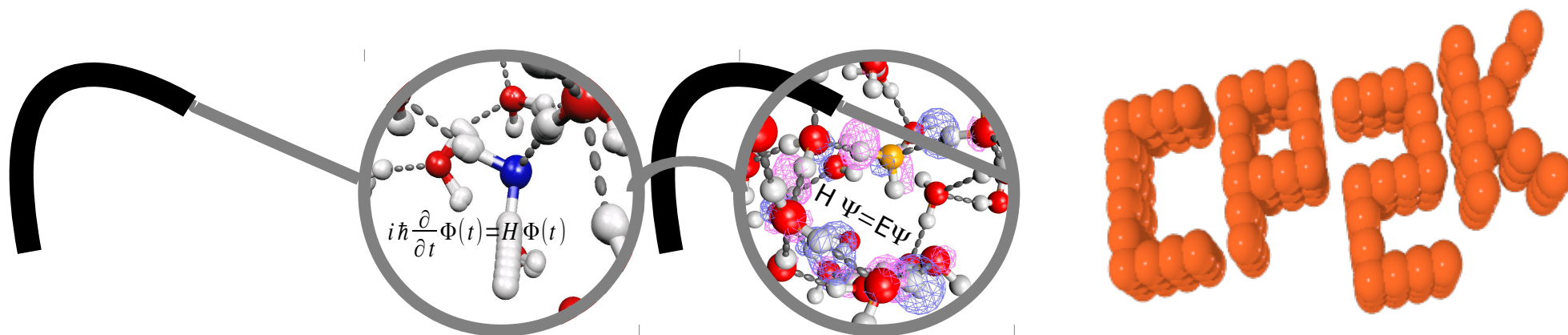




Simulating X-ray Spectroscopies with CP2K

Axel Erbing
Department of Physics

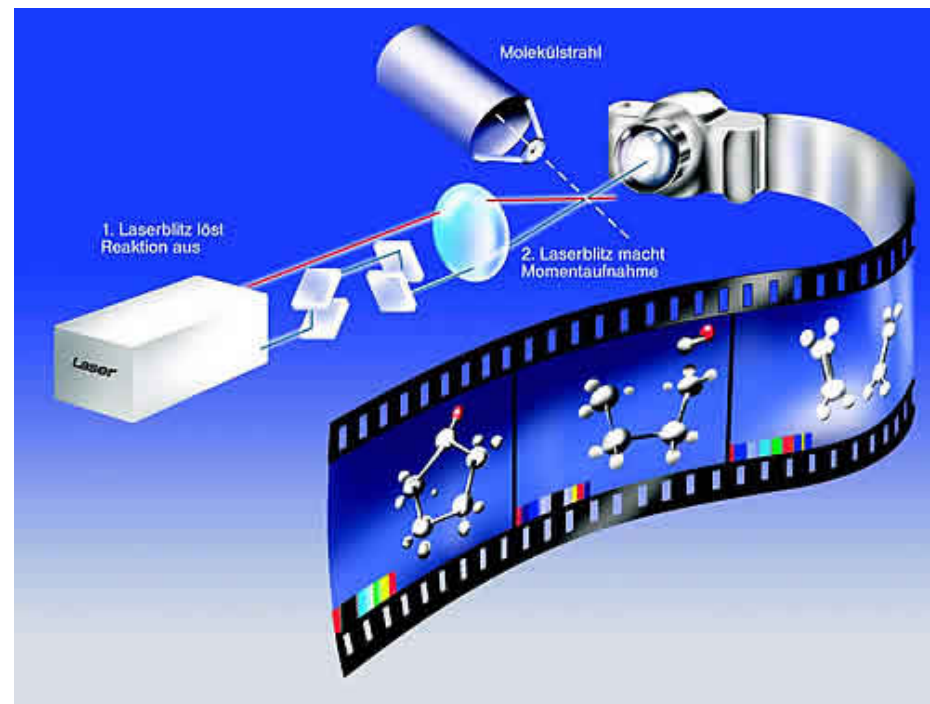
CONEXS SUMMER SCHOOL 2019:
Analysing X-ray Spectroscopy



Stockholm
University

Theoretical spectrum simulations

- Why bother?

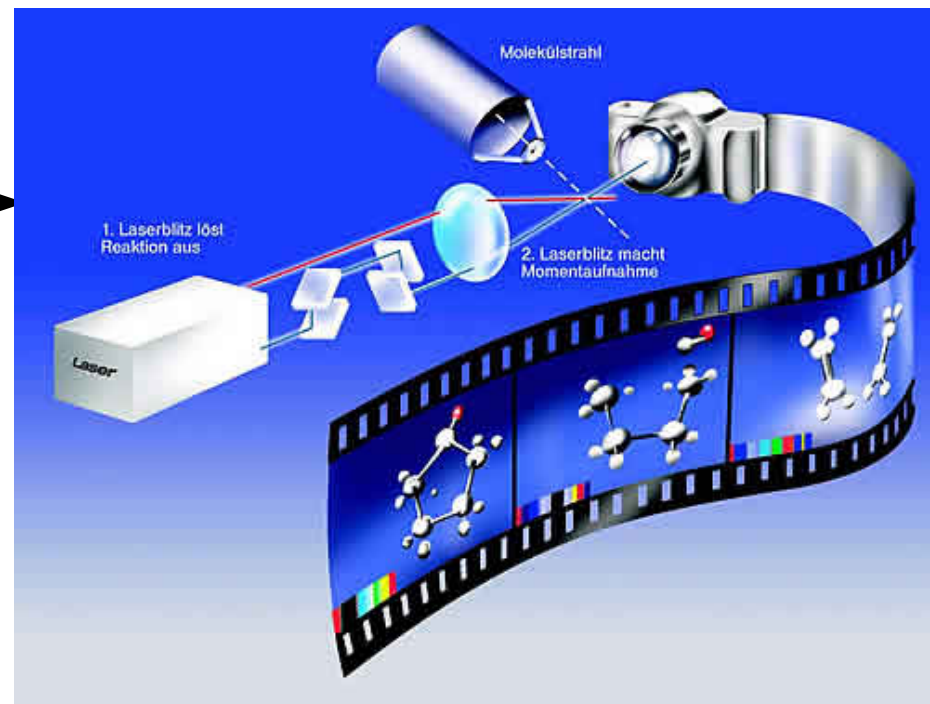


Femtochemistry: "Filming" chemical reactions using ultra-fast lasers.
(Source: DESY Hamburg)

Theoretical spectrum simulations

- Why bother?

**Theory is required
to develop the film**



Qualitative
assignment

CP2K

Evaluate
theo. models

Quantitative
analysis

Evaluate
approximations

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

Outline

Introduction

X-ray photo-electron spectroscopy (XPS)

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

Molecular dynamics (MD)

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

X-ray emission spectroscopy (XES)

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

Bonus example: XPS on perovskite solar cells

Quantum Chemistry $H\Psi=E\Psi$

Hartree-Fock

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

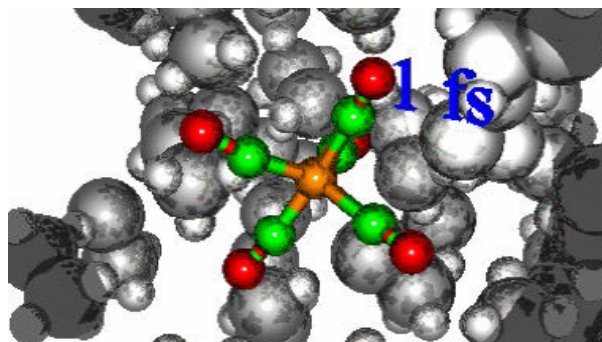
$$\Psi_{\text{HF}} = \det | \phi_1, \phi_2, \dots, \phi_N |$$

Momentary
e⁻ - e⁻ correlation
missing!

DFT

Singlet determinant

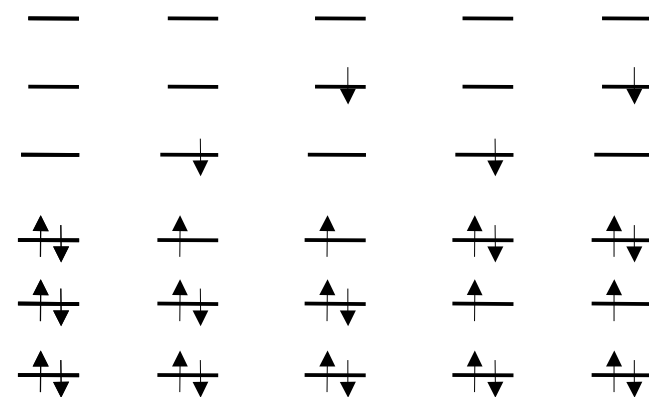
Correlation in **H**



Post-HF

Multi-determinant

Wave function correlated



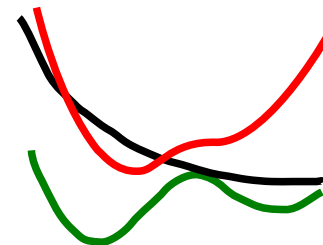
Ab initio Molecular dynamics

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

$$\mathbf{F}_I = -\nabla_I \min_{\phi_i} \{ E_{\text{KS}}(\{\phi_i\}; \mathbf{R}_I) \}$$

Quantum dynamics

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



AIMD: CPMD CP2K

QMD: Wave packet simulations

Quantum Chemistry $H\Psi=E\Psi$

Hartree-Fock

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

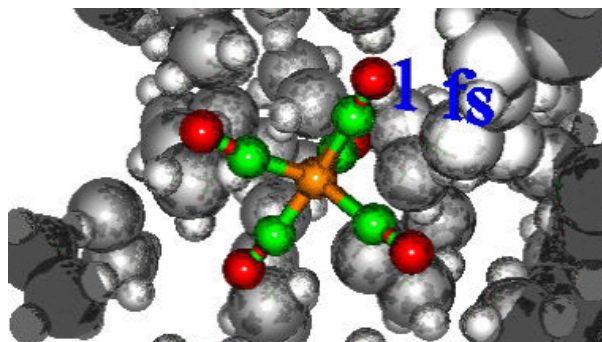
$$\Psi_{\text{HF}} = \det | \phi_1, \phi_2, \dots, \phi_N |$$

Momentary
e⁻ - e⁻ correlation
missing!

