Calculations of X-ray photoemission spectra

- X-ray photoemission spectroscopy
- Multiple splitting of binding energies
- Energy expression of absolute energies
- Core hole calculations
- Benchmark calculations and Applications
- Usage of OpenMX for the XPS calc.
- Exercises

Taisuke Ozaki (ISSP, Univ. of Tokyo)

X-ray photoemission spectroscopy (XPS)

- Information of chemical composition, surface structure, surface adsorbate
- XPS with synchrotron radiation extends its usefulness, e.g., satellite analysis, core level vibrational fine structure, XPS circular dichroism, spin-resolved XPS, and XPS holography.
- How to calculate the absolute binding energies in solids?

We have developed a general method to calculate absolute binding energies of core levels in solids with the following features:

- applicable to insulators and metals
- accessible to absolute binding energies
- screening of core and valence electrons on the same footing
- SCF treatment of spin-orbit coupling
- exchange interaction between core and valence states
- geometry optimization with a core hole state
XPS experiments

In general, XPS requires high vacuum (P ~ 10^{-8} millibar) or ultra-high vacuum (UHV; P < 10^{-9} millibar) conditions.

Basic physics in X-ray photoelectron spectroscopy (XPS)

Escape time of photoelectron seems to be considered around $10^{-16}$ sec., resulting in relaxation of atomic structure would be ignored.
Surface sensitivity


Fig. 2. Inelastic mean free paths (IMFPs) for 41 elements, calculated using the TPP-2M formula: Li, Be, three forms of carbon (graphite, diamond, glassy C), Na, Mg, Al, Si, K, Sc, Ti, V, Cr, Fe, Co, Ni, Cu, Ge, Y, Nb, Mo, Ru, Rh, Pd, Ag, In, Sn, Cs, Gd, Tb, Dy, Hf, Ta, W, Re, Os, Ir, Pt, Au, and Bi. Five “outlier” elements are indicated to provide some idea of what electronic structure characteristics can give rise to deviations from the majority behavior: diamond and the alkali metals. The dashed straight line for higher energies represents a variation as $\lambda_e \propto E_{kin}^{0.78}$, and is a reasonable first approximation to the variation for all of the elements shown (from Ref. [23]).

- Inelastic Mean Free Path (IMFP) of photo excited electron for 41 elemental solids is shown the left figure.

- In case of the widely used aluminum K-alpha X-ray having 1486.7 eV, the IMFP is found to be $15 \sim 100$ Å.

- On the other hand, when X-rays generated by synchrotron radiation is utilized, which have energy up to 15 keV, the IMFP can be more than 100 Å.
Multiple splitting of core level binding energies

There are four kinds of physical origins for multiple splitting of core level binding energies at least.

- Chemical shift
- Spin-orbit coupling
- Exchange interaction
- Chemical potential shift
The binding energy shifts depending on its chemical environment. The amount of shift is primarily determined by its charge state, known to be initial state effect. After creating the core hole, the screening of the core hole is also an important factor to determine chemical shift, known to be final state effect.
Core level multiplet splittings: Spin-orbit splitting

In addition to the chemical shift, there are other multiplet splittings.

**Spin-orbit coupling of core level**

- Due to the strong SOC of core level states, the binding energy is split into two levels.
- The intensity ratio is $2l: 2(l+1)$ for $l-1/2$ and $l+1/2$, respectively.

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Core level multiplet splittings: Exchange interaction

Exchange interaction between core and valence electrons

Molecules

Hedman et al.,
Phys. Lett. 29A,

Solids

Fadley and Shirley,
PRA 2, 1109 (1970).

Fig. 1. ESCA spectra of core electron levels in N_2,
O_2, and NO. Paramagnetic splitting is observed for
the ls levels in the O_2 and NO molecules.

FIG. 1. Photoelectron spectra from MnF_2, MnO, and
MnO_2 in the kinetic-energy region corresponding to
ejection of Mn 3s and 3p electrons by Mg K\alpha x rays.
Energy conservation in XPS

\[ E_i (N) + h\nu = E_f (N - 1) + V_{\text{spec}} + K_{\text{spec}} \]
Core level binding energies in XPS #1

\[ E_i(N) + h\nu = E_f(N - 1) + V_{\text{spec}} + K_{\text{spec}} \]

Using a relation: \( V_{\text{spec}} = \mu + \varphi_{\text{spec}} \) we have

\[ E_b = h\nu - K_{\text{spec}} - \phi_{\text{spec}} = E_f(N - 1) - E_i(N) + \mu \]

