Multi channel multiple scattering theory for X-ray absorption spectroscopy

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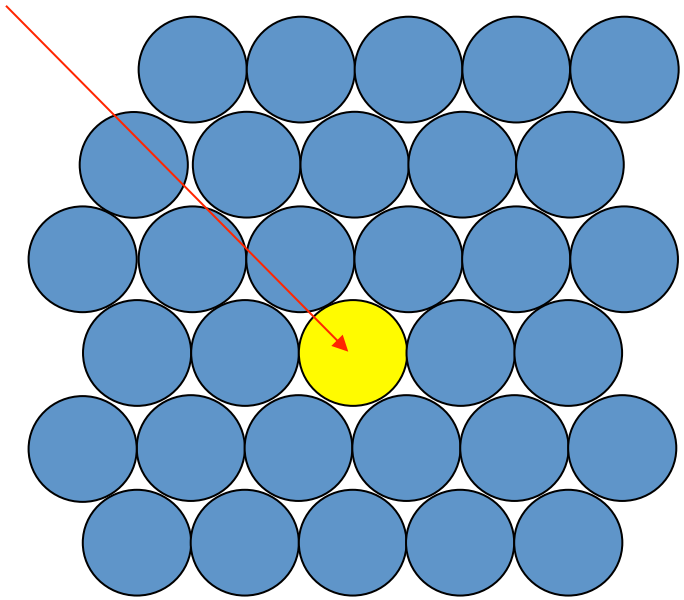
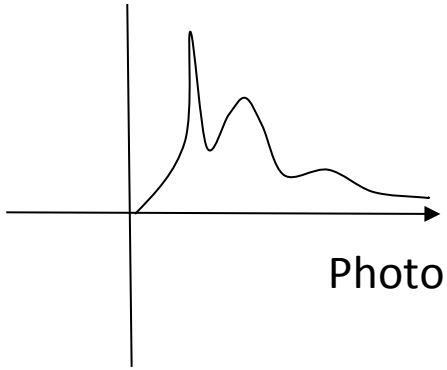
Introduction to XAFS based on the interpretation of multiple scattering approach

X-ray Absorption Fine Structure (XAFS)

Photon



XAFS spectrum



Interpretation

- Molecular Orbital
- Band structure
- Ligand field splitting
- Interference of photoelectron

Absorption coefficient

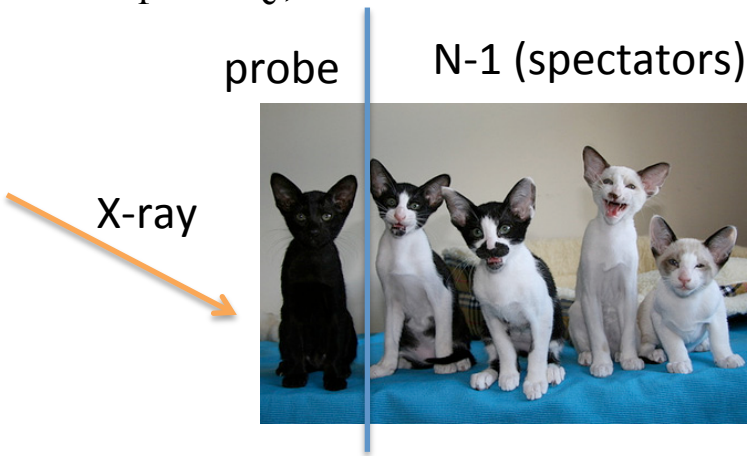
Fermi's golden rule

$$\sigma(\omega) = 4\pi^2 \alpha \omega \sum_f \left| \left\langle \Psi_f^N \left| \vec{\varepsilon} \cdot \vec{r} \right| \Psi_G^N \right\rangle \right|^2 \delta(\omega - E_f + E_c)$$

Independent particle approximation

$$\Psi_G^N = \Phi_0^{(N-1)} \times \phi_{core}$$

$$\Psi_f^N = \Phi_0^{(N-1)} \times \phi_{photo-electron}$$



$$\sigma(\omega) = 4\pi^2 \alpha \omega \sum_f \left| \left\langle \phi_{photo-el} \left| \vec{\varepsilon} \cdot \vec{r} \right| \phi_c \right\rangle \right|^2 \delta(\omega - E_f + E_c)$$

Use Green's function

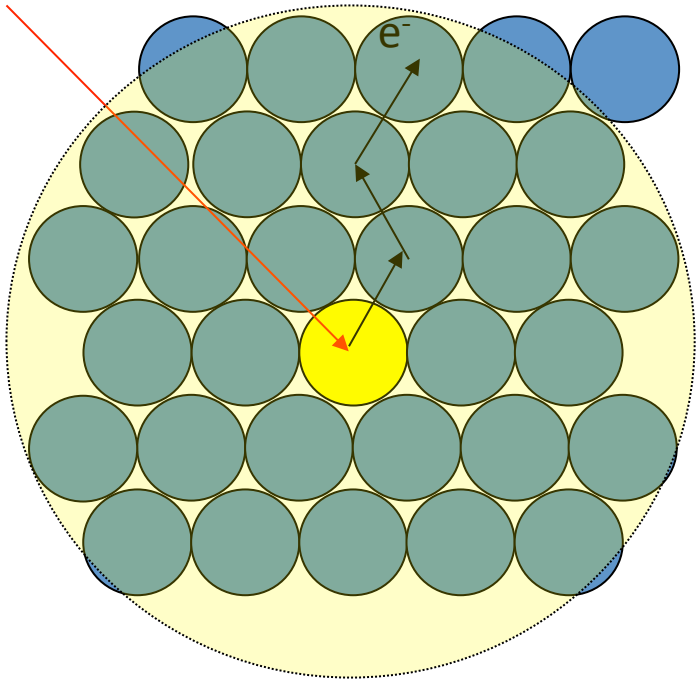
$$\sum_f \left| \phi_{photo-el} \right\rangle \left\langle \phi_{photo-el} \right| \delta(\omega - E_f + E_c) = -\frac{1}{\pi} \mathrm{Im}\, G(\omega + E_c)$$

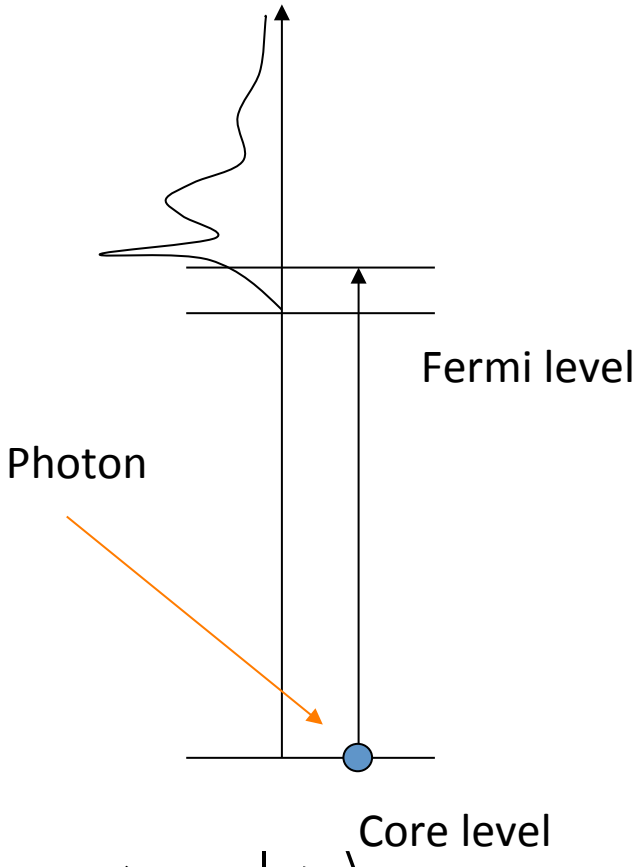
$$\sigma(\omega) = -4\pi\alpha\omega \left\langle \phi_c \left| \varepsilon \cdot r \, \mathrm{Im}\, G(\omega + E_c) \varepsilon \cdot r \right| \phi_c \right\rangle$$

Image:https://www.flickr.com/photos/rcoldbreath/

Absorption

Photon

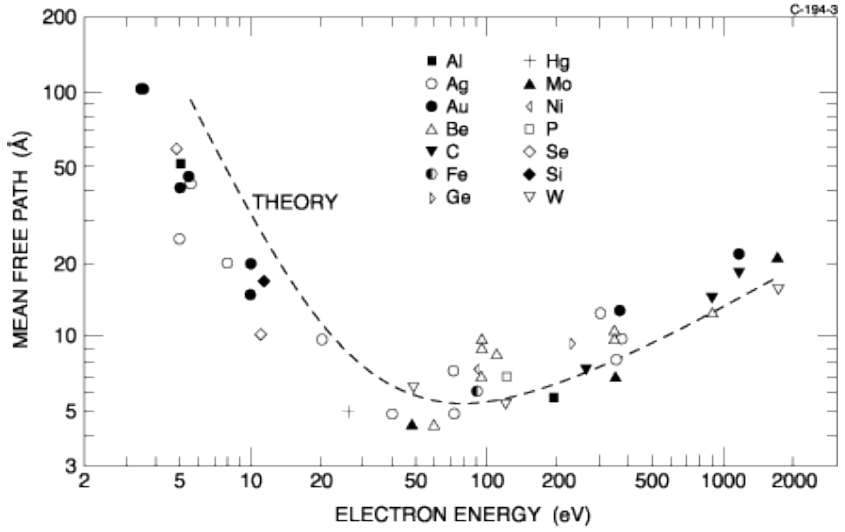




$$\sigma(\omega) = -4\pi\alpha\omega \left\langle \phi_c \middle| \varepsilon \cdot r \, \mathrm{Im}\, G(\omega + E_c) \varepsilon \cdot r \middle| \phi_c \right\rangle$$

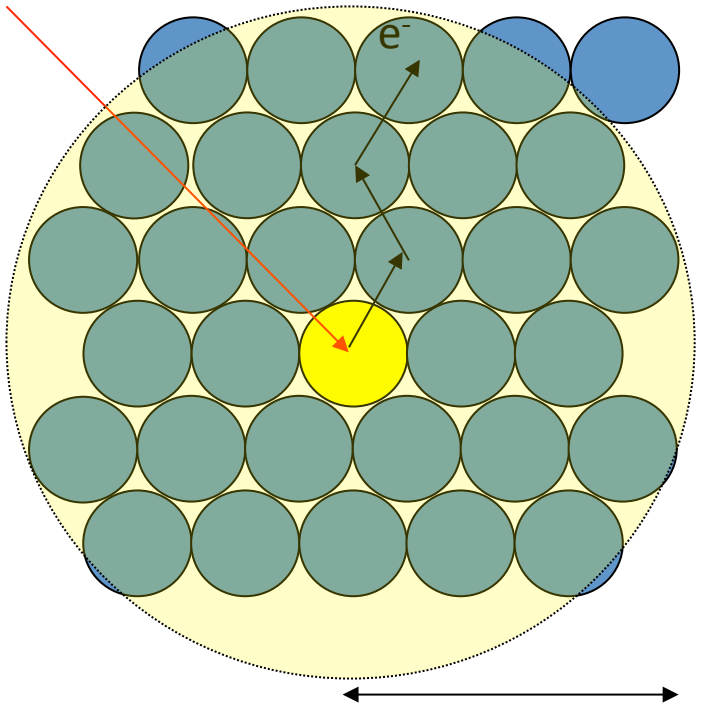
Cluster size

- Due to a finite lifetime of corehole and a mean free path of excited electron, it can travel only up to a few Å (depending on energy)

