space

Self energy and line-width

A local multiplet can decay due to covalent interaction with the continuum



Elastic line

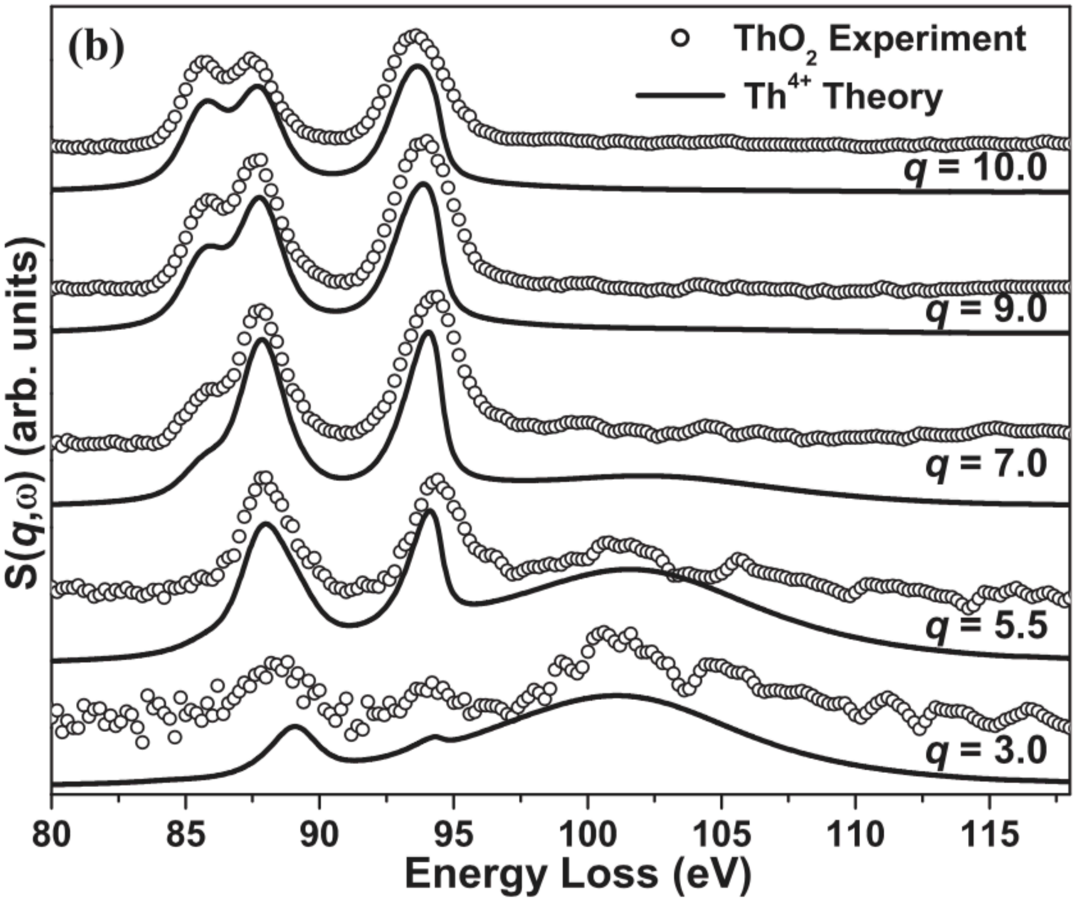
Local excitons (d-d excitations)

Itinerant excitations (charge-transfer)

Self energy and line-width

A local multiplet can decay due to covalent interaction with the continuum

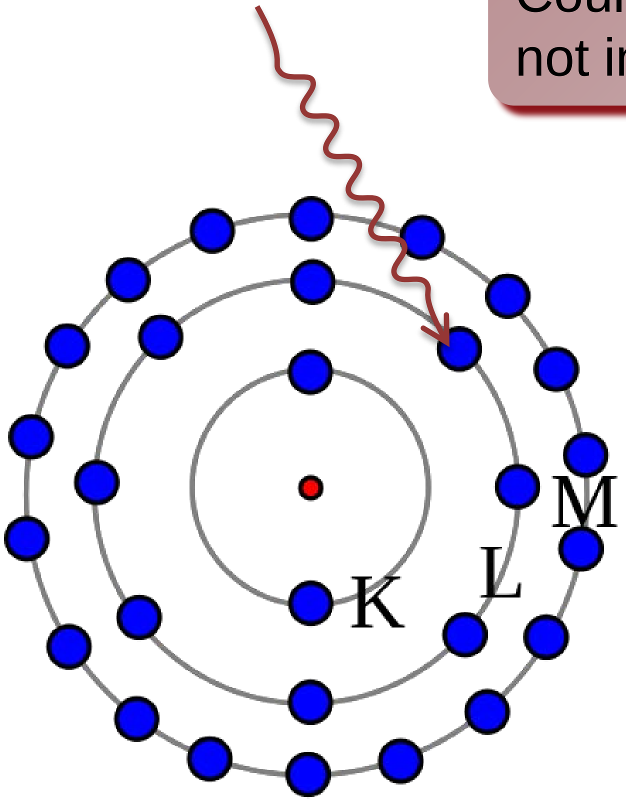
Coexistence of bound and virtual-bound states in shallow-core to valence x-ray spectroscopies



PHYSICAL REVIEW B **84**, 075134 (2011)

Self energy and line-width

A local multiplet decays by the Auger Meitner process



Coulomb interaction to states with free electrons not included in the Hilbert space sofar

Photon excitation of core electron

Self energy and line-width

A local multiplet decays by the Auger Meitner process

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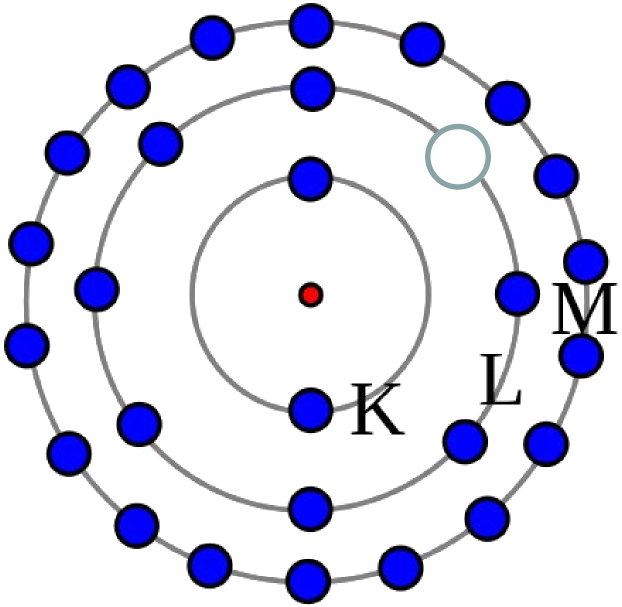

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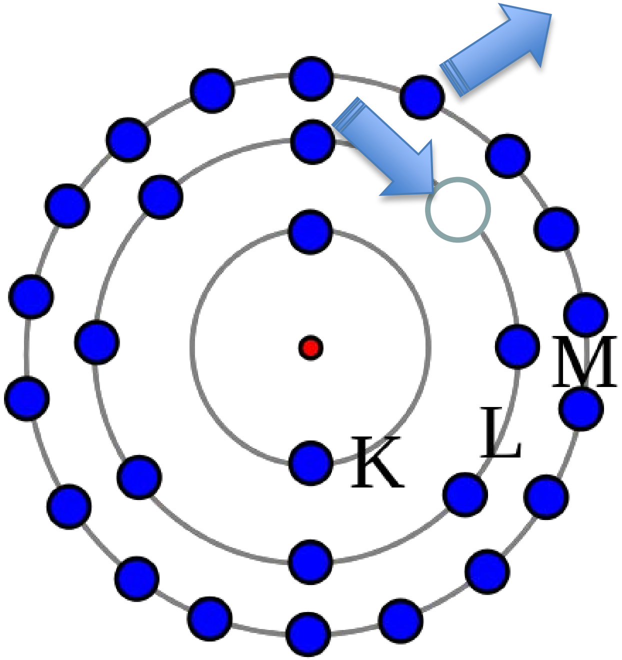
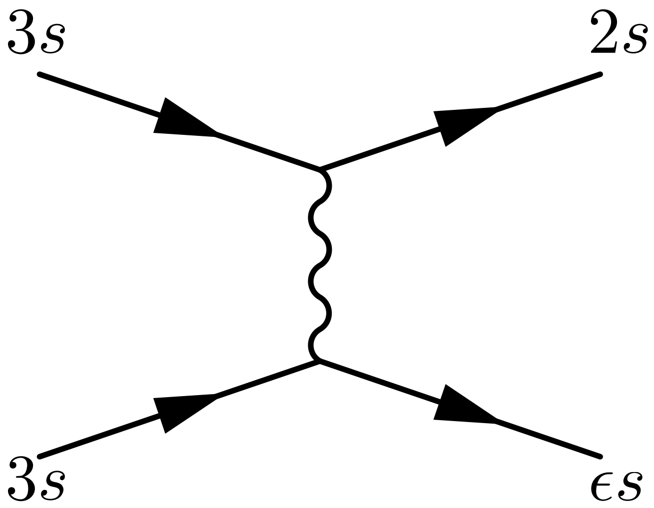


Photon excitation of core electron

Core-hole decays via Auger Meitner process



Self energy and line-width

A local multiplet decays by the Auger Meitner process

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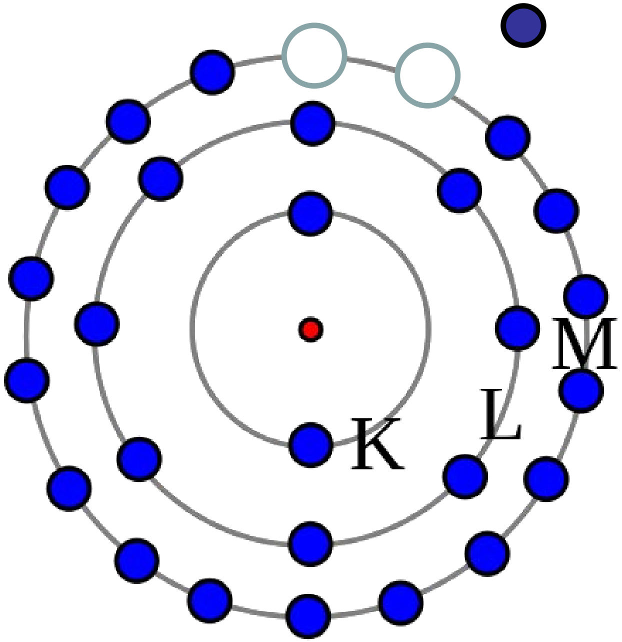

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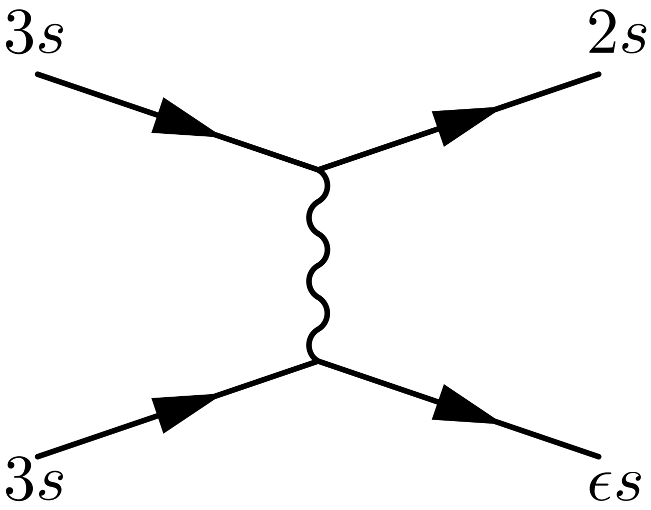
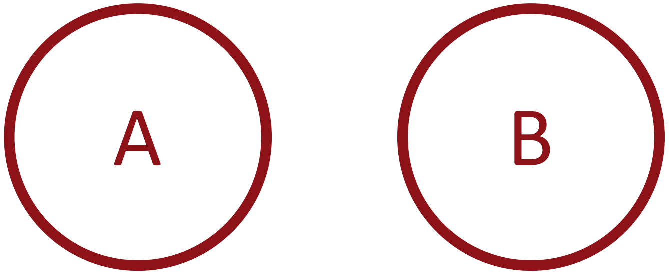


Calculate the lifetime – From Γ to $\Sigma(\omega)$

In order to calculate the lifetime we split the Hilbert-space into two parts



Hilbert space A contains all local states, Hilbert-space B contains the states after decay. (e.g. with one electron in the continuum)

Hamiltonian H_A acts within subspace A, Hamiltonian H_B within subspace B and H_{AB} couples the two spaces

The original Green's function describing the propagation of an excitation made with operator T, without lifetime is given as:

$$G^{+} = \lim_{\Gamma\to 0^{+}} \left\langle i \left| T^{\dagger} \frac{1}{\omega - H_A + \mathrm{i}\frac{\Gamma}{2}} T \right| i \right\rangle$$

Calculate the lifetime – From Γ to $\Sigma(\omega)$

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If we add the interaction with the continuum (H_{AB}) to the propagator we find (using the Dyson equations or diagonalization of a Block Matrix)

$$G^{+} = \lim_{\Gamma\to 0^{+}} \left\langle i \left| T^{\dagger} \frac{1}{\omega - H_A - H_{AB}^{\dagger} \frac{1}{\omega - H_B + \mathrm{i}\frac{\Gamma}{2}} H_{AB}} T \right| i \right\rangle$$

Where the lifetime of the state now is given by the propagator making excitations into the continuum

Calculate the lifetime – From Γ to $\Sigma(\omega)$

If we add the interaction with the continuum (H_{AB}) to the propagator we find (using the Dyson equations or diagonalization of a Block Matrix)

$$G^{+} = \lim_{\Gamma\to 0^{+}} \left\langle i \left| T^{\dagger} \frac{1}{\omega - H_A - H^{\dagger}_{AB} \frac{1}{\omega - H_B + \mathrm{i}\frac{\Gamma}{2}} H_{AB}} T \right| i \right\rangle$$

Where the lifetime of the state now is given by the propagator making excitations into the continuum

$$\hat{\Sigma}(\omega) = \lim_{\Gamma\to 0^{+}} H^{\dagger}_{AB} \frac{1}{\omega - H_B + \mathrm{i}\frac{\Gamma}{2}} H_{AB}$$

We can create a Krylov basis for H_A and calculate the Green's function describing the spectra of these states after making an excitation with operator H_{AB}

From Γ to $\Sigma(\omega)$ – for Auger Meitner decay

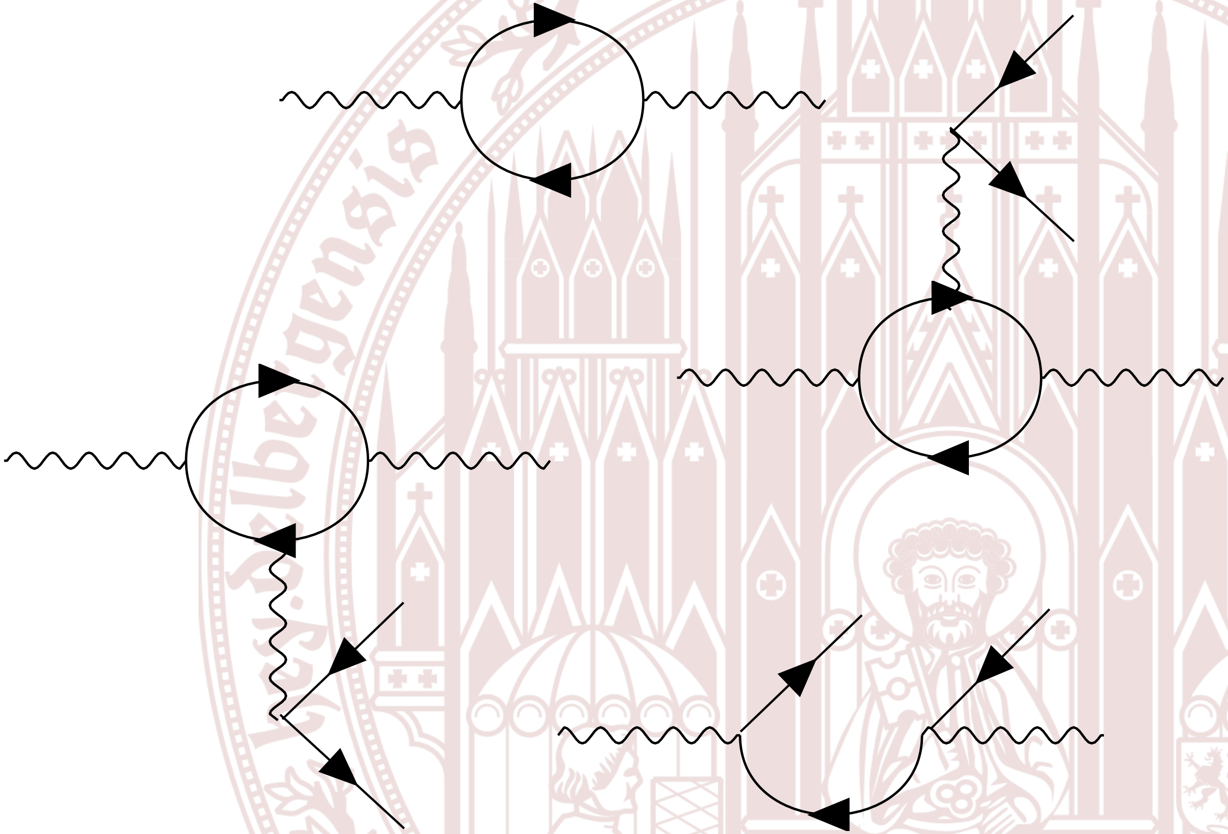
$$I = -\frac{1}{\pi}\mathrm{Im}\left\langle I \left| T^{\dagger} \frac{1}{\omega - H - H_{Auger}\frac{1}{\omega - H + \mathrm{I}\frac{\Gamma}{2}} H_{Auger}} T \right| I \right\rangle$$

$$\hat{\Sigma}(\omega) = H_{Auger}\frac{1}{\omega - H + \mathrm{I}\frac{\Gamma}{2}} H_{Auger}$$

$$I = -\frac{1}{\pi}\mathrm{Im}\left\langle I \left| T^{\dagger} \frac{1}{\omega - H - \Sigma(\omega)} T \right| I \right\rangle$$

RIXS – competition between decay processes

A non-perturbative absolute converging series expansion as alternative to traditional (diagrammatic) methods