The experimental chemical potential can be transformed as

\[ E_b = E_f^{(0)}(N - 1) + (N - 1)\Delta\mu - \left( E_i^{(0)}(N) + N\Delta\mu \right) + \mu_0 + \Delta\mu \]

A general formula of core level binding is given by

\[ E_b = E_f^{(0)}(N - 1) - E_i^{(0)}(N) + \mu_0 \]

This is common for metals and insulators.
Core level binding energies in XPS #2

For metals, the Janak’s theorem simplifies the formula:

\[ E^{(0)}_f (N - 1) - E^{(0)}_f (N) = \int \frac{d\eta}{\partial E^{(0)}_f} / \partial \eta = -\mu_0 \]

\[ E_b = E^{(0)}_f (N) - E^{(0)}_i (N) \]

The formulae of core level binding energies are summarized as

- **Solids (gapped systems, metals)**
  \[ E_b = E^{(0)}_f (N - 1) - E^{(0)}_i (N) + \mu_0 \]

- **Metals**
  \[ E_b = E^{(0)}_f (N) - E^{(0)}_i (N) \]

- **Gases**
  \[ E_b = E^{(0)}_f (N - 1) - E^{(0)}_i (N) \]
Chemical potential shift in gapped systems

In gapped systems, the chemical potential is highly sensitive to dopants, surface structure, and adsorbates.

This may explain the fact that reported binding energies are more dispersive for gapped systems than that for metals.
Within DFT, there are at least three ways to calculate the binding energies of core states as summarized below:

1. **Initial state theory**
   
   Simply the density of states is taken into account

2. **Core-hole pseudopotential method**
   
   Full initial and semi-final state effects are taken into account
   

3. **Core-hole SCF method**
   
   The initial and final state effects are fully taken into account on the same footing.
   
DFT calculation with a core hole

✓ How to create a core hole?

✓ How to eliminate the spurious interaction between supercells?
Constraint DFT with a penalty functional

\[ E_f = E_{\text{DFT}} + E_p \]

\( E_{\text{DFT}} \) is a conventional functional of DFT, and \( E_p \) is a penalty functional defined by

\[ E_p = \frac{1}{V_B} \int dk^3 \sum_{\mu} f^{(k)}_{\mu} \langle \psi^{(k)}_{\mu} | P | \psi^{(k)}_{\mu} \rangle \]

\[ P = \left| R\Phi^M_J \right\rangle \Delta \left\langle R\Phi^M_J \right| \]

R: radial function of the core level

The projector is given by a solution of Dirac eq. for atoms.

\[ J = l + \frac{1}{2}, M = m + \frac{1}{2} \quad J = l - \frac{1}{2}, M = m - \frac{1}{2} \]

\[ |\Phi^M_J\rangle = \left( \frac{l+m+1}{2l+1} \right)^{\frac{1}{2}} |Y^m_l\rangle + \left( \frac{l-m}{2l+1} \right)^{\frac{1}{2}} |Y^{m+1}_l\rangle \]

\[ |\Phi^M_J\rangle = \left( \frac{l-m+1}{2l+1} \right)^{\frac{1}{2}} |Y^{m-1}_l\rangle + \left( \frac{l+m}{2l+1} \right)^{\frac{1}{2}} |Y^m_l\rangle \]
Elimination of inter-core hole interaction

$$\rho_f(\mathbf{r}) = \rho_i(\mathbf{r}) + \Delta \rho(\mathbf{r})$$

\[\Delta \rho(\mathbf{r}) = \rho_f(\mathbf{r}) - \rho_i(\mathbf{r})\]

- Periodic Hartree potential is calculated by charge density of the initial state.
- Potential by induced charge is calculated by an exact Coulomb cutoff method.
Exact Coulomb cutoff method #1

If the charge induced by a core hole localizes within a radius of $R$, we can set $R_c = 2R$, and the cutoff condition becomes $2R_c < L$ to eliminate the inter-core hole interaction.

$$v_H(r) = \sum_G \tilde{n}(G)\tilde{v}(G)e^{iG \cdot r} \quad \tilde{v}(G) = \frac{4\pi}{G^2} (1 - \cos GR_c)$$

Jarvis et al., PRB 56, 14972 (1997).
Convergence w. r. t. cell size

General formula

\[ E_b = E_f^{(0)}(N - 1) - E_i^{(0)}(N) + \mu_0 \]  

(3)

