Simulating X-ray Spectroscopies with CP2K

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CONEXS SUMMER SCHOOL 2019:
Analysing X-ray Spectroscopy
Theoretical spectrum simulations – Why bother?

Femtochemistry: "Filming" chemical reactions using ultra-fast lasers.
(Source: DESY Hamburg)
Theory is required to develop the film

Qualitative assignment

Quantitative analysis

Evaluate theo. models

Evaluate approximations

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

Introduction

X-ray photo-electron spectroscopy (XPS)
- Example: XPS on $\text{H}_2\text{O}(g,l,s)$
- CP2K input

Molecular dynamics (MD)
- Basic theory
- Example: H-bond dynamics in $\text{H}_2\text{O}(l)$
- CP2K input

X-ray emission spectroscopy (XES)
- Example: XES on $\text{NH}_3(aq)$
- CP2K input

Bonus example: XPS on perovskite solar cells
Quantum Chemistry $\hat{H}\Psi=E\Psi$

<table>
<thead>
<tr>
<th>Hartree-Fock</th>
<th>DFT</th>
<th>Post-HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Born-Oppenheimer</td>
<td>Singlet determinant</td>
<td>Multi-determinant</td>
</tr>
<tr>
<td>2) Mean-field approx.</td>
<td>Correlation in $\hat{H}$</td>
<td>Wave function correlated</td>
</tr>
</tbody>
</table>

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

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

Ab initio Molecular dynamics

$$-\nabla I V = F_I = m_I a_I$$

$$F_I = -\nabla I \min_{\phi_i} \{ E_{KS}(\phi_i); R_I \}$$

Quantum dynamics

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

AIMD: CPMD CP2K

QMD: Wave packet simulations
Quantum Chemistry $H\Psi = E\Psi$

Hartree-Fock

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

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

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

Post-HF

Singlet determinant

Correlation in $H$

Wave function correlated

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

Ab initio Molecular dynamics

$-\nabla I V = F_I = m_I a_I$

$F_I = -\nabla I \min_{\phi_i} \{ E_{KS}(\{\phi_i\}; R_I) \}$

Quantum dynamics

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

AIMD: CPMD CP2K

QMD: Wave packet simulations
Core-level spectroscopy

- X-ray photo-electron spectroscopy
- X-ray absorption spectroscopy
- X-ray emission spectroscopy

Core-ionization (Valence-ionization)
Core-excitation
Fluorescence decay

XPS  XAS  XES
Spectrum simulations $\hat{H} \Psi = E\Psi$

Accurate methods
Electronic states

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

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

Core-excited

Valence excited

Ground state

Approximate methods
Molecular orbitals

Transition potential DFT

$|<\Psi_i|O|\Psi_j>|^2 = |<\phi_n|O|\phi_m>|^2$
Orbital representation of the XPS and XES processes

Photo-ionization

XPS

Photo-ionization

XPS

X-rays emission

XES
Orbital representation of the XPS and XES processes

Photo-ionization

XPS

\[ \hbar n \]

X-ray emission

XES

\[ \hbar n \]

Ground state orbitals

\[ \phi_1, \varepsilon_1 \]
\[ \phi_2, \varepsilon_2 \]
\[ \phi_3, \varepsilon_3 \]
\[ \phi_4, \varepsilon_4 \]
\[ \phi_5, \varepsilon_5 \]
\[ \phi_6, \varepsilon_6 \]
\[ \phi_7, \varepsilon_7 \]
Broadening:

\[ E_{\text{tot}}(\Psi_i) - E_{\text{tot}}(\Psi_j) \]

\[ |<\Psi_j|O|\Psi_i>|^2 \]

Core-hole life-time
Vibrational
Configurational
Experimental
**Broadening:**

How to simulate it?

Simplest approach:
Convolution with Gaussian functions

\[
I(E) = \sum_{i} f(\epsilon_i) e^{-(E-\epsilon_i)^2/2\sigma^2}
\]

**Width parameter**

\[
\text{FWHM} = 2\sqrt{2}\log(2)\sigma
\]

Other functions, e.g. Lorentzians
Molecular orbitals of $\text{H}_2\text{O(g)}$ - $\text{C}_{2v}$ Point group

$4a_1$ $2b_2$

$1b_1$

$3a_1$

$1b_2$

O2s ($2a_1$)

O1s ($1a_1$)
X-ray spectroscopy Case study: H$_2$O(g)

**XPS**

Photoelectron spectroscopy

**XES**

Decay channels to valence-ionized states

X-ray Absorption and Emission Spectroscopy
Photo-electron spectroscopy of $\text{H}_2\text{O}(g,l,s)$

$E_{\text{binding}} = E_{\text{photon}} - E_{\text{kin}}$

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 $\text{H}_2\text{O}(g, l, s)$

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 $\text{H}_2\text{O}(g,l,s)$

Cross sections vary with photon energy

C. binding energies (eV) are:
- 1s (2) 290.860
- 2s (2) 17.5409
- 2p (2) 8.98202
Notice: In $C_{2v}$ symmetry only $a_1$ can have oxygen s-sym.
In CP2K:

**PDOS section**

```plaintext
&FORCE_EVAL
  &DFT
  ... 
  &SCF
  ...
  &END SCF
  &PRINT
  ...
  &PDOS
  FILENAME ./PDOS_H2O
  NLUMO 10
  &LDOS
    LIST 1 4 7
  &END
  &LDOS
    LIST 2
  &END
  &END PDOS
  &END PRINT
  &END DFT
  &END FORCE_EVAL
```

**Output**

![Projected DOS for atomic kind 0 at iteration step 1 = 0, E(Fermi) = -0.092095 a.u.](image)

![Projected DOS for atomic kind 0 at iteration step 1 = 0, E(Fermi) = -0.242711 a.u.](image)

E.g. `PDOS_H2O-k1-1.pdos`
Molecular Dynamics

Molecular dynamics (MD)

Why bother with MD?

