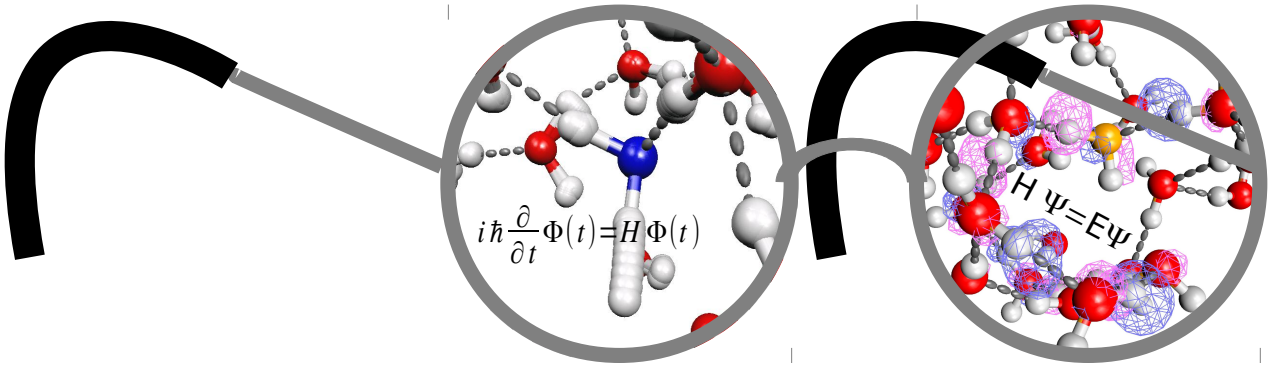


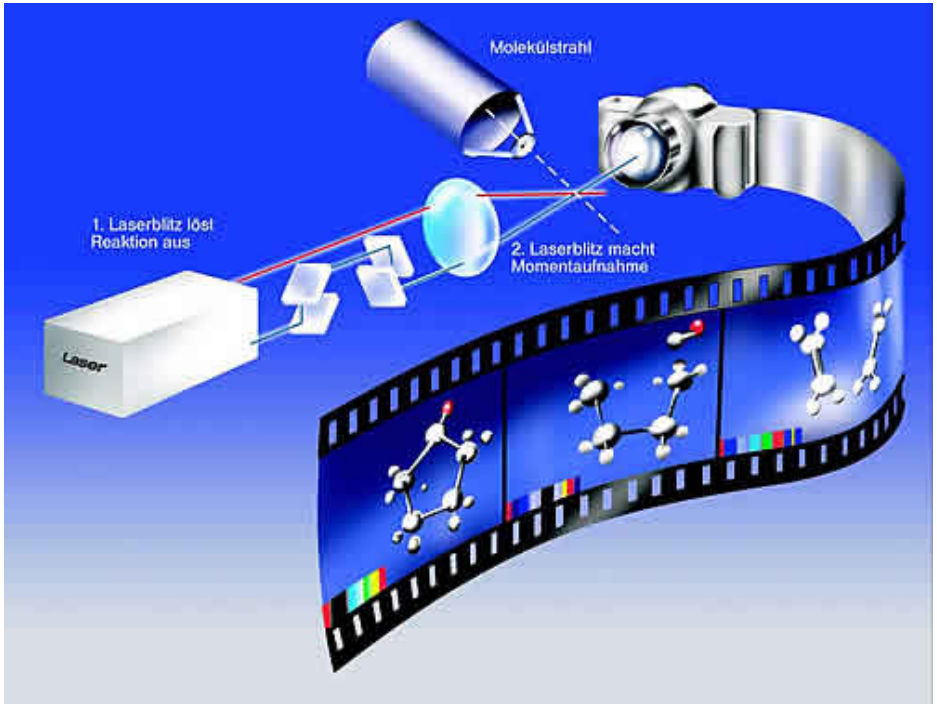
Simulating X-ray Spectroscopies with CP2K

Axel Erbing
Department of Physics

CONEXS SUMMER SCHOOL 2019:
Analysing X-ray Spectroscopy

Stockholm University

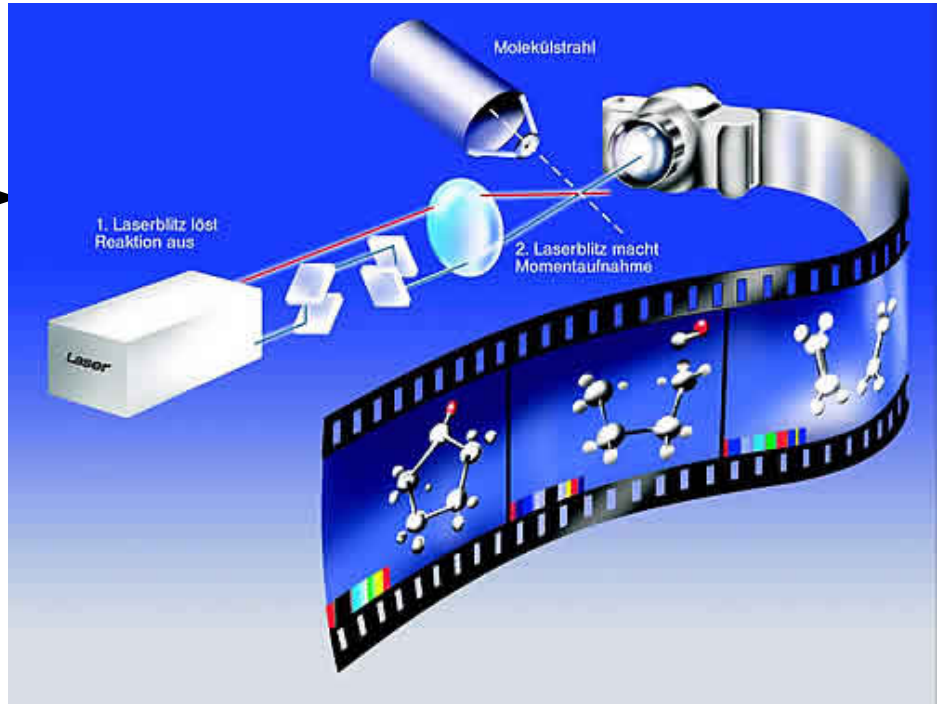
Theoretical spectrum simulations – Why bother?



<u>Femtochemistry</u>: "Filming" chemical reactions using ultra-fast lasers. (Source: DESY Hamburg)

Theoretical spectrum simulations – Why bother?

Theory is required to develop the film



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

Qualitative assignment

Evaluate theo. models

Quantitative analysis

Evaluate approximations

Outline

Introduction

X-ray photo-electron spectroscopy (XPS)

- Example: XPS on H_2O(g,l,s)
- CP2K input

Molecular dynamics (MD)

- Basic theory
- Example: H-bond dynamics in H_2O(l)
- CP2K input

X-ray emission spectroscopy (XES)

- Example: XES on NH_3(aq)
- CP2K input

Bonus example: XPS on perovskite solar cells

Quantum Chemistry $H\Psi = E\Psi$

Hartree-Fock

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

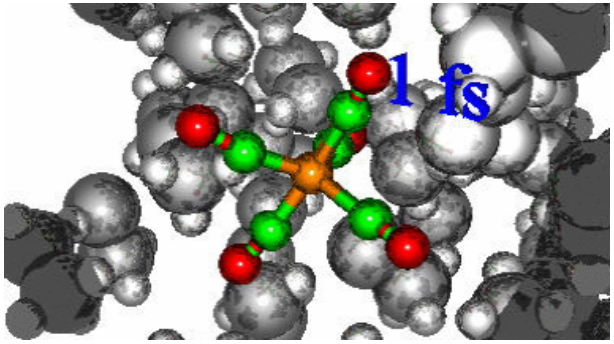
$\Psi_{HF} = \det | \phi_1, \phi_2, \ldots \phi_N |$

Momentary
e^- - e^- correlation
missing!

DFT

Singlet determinant

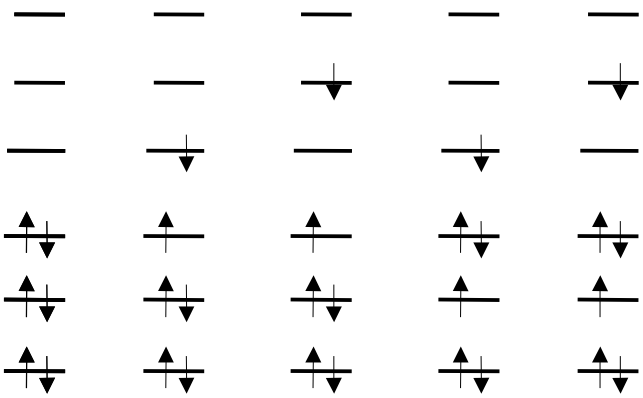
Correlation in **H**



Post-HF

Multi-determinant

Wave function correlated



Ab initio Molecular dynamics

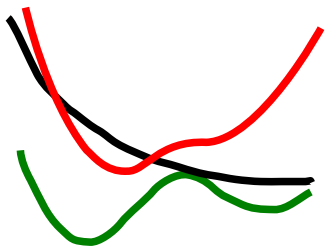
$$-\nabla_I V = \boldsymbol{F}_I = m_I \boldsymbol{a}_I$$

$$\boldsymbol{F}_I = -\nabla_I \min_{\phi_i} \left\{ E_{\mathrm{KS}}(\{\phi_i\}; \boldsymbol{R}_I) \right\}$$

AIMD: CPMD CP2K

Quantum dynamics

$$i\hbar \frac{\partial}{\partial t} \Phi(\{\boldsymbol{r}_i\}, \{\boldsymbol{R}_I\}; t) = H\, \Phi(\{\boldsymbol{r}_i\}, \{\boldsymbol{R}_I\}; t)$$



QMD: Wave packet simulations

Quantum Chemistry $H\Psi = E\Psi$

Hartree-Fock

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

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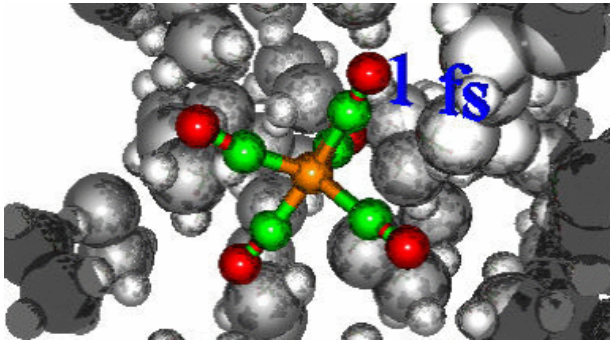
missing!

DFT

Singlet determinant

Correlation in **H**



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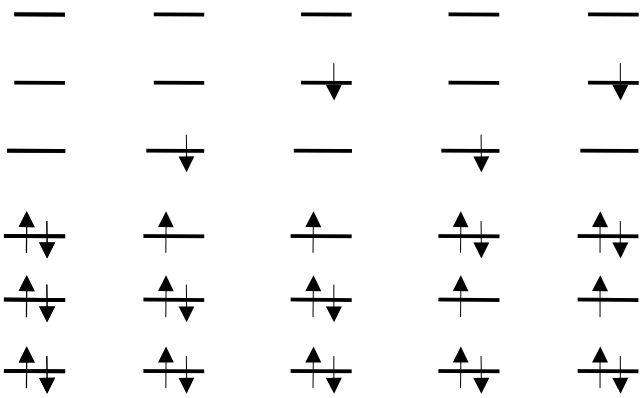

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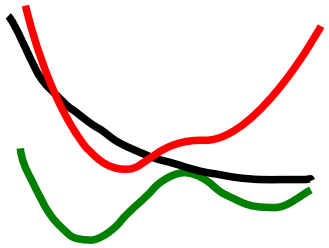
AIMD: CPMD CP2K

Quantum dynamics

$$i\hbar \frac{\partial}{\partial t} \Phi(\{\boldsymbol{r}_i\}, \{\boldsymbol{R}_I\}; t) = H\, \Phi(\{\boldsymbol{r}_i\}, \{\boldsymbol{R}_I\}; t)$$



QMD: Wave packet simulations

Core-level spectroscopy

X-ray photo-electron spectroscopy	**Core-ionization (Valence-ionization)**
X-ray absorption spectroscopy	**Core-excitation**
X-ray emission spectroscopy	**Fluorescence decay**