DFT

Singlet determinant

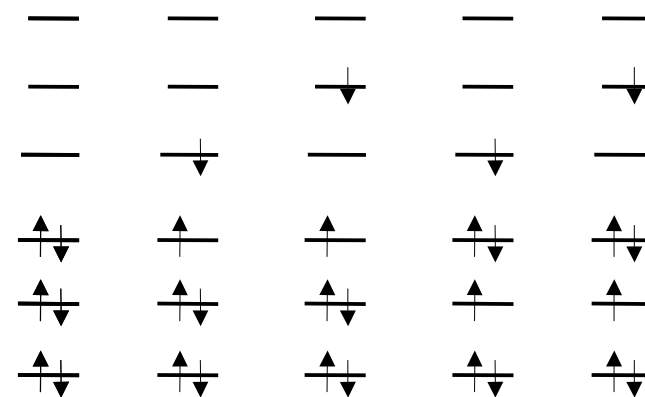
Correlation in **H**



Post-HF

Multi-determinant

Wave function correlated



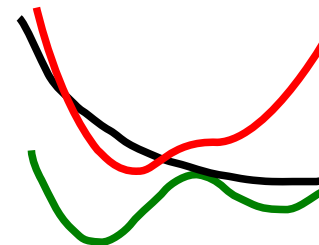
Ab initio Molecular dynamics

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

$$\mathbf{F}_I = -\nabla_I \min_{\phi_i} \{ E_{\text{KS}}(\{\phi_i\}; \mathbf{R}_I) \}$$

Quantum dynamics

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



AIMD: CPMD **CP2K**

QMD: Wave packet simulations

Core-level spectroscopy

X-ray photo-electron spectroscopy

**Core-ionization
(Valence-ionization)**

X-ray absorption spectroscopy

Core-excitation

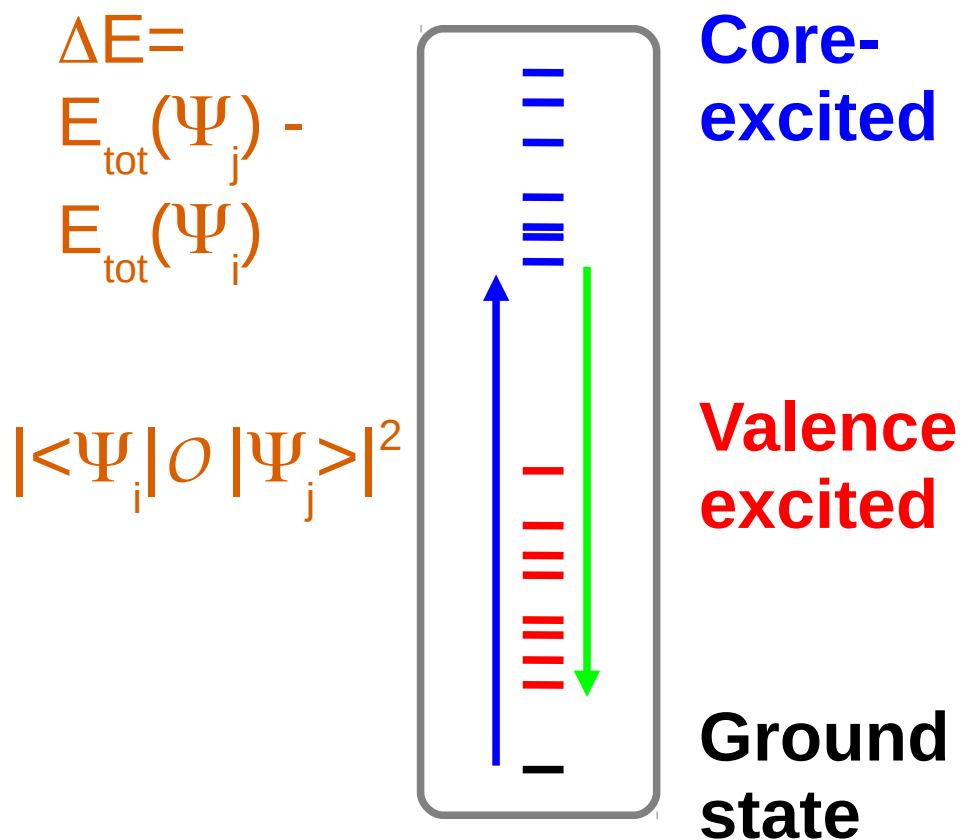
X-ray emission spectroscopy

Fluorescence decay

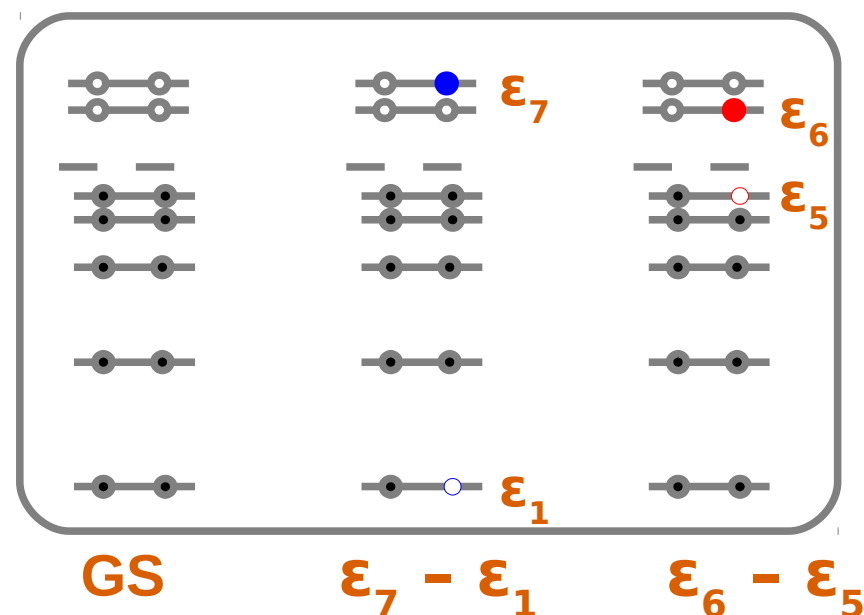
XPS XAS XES

Spectrum simulations $\hat{H} \Psi = E \Psi$

Accurate methods Electronic states



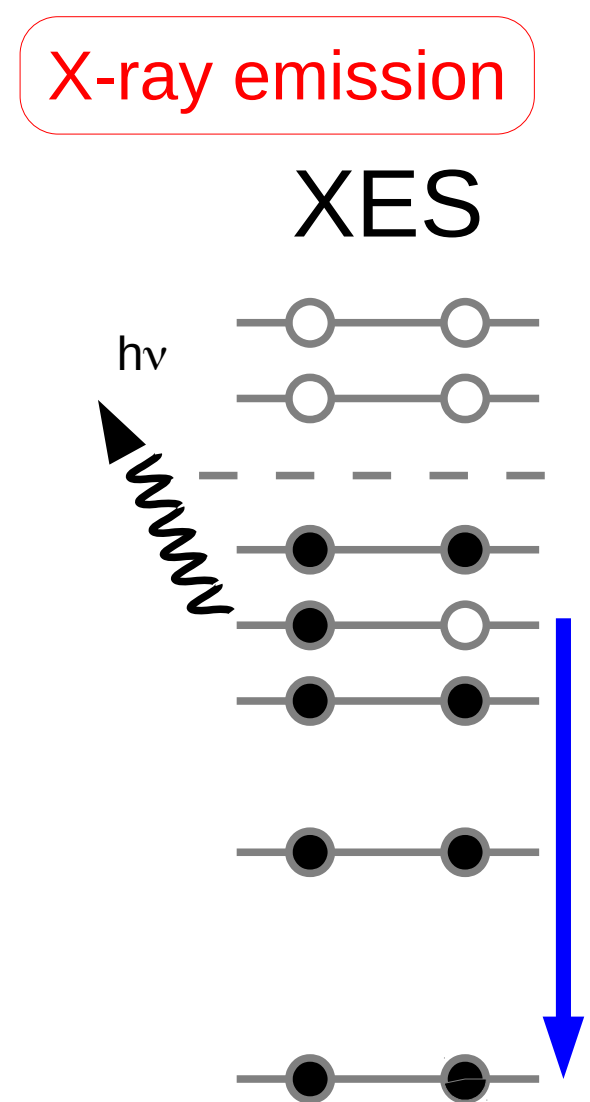
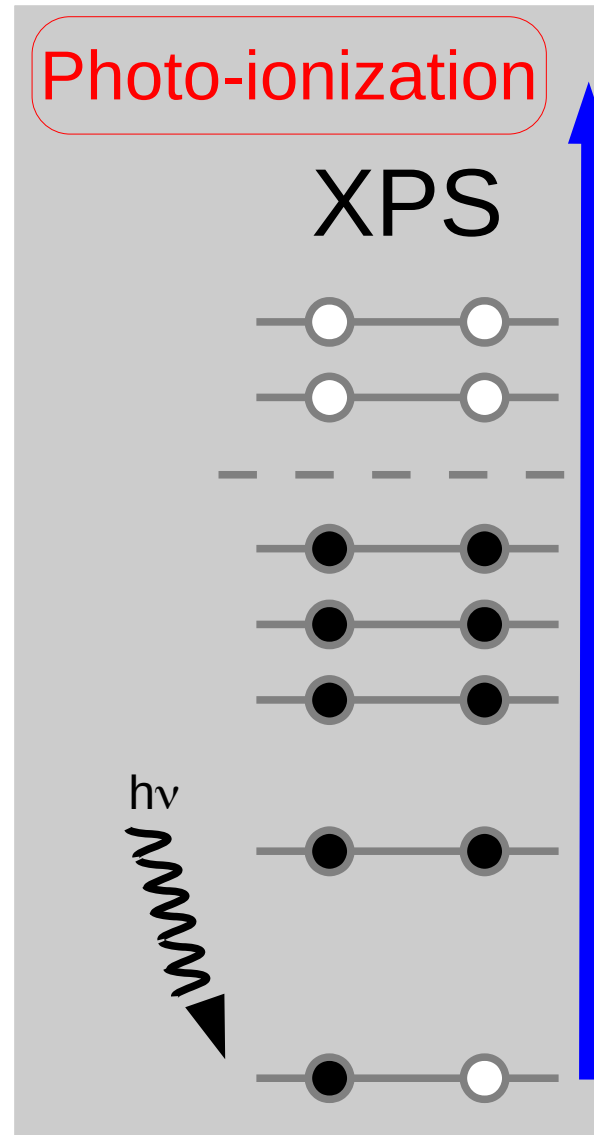
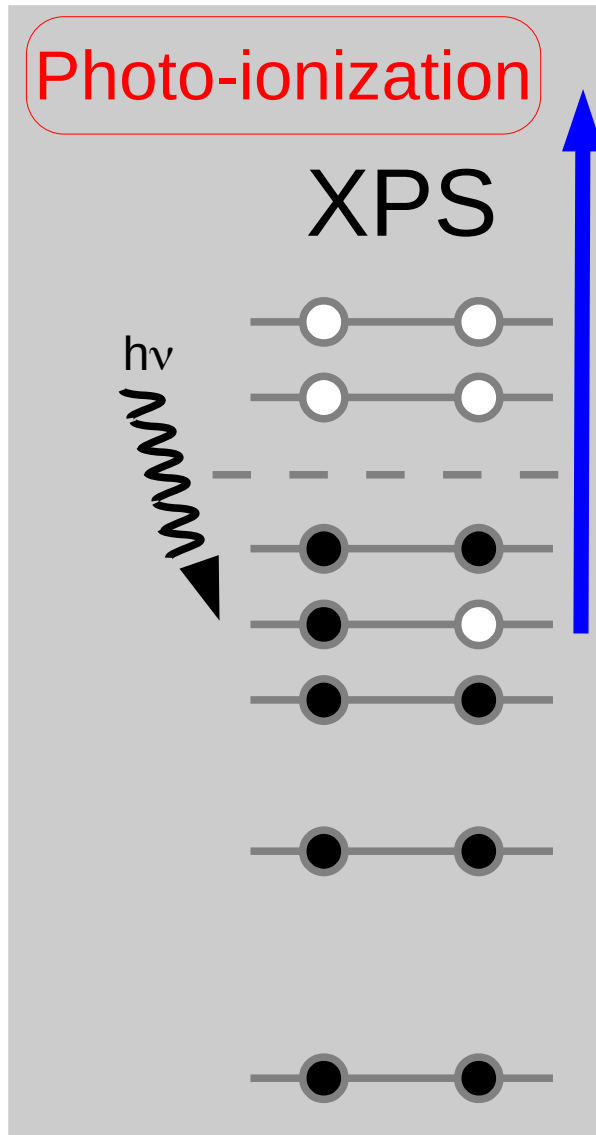
Approximate methods Molecular orbitals