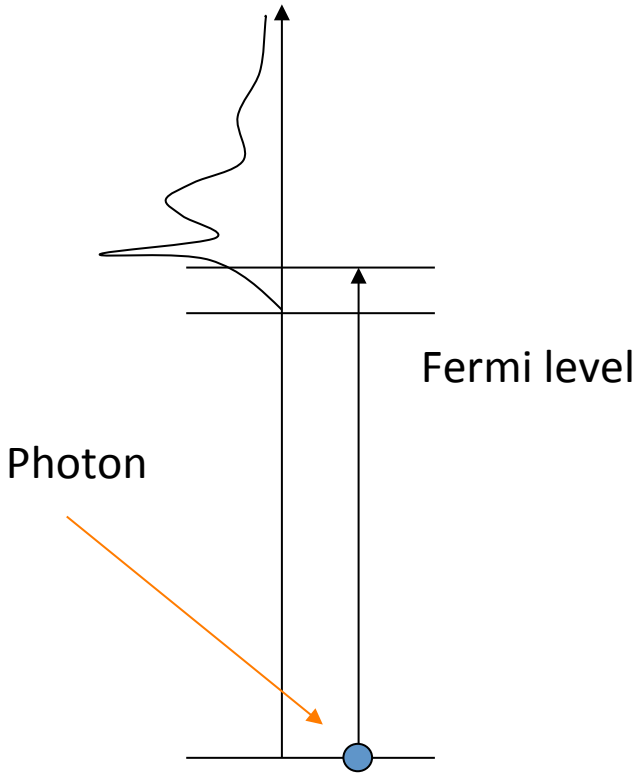


Absorption

Photon

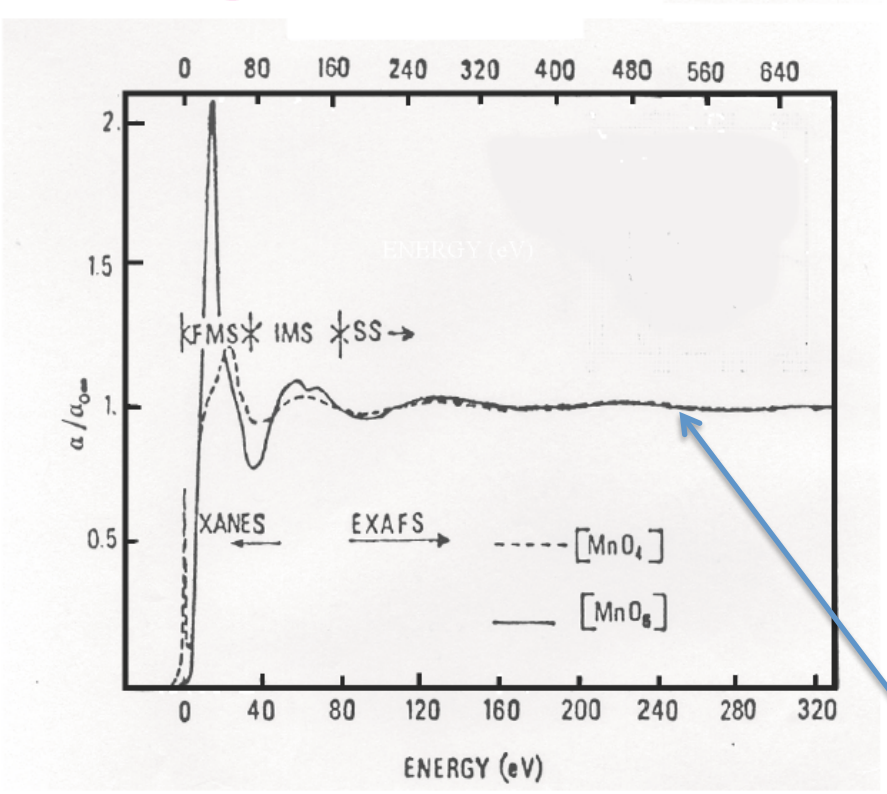


5~10 Å



$$\sigma(\omega) = -4\pi\alpha\omega \left\langle \phi_c \middle| \varepsilon \cdot r \, \mathrm{Im}\, G(\omega + E_c) \varepsilon \cdot r \middle| \phi_c \right\rangle$$

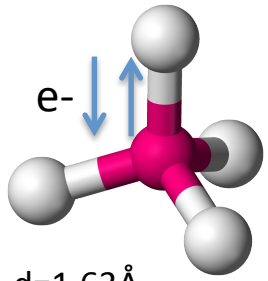
Mn K-edge



The energy scale are in the ratio 0.47 to account for the different distance between Mn and O in MnO_6 and MnO_4

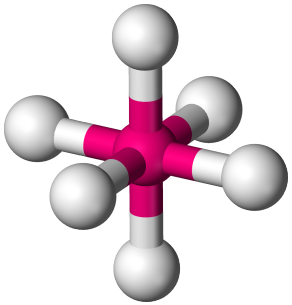
The amplitude has been corrected for the different number of neighbourings

MnO_4



d=1.63Å

MnO_6



d=2.17Å

EXAFS shows sin(kR) oscillations

The two spectra are the same beyond 150 eV → MS contributions

M. Benfatto et al. Phys. Rev B34, 5774 (1986)

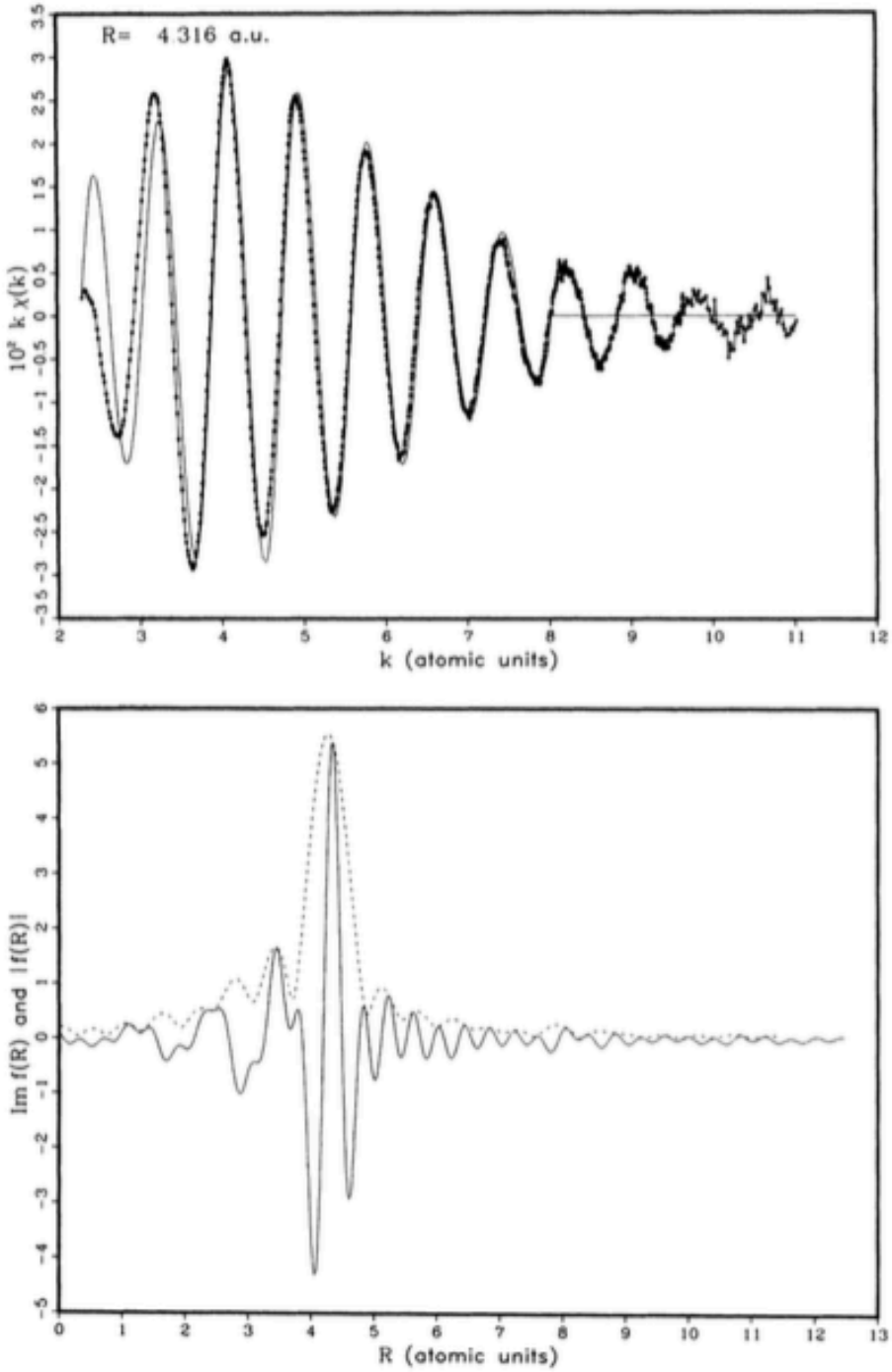


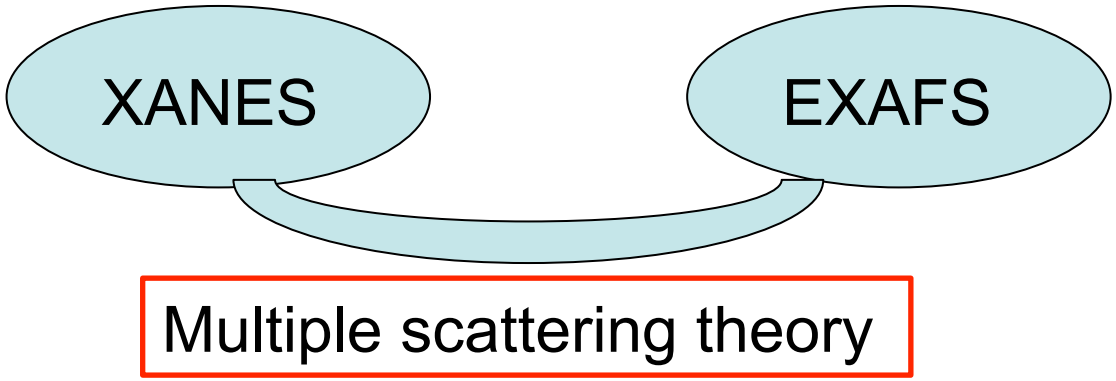
FIG. 7. (a) Comparison of theory (solid line) with the normalized experimental EXAFS spectrum (circles linked by solid line) for Br_2. E_0 has been chosen to be 13 eV above the bound state. Theoretical curve stops at $k = 8$. Theory curve has been reduced by a factor of 0.62 to fit the overall magnitude. (b) Fourier transform of the EXAFS data as defined by Eq. (3.4). Solid line is the imaginary part and dashed line the absolute value of the transform.

Lee&Beni PRB (1976)

K-edge XAFS

	Structure
EXAFS	1d distance
XANES	3d structure

By using Scattering theory, one can have a seamless connection in whole energy range for XAFS.



Multiple scattering Theory

- Multiple Scattering Theory (MST) is a powerful tool for core-electron spectroscopies.

it is a general method, namely,

- good convergence for wide energy range (-50 ~ 1000eV)
- no limitation for atomic species
- complex energy dependent potential

ex.) $\Sigma_{opt} \sim GW \sim V^{ex}_c + G_c v P_c v + G_v W_v$ ($r \approx \infty, \sim 1/r^4$)

T. Fujikawa, K. Hatada and L. Hedin, PRB (2000)

Application of Multiple scattering approach

KKR (band): Korringa (1947), Kohn and Rostoker (1954)
SCF-SW (Quantum Chemistry:MO): Slater and Johnson (1966),
Smith and Johnosn (1969)

For core electron spectroscopy,

PHD (Photo Electron Diffraction) :
Sebilleau (MsSpec), Rennert, Van Hove, Saldin, De Abajo

XAFS (X-ray Absorption Fine Structure):
Natoli (1980), Vedrinsky, Pendry, Fujikawa, Rehr (FEFF code),
Benfatto, Brouder, Foulis, Ebert (SPRKKR), Hatada (FPMS) …

Also for EELS (Electron Energy Loss Spectroscopy),
RXS (Resonant X-ray Scattering)