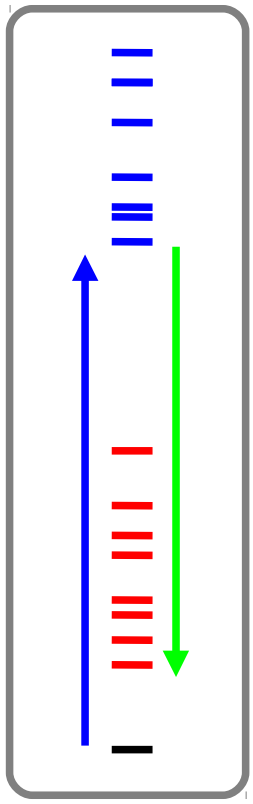
XPS XAS XES

Spectrum simulations $H\Psi = E\Psi$

Accurate methods
Electronic states

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

$|\langle\Psi_i|\mathcal{O}|\Psi_j\rangle|^2$

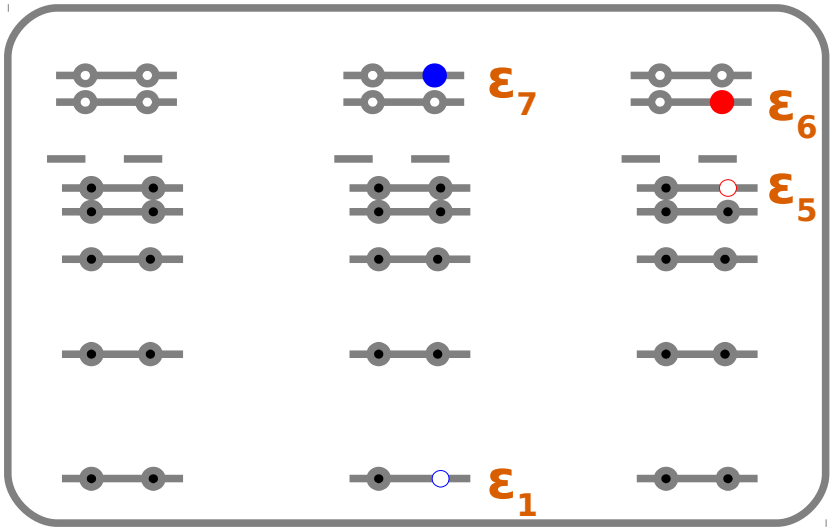


Core-excited

Valence excited

Ground state

Approximate methods
Molecular orbitals



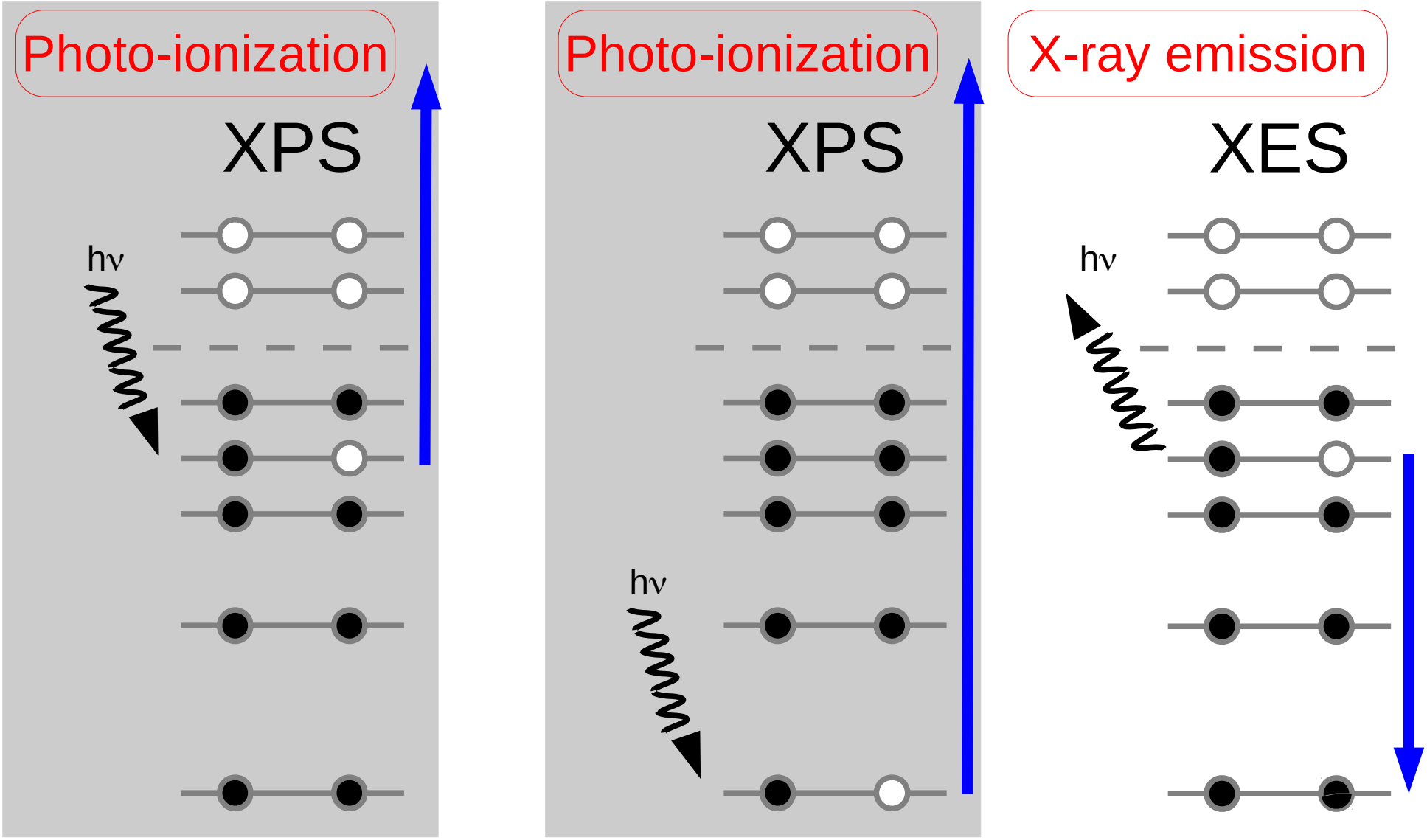
GS $\quad \varepsilon_7 - \varepsilon_1 \quad \varepsilon_6 - \varepsilon_5$

Transition potential DFT

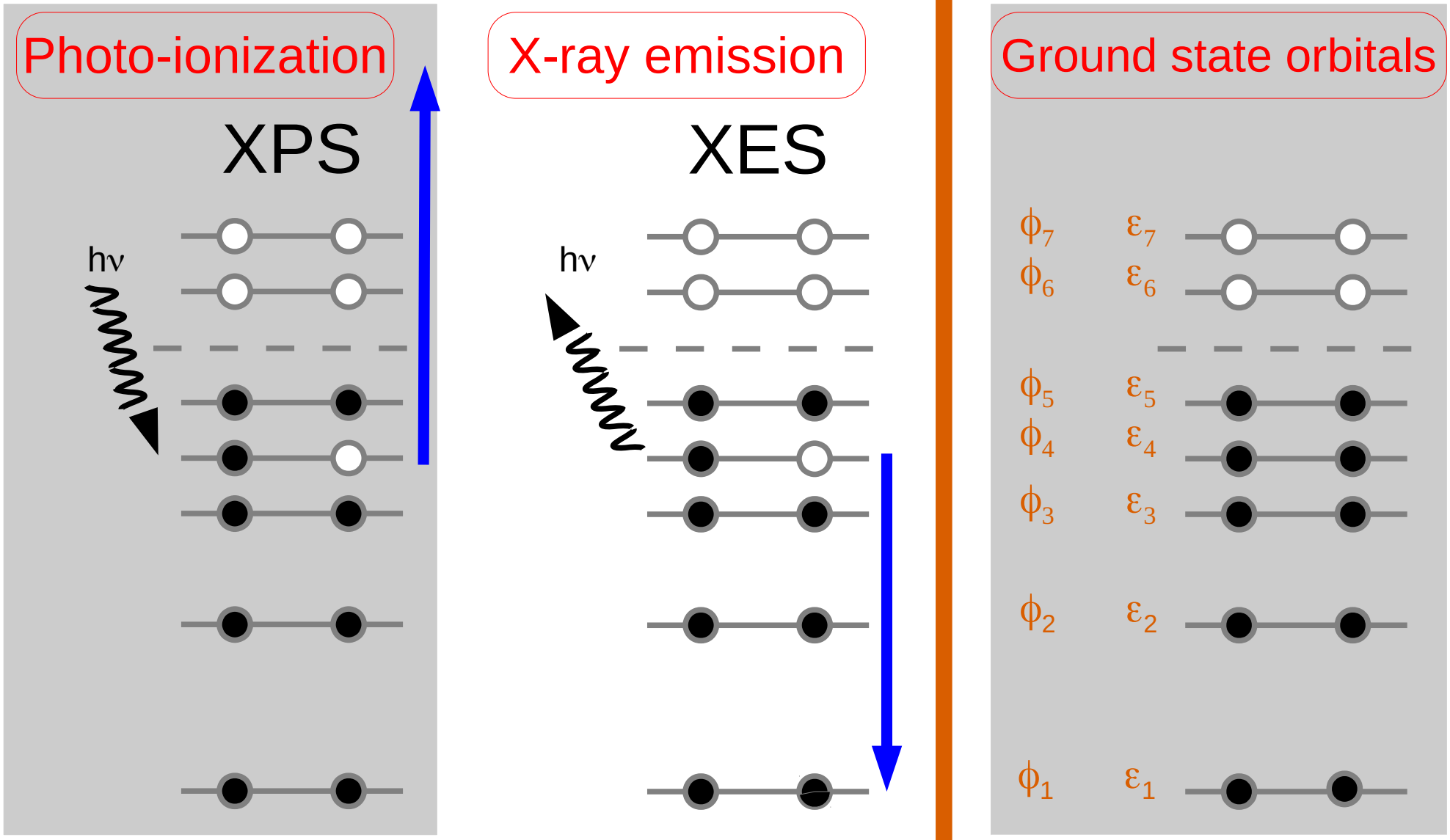
$|\langle\Psi_i|\mathcal{O}|\Psi_j\rangle|^2 =$

$|\langle\phi_n|\mathcal{O}|\phi_m\rangle|^2$

Orbital represention of the XPS and XES processes



Orbital represention of the XPS and XES processes

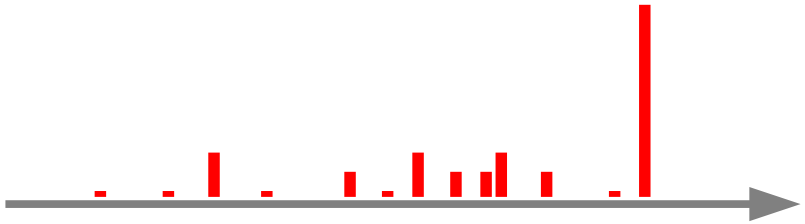


Spectrum simulations $H\,\Psi = E\Psi$

Broadening:

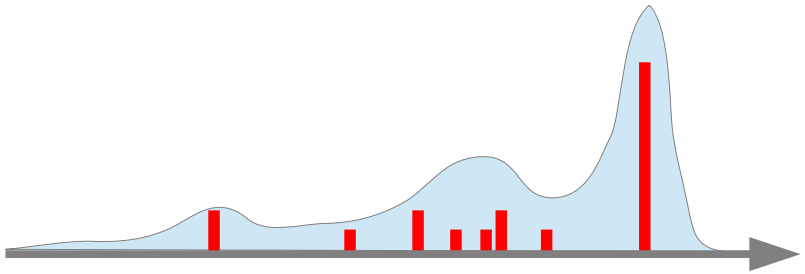
$$E_{tot}(\Psi_i) - E_{tot}(\Psi_j)$$

$$|\langle\Psi_j|\mathcal{O}\,|\Psi_i\rangle|^2$$



Core-hole life-time

Vibrational



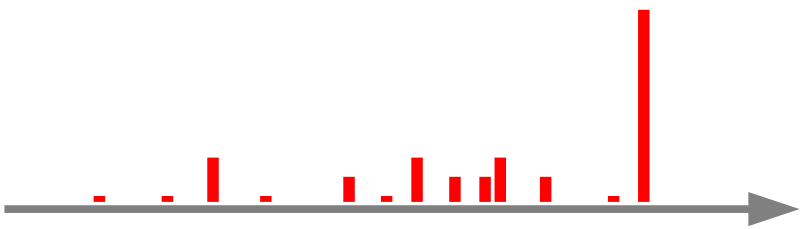
Configurational

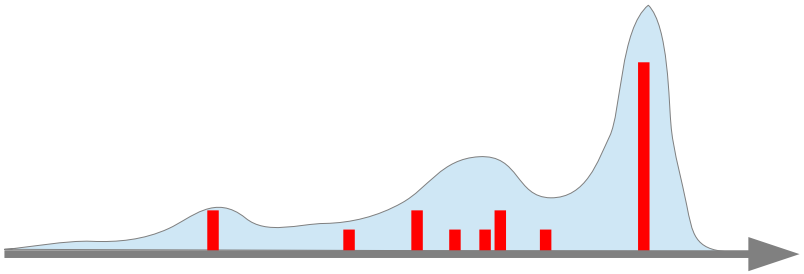
Experimental

Spectrum simulations $H\Psi = E\Psi$

Broadening:

How to simulate it?





Simplest approach:
Convolution with Gaussian functions

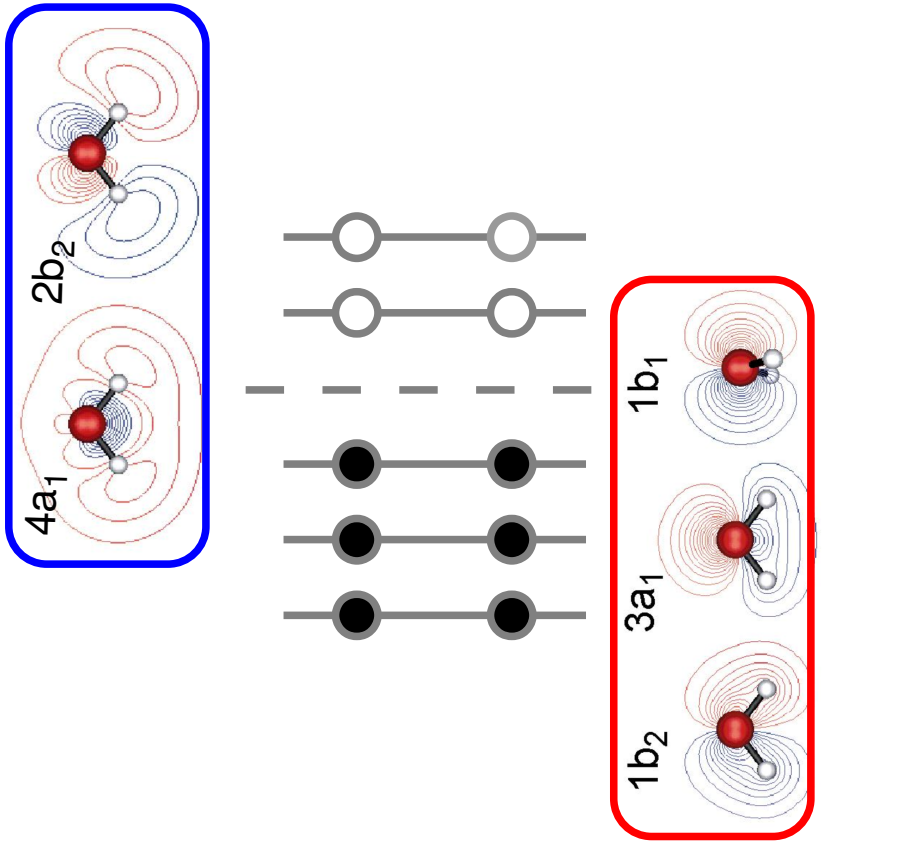
$$I(E) = \sum_i f(\epsilon_i) e^{-(E-\epsilon_i)^2/2\sigma^2}$$

Width parameter

$$\mathrm{FWHM} = 2\sqrt{2}\log(2)\sigma$$

Other functions, e.g. Lorentzians

Molecular orbitals of $H_2O(g)$ – C_{2v} Point group



O2s ($2a_1$)

O1s ($1a_1$)

