

Density functional theory for surface science, Auger spectroscopy and simple thermodynamics

Peter Krüger

Outline

- 1) What is density functional theory ?
→ Examples of recent work with Yamada group
- 2) Theory of resonant Auger electron spectroscopy + diffraction
- 3) Basic physical chemistry. Thermodynamic information from the pair correlation function / structure factor

First-principles calculations / density functional theory

Nowadays, the structural, dynamic, electronic, magnetic, optical properties of most materials can be calculated “**from first principles**”, that is without input from experiment

Start from some structural model (and refine it later if necessary)

calculate the electronic state: molecular orbitals / bands in a molecule, electronic band structure in a solid

- use density functional theory (or Hartree-Fock or ..)
- solve Kohn-Sham (~Schrodinger) equations
- molecular orbitals / bands, electronic (and spin) density, total energy.

- once the electronic state is known, many chemical, optical and transport properties can be understood.

- forces between atoms
- find equilibrium atomic structure by “structural optimization”:
move atoms along forces until all forces are zero.
- compute atomic dynamics, vibrational spectra etc

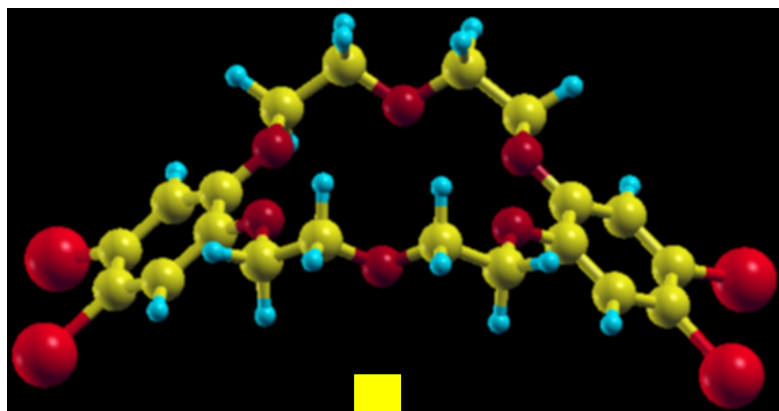
Well-ordered monolayer growth of Crown-Ether ring molecules on Cu(111) in ultra-high vacuum: a STM, UPS and DFT study, Ryohei Nemoto, Peter Krüger, Ayu Novita Putri Hartini, Takuya Hosokai, Masaki Horie, Satoshi Kera and Toyo Kazu Yamada, J. Phys. Chem. C 123, 18939-18950 (2019)

Direct Imaging of Precursor Adcomplex States during Cryogenic-Temperature On-Surface Metalation: Scanning Tunneling Microscopy Study on Porphyrin Array with Fe Adsorption at 78.5 K
Eiichi Inami, Masataka Yamaguchi, Ryohei Nemoto, Hideki Yorimitsu, Peter Krüger, and Toyo Kazu Yamada, J. Phys. Chem. C 2020, 124, 3621

Carbon Monoxide Stripe Motion Driven by Correlated Lateral Hopping in a 1.4×1.4 Monolayer Phase on Cu(111),
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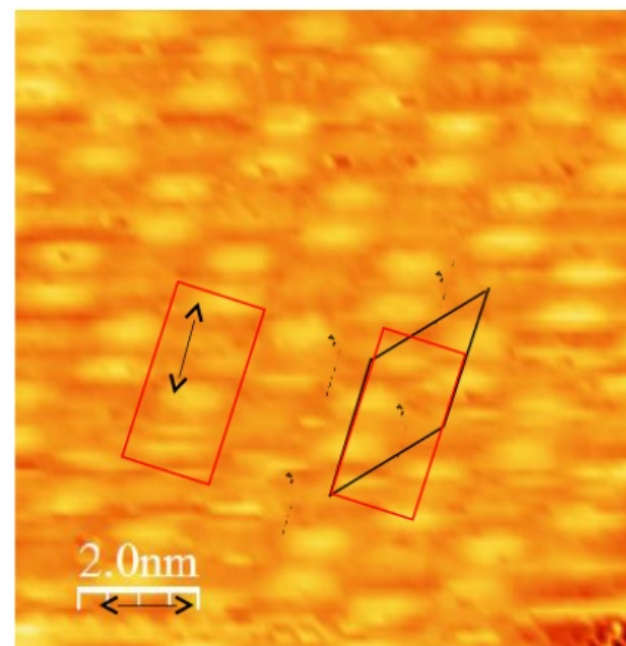
有機分子の2次元構造

単層 → 2次元のテンプレート

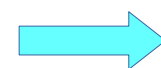


基板 銅 Cu(111)

走査トンネル顕微鏡
(山田研究室)

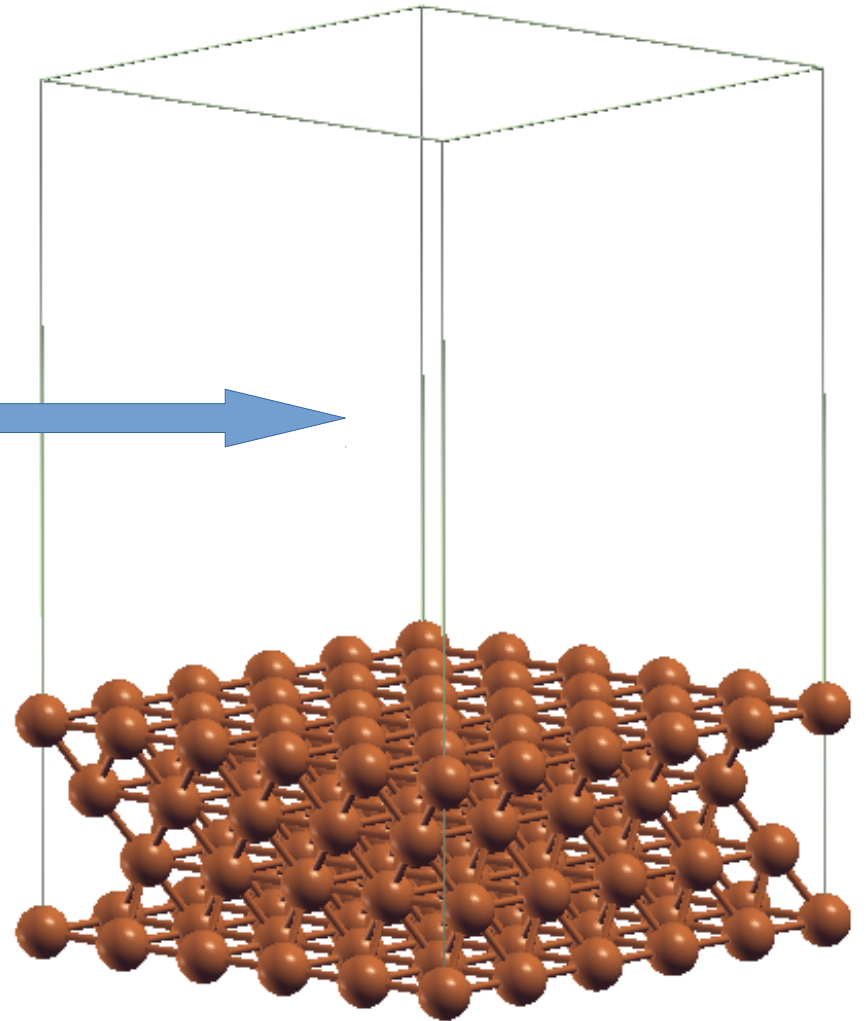
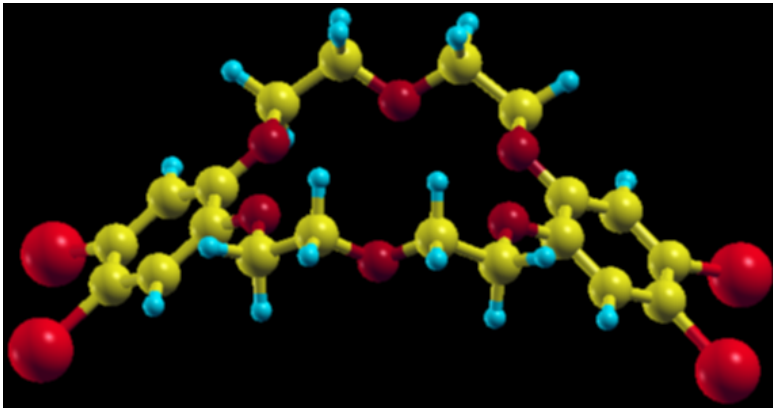


周期性 OK
細かい構造?

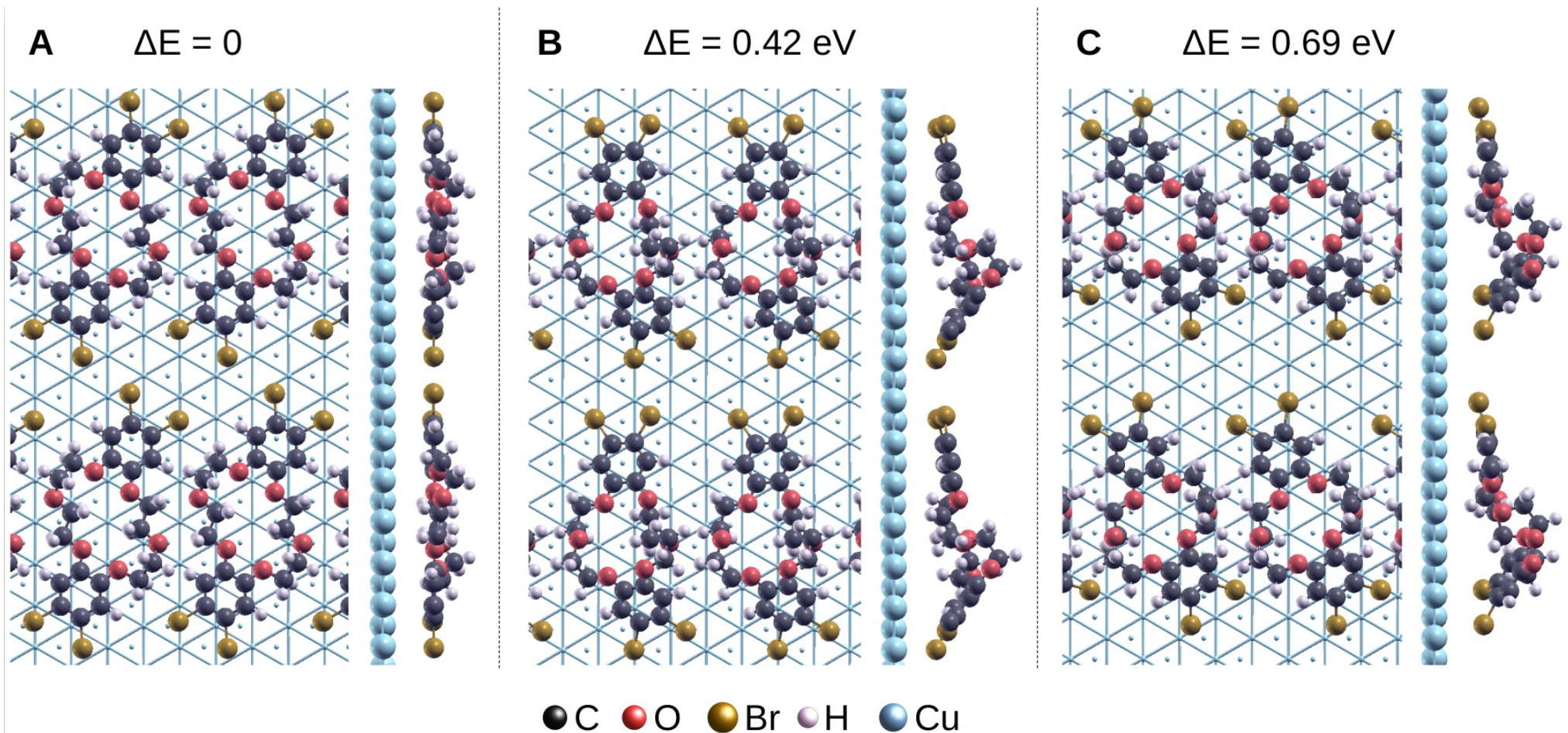


理論計算

基板シミュレーションモデル



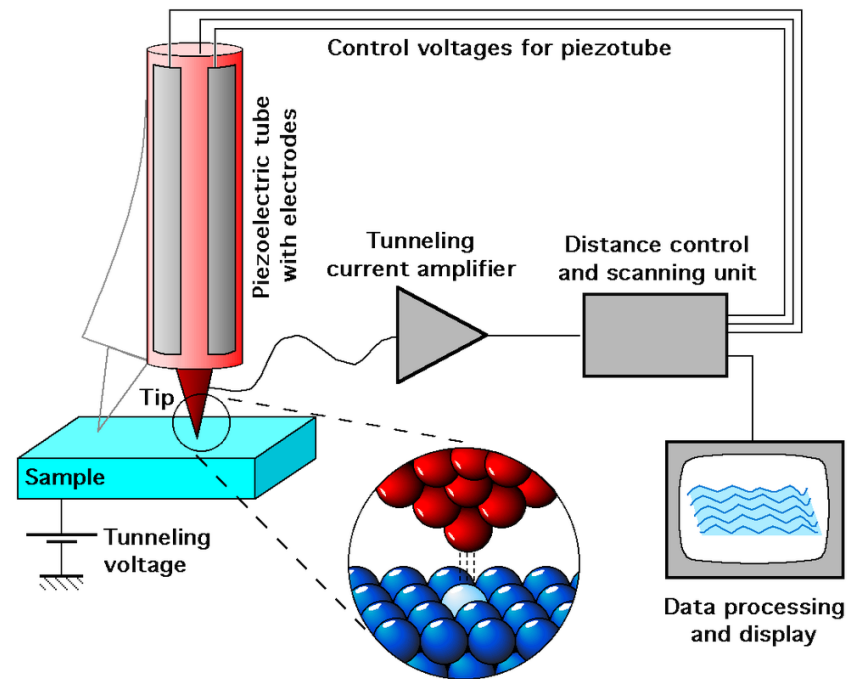
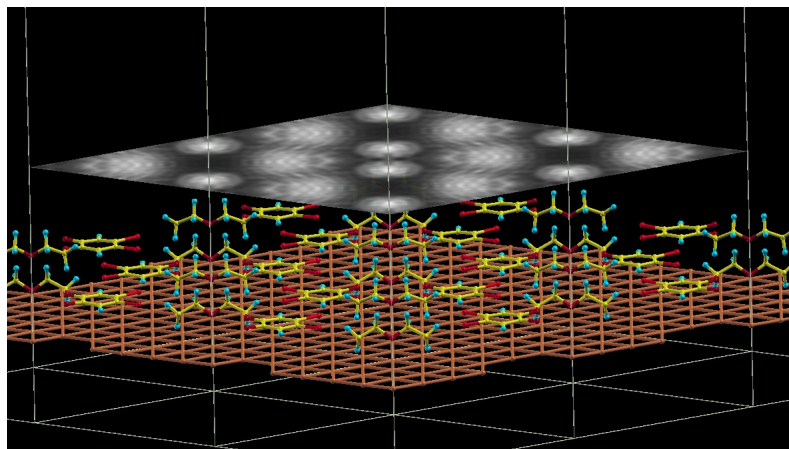
計算結果 安定な構造



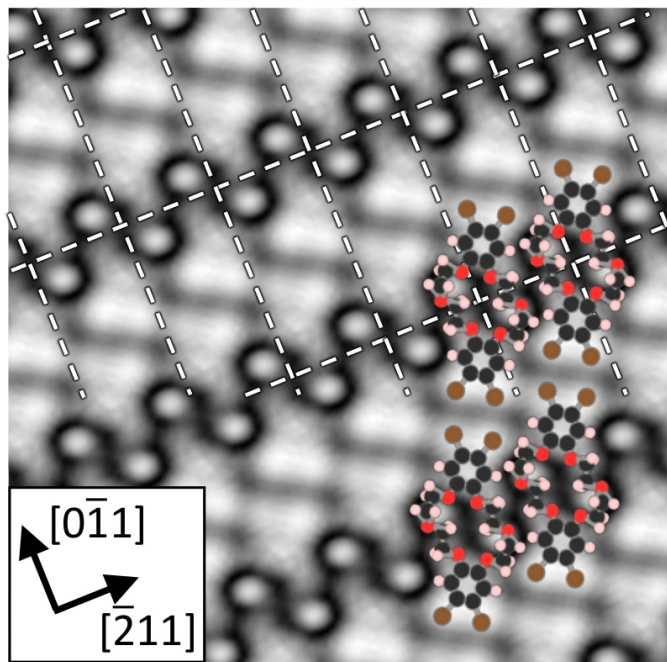
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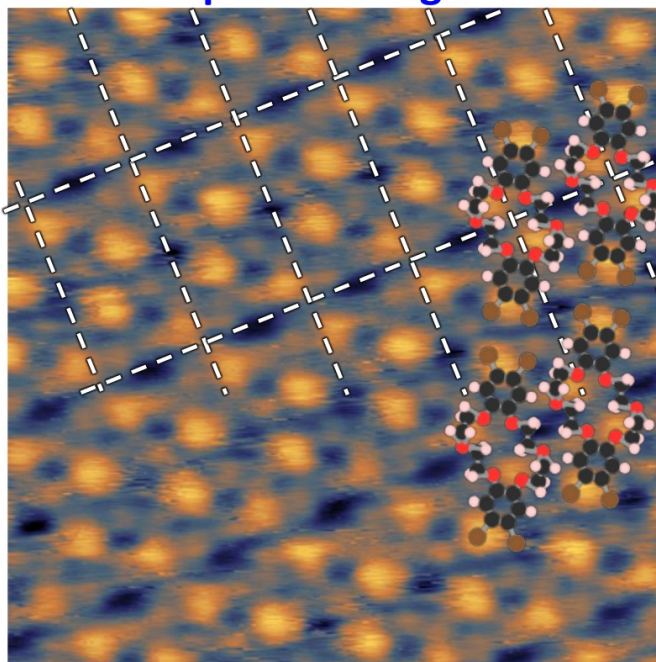
STM 顕微鏡