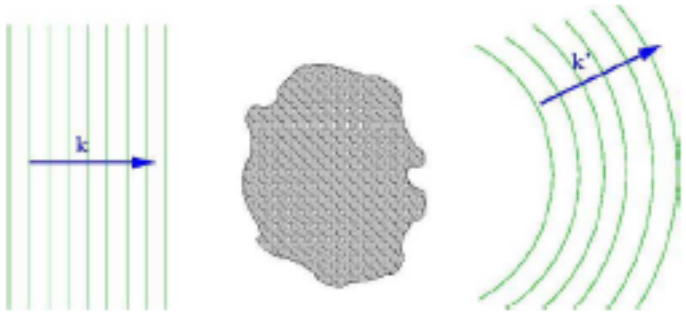
wide application of MS theory

K. Hatada, *IXAS Web Magazine* (2010)

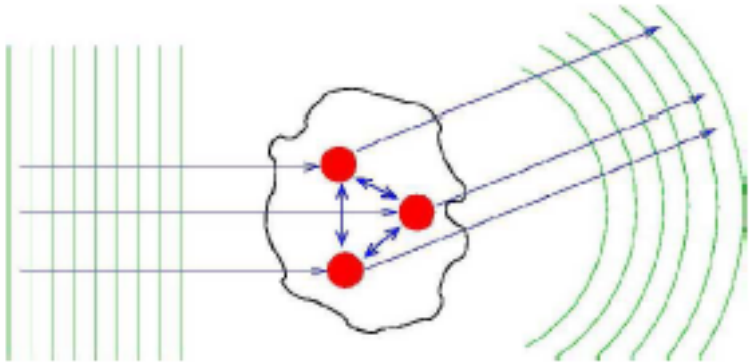
Multiple Scattering Theory for XAS

XAS: initial: core state → final continuum → scattering state

scattering problem



method of multiple scattering



$\Psi(\mathbf{x}) \rightarrow e^{i\mathbf{k}\cdot\mathbf{x}} - 2\pi \langle \mathbf{k}'|T|\mathbf{k}\rangle \, e^{ikr}/r$

- solve single scattering → t_i
- free propagation between sites → G_{ij}

$$T = \sum_i t_i + \sum_{i\neq j} t_i G_{ij} t_j + \sum_{i\neq j\neq k} t_i G_{ij} t_j G_{jk} t_k + \ldots \quad = \sum_{ij} \tau_{ij}$$

$$\tau_{ij} = [\delta_{ij} {t_i}^{-1} - G_{ij}]^{-1}$$

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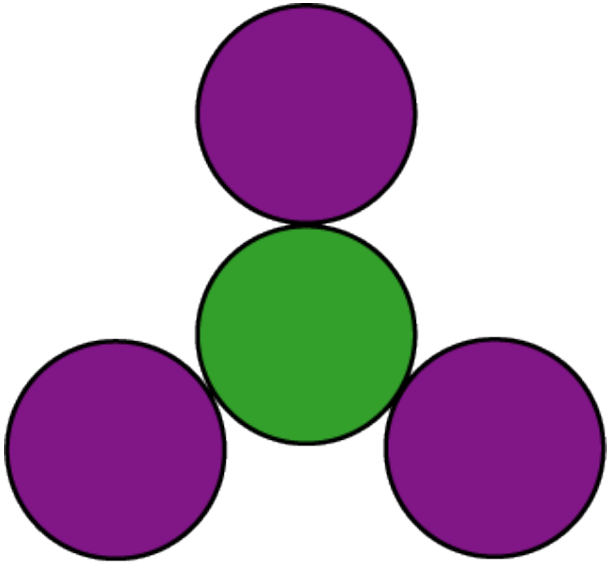
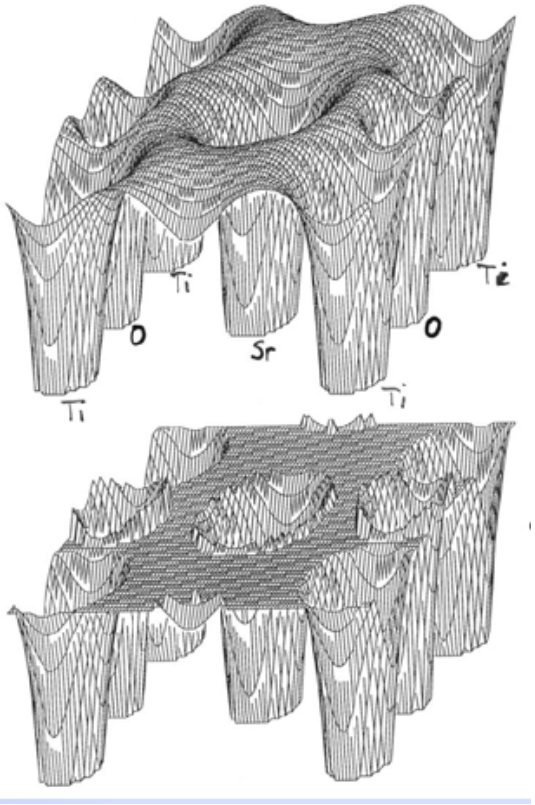
Approximation of potential: Muffin-tin (MT) approximation





Spherical shaped

Spherical averaged

Constant in interstitial region

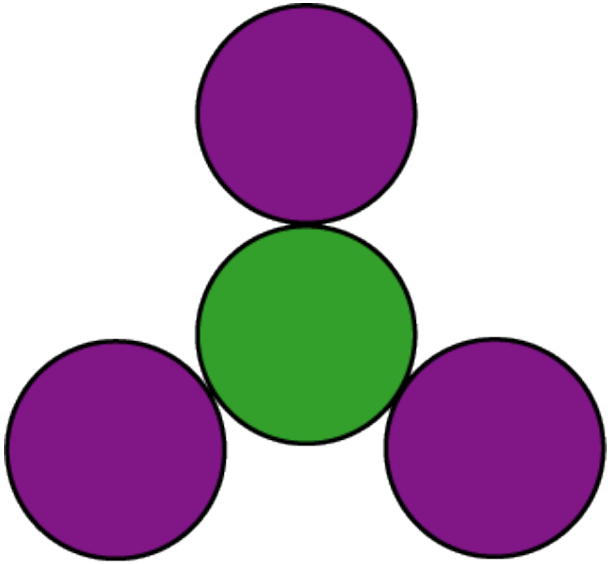
This approximation works well for :

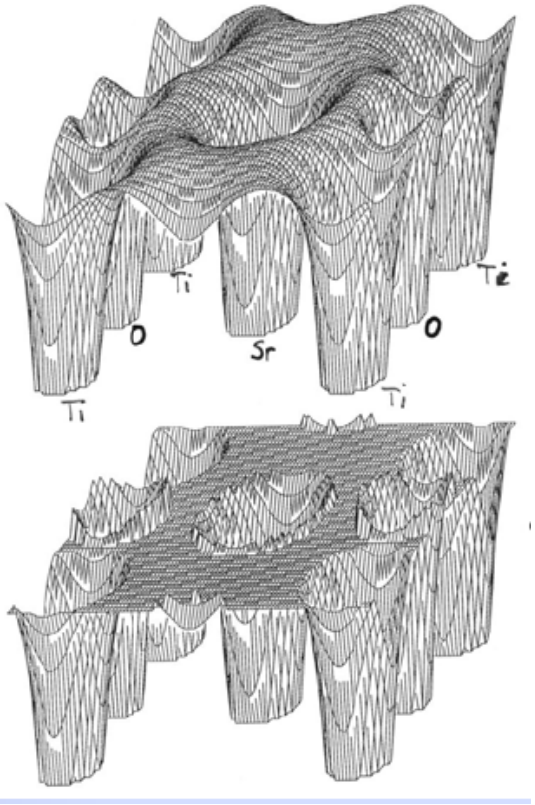
Closed packed system

Higher energy region ~20 eV

Image: https://www.flickr.com/photos/piez/529412931/

Approximation of potential: Muffin-tin (MT) approximation





Spherical shaped

Spherical averaged

Constant in interstitial region

MT scatterer

This approximation works well for :

Closed packed system

Higher energy region ~20 eV

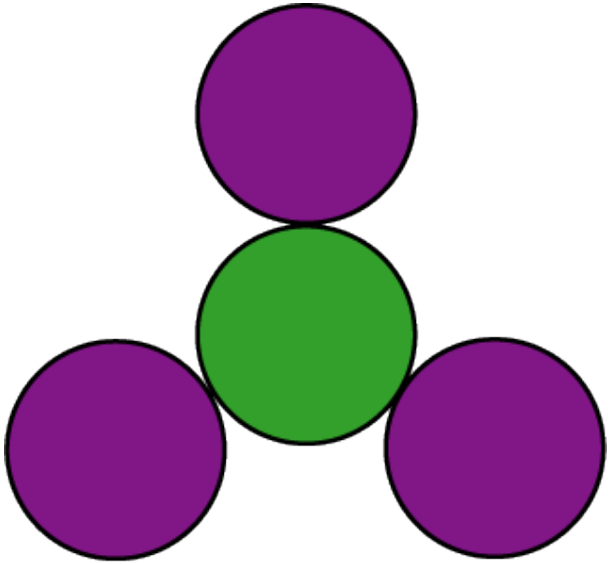
Programs

- CONTINUUM (Natoli)
- FEFF (Rehr)
- GNXAS (Fillipponi&Di Cicco)
- MXAN (Benfatto&Della Longa (Hatada))
- **FPMS** (Hatada)

FPMS school by COST in Rennes the last week of June 2016!

For requests of FPMS and MXAN send email:
keisuke.hatada.gm@gmail.com

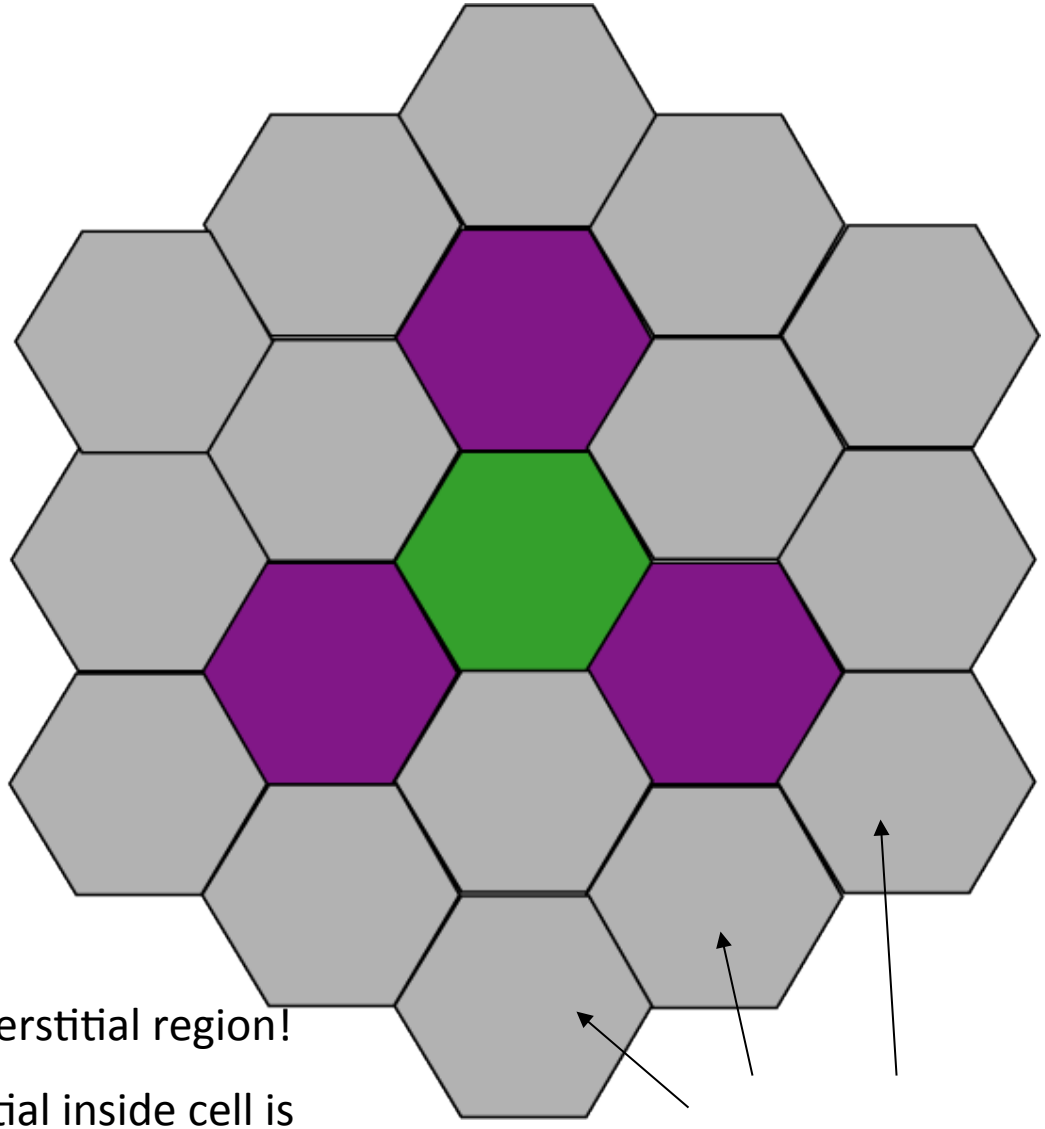
MT approximation (MXAN)