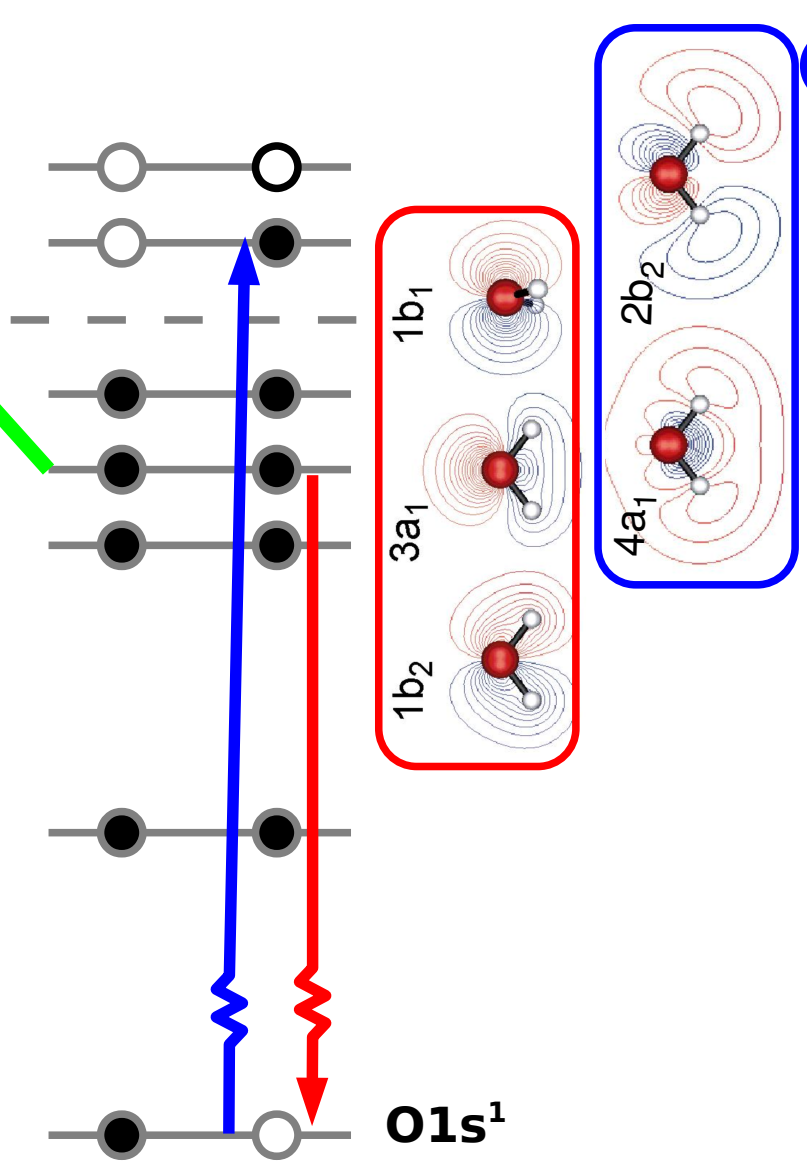
X-ray spectroscopy Case study: $H_2O(g)$

XPS

Photoelectron spectroscopy

XES

Decay channels to valence-ionized states

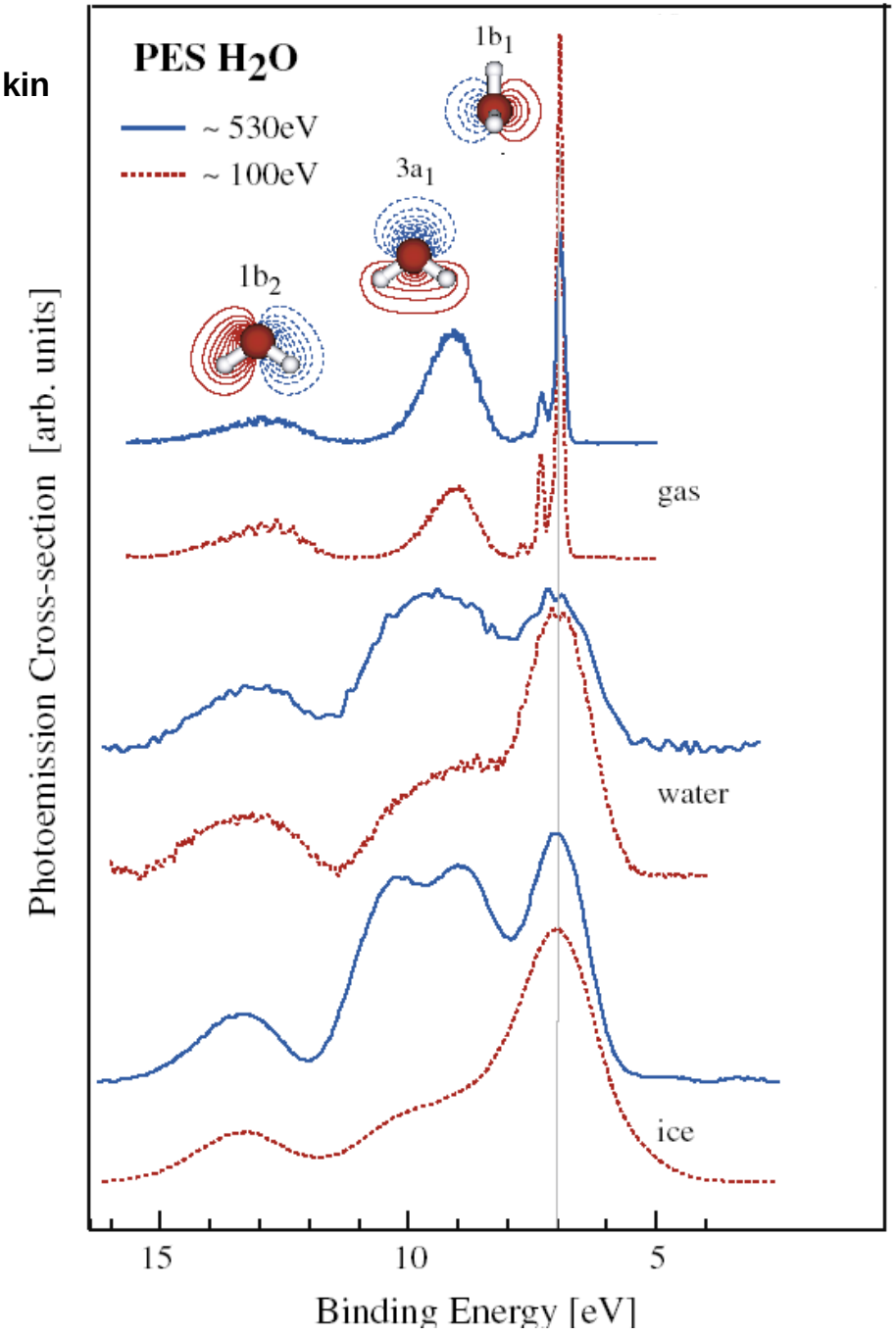


XAS

X-ray Absorption and Emission Spectroscopy

Photo-electron spectroscopy of H_2O(g,l,s)

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



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)

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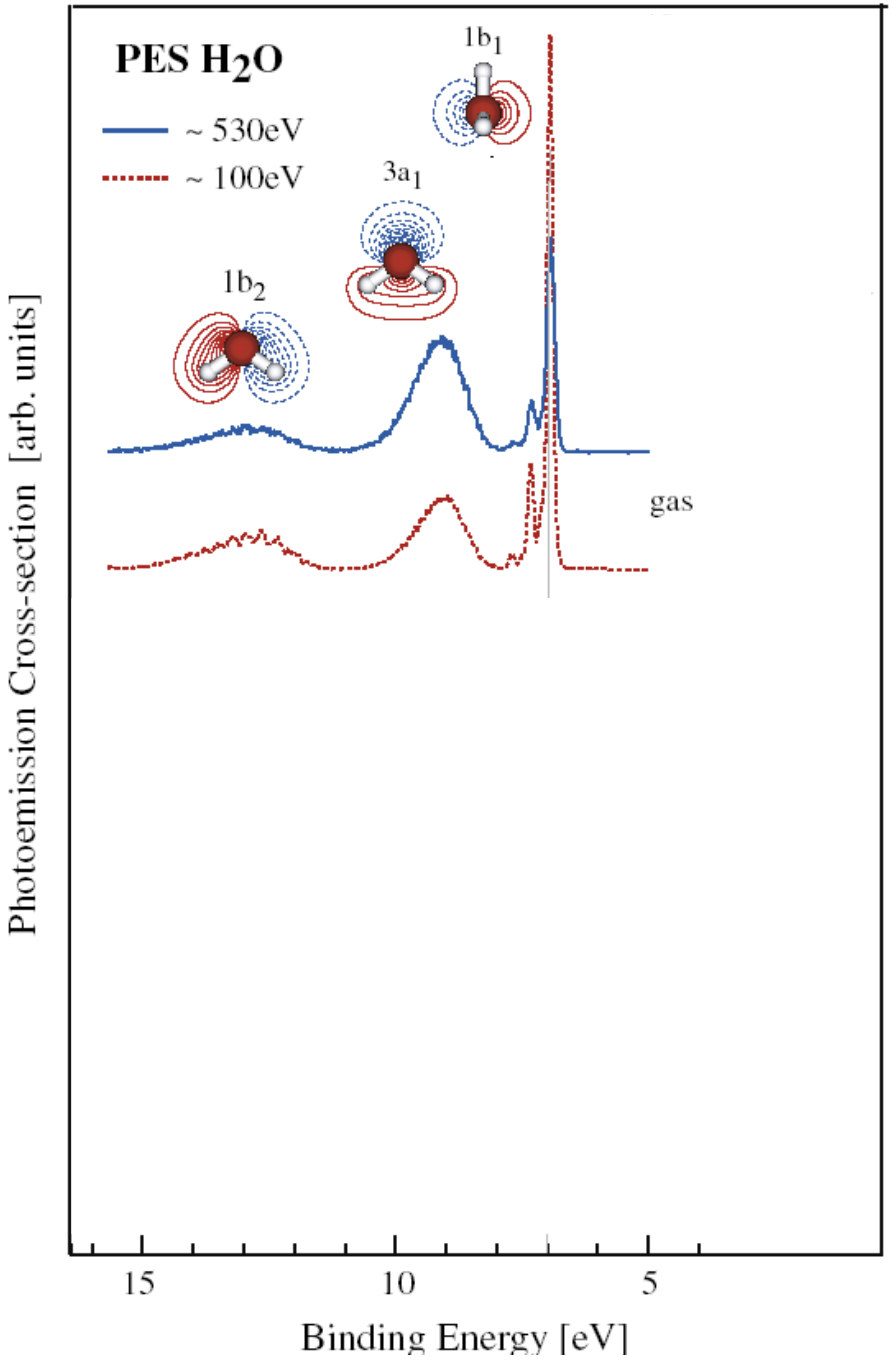
Photo-electron spectroscopy of H_2O(g,l,s)



Franck-Condon

Vibrational excitations

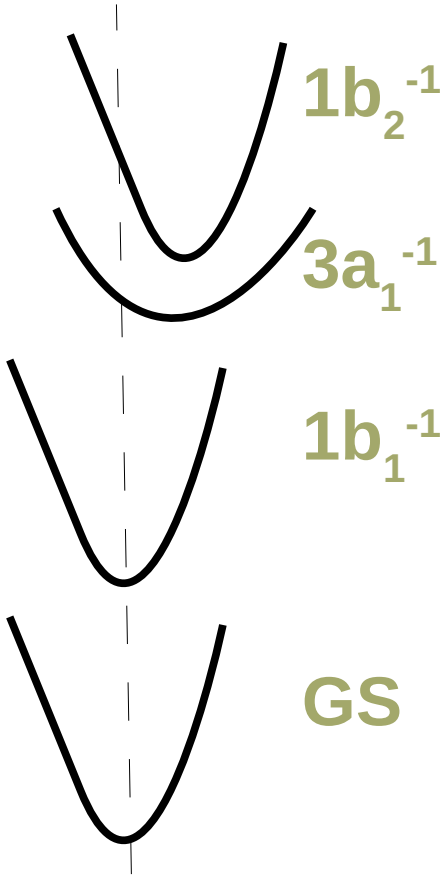


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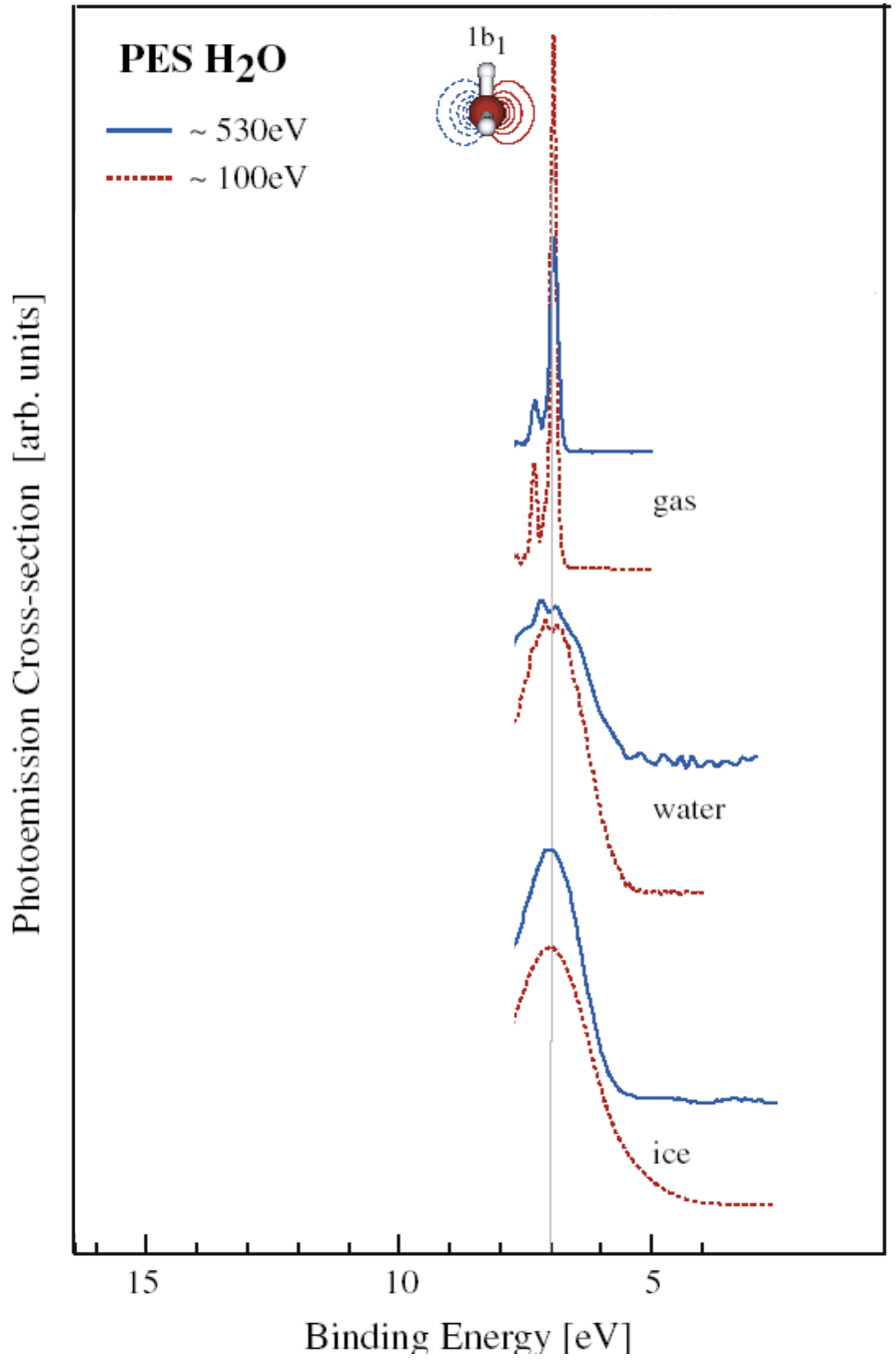
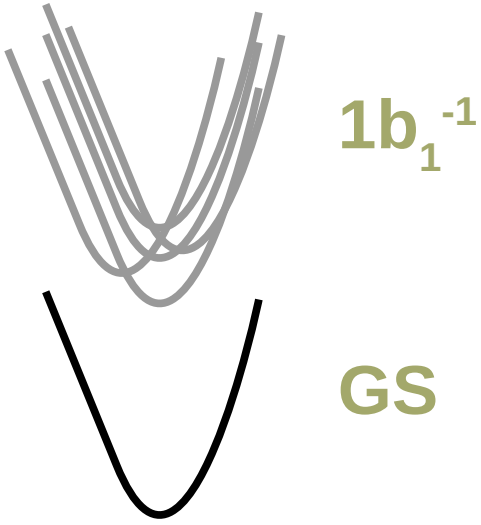
Photo-electron spectroscopy of H_2O(g,l,s)