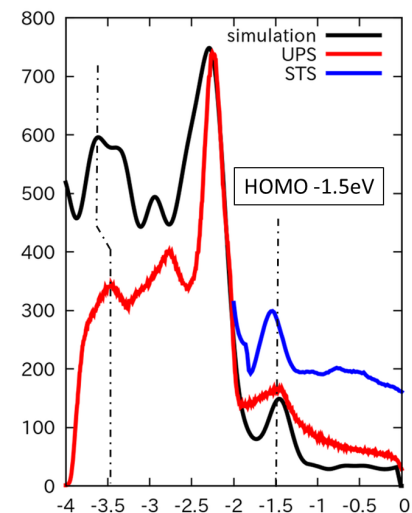
B DFT STM simulation



C Exp. STM image

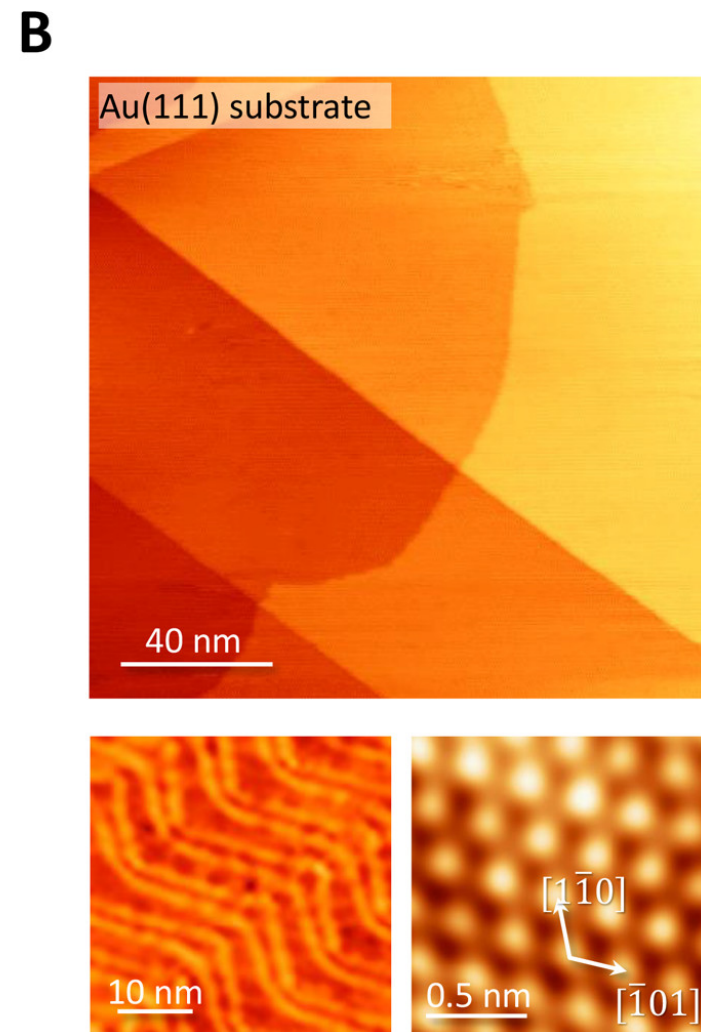
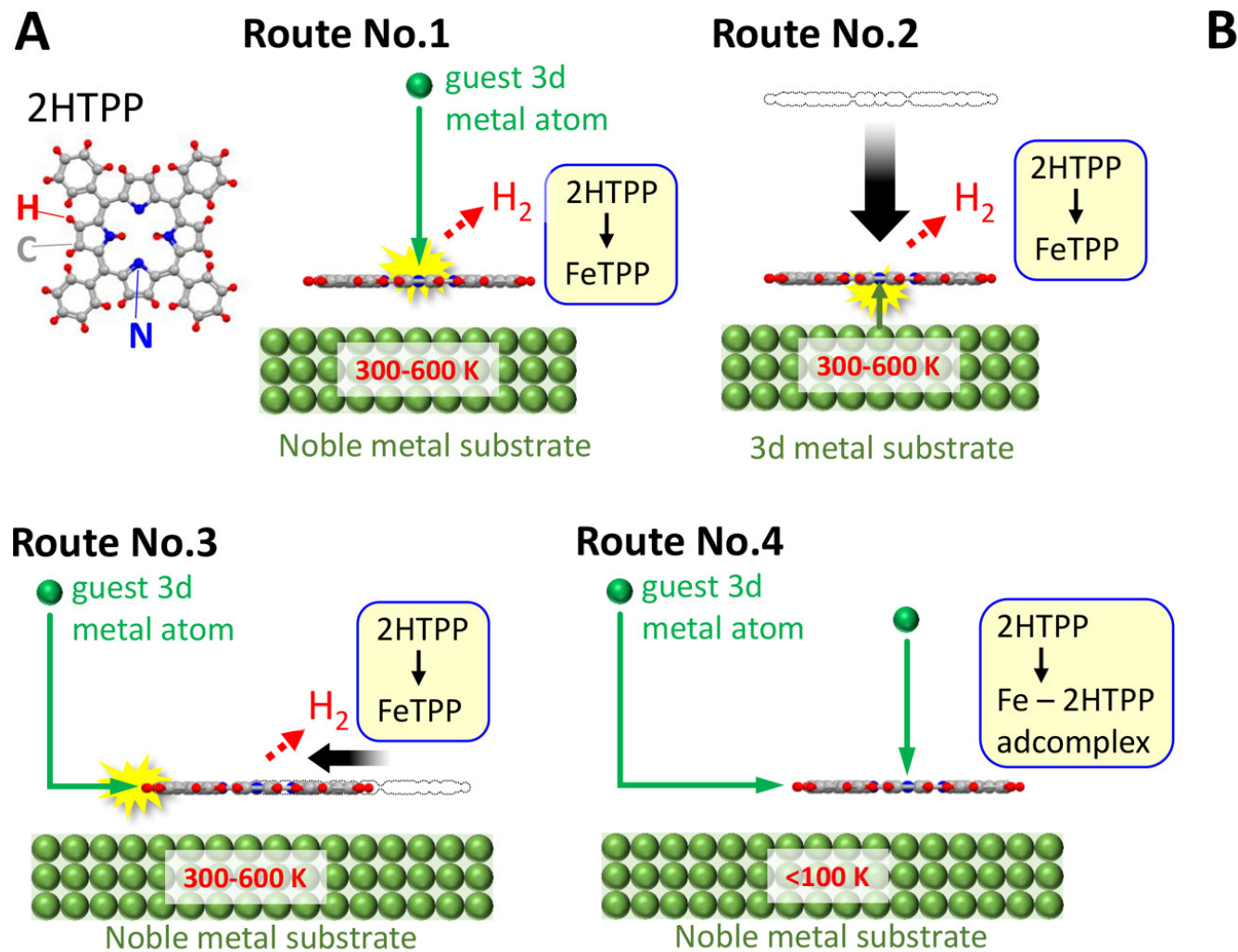


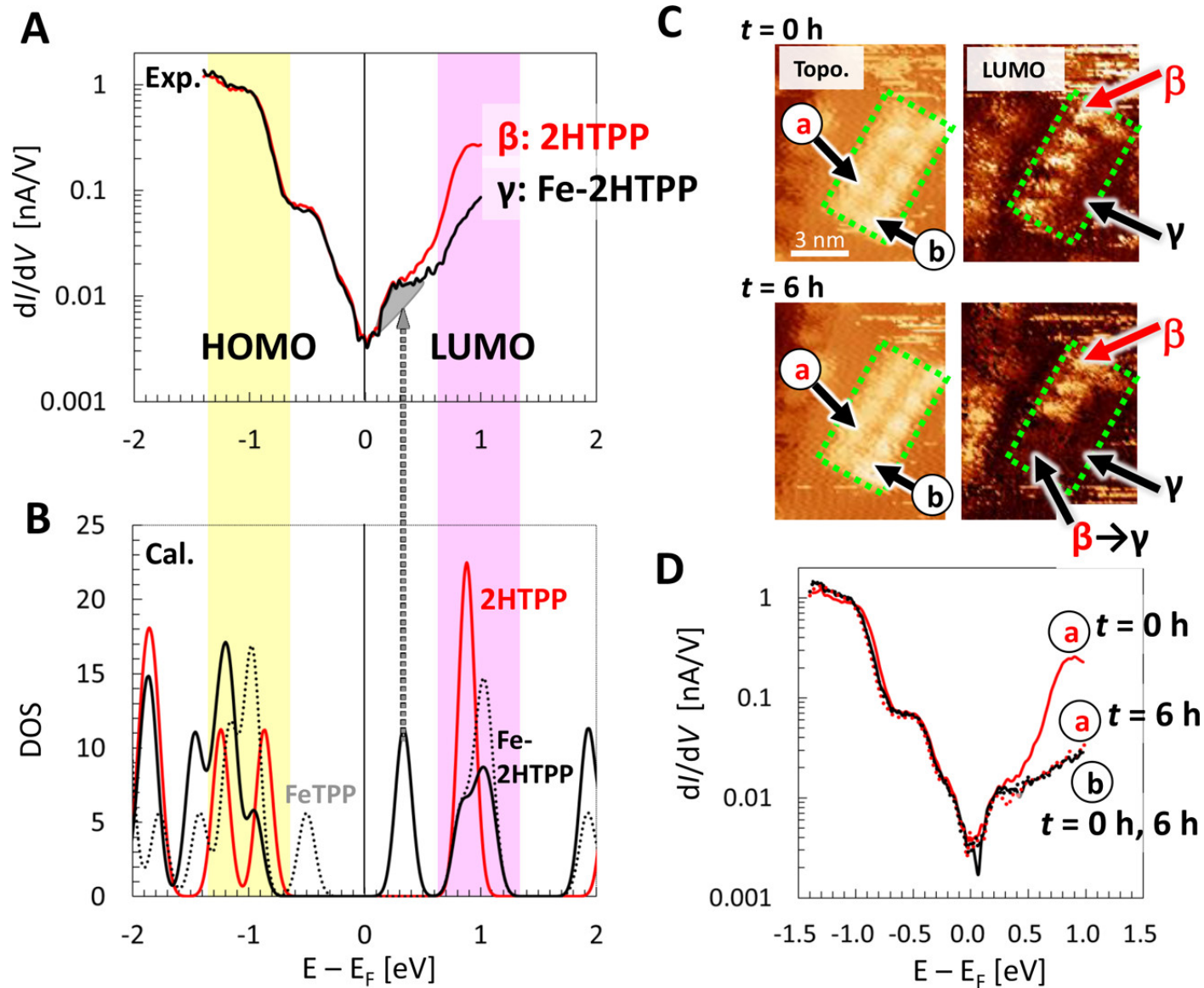
エネルギー スペクトル



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Computed STS spectra (electronic density of states)

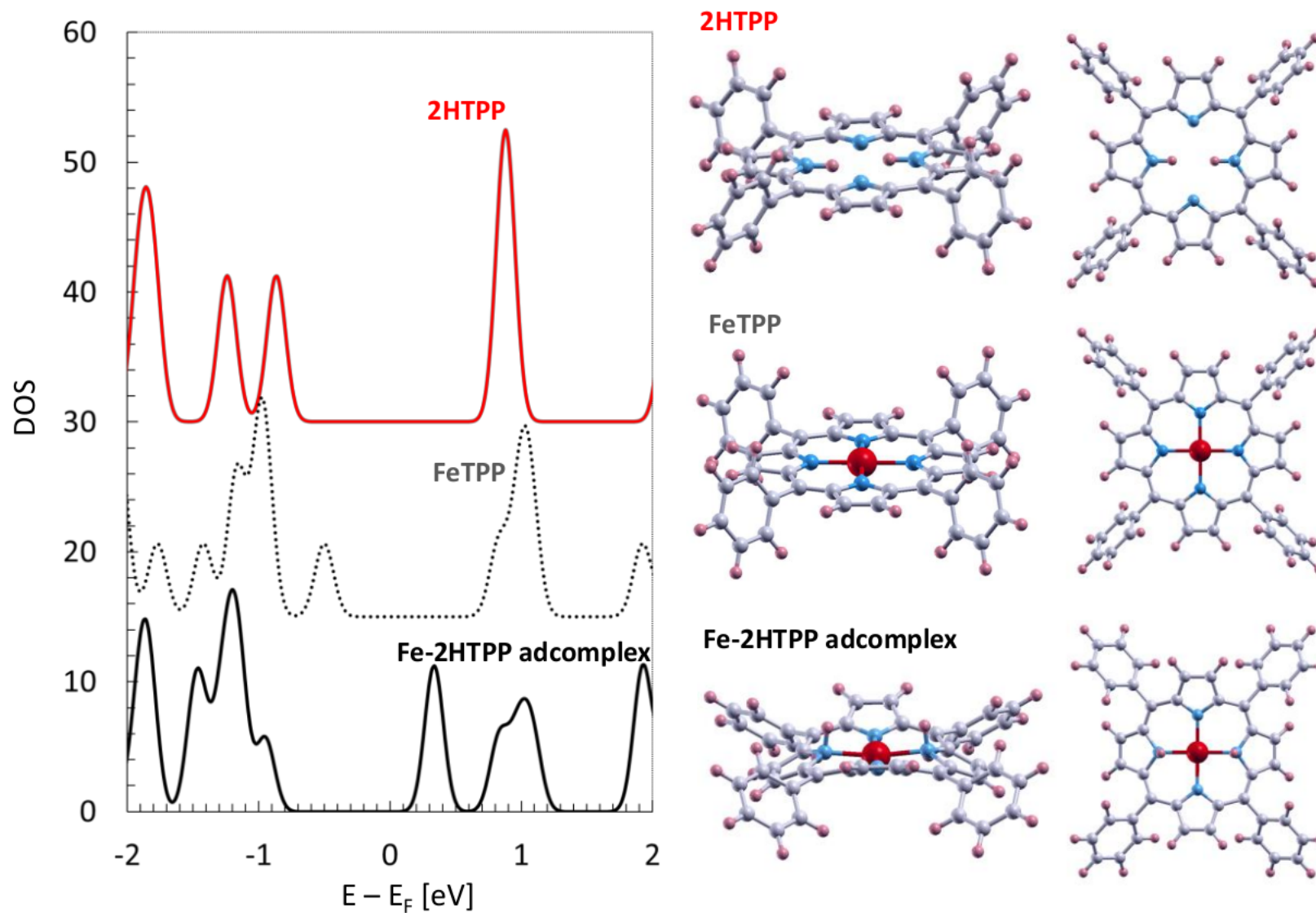
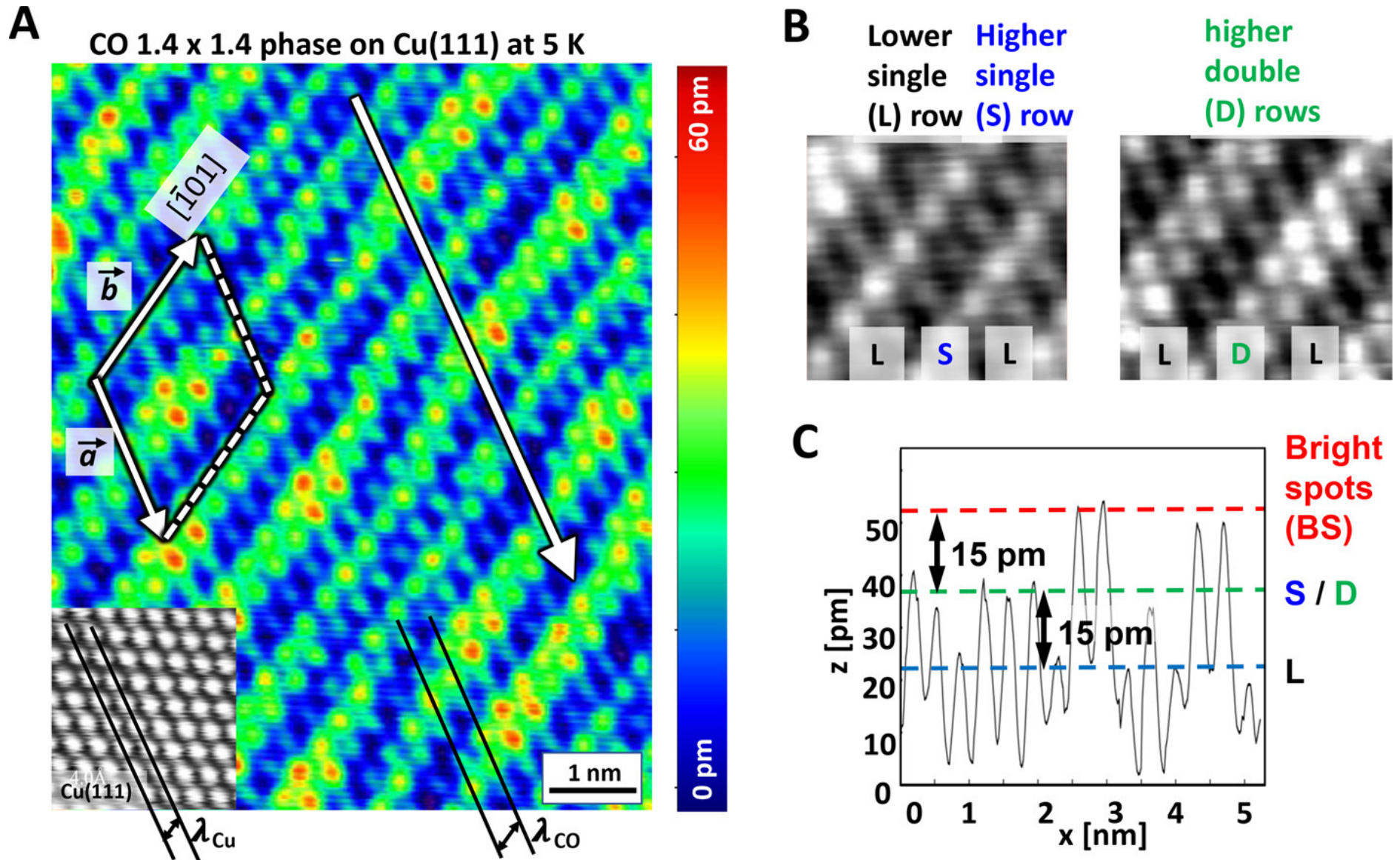
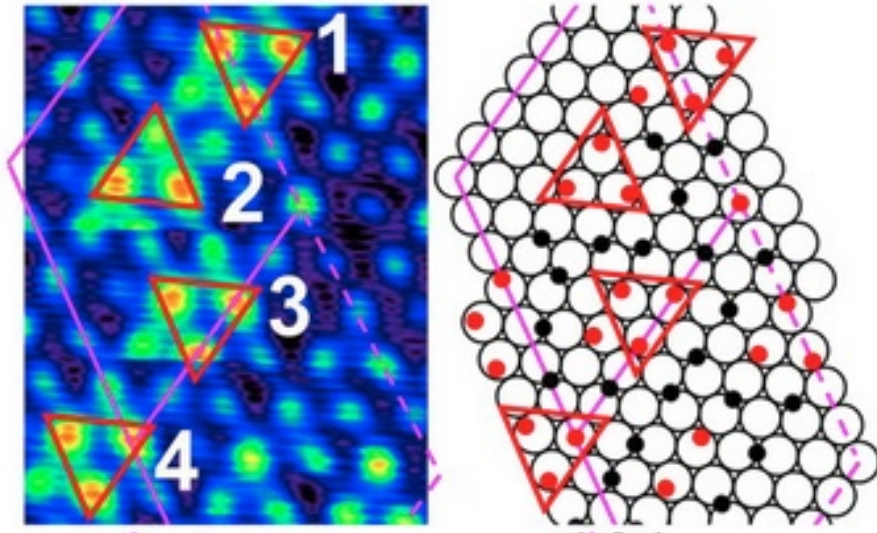


Figure S3. DFT calculated DOS of 2HTPP [red line], FeTPP [dotted line] and Fe-2HTPP adcomplex [black line]. Right panels denote models of calculated molecular structures: 3D and top views.