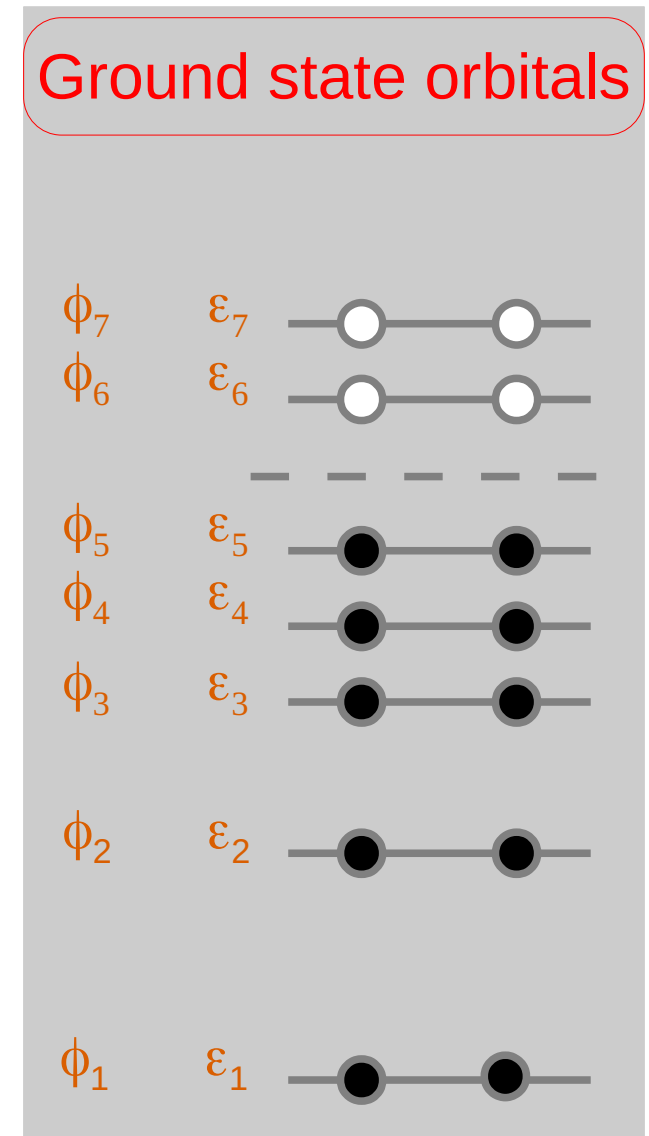
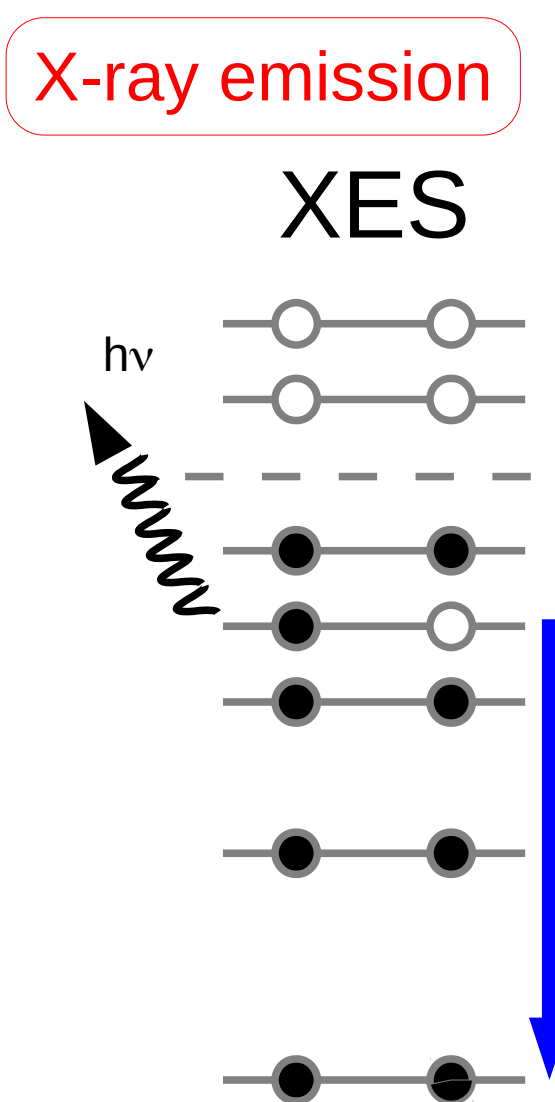
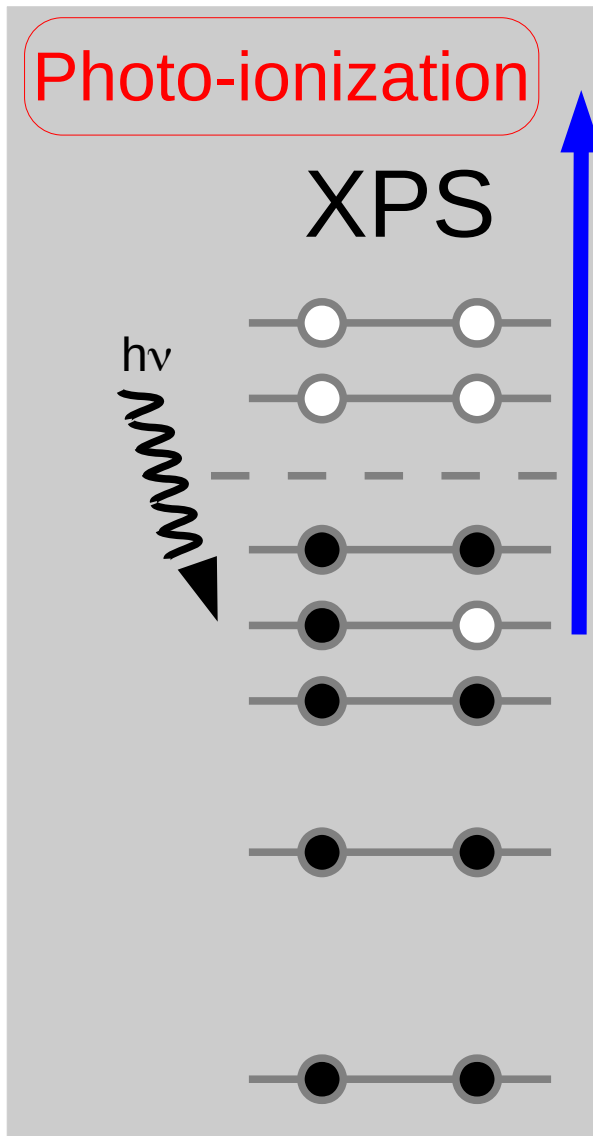
Transition potential DFT

$$|\langle \Psi_i | \hat{O} | \Psi_j \rangle|^2 = |\langle \phi_n | \hat{O} | \phi_m \rangle|^2$$

Orbital representation of the XPS and XES processes



Orbital representation of the XPS and XES processes

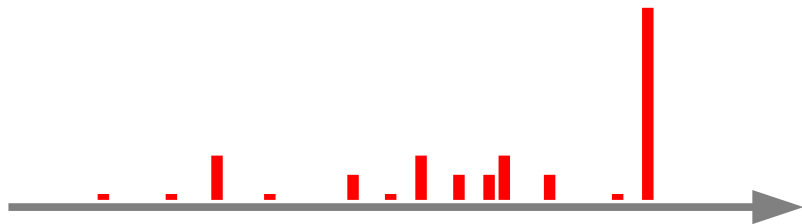


Spectrum simulations $H \Psi = E \Psi$

Broadening:

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

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

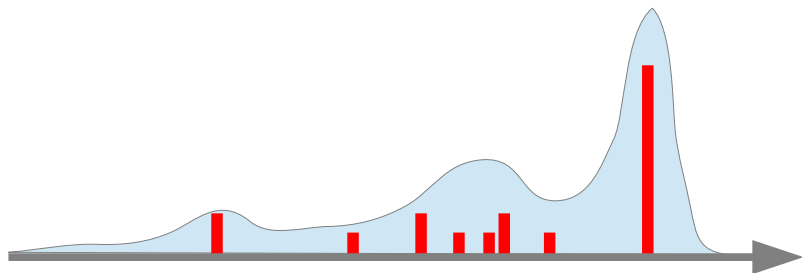


Core-hole life-time

Vibrational

Configurational

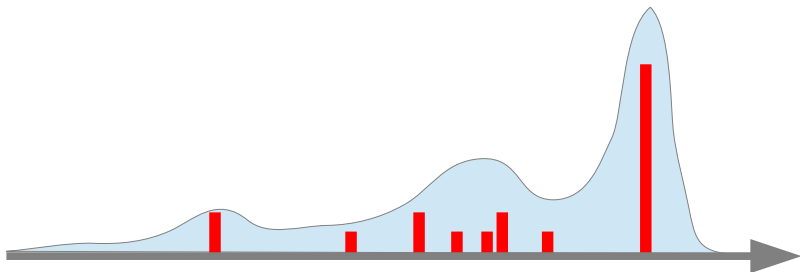
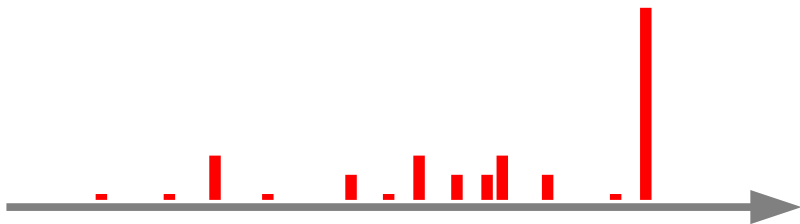
Experimental



Spectrum simulations $H \Psi = E \Psi$

Broadening:

How to simulate it?



Simplest approach:

Convolution with Gaussian functions

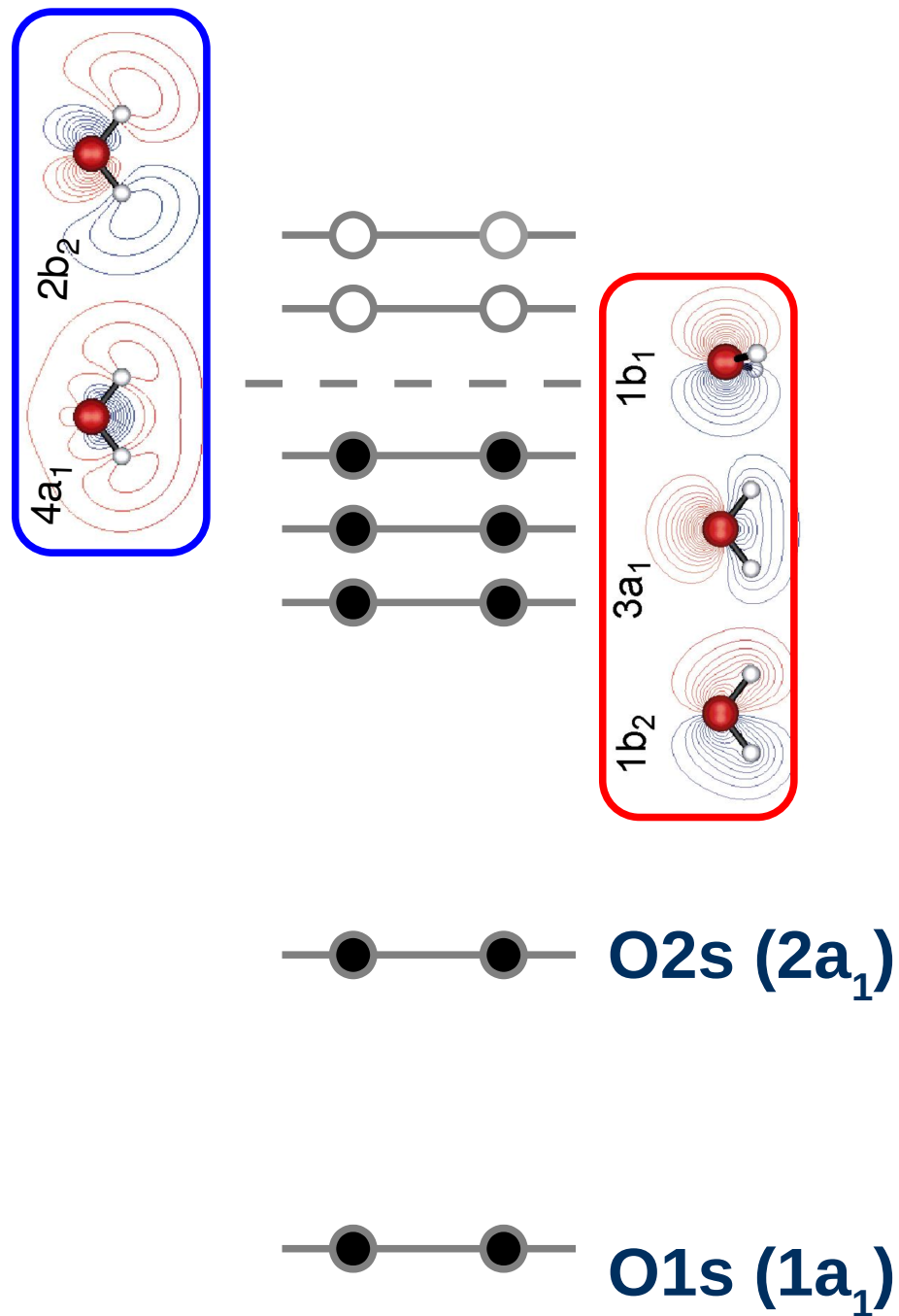
$$I(E) = \sum_i f(\epsilon_i) e^{-(E-\epsilon_i)^2/2\sigma^2}$$

Width parameter

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

Other functions, e.g. Lorentzians

Molecular orbitals of $\text{H}_2\text{O}(\text{g})$ - C_{2v} Point group



X-ray spectroscopy Case study: $\text{H}_2\text{O}(\text{g})$

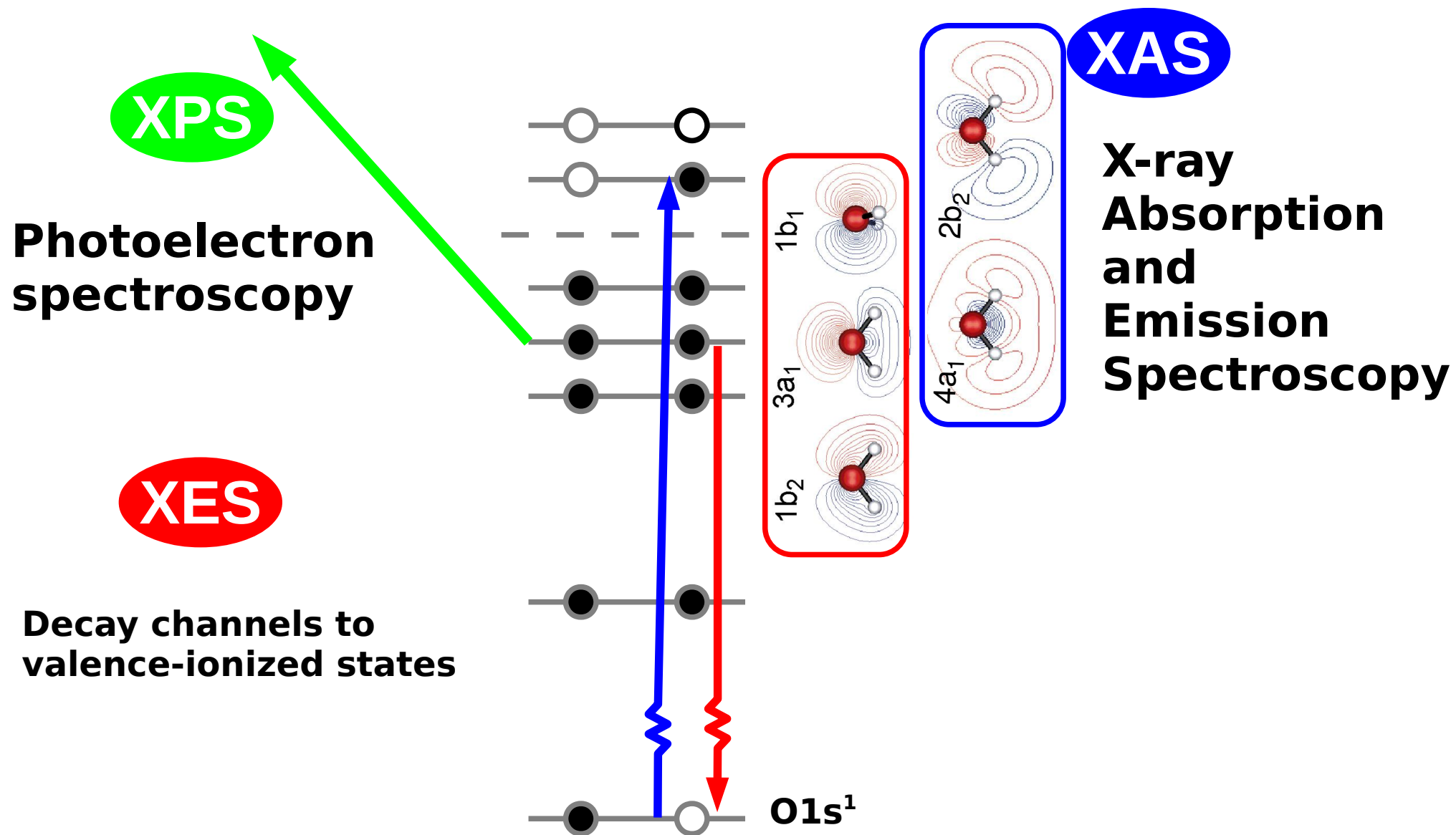
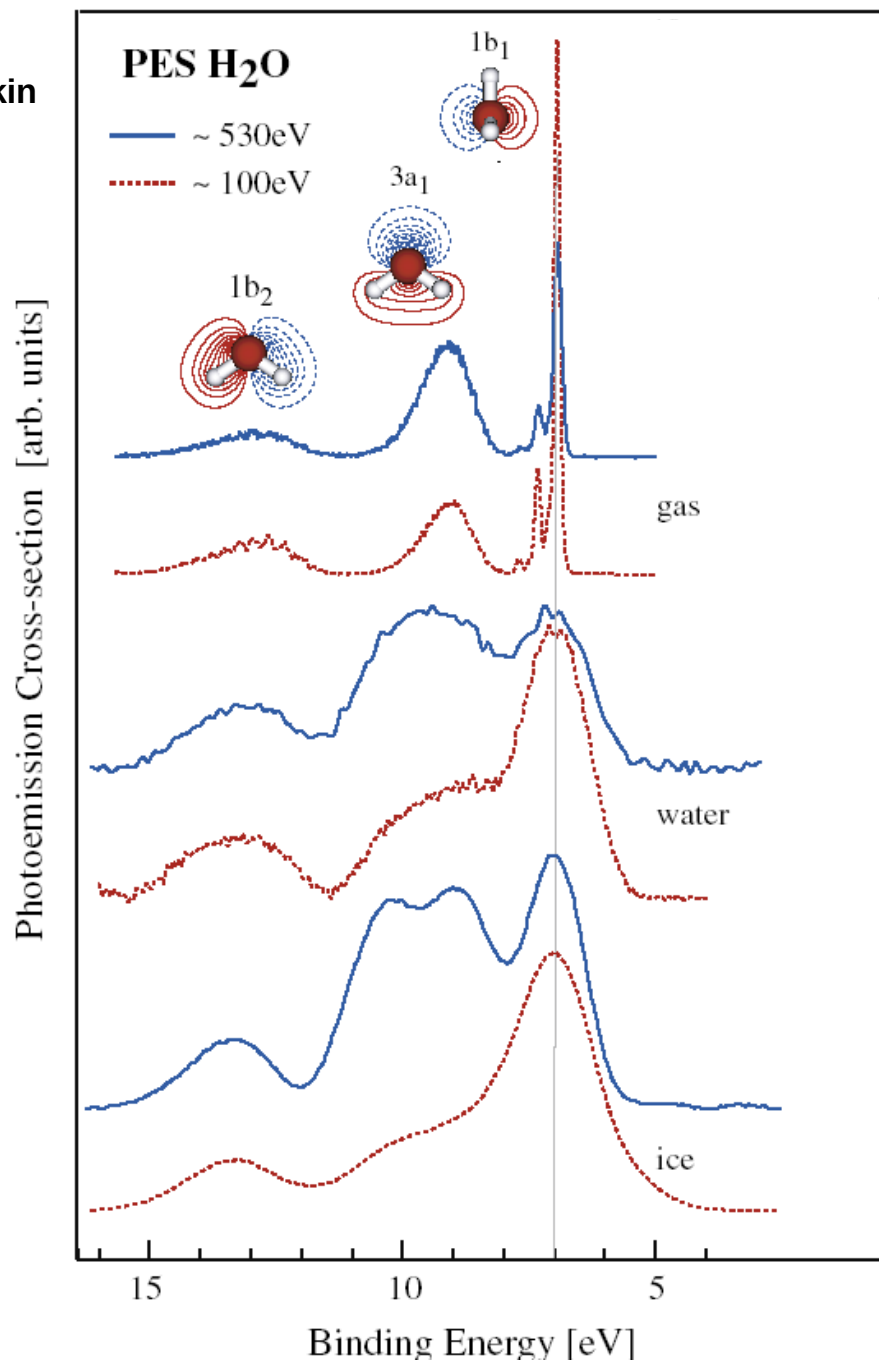


Photo electron spectroscopy of $\text{H}_2\text{O}(\text{g}, \text{l}, \text{s})$