Use spherical shaped and averaged potential

outside the cells potential is flat

Non-MT (FPMS)



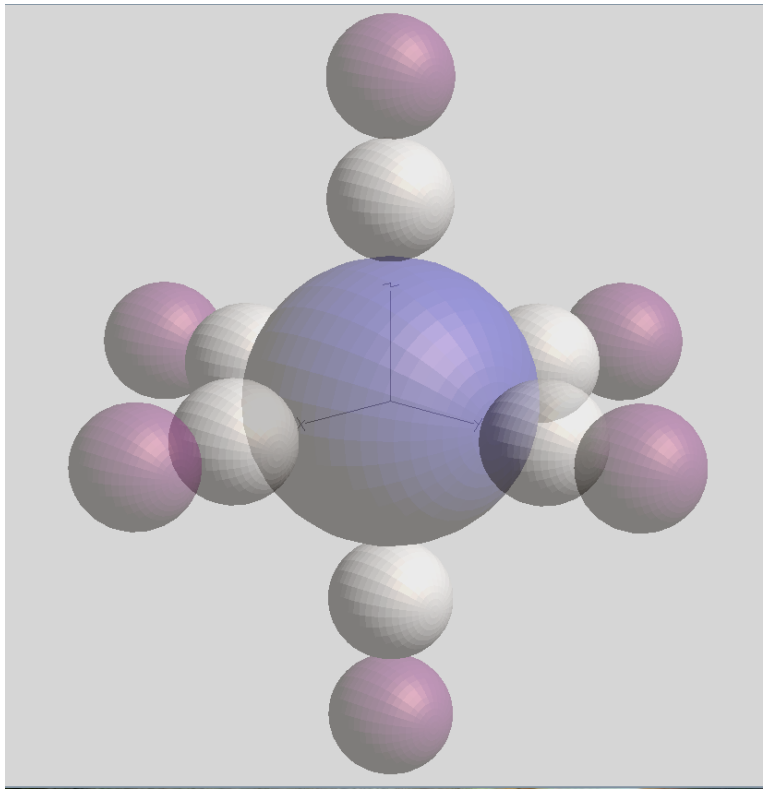
No interstitial region!

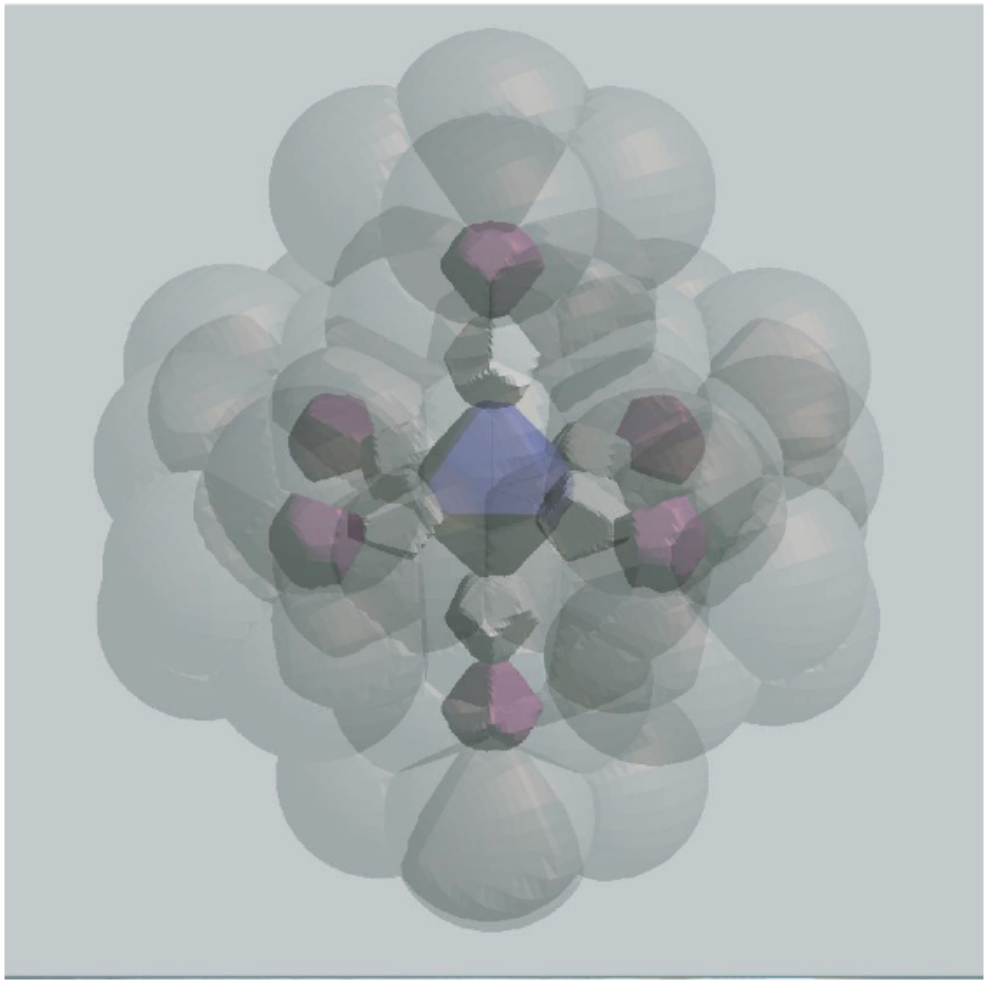
Potential inside cell is anisotropic

Empty Cells (EC)

3d images of MT & NMT

$Fe(CN)_6$





L_{23} edge of transition metal

- We have seen XAFS can be separated by energy region. What about the edges? Different?

Yes…

3 main types of work for XAFS

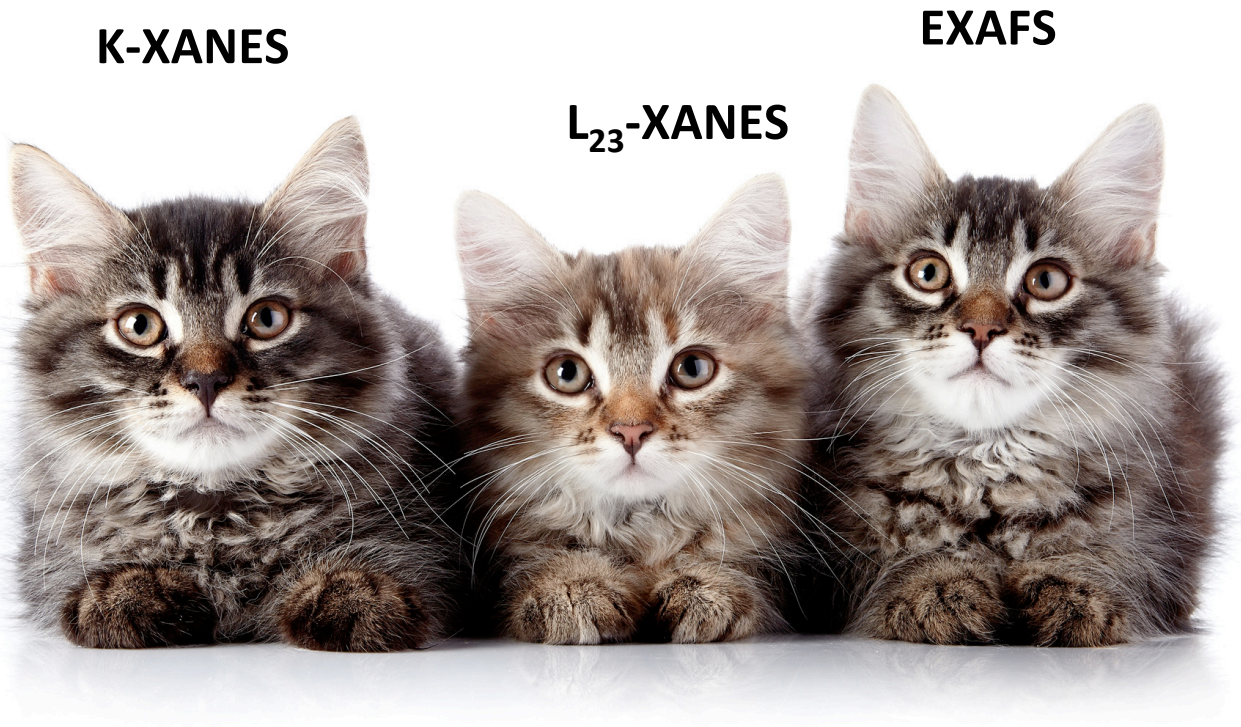


Image:http://www.scrippsranchpetwatch.com/cat-sitter/

3 main types of work for XAFS

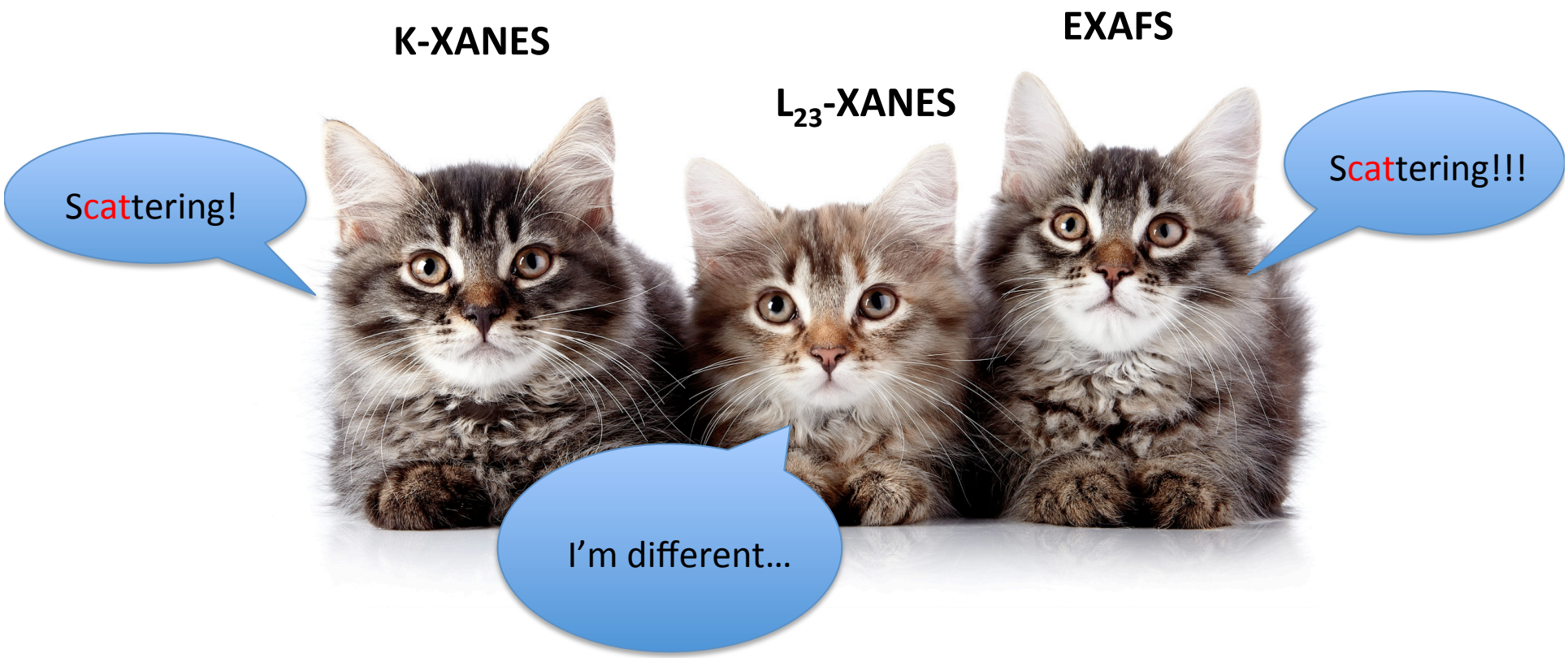


Image:http://www.scrippsranchpetwatch.com/cat-sitter/

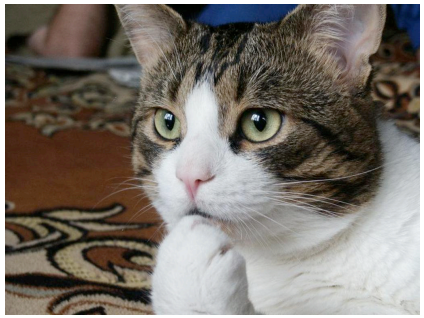
L_{23} edge of transition metal

- We have seen XAFS can be separated by energy region. What about the edges? Different?