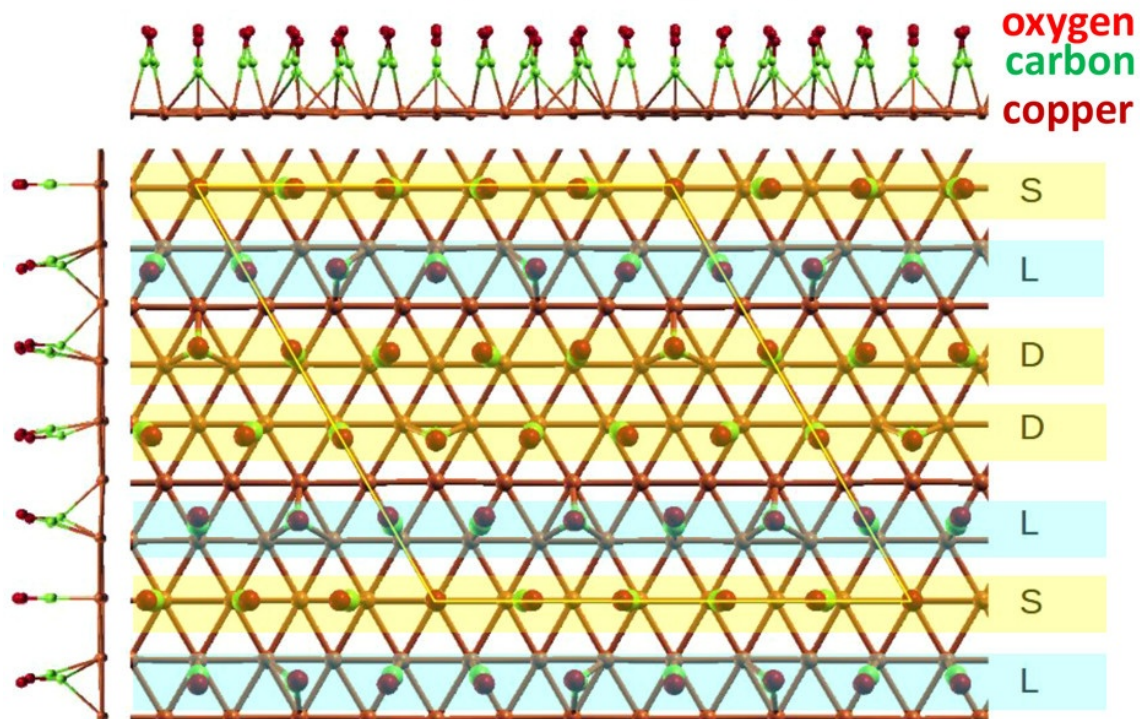
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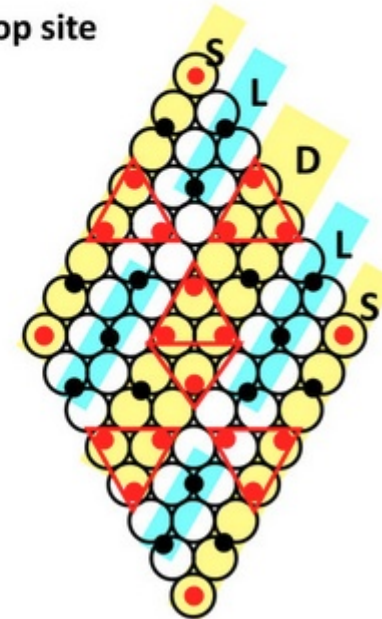
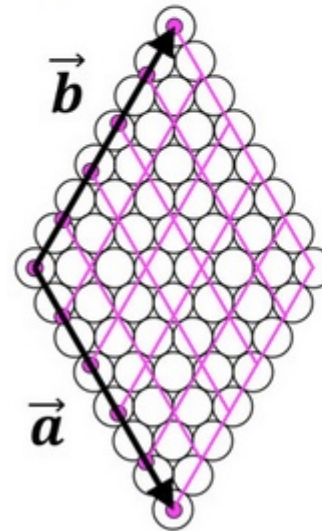


A DFT optimized structure of CO monolayer on Cu(111)



1.4 x 1.4 phase
top (T) : bridge (B) = 13 : 12

- Cu
- CO at bridge site
- CO at off-centered top site



First real space evidence of 1.4 x 1.4 structure

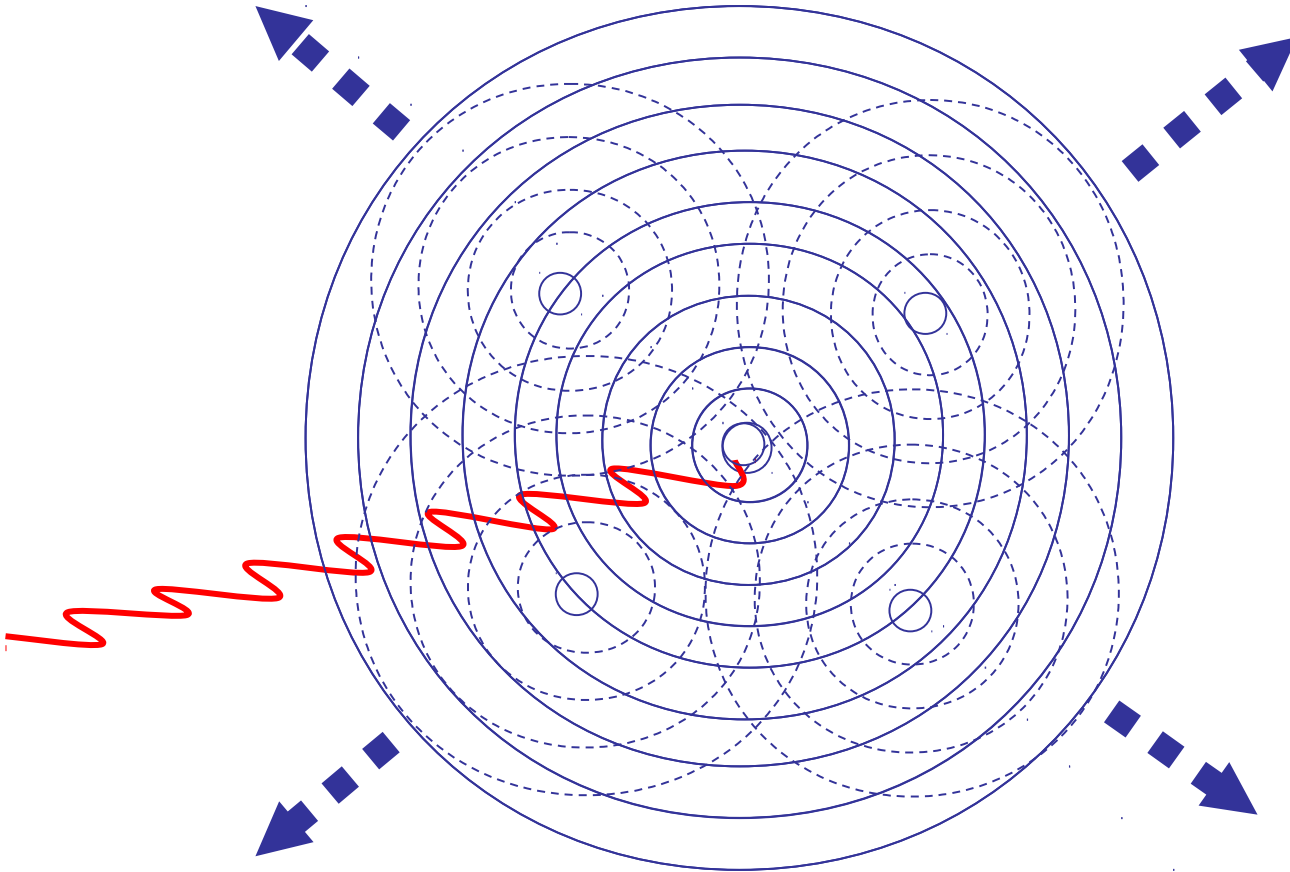
stripe formation and stripe motion explained

(2) Theory of resonant Auger electron spectroscopy / diffraction

Application to Ni(111)

→ Daimon effect with reversed angular momentum transfer

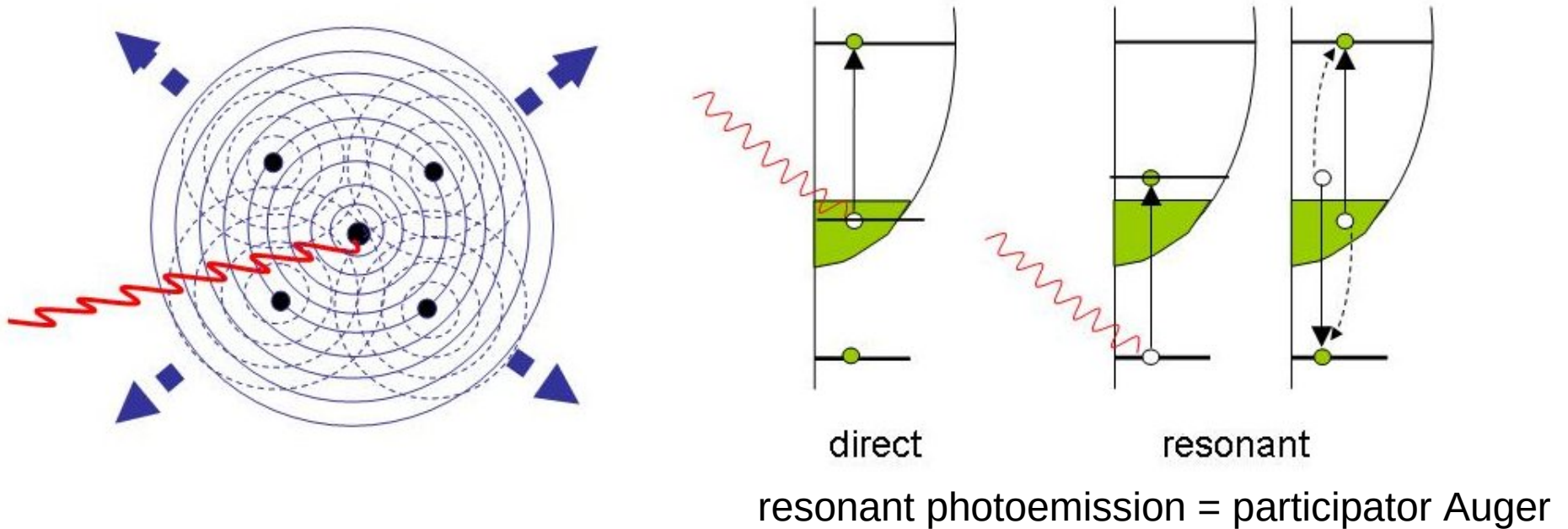
Principle of photoelectron diffraction



Interference between primary and scattered waves

- intensity modulation as function of angle = diffraction pattern
- information about local structure around emitter species

Resonant Photo-/ Auger-Electron Diffraction



- X-ray photoelectron diffraction → geometrical structure
- X-ray absorption → element selective information on unoccupied states
- valence photoemission → occupied states

Resonant valence band photoemission / Auger-electron diffraction

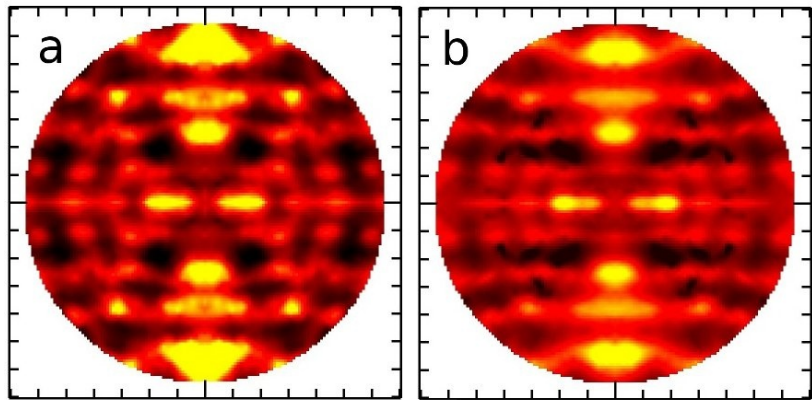
→ **element and site-specific electronic structure**

- easy to do on modern synchrotron sources
- rarely reported ... difficult to understand... no calculation method available

Ti 2p-3d resonant photoelectron diffraction from in-gap state of TiO₂(110)

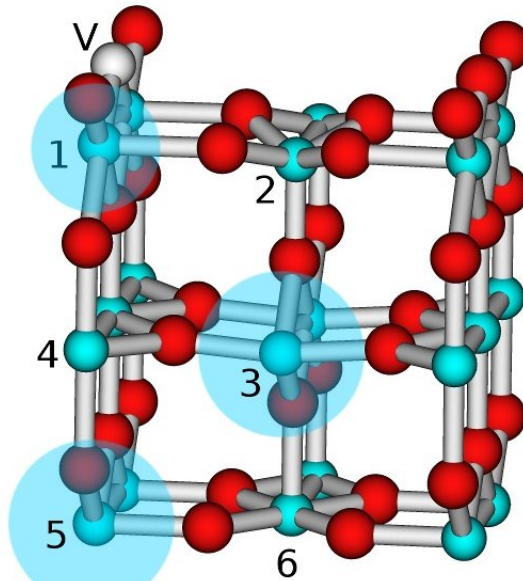
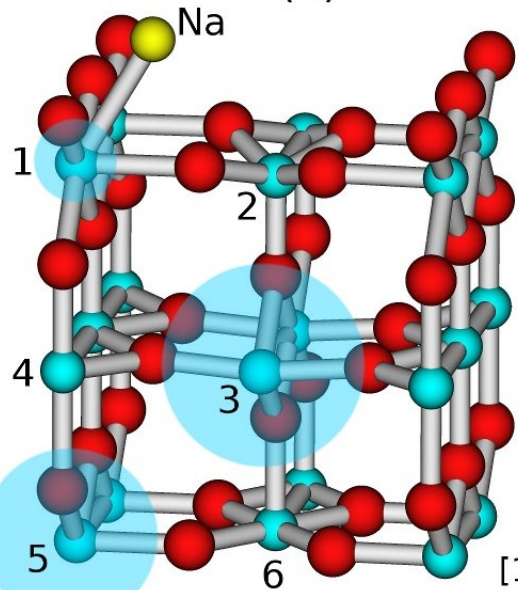
Exp. Na/TiO₂

O-vacancy TiO₂



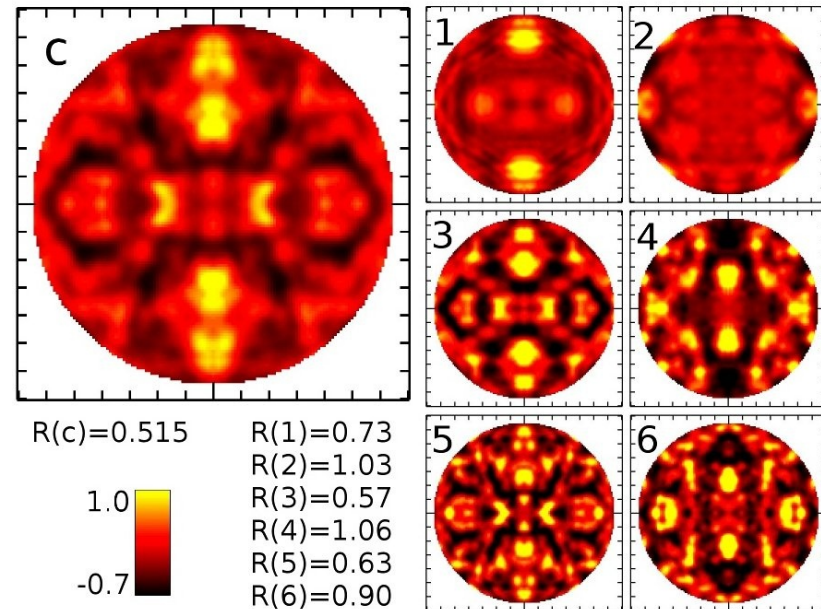
(a)

(b)



[110]
[001]
[1 $\bar{1}$ 0]

Simple PED calculation



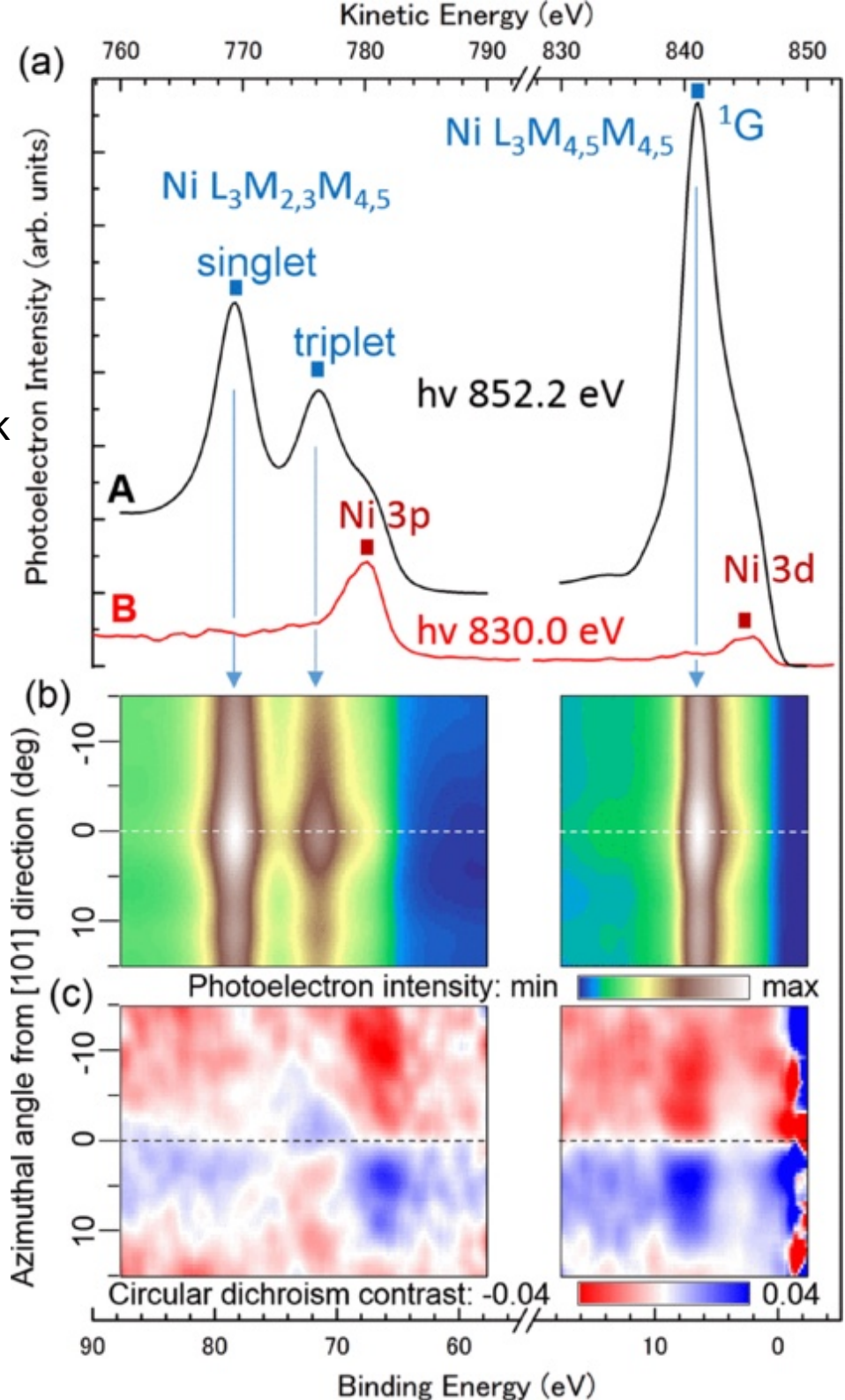
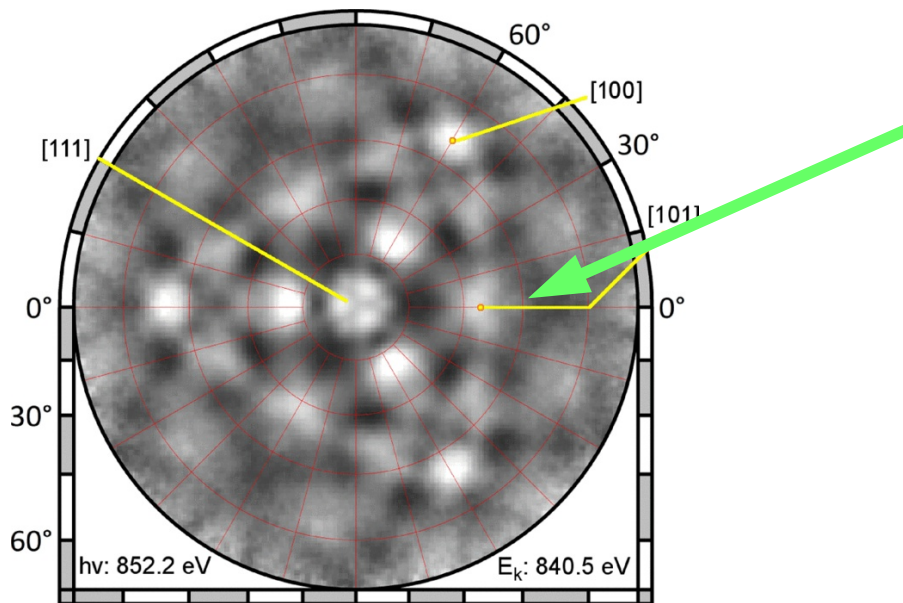
P. Krüger et al,
PRL 108 (2012) 126803