Inhomogeneous Broadening



(Homogeneous broadening is due to finite life-times)

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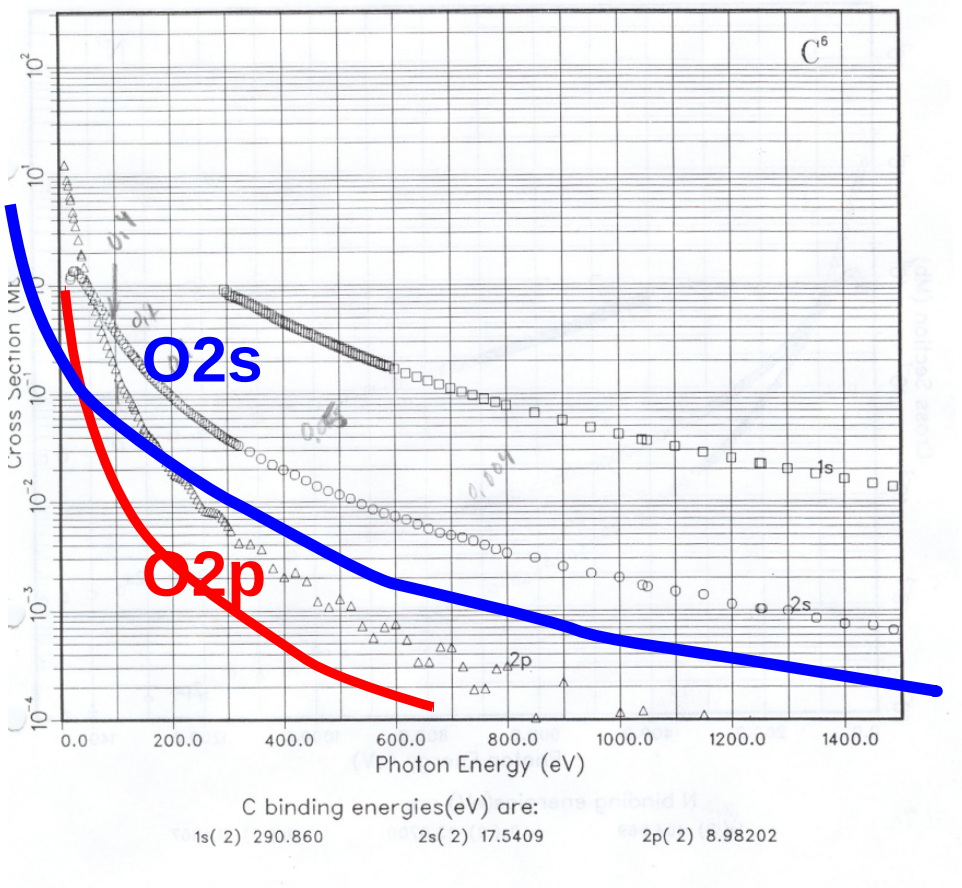
Photo-electron spectroscopy of H_2O(g,l,s)

Cross sections vary with photonenergy



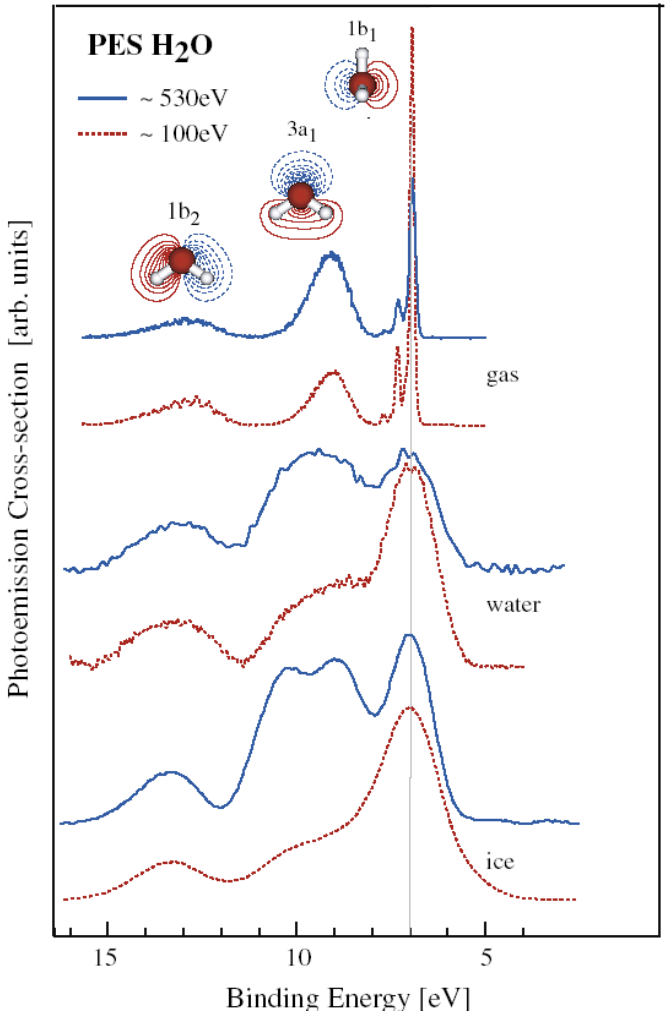


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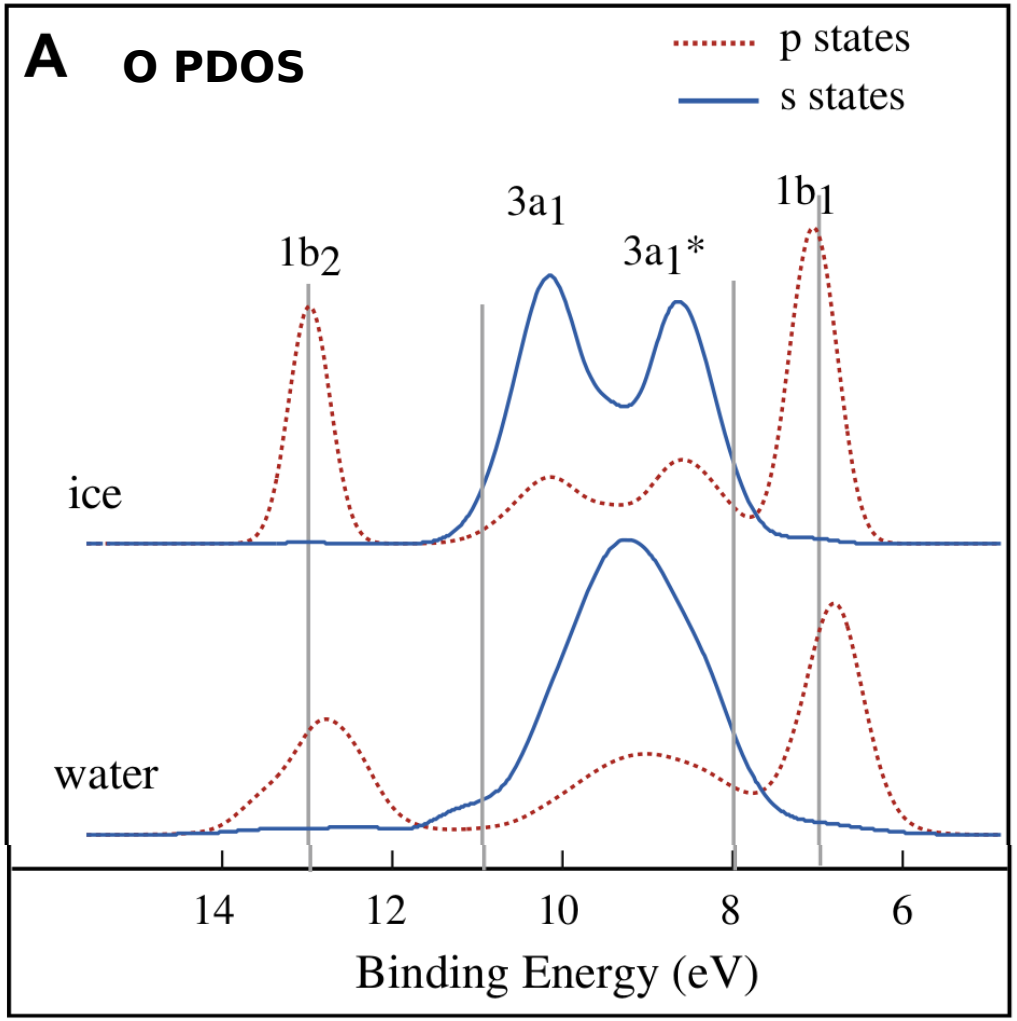
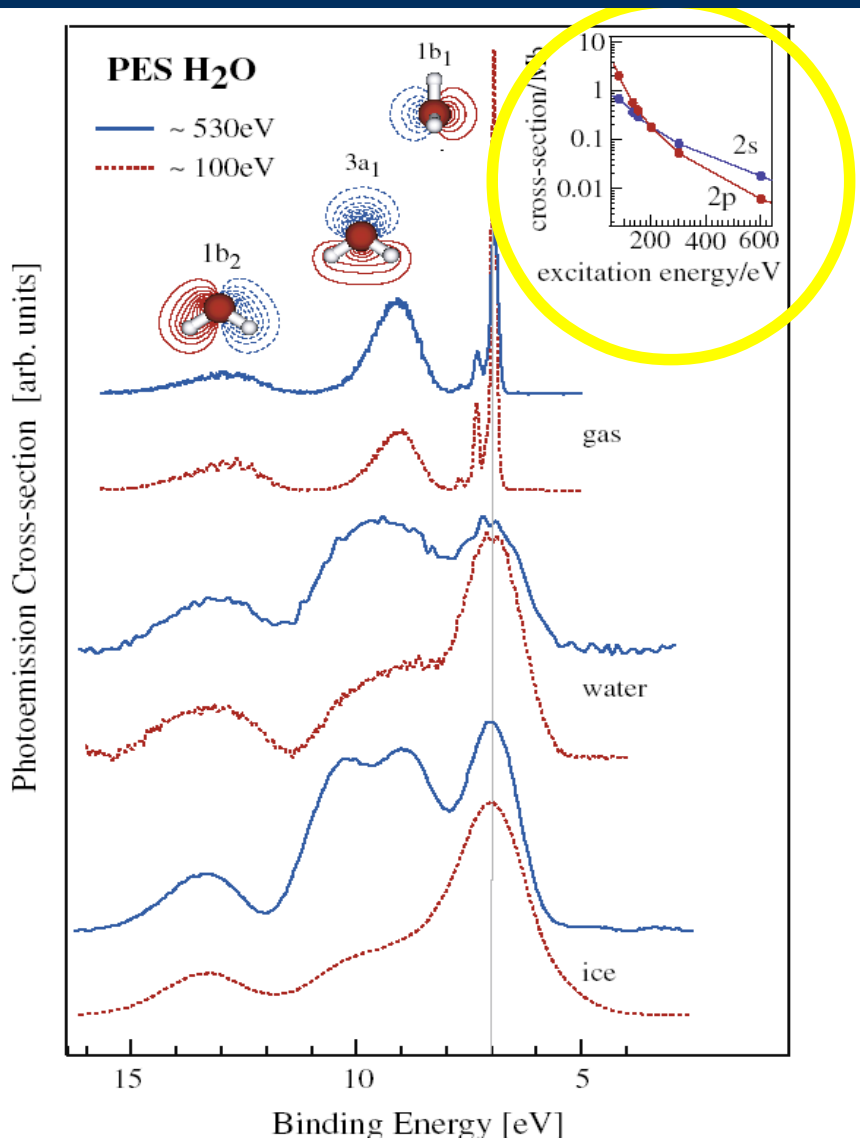
Photo-electron spectroscopy of H_2O(g,l,s)





Notice: In C_{2v} symmetry only a_1 can have oxygen s-sym.