Yes…

- K-edge XANES and EXAFS provide mainly structural info.

- While shallow core edges, what happens?



?

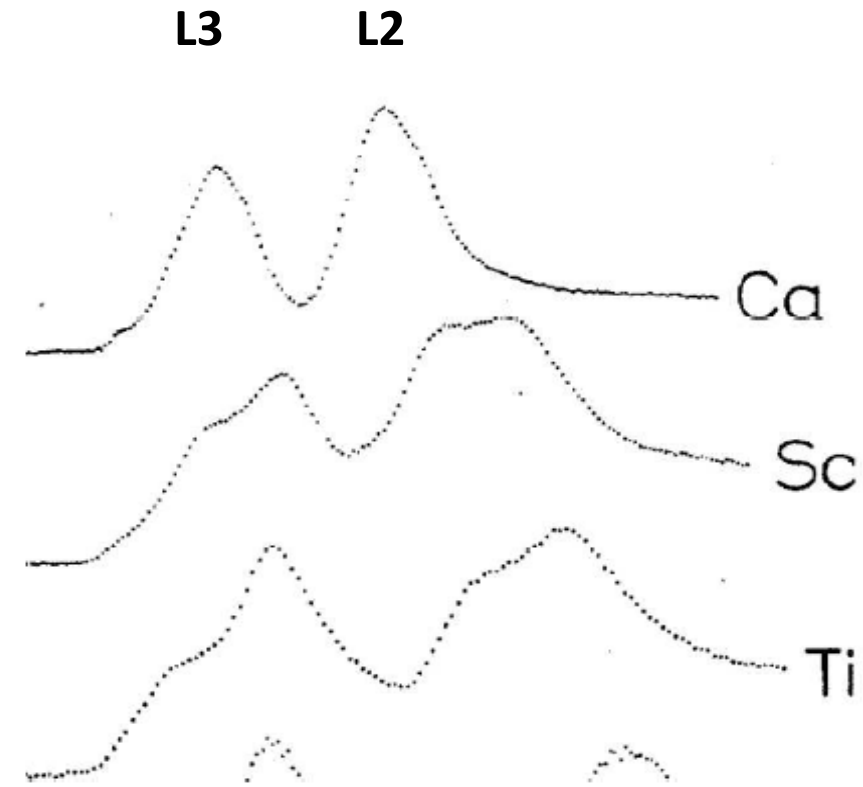
More electron information.

- L_{23} 3d transition metal case is particular.

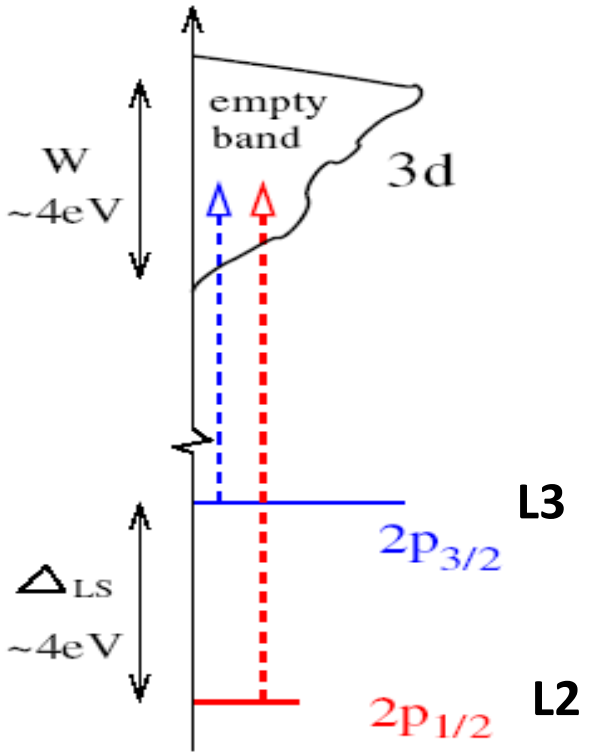
(L_{23} edge is important also for XMCD to study magnetism)

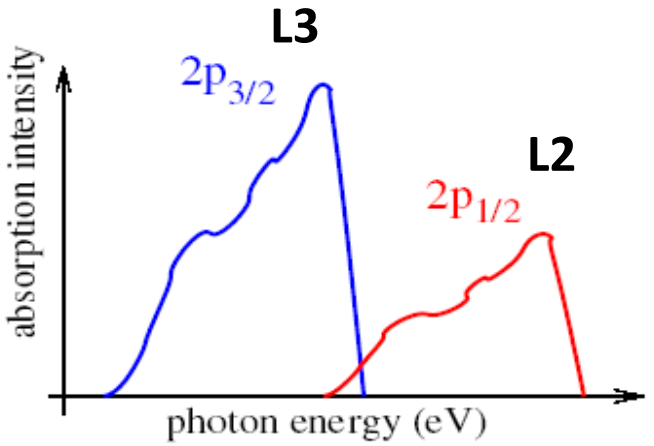
Image: http://photoity.com/the-32-graceful-pictures-of-surprised-cats/

$L_{2,3}$-XAS of early 3d elements



J. Fink et al. Phys. Rev. B 32, 4899 (1985)





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Experiment

Independent particle picture

2:1

$L_{2,3}$-XAS of d^0-system in atomic multiplet theory

Many-electron states

$|g\rangle = |\, 2p^6 3d^0, J=0\rangle$

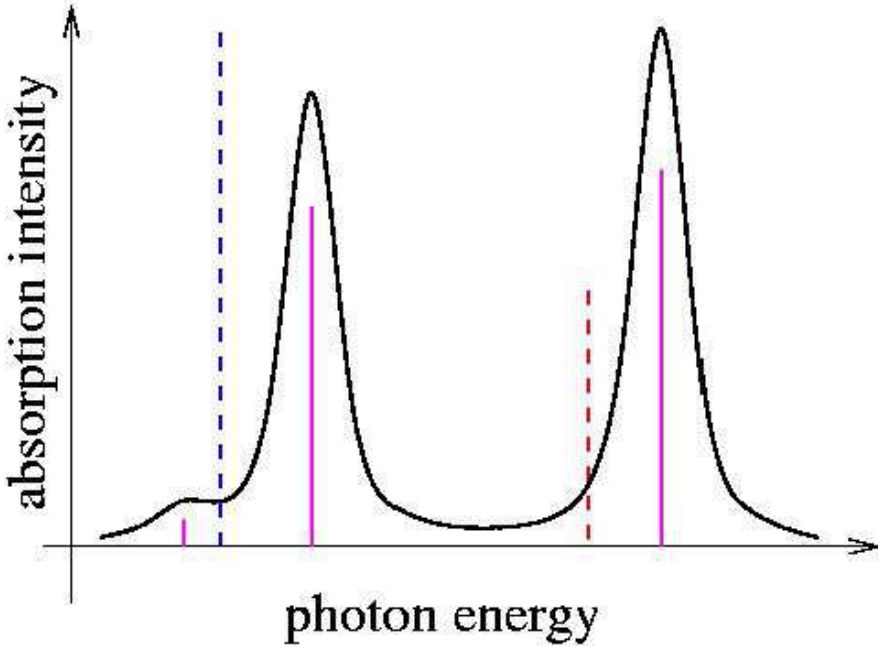
$|\, f\rangle = |\, 2p^5 3d^1, J=1\rangle$

2p-s.-o. ~ 2p-3d Coulomb

Intermediate coupling

$2p_{1/2}$, $2p_{3/2}$ holes mixed

L_2-L_3 channel coupling



(dotted: without 2p-3d Coulomb)

- **correct branching ratio**
- **no band structure / ligand field**

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Can we put multiplets in multiple scattering?

Many body… identical… Fermionic…

Image:http://connect.everythingzoomer.com/profiles/blogs/when-do-you-have-too-many-cats

First attempts were done in Natoli (Frascati) and Vedrinskii (Rostov) groups in 1990
In this way ligand field is automatically taken into account by multiple scattering part

No ligand field parameters!

PHYSICAL REVIEW B VOLUME 42, NUMBER 4 1 AUGUST 1990

Multichannel multiple-scattering theory with general potentials

C. R. Natoli and M. Benfatto
Laboratori Nazionali di Frascati dell'Istituto Nazionale di Fisica Nucleare, P.O. Box 13, I-00044 Frascati, Italy

C. Brouder
Laboratoire de Physique du Solide, Université de Nancy I, Boîte Postale 239, F-54506 Vandoeuvre-les-Nancy CEDEX, France

M. F. Ruiz López
Laboratoire de Chimie Théorique, Université de Nancy I, Boîte Postale 239, F-54506 Vandoeuvre-les-Nancy CEDEX, France

D. L. Foulis
Department of Physics, University of Warwick, Coventry, CV4 7AL, United Kingdom
(Received 13 November 1989)

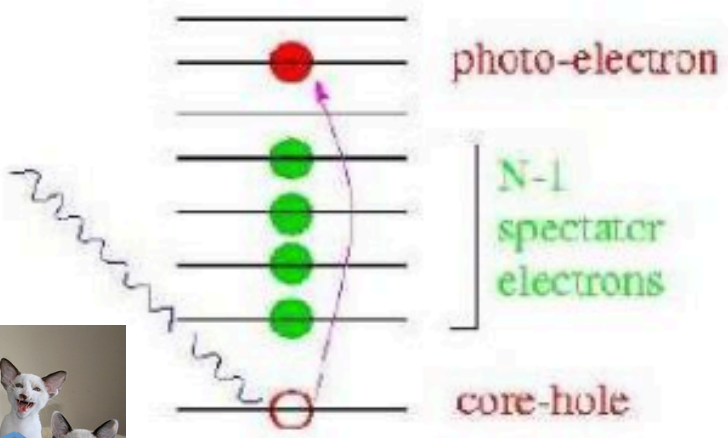
Multichannel multiple scattering theory

Standard M.S. theory:

independent particle approx.

$$\Psi_g^{(N)} = \Phi_0^{(N-1)} \times \phi_{\text{core}}$$

$$\Psi_f^{(N)} = \Phi_0^{(N-1)} \times \phi_{\text{photo-el}}$$



Multichannel M.S. theory

$$\Psi_f^{(N)} = \sum_\alpha \Phi_\alpha{}^{(N-1)} \times \phi_\alpha$$

"close coupling expansion" = C.I. over $\Phi_\alpha^{(N-1)}$ eigenstates

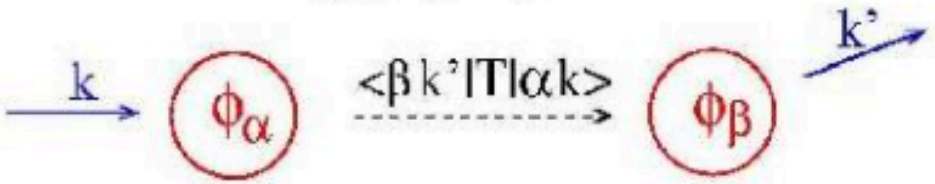
photo-electron interacts with core-hole and "spectators"

⇒ exchanges quantum numbers: energy, spin, . . .