PRL **119**, 256401 (2017)

RIXS – competition between decay processes

Projection expansions for functions

$$f(x) = \sum_{n=0}^{\infty} \alpha_n \, g_n(x) \quad \text{with} \quad \alpha_n = \left\langle g_n(x) \middle| f(x) \right\rangle$$

$$\text{if} \quad \left\langle g_n(x) \middle| g_m(x) \right\rangle = \delta_{n,m}$$

Projection expansions for operators

$$P = \sum_{m,n}^{\infty,\infty} \alpha_{m,n} O^{m,n} \quad \text{with} \quad \alpha_{m,n} = \frac{\left\langle O^{m,m} P O^{n,n} \right\rangle}{\left\langle O^{m,n} \right\rangle}$$

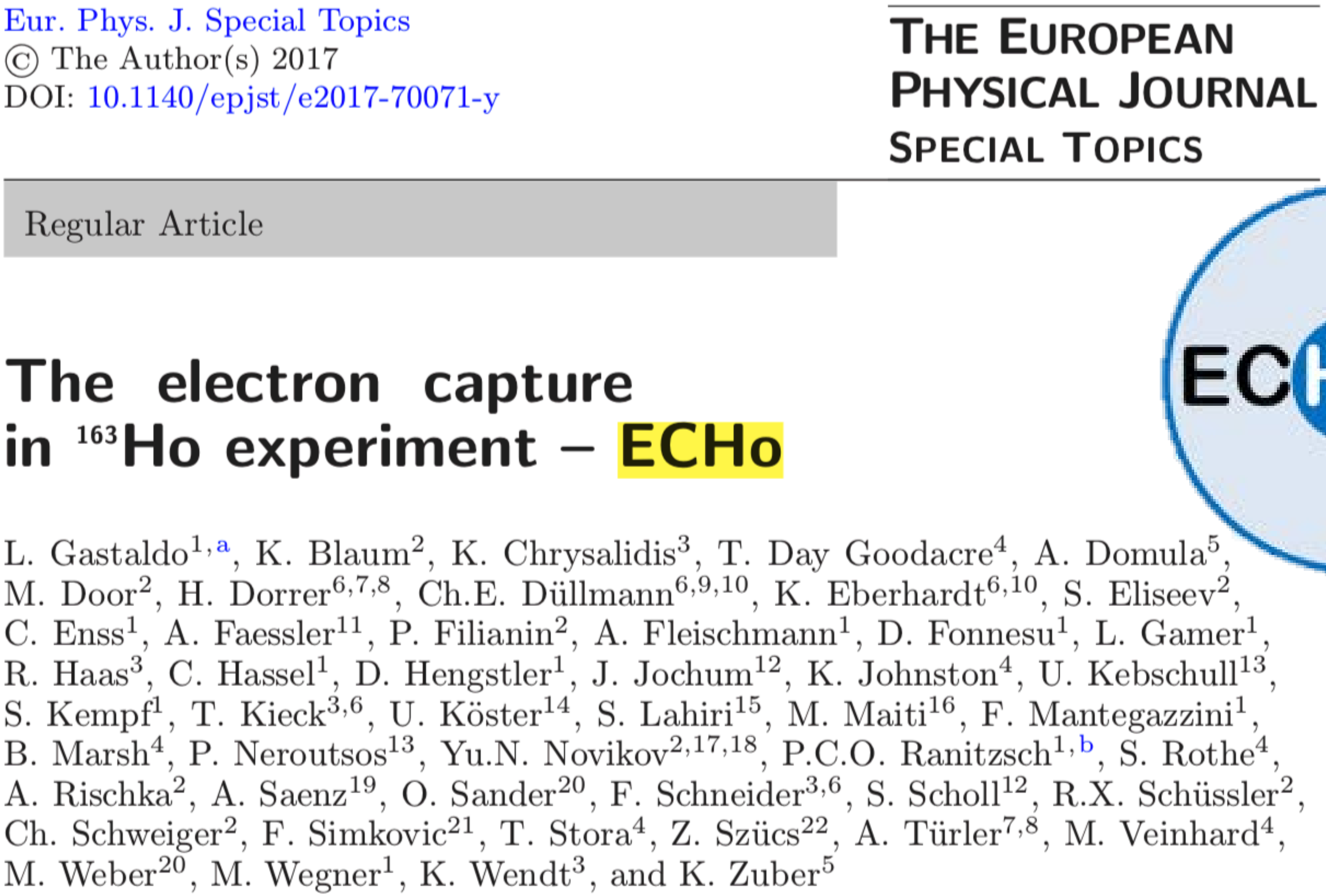
$$\text{if} \quad O^{m,n\dagger} = O^{n,m}$$

$$O^{s,t} O^{m,n} = \delta_{t,m} O^{s,n}$$

PRL **119**, 256401 (2017)

Accurate determination of Σ of a core excited state

Determining the neutrino mass - Nuclear decay of Ho



Eur. Phys. J. Special Topics

DOI: 10.1140/epjst/e2017-70071-y

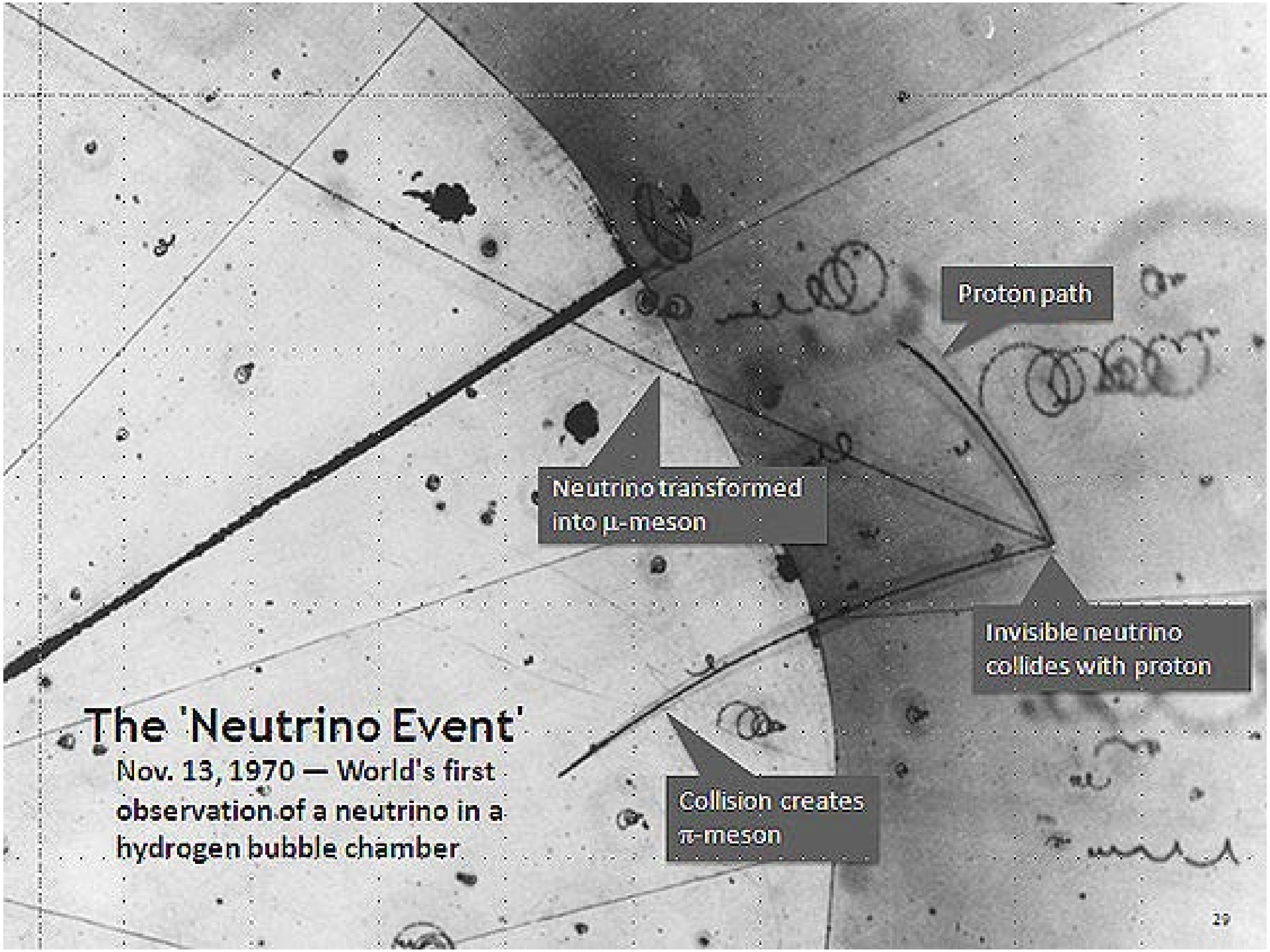
THE EUROPEAN
PHYSICAL JOURNAL
SPECIAL TOPICS

Regular Article

The electron capture in ^{163}Ho experiment – ECHo

L. Gastaldo[1,a], K. Blaum[2], K. Chrysalidis[3], T. Day Goodacre[4], A. Domula[5], M. Door[2], H. Dorrer[6,7,8], Ch.E. Düllmann[6,9,10], K. Eberhardt[6,10], S. Eliseev[2], C. Enss[1], A. Faessler[11], P. Filianin[2], A. Fleischmann[1], D. Fonnesu[1], L. Gamer[1], R. Haas[3], C. Hassel[1], D. Hengstler[1], J. Jochum[12], K. Johnston[4], U. Kebschull[13], S. Kempf[1], T. Kieck[3,6], U. Köster[14], S. Lahiri[15], M. Maiti[16], F. Mantegazzini[1], B. Marsh[4], P. Neroutsos[13], Yu.N. Novikov[2,17,18], P.C.O. Ranitzsch[1,b], S. Rothe[4], A. Rischka[2], A. Saenz[19], O. Sander[20], F. Schneider[3,6], S. Scholl[12], R.X. Schüssler[2], Ch. Schweiger[2], F. Simkovic[21], T. Stora[4], Z. Szücs[22], A. Türler[7,8], M. Veinhard[4], M. Weber[20], M. Wegner[1], K. Wendt[3], and K. Zuber[5]

How to determine the neutrino mass from nuclear decay



Proton path

Neutrino transformed into μ-meson

Invisible neutrino collides with proton

Collision creates π-meson

The 'Neutrino Event'

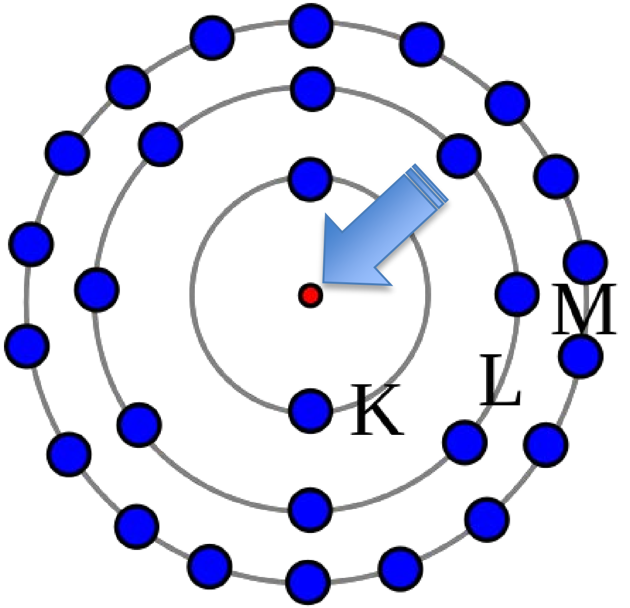
Nov. 13, 1970 — World's first observation of a neutrino in a hydrogen bubble chamber

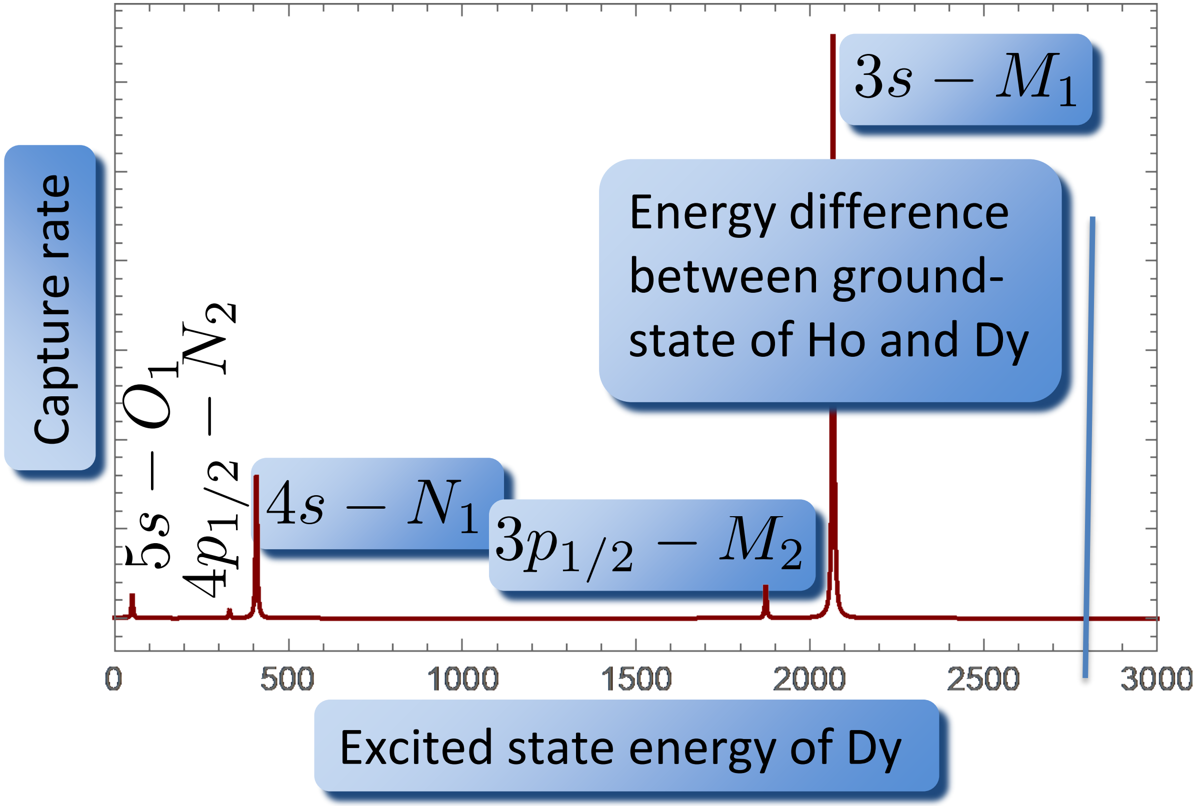
Electron capture in Ho and the neutrino mass

Detailed analyses of electron capture

$$p^+ + e^- \to n^0$$

$$^{163}_{67}Ho \to {}^{163}_{66}Dy^* + \nu_e$$



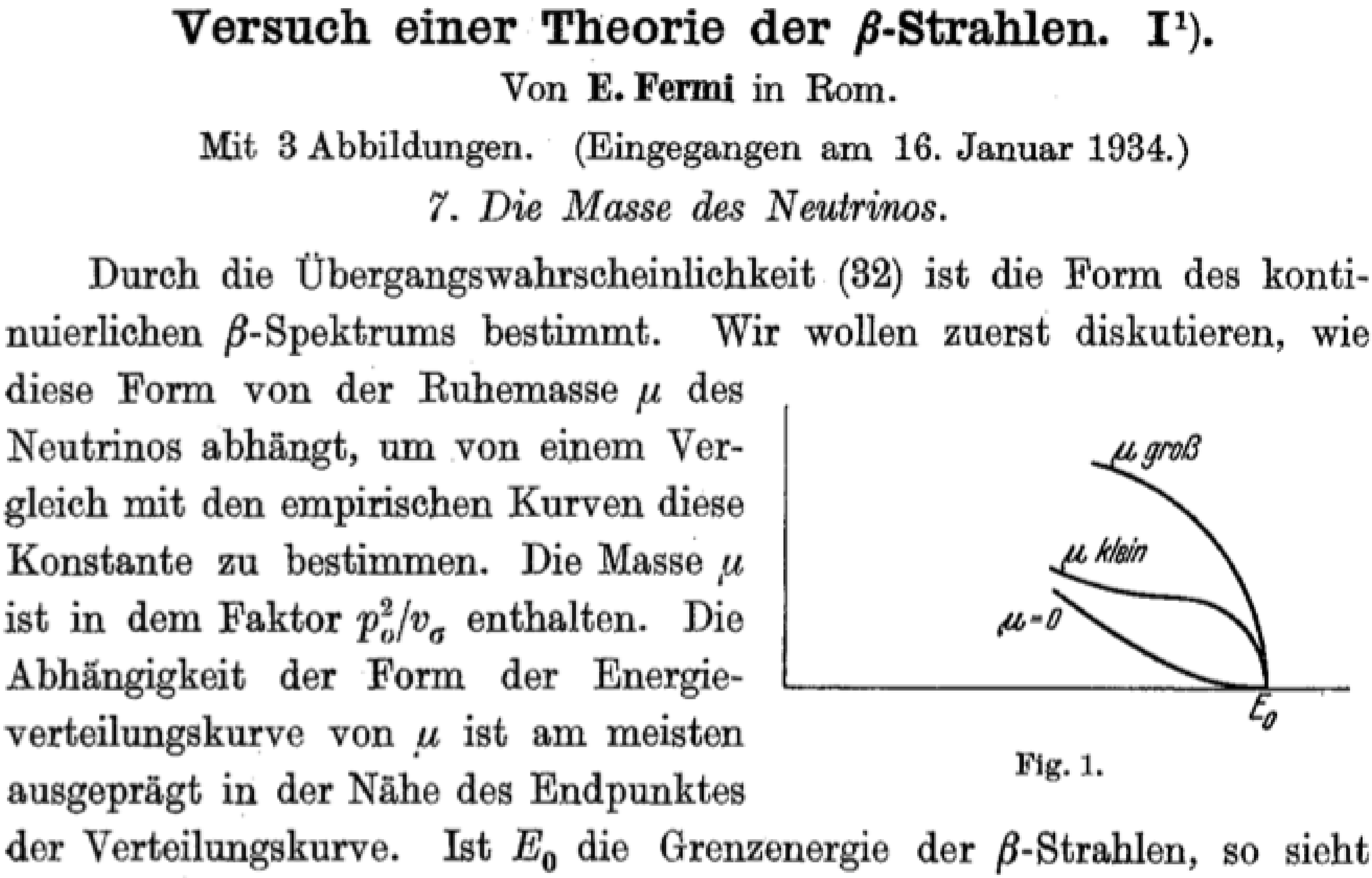


Capture rate

Energy difference between ground-state of Ho and Dy

Excited state energy of Dy

How to determine the neutrino mass from nuclear decay



Versuch einer Theorie der β-Strahlen. I[1]).