Resonant Auger electron diffraction from Ni(111)

F. Matsui et al, PRB 97, 035424 (2018)

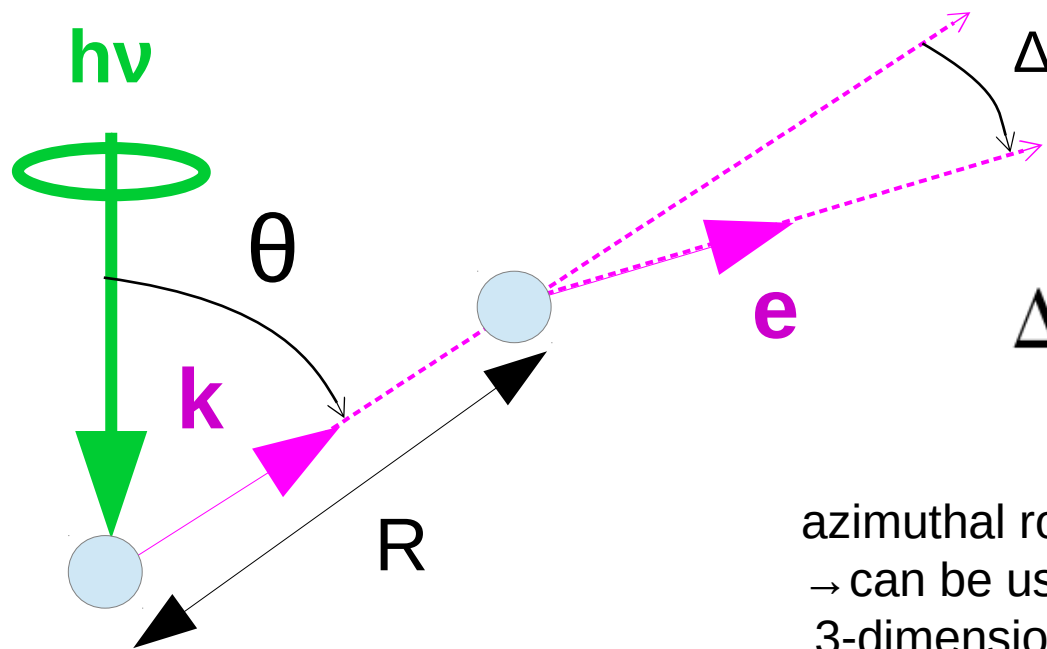
Circular dichroism around forward scattering peak (Daimon effect)

Auger electron angular momentum as photon (L3M45M45) or reversed (L3M23M45 triplet)



Daimon effect

X-ray photoelectron diffraction with circular polarized light
Light angular momentum transferred to photo-electron $m = \langle L_z \rangle$



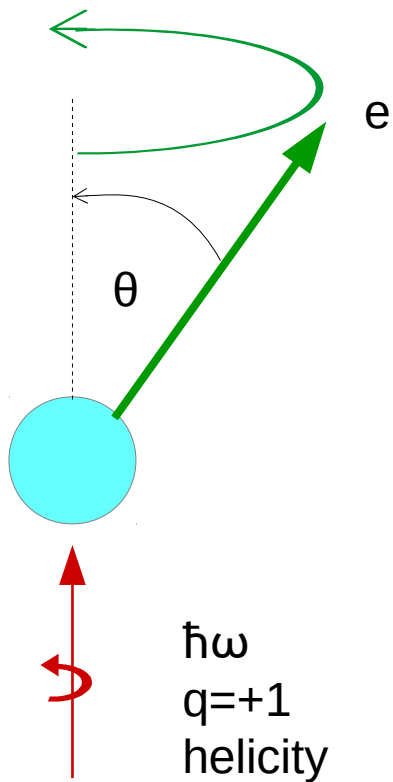
$$\Delta = \tan^{-1} \frac{m}{kR \sin^2 \theta}$$

azimuthal rotation of forward focusing peak
→ can be used for stereoscopic microscopy of
3-dimensional atomic structure

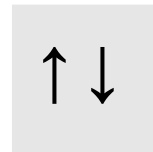
H. Daimon, PRL 86, 2034 (2001)

Angular momentum transfer in direct photoemission

Electric dipole transition
 $\Delta L_z = q$ $\Delta S_z = 0$

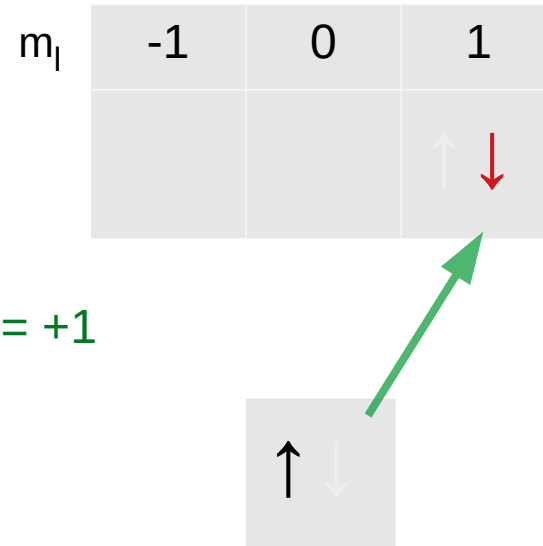


initial state



initial shell $\langle m_l \rangle$ photo-el.
 s 1
 p,d,f > 0

final state



$\Delta L_z = +1$

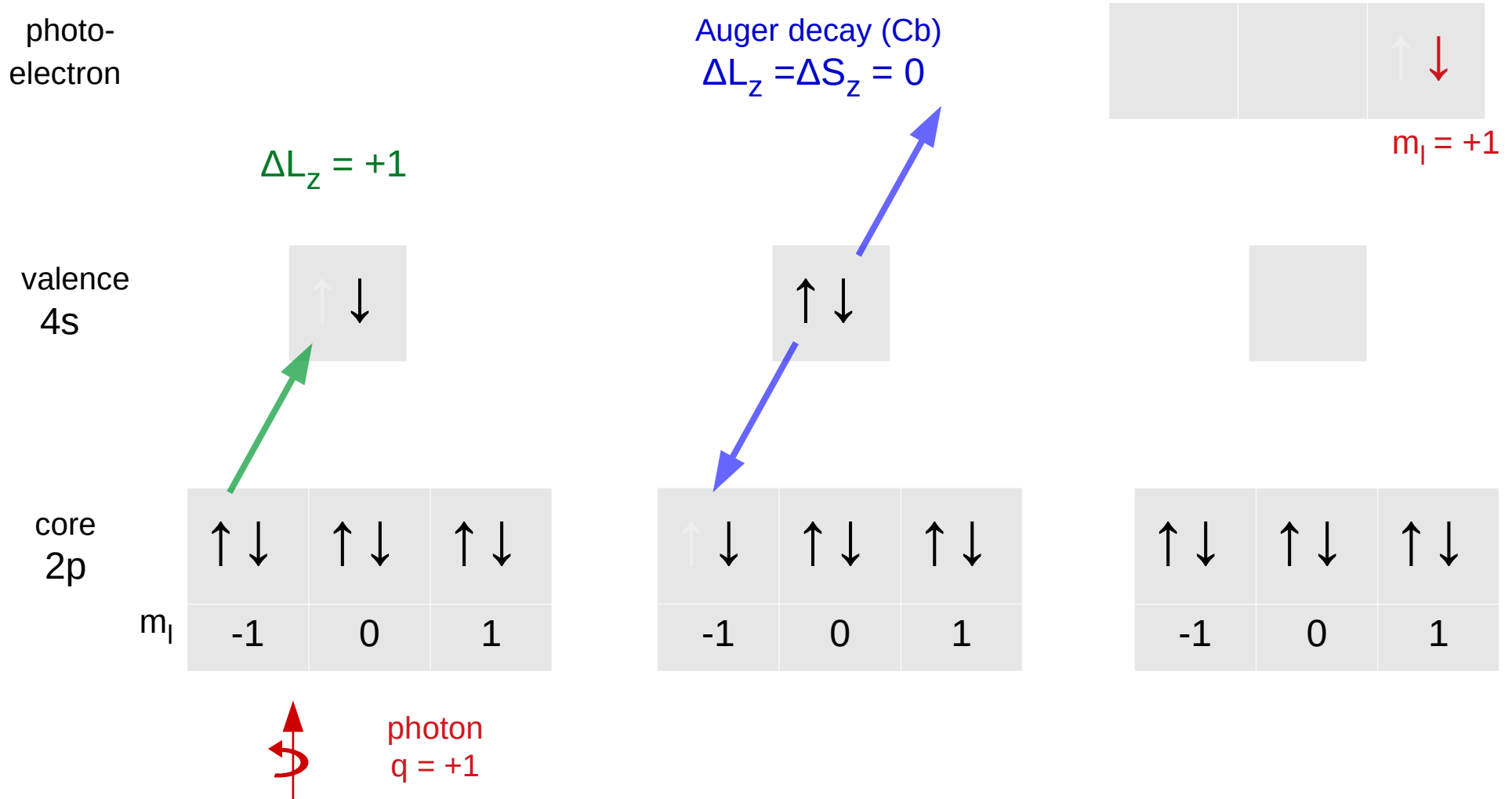
continuum p
 $m_l = q = +1$

1s

photon
 $q = +1$

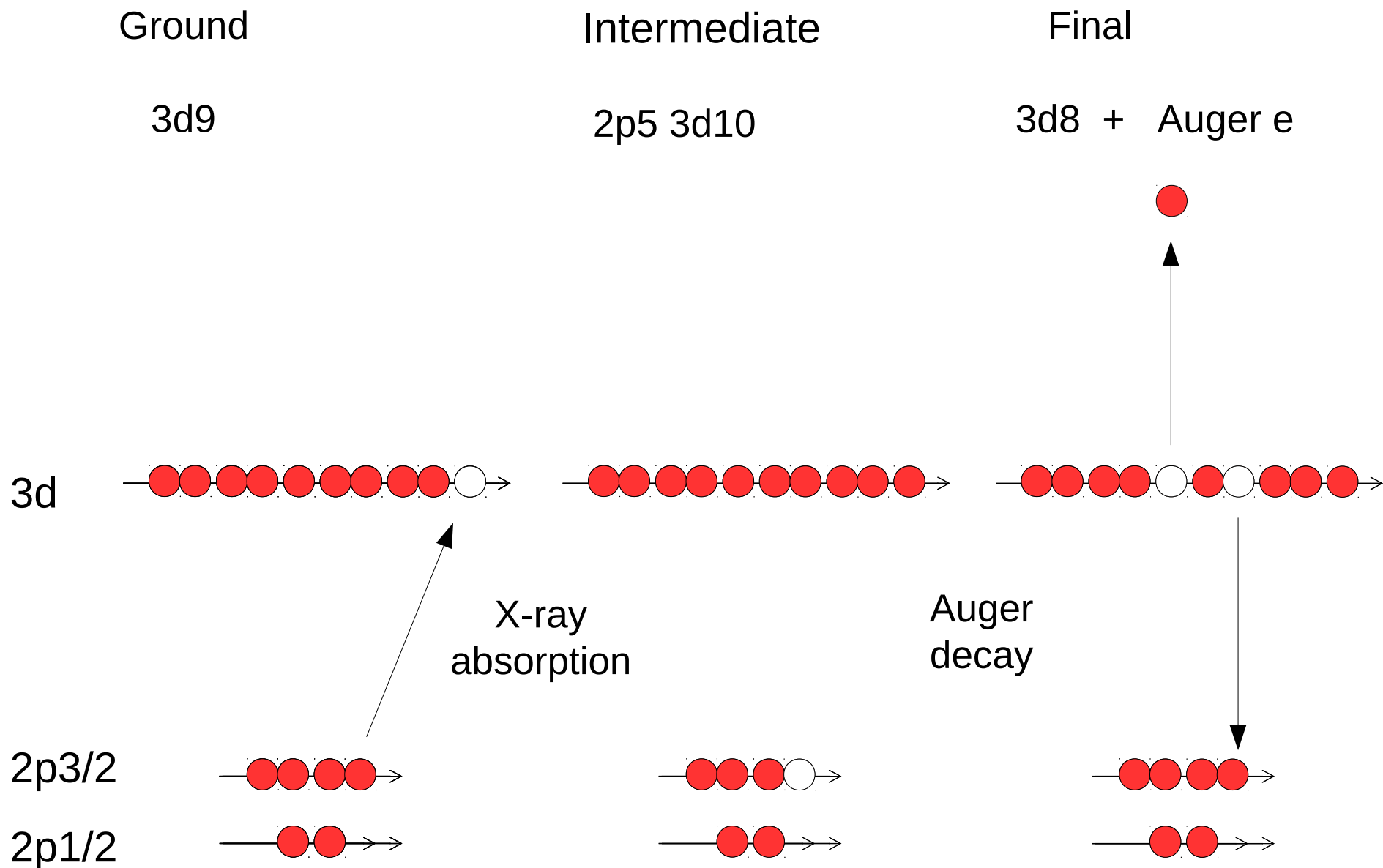
→ positive AM transfer

Angular momentum transfer in resonant photoemission



here: full AM transfer from light to photoelectron, same as direct 4s-PES
in general: partial AM transfer to photoelectron and to valence electrons
photoelectron AM depends on valence final state

Resonant L3M45M45 Auger emission of 3d⁹ atom



Resonant photoemission calculation method

Second order perturbation theory (Kramers-Heisenberg)

$$I(\omega, \epsilon) = \sum_F \left| \langle F(\epsilon) | T_{opt} | G \rangle + \sum_M \frac{\langle F(\epsilon) | T_{AI} | M \rangle \langle M | T_{opt} | G \rangle}{\hbar\omega + E_G - E_M - i\Gamma_M/2} \right|^2 \delta(\hbar\omega + E_G - E_F)$$

Resonant photoelectron amplitudes computed in atomic multiplet model

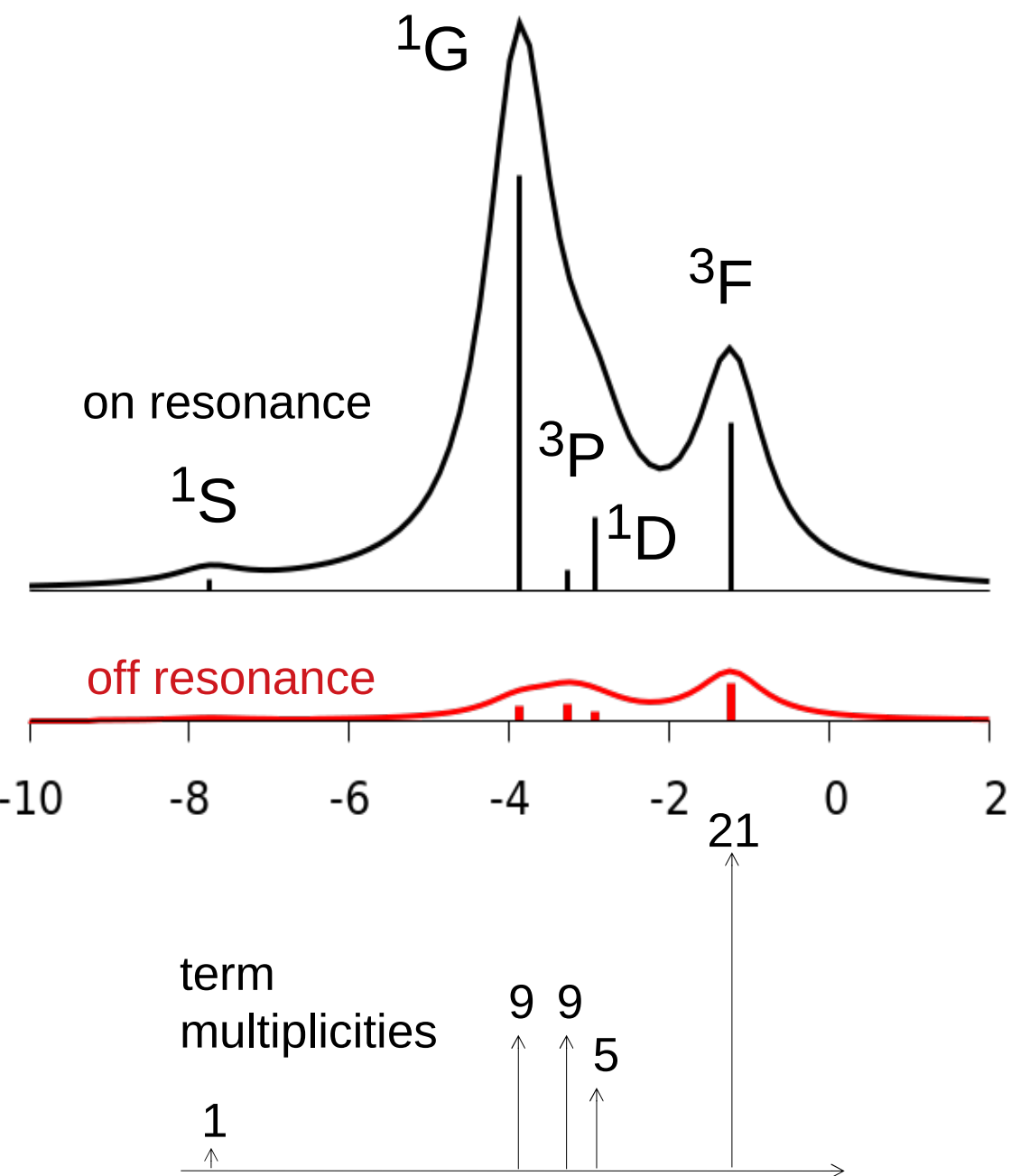
$$A_{Gf}(E_e, ilms) = \langle f, E_e, ilms | T_{opt} | G \rangle + \sum_M \frac{\langle f, E_e, ilms | T_{AI} | M \rangle \langle M | T_{opt} | G \rangle}{\hbar\omega + E_G - E_M - i\Gamma_M/2}$$