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



Koopman's theorem

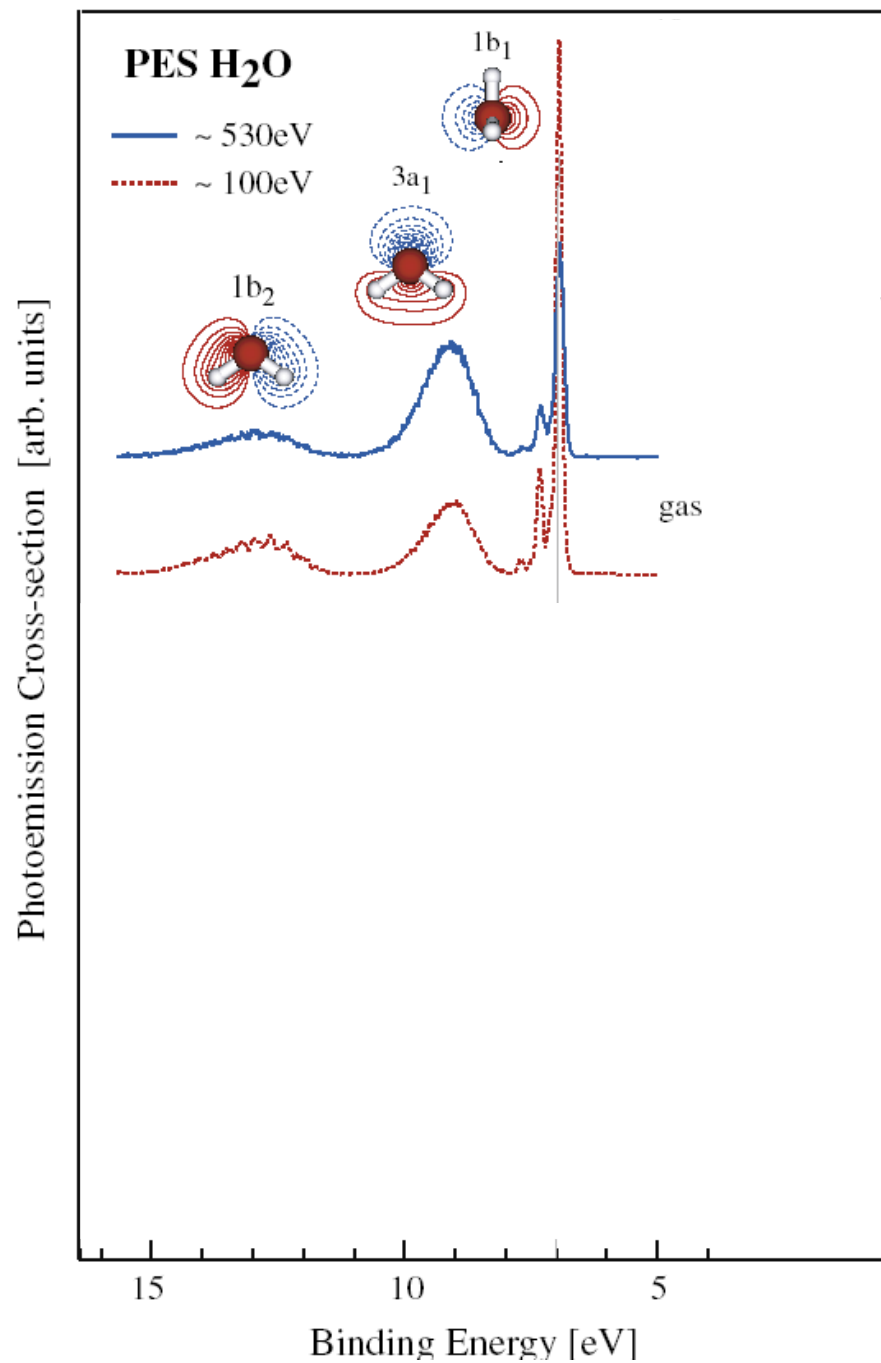
HF orbital energies

approximate

Ionization binding energies

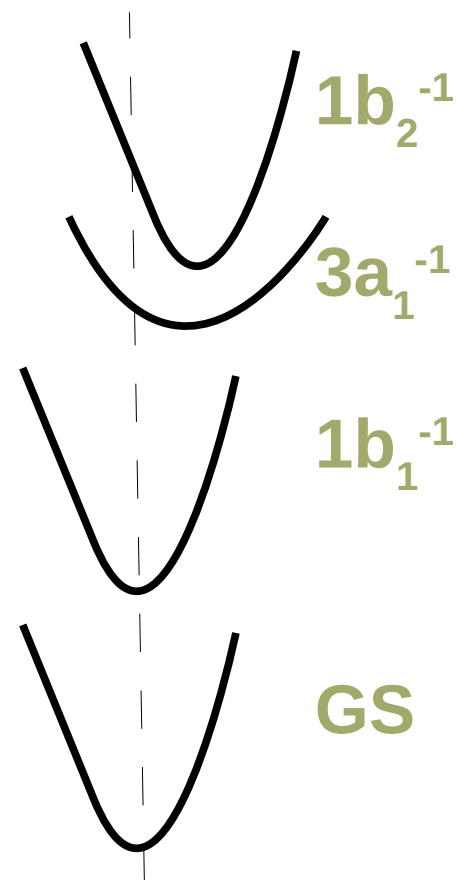
(However, we will cheat and also use DFT Kohn-Sham energies which require ad hoc shifts)

Photo electron spectroscopy of $\text{H}_2\text{O}(\text{g}, \text{l}, \text{s})$



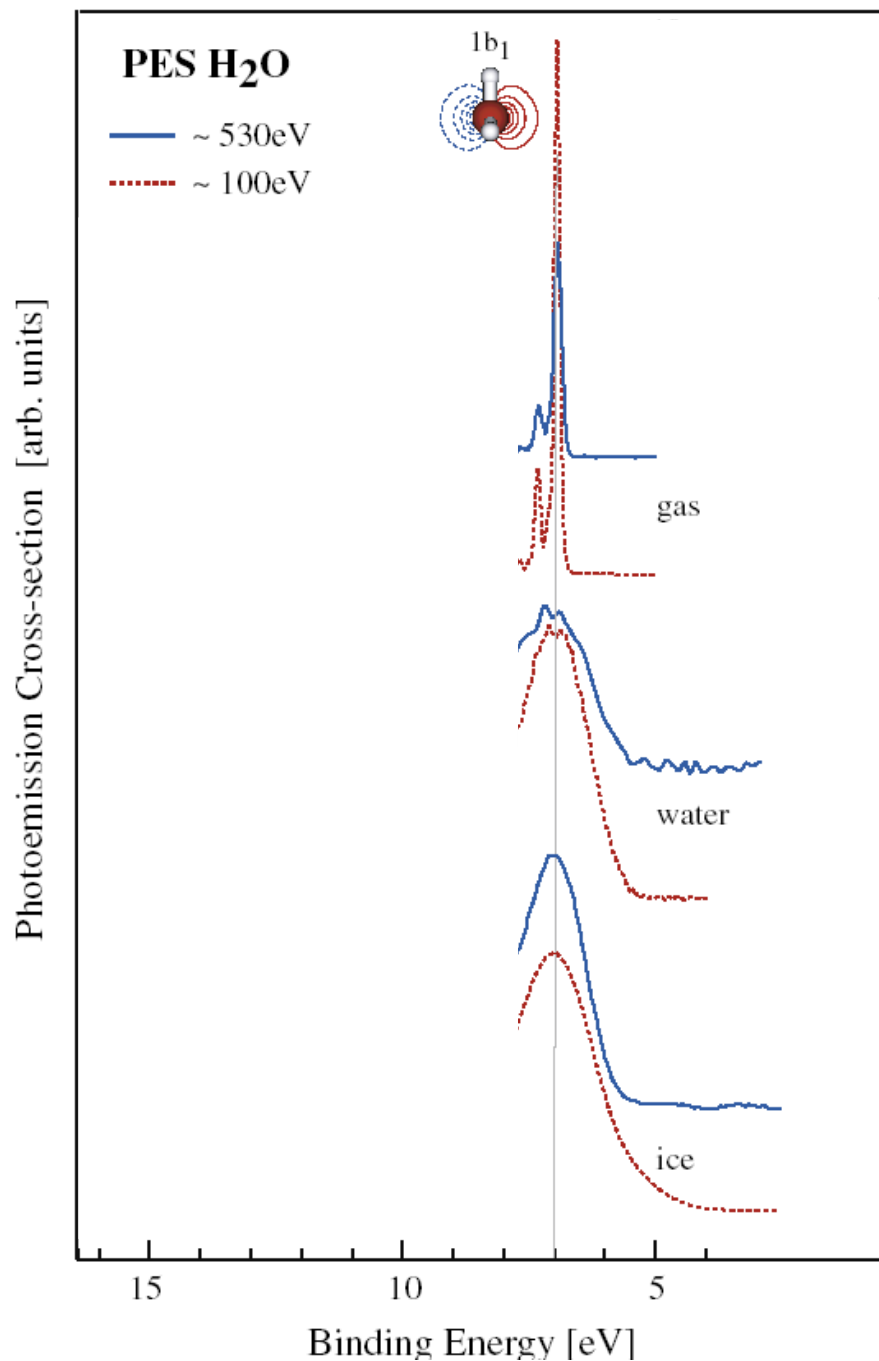
Franck-Condon

Vibrational excitations

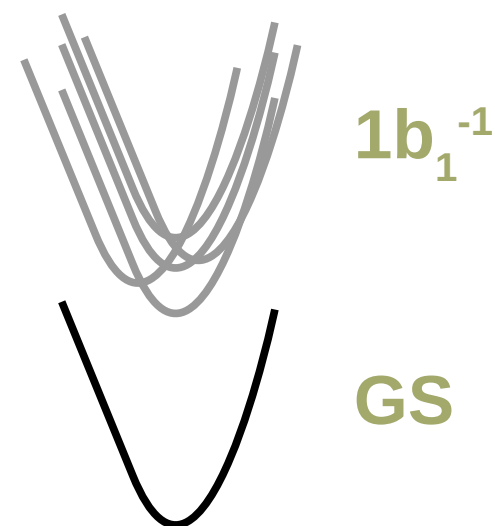


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Photo-electron spectroscopy of $\text{H}_2\text{O}(\text{g}, \text{l}, \text{s})$



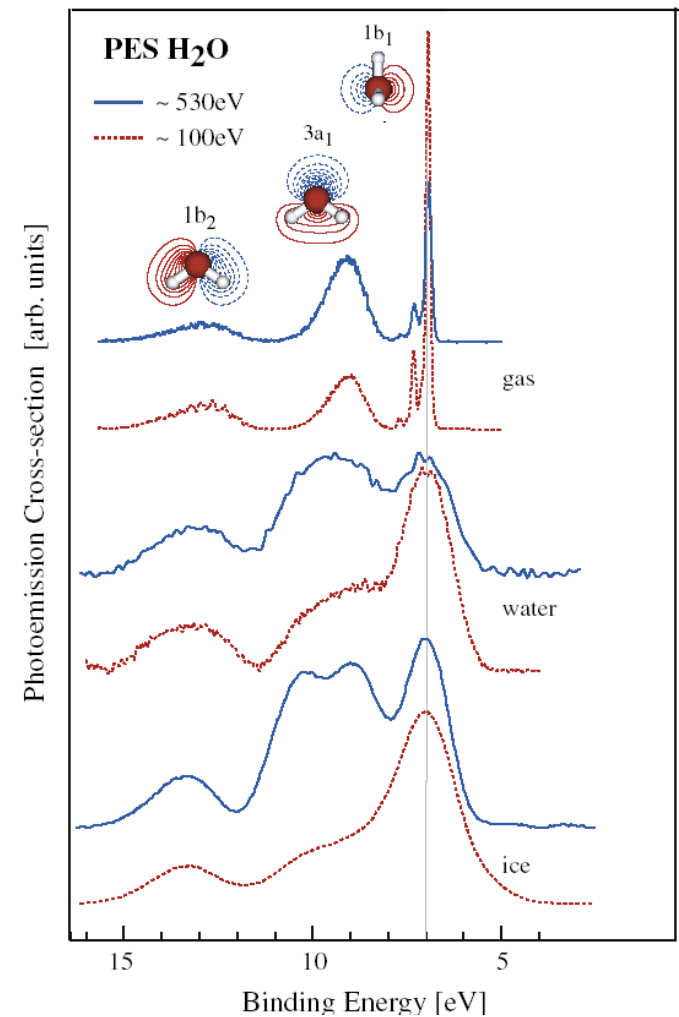
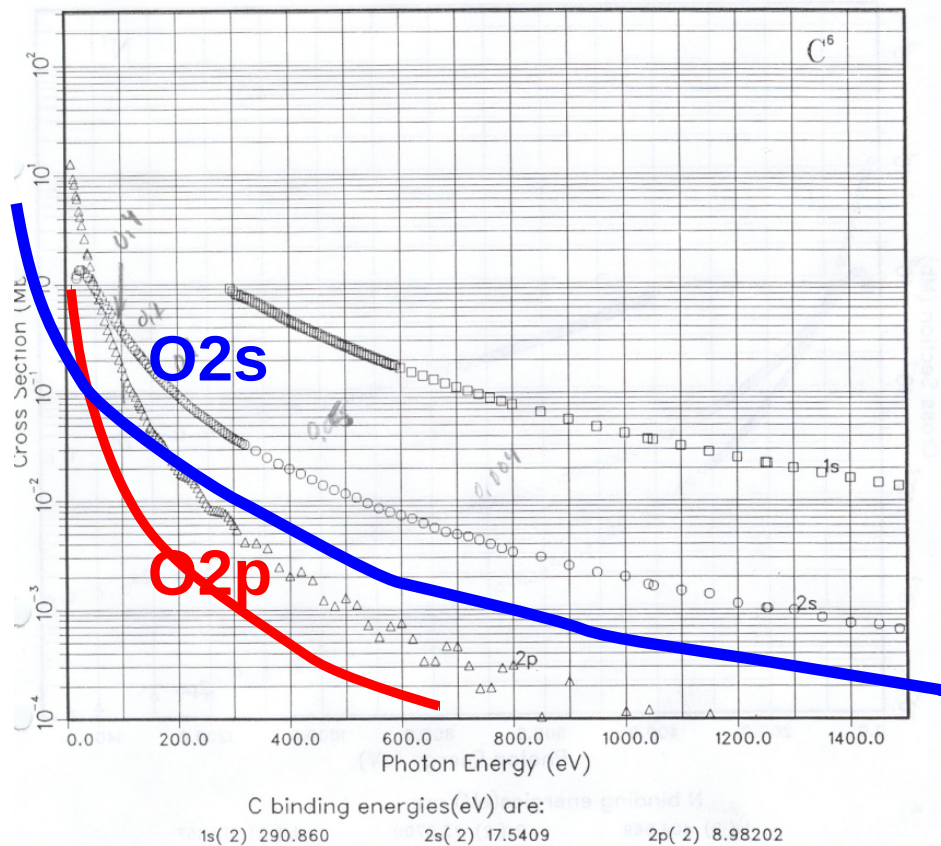
Inhomogeneous Broadening