Von **E. Fermi** in Rom.

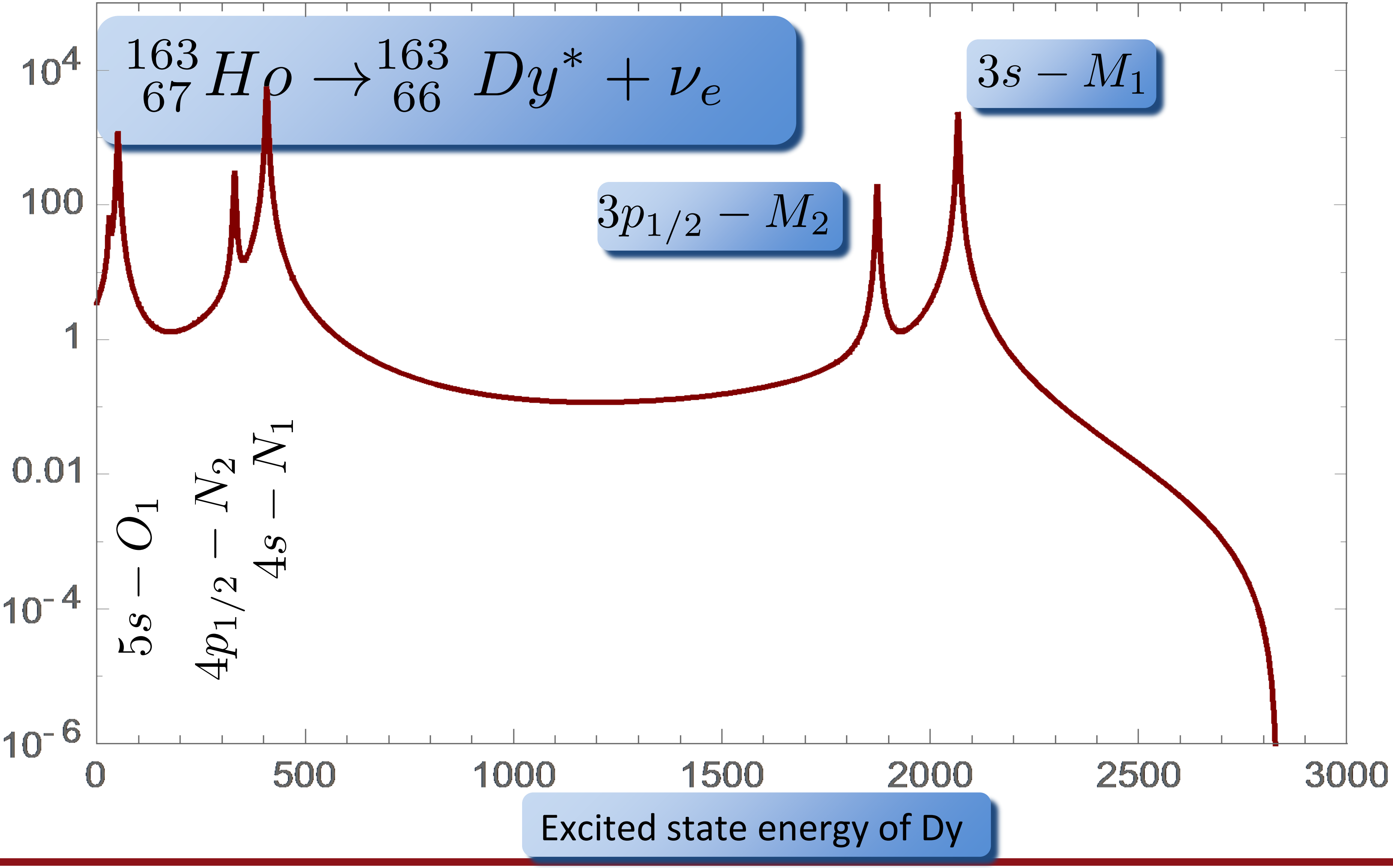
Mit 3 Abbildungen. (Eingegangen am 16. Januar 1934.)

7. *Die Masse des Neutrinos.*

Durch die Übergangswahrscheinlichkeit (32) ist die Form des kontinuierlichen β-Spektrums bestimmt. Wir wollen zuerst diskutieren, wie diese Form von der Ruhemasse μ des Neutrinos abhängt, um von einem Vergleich mit den empirischen Kurven diese Konstante zu bestimmen. Die Masse μ ist in dem Faktor p_0^2/v_σ enthalten. Die Abhängigkeit der Form der Energieverteilungskurve von μ ist am meisten ausgeprägt in der Nähe des Endpunktes der Verteilungskurve. Ist E_0 die Grenzenergie der β-Strahlen, so sieht

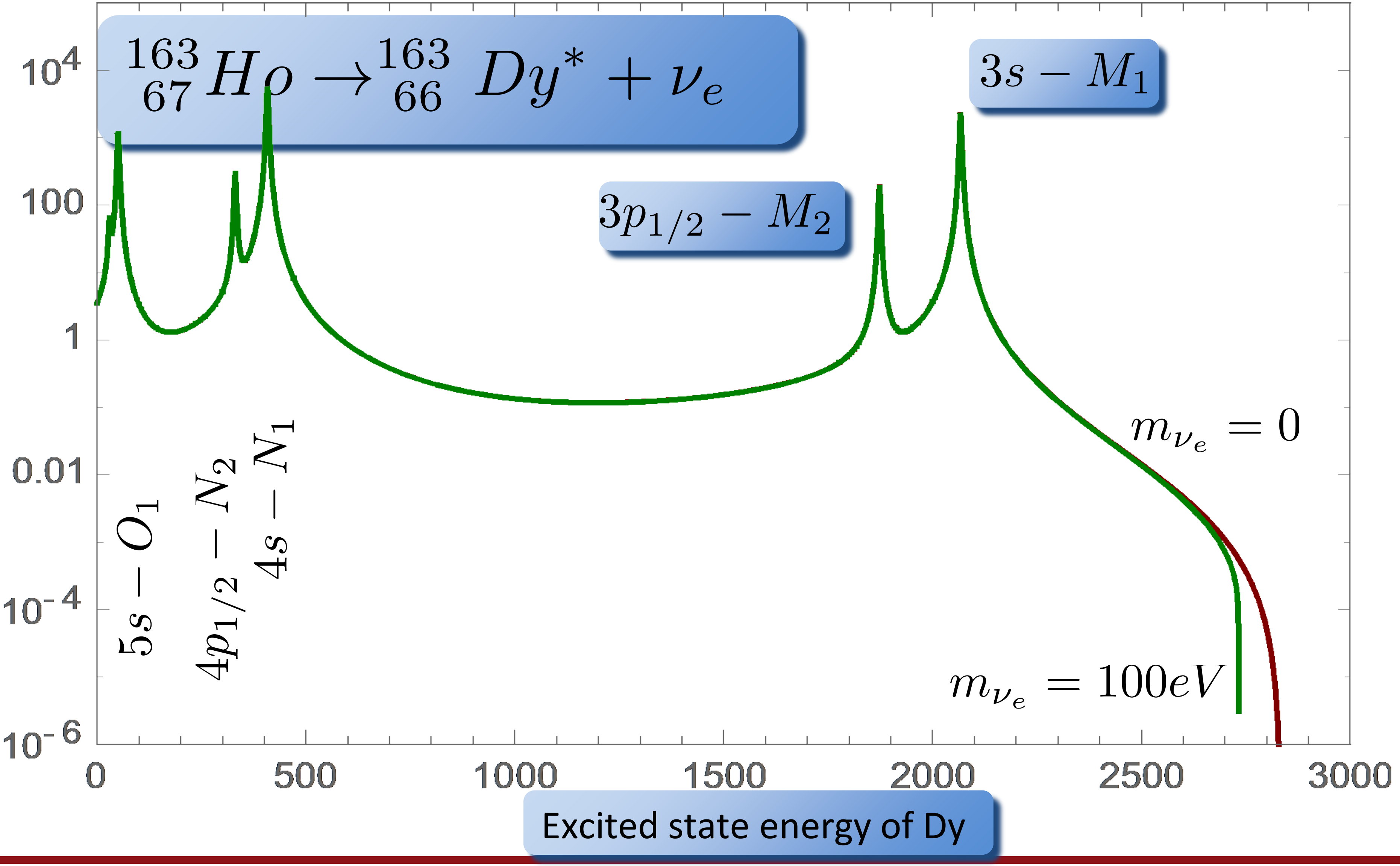
Fig. 1.

Electron capture in Ho and the neutrino mass



$$^{163}_{67}Ho \rightarrow ^{163}_{66}Dy^* + \nu_e$$

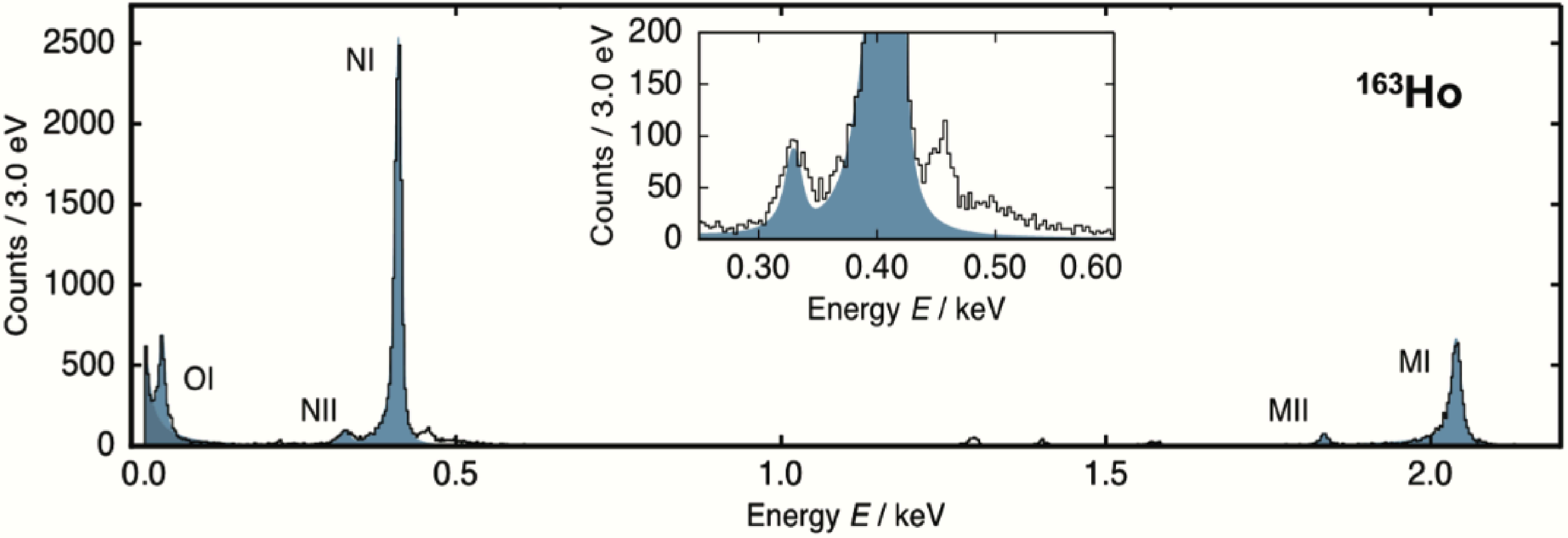
Electron capture in Ho and the neutrino mass



$$^{163}_{67}Ho \rightarrow ^{163}_{66}Dy^{*} + \nu_e$$

Status quo of the theory of the EC spectrum in Ho

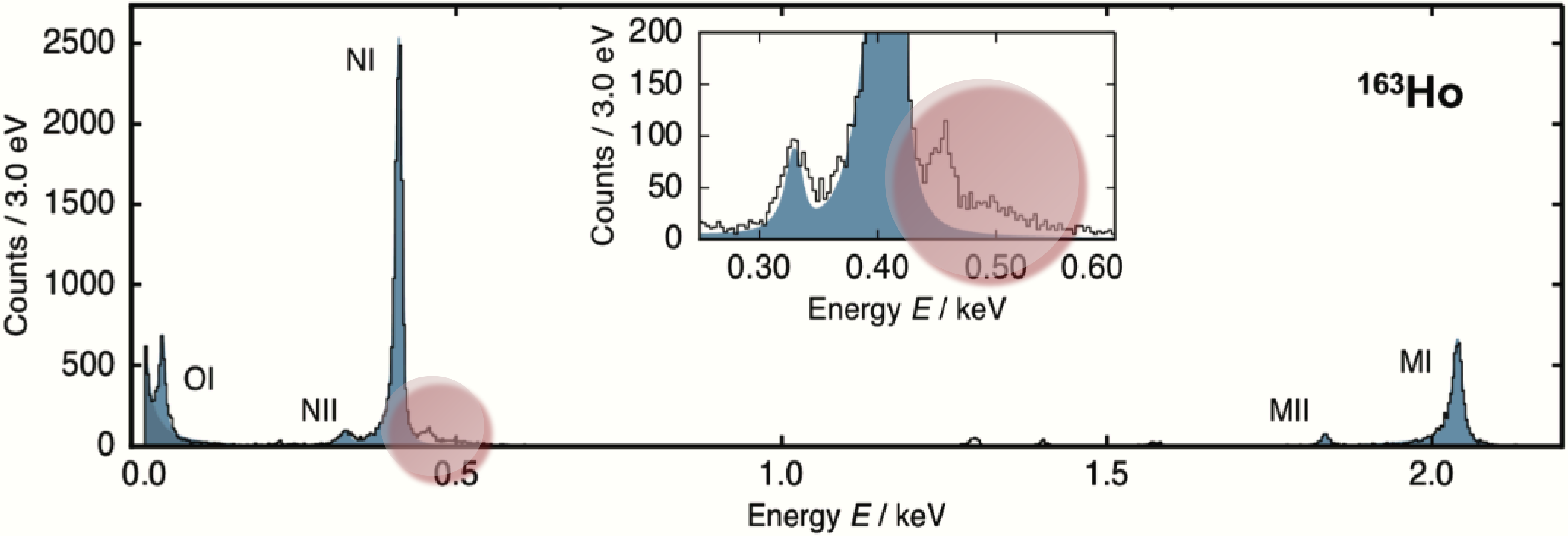
ECHo data recently published PRL **119**, 122501 (2017)



Status quo of the theory of the EC spectrum in Ho

ECHo data recently published PRL **119**, 122501 (2017)

Additional (unexplained) peaks

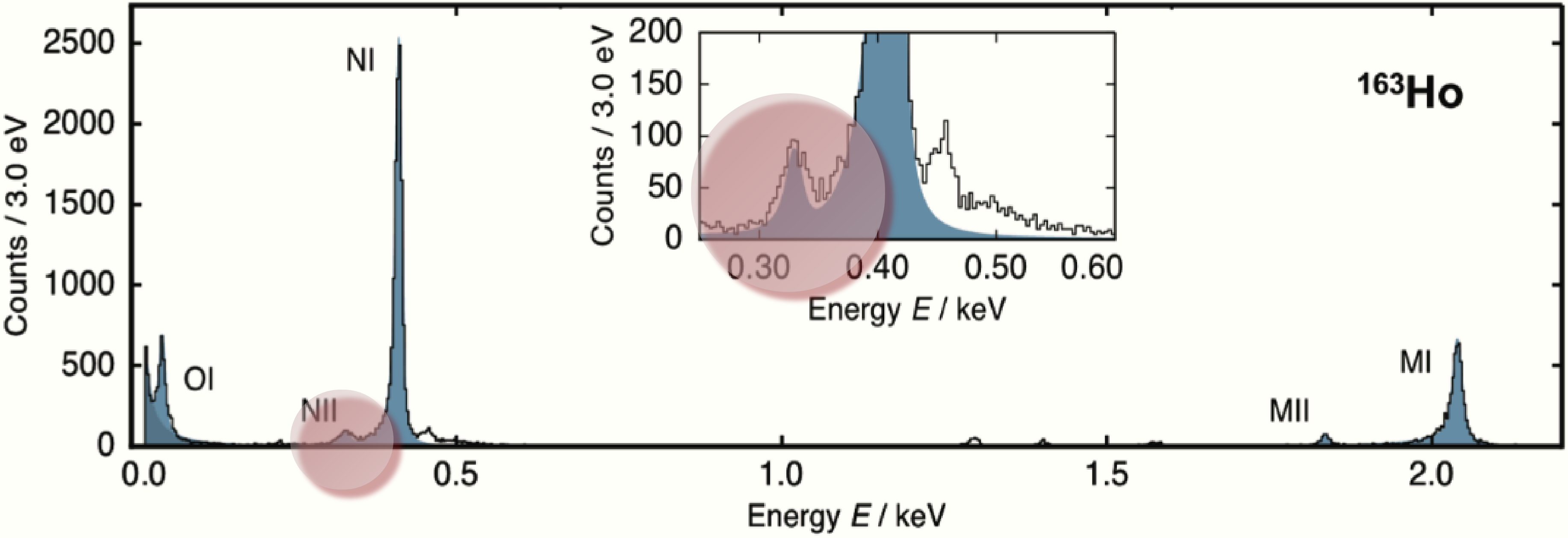


Status quo of the theory of the EC spectrum in Ho

ECHo data recently published PRL **119**, 122501 (2017)

Additional (unexplained) peaks

Unexplained line-broadening (and missing intensity)