Diffraction calculation:

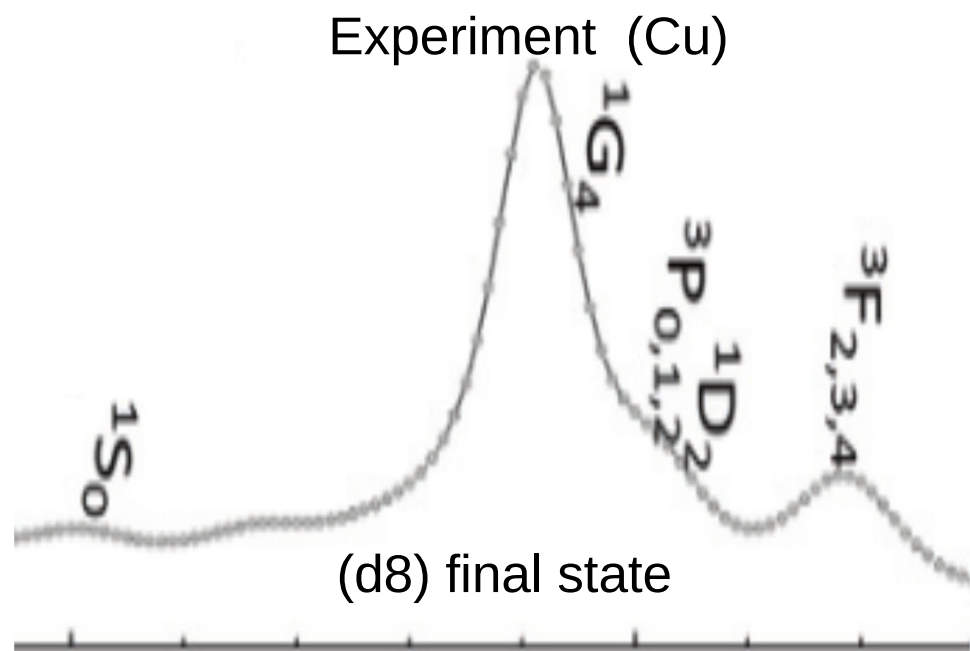
A → multiple scattering code EDAC [Garcia de Abajo]

$$I(\omega, E_e \hat{\mathbf{k}}s, i_0) = \sum_{Gf} w_G \left| \sum_{lm} B_{i_0lm}^*(E_e, \hat{\mathbf{k}}) A_{Gf}(E_e, i_0lms) \right|^2 \delta(\hbar\omega + E_g - E_f - E_e)$$

ResPES spectrum of Ni⁺ ion (3d⁹) in multiplet calculation

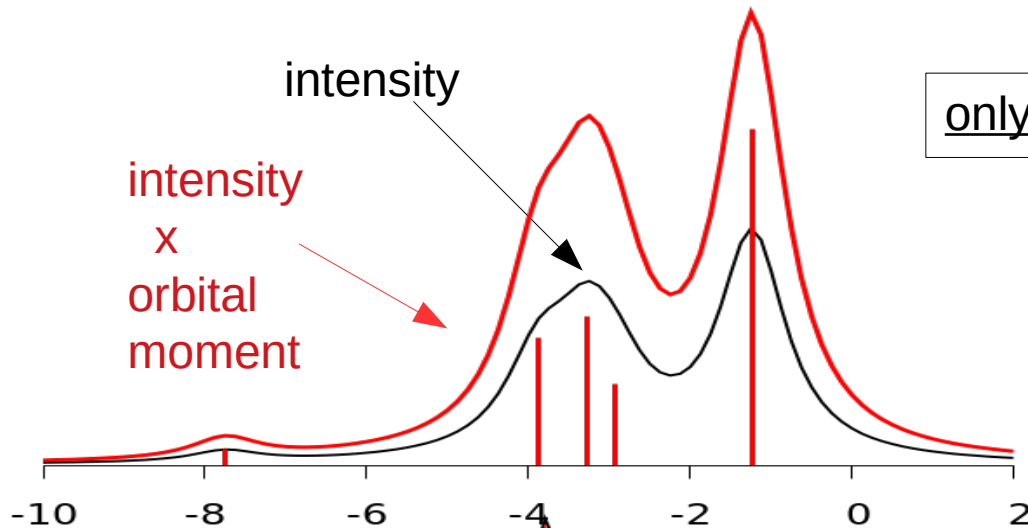


2p, 3d shells
 Coulomb + S.O. interaction
 parameters from
 A. Tanaka, T. Jo, JPSJ 1993



F. Matsui et al , Z. Phys. Chem 230,
 519 (2016)

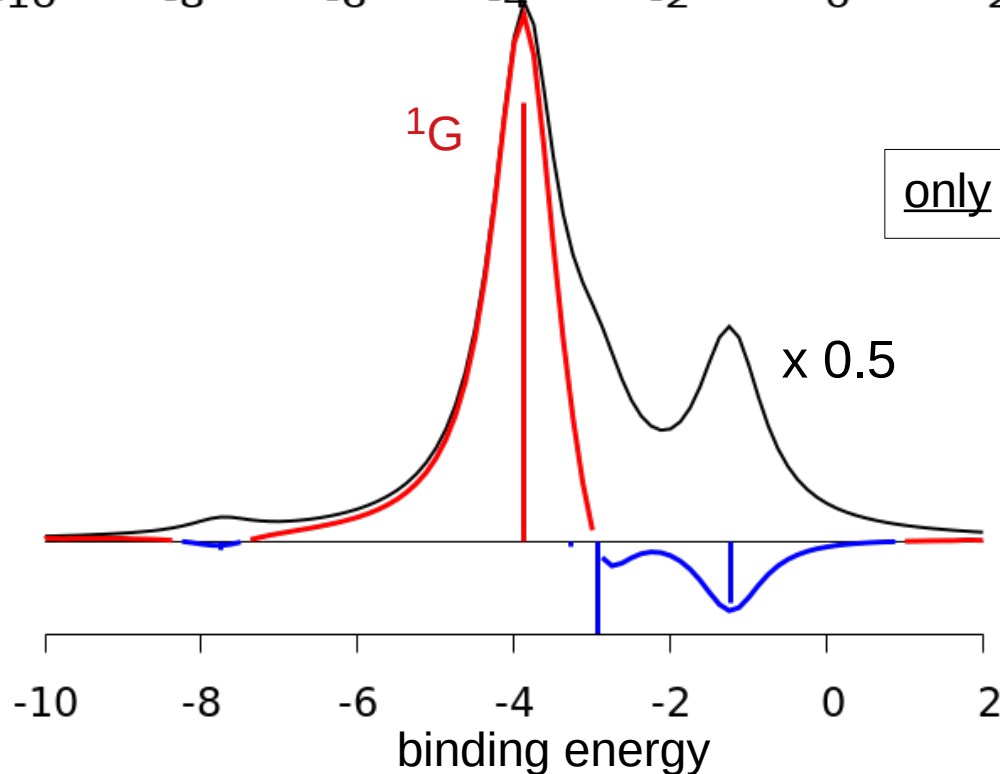
Orbital angular momentum of emitted electron for $q = +1$ helicity



only direct 3d emission

$$\langle L_z \rangle \sim 1.9 \hbar$$

independent of final state multiplet
always positive AM transfer



only 2p3d3d resonant emission process

$$|\langle L_z \rangle| < 0.5 \hbar \quad \text{-- much weaker}$$

$$\langle L_z \rangle > 0 \quad \text{for dominating } {}^1G$$

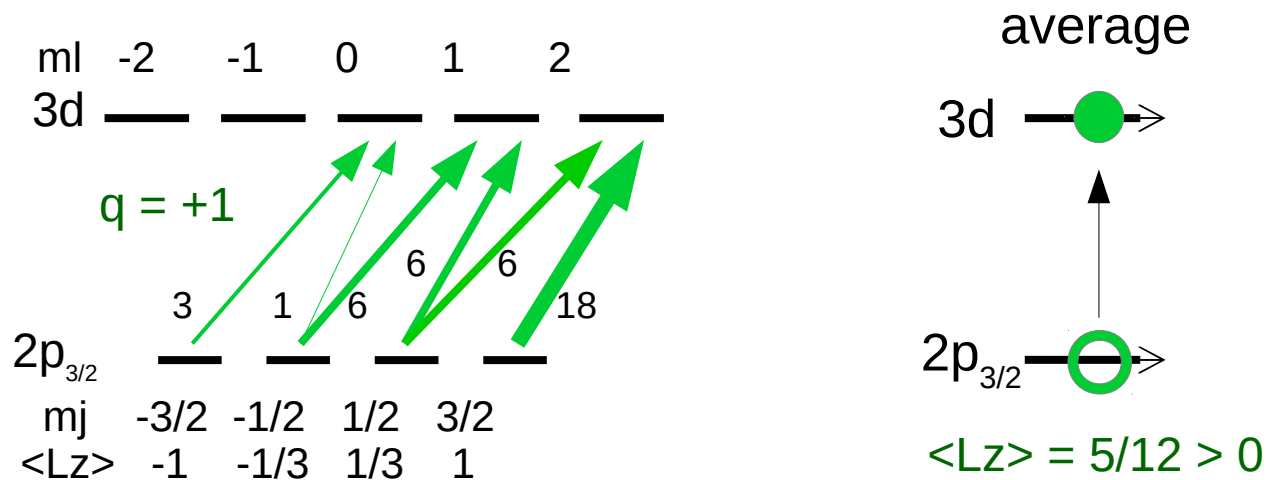
$$\langle L_z \rangle < 0 \quad \text{for all other multiplets}$$

→ **reversed** AM transfer

Why orbital momentum reversal ?

1. Core-hole alignment

$2p_{3/2} \rightarrow 3d$ transition with $q = +1$ light helicity



- core-hole orbital momentum $\langle L_z \rangle$ partially aligned (42%) with light helicity
- $m_j=3/2$ ($m_l=1$) hole has largest probability (45%)

Why orbital momentum reversal ?

2. Auger decay

Coulomb interaction
total L_z conservation

$$|dd\rangle \rightarrow |ce\rangle$$

$$M(dd) = m(c) + m(e)$$

If all M equally likely $\langle M(dd) \rangle = 0$

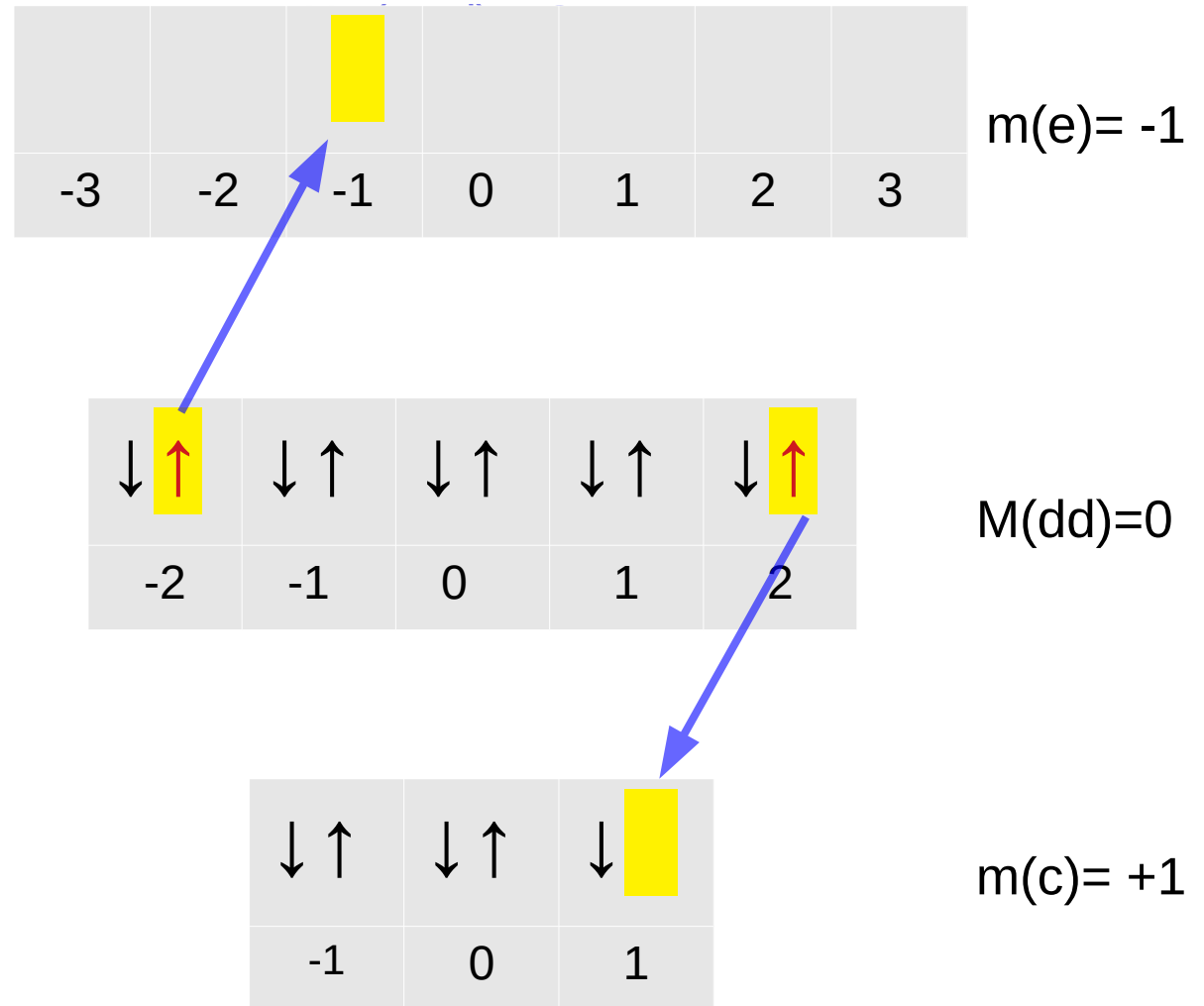
$$\langle m(e) \rangle = 0 - \langle m(c) \rangle = -5/12$$

on average

→ orbital momentum reversal

→ occurs for resonant 3F 1D 3P 1S

$\langle L_z \rangle$ (Auger-el.) opposite to helicity



Why orbital momentum **not always** reversed?

1G multiplet

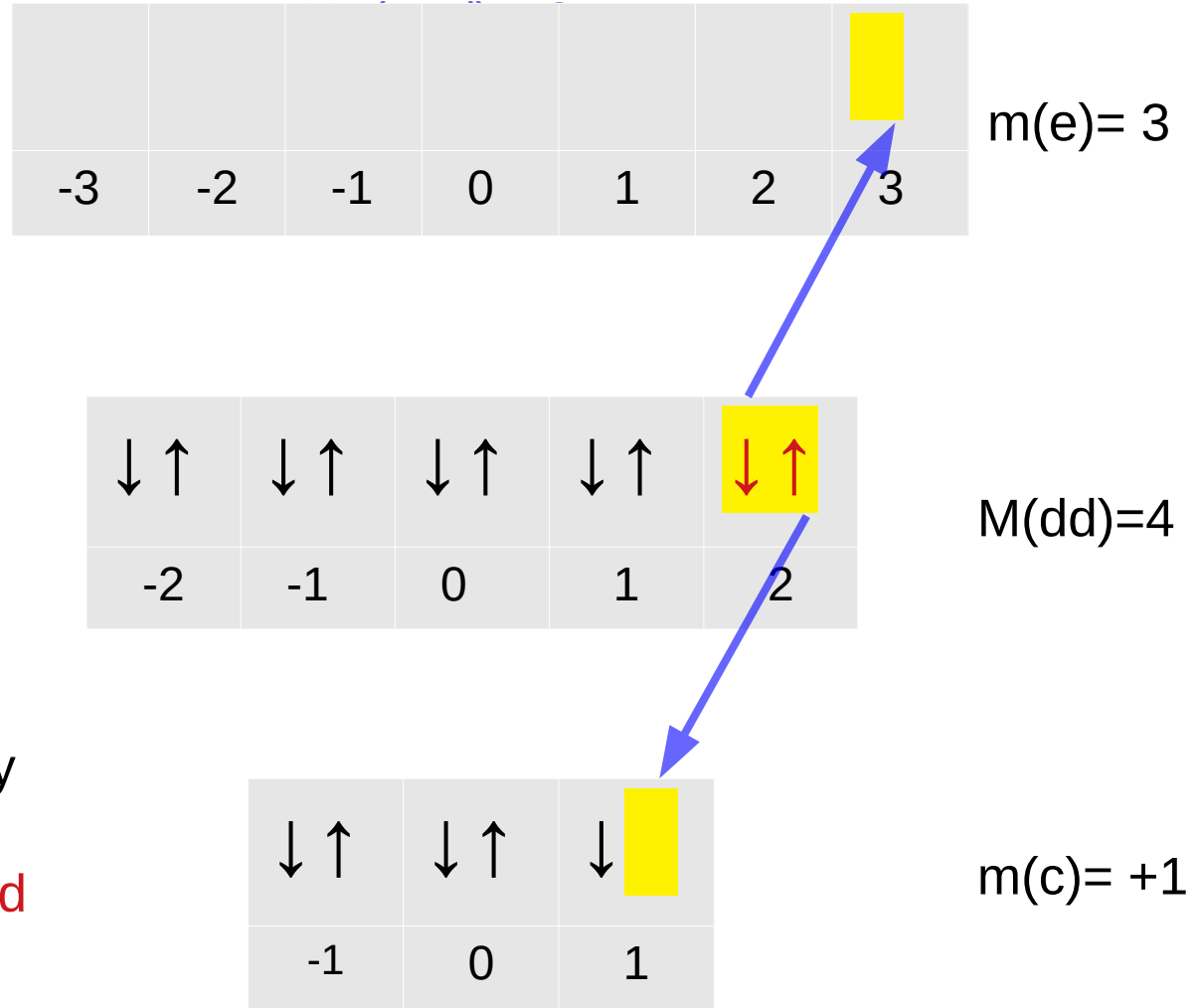
two same d-orbitals scatter
 → by far largest intensity