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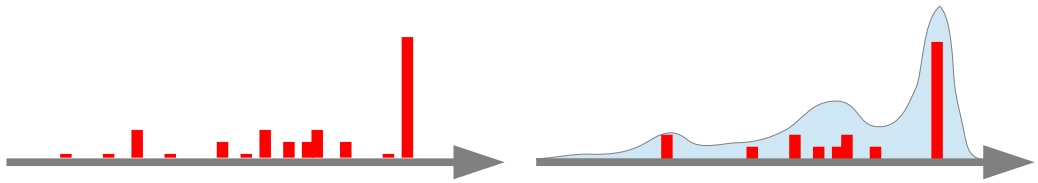
XPS in CP2K

In CP2K:

PDOS section

```
&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 O at iteration step i = 0, E(Fermi) =    -0.092095 a.u.
#     MO Eigenvalue [a.u.]      Occupation                s                 p                 d
      1         -0.813984        2.000000        0.60602572        0.01485316        0.00068085
      2         -0.811458        2.000000        0.59241283        0.02442027        0.00070482
      3         -0.805771        2.000000        0.60812885        0.01594420        0.00052020
      4         -0.804528        2.000000        0.59910583        0.02034290        0.00058688
      5         -0.803092        2.000000        0.60470405        0.01908272        0.00068245
      6         -0.799728        2.000000        0.60995065        0.02078783        0.00054705
      7         -0.799365        2.000000        0.61494883        0.01871139        0.00061605
      8         -0.796444        2.000000        0.60950411        0.01896750        0.00060187
      9         -0.795593        2.000000        0.60359670        0.01937689        0.00061605
     10         -0.794065        2.000000        0.60611548        0.02118279        0.00058782
     11         -0.792778        2.000000        0.60035120        0.02380201        0.00062264
     12         -0.792114        2.000000        0.61390238        0.01770367        0.00056747
     13         -0.791049        2.000000        0.61781343        0.02008600        0.00057487
     14         -0.789865        2.000000        0.61436528        0.02173526        0.00060204
     15         -0.787285        2.000000        0.61022220        0.01937101        0.00072422
     16         -0.786506        2.000000        0.60903629        0.02144700        0.00059809
     17         -0.785677        2.000000        0.61293620        0.01899232        0.00056839
```

```
# Projected DOS for atomic kind O at iteration step i = 0, E(Fermi) =    -0.242711 a.u.
#     MO Eigenvalue [a.u.]      Occupation                s                 p                 d
      1         -0.901554        2.000000        0.60829071        0.02924920        0.00078405
      2         -0.454223        2.000000        0.00000000        0.66362894        0.01043279
      3         -0.318901        2.000000        0.12519439        0.78167809        0.00218947
      4         -0.242711        2.000000        0.00000000        0.94836955        0.00021426
      5          0.031826        0.000000        0.06525583        0.08045666        0.00491060
      6          0.114429        0.000000        0.00000000        0.16861035        0.01700454
```

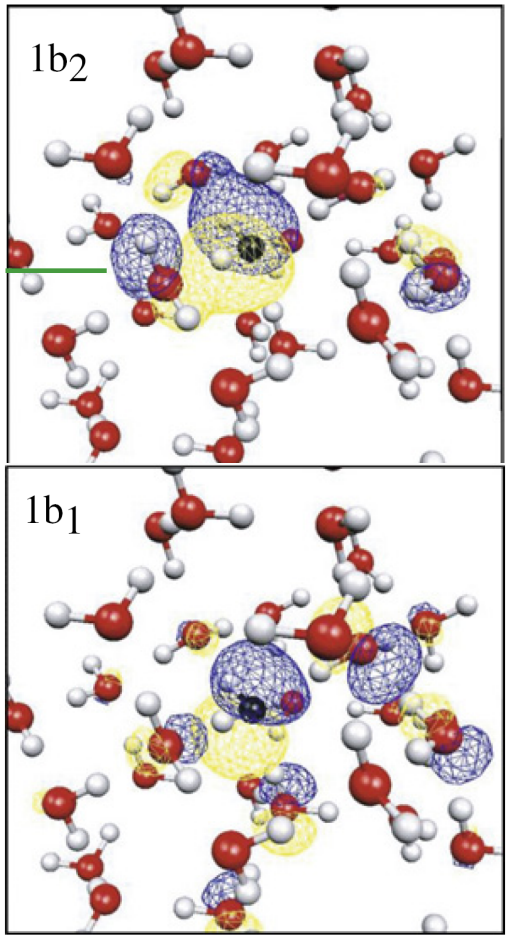
e.g. PDOS_H2O-k1-1.pdos

Molecular Dynamics

Molecular dynamics (MD)

Why bother with MD?

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



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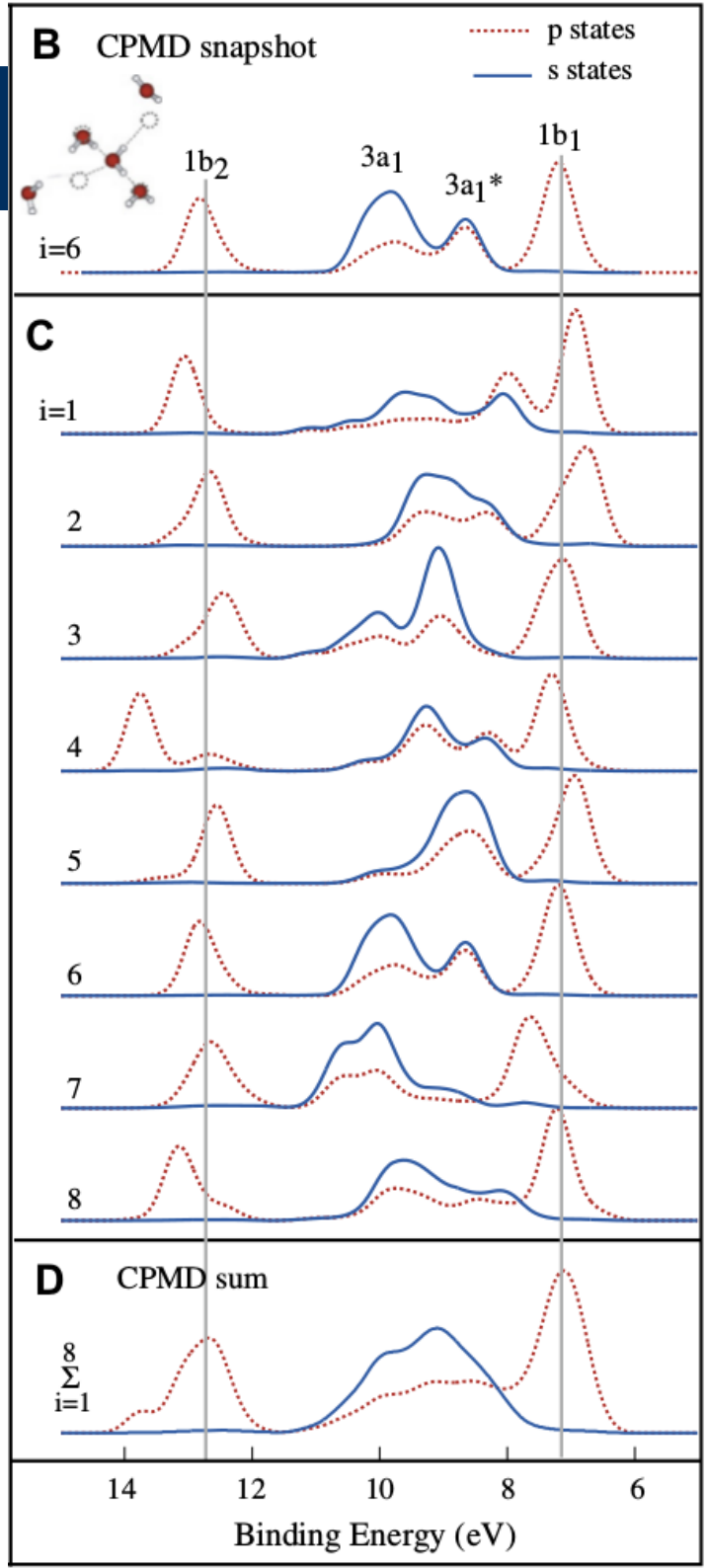


Molecular dynamics (MD)

Newton's equations of motion

$$\boldsymbol{F}_I = m_I \boldsymbol{a}_I$$

Molecular dynamics (MD)

Newton's equations of motion

$$\boldsymbol{F}_I = m_I \boldsymbol{a}_I \ , \qquad \boldsymbol{F}_I = -\nabla_I V$$

Two problems: Calculating forces and integrating EoMs

Velocity Verlet

$$\boldsymbol{R}(t+\delta t) = \boldsymbol{R}(t) + \boldsymbol{V}(t)\delta t + \frac{1}{2M}\boldsymbol{F}(t)\delta t^2$$

$$\boldsymbol{V}(t+\delta t) = \boldsymbol{V}(t) + \frac{1}{2M}\left[\boldsymbol{F}(t) + \boldsymbol{F}(t+\delta t)\right]\delta t$$

Molecular dynamics (MD)

Newton's equations of motion

$$\boldsymbol{F}_I = m_I \boldsymbol{a}_I \ , \qquad \boldsymbol{F}_I = -\nabla_I V$$

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

$$\boldsymbol{F}_I = m_I \boldsymbol{a}_I \ , \qquad \boldsymbol{F}_I = -\nabla_I V$$

Two problems: Calculating forces and integrating EoMs

Classical MD:

Force fields

- Less expensive
- Good for larger systems

Ab initio MD (AIMD):

Born-Oppenheimer MD

- In CP2K

Car-Parrinello MD

- In CPMD

Molecular Dynamics

Born-Oppenheimer MD

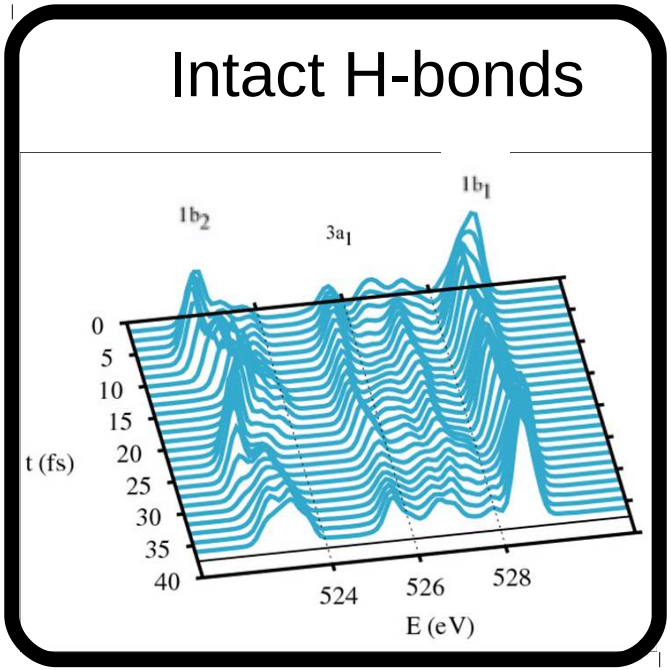
Parameter-free force expression

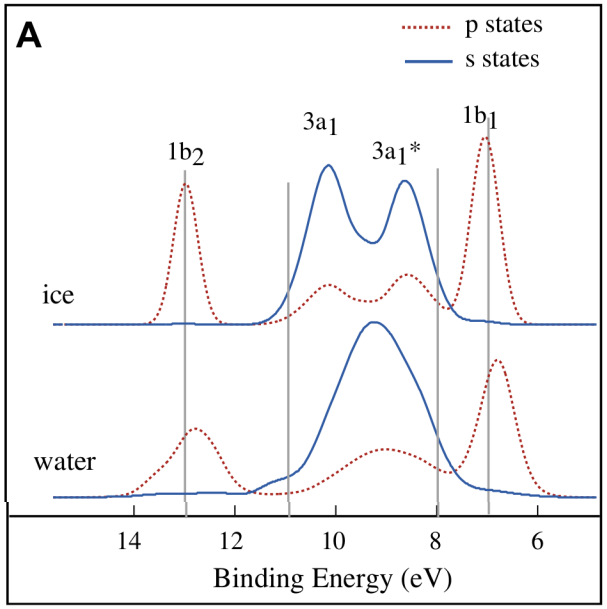
$$\boldsymbol{F}_I = -\nabla_I \min_{\phi_i} \left\{ E_{\mathrm{KS}}(\{\phi_i\}; \boldsymbol{R}_I) + \mathrm{constr.} \right\}$$

Electronic orbitals optimized at each step

Time evolution of the electronic structure due to hydrogen bond dynamics

Hydrogen bond dynamics





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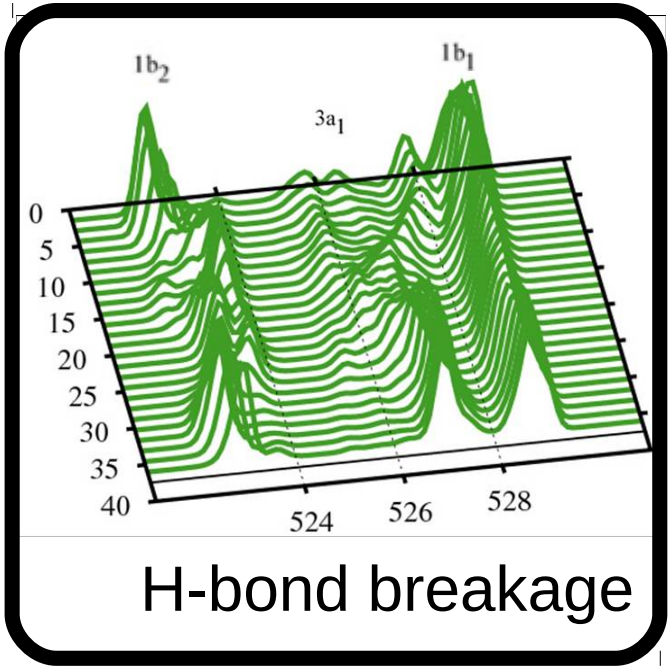
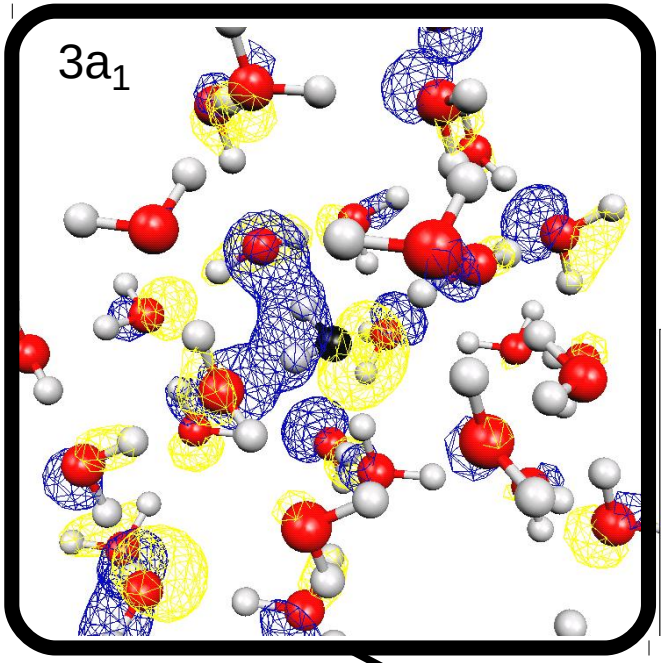
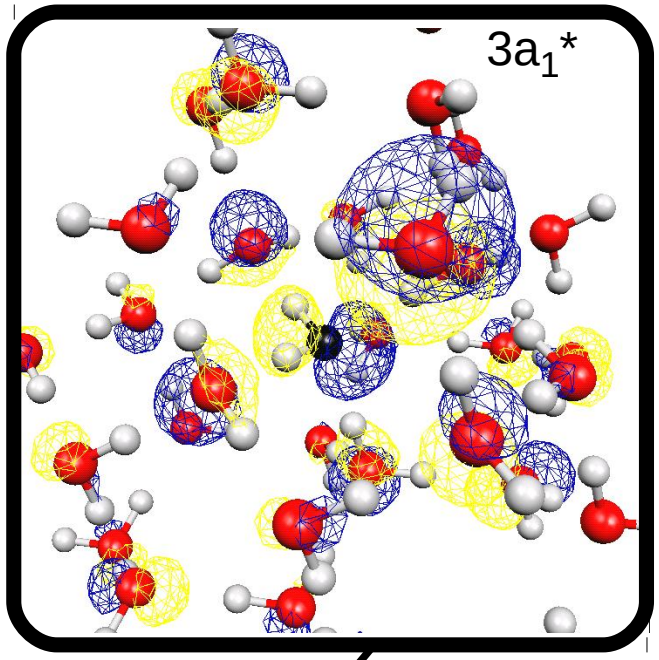
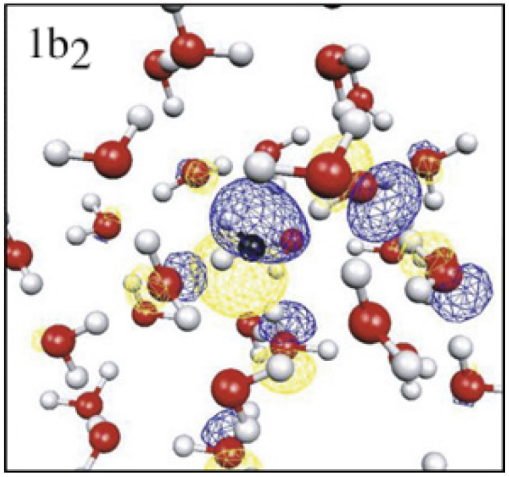