⇒ transitions $\Phi_\alpha \rightarrow \Phi_\beta$

"inelastic" scattering

→ multi-channel



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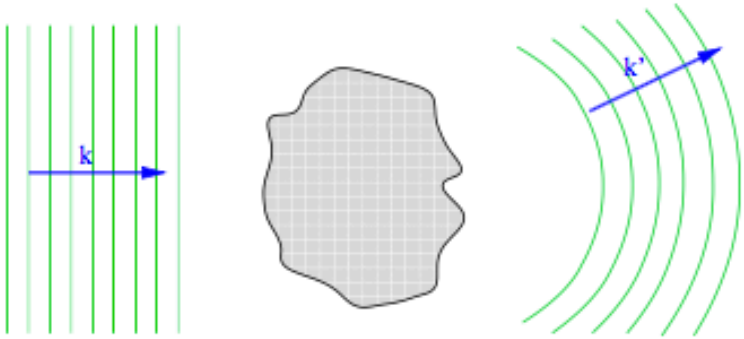
Multiple Scattering Theory

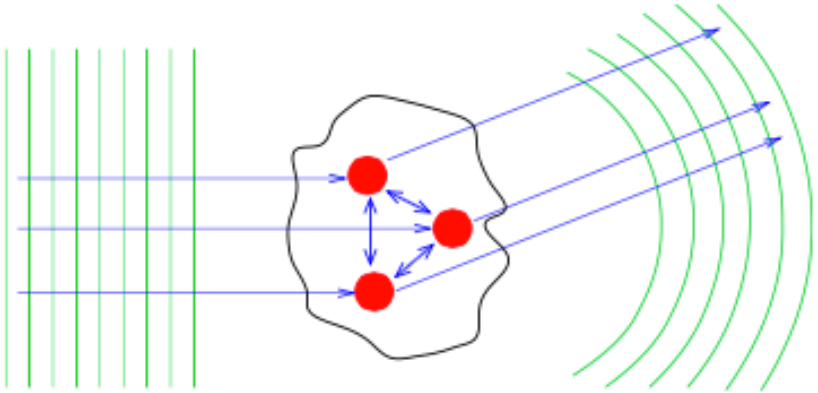
scattering problem



$$\Psi(\mathbf{x}) \rightarrow e^{i\mathbf{k}\cdot\mathbf{x}} - 2\pi \langle \mathbf{k}'|T|\mathbf{k}\rangle \; e^{ikr}/r$$

$$\Psi(\mathbf{x}) \rightarrow e^{i\mathbf{k}_\alpha\cdot\mathbf{x}} - 2\pi \langle \mathbf{k}'_\beta|T|\mathbf{k}_\alpha\rangle \; e^{ikr}/r$$

method of multiple scattering



- solve single scattering $\rightarrow t^i, t^i_{\alpha\beta}$
- free propagation between sites $\rightarrow G^{ij}$

$$T = \sum_i t^i + \sum_{i\neq j} t^i G^{ij} t^j + \sum_{i\neq j\neq k} t^i G^{ij} t^j G^{jk} t^k + \ldots$$

$$T_{\alpha\beta} = \sum_i t^i_{\alpha\beta} + \sum_{i\neq j} \sum_{\mu} t^i_{\alpha\mu} G^{ij}_{\mu} t^j_{\mu\beta} + \sum_{i\neq j\neq k} \sum_{\mu\nu} t^i_{\alpha\mu} G^{ij}_{\mu} t^j_{\mu\nu} G^{jk}_{\nu} t^k_{\mu\beta} + \ldots$$

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Calculation of T-matrix

(1) integration of Schrödinger equation inside atomic sphere

$$(-\nabla^2 + \mathbf{V_0}(\vec{\mathbf{r}}) - \epsilon_\alpha)\,\phi_\alpha(\vec{\mathbf{r}}) = -\sum_\beta \int \mathbf{V}_{\alpha\beta}(\vec{\mathbf{r}},\vec{\mathbf{r}}')\phi_\beta(\vec{\mathbf{r}}')\,\mathbf{d^3r'}$$

where

$$\epsilon_\alpha = \hbar\omega + \mathbf{E_g^N} - \mathbf{E_\alpha^{N-1}}$$

Problem:
interchannel potential, coupled integro-differential equations

(2) R-matrix methods [Wigner, Eisenbud, Kohn $\sim$ 1940']

R-matrix = logarithmic derivative in multi-channel case

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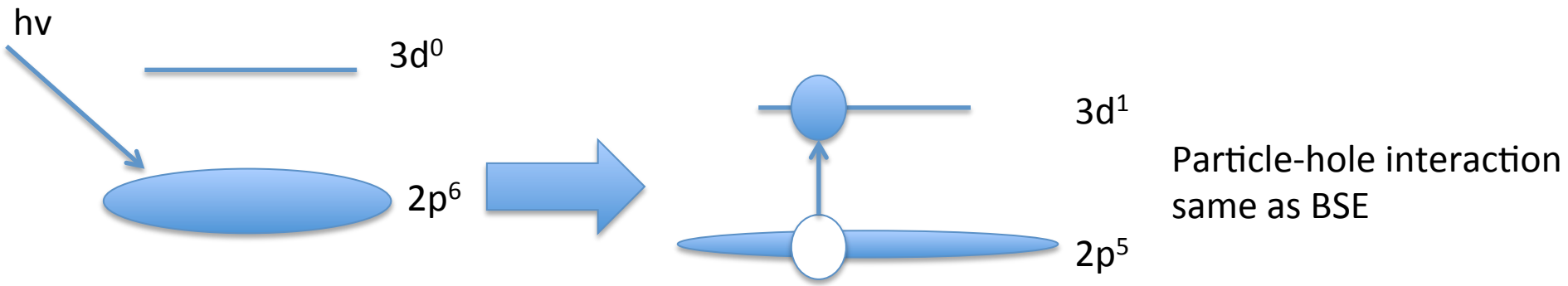
Multi Channel Multiple Scattering (MCMS)

- First rigorous practical calculation was published by Kruger and Natoli (PRB 2004)



Eigen-channel R-matrix method

variational principle for logarithmic derivative [W. Kohn 1948]

$$b[\Psi] \equiv \frac{\langle \Psi | E - \hat{H} - \hat{L} | \Psi \rangle}{\langle \Psi | Q | \Psi \rangle} \quad , \quad \delta b[\Psi] = 0 \, ,$$

where $\hat{L} \equiv \sum_j \delta(r_j - r_0) \frac{\partial}{\partial r_j}$ and $\hat{Q} \equiv \sum_j \delta(r_j - r_0)$

solutions $b_k, \ \Psi_k$

$$H\Psi_k = E\Psi_k \quad and \quad \left. \frac{\partial \Psi_k}{\partial r} \right|_{r_0} = -b_k \, \Psi_k(r_0)$$

develop $\Psi_k = \sum_\nu \Phi_\nu c_{\nu k} \quad \Rightarrow$

$$\sum_\nu [E - H - L]_{\mu\nu} \, c_{\nu k} = \sum_\nu Q_{\mu\nu} \, c_{\nu k} \, b_k$$

generalized eigenvalue problem: dim $\gg$ rank, metric Q singular

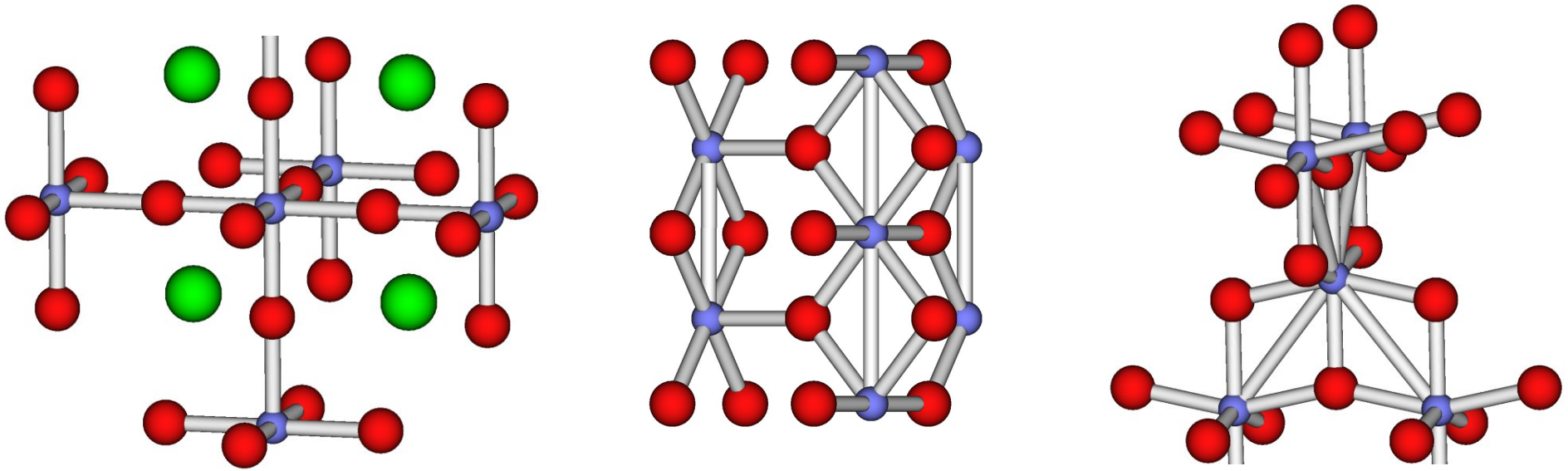
PK

Kruger&Natoli PRB **71** 245120 (2004)

