

Computational X-Ray Spectroscopy

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Section 1

Background

What Is X-Ray Spectroscopy?

- Use X-Rays to investigate molecular physics
- Probes electronic structure
- Chemical properties
- Study collective excitations
- Important applications in nano-science, materials science, chemical physics, and condensed matter physics

What is X-Ray Photoelectron Spectroscopy

- Photoelectric effect
- Intensity of ejected electrons vs. kinetic energy
- Study quasi-particle excitations
- Experiments conducted in high-vacuum
- Often use high-energy synchrotron x-rays

Goal

To calculate a spectrum from first principles and have it agree with experiment.

- Typically ~ 10 atoms
- Typically ~ 10 electron per atom
- **Many** body problem
- Often ignore core electrons
- Often ignore nuclear motion

Fermi Rule

The XPS photocurrent is given by $J_k(\omega)$ ¹

$$J_k(\omega) = \sum_f |\langle f, N-1; \vec{k} | \hat{H}_{\text{dipole}} | 0, N \rangle|^2 \delta(\omega - \omega_s) \quad (1)$$

Looks simple to calculate! But it isn't...

- Need eigenstates
- Must sum over **many** states
- Photoelectron not separable
- Core-hole also interacts

¹ J.J. Kas, F.D. Vila, J.J. Rehr, S.A. Chambers, Physical Review B 91, 12112(R) (2015): d.o.i. 10.1103/PhysRevB.91.121112

Electrons and Photons

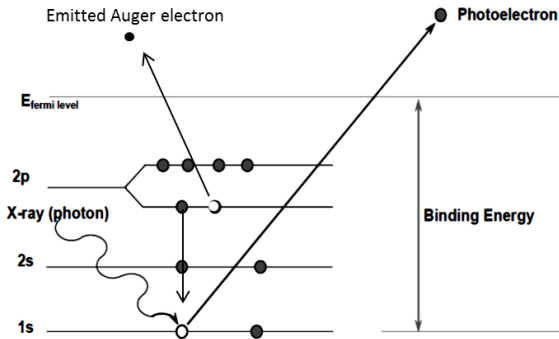


Figure 1: A diagram demonstrating the XPS interaction

Excitations

- Appear as secondary “satellite” peaks
- Due to inelastic losses
- Collective excitations absorb energy
- Mostly plasmons

Plasmon

Quanta of valence electron oscillation. Analogous to phonons and lattice vibrations. Couples to both photoelectron and core-hole.

Spectral Function $A(\omega)$

- Roughly proportional to $J_k(\omega)$
- Represents distribution of energies
- Are normalized to one
- Calculated using density fluctuations

$A(\omega)$

$$A(\omega) = -\frac{1}{\pi} \text{Im} \int d\omega e^{i\omega t} G_c(t) \quad (2)$$

where $G_c(t)$ is the Green's function for the core-hole²

²Ibid

Project Background

- Used RT-SIESTA
- DFT/TD-DFT calculation of electron density
- Pseudo-potentials
- Basis set of LCAO
- Relax to ground state
- Add core-level Coulomb potential
- Calculate density fluctuations in **real time**
- Effective to ~ 300 atoms

Section 2

Project

Subsection 1

Sexithiophene

Sexithiophene

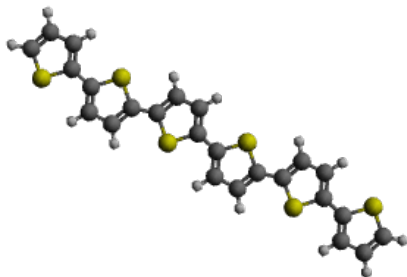


Figure 2: Sexithiophene

What is sexithiophene?

- Planar molecule
- Rotationally symmetric 180° about midpoint
- Formula is $C_{24}S_6H_{10} \Rightarrow 250e^-$
- Possible uses as organic semiconductor
- Label Sulphur from outermost (*S1*) to innermost (*S3*)

Experimental Data

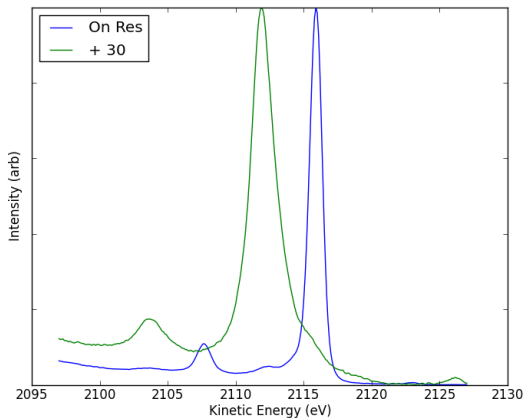


Figure 3: The “On Res” curve is the XPS for sexithiophene on the Sulphur resonant energy.