(Homogeneous broadening is due to finite life-times)

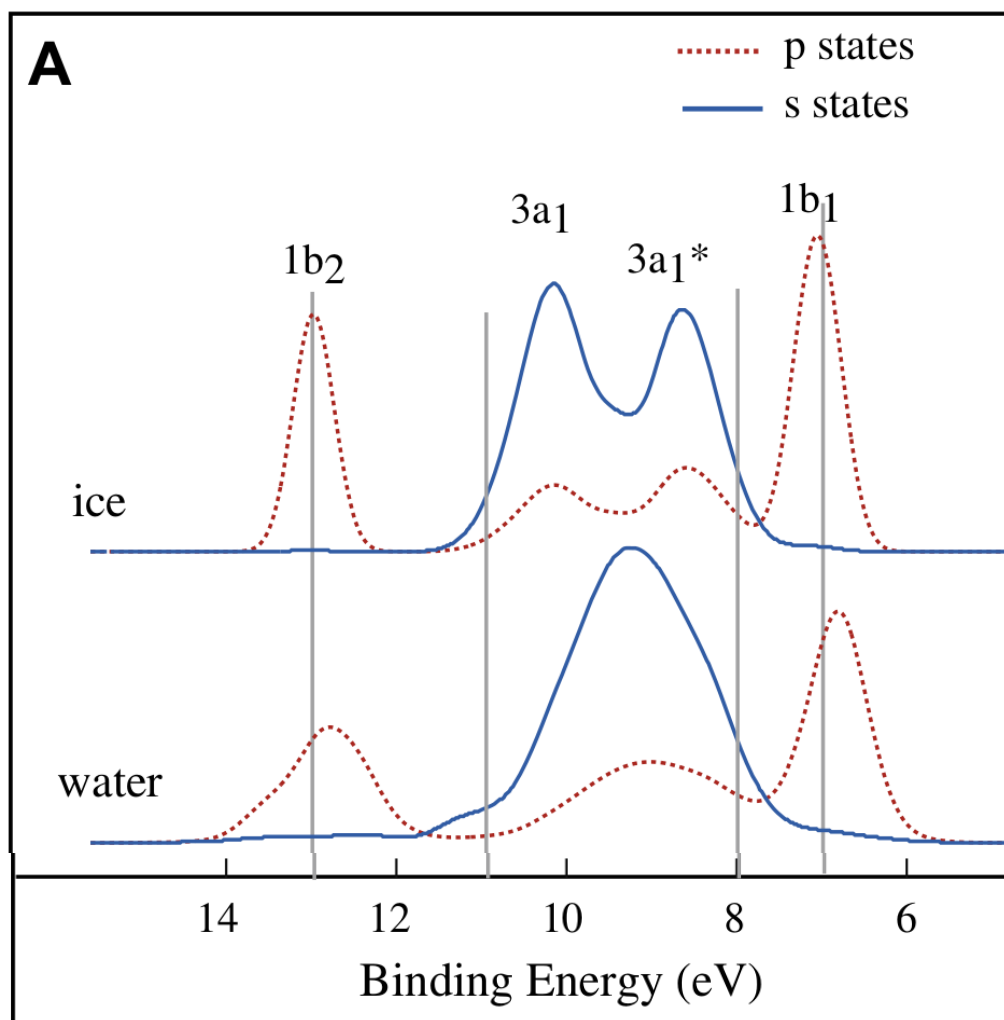
Photo electron spectroscopy of $\text{H}_2\text{O}(\text{g}, \text{l}, \text{s})$

Cross sections vary with photonenergy

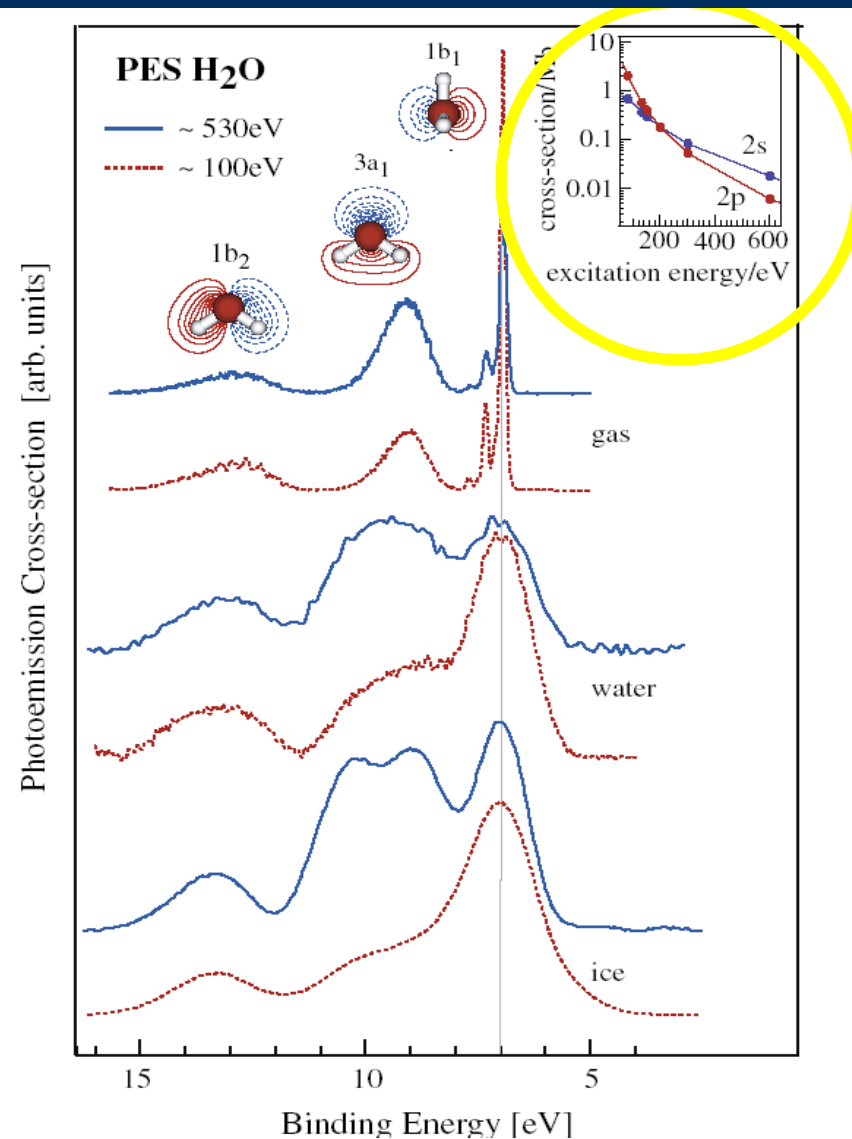


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Photo electron spectroscopy of H₂O(g,l,s)



Notice: In C_{2v} symmetry only a₁ can have oxygen s-sym.



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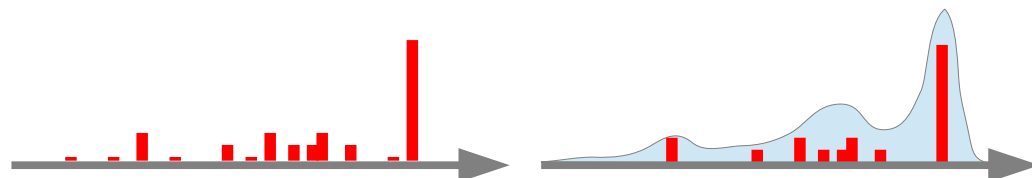
XPS in CP2K

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 0 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 0 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