$SrTiO_3$

TiO_2 rutile

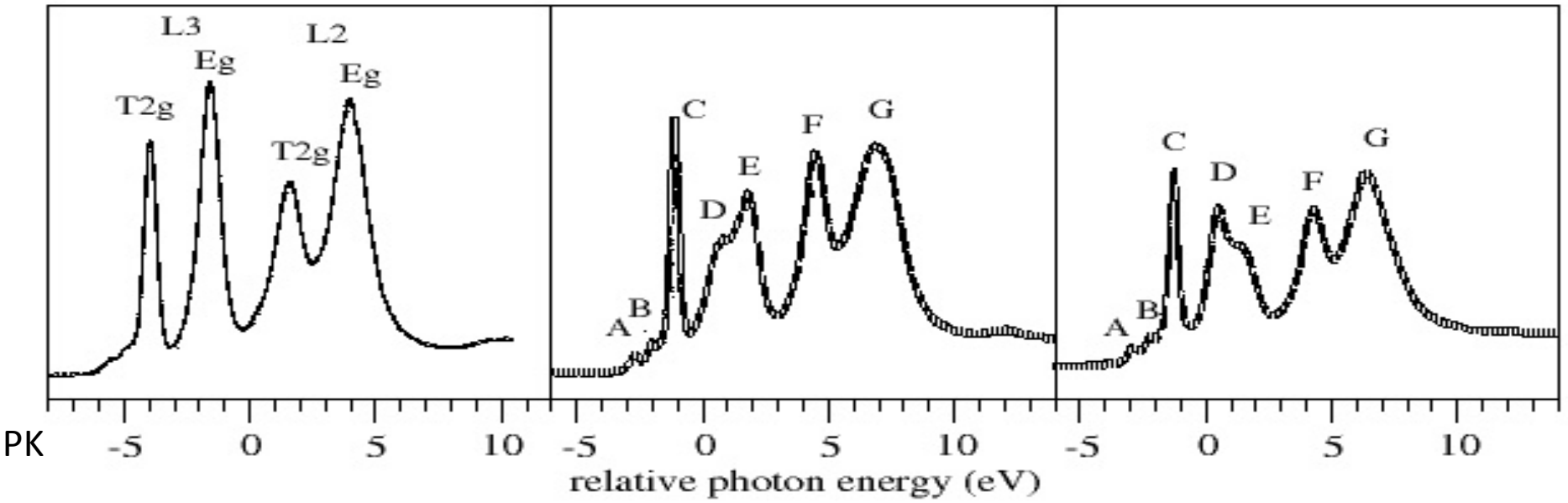
TiO_2 anatase



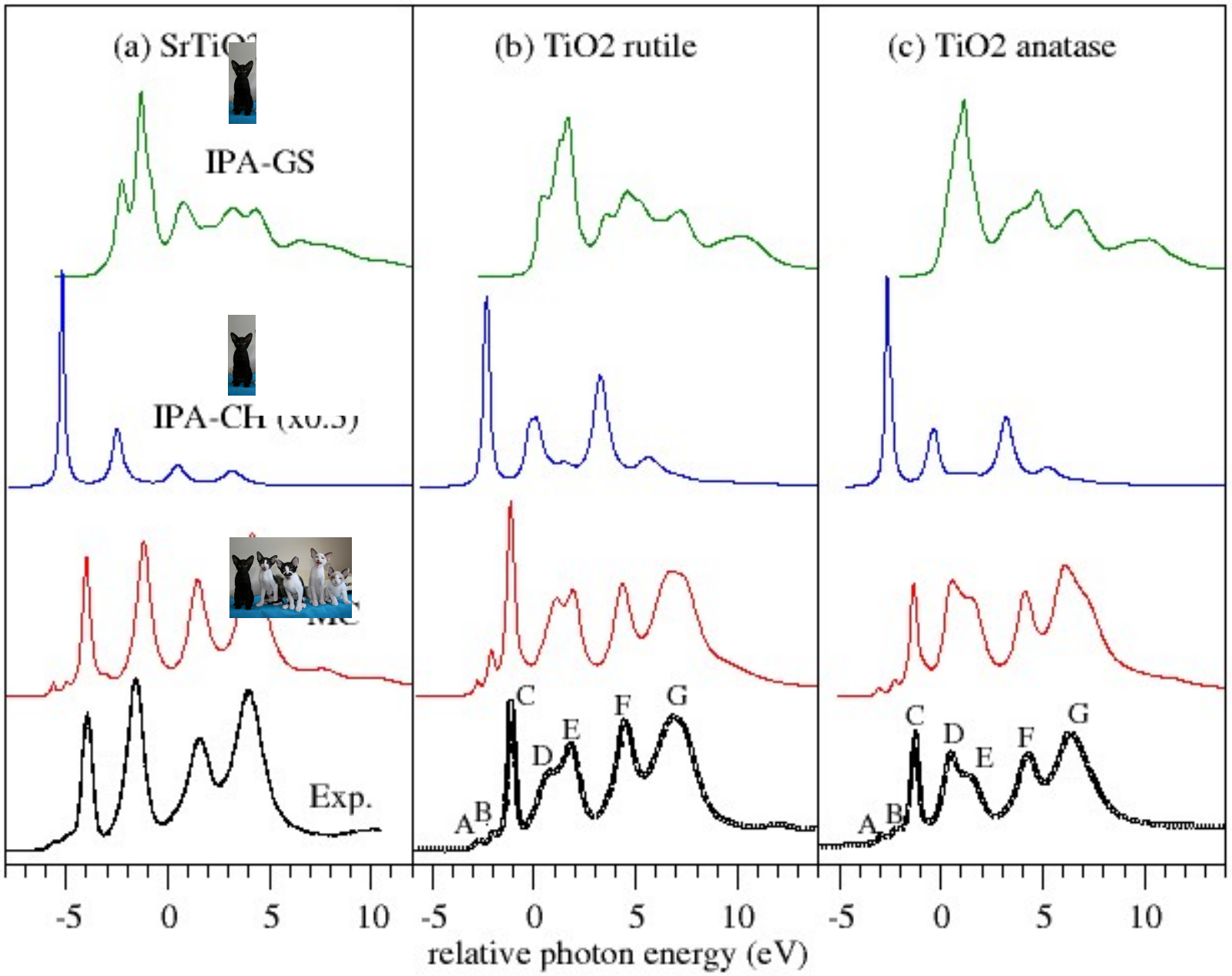
cubic, Oh

tetragonal, D2h

tetragonal, D2d



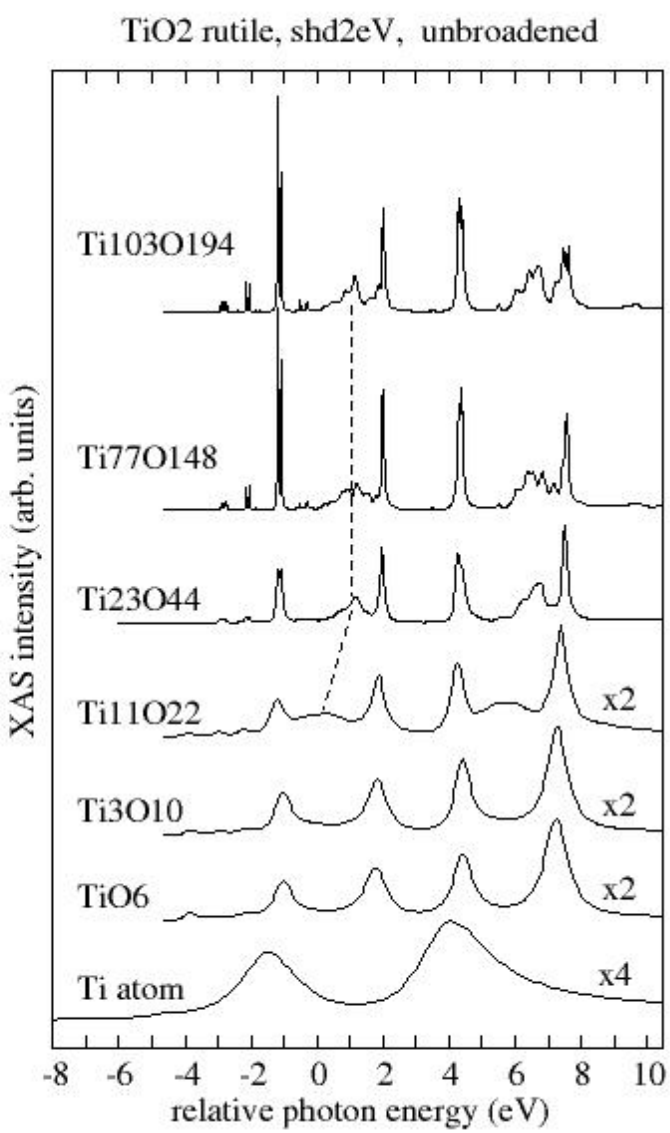
PK

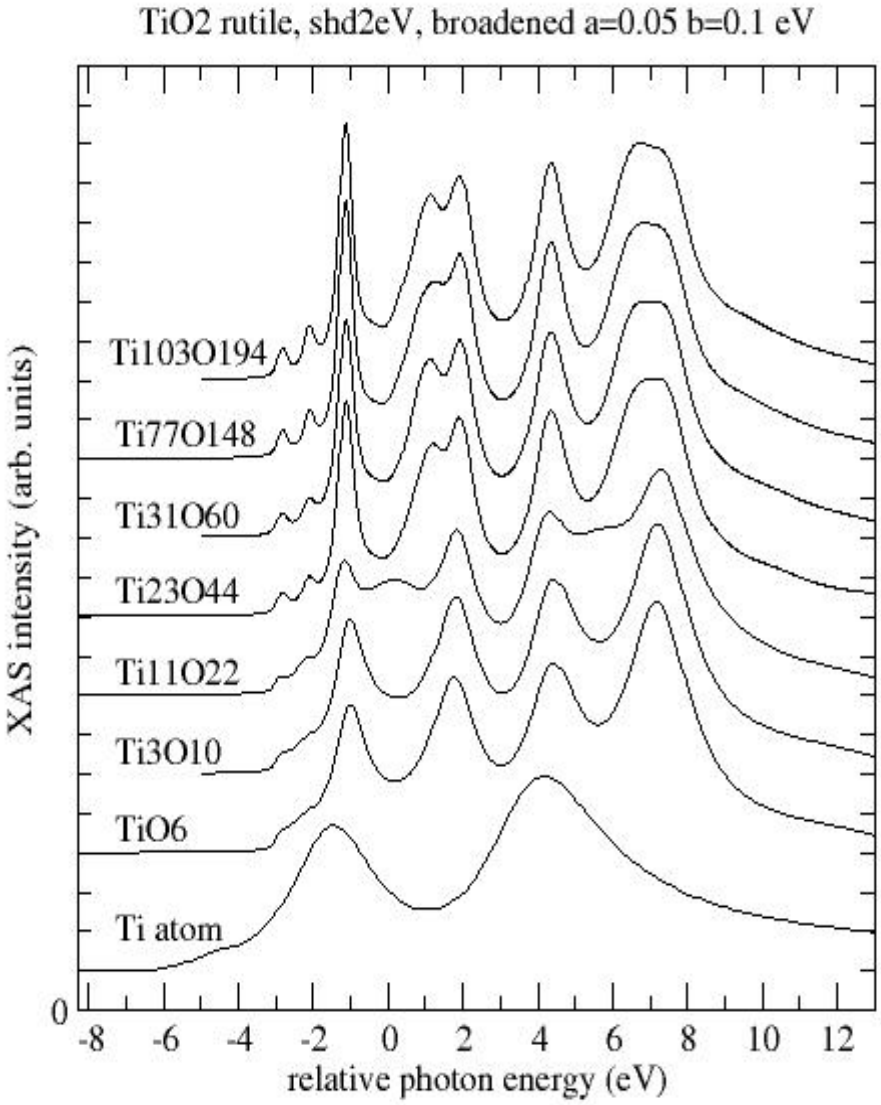


PK

Kruger PRB (2010), J. Phys. Conf. Ser (2009)

TiO_2 rutile - cluster size dependence





PK

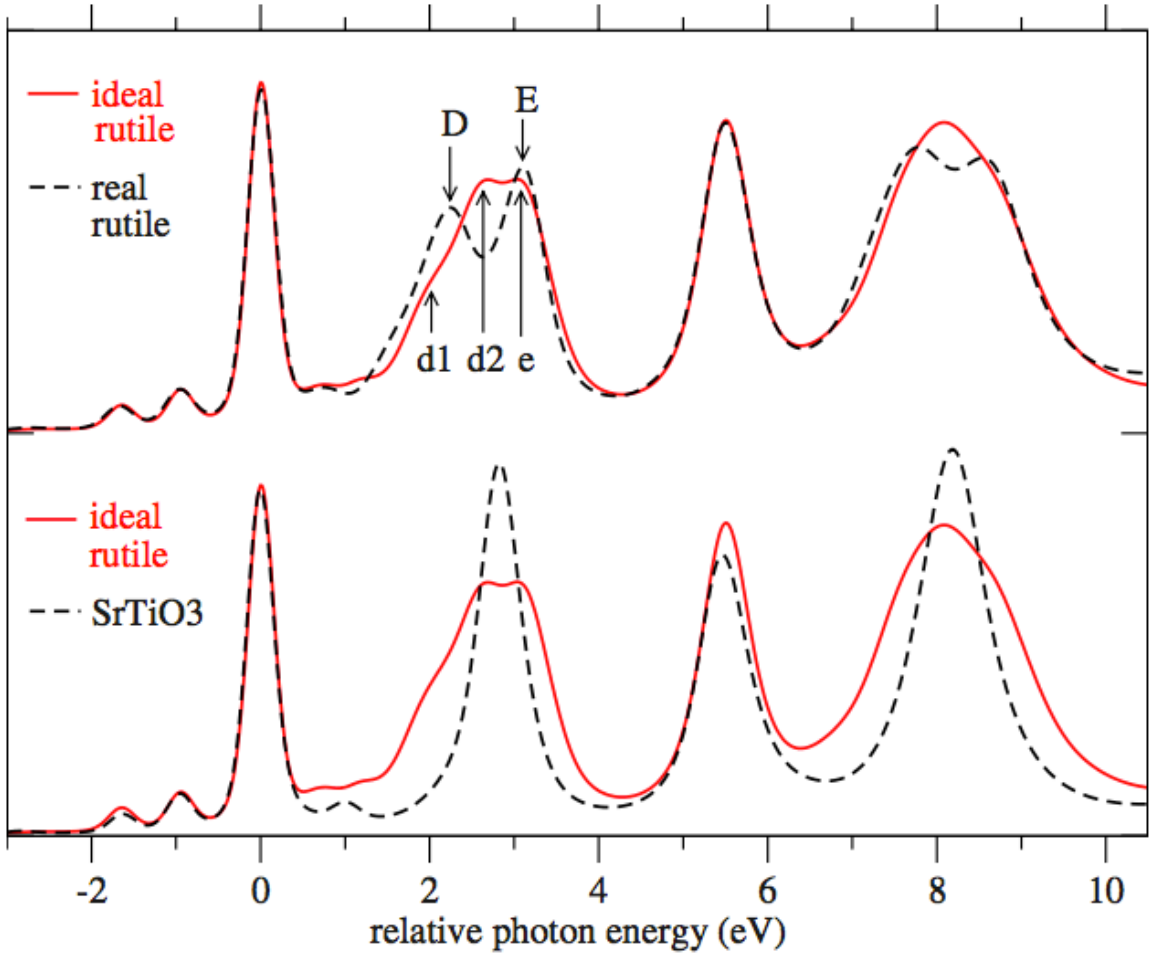


FIG. 4. (Color online) $L_{2,3}$-edge spectra calculated with MC-PS with clusters of about 300 atoms. Comparison between $SrTiO_3$ and rutile TiO_2 with either the real structure or an ideal rutile structure made of undistorted TiO_6 octahedra.