$M(dd) = 4 \rightarrow m(e) = 3 > 0$

$M(dd) = -4$ impossible
 in dominant $d \rightarrow f$ channel

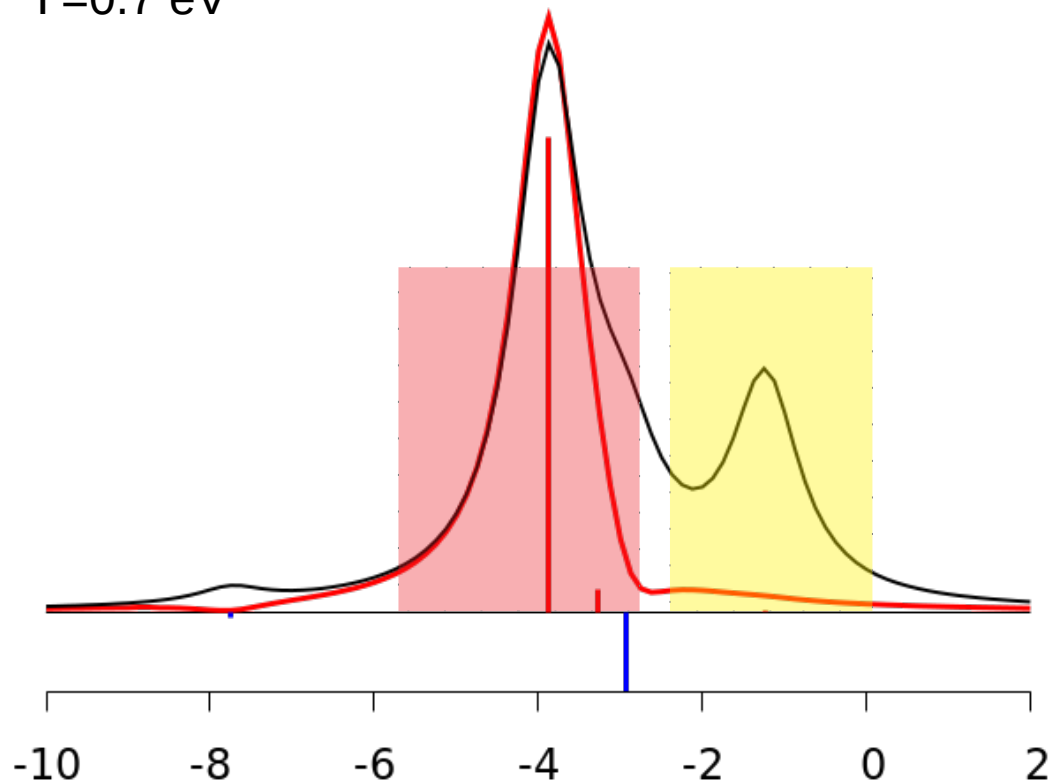
$\langle L_z \rangle$ (Auger-el.) parallel to helicity

→ orbital momentum **not reversed**

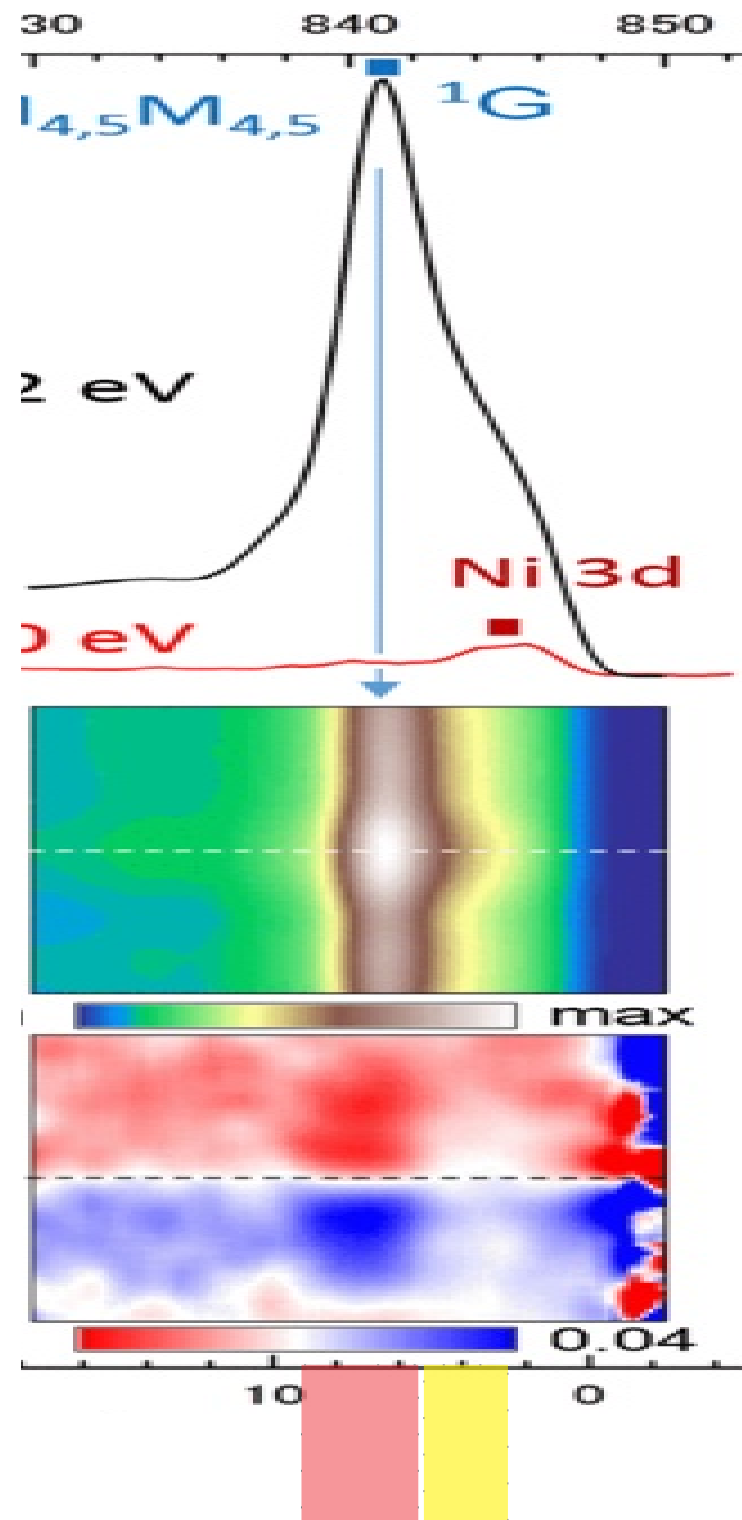


Comparison with experiment

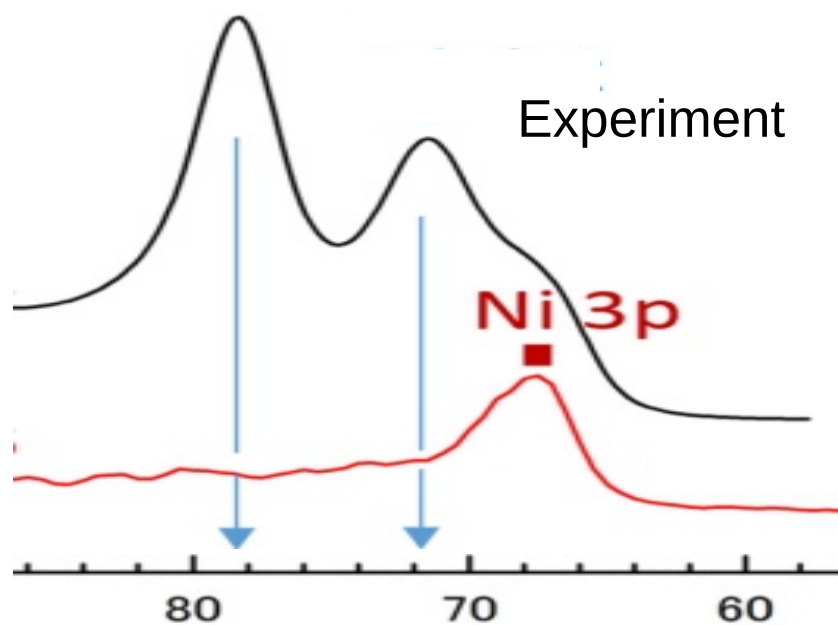
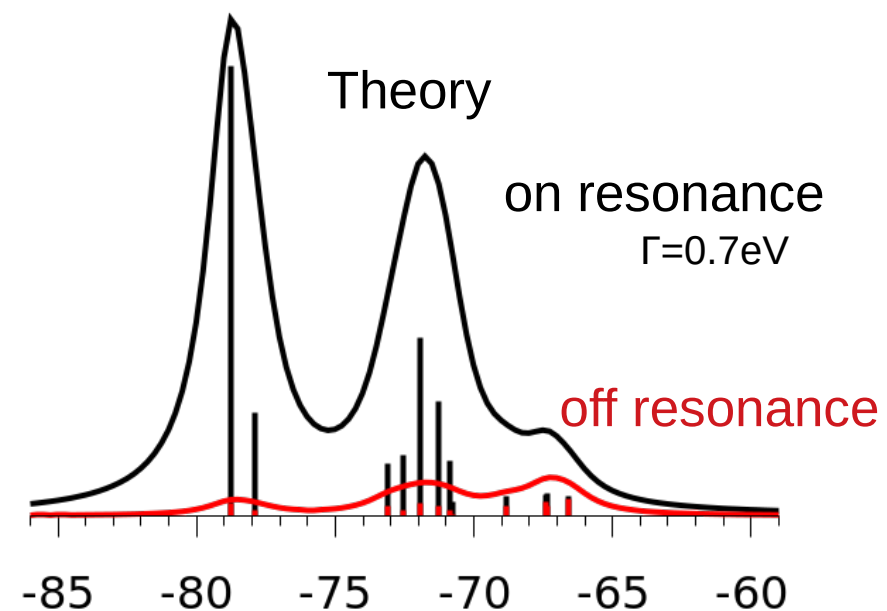
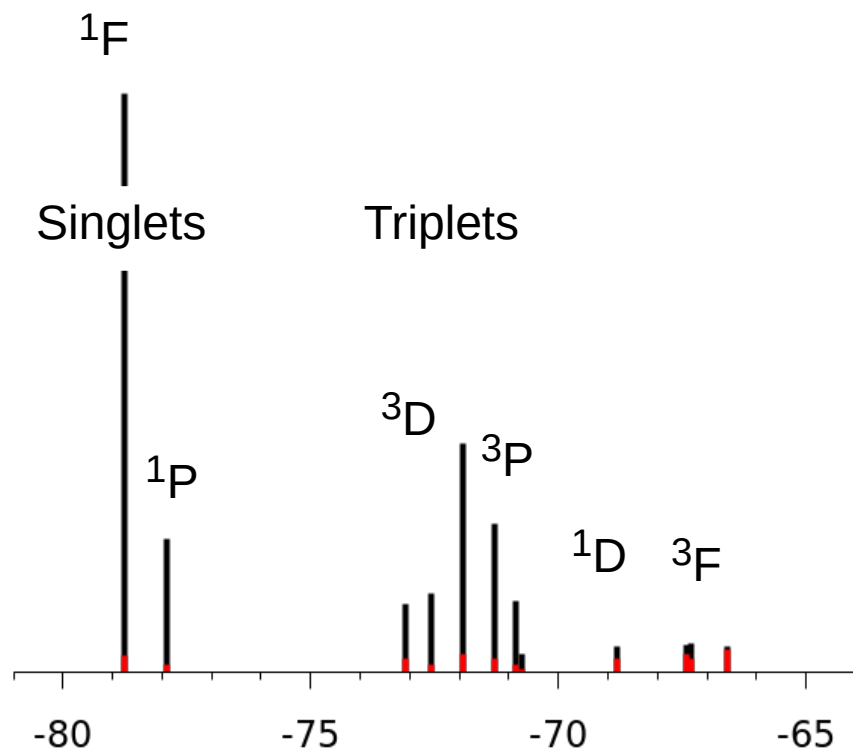
Total: direct + resonant
 $\Gamma=0.7$ eV



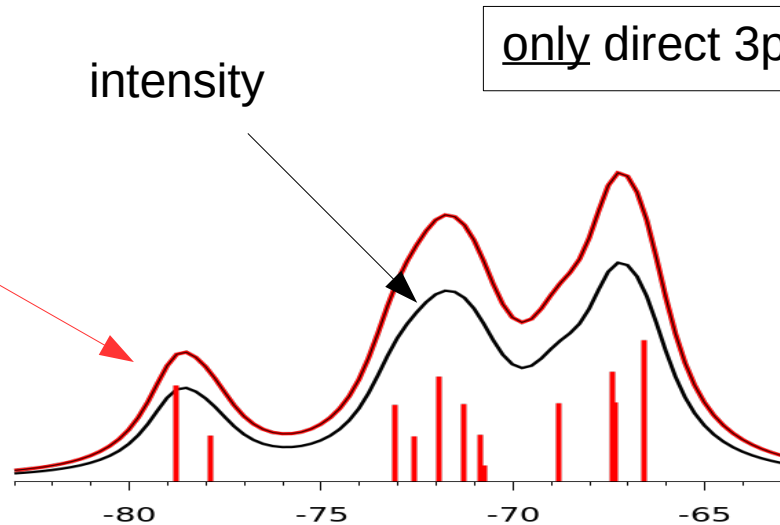
resonant emission $\langle L_z \rangle < 0$
 + normal emission $\langle L_z \rangle > 0$ mostly cancel
 except for very dominant 1G



3p3d resonant Auger spectrum

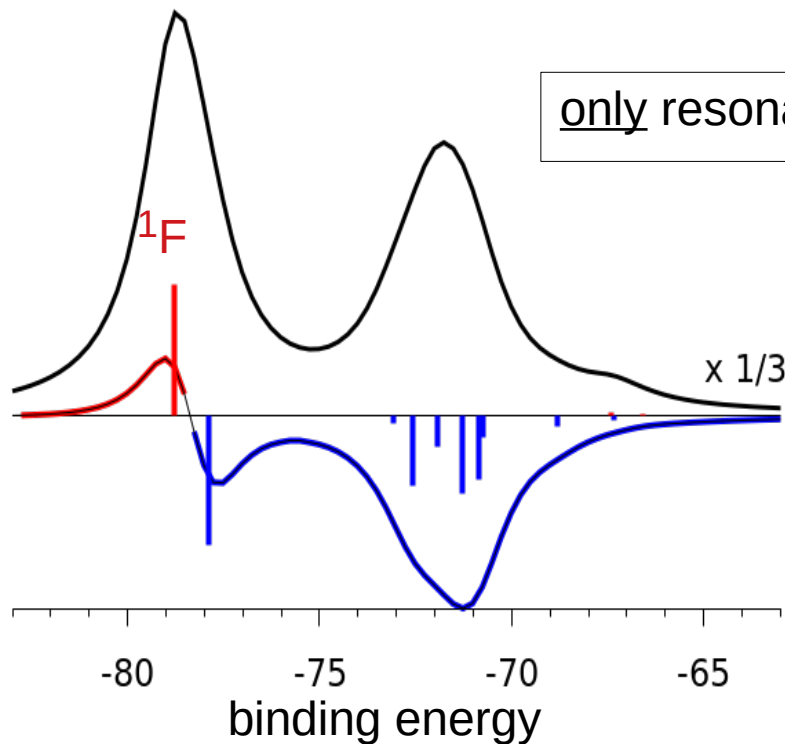


orbital angular momentum of emitted electron



$$\langle L_z \rangle \sim 1.4 \hbar$$

independent of final state multiplet
always positive AM transfer



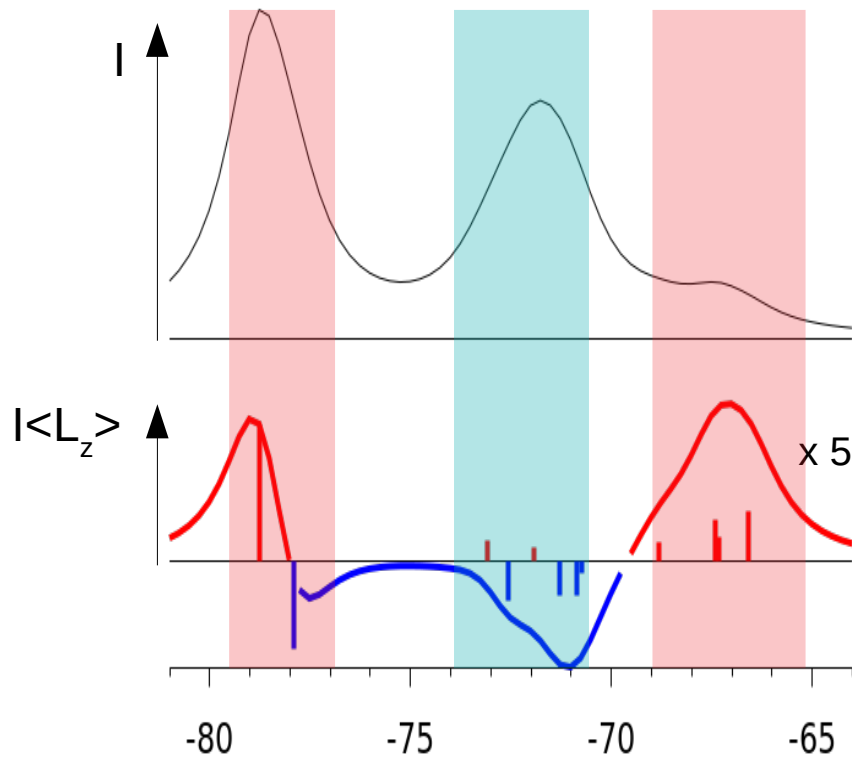
$$\langle L_z \rangle < 0$$

→ **reversed** AM transfer for all

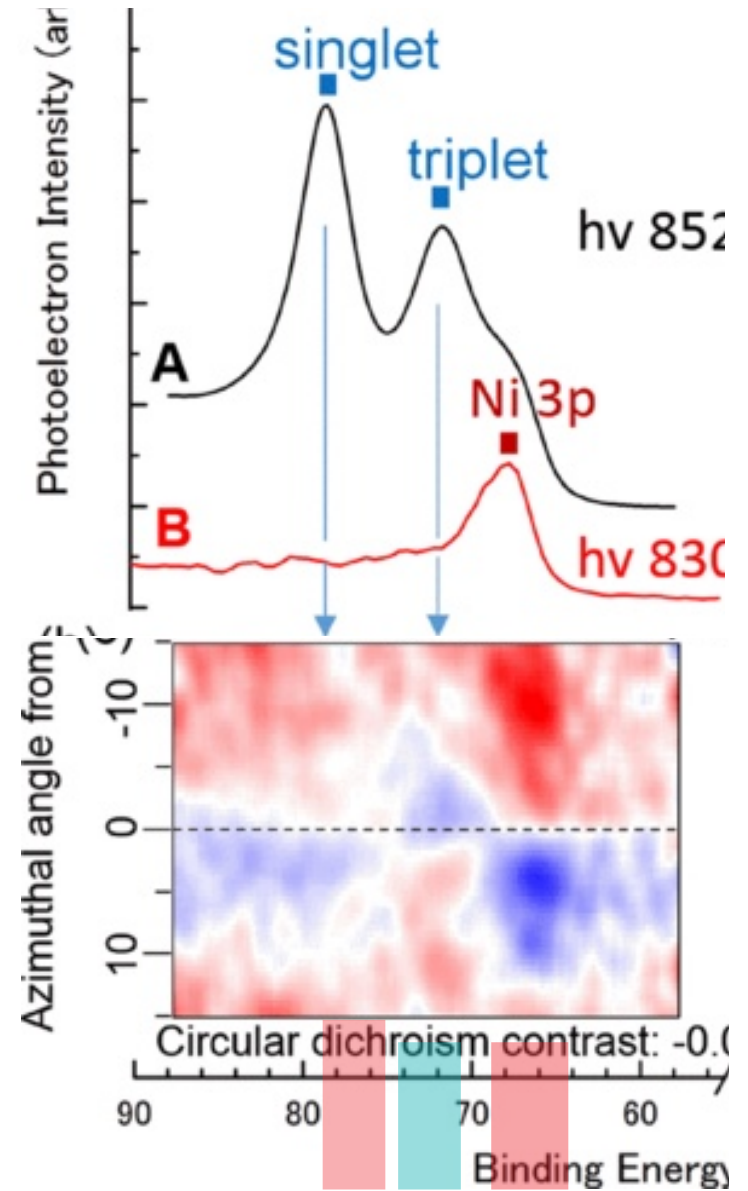
but most intense multiplet line 1F

Comparison with experiment

Total: direct + resonant
 $\Gamma=0.7$ eV



normal – reversed – normal
 angular momentum transfer
 in agreement with experiment