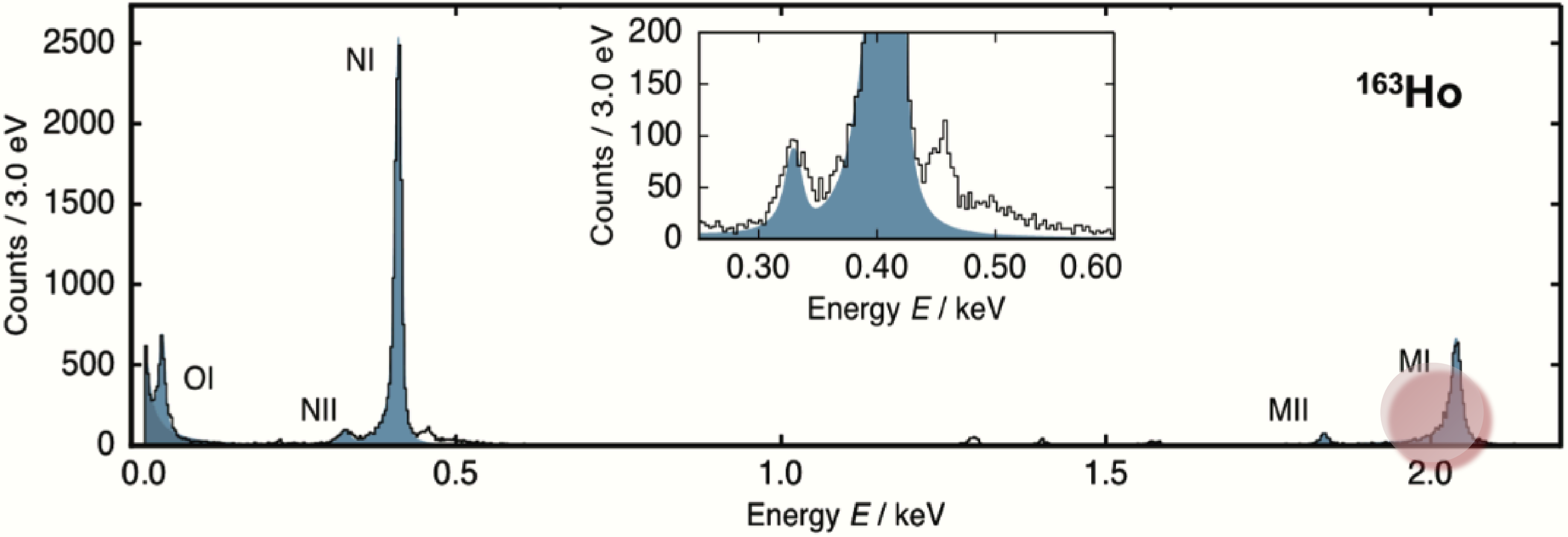
Status quo of the theory of the EC spectrum in Ho

ECHo data recently published PRL **119**, 122501 (2017)

Additional (unexplained) peaks

Unexplained line-broadening (and missing intensity)

Asymmetric line shapes

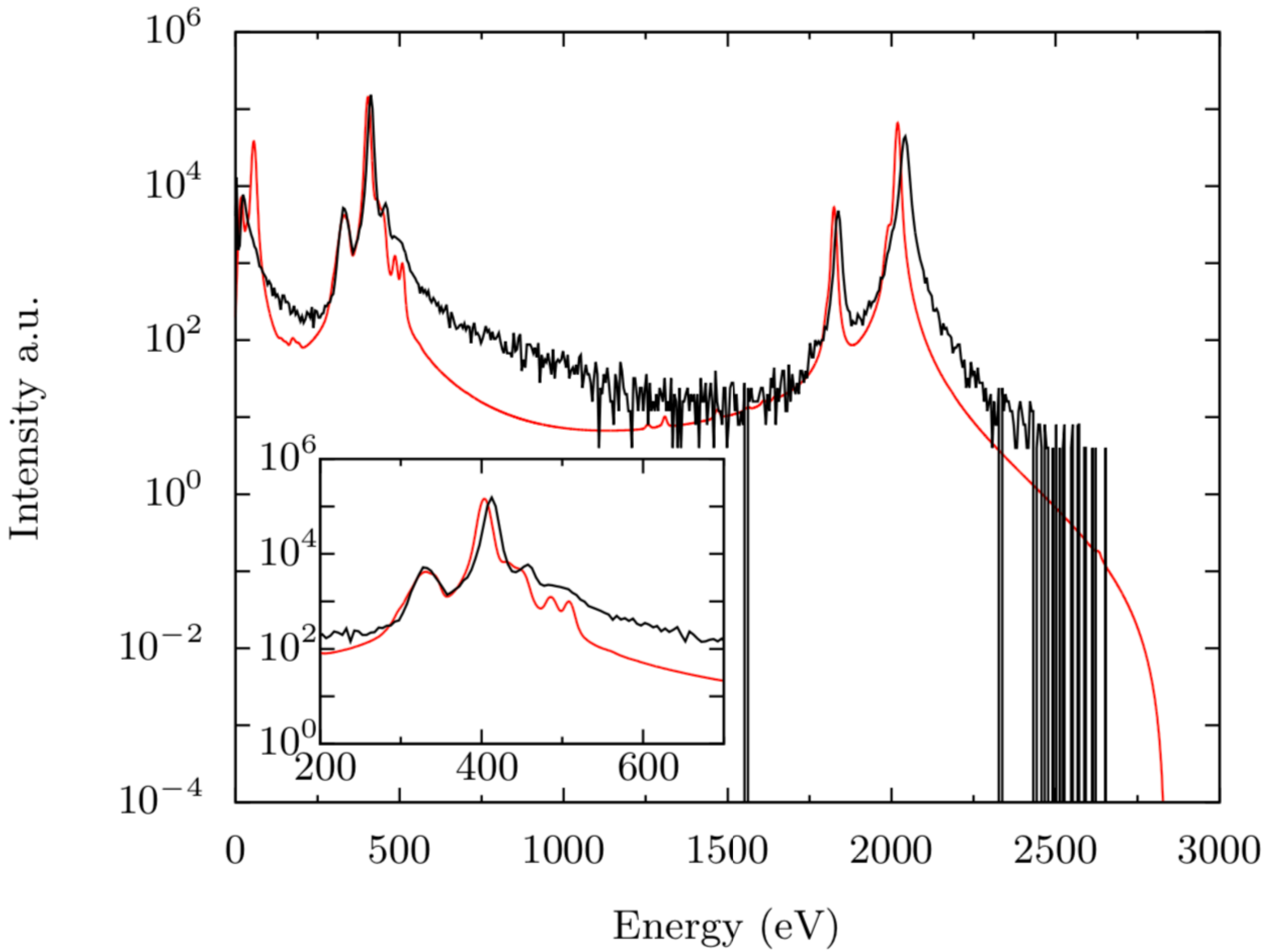


Nuclear decay of Ho theory including locally bound states

Calculate the electron capture spectrum of atomic Ho including all bound orbitals for Ho in Au.
(1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f) and 67 electrons

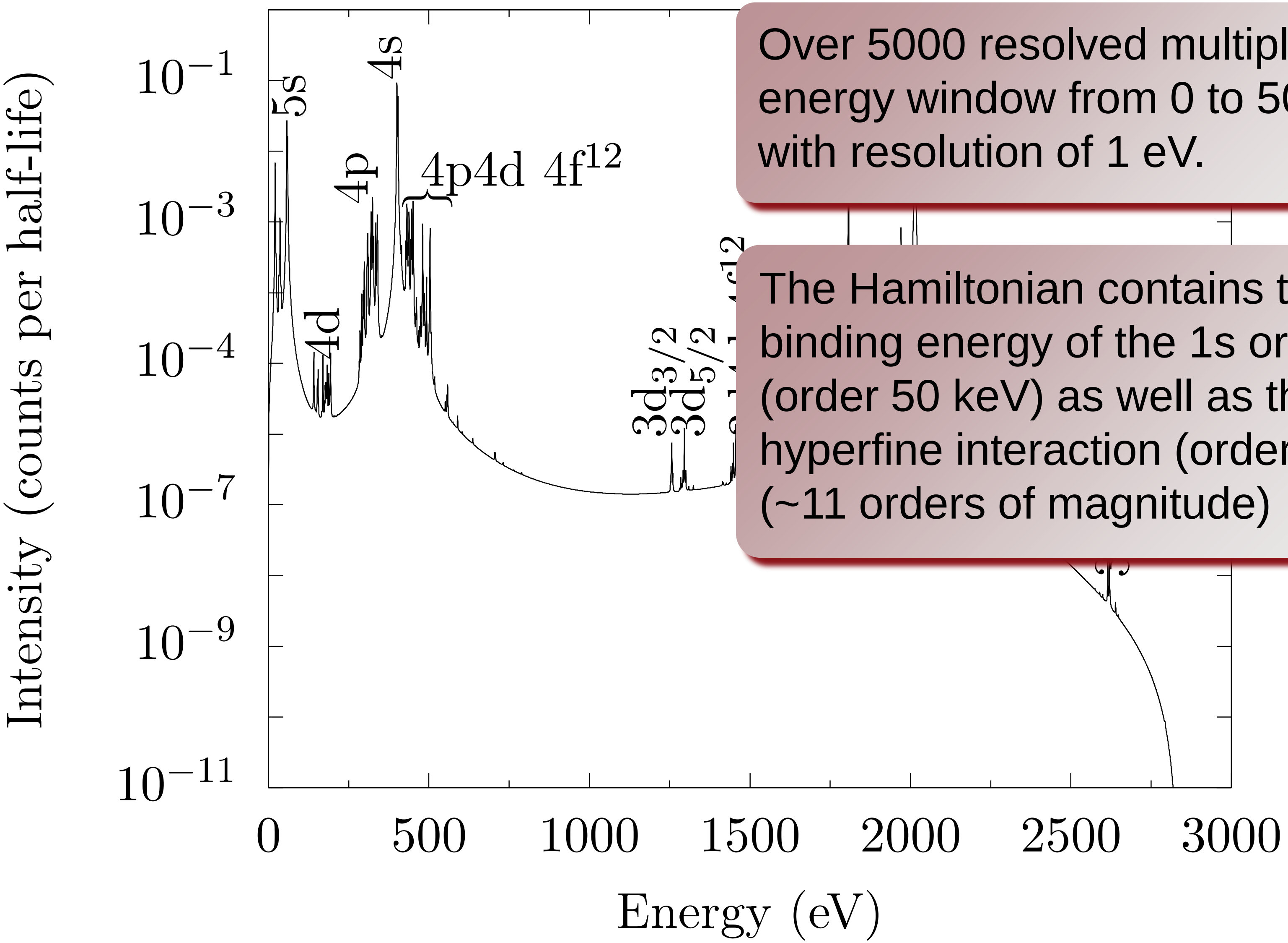
Operator T is the weak interaction, turning the Ho nucleus into a Dy nucleus, creating a neutrino and annihilating an s or $p_{1/2}$ electron.

Nuclear decay of Ho theory including locally bound states



PHYSICAL REVIEW C **97**, 054620 (2018)

High resolution theory (Lorenzian FWHM = 1 eV)



Over 5000 resolved multiplets in an energy window from 0 to 50 keV, with resolution of 1 eV.

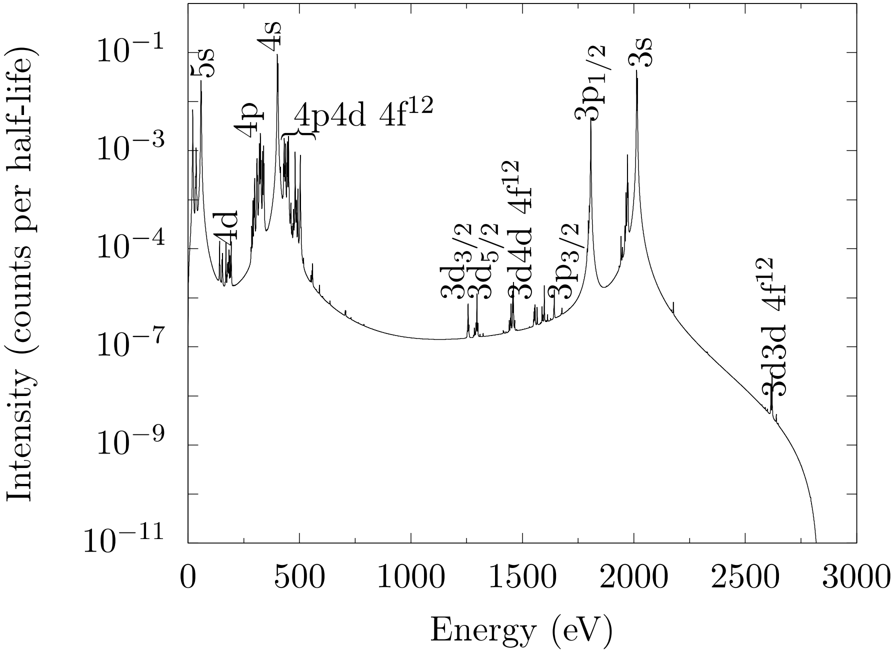
The Hamiltonian contains the binding energy of the 1s orbital (order 50 keV) as well as the hyperfine interaction (order μeV) (~11 orders of magnitude)

PHYSICAL REVIEW C **97**, 054620 (2018)

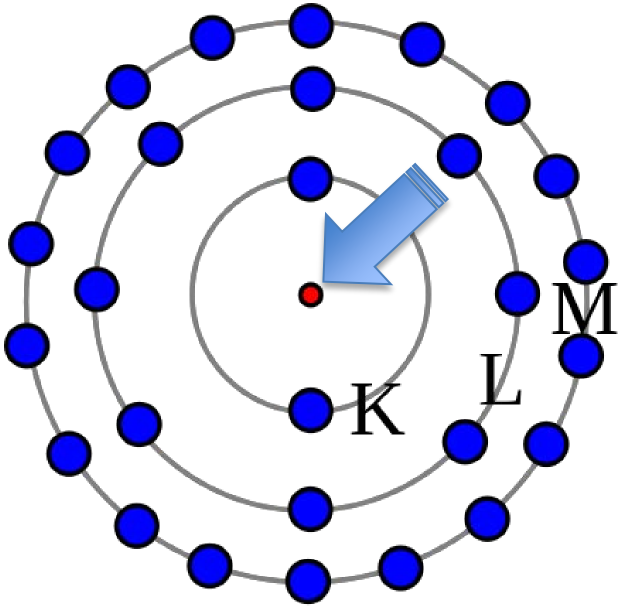
Calculate the lifetime of these excitations

Green’s function – spectral representation (energy domain)

$$I = -\frac{1}{\pi}\mathrm{Im}\left\langle i \middle| T^{\dagger}\frac{1}{\omega - H + \mathrm{i}\frac{\Gamma}{2}} + \frac{1}{\omega + H + \mathrm{i}\frac{\Gamma}{2}} T \middle| i \right\rangle$$

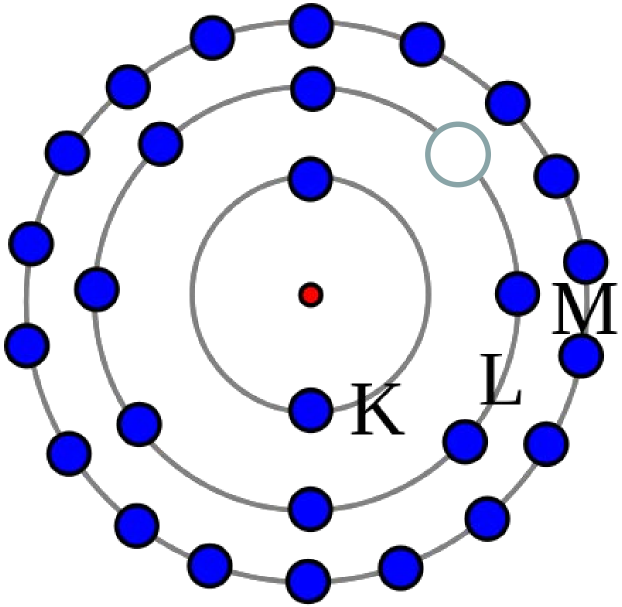


Calculate the lifetime of these excitations



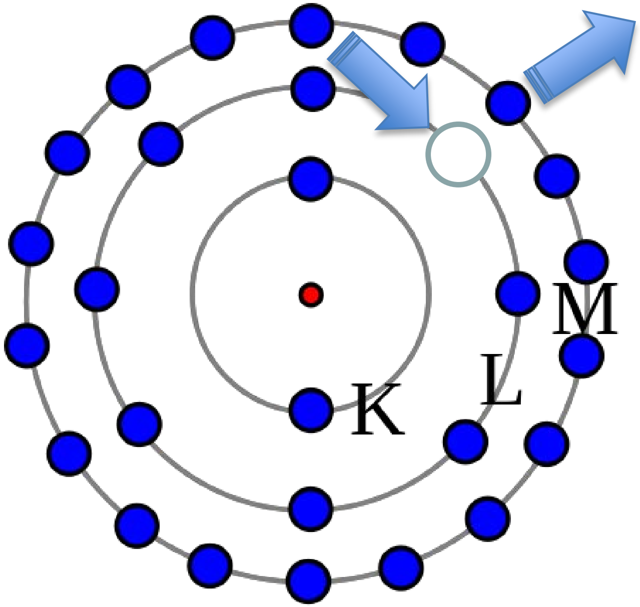
Electron captured from inner shell

Calculate the lifetime of these excitations

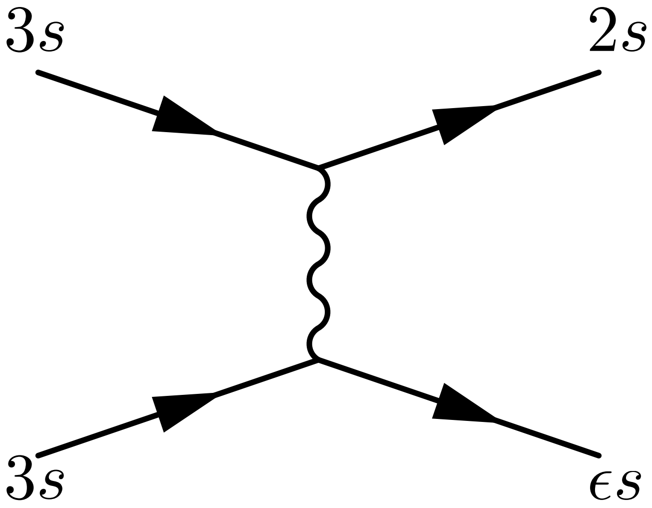


Electron captured from inner shell

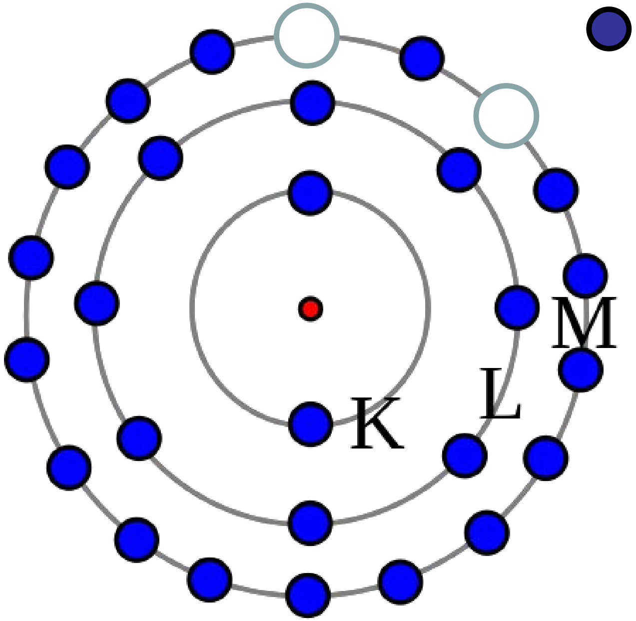
Calculate the lifetime of these excitations