Computed Results

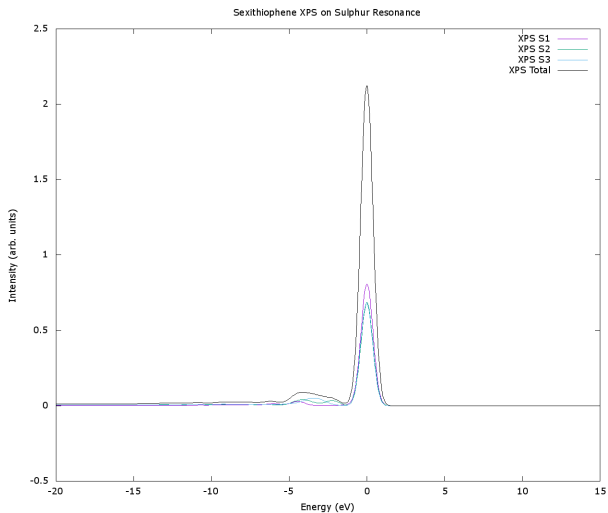


Figure 4: The XPS for each individual sulphur atom and their sum

Subsection 2

C_{60} Fullerene

C_{60} Fullerene

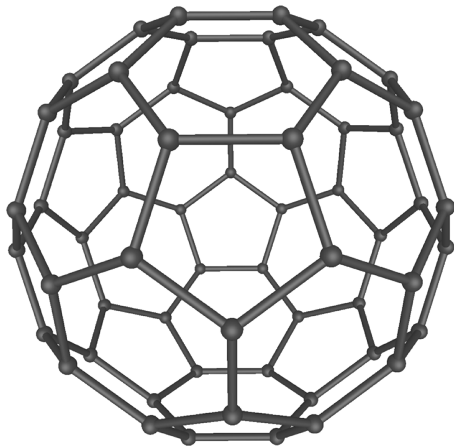


Figure 5: C_{60} Fullerene “Bucky-ball”

C_{60} Fullerene Crystal

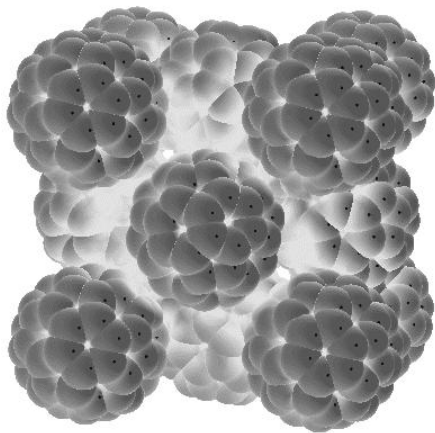


Figure 6: C_{60} fcc crystal

What is Fullerene?

- Most common of the fullerenes
- Molecule has diameter ~ 1 nm
- Forms face-centered cubic (fcc) crystals in solid phase
- Natural semi-conductor
- Can be doped to become super-conducting
- Nano-engineering

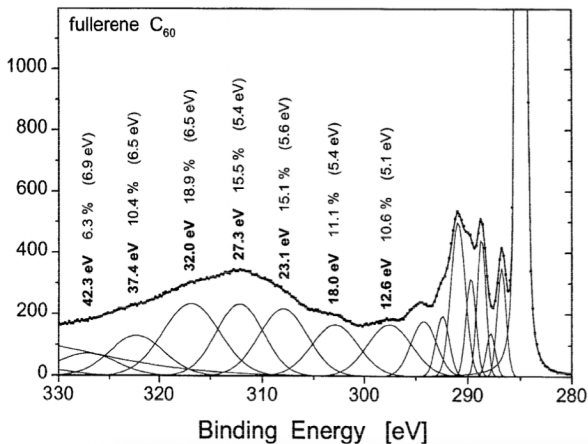


Figure 7: Measured C60 XPS

Comparison

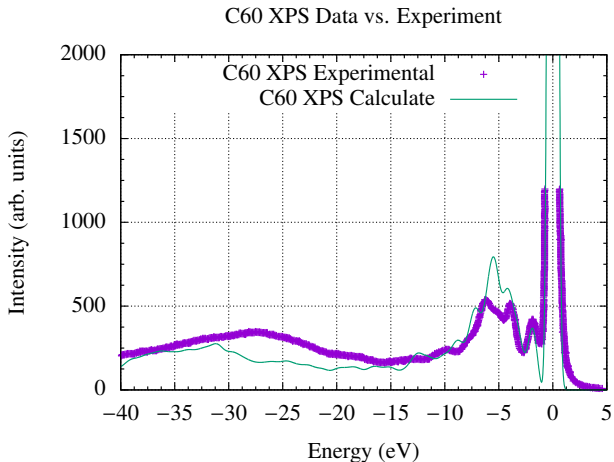


Figure 8: Comparison of calculated and measured. Centered and rescaled to same sizes

