Modeling of X-ray spectroscopies

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4FUTURE Intensive course 2019:
Methods for Image and Spectral Data Analysis and Interpretation
Ultrafast dynamics in solution

Dynamics

- Electronic structure
- Solvation

Solar cell materials

Hybrid perovskites: Methylammonium lead triiodide

Great photovoltaic properties, but environmental hazards and instability
Theoretical spectrum simulations - Why bother?

Femtochemistry: "Filming" chemical reactions using ultra-fast lasers.
(Source: DESY Hamburg)
Theoretical spectrum simulations - Why bother?

Theory is required to develop the film

- Qualitative assignment
- Evaluate theoretical models
- Quantitative analysis
- Evaluate approximations

Femtochemistry: "Filming" chemical reactions using ultra-fast lasers. (Source: DESY Hamburg)
Outline

Spectrum simulations – Part I

Molecular orbital approach

Spectrum simulations – Part II

Electronic states approach

Dynamical effects

Excited state X-ray spectra
<table>
<thead>
<tr>
<th>Core-level spectroscopy</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray photo-electron spectroscopy</td>
<td>Core-ionization (Valence-ionization)</td>
</tr>
<tr>
<td>X-ray absorption spectroscopy</td>
<td>Core-excitation</td>
</tr>
<tr>
<td>X-ray emission spectroscopy</td>
<td>Fluorescence decay</td>
</tr>
<tr>
<td>Resonant inelastic X-ray Scattering</td>
<td>Fluorescence decay</td>
</tr>
</tbody>
</table>

**XPS XAS XES RIXS**

| Resonant photo-electron spectrosc. | Auger decay (dominate for small Z) |
Quantum Chemistry $\hat{H} \Psi = E \Psi$

**Hartree-Fock**

1) Born-Oppenheimer
2) Mean-field approx.

$\Psi_{HF} = \text{det} | \phi_1, \phi_2, \ldots, \phi_N |$

Momentary $e^- - e^-$ correlation missing!

**DFT**

Singlet determinant

Correlation in $\hat{H}$

**Post-HF**

Multi-determinant

Wave function correlated

**Ab initio Molecular dynamics**

F=ma

$F_i = -\nabla_i \langle H_e \rangle \approx -\langle \Psi_0 | \nabla_i H_e | \Psi_0 \rangle$

AIMD: CPMD Cp2k

**Quantum dynamics**

$i \hbar \frac{\partial}{\partial t} \Phi(\{r_i\}, \{R_I\}; t) = H \Phi(\{r_i\}, \{R_I\}; t)$

QMD: Wave packet simulations
Molecular orbitals of $\text{H}_2\text{O}(g)$ – $C_{2v}$ Point group

- $2a_1$ (02s)
- $1a_1$ (01s)
- $2b_2$ (4a_1)
- $1b_1$ (3a_1)
- $1b_2$
Spectrum simulations $\mathcal{H}\Psi=E\Psi$

Accurate methods
Electronic states

$\Delta E = E_{\text{tot}}(\Psi_i) - E_{\text{tot}}(\Psi_j)$

$|\langle \Psi_i | O | \Psi_i \rangle|^2$

Core-excited

Valence excited

Ground state

Approximate methods
Molecular orbitals

Transition potential DFT

$|\langle \Psi_i | O | \Psi_i \rangle|^2 = |\langle \phi_m | O | \phi_n \rangle|^2$
Spectrum simulations $\mathcal{H}\Psi = E\Psi$

$$E_{\text{tot}}(\Psi_i) - E_{\text{tot}}(\Psi_j)$$

$$|<\Psi_i|O|\Psi_i>|^2$$

**Broadening:**
- Core-hole life-time
- Vibrational
- Configurational
- Experimental
Orbital representation of the XPS and XES processes

- **XPS**: Photo-ionization
- **XES**: X-ray emission

The diagram illustrates the processes using orbital representations.
Orbital representation of the XPS and XES processes

**Photo-ionization**

**XPS**

**X-ray emission**

**XES**

**Ground state orbitals**

\[
\begin{align*}
\phi_1 & \quad \varepsilon_1 \\
\phi_2 & \quad \varepsilon_2 \\
\phi_3 & \quad \varepsilon_3 \\
\phi_4 & \quad \varepsilon_4 \\
\phi_5 & \quad \varepsilon_5 \\
\phi_6 & \quad \varepsilon_6 \\
\phi_7 & \quad \varepsilon_7
\end{align*}
\]
Orbital representation of the XA process

XAS

Half-core-hole

\[ \phi_1 \quad \epsilon_1 \]
\[ \phi_2 \quad \epsilon_2 \]
\[ \phi_3 \quad \epsilon_3 \]
\[ \phi_4 \quad \epsilon_4 \]
\[ \phi_5 \quad \epsilon_5 \]
\[ \phi_6 \quad \epsilon_6 \]
\[ \phi_7 \quad \epsilon_7 \]

Full-core-hole

\[ \text{FH} \]
X-ray spectroscopy Case study: H₂O(g)

XPS
Photoelectron spectroscopy

XES
Decay channels to valence-ionized states

XAS
X-ray Absorption and Emission Spectroscopy

RIXS
Decay channels to valence-excited states

O₁s¹
Photo electron spectroscopy of H$_2$O(g,l,s)

\[ E_{\text{binding}} = E_{\text{photon}} - E_{\text{kin}} \]