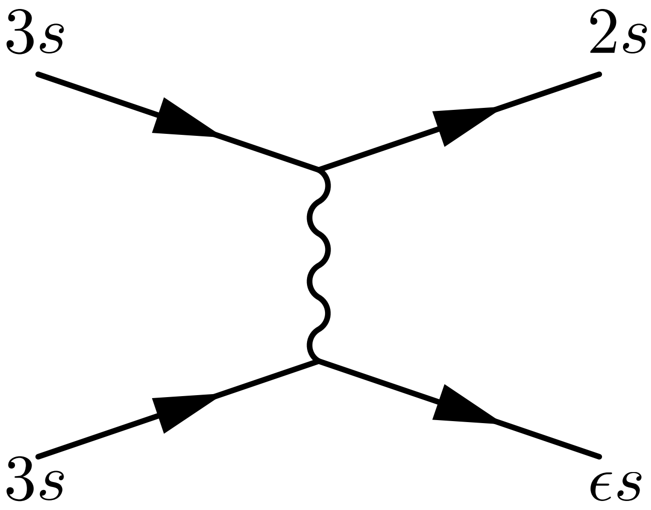
Core-hole decays via Auger process



Calculate the lifetime of these excitations



Core-hole decays via Auger process



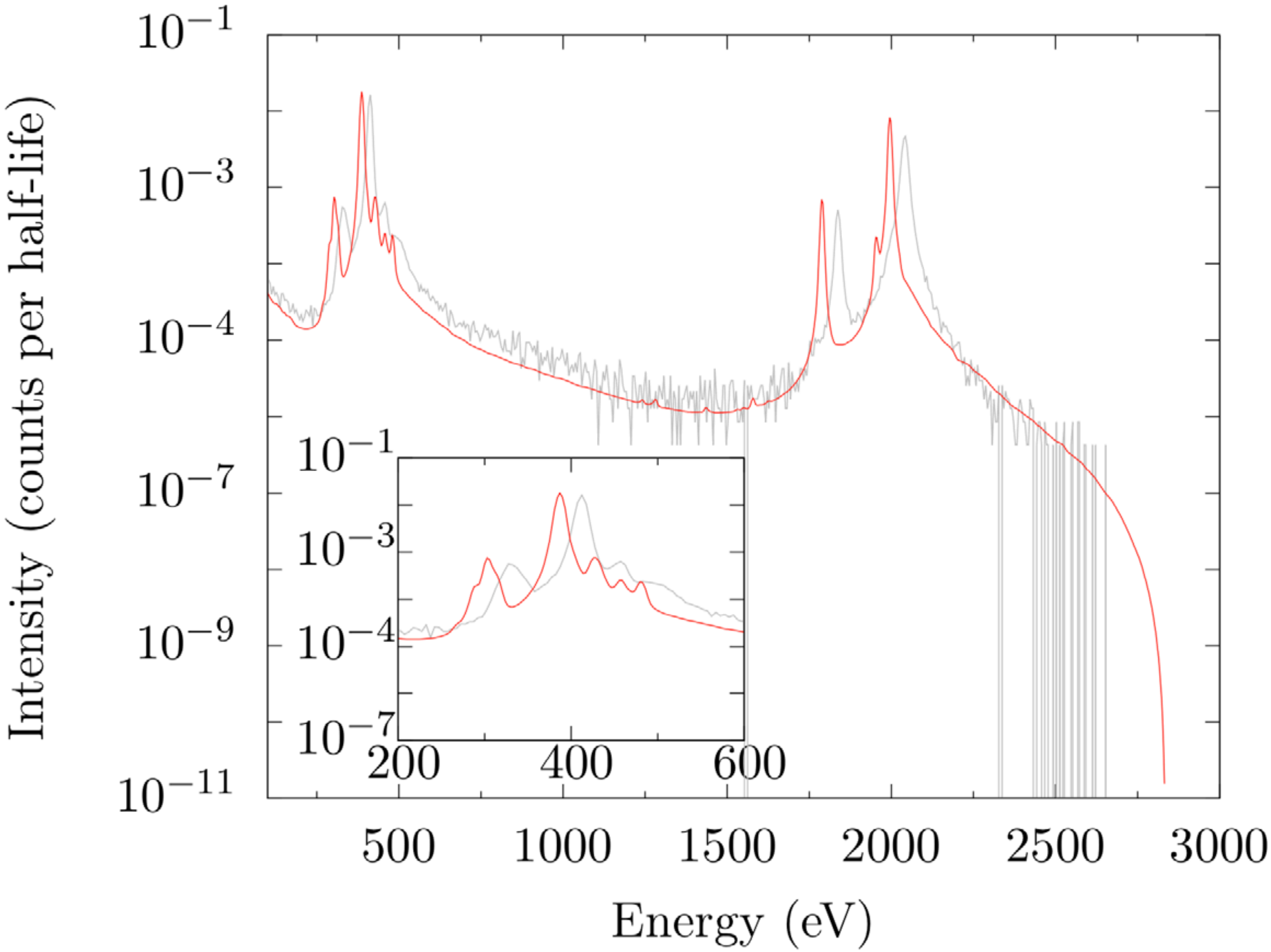
Auger decay – self-energy of the many particle propagator

$$I = -\frac{1}{\pi}\mathrm{Im}\left\langle I \left| T^{\dagger} \frac{1}{\omega - H - H_{Auger}\frac{1}{\omega - H + \mathrm{I}\frac{\Gamma}{2}} H_{Auger}} T \right| I \right\rangle$$

$$\hat{\Sigma}(\omega) = H_{Auger} \frac{1}{\omega - H + \mathrm{I}\frac{\Gamma}{2}} H_{Auger}$$

$$I = -\frac{1}{\pi}\mathrm{Im}\left\langle I \left| T^{\dagger} \frac{1}{\omega - H - \Sigma(\omega)} T \right| I \right\rangle$$

Nuclear decay of Ho – local multiplets and Auger decay

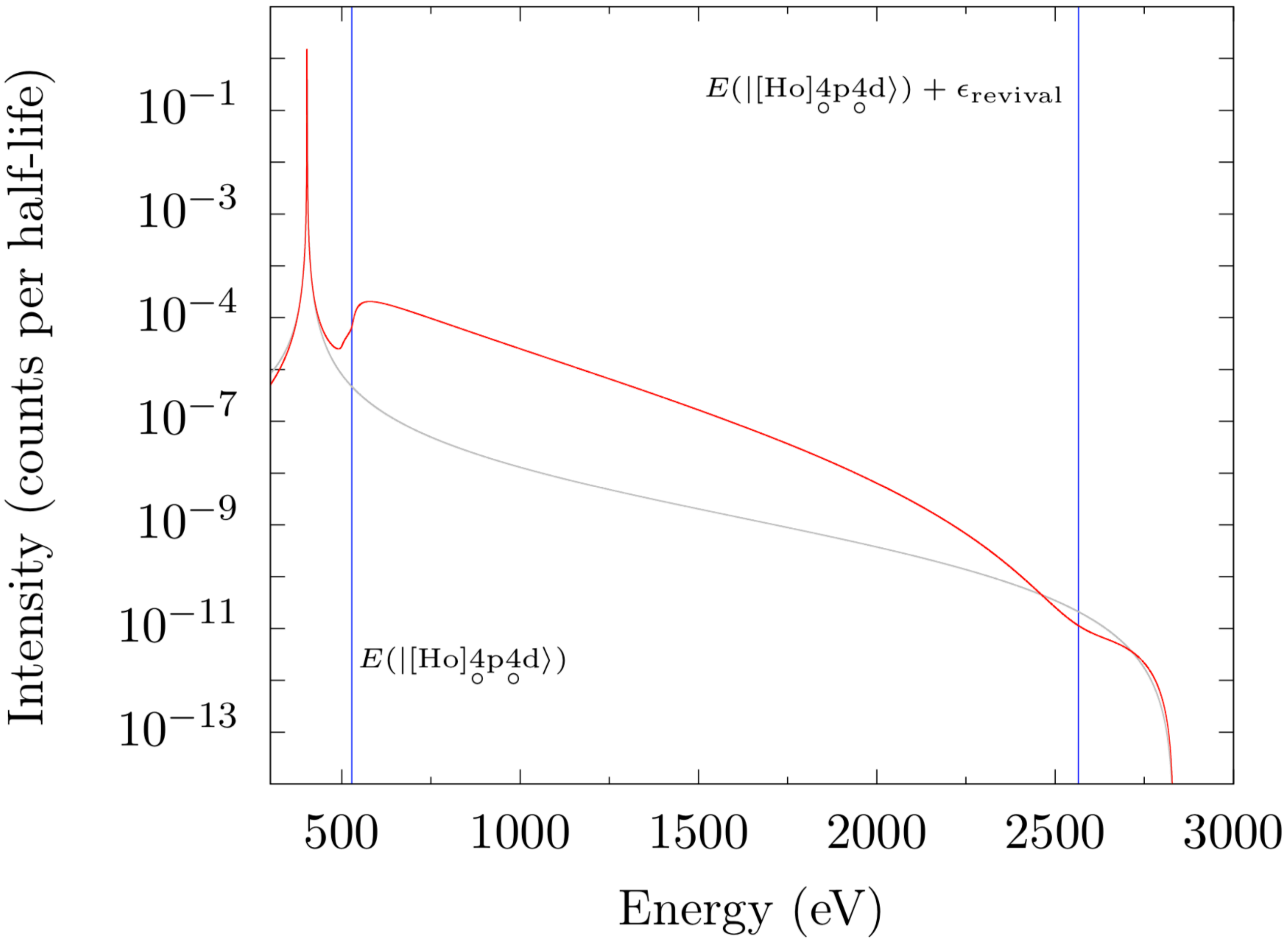


Nuclear decay of Ho – local multiplets and Auger decay

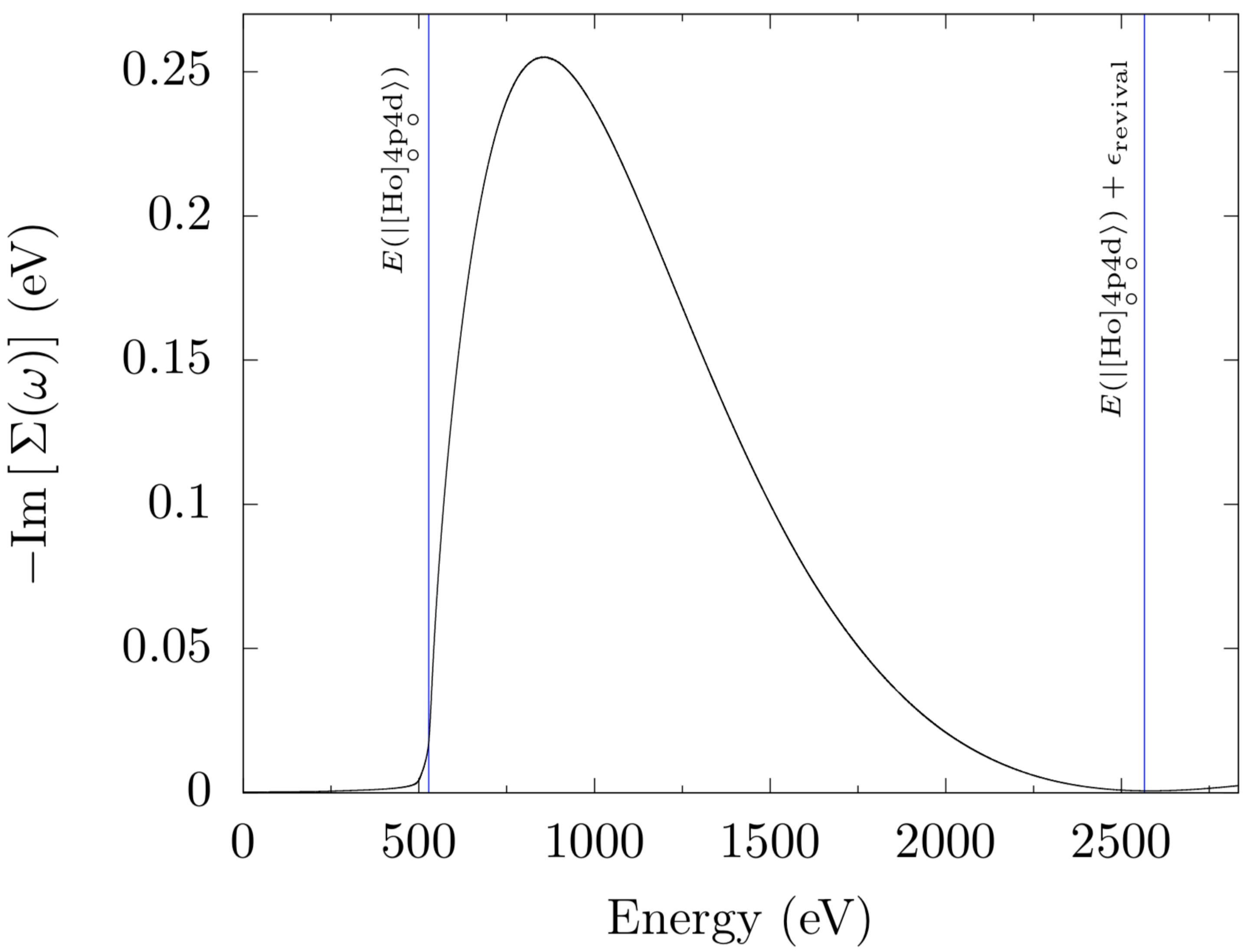
These peaks do not have a lorenzian line-shape. Focus on one decay to see what happens

$$[\mathrm{Ho}]\underset{\circ}{4}s \rightarrow [\mathrm{Ho}]\underset{\circ}{4}p\underset{\circ}{4}d + e^{-}_{\epsilon f}$$

Nuclear decay of Ho – local multiplets and Auger decay



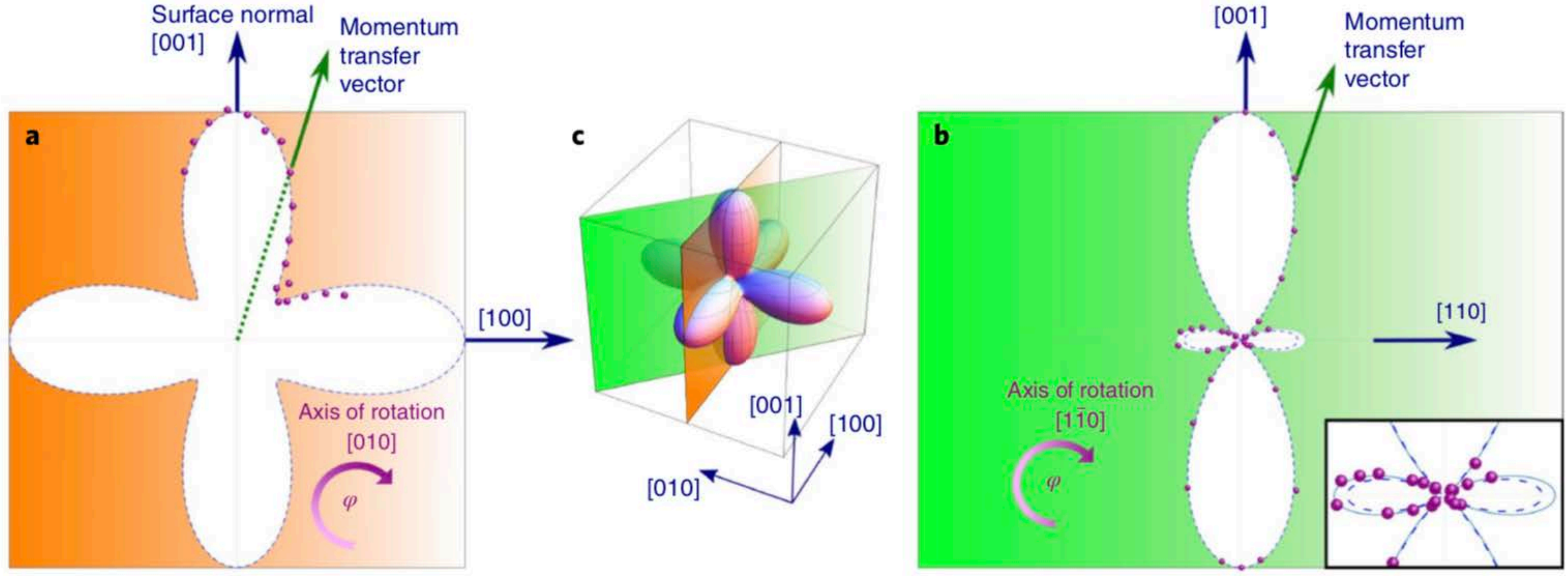
Nuclear decay of Ho – Energy dependence of the lifetime