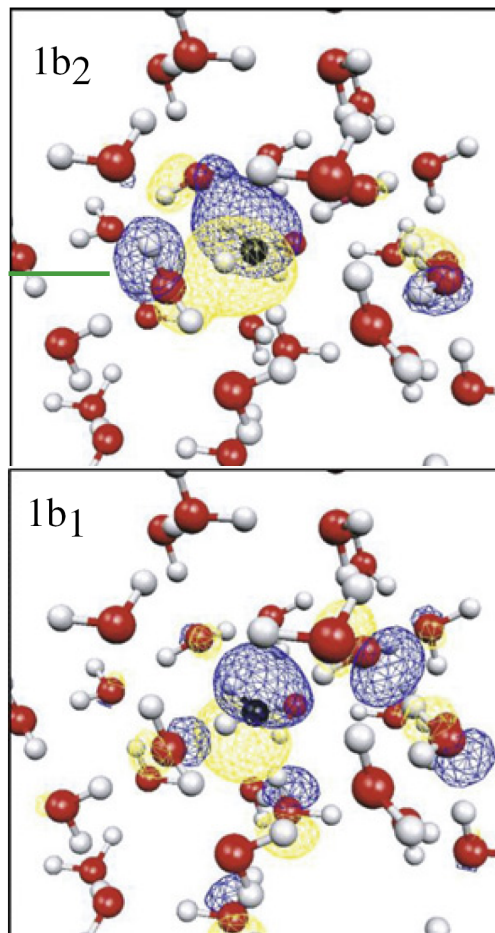
e.g. PDOS_H2O-k1-1.pdos

Molecular Dynamics

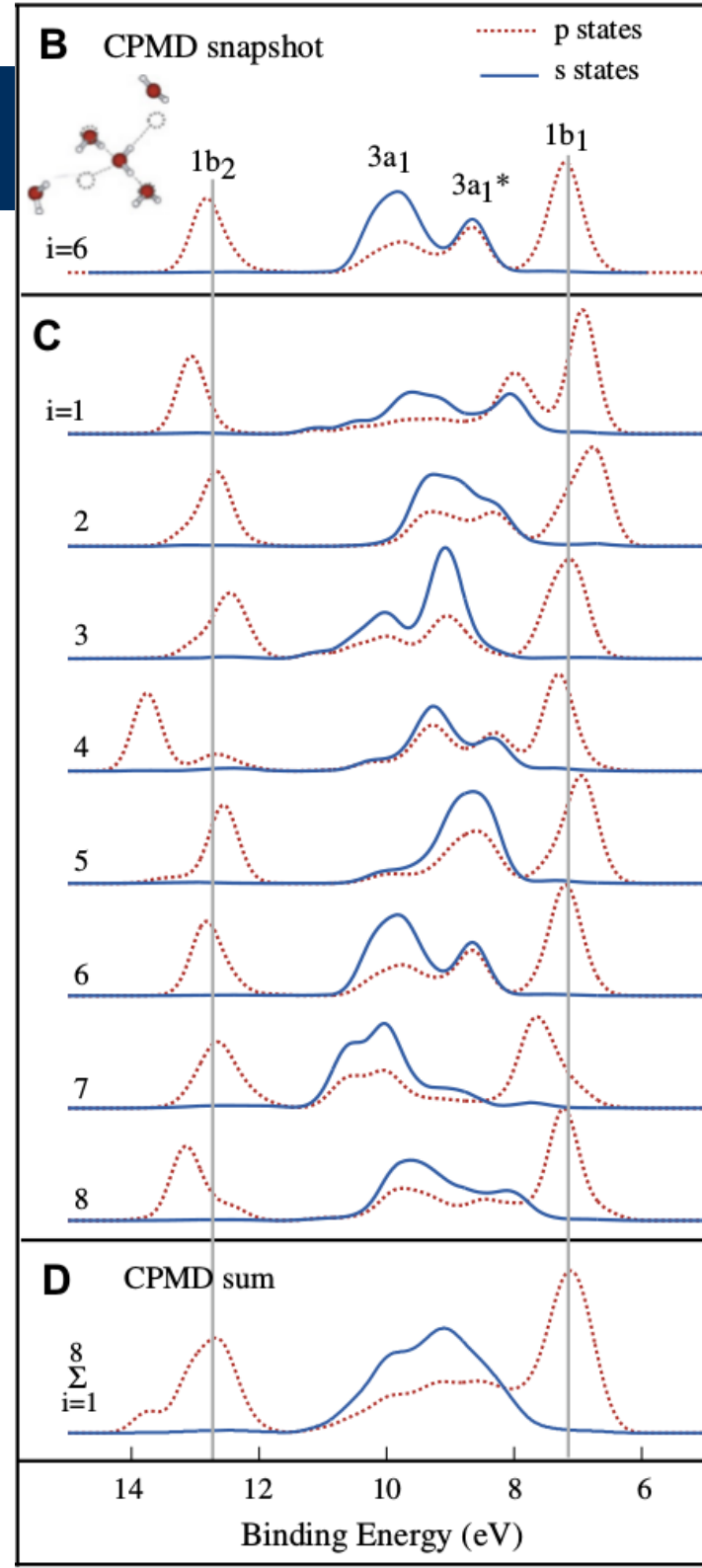
Molecular dynamics (MD)

Why bother with MD?

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



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Molecular Dynamics

Molecular dynamics (MD)

Newton's equations of motion

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

Molecular Dynamics

Molecular dynamics (MD)

Newton's equations of motion

$$\mathbf{F}_I = m_I \mathbf{a}_I, \quad \mathbf{F}_I = -\nabla_I V$$

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

Molecular dynamics (MD)

Newton's equations of motion

$$\mathbf{F}_I = m_I \mathbf{a}_I , \quad \mathbf{F}_I = -\nabla_I V$$

Two problems: Calculating forces and integrating EoMs

Classical MD:

Force fields

- Less expensive
- Good for larger systems

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

Molecular Dynamics

Molecular dynamics (MD)

Newton's equations of motion

$$\mathbf{F}_I = m_I \mathbf{a}_I, \quad \mathbf{F}_I = -\nabla_I V$$

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

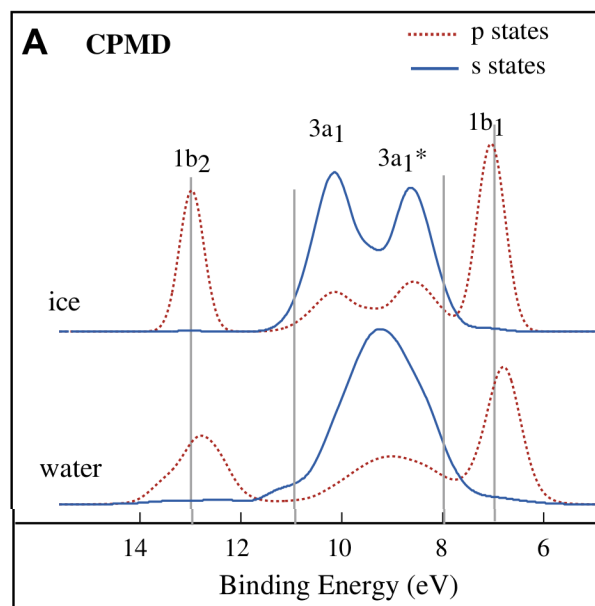
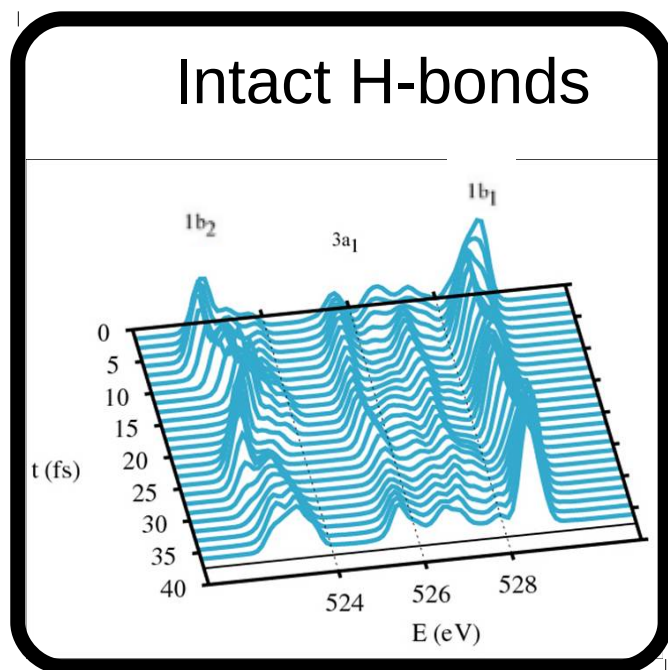
Parameter-free force expression

$$\mathbf{F}_I = -\nabla_I \min_{\phi_i} \{ E_{\text{KS}}(\{\phi_i\}; \mathbf{R}_I) \}$$

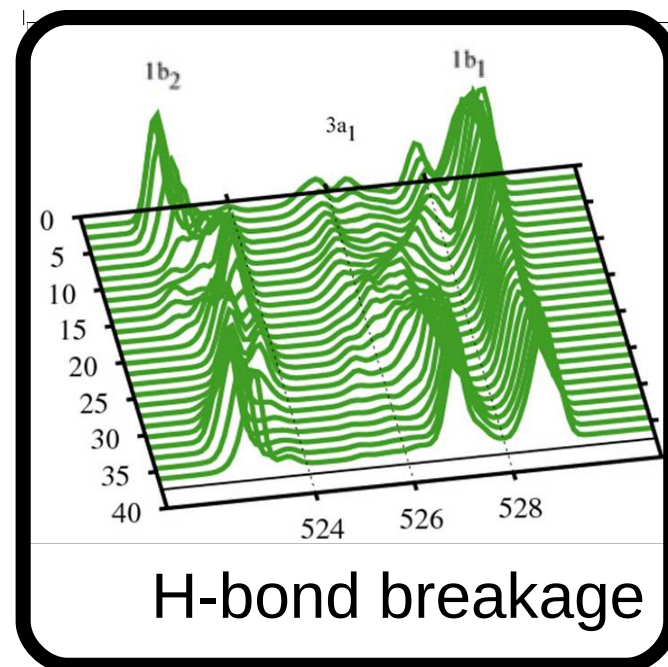
Electronic orbitals optimized at each step

Time evolution of the electronic structure due to hydrogen bond dynamics

Hydrogen bond dynamics

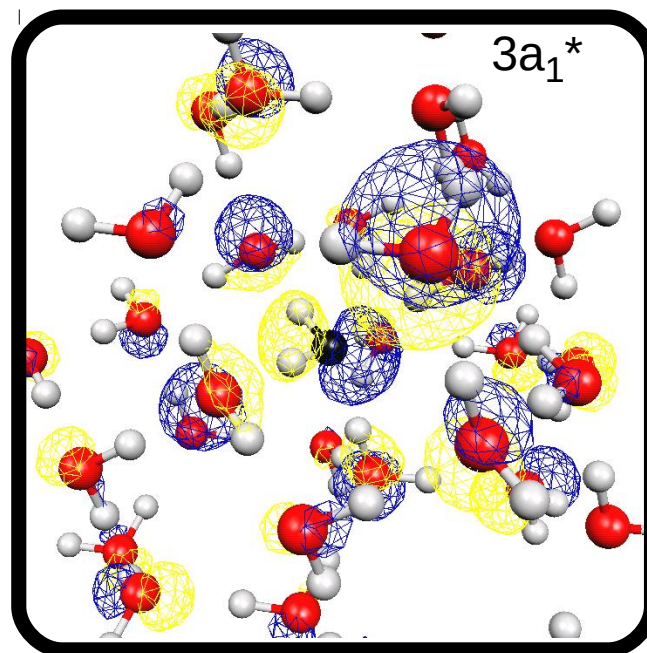
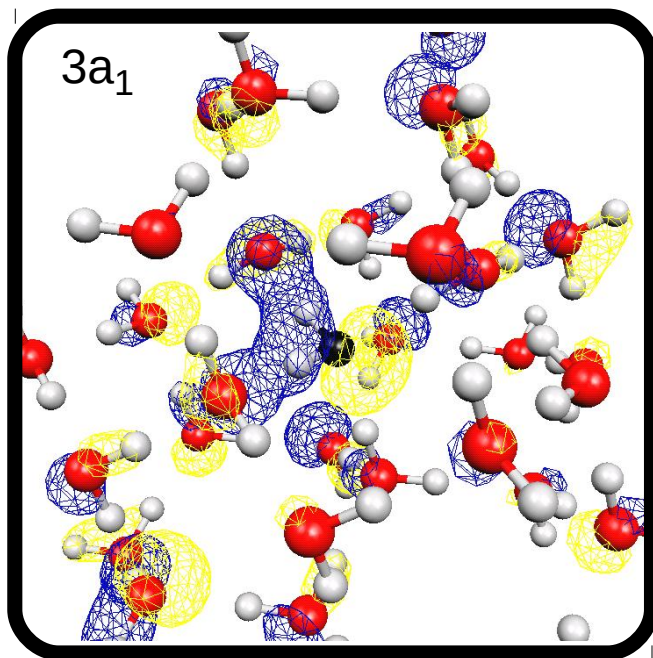