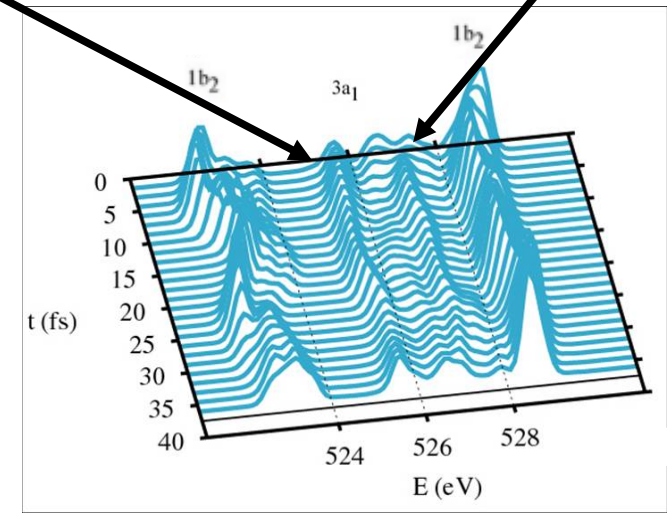
Hydrogen bonding in water

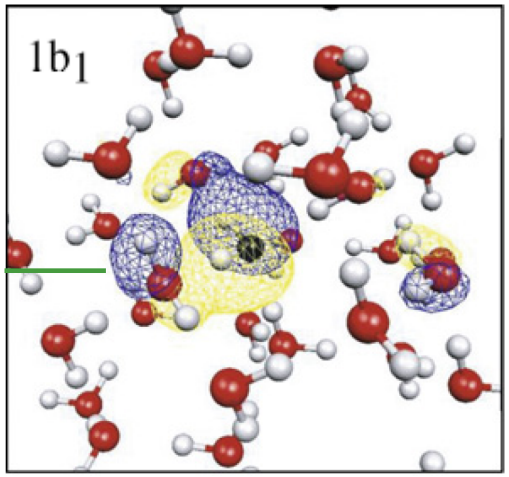




Strong overlap in $3a_1$







D. Nordlund et al
CPL **460** 86 (2008)

Molecular Dynamics in CP2K

In CP2K:

Use MD as run type

```
&GLOBAL
  PROJECT liquid_water_md
  RUN_TYPE MD
  IOLEVEL LOW
&END GLOBAL
```

MD Section

- Ensemble
- Time step
- Temperature
- Thermostat
- Printing

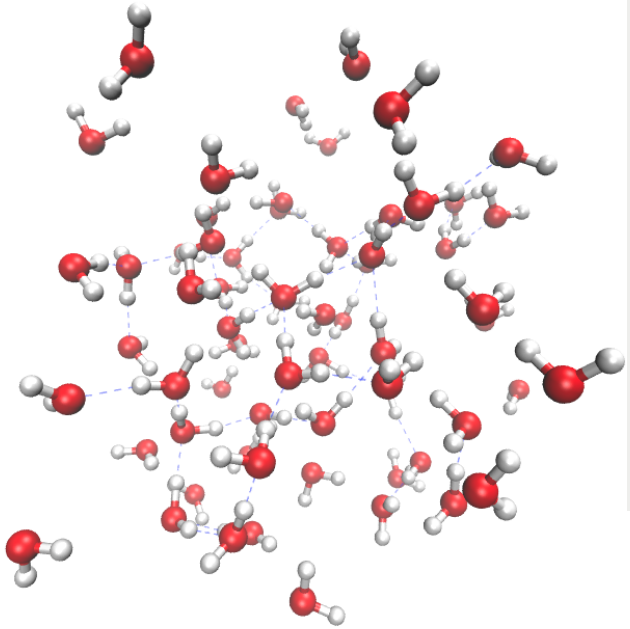
```
&MOTION
  &MD
    ENSEMBLE NVT
    STEPS 500
    TIMESTEP 1
    TEMPERATURE 300.0
    &THERMOSTAT
      REGION MASSIVE
      TYPE CSVR
      &CSVR
        TIMECON 20
      &END CSVR
    &END THERMOSTAT
  &END MD
  &PRINT
    &TRAJECTORY
      &EACH
        MD 5
      &END
    &END TRAJECTORY
    &VELOCITIES OFF
    &END
    &RESTART
      &EACH
        MD 10
      &END
      ADD_LAST NUMERIC
    &END
    &RESTART_HISTORY OFF
    &END
  &END PRINT
&END MOTION
```

Molecular Dynamics in CP2K

In CP2K:

Output

Trajectory



Time, temperature, and energies

# Step Nr.	Time[fs]	Kin.[a.u.]	Temp[K]	Pot.[a.u.]	Cons Qty[a.u.]	UsedTime[s]
0	0.000000	0.273612846	300.000000000	-1101.195048677	-1100.921435831	0.000000000
1	1.000000	0.260788851	285.939262507	-1101.187798871	-1100.921315744	185.706952075
2	2.000000	0.251306678	275.542630917	-1101.180757600	-1100.920989497	79.281784041
3	3.000000	0.245390724	269.056143752	-1101.180382929	-1100.921719691	74.824822441
4	4.000000	0.242953031	266.383360562	-1101.180715807	-1100.922038801	74.627564488
5	5.000000	0.244483398	268.061315781	-1101.173607104	-1100.921241154	81.450230681
6	6.000000	0.248146396	272.077572772	-1101.170366895	-1100.920782952	80.918141057
7	7.000000	0.243194901	266.648556557	-1101.176391675	-1100.920844694	68.497354319
8	8.000000	0.266614350	292.326571080	-1101.193920451	-1100.921755529	79.407844959
9	9.000000	0.282143251	309.353075672	-1101.207672144	-1100.922823669	50.431842566
10	10.000000	0.277957975	304.764172501	-1101.205146651	-1100.922196436	67.354678559
11	11.000000	0.267186222	292.953594182	-1101.193865916	-1100.920825588	62.275034669
12	12.000000	0.268798850	294.721743890	-1101.190595790	-1100.920813534	74.036419125
13	13.000000	0.273868615	300.280435755	-1101.192085651	-1100.921504962	82.080369944
14	14.000000	0.260863451	286.021057303	-1101.188315315	-1100.921489325	60.489270956
15	15.000000	0.246732390	270.527199517	-1101.178095043	-1100.920685259	73.977594214
16	16.000000	0.241390703	264.670361900	-1101.173192957	-1100.920360170	68.257580375
17	17.000000	0.243886285	267.406617622	-1101.176766365	-1100.920488230	77.877416690
18	18.000000	0.263436205	288.841926755	-1101.190322074	-1100.921032269	73.244974266
19	19.000000	0.280008882	307.012868808	-1101.205372283	-1100.922310150	66.950812683
20	20.000000	0.278566222	305.431079195	-1101.203508831	-1100.921750388	74.972466874
21	21.000000	0.274697146	301.188869741	-1101.198046242	-1100.920612145	124.051279855
22	22.000000	0.280446095	307.492246630	-1101.202198249	-1100.920967212	101.725280184
23	23.000000	0.290504788	318.520996969	-1101.213382017	-1100.921909393	92.342588647
24	24.000000	0.293909603	322.254171119	-1101.217940920	-1100.922053166	79.395465549
25	25.000000	0.293316279	321.603627108	-1101.213950635	-1100.921493397	81.616674579
26	26.000000	0.287446640	315.167922262	-1101.207388779	-1100.920908335	72.550315438
27	27.000000	0.284613311	312.061347630	-1101.204539539	-1100.920300885	63.716598709
28	28.000000	0.294791092	323.220671590	-1101.211853416	-1100.920806870	60.495320910
29	29.000000	0.306880839	336.476350649	-1101.224396577	-1100.922196413	67.581873094
30	30.000000	0.311467278	341.505104356	-1101.224802819	-1100.922263794	76.707186854
31	31.000000	0.296048848	324.599725054	-1101.210297945	-1100.921193445	63.403624347
32	32.000000	0.272354495	298.620293893	-1101.192294399	-1100.920210519	80.945801291
33	33.000000	0.266102466	291.765321428	-1101.189084729	-1100.919903498	68.794831039
34	34.000000	0.279966618	306.966528169	-1101.202928165	-1100.921652109	68.256335506
35	35.000000	0.283080611	310.380834476	-1101.205777712	-1100.922353383	67.731184330
36	36.000000	0.265191010	290.765964080	-1101.190904656	-1100.920629662	75.648185624
37	37.000000	0.264772100	290.306655409	-1101.187644821	-1100.919933361	71.631821207
38	38.000000	0.271314857	297.480393587	-1101.201295622	-1100.921645440	89.441283940
39	39.000000	0.278730201	305.610871415	-1101.214567322	-1100.922515588	72.446101384
40	40.000000	0.277284941	304.026231399	-1101.217693627	-1100.922521564	65.982694265
41	41.000000	0.266674230	292.392225474	-1101.209732017	-1100.921575999	96.955513053
42	42.000000	0.265563288	291.174144961	-1101.203958115	-1100.920208762	97.002539299
43	43.000000	0.278680121	305.555962096	-1101.217371396	-1100.921302690	73.838125673
44	44.000000	0.295775609	324.300134456	-1101.232465712	-1100.922643814	69.464185646
45	45.000000	0.293090207	321.355753173	-1101.227676679	-1100.921663414	77.113984438
46	46.000000	0.271676677	297.877107791	-1101.215412194	-1100.919890371	100.363709472
47	47.000000	0.280631093	307.695085597	-1101.223582008	-1100.921162812	56.928944765
48	48.000000	0.284931900	312.410661506	-1101.235919778	-1100.921945724	75.435754369
49	49.000000	0.282037030	309.236610536	-1101.239173849	-1100.921834984	69.919304038
50	50.000000	0.284386775	311.812964849	-1101.236343611	-1100.921655594	73.850114970

E.g. water_liquid-1.ener

Molecular Dynamics in CP2K

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

```
&FORCE_EVAL
  &DFT
    ...
    &QS
      METHOD                GPW
      EPS_DEFAULT           1.0E-10
      !EXTRAPOLATION         USE_GUESS
      EXTRAPOLATION         ASPC
      EXTRAPOLATION_ORDER   4
  &END DFT
&END FORCE_EVAL
```

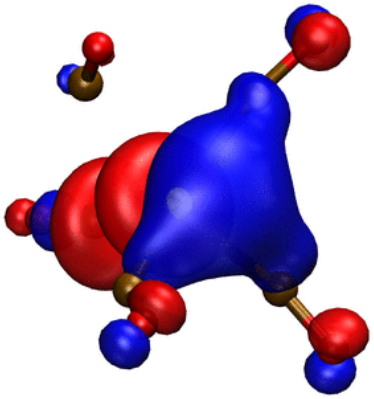
Molecular Orbitals in CP2K

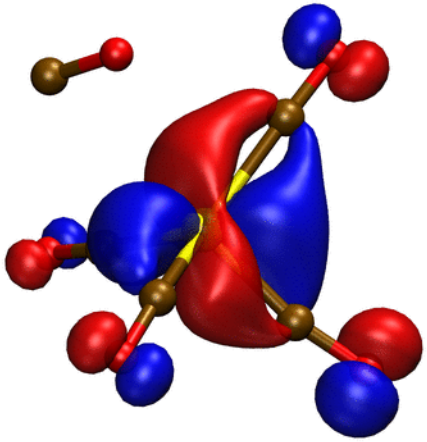
In CP2K:

Plotting molecular orbitals

- Cube-file format **.cube**
- Can be visualized in software like VMD, VESTA, or GaussView
- Be careful when writing and storing cube-files as they take up alot of space!