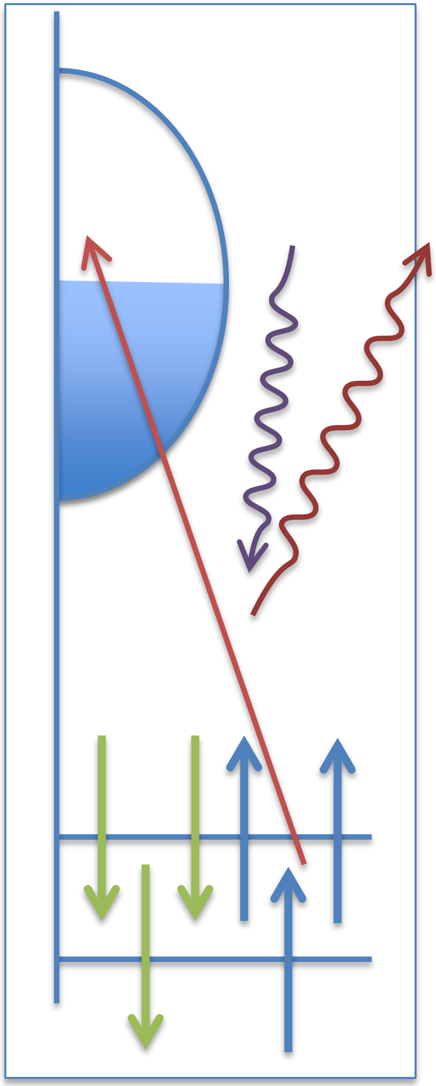
Measuring orbitals

Direct imaging of orbitals in quantum materials

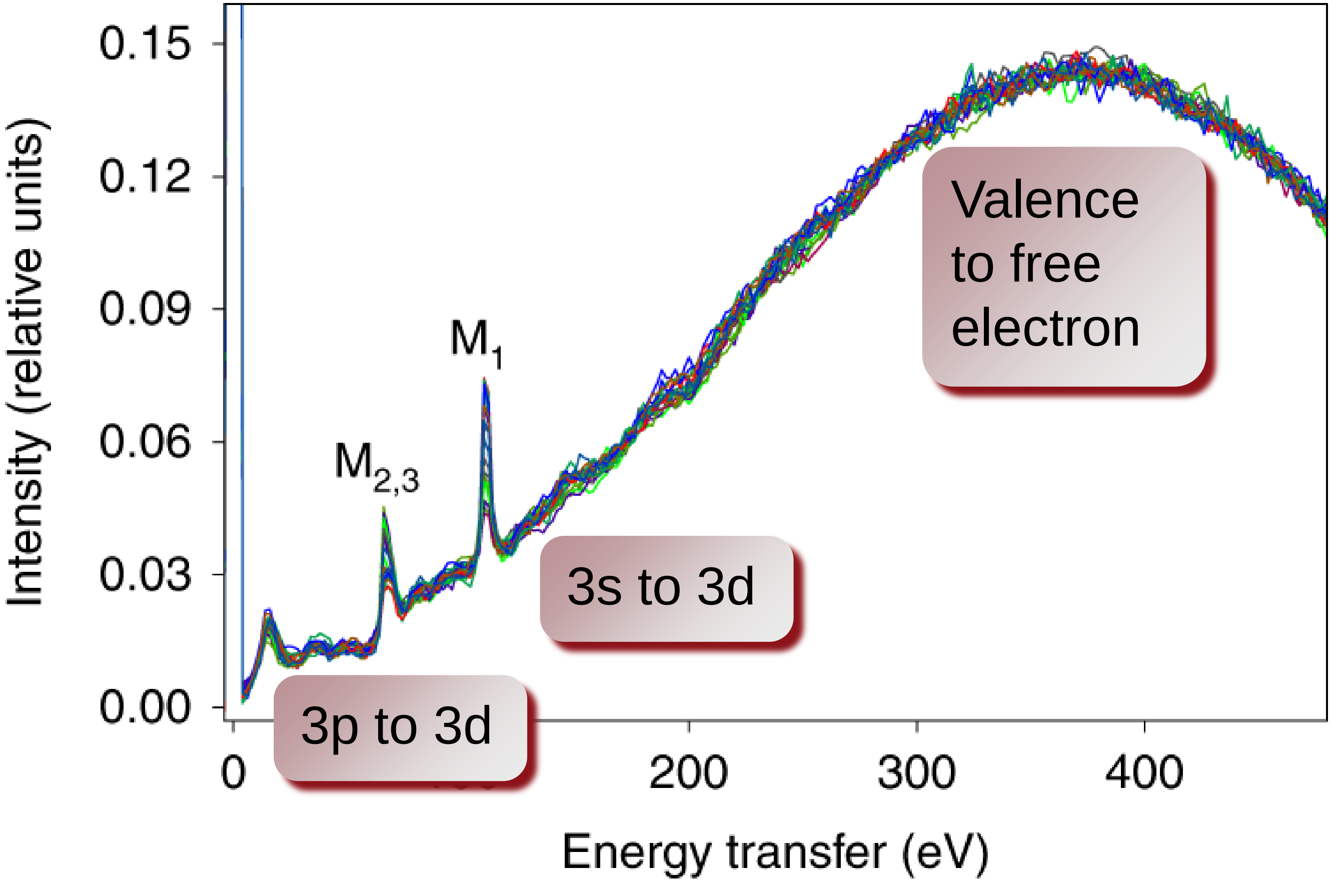
Hasan Yavaş[1,2,5], Martin Sundermann[1,3], Kai Chen[3,6], Andrea Amorese[1,3], Andrea Severing[1,3], Hlynur Gretarsson[1,2], Maurits W. Haverkort[4] and Liu Hao Tjeng[1*]



Measuring orbitals – resonances in non-resonant IXS



IXS spectrum of NiO



Valence to free electron

3s to 3d

3p to 3d

Measuring orbitals – sum-rules in nIXS

$$\int -\frac{1}{\pi}\mathrm{Im}\left\langle i \left| T^{\dagger}\frac{1}{\omega - H + \mathrm{i}\frac{\Gamma}{2}} T \right| i \right\rangle d\omega =$$

$$\left\langle i \left| T^{\dagger} T \right| i \right\rangle$$

For s-nIXS integrated over a single core resonance (c) the operator one measures is the projection operator to the one particle orbital:

$$R_{c,s}(r)j_l(qr)Y_{l,m}(\theta,\phi)$$

For the angular part this is a complete orthonormal set. For the radial part this is a complete set, non-orthogonal and with a norm proportional to $|R_{cs}(r)|$. One measures the projected partial density matrix around the atom of the resonance with a radius related to the size of the core orbital.

Team and funding

ECHo

Martin Brass

Marc Merstorf

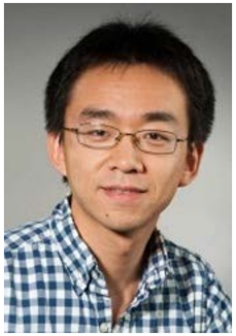
Maurits W. Haverkort

Simon Heinze

MεtrOMMC

Center for Quantum Dynamics

Nadejda Bouldi



Yi Lu

Robert Green

UBC

Marius Retegan

ESRF

UNIVERSITÄT
HEIDELBERG

Quanty workshop in Heidelberg

7-11 October 2019

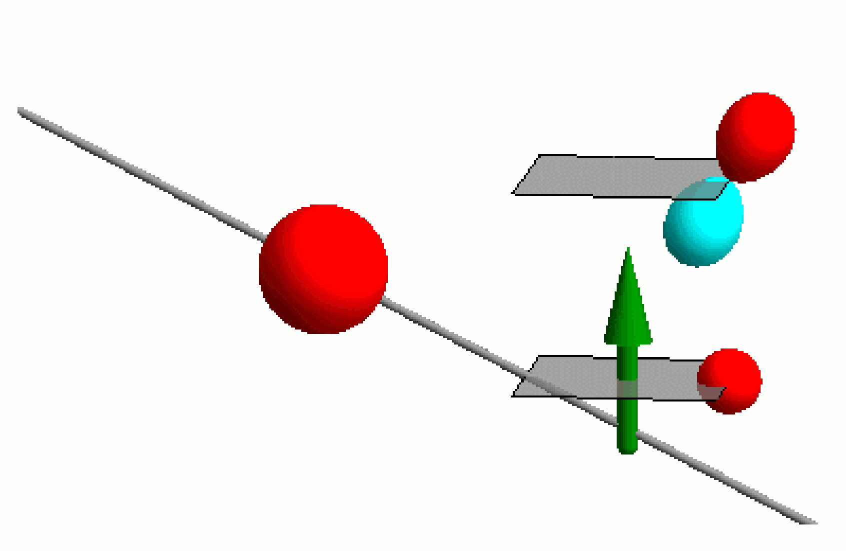
www.Quanty.org/workshop

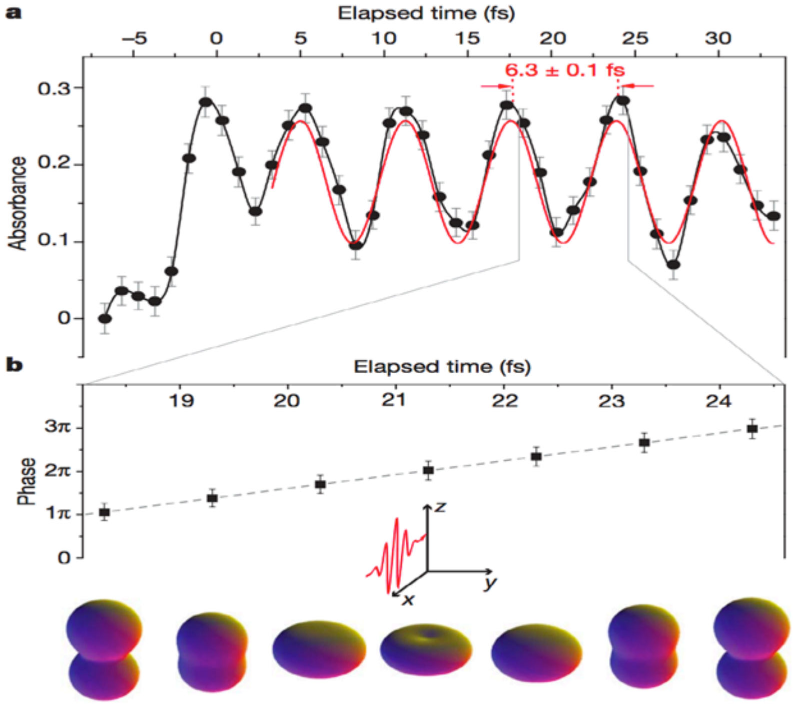
INSTITUTE FOR
THEORETICAL PHYSICS

Understanding quantum materials

For very small systems there is a nearly perfect theoretical understanding of quantum materials and their dynamics

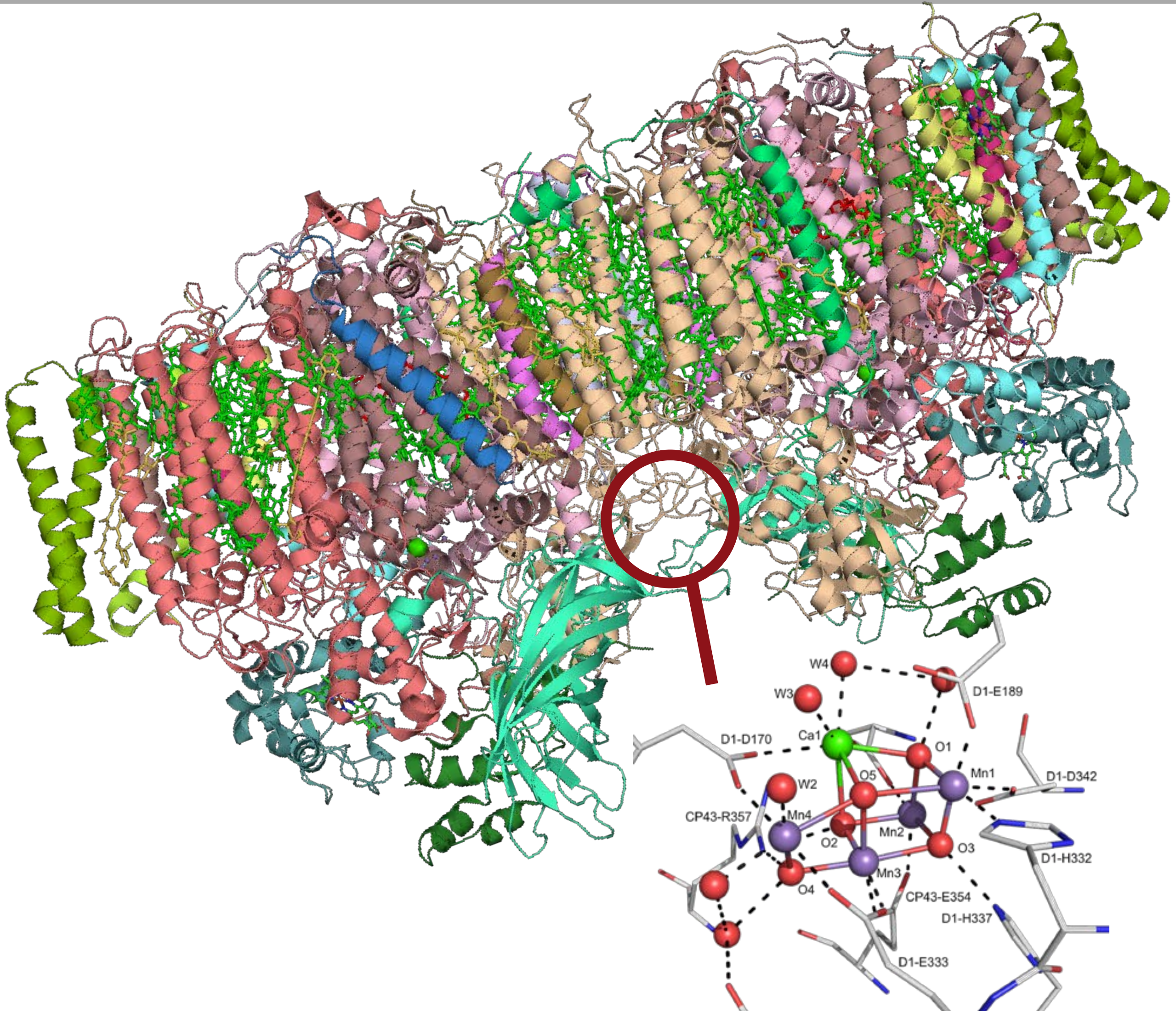
Experiment – For example: *Real-time observation of valence electron motion* (Nature **466** 2010)