P. Krüger, Phys. Rev. B, 81 (2010) 125121

Calculation of T-matrix

(1) integration of Schrödinger equation inside atomic sphere

$$(-\nabla^2 + \mathbf{V_0}(\vec{\mathbf{r}}) - \epsilon_\alpha)\,\phi_\alpha(\vec{\mathbf{r}}) = -\sum_\beta \int \mathbf{V}_{\alpha\beta}(\vec{\mathbf{r}},\vec{\mathbf{r}}')\phi_\beta(\vec{\mathbf{r}}')\,\mathbf{d^3r'}$$

where

$$\epsilon_\alpha = \hbar\omega + \mathbf{E_g^N} - \mathbf{E_\alpha^{N-1}}$$

Problem:
interchannel potential, coupled integro-differential equations

(2) R-matrix methods [Wigner, Eisenbud, Kohn $\sim$ 1940']

R-matrix = logarithmic derivative in multi-channel case

PK

Dyson equation for multichannel potential

$$G^{(+)}(E) = g^{(+)}(E) + g^{(+)}(E)\Delta V\, G^{(+)}(E)$$

Manybody correction

With multiple scattering frame work

$$G_{\alpha\beta} = g_{\alpha\beta} + \sum_{\gamma\delta} g_{\alpha\gamma}\, \Delta t_{\gamma\delta}\, G_{\delta\beta}$$

T-matrix is calculated by

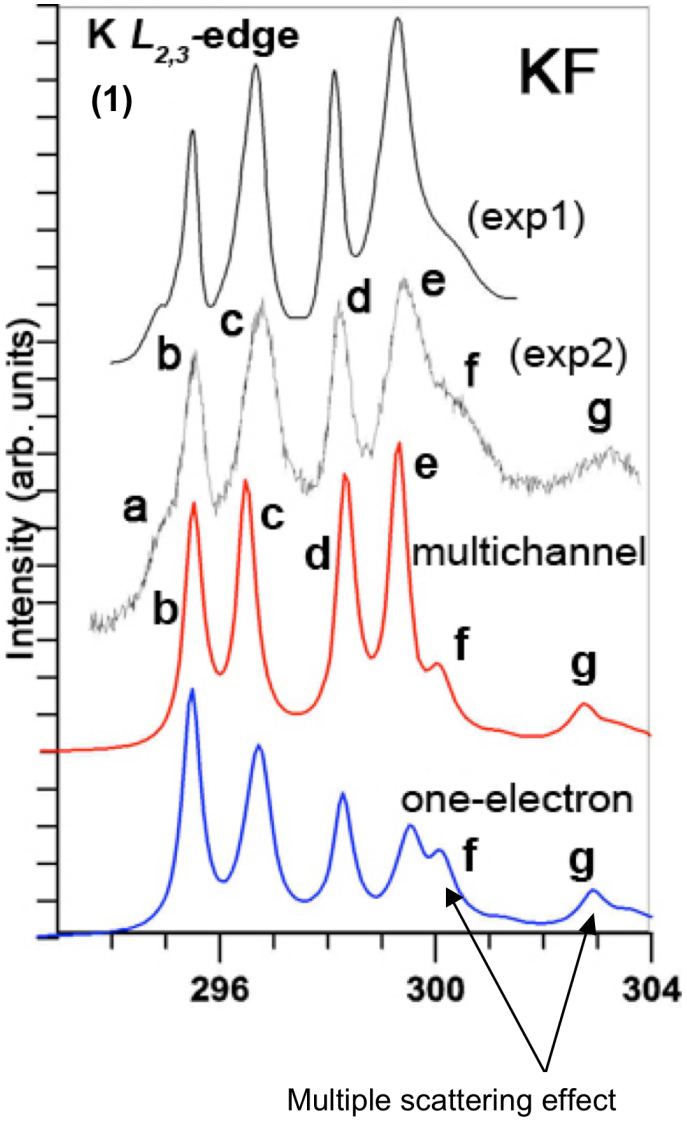
$$\left(\frac{d^2}{dr^2} - \frac{l_\alpha(l_\alpha+1)}{r^2} + \frac{2Z}{r} + k_\alpha^2 \right)\phi_\alpha(r) - \sum_\beta \int dr' V_{\alpha\beta}(r,r')\phi_\beta(r') = 0$$

No approximation for estimation of T-matrix

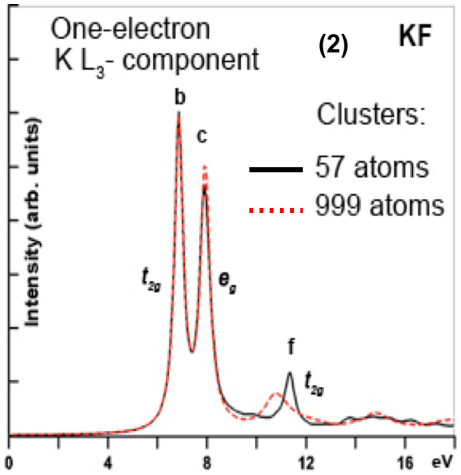
Taranukhina&Novakovich

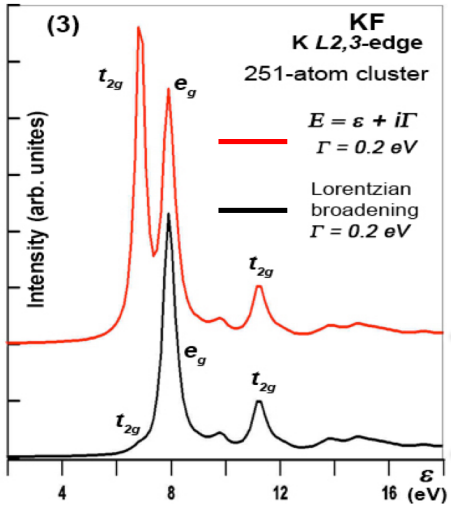
AT

Image:http://www.cutestpaw.com/images/stalin-the-cat/



Multiple scattering effect





Complex energy calculation

Just broadening

Step=0.005 eV (300 points for all spectra on Panels (1)-(3)

Taranukhina&Novakovich
(to be published)

AT

Multichannel scattering equation

$$\left(\nabla^2 + k_\alpha^2\right)\phi_\alpha^f(\mathbf{r}) = \sum_\beta \int V_{\alpha\beta}(\mathbf{r},\mathbf{r}')\phi_\beta^f(\mathbf{r}')\,\mathrm{d}\mathbf{r}'$$

$$\begin{aligned}
V_{\alpha\beta}(\mathbf{r},\mathbf{r}') &= V^d_{\alpha\beta} + V^{ex}_{\alpha\beta} + V^2_{\alpha\beta} \\
V^d_{\alpha\beta}(\mathbf{r},\mathbf{r}') &= \delta(\mathbf{r}-\mathbf{r}')\left[\int \rho_{\alpha\beta}(\mathbf{r}'',\mathbf{r}'')\,\frac{2}{|\mathbf{r}-\mathbf{r}''|}\,\mathrm{d}\mathbf{r}'' + \delta_{\alpha\beta}\Phi_Z(\mathbf{r})\right] \\
V^{ex}_{\alpha\beta}(\mathbf{r},\mathbf{r}') &= -\rho_{\alpha\beta}(\mathbf{r}',\mathbf{r})\left[\frac{2}{|\mathbf{r}-\mathbf{r}'|} - 1 + \frac{1}{2}(\Phi_Z(\mathbf{r}) + \Phi_Z(\mathbf{r}'))\right] \\
V^2_{\alpha\beta}(\mathbf{r},\mathbf{r}') &= -\int \rho^2_{\alpha\beta}(\mathbf{r},\mathbf{r}'';\mathbf{r}',\mathbf{r}'')\left(\frac{2}{|\mathbf{r}''-\mathbf{r}|} + \frac{2}{|\mathbf{r}''-\mathbf{r}'|}\right)\mathrm{d}\mathbf{r}''
\end{aligned}$$

Multiple scattering theory for non-local and multichannel potentials

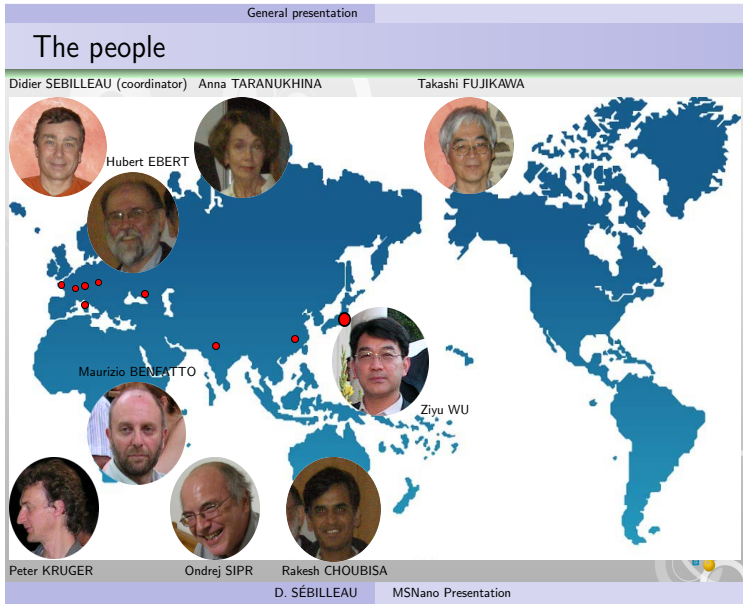
CN

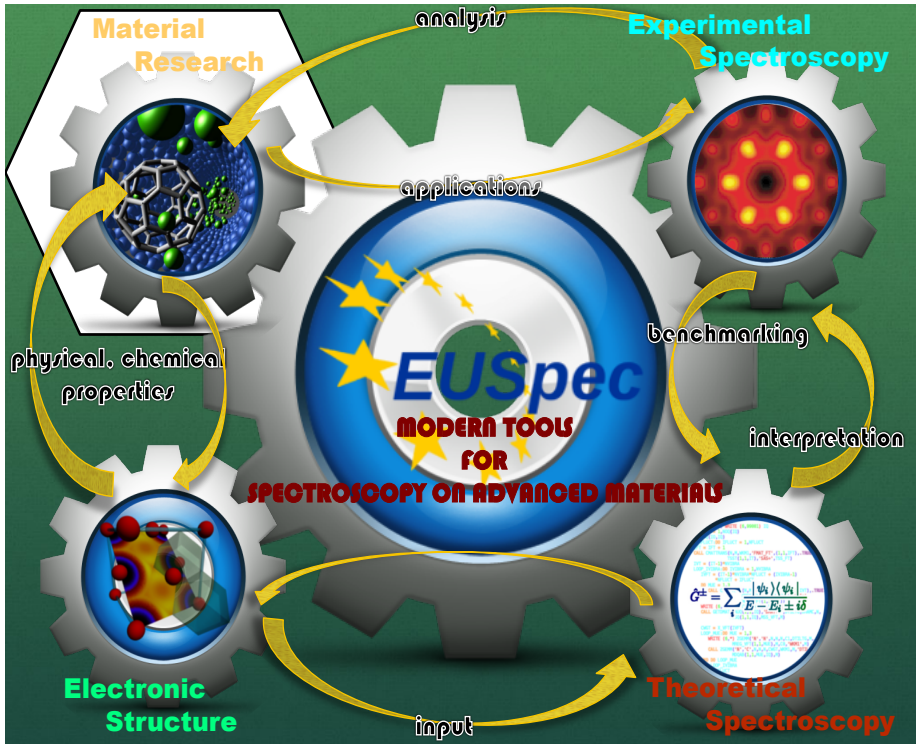
Calogero R Natoli[1,2], Peter Krüger[1], Keisuke Hatada[2,3], Kuniko Hayakawa[2,4], Didier Sébilleau[5] and Ondřej Šipr[6]

JPCM (2012)

The code is not yet implemented!

MSNano (IRSES)





From Sept/2012 to Aug/2016

Conclusions

- multichannel theory with particle-hole wave function by Kruger&Natoli (R-matrix) and Taranukhina&Novakovich (Dyson eq.)
- TiO_2 spectra perfectly reproduced for the first time by KN.
- D-E splitting is a long range band structure effect, local distortions play no role
- TN's approach has less restriction for theory, but numerically it is difficult for developers.
- methods work well for light 3d elements
- $3d^n$ case is under development

Acknowlegdements

Several slides are provided as a courtesy of Peter Kruger (PK), Calogero Natoli (CN) and Anna Taranukhina (AT), those are indicated by their initials at the low left corner


Thank you for your attention!!
Hvala!