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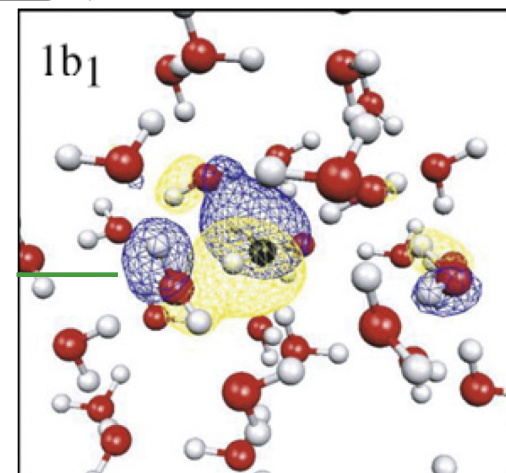
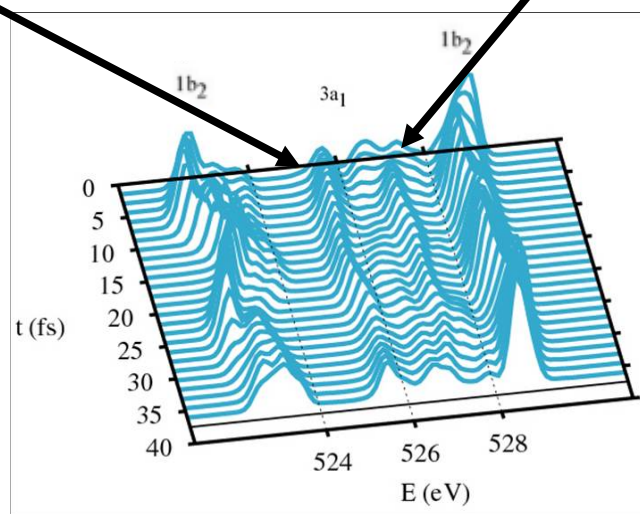
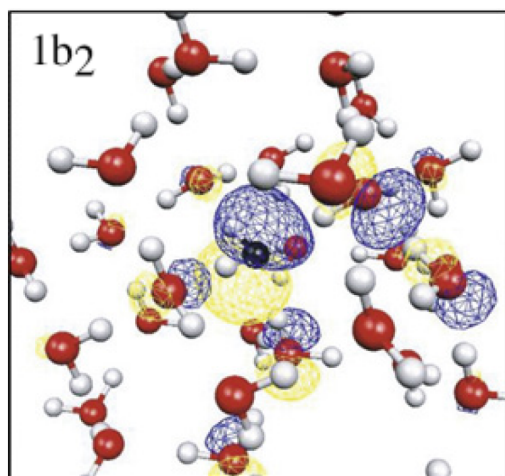


Car-Parrinello MD
simulations

Hydrogen bonding in water



Strong
overlap
in $3a_1$



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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 2 !fs  
    → TEMPERATURE 300.0 !K  
    &THERMOSTAT  
      REGION MASSIVE  
    → TYPE CSVR  
      &CSVR  
        TIMECON 50  
      &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

Time, temperature, and energies

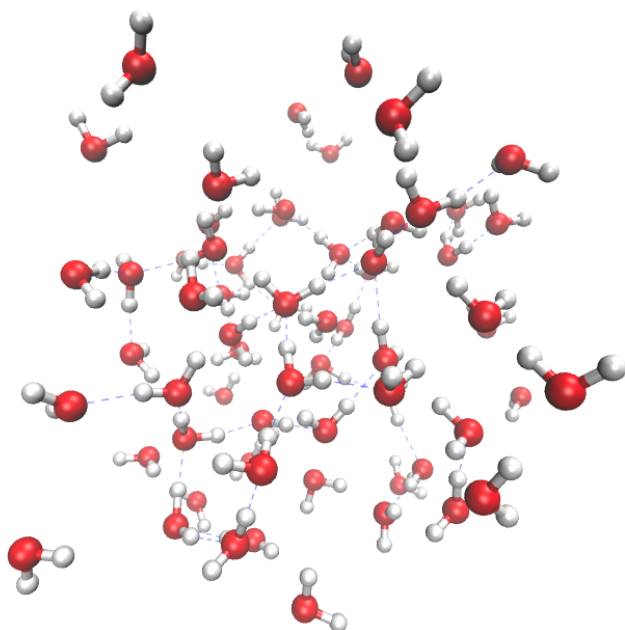
In CP2K:

Output

Trajectory

#	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	-1100.920661215	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	96.95513053
	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



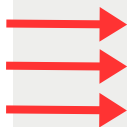
Molecular Dynamics in CP2K

In CP2K:

Initial guess of wave function

- ASPC (default) or PS for faster convergence in the SCFs
- USE_GUESS for the same initial guess in all MD steps (e.g. ATOMIC) for better stability

```
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  &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
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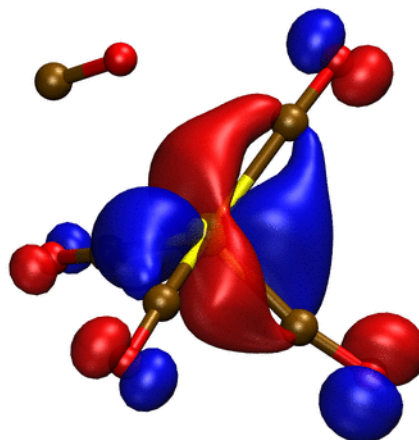
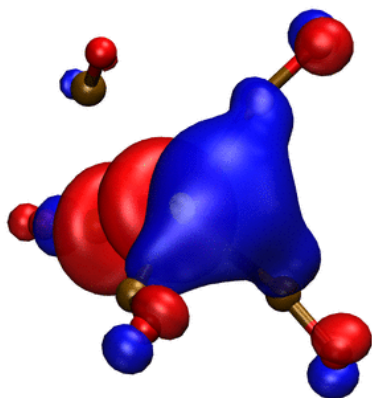
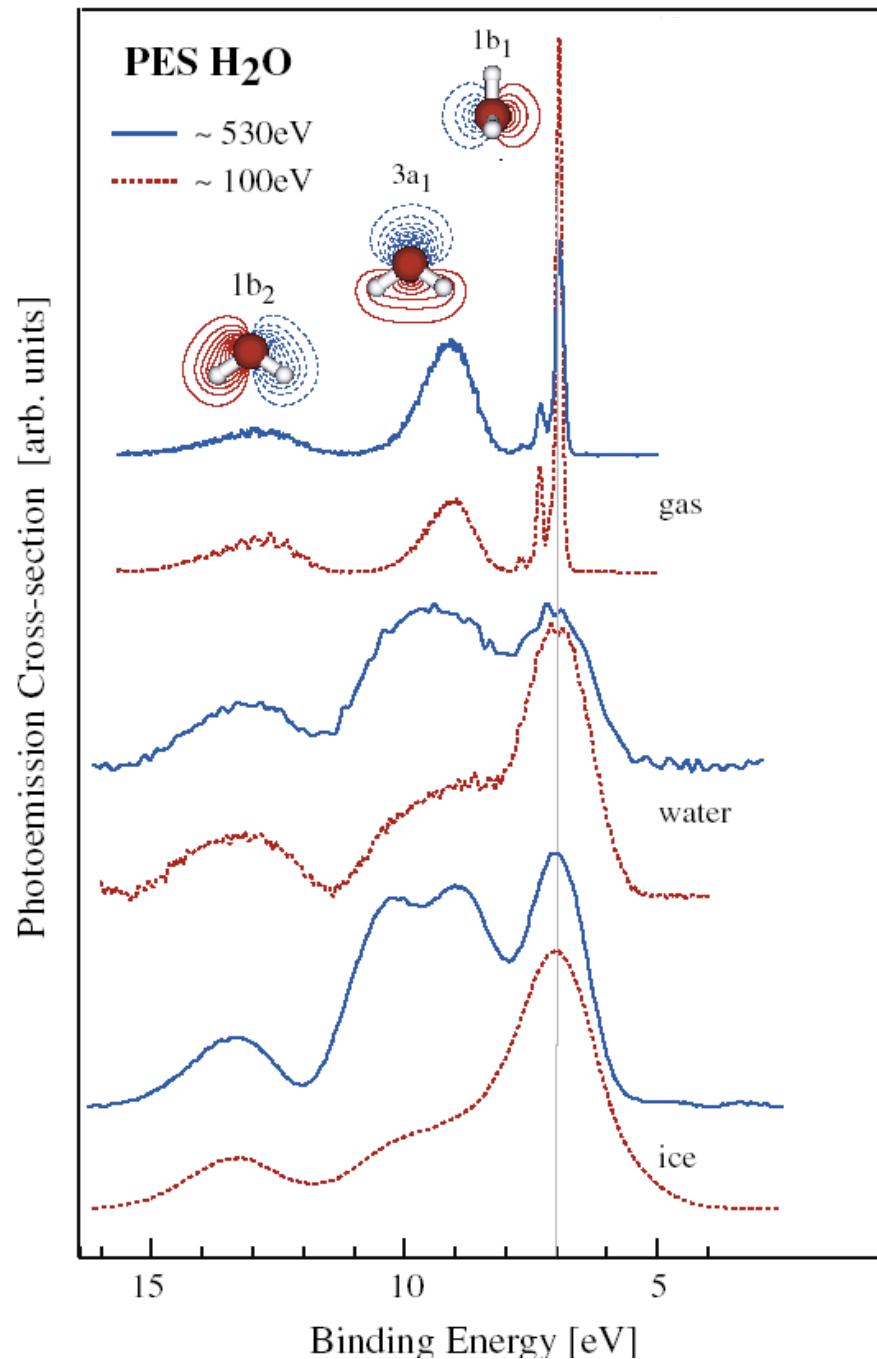


Photo electron spectroscopy of $\text{H}_2\text{O}(\text{g}, \text{l}, \text{s})$



Franck-Condon

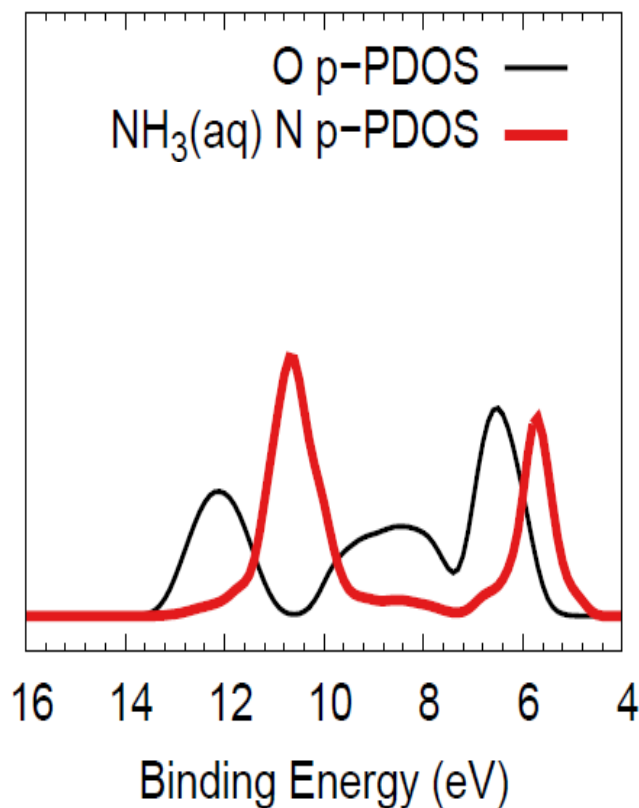
Inhomogeneous broadening

Chemical bonding

Hydrogen bonding and dynamics

XES allows us to access N p