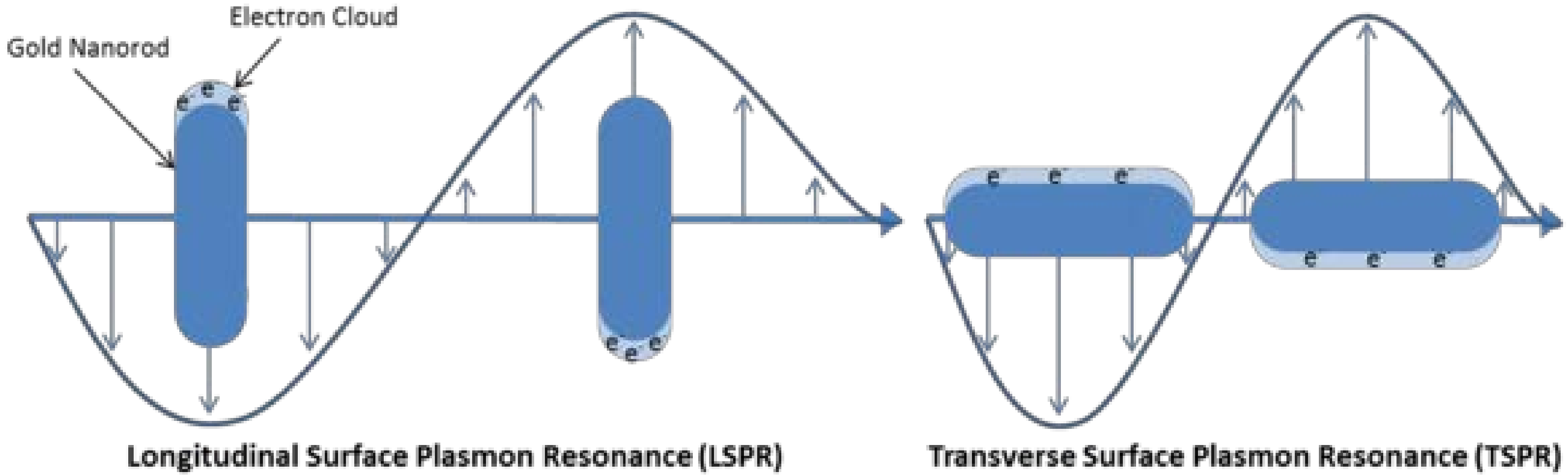
Reconstructed wave-package

But what happens if we put a larger molecule in a field



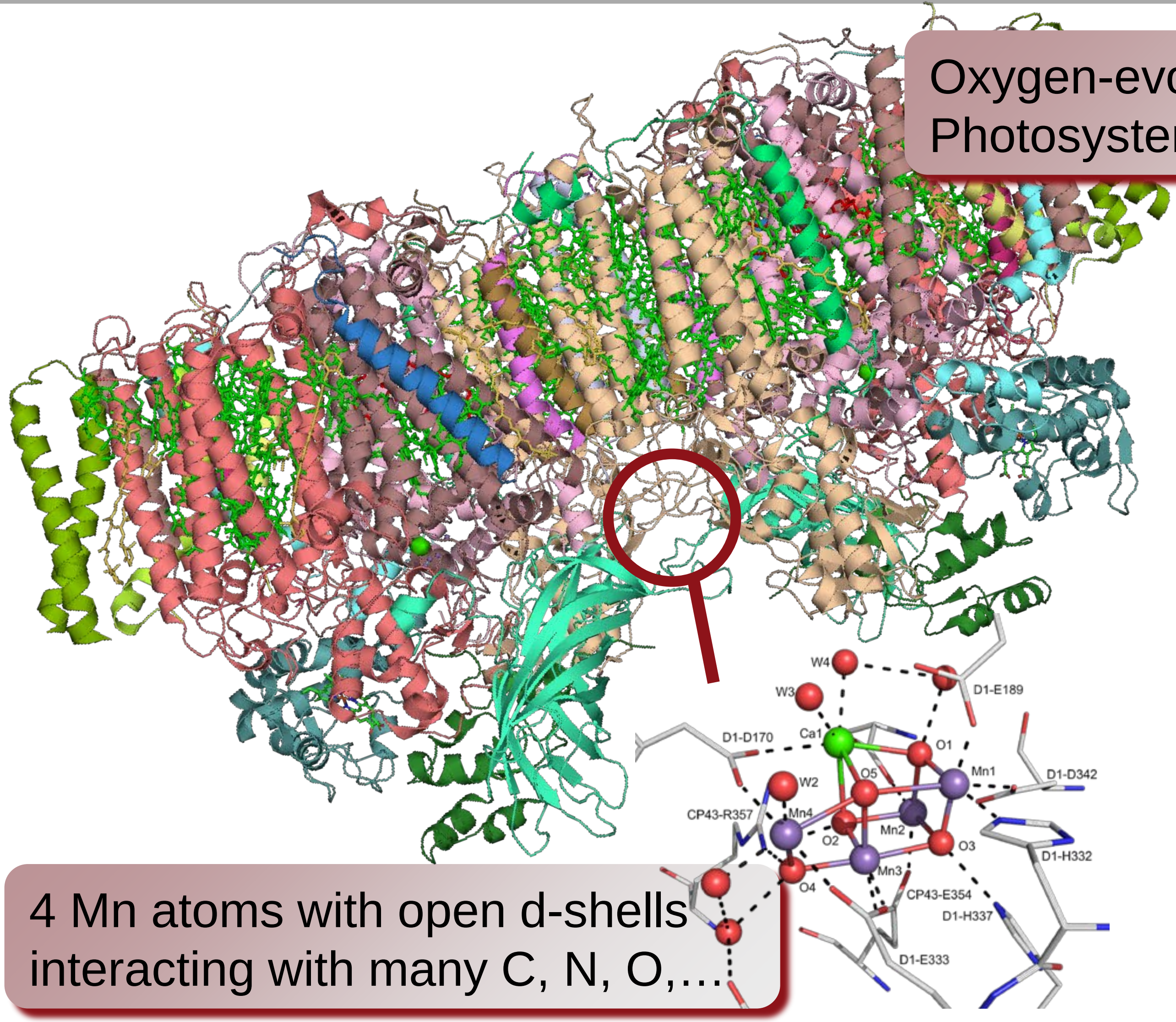
Pictures from wikipedia

Simple metals (Li, Al, …) in a field – Plasmon oscillations



Pictures from wikipedia

How about this molecule

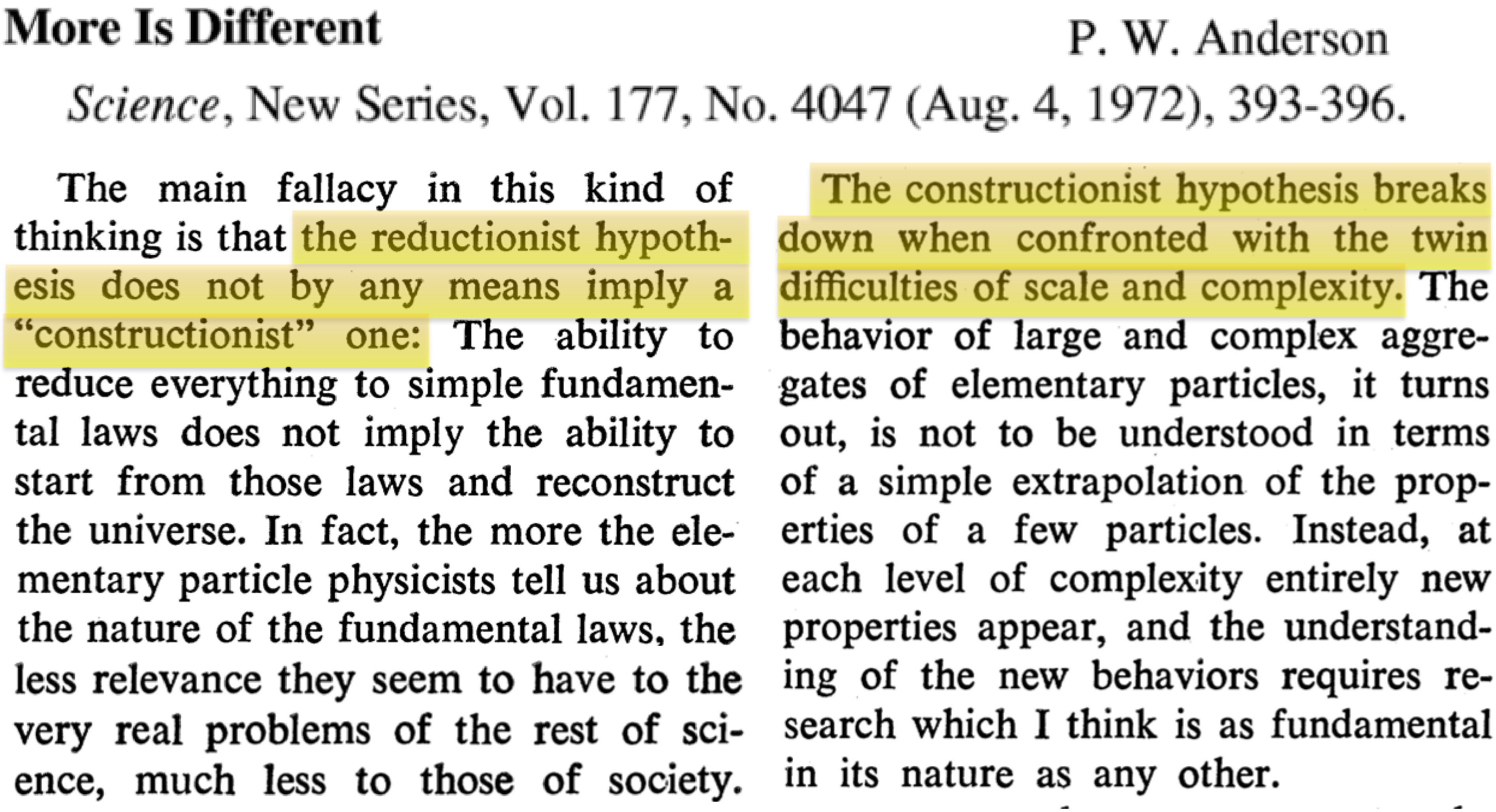


Oxygen-evolving complex in Photosystem II

4 Mn atoms with open d-shells interacting with many C, N, O,…

Pictures from wikipedia

No intuitive extrapolation from small to large systems



More Is Different

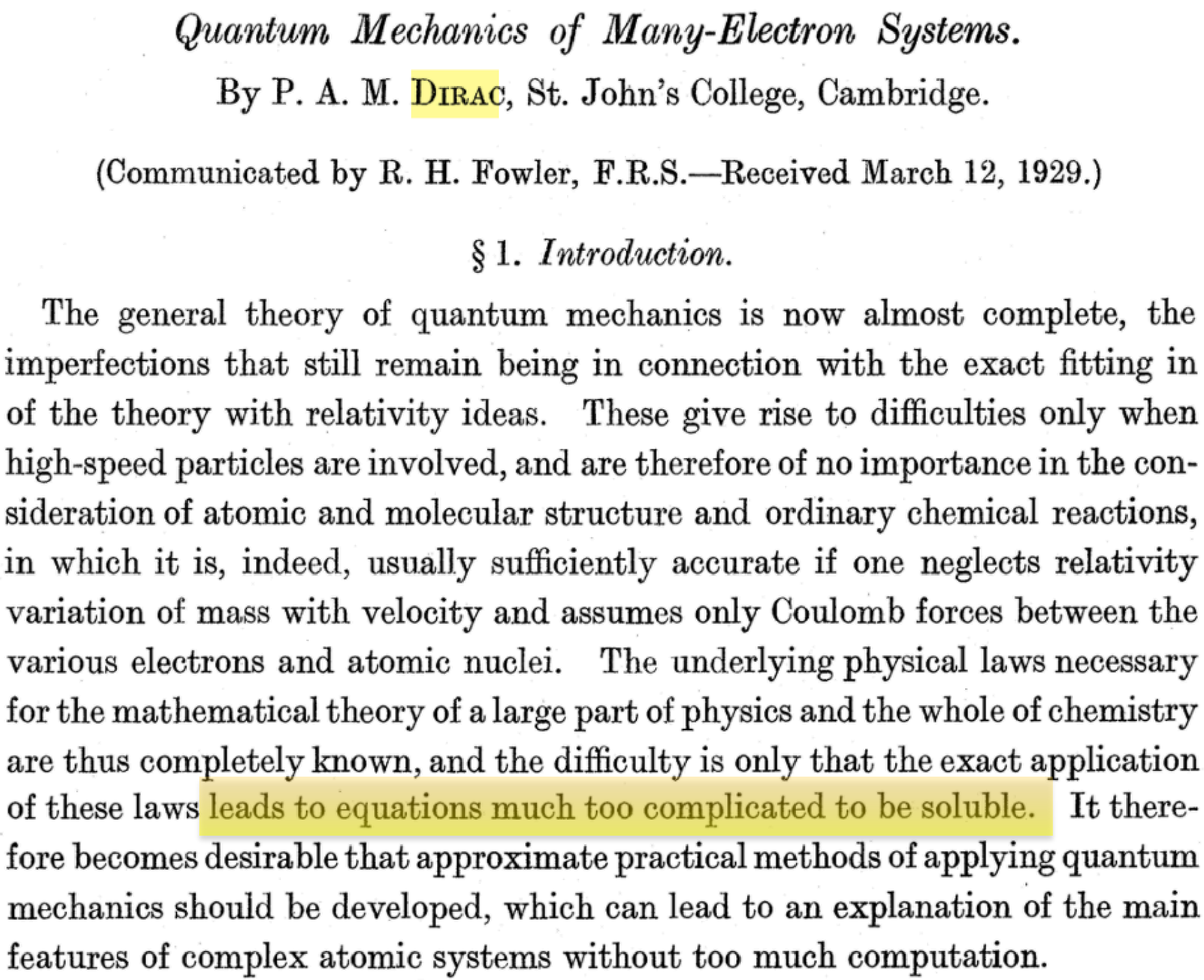
P. W. Anderson

Science, New Series, Vol. 177, No. 4047 (Aug. 4, 1972), 393-396.

The main fallacy in this kind of thinking is that the reductionist hypothesis does not by any means imply a "constructionist" one: The ability to reduce everything to simple fundamental laws does not imply the ability to start from those laws and reconstruct the universe. In fact, the more the elementary particle physicists tell us about the nature of the fundamental laws, the less relevance they seem to have to the very real problems of the rest of science, much less to those of society.

The constructionist hypothesis breaks down when confronted with the twin difficulties of scale and complexity. The behavior of large and complex aggregates of elementary particles, it turns out, is not to be understood in terms of a simple extrapolation of the properties of a few particles. Instead, at each level of complexity entirely new properties appear, and the understanding of the new behaviors requires research which I think is as fundamental in its nature as any other.

How far can we get *ab initio*



Quantum Mechanics of Many-Electron Systems.

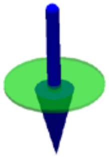
By P. A. M. Dirac, St. John's College, Cambridge.

(Communicated by R. H. Fowler, F.R.S.—Received March 12, 1929.)

§ 1. *Introduction.*

The general theory of quantum mechanics is now almost complete, the imperfections that still remain being in connection with the exact fitting in of the theory with relativity ideas. These give rise to difficulties only when high-speed particles are involved, and are therefore of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions, in which it is, indeed, usually sufficiently accurate if one neglects relativity variation of mass with velocity and assumes only Coulomb forces between the various electrons and atomic nuclei. 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 equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

Theoretical challenges – NP-hard scaling

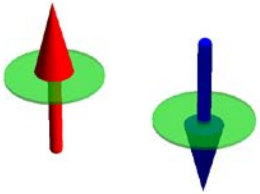


Example cluster of H atoms

# atoms	# spin-orbitals	# electrons	# states
1	2	1	$\binom{2}{1}$ 2

Cluster of H atoms
Only include the 1s orbital
(Hubbard model)

Theoretical challenges – NP-hard scaling

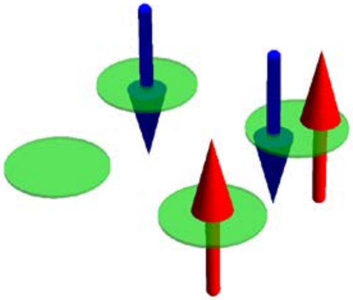


Example cluster of H atoms

# atoms	# spin-orbitals	# electrons	# states
1	2	1	$\binom{2}{1}$ 2
2	4	2	$\binom{4}{2}$ 6

Cluster of H atoms
Only include the 1s orbital
(Hubbard model)

Theoretical challenges – NP-hard scaling



Example cluster of H atoms

# atoms	# spin-orbitals	# electrons	# states
1	2	1	$\binom{2}{1}$ 2
2	4	2	$\binom{4}{2}$ 6
4	8	4	$\binom{8}{4}$ 70

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Only include the 1s orbital
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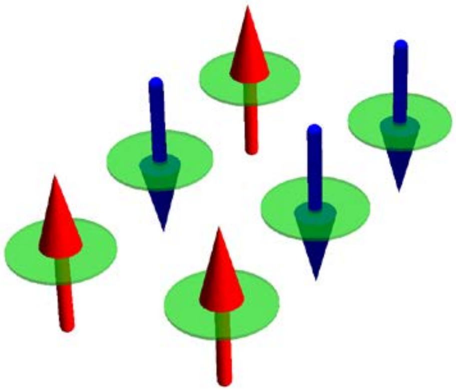
Theoretical challenges – NP-hard scaling



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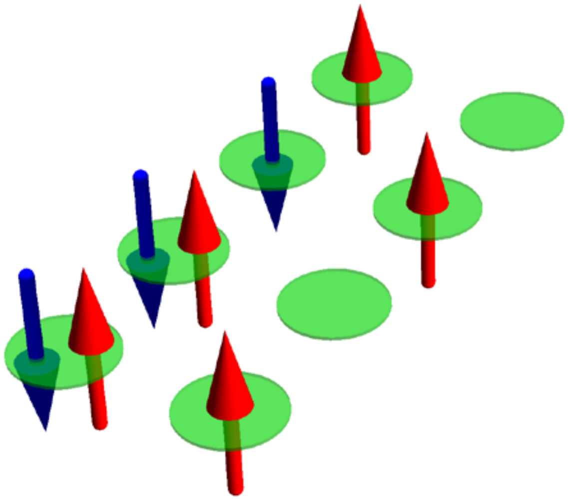
Example cluster of H atoms

# atoms	# spin-orbitals	# electrons	# states
1	2	1	$\binom{2}{1}$ 2
2	4	2	$\binom{4}{2}$ 6
4	8	4	$\binom{8}{4}$ 70
6	12	6	$\binom{12}{6}$ 924

Theoretical challenges – NP-hard scaling



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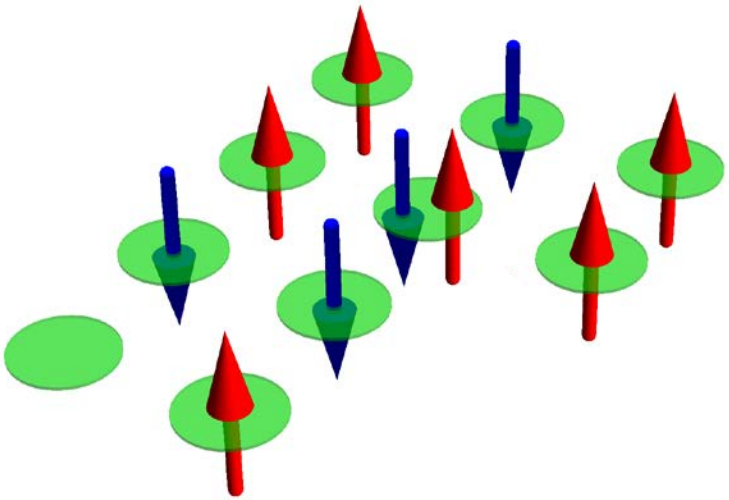
4	8	4	$\binom{8}{4}$ 70
6	12	6	$\binom{12}{6}$ 924
8	16	8	$\binom{16}{8}$ 12 870

Theoretical challenges – NP-hard scaling



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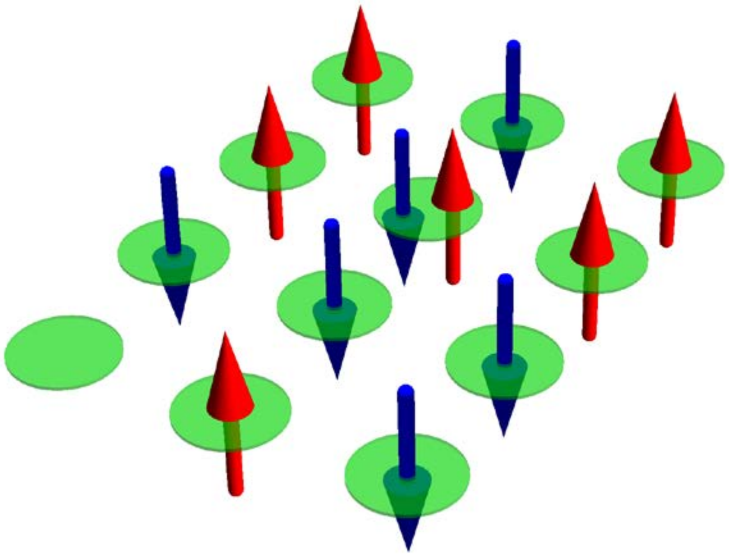
6	12	6	$\binom{12}{6}$ 924
8	16	8	$\binom{16}{8}$ 12 870
10	20	10	$\binom{20}{10}$ 184 756

Theoretical challenges – NP-hard scaling



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Example cluster of H atoms

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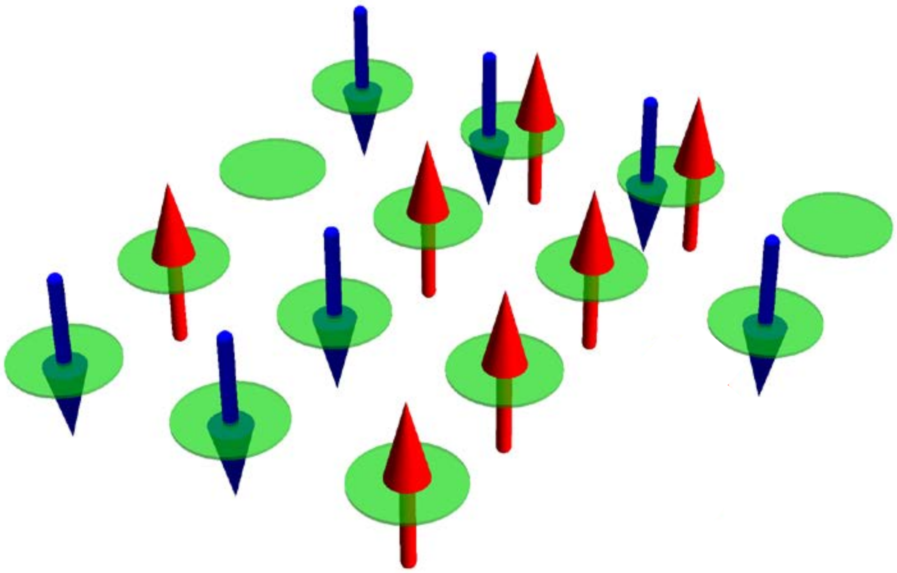
6	12	6	$\binom{12}{6}$ 924
8	16	8	$\binom{16}{8}$ 12 870
10	20	10	$\binom{20}{10}$ 184 756
12	24	12	$\binom{24}{12}$ 2 704 156