- Temperature
- Bond dynamics
- Reactions
- (Much more!)

D. Nordlund et al
CPL 460 86 (2008)
Molecular dynamics (MD)

Newton’s equations of motion

\[ F_I = m_I a_I \]
Molecular dynamics (MD)

Newton’s equations of motion

\[ F_I = m_I a_I , \quad F_I = -\nabla_I V \]

Two problems: Calculating forces and integrating EoMs

Velocity Verlet

\[ \mathbf{R}(t + \delta t) = \mathbf{R}(t) + \mathbf{V}(t)\delta t + \frac{1}{2M} \mathbf{F}(t)\delta t^2 \]

\[ \mathbf{V}(t + \delta t) = \mathbf{V}(t) + \frac{1}{2M} [\mathbf{F}(t) + \mathbf{F}(t + \delta t)] \delta t \]
Molecular dynamics (MD)

Newton’s equations of motion

\[ F_I = m_I a_I , \quad F_I = -\nabla_I V \]

Two problems: Calculating forces and integrating EoMs

Classical MD:

Force fields

- Good for larger systems

\[ V = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - 2 \left( \frac{\sigma}{r} \right)^6 \right] \]
Molecular dynamics (MD)

Newton’s equations of motion

\[ F_I = m_I a_I , \quad F_I = -\nabla_I V \]

Two problems: Calculating forces and integrating EoMs

Classical MD:

- Force fields
  - Good for larger systems

Ab initio MD (AIMD):

- Born-Oppenheimer MD
  - In CP2K
- Car-Parrinello MD
  - In CPMD
Born-Oppenheimer MD

Parameter-free force expression

\[ F_I = -\nabla_I \min_{\phi_i} \left\{ E_{KS}(\{\phi_i\}; R_I) + \text{constr.} \right\} \]

Electronic orbitals optimized at each step
Hydrogen bond dynamics

Time evolution of the electronic structure due to hydrogen bond dynamics

D. Nordlund et al
CPL 460 86 (2008)
Hydrogen bonding in water

Strong overlap in $3a_1$
In CP2K:

Use MD as run type

MD Section

- Ensemble
- Time step
- Temperature
- Thermostat
- Printing
Molecular Dynamics in CP2K

In CP2K:

Output

Trajectory

E.g. water_liquid-1.ener
In CP2K:

Initial guess of wave function

- ASPC (recommended) for faster convergence in the SCFs while keeping stability
- USE_GUESS for the same initial guess for all steps
In CP2K:

Plotting molecular orbitals

- Cube-file format \texttt{.cube}
- Can be visualized in software like VMD, VESTA, or GaussView
- Be careful when writing and storing cube-files as they take up a lot of space!
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
Electronic structure of NH$_3$(g) and NH$_3$(aq)
X-ray emission spectroscopy of NH$_3$ (g) and NH$_3$ (aq)

XES in CP2K

In CP2K:

XAS section

- Choose method to compute transition potential
- Remember to use an all electron potential / basis set
- The optimal method might vary between systems

Output spectrum

<table>
<thead>
<tr>
<th>Emission spectrum for atom</th>
<th>1, index of excited core M0 is</th>
<th>1, # of lines</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00000000</td>
<td>0.00000000</td>
<td>-0.00000000</td>
</tr>
<tr>
<td>2</td>
<td>485.71459420</td>
<td>-0.00563467</td>
<td>-0.22020527</td>
</tr>
<tr>
<td>3</td>
<td>497.86840667</td>
<td>-0.87279925</td>
<td>0.01937984</td>
</tr>
<tr>
<td>4</td>
<td>501.75564296</td>
<td>-0.02221183</td>
<td>0.87187036</td>
</tr>
<tr>
<td>5</td>
<td>504.10422332</td>
<td>-0.00300028</td>
<td>0.32795079</td>
</tr>
</tbody>
</table>
Perovskite solar cells: \( \text{CH}_3\text{NH}_3\text{PbI}_3 \)

Photo-energy dependence in XPS

J. Phys. Chem. C 121 48
Perovskite solar cells: $\text{CH}_3\text{NH}_3\text{PbI}_3$

Photo-energy dependence in XPS

Perovskite solar cells: $\text{CH}_3\text{NH}_3\text{PbI}_3$

Photo-energy dependence in XPS

Perovskite solar cells: $\text{CH}_3\text{NH}_3\text{PbI}_3$

Understanding the valence band from orbitals

J. Phys. Chem. C 121 48
Thank you for your attention!

Questions?