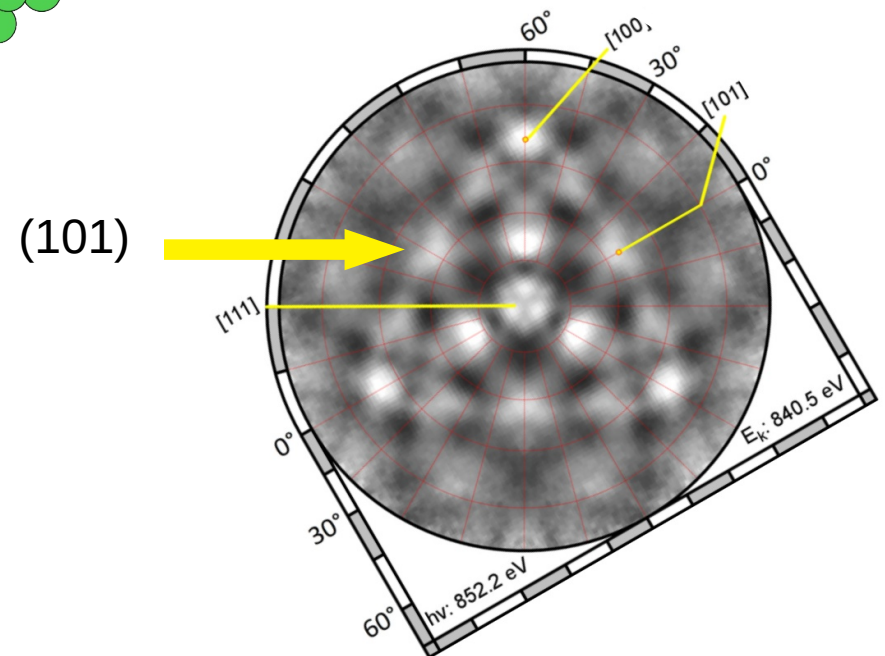
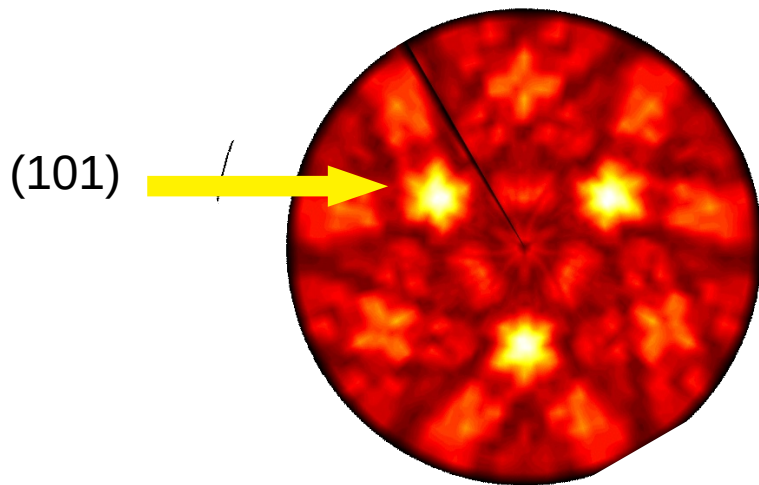
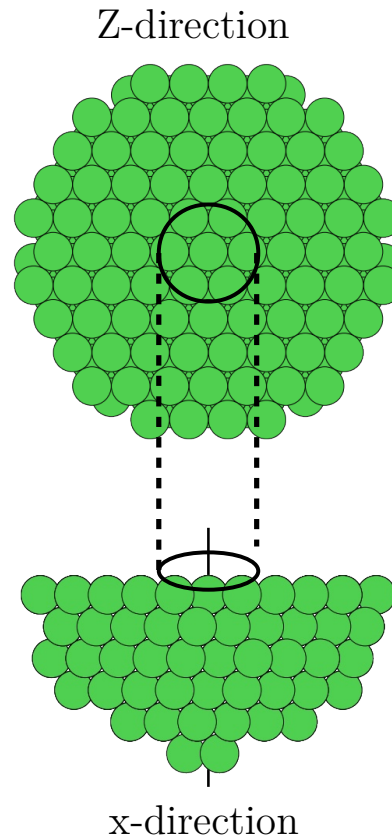


Resonant photoelectron diffraction calculation

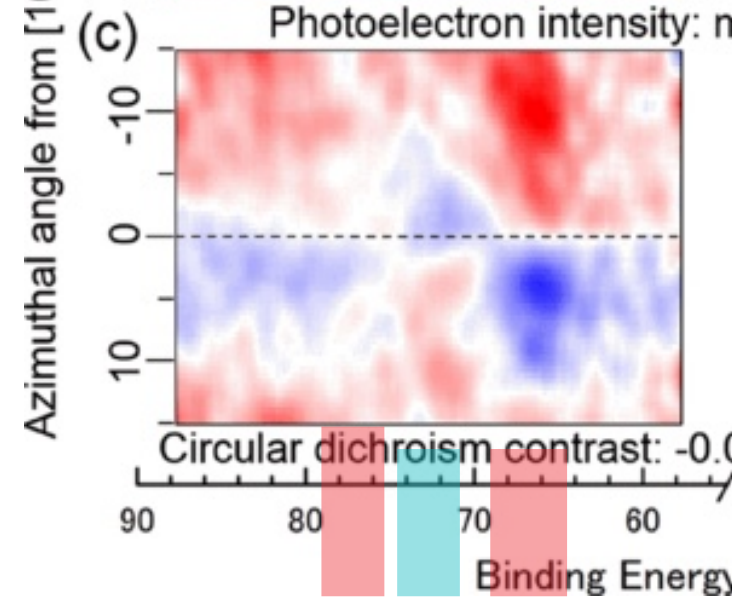
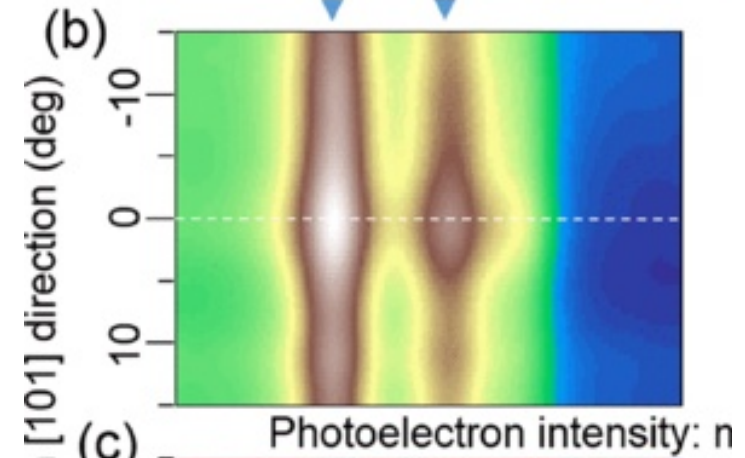
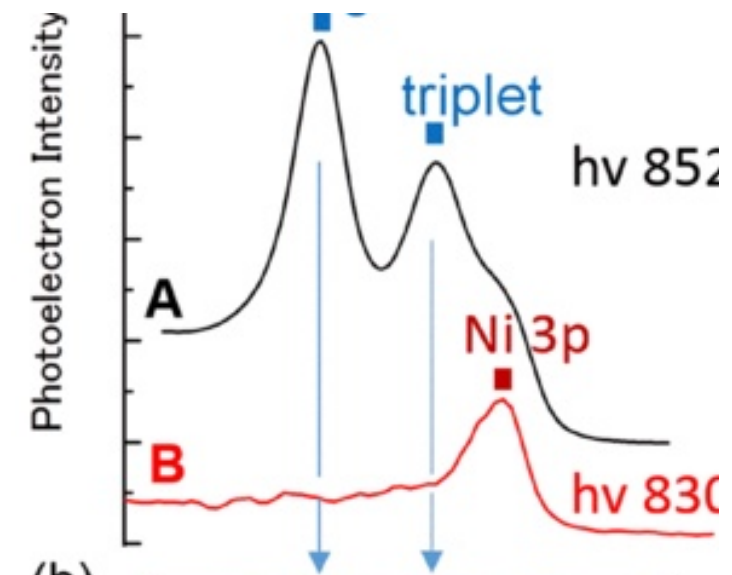
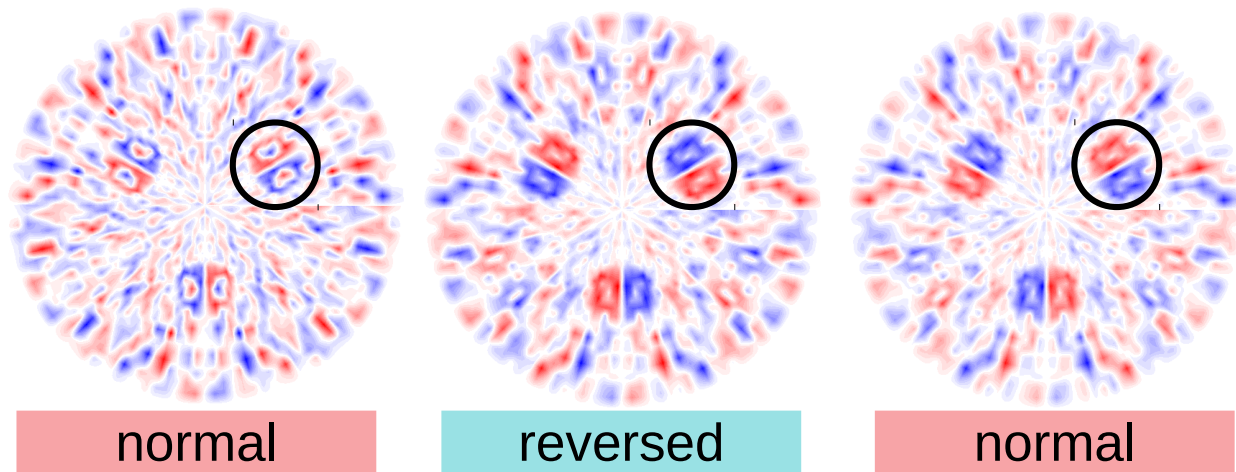
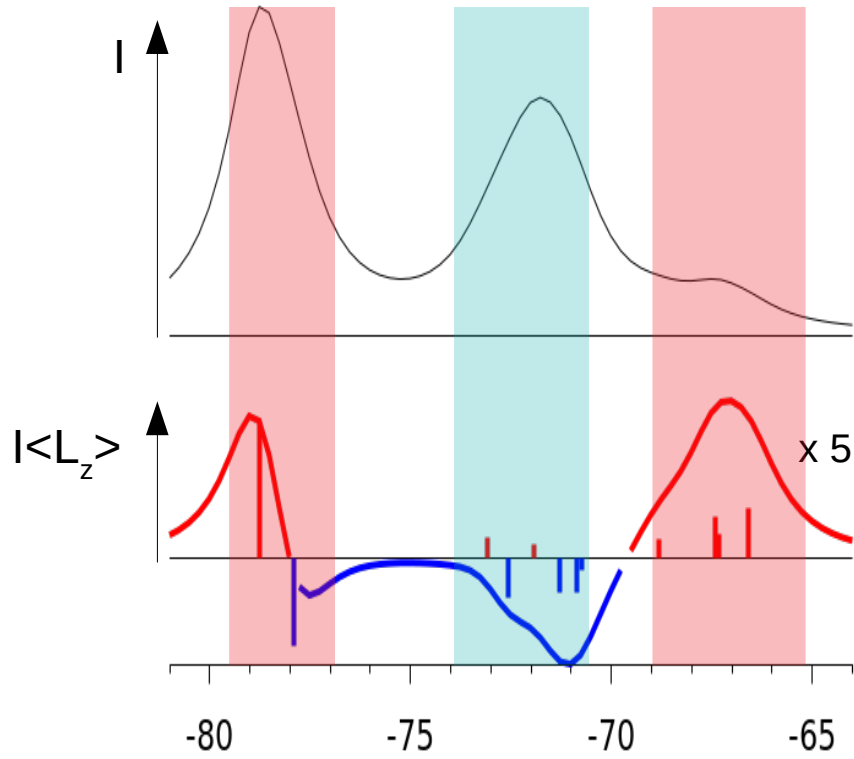
- EDAC code
- $E_{kin} \sim 850$ eV
- single scattering
- source waves:
resonant ResPES
multiplet amplitudes for
each final state



G. Park (M2)



Circ. Dichroism at diffraction peak



Conclusions

- ResPES spectrum of Ni successfully modeled using multiplet model
- photon to electron angular momentum (AM) transfer occurs in ResPES, but effect is weaker than in non-res PES and strongly multiplet term dependent
- exp. observed reversal of AM transfer in 2p3p3d ResPES fully reproduced
- AM reversal explained by core-hole alignment in 2p-3d excitation and Lz conservation in Auger decay
- ResPE diffraction patterns modeled for the first time by combining atomic multiplet final state with Multiple Scattering calculation (EDAC)
- Daimon effect in Res PE diffraction reproduced

Introduction: atomic structure of matter

How do we know the atomic structure of matter?

Diffraction experiments: X-ray, neutrons, electrons

$$\Delta x = \mathbf{R} \cdot \hat{\mathbf{k}} - \mathbf{R} \cdot \hat{\mathbf{k}}'$$

$$\Delta \phi = 2\pi \Delta x / \lambda = \mathbf{R} \cdot (\mathbf{k} - \mathbf{k}') \equiv -\mathbf{R} \cdot \mathbf{q}$$

scattered wave amplitude:

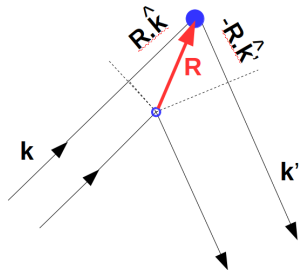
$$A \sim \sum_i \exp(-i\mathbf{q} \cdot \mathbf{R}_i)$$

intensity:

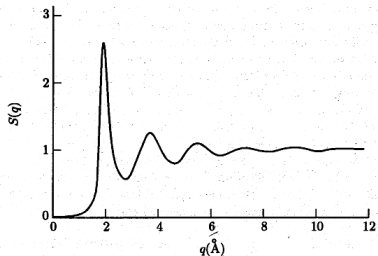
$$I \sim |A|^2 = \sum_{ij} \exp[-i\mathbf{q} \cdot (\mathbf{R}_i - \mathbf{R}_j)]$$

→ structure factor:

$$S(\mathbf{q}) = \frac{1}{N} \sum_{ij} \exp[-i\mathbf{q} \cdot (\mathbf{R}_i - \mathbf{R}_j)]$$

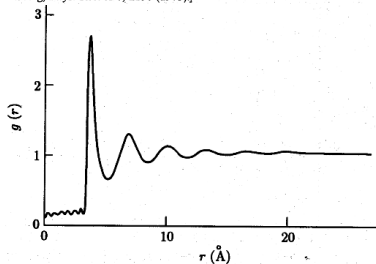


Structure factor and pair distribution function



structure factor of liquid Ar

Fig. 2.4.4. The static structure factor $S(q)$ for liquid argon for the same conditions as Fig. 2.4.3. [J.L. Yarnell, M.J. Katz, R.G. Wenzel, and S.H. Koenig, *Phys. Rev. A* 7, 2130 (1973).]



$$g(\mathbf{r}) - 1 = \frac{1}{8\pi^3\rho_0} \int [S(\mathbf{q}) - 1] e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{q}$$

pair distribution function

Meaning of pair distribution function

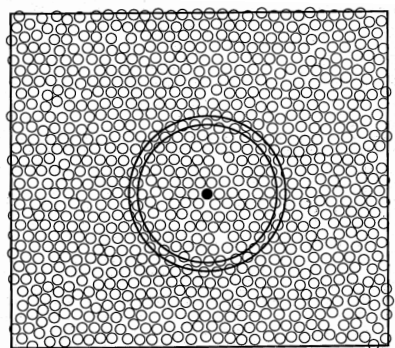
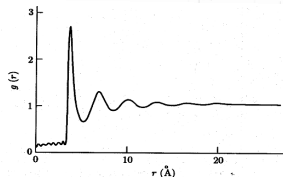


Fig. 23.1. Typical atomic configuration in a hard-sphere fluid. The pair distribution function can be obtained by choosing an arbitrary particle as the origin and counting the number of atoms whose centers lie within a distance dr of a circle of radius r of the origin.



$$dN = g(r)\rho 4\pi r^2 dr$$

= average number of particles at distance $(r, r+dr)$ from chosen one. (\sim conditional probability)

If particle positions are uncorrelated (ideal gas)

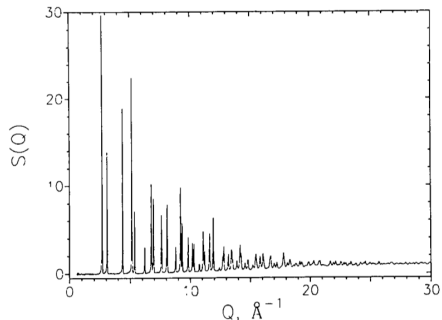
$$\rightarrow g(r) = 1$$

$g < 1$ depletion

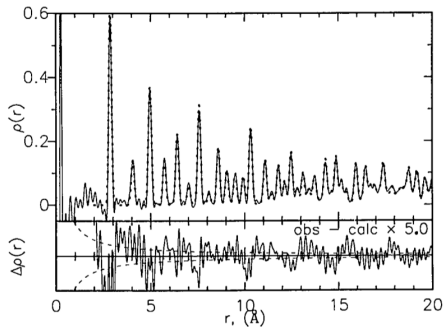
$g > 1$ accumulation

Crystals?

powder diffraction $\rightarrow S(q)$



Aluminum (neutron diffraction)



corresponding PDF

[B. H. Toby and T. Egami, Acta Cryst. A48 (1992) 336.]