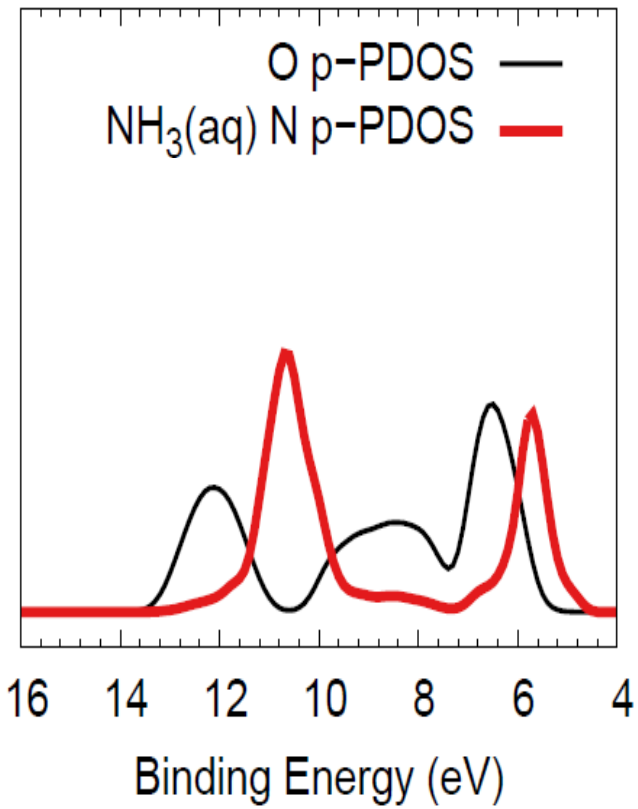
```
&FORCE_EVAL
  &DFT
    ...
    &SCF
      ...
    &END SCF
    &PRINT
      &MO_CUBES
        NHOMO 3
        NLUMO 2
        &EACH
          MD 10
        &END
        WRITE_CUBE .TRUE.
      &END
    &END PRINT
  &END DFT
&END FORCE_EVAL
```





XES allows us to access N p-PDOS in NH_3(aq)

Aqueous ammonia:
Energy mismatch in orbital mixing

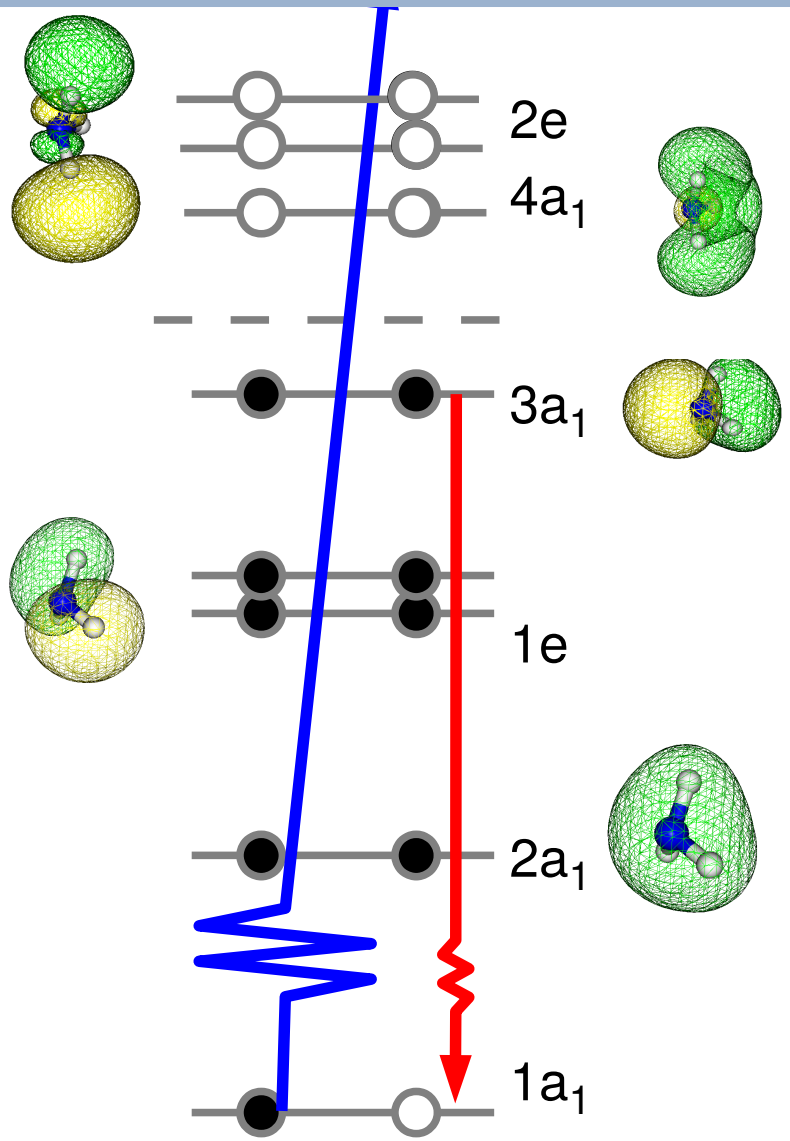


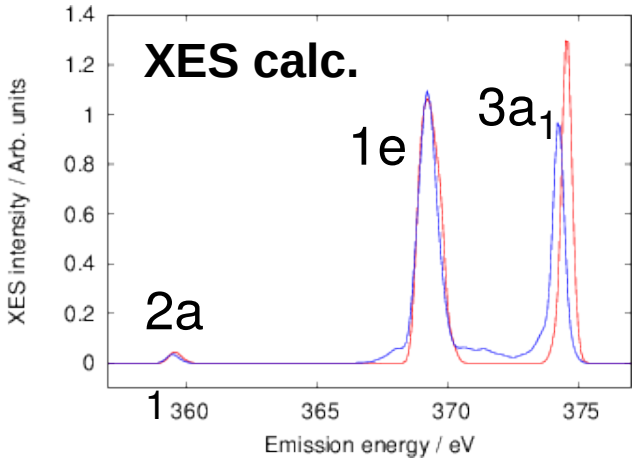
O PDOS would dominate in valence XPS

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

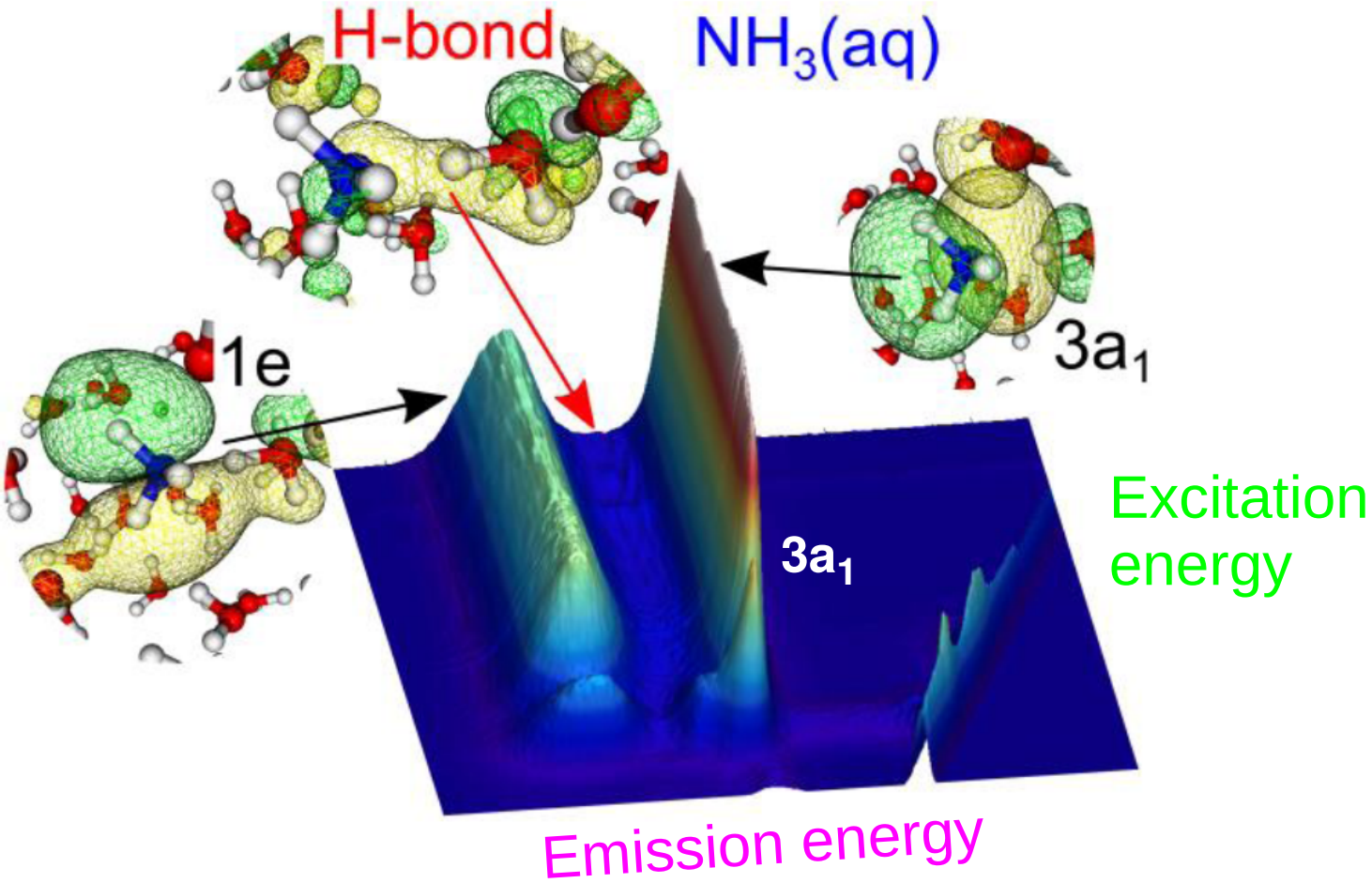
M. Ekimova et al. DOI: 10.1021/jacs.7b07207
J. Am. Chem. Soc. 2017, 139, 12773–12783

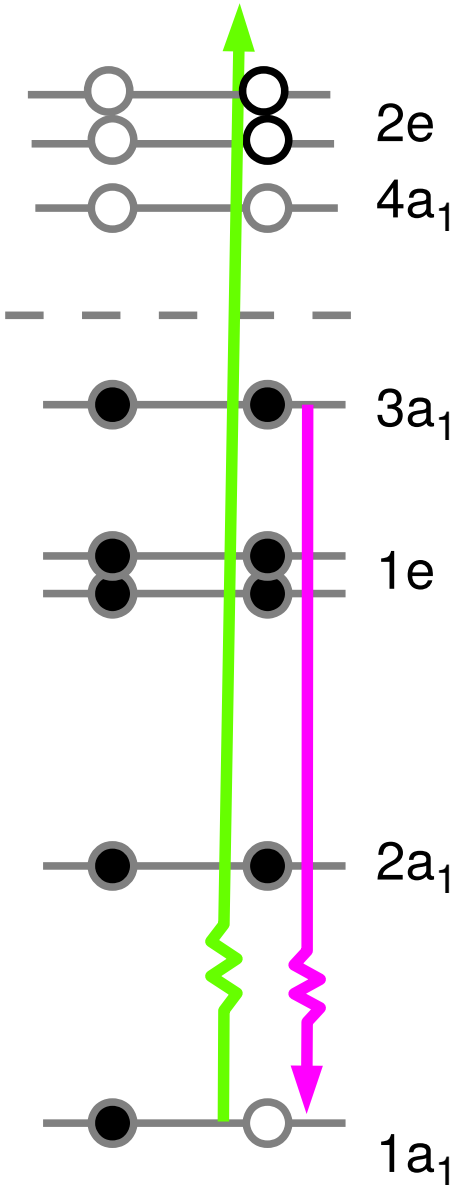
Electronic structure of NH_3(g) and NH_3(aq)





X-ray emission spectroscopy of NH_3(g) and NH_3(aq)





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.
Phys. Chem. Chem.Phys., **17**, 27145 (2015)

XES in CP2K

In CP2K:

XAS section

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

```
&FORCE_EVAL
  &DFT
    ...
    LSD
    &QS
      METHOD GAPW
      EPS_DEFAULT 1.0E-10
    &END QS
    ...
    &XAS
      DIPOLE_FORM   VELOCITY
      STATE_TYPE    1s
      ATOMS_LIST    1
      METHOD        TP_VAL
      XES_CORE      1.0
      &SCF
        !DSCF
      &END SCF
      &LOCALIZE
      &END
      &PRINT
        &XES_SPECTRUM
          FILENAME ./h2o
        &END
      &END
    &END XAS
  &END DFT
```

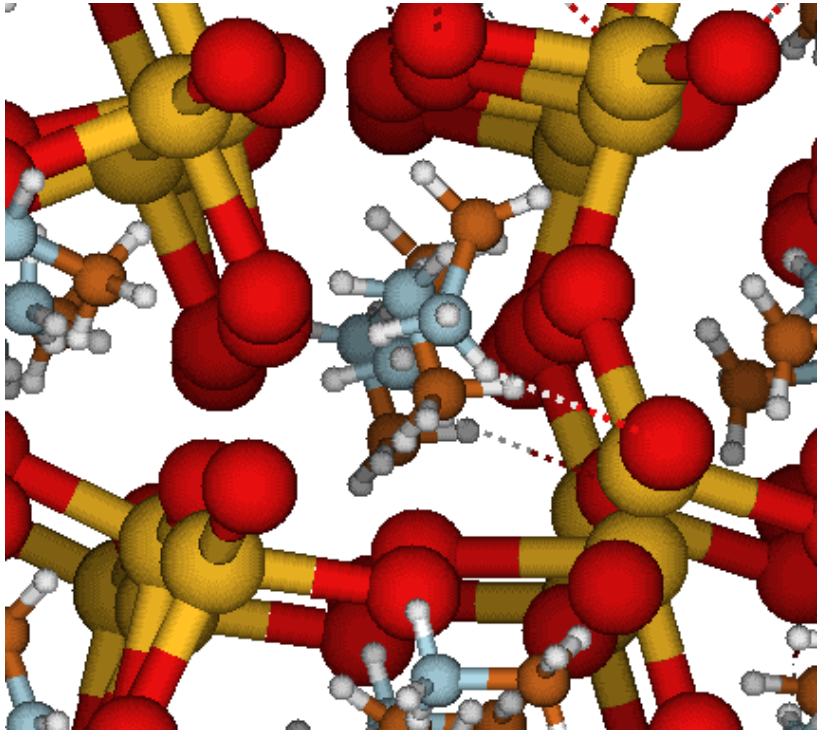
```
METHOD        TP_FLEX
XAS_CORE      1.0
XAS_TOT_EL    5
```

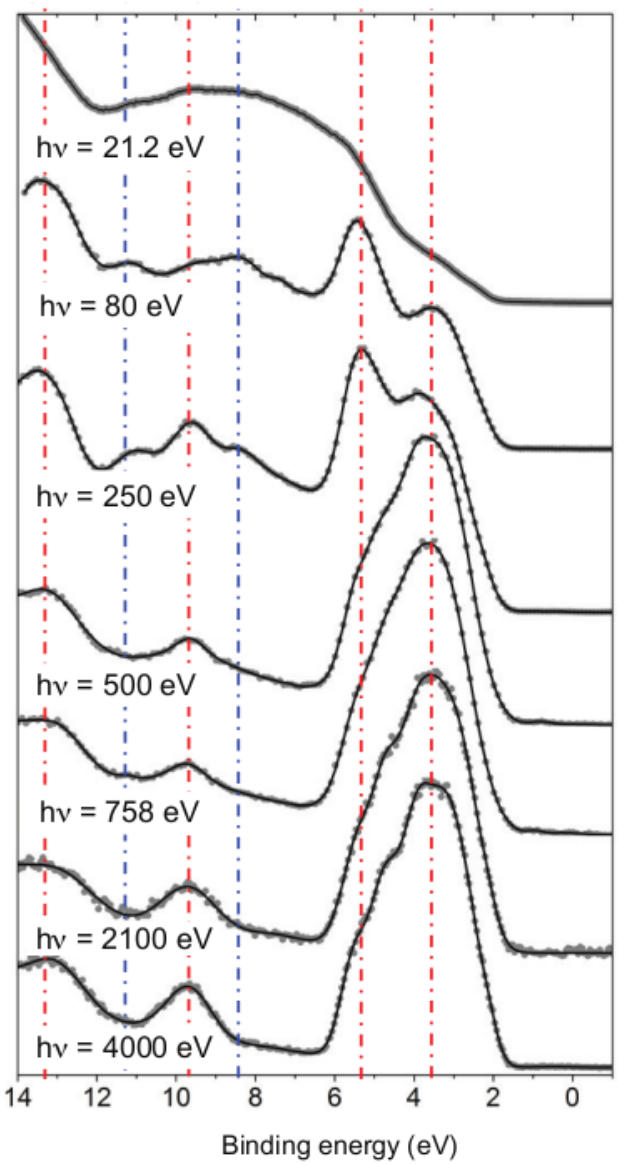
Output spectrum

```
Emission spectrum for atom      1, index of excited core MO is     1, # of lines      5
    1      0.00000000      0.00000000      0.00000000     -0.00000000      0.00000000   1.00000
    2    485.71459420     -0.00563467     -0.22020527     -0.07102793      0.05356708   1.00000
    3    497.86840667     -0.87279925      0.01937984      0.00882570      0.76223201   1.00000
    4    501.75564296     -0.02221103     -0.87187036     -0.28115240      0.83969793   1.00000
    5    504.10422332     -0.00300028      0.32795079     -1.01658135      1.14099837   1.00000
```