Subsection 3

Transition Metals

Transition Metals

- Metals like *Ni*, *Co*, and *Fe*
- Many-body effects are very important
- Possible applications to highly-correlated systems
- “High T_c ” super conductors
- Crystalline structure requires band-theory in addition to molecular theory

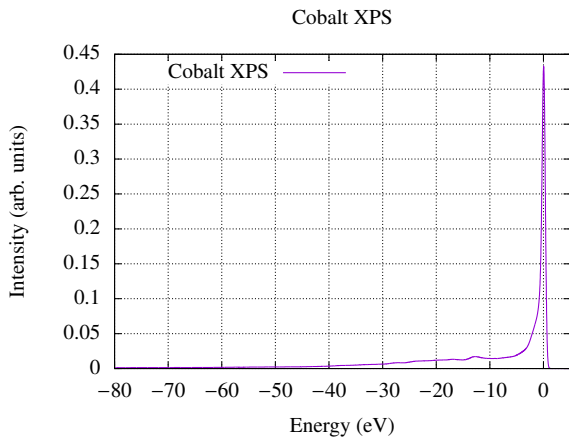


Figure 9: Calculated Cobalt XPS

Section 3

Future Efforts

Sexithiophene

- Include ghost atoms
- Examine different core charges
- Density fluctuations at frequency
- Ongoing investigation

- Examine crystal effects
- Compute XAS with many body effects
- Include extrinsic interactions
- Compare with graphene

Transition Metals

- Check for supercell convergence
- Analyze other metals
- Compare to experiment
- Check accuracy of quasi-peak weights
- Apply to correlated materials

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Section 4

Backup Slides

Energy Spectrum⁴

SIESTA outputs potential energy of density fluctuations $\Delta(t)$.
First compute the energy spectrum $\beta(\omega)$

$$\beta(\omega)/\omega = \text{Re} \int dt e^{-i\omega t} \Delta(t) \quad (3)$$

and then the cumulant $C(t)$

$$C(t) = \int \beta(\omega) \left(\frac{e^{i\omega t} - i\omega t - 1}{\omega^2} \right) d\omega \quad (4)$$

Finally, the spectral function

$$A(\omega) = -\frac{1}{\pi} \text{Re} \int e^{i\omega t} e^{C(t)} dt \quad (5)$$

⁴ J.J. Kas, F.D. Vila, J.J. Rehr, S.A. Chambers, Physical Review B 91, 12112(R) (2015): d.o.i. 10.1103/PhysRevB.91.121112

Calculated XPS

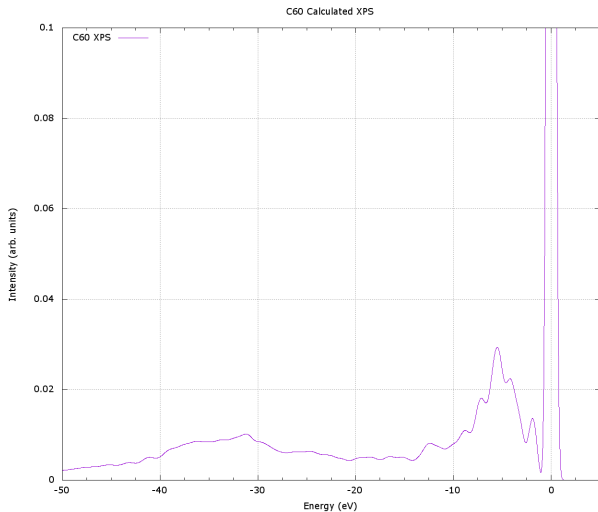


Figure 10: Calculated XPS of C60. Quasi-peak weight of $Z = 58.4\%$

Peak Weights

Material	Z	$1 - Z$
S1	.768	.232
S2	.666	.334
S3	.667	.333
C ₆₀	.584	.416
Fe	.316	.684
Co	.283	.717
Ni	.147	.853

Table 1: Quasi-particle peak weights, in increasing order of satellite weight. Z for metals may be inaccurate.

S1, S2, S3 refer to the various Sulphurs in sexithiophene