Particle number fluctuations in fluids

fluctuations \sim 2nd derivatives of thermodynamic potentials

canonical ensemble (T,V,N)

$$C_V = \left(\frac{\partial \langle E \rangle}{\partial T} \right)_{V,N} = \frac{\langle E^2 \rangle - \langle E \rangle^2}{k_B T^2}$$

grand-canonical ensemble (T,V, μ) particle number fluctuations

$$\frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} = \frac{k_B T}{\langle N \rangle} \left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} \equiv \frac{1}{\Gamma}$$

Γ = “thermodynamical correction factor”

Compressibility equation

$$dG = -SdT - PdV - Nd\mu \quad \left(\frac{\partial P}{\partial \mu}\right)_T = \left(\frac{\partial N}{\partial V}\right)_T = \rho$$

$$\frac{1}{\langle N \rangle} \left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{T,V} = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial \mu}\right)_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P}\right)_T \left(\frac{\partial P}{\partial \mu}\right)_T = \left(\frac{\partial \rho}{\partial P}\right)_T$$

$$\frac{1}{\Gamma} = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} = \frac{k_B T}{\langle N \rangle} \left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{T,V} = k_B T \left(\frac{\partial \rho}{\partial P}\right)_T$$

isothermal compressibility

$$-\frac{1}{\langle V \rangle} \left(\frac{\partial \langle V \rangle}{\partial P}\right)_{T,N} = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P}\right)_T$$

Kirkwood Buff theory: thermodynamics from structure

[J. Kirkwood and F. P. Buff, J.Chem.Phys. 19, 774 (1952)]

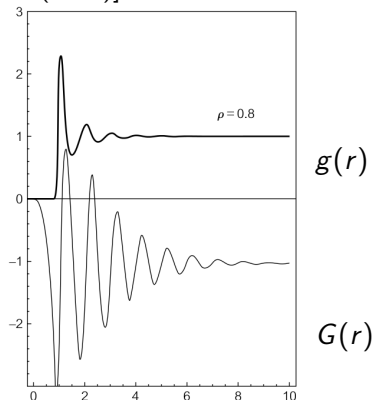
$$\frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} = 1 + \rho G$$

$$G = \int_0^\infty [g(r) - 1] 4\pi r^2 dr$$

G = "Kirkwood-Buff integral"

$g(r)$ = pair distribution function

$g(r)$ from FT of structure factor
or molecular simulations



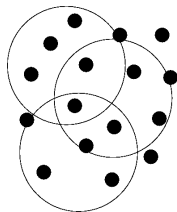
A. Ben-Naim

Molecular Theory of Solutions

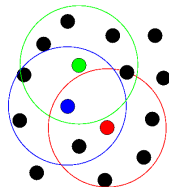
Relation to fluctuations

Fluctuations in V

$$G(V) \equiv \frac{1}{V} \int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 h(|\mathbf{r}_1 - \mathbf{r}_2|) \neq \int_V h(r) d\mathbf{r} \equiv G_0(V)$$



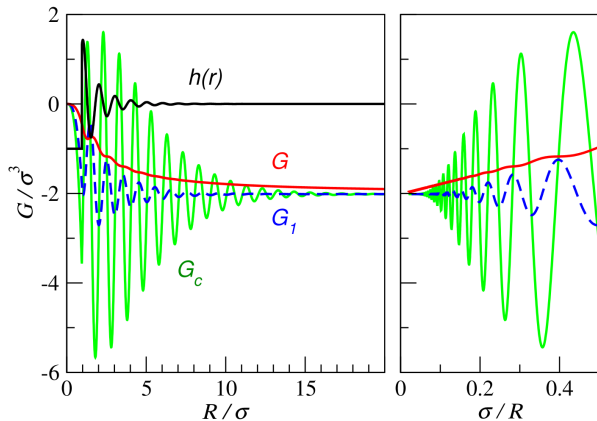
Particle excess in V



$$\frac{1}{V} \int_V d\mathbf{r}_2 \int_{V-r_2} d\mathbf{r} h(r) \neq \int_V d\mathbf{r} h(r)$$

Model pair distribution function

$$h(r) = \begin{cases} \frac{1.5}{r/\sigma} \exp\left(-\frac{r/\sigma-1}{\chi}\right) \cos[2\pi(r/\sigma - 1.05)], & r \geq 0.95\sigma, \\ -1, & r < 0.95\sigma. \end{cases}$$



$\chi = 2$

$h(r)$

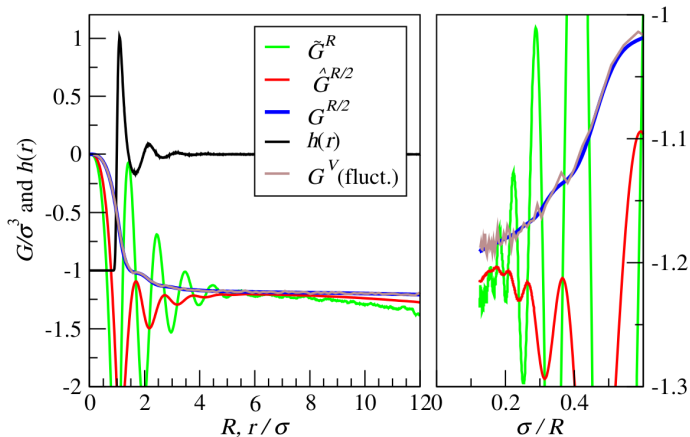
cut-off

exact finite V

extrapolated

Molecular dynamics simulations

Simple model for liquid Argon. 10000 atoms, Lennard-Jones potential.



Density $\rho/\sigma^3 = 0.551$. Temperature $k_B T/\epsilon = 1.40$.

Extension of Kirkwood-Buff theory to solids and its application to the compressibility of fcc argon

Masafumi Miyaji, Bastien Radola, Jean-Marc Simon, Peter Krüger,

J. Chem. Phys. (2021) accepted

Validity of compressibility equation and Kirkwood-Buff theory in crystalline matter

P. Krüger

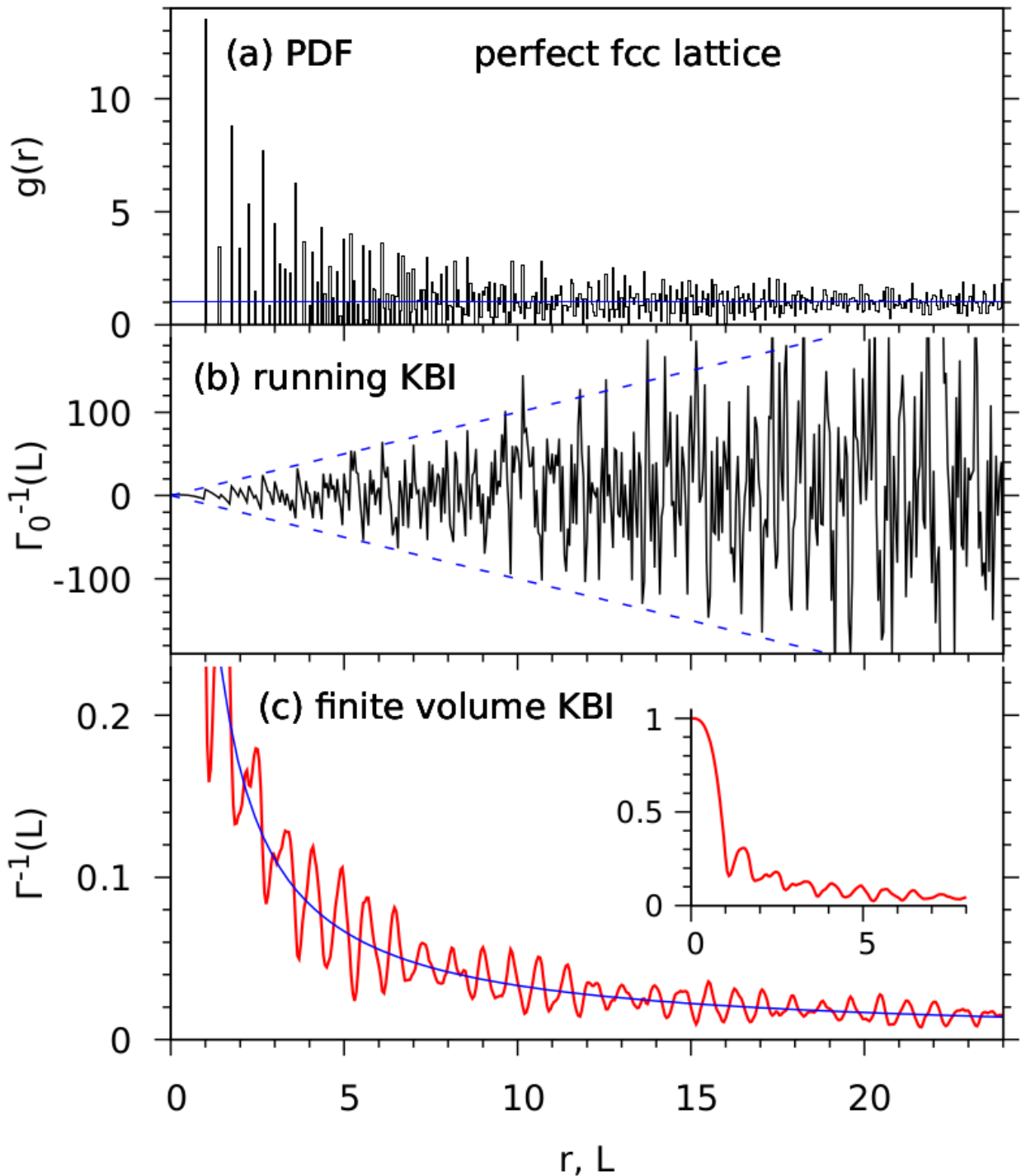
<https://arxiv.org/abs/2101.03515>

Volume integrals over the radial pair-distribution function, so-called Kirkwood-Buff integrals (KBI) play a central role in the theory of solutions, by linking structural with thermodynamic information. The simplest example is the compressibility equation, a fundamental relation in statistical mechanics of fluids. Until now, KBI theory could not be applied to crystals, because the integrals strongly diverge when computed in the standard way. We solve the divergence problem and generalize KBI theory to crystalline matter by using the recently proposed finite-volume theory. For crystals with harmonic interaction, we derive an analytic expression for the peak shape of the pair-distribution function at finite temperature. From this we demonstrate that the compressibility equation holds exactly in harmonic crystals.

fcc crystal at $T=0$

Standard theory:
integral strongly
diverges

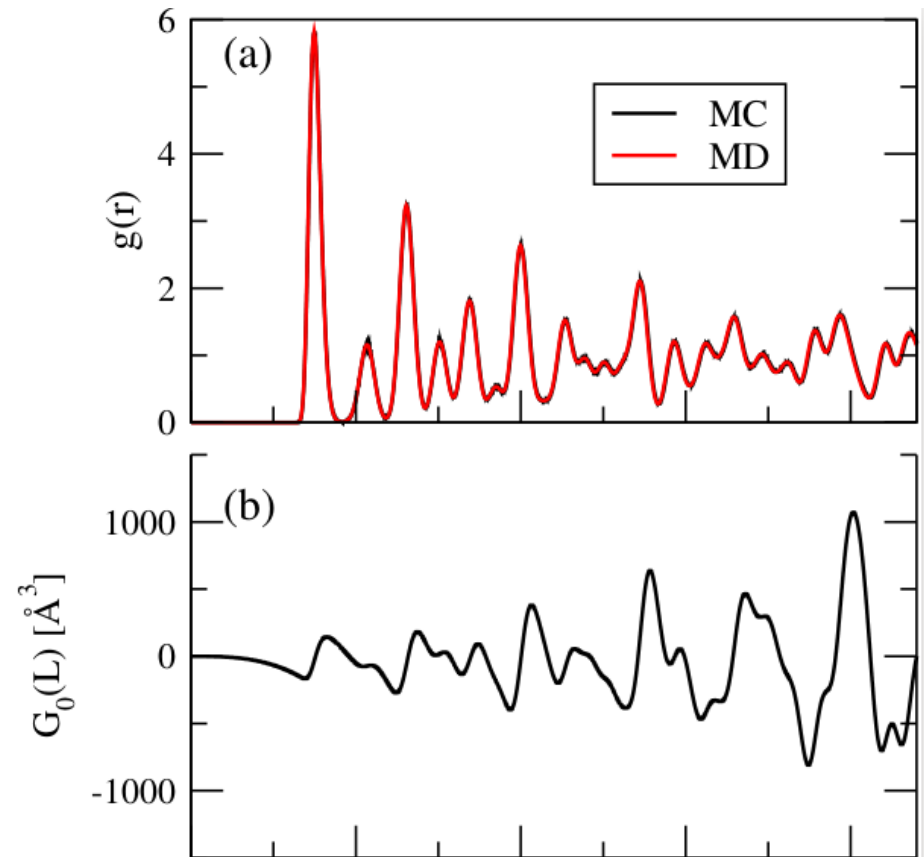
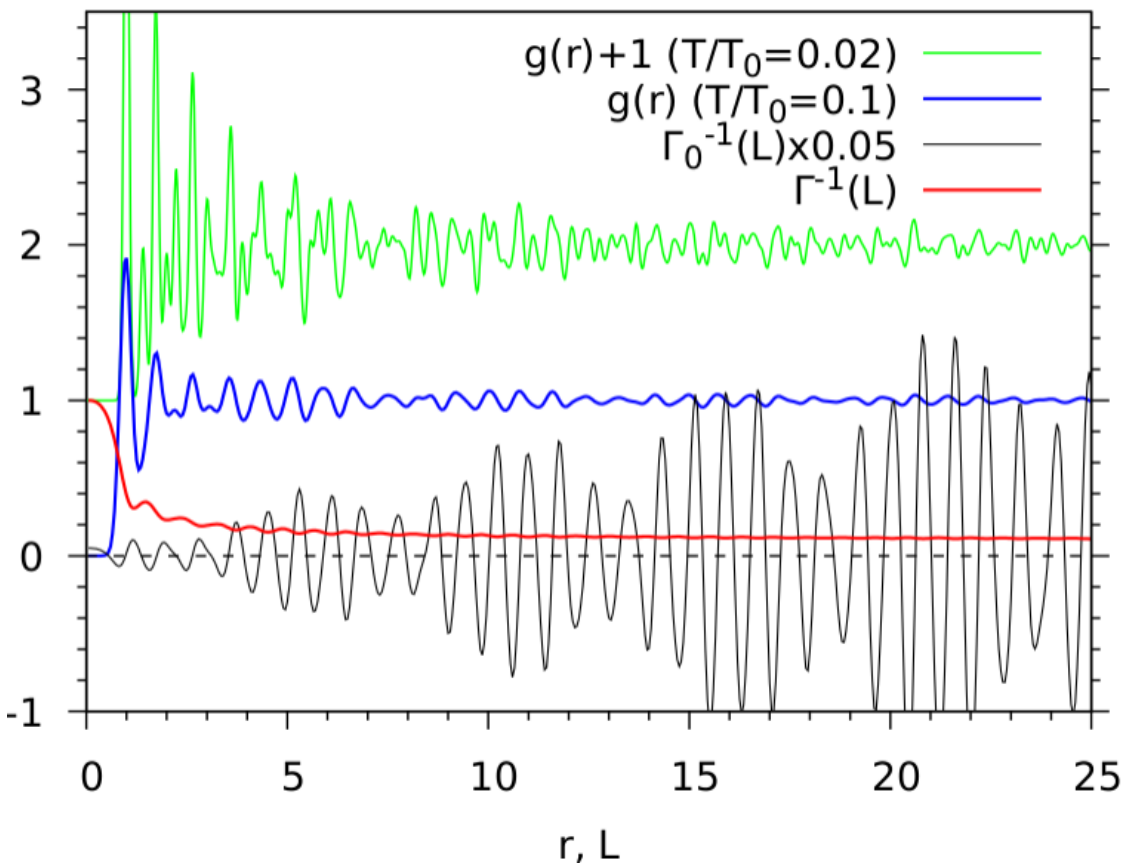
our theory:
integral converges
to exact limit (0)



Finite temperature

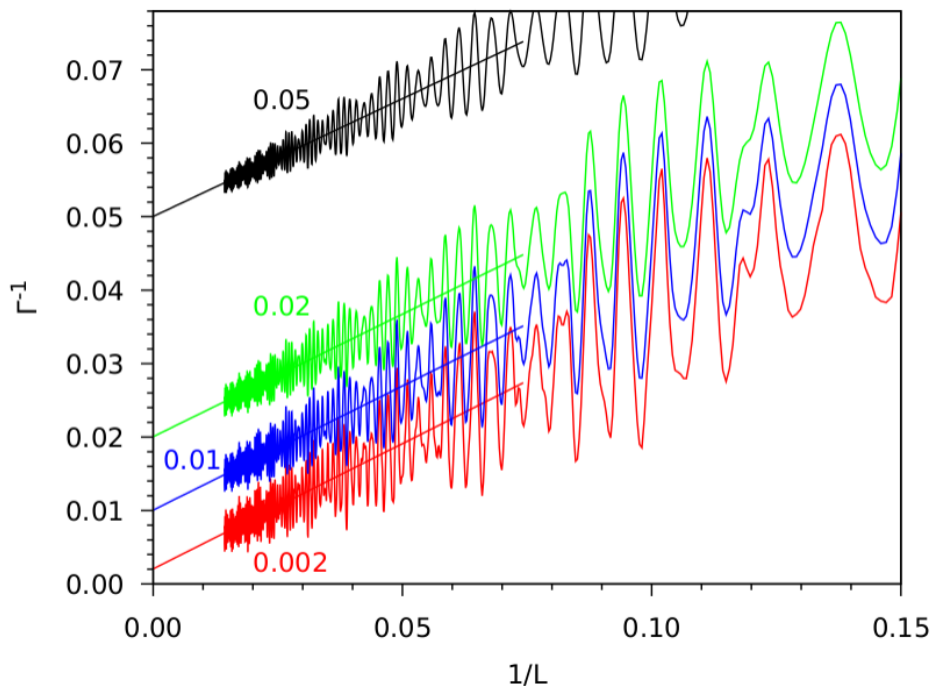
Harmonic crystal
(analytic theory)

Solid argon →
anharmonic effects.
molecular simulation



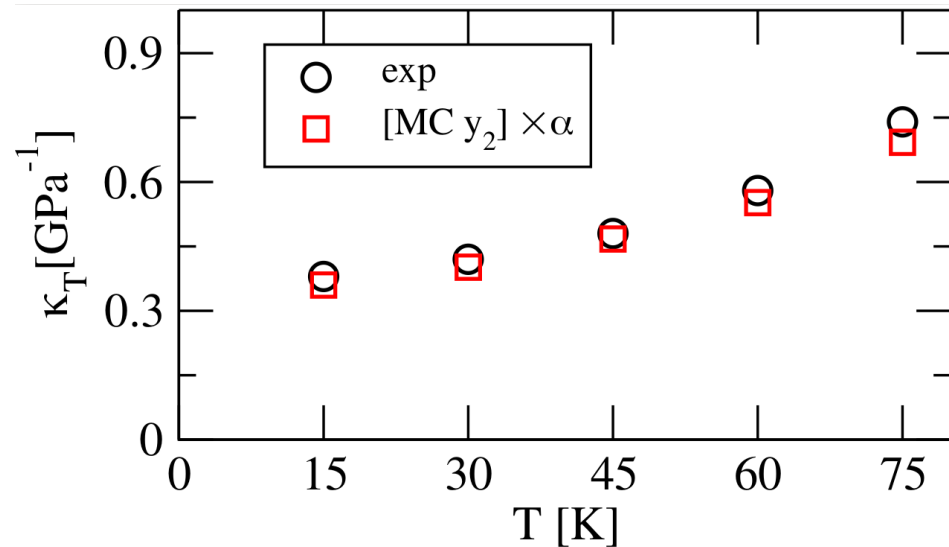
Convergence, compressibility

Harmonic crystal



Integral converges to exact limit for all $T \rightarrow$ exact (const) compressibility

Solid argon



Integral converges (after many tricks)

Compressibility has correct temperature dependence, but large systematic error (scaling factor), can be fixed.