For metals

\[ E_b = E_f^{(0)}(N) - E_i^{(0)}(N) \]  

(4)

- Convergence is attainable around 15~20Å.
- The formula for metals is not applicable for gapped systems.
- Very fast convergence by Eq. (4) for metals.
Difference charge induced by a core hole in Si

- The effective radius is about 7 Å.
- The core hole is almost screened on the same Si atom.
# Absolute values: Expt. vs. Calcs. for **solids**

<table>
<thead>
<tr>
<th>Material</th>
<th>State</th>
<th>Calc. (eV)</th>
<th>Expt. (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gapped system</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c-BN</td>
<td>N-1s</td>
<td>398.87</td>
<td>398.1*</td>
</tr>
<tr>
<td>bulk NH₃</td>
<td>N-1s</td>
<td>398.92</td>
<td>399.0⁺</td>
</tr>
<tr>
<td>Diamond</td>
<td>C-1s</td>
<td>286.50</td>
<td>285.6†</td>
</tr>
<tr>
<td>Si</td>
<td>Si-2p₁/₂</td>
<td>100.13</td>
<td>99.8*</td>
</tr>
<tr>
<td>Si</td>
<td>Si-2p₃/₂</td>
<td>99.40</td>
<td>99.2*</td>
</tr>
<tr>
<td><strong>Semimetal or Metal</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graphene</td>
<td>C-1s</td>
<td>284.23</td>
<td>284.4†</td>
</tr>
<tr>
<td>TiN</td>
<td>N-1s</td>
<td>396.43</td>
<td>397.1§</td>
</tr>
<tr>
<td>TiC</td>
<td>C-1s</td>
<td>281.43</td>
<td>281.5*</td>
</tr>
</tbody>
</table>

Mean absolute error: 0.4 eV, Mean relative error: 0.16 %
## Absolute values: Expt. vs. Calcs. for gases

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Calc. (eV)</th>
<th>Expt.* (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>C-1s state</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>295.87</td>
<td>296.19</td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
<td>291.24</td>
<td>291.17</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>296.89</td>
<td>297.66</td>
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<tr>
<td>HCN</td>
<td>293.35</td>
<td>293.50</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>290.50</td>
<td>290.79</td>
</tr>
<tr>
<td>H$_2$CO</td>
<td>294.00</td>
<td>294.47</td>
</tr>
<tr>
<td><strong>N-1s state</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N$_2$</td>
<td>409.89</td>
<td>409.83</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>404.70</td>
<td>405.60</td>
</tr>
<tr>
<td>N$_2$H$_4$</td>
<td>404.82</td>
<td>406.1</td>
</tr>
<tr>
<td>HCN</td>
<td>406.16</td>
<td>406.36</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>408.24</td>
<td>408.66</td>
</tr>
<tr>
<td>N$_2$O$_5$</td>
<td>411.98</td>
<td>412.57</td>
</tr>
<tr>
<td>NO(S=0)</td>
<td>410.62</td>
<td>411.6</td>
</tr>
<tr>
<td>NO(S=1)</td>
<td>410.10</td>
<td>410.2</td>
</tr>
<tr>
<td><strong>O-1s state</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>542.50</td>
<td>542.4</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>541.08</td>
<td>541.2</td>
</tr>
<tr>
<td>O$_2$(S=1/2)</td>
<td>543.15</td>
<td>544.2</td>
</tr>
<tr>
<td>O$_2$(S=3/2)</td>
<td>542.64</td>
<td>543.1</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>539.18</td>
<td>539.9</td>
</tr>
<tr>
<td><strong>Si-2p state</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiH$_4$</td>
<td>106.56</td>
<td>107.3</td>
</tr>
<tr>
<td>Si$_2$H$_6$</td>
<td>106.21</td>
<td>106.86</td>
</tr>
<tr>
<td>SiF$_4$</td>
<td>111.02</td>
<td>111.7</td>
</tr>
<tr>
<td>SiCl$_4$</td>
<td>109.32</td>
<td>110.2</td>
</tr>
</tbody>
</table>

Mean absolute error: 0.5 eV  
Mean relative error:  0.22 %
The XPS data is well compared with the calculated binding energy of planar-like structure.

By the Yoshinobu-lab. in ISSP

Borophene on Ag

Computational model

STM images from Feng et al, PRB 94, 041408 (2016).

DFT-GGA

B-1s binding energies

I. Matsuda group in ISSP

experiment

Bonding in borophene

The higher coordination number, the lower number of bondings.