Theoretical challenges – NP-hard scaling



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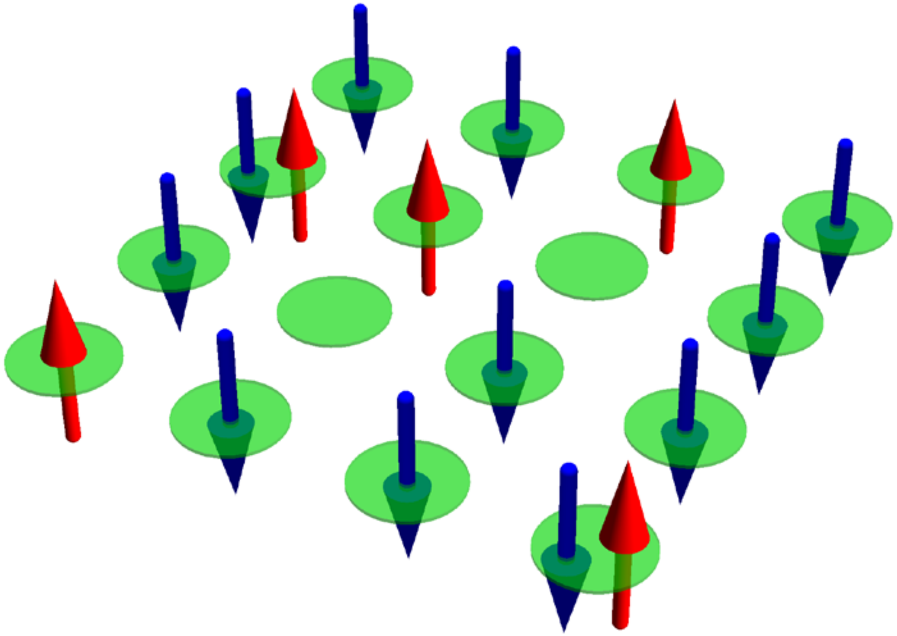
6	12	6	$\binom{12}{6}$ 924
8	16	8	$\binom{16}{8}$ 12 870
10	20	10	$\binom{20}{10}$ 184 756
12	24	12	$\binom{24}{12}$ 2 704 156
14	28	14	$\binom{28}{14}$ 40 116 600

Theoretical challenges – NP-hard scaling



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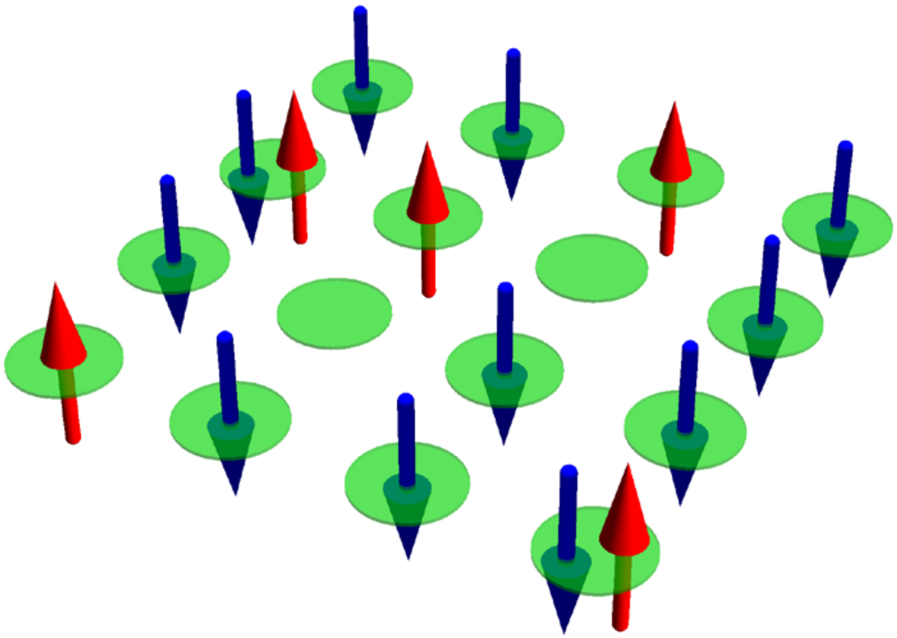
10	20	10	$\binom{20}{10}$ 184 756
12	24	12	$\binom{24}{12}$ 2 704 156
14	28	14	$\binom{28}{14}$ 40 116 600
16	32	16	$\binom{32}{16}$ 601 080 390

Theoretical challenges – NP-hard scaling



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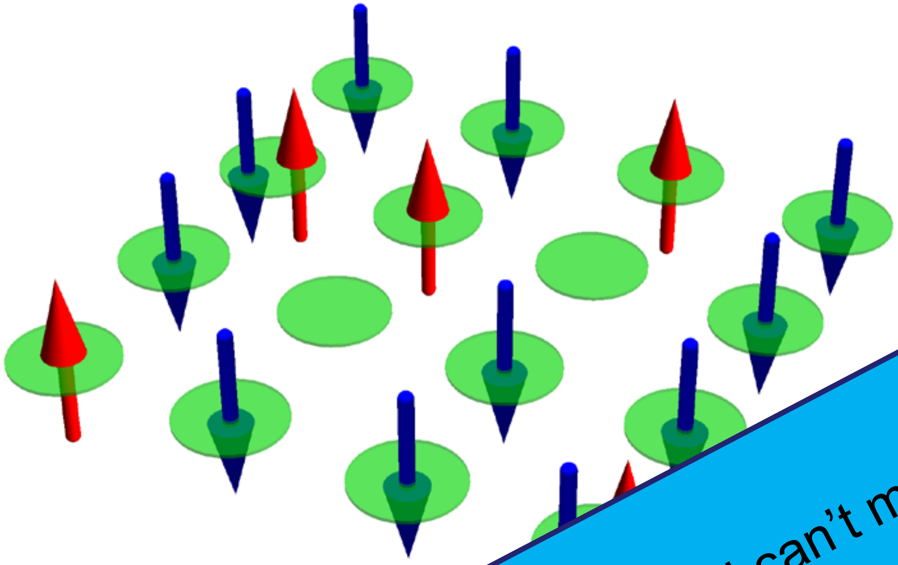
8	16	8	$\binom{16}{8}$ 12 870
10	20	10	$\binom{20}{10}$ 184 756
12	24	12	$\binom{24}{12}$ 2 704 156
14	28	14	$\binom{28}{14}$ 40 116 600
16	32	16	$\binom{32}{16}$ 601 080 390
18	36	18	$\binom{36}{18}$ 9 075 135 300

Theoretical challenges – NP-hard scaling



What can and can't mean-field do for you

Replace $\sum_{i,j} \frac{1}{r_i - r_j}$ by $V(r,t)$.

No direct exa

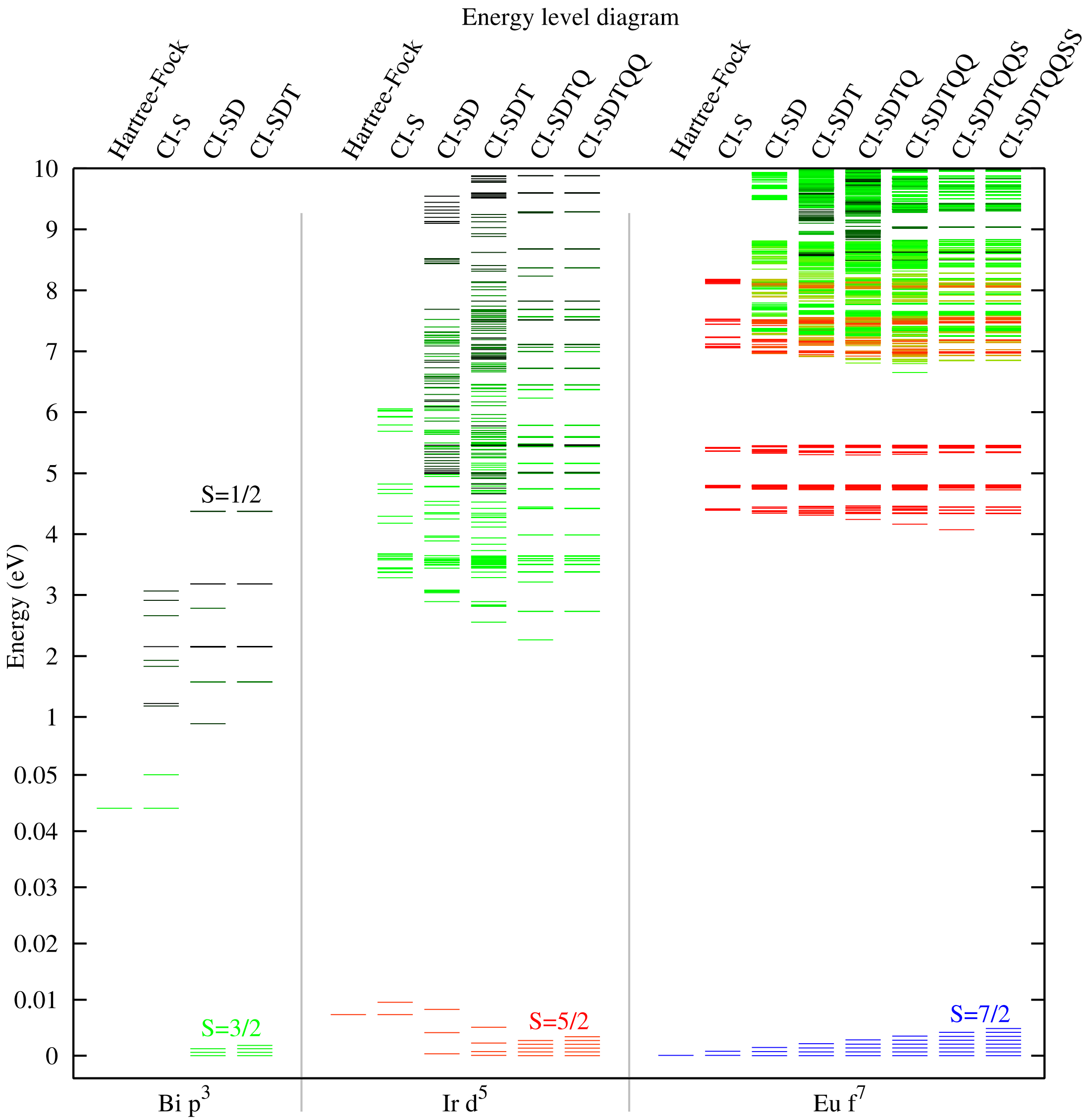
possible

olution (1):

Approximate the Coulomb interaction by a (time dependent) potential.

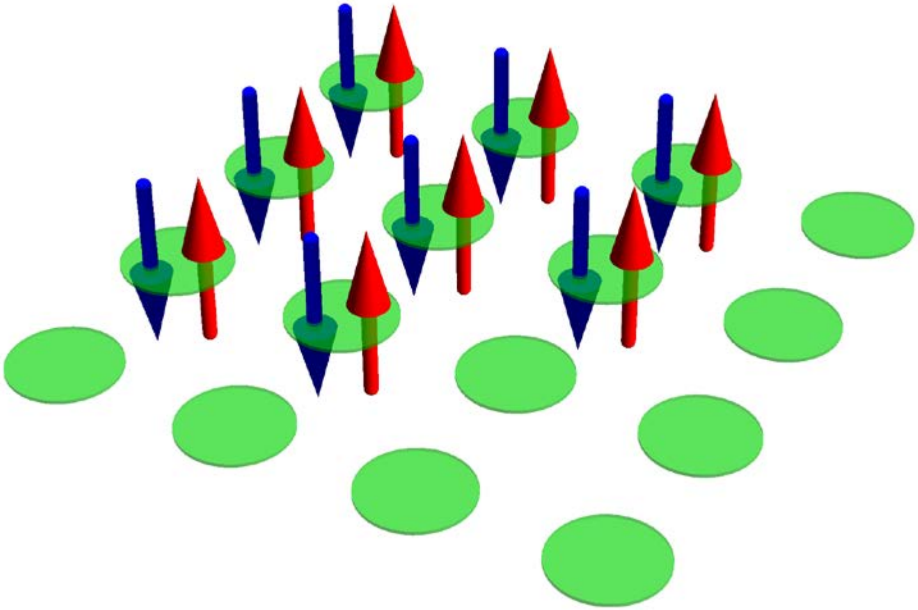
(LDA, GGA, Hartree-Fock)

Multi-electron excitations – excited state v.s. ground-state



Eigen-state energies of half filed atoms (p^3, d^5 and f^7) using different levels of configuration interaction (singles, doubles, triples, quadruples, quintuples, …)

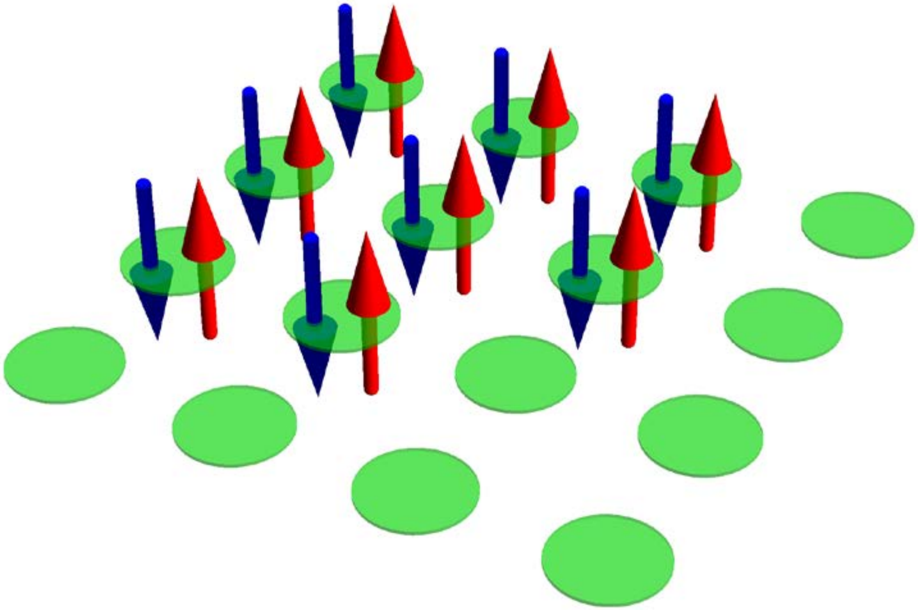
Theoretical challenges – NP-hard scaling



Solution (1):
Approximate the Coulomb interaction by a (time dependent) potential.
(LDA, GGA, Hartree-Fock)

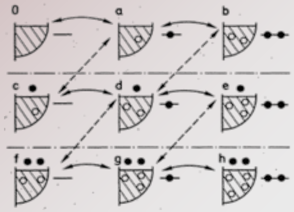
Solution (2):
Many determinants are highly improbable and do not contribute to the state of interest. Therefore do not include those in the basis

Minimize the exponent of the exponential scaling



Many determinants are highly improbable and do not contribute to the state of interest. Therefore do not include those in the basis

O. Gunnarsson and
K. Schönhammer,
PRL **50**, 604 (1983)



Configuration interaction

Renormalization group

Improve on Configuration interaction by systematically optimizing the one orbital basis and remove the unimportant many electron determinants.

Mix ideas from quantum chemistry and renormalization group theory
PRB **85**, 165113 (2012).
PRB **90**, 085102 (2014).

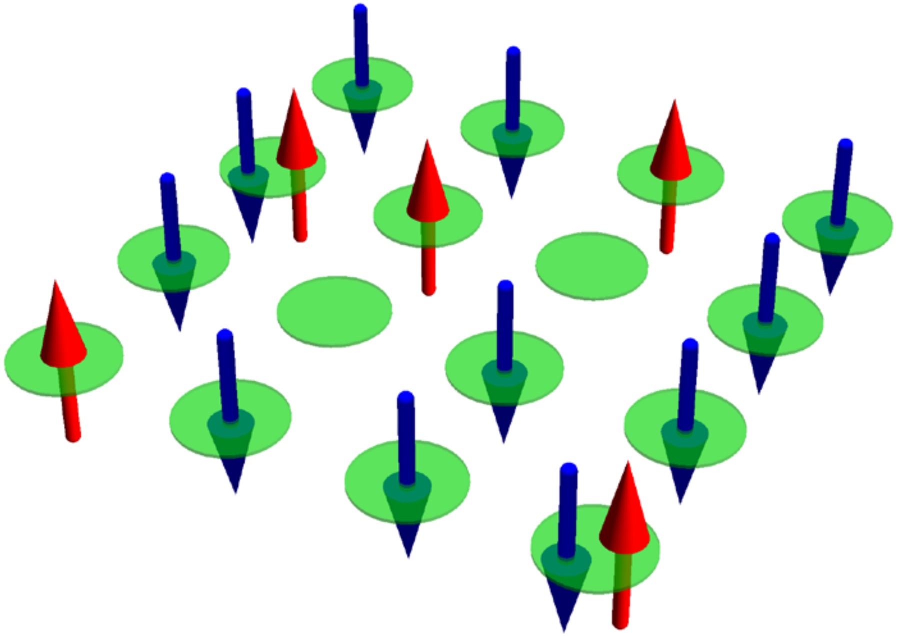
Quanty – www.quanty.org

Ground-state by
Quantum chemistry (CI (S,D,T,…), RAS, …)
Renormalization group
Matrix product states
Or combinations of these with basis set truncations

Spectroscopy using Green’s functions.
Any order of response for any operator
Diagrammatic expansions
Self energy of excited states due to decay of quasi particles

Implemented as script language
Freedom to choose your model and level of theory

Theoretical challenges – NP-hard scaling



Solution (3):
Combined with (2):
Include locally all interactions, make non-local approximations.

- Multiplet Crystal-Field Theory
- Multiplet Ligand-Field Theory
- Embedded Cluster Theory
- Dynamical mean-field theory
- (connected to DFT or HF)

Solution (1):
Approximate the Coulomb interaction by a (time dependent) potential.
(LDA, GGA, Hartree-Fock)

Solution (2):
Many determinants are highly improbable and do not contribute to the state of interest. Therefore do not include those in the basis