Perovskite solar cells: $CH_3NH_3PbI_3$

Photo-energy dependence in XPS

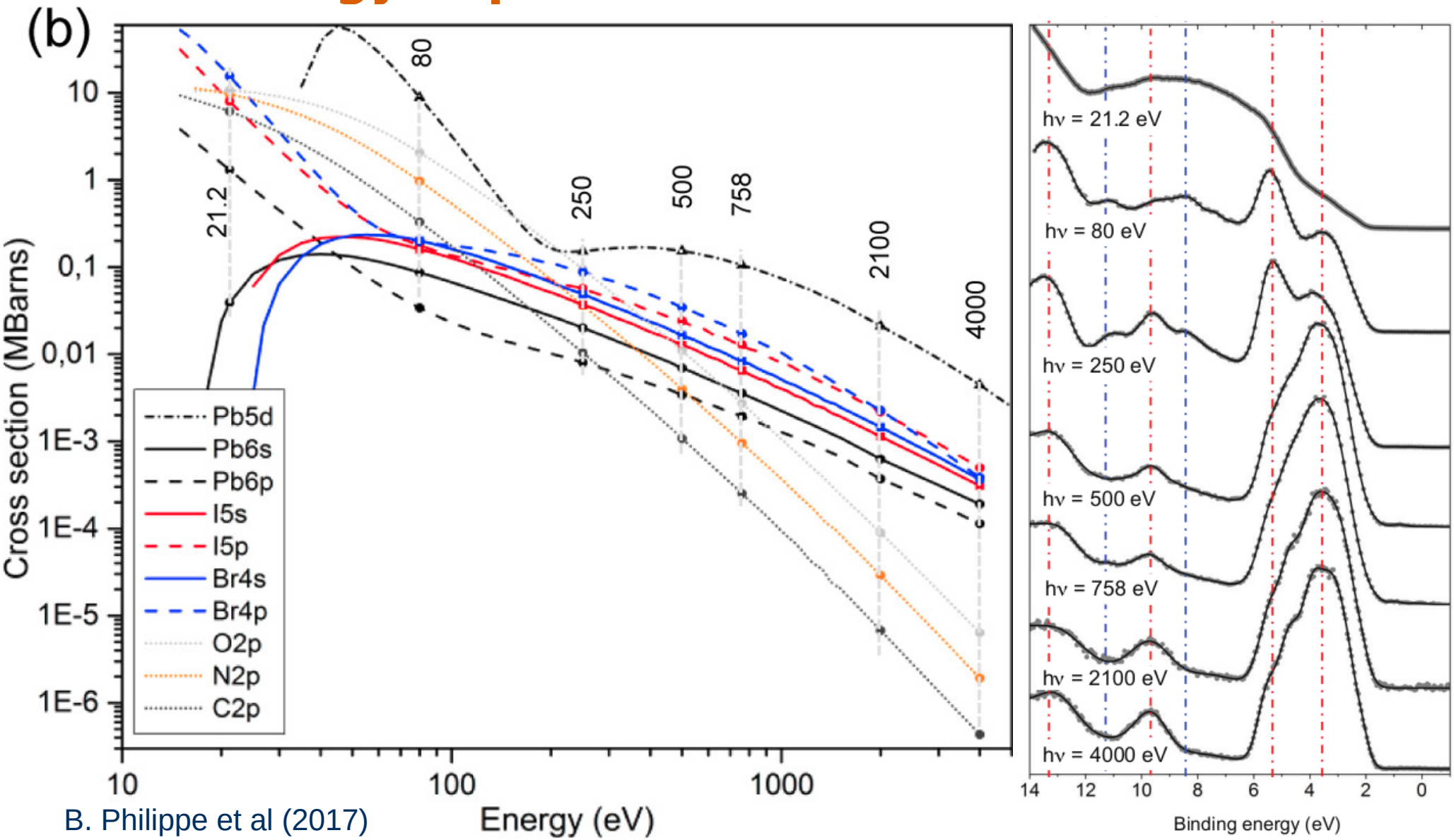




B. Philippe et al (2017)
J. Phys. Chem. C **121** 48

Perovskite solar cells: $CH_3NH_3PbI_3$

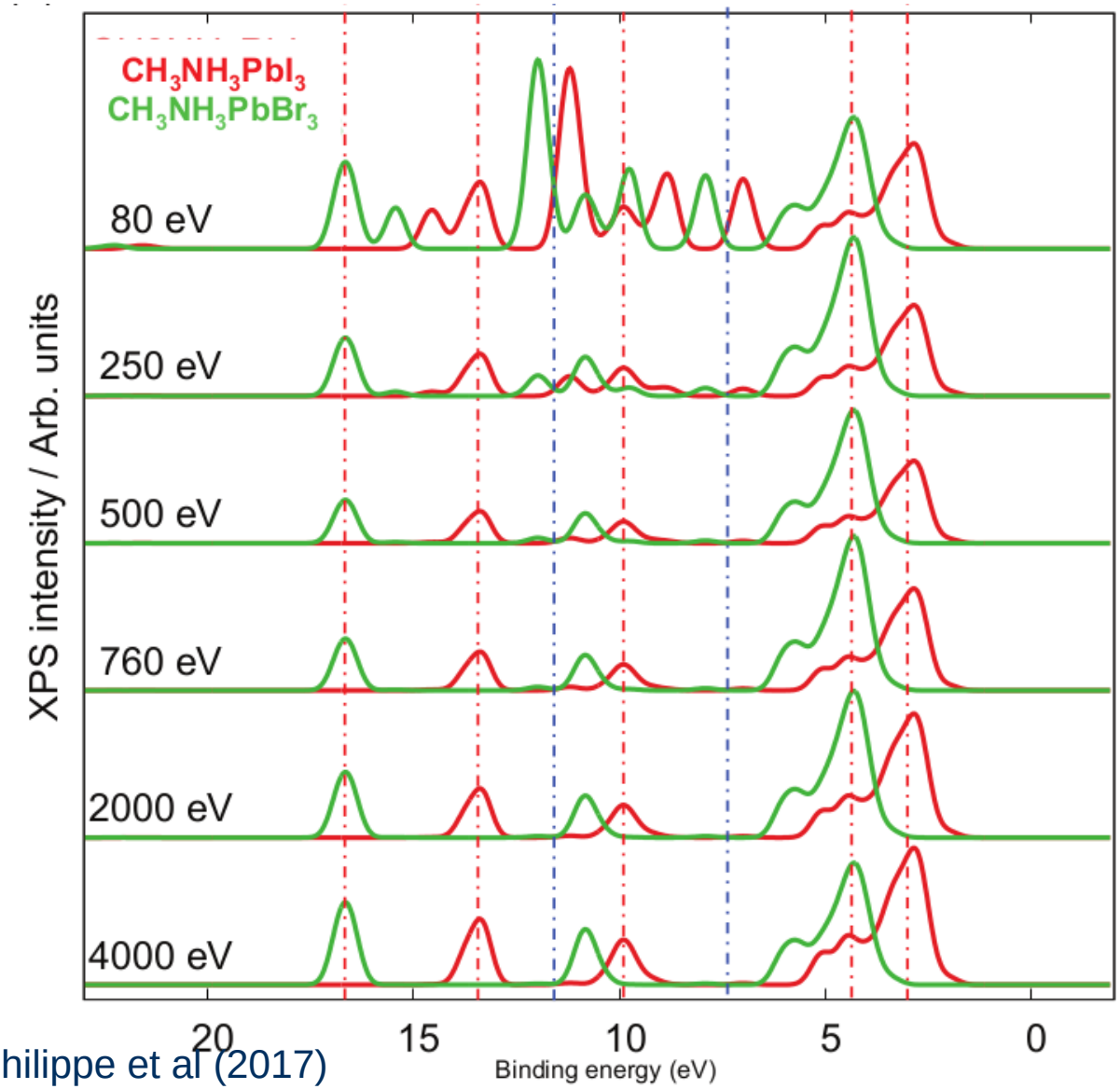
Photo-energy dependence in XPS

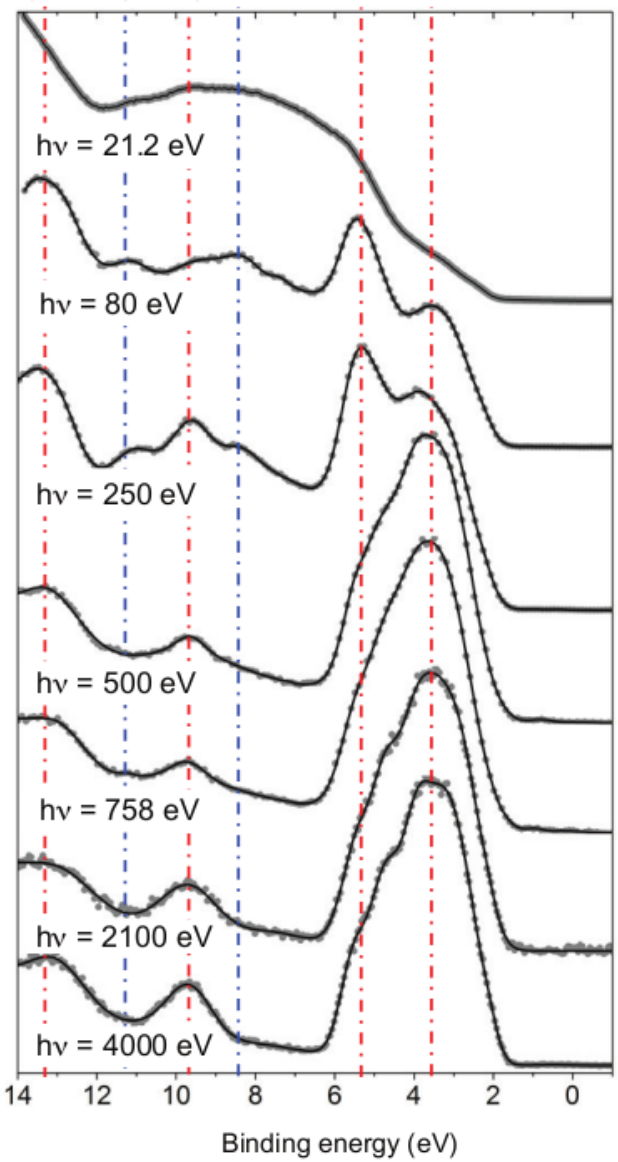


B. Philippe et al (2017)
J. Phys. Chem. C **121** 48

Perovskite solar cells: $CH_3NH_3PbI_3$

Photo-energy dependence in XPS

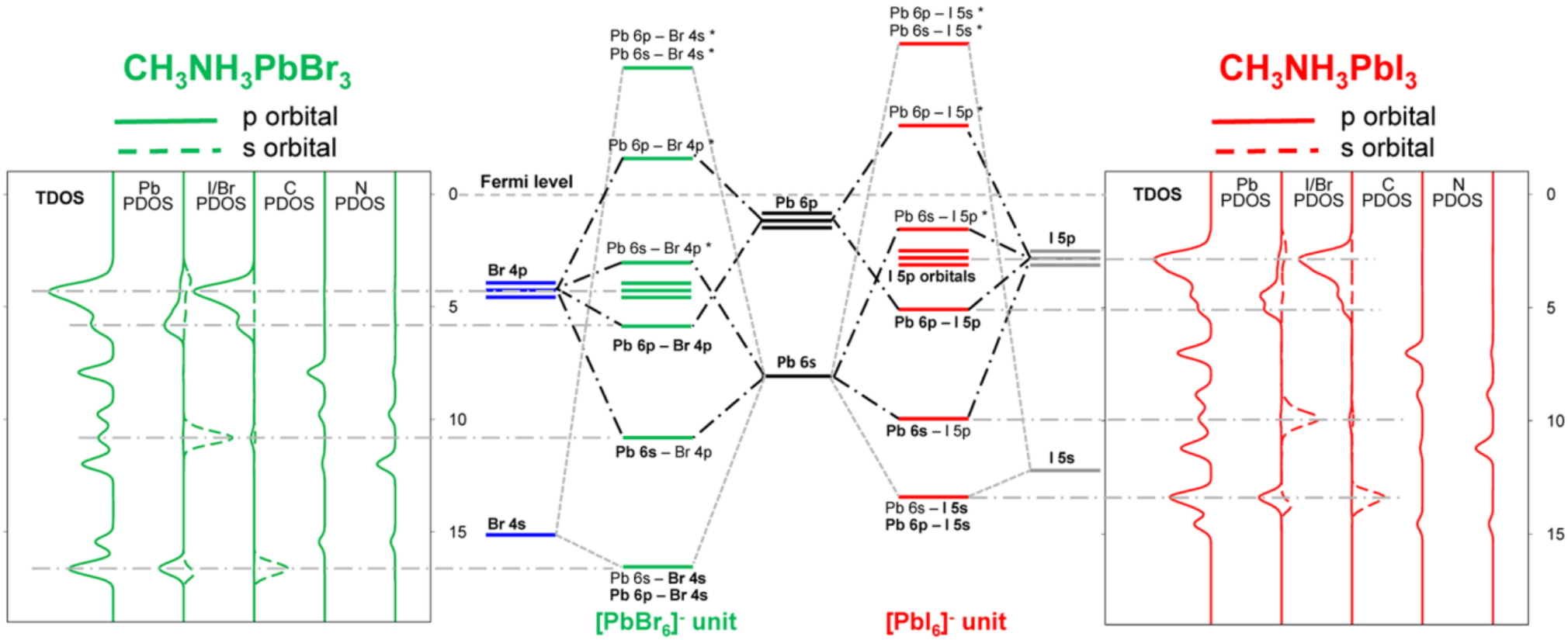




B. Philippe et al (2017)
J. Phys. Chem. C **121** 48

Perovskite solar cells: $CH_3NH_3PbI_3$

Understanding the valence band from orbitals



B. Philippe et al (2017)
J. Phys. Chem. C **121** 48

Thank you for your attention!

Questions?