<table>
<thead>
<tr>
<th>Binding energy</th>
<th>Coordination</th>
<th>Bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>186.228 eV</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>186.946 eV</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>188.646 eV</td>
<td>6</td>
<td>2</td>
</tr>
</tbody>
</table>

0.125 e/bohr$^3$
In collaboration with experiments and simulations, the local structure and the electronic states of Pt atoms monodispersed on graphene were clarified in details.


Calculated XPS binding energies of Pt 4f\textsubscript{7/2}
Let me explain the usage by taking an example, TiC, where the unit cell contains 8 atoms. We define atomic species and unit vectors for both the ground and exited states as

```
Species.Number  3
<Definition.of.Atomic.Species
  Ti  Ti7.0-s3p2d2       Ti_PBE19
  C   C6.0_1s-s3p2d1     C_PBE19_1s
  C1  C6.0_1s_CH-s3p2d1  C_PBE19_1s
Definition.of.Atomic.Species>

Atoms.UnitVectors.Unit   Ang  # Ang|AU
<Atoms.UnitVectors
  4.327000000000  0.000000000000  0.000000000000
  0.000000000000  4.327000000000  0.000000000000
  0.000000000000  0.000000000000  4.327000000000
Atoms.UnitVectors>
```

The atomic coordinates are specified for both the cases as follows:

### Ground state

```
<Atoms.SpeciesAndCoordinates
  1  Ti  0.000000000000  0.000000000000  0.000000000000  6.0 6.0
  2  Ti  2.163500000000  2.163500000000  0.000000000000  6.0 6.0
  3  Ti  0.000000000000  2.163500000000  2.163500000000  6.0 6.0
  4  Ti  2.163500000000  0.000000000000  2.163500000000  6.0 6.0
  5  C   2.163500000000  0.000000000000  0.000000000000  3.0 3.0
  6  C   0.000000000000  0.000000000000  2.163500000000  3.0 3.0
  7  C   0.000000000000  2.163500000000  0.000000000000  3.0 3.0
  8  C   2.163500000000  2.163500000000  2.163500000000  3.0 3.0
Atoms.SpeciesAndCoordinates>
```

### Excited state

```
<Atoms.SpeciesAndCoordinates
  1  Ti  0.000000000000  0.000000000000  0.000000000000  6.0 6.0
  2  Ti  2.163500000000  2.163500000000  0.000000000000  6.0 6.0
  3  Ti  0.000000000000  2.163500000000  2.163500000000  6.0 6.0
  4  Ti  2.163500000000  0.000000000000  2.163500000000  6.0 6.0
  5  C1  2.163500000000  0.000000000000  0.000000000000  3.0 3.0
  6  C   0.000000000000  0.000000000000  2.163500000000  3.0 3.0
  7  C   0.000000000000  2.163500000000  0.000000000000  3.0 3.0
  8  C   2.163500000000  2.163500000000  2.163500000000  3.0 3.0
Atoms.SpeciesAndCoordinates>
```

It should be noted that a core hole is created in the atom 5 for the excited state by the following keyword:

```
<core.hole.state
  5  s 1
core.hole.state>
```

The first: atomic index
The second: target l-channel (s, p, d, or f)
The third: orbital index (1 to 4l+2)

Note that the ground and excited state calculations have to be performed with “scf.SpinPolarization” = “on” or “nc”.
Usage #2

The orbital index corresponds to a state listed below:

### Collinear case

<table>
<thead>
<tr>
<th>s</th>
<th>1: s↑</th>
<th>2: s↓</th>
<th>3: p̴</th>
<th>4: p↓</th>
<th>5: p↓</th>
<th>6: p↓</th>
</tr>
</thead>
<tbody>
<tr>
<td>d</td>
<td>1: d₃z²-r²↑</td>
<td>2: dₓ₂-y₂↑</td>
<td>3: dₓ↑</td>
<td>4: dₓ↑</td>
<td>5: dᵧ↑</td>
<td>6: dₓ↓</td>
</tr>
<tr>
<td></td>
<td>6: d₃z²-r²↓</td>
<td>7: dₓ₂-y₂↓</td>
<td>8: dₓ↓</td>
<td>9: dₓ↓</td>
<td>10: dᵧ↓</td>
<td></td>
</tr>
<tr>
<td>f</td>
<td>1: f₅z²-3r²↑</td>
<td>2: f₅x₂-yr²↑</td>
<td>3: f₅y²-yr²↑</td>
<td>4: fₓ₂-zy²↑</td>
<td>5: fₓz↑</td>
<td>6: fₓ₁-3xy²↑</td>
</tr>
<tr>
<td></td>
<td>8: f₅z²-3r²↓</td>
<td>9: f₅x₂-yr²↓</td>
<td>10: f₅y²-yr²↓</td>
<td>11: f₅y²-yr²↓</td>
<td>12: fₓz↓</td>
<td>13: fₓ₁-3xy²↓</td>
</tr>
</tbody>
</table>