Koopman’s theorem

HF orbital energies approximate

Ionization binding energies

(However, we will cheat and also use DFT Kohn-Sham energies which require ad hoc shifts)

D. Nordlund et al
CPL 460 86 (2008)
Photo electron spectroscopy of H$_2$O(g,l,s)

Franck-Condon

Vibrational excitations

D. Nordlund et al
CPL 460 86 (2008)
Photo electron spectroscopy of H$_2$O(g,l,s)

Inhomogeneous Broadening

(Homogeneous broadening is due to finite life-times)

D. Nordlund et al
CPL 460 86 (2008)
Photo electron spectroscopy of H$_2$O(g,l,s)

Cross-sections vary with photon energy

D. Nordlund et al
CPL 460 86 (2008)
Photo electron spectroscopy of H₂O(l,s)

Notice: In C₂ᵥ symmetry only a₁ can have oxygen s-sym.

D. Nordlund et al
CPL 460 86 (2008)
Hydrogen bond dynamics

Intact H-bonds

H-bond breakage

D. Nordlund et al
CPL 460 86 (2008)

Car-Parrinello MD simulations

Time evolution of the electronic structure due to hydrogen bond dynamics
Hydrogen bonding in water

Strong overlap in $3a_1$

D. Nordlund et al
CPL 460 86 (2008)
Franck-Condon

Inhomogeneous broadening

Chemical bonding

Hydrogen bonding and dynamics
Aqueous ammonia:
Energy mismatch in orbital mixing

O PDOS would dominate in valence XPS

N K-edge XES can cut-out N p-PDOS

M. Ekimova et al. DOI: 10.1021/jacs.7b07207
J. Am. Chem. Soc. 2017, 139, 12773–12783
X-ray emission spectroscopy of NH$_3$ (g) and NH$_3$ (aq)

L. Weinhardt, E. Ertan, M. Iannuzzi, M. Weigand, O. Fuchs, M. Bär, M. Blum, J. D. Denlinger, W. Yang, M. Odelius E. Umbach, and C. Heske.
Electronic structure of \( \text{NH}_3 \) (g) and \( \text{NH}_3 \) (aq)

XES calc.
RIXS spectroscopy of NH$_3$(aq)
The effect of pH

Aqueous ammonia: Energy mismatch

M. Ekimova et al. DOI: 10.1021/jacs.7b07207
J. Am. Chem. Soc. 2017, 139, 12773–12783
Hydration structure of $\text{NH}_3(\text{aq})$ and $\text{NH}_4^+(\text{aq})$

pH dependence in N K-edge X-ray absorption

M. Ekimova et al. DOI: 10.1021/jacs.7b07207
J. Am. Chem. Soc. 2017, 139, 12773–12783

![Diagram showing hydration structures and XAS intensity plots for $\text{NH}_3(\text{aq})$ and $\text{NH}_4^+(\text{aq})$. The plots compare XFH calculation with experiment, noting 180 configurations.]
Transition potential approximations of N K-edge XAS

In our case, XFH and FH are superior to HH

M. Ekimova et al. DOI: 10.1021/jacs.7b07207
J. Am. Chem. Soc. 2017, 139, 12773–12783
Electronic relaxation in the presence of the core-hole
N K-edge XAS of NH$_3$(aq) and NH$_4^+$(aq)

(a) $\text{NH}_3$ (red) and $\text{NH}_4^+$ (blue) XAS intensities. 
- **XFH Calculation**

(b) XAS intensities from experiment.
- **Excitation energy / eV**

M. Ekimova et al. DOI: 10.1021/jacs.7b07207

*J. Am. Chem. Soc.* 2017, 139, 12773–12783
N K-edge XAS of NH$_3$(aq) and NH$_4^+$(aq)

NH$_3$(aq):
Whole XAS blue-shifted by accepting H-bonding

NH$_4^+$(aq):
Pre-edge intensity due to distortions
Main-edge slightly red-shifted by donating H-bonding
Post-edge not well reproduced

M. Ekimova et al. DOI: 10.1021/jacs.7b07207
J. Am. Chem. Soc. 2017, 139, 12773–12783
Perovskite solar cells: PbI$_3$CH$_3$NH$_3$

**XPS and XES**

R. Wilks, M. Bär ....A. Erbing, M. Odelius

![Graph showing XPS and XES data](image-url)
Perovskite solar cells: $\text{PbI}_3\text{CH}_3\text{NH}_3$

Photo-energy dependence in XPS
Perovskite solar cells: PbI$_3$CH$_3$NH$_3$

Photo-energy dependence in XPS

![XPS Spectra](image)
Orbital energies derived from XAS and XPS of an organic dye

Molecular structure of D5.

XAS

ΔE?

E. Johansson et al

Orbital energies derived from XAS and XPS of an organic dye

Molecular structure of D5.

Valence XPS show that HOMO resides on TAA

Lowest UV excitation is a TAA → CN charge transfer

E. Johansson et al

Outline

Spectrum simulations – Part I

Molecular orbital representation

XPS  - Chemical environment
   - Chemical bonding

XES  - Local element-specific projection

XAS  - Local element-specific projection
   - Relaxation in presence of core-hole
   - Alignment of energy scales