### Non-collinear case

<table>
<thead>
<tr>
<th>s</th>
<th>1: J = 1/2 M = 1/2</th>
<th>2: J = 1/2 M = -1/2</th>
<th>3: J = 3/2 M = -1/2</th>
<th>4: J = 3/2 M = -3/2</th>
<th>5: J = 1/2 M = 1/2</th>
<th>6: J = 1/2 M = -1/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>d</td>
<td>1: J = 5/2 M = 5/2</td>
<td>2: J = 5/2 M = 3/2</td>
<td>3: J = 5/2 M = 1/2</td>
<td>4: J = 5/2 M = -1/2</td>
<td>5: J = 5/2 M = -3/2</td>
<td>6: J = 5/2 M = -5/2</td>
</tr>
<tr>
<td></td>
<td>7: J = 3/2 M = 3/2</td>
<td>8: J = 3/2 M = 1/2</td>
<td>9: J = 3/2 M = -1/2</td>
<td>10: J = 3/2 M = -3/2</td>
<td>11: J = 5/2 M = 3/2</td>
<td>12: J = 5/2 M = 1/2</td>
</tr>
<tr>
<td>f</td>
<td>1: J = 7/2 M = 7/2</td>
<td>2: J = 7/2 M = 5/2</td>
<td>3: J = 7/2 M = 3/2</td>
<td>4: J = 7/2 M = 1/2</td>
<td>5: J = 7/2 M = -1/2</td>
<td>6: J = 7/2 M = -3/2</td>
</tr>
<tr>
<td></td>
<td>7: J = 7/2 M = -5/2</td>
<td>8: J = 7/2 M = -7/2</td>
<td>9: J = 5/2 M = 5/2</td>
<td>10: J = 5/2 M = 3/2</td>
<td>11: J = 5/2 M = 1/2</td>
<td>12: J = 5/2 M = -1/2</td>
</tr>
<tr>
<td></td>
<td>13: J = 5/2 M = -3/2</td>
<td>14: J = 5/2 M = -5/2</td>
<td>15: J = 5/2 M = -7/2</td>
<td>16: J = 5/2 M = -9/2</td>
<td>17: J = 5/2 M = -11/2</td>
<td>18: J = 5/2 M = -13/2</td>
</tr>
</tbody>
</table>
The other keywords for the core hole calculation are given as

- scf.restart on
- scf.restart.filename TiC8
- scf.coulomb.cutoff on
- scf.core.hole on

<core.hole.state
  5 s 1
core.hole.state>

- scf.system.charge 0.0

- In the final state, the restart files, generated by the initial state calculation, has to be read. The relevant keywords are scf.restart and scf.restart.filename.

- Also, the non-periodic charge density is treated by the exact Coulomb cutoff method, specified by the keyword: scf.coulomb.cutoff.

- The core hole is introduced by the keywords: scf.core.hole and core.hole.state.

- Also, due to the creation of core hole, the system is charged up by the keyword: scf.system.charge.
Examples of the calculations can be found at
https://t-ozaki.issp.u-tokyo.ac.jp/vps_pao_core2019/

Examples

Database (2019) of optimized VPS and PAO for core level excitations

The database (2019) of fully relativistic pseudopotentials (VPS) and pseudo-atomic orbitals (PAO) which can be used for calculations of core level excitations in OpenMX. The VPS and PAO files were generated by ADPACK. The VPS and PAO files of elements with the underline are currently available. When you use these data, VPS and PAO, in the program package, OpenMX, then copy them to the directory, openmx*:.*/DFT_DATA19/VPS/ and openmx*:.*/DFT_DATA19/PAO/, respectively.
Exercises

• Calculate the core level binding energy of C-1s state in acetylene molecule. Please follow the guidance in the pages 278-281 of the manual.

• Calculate the core level binding energy of C-1s state in TiC bulk. Please copy the input files (TiC8.dat and TiC8-CH3.dat) in /home/hands-on/, and follow the guidance in the pages 281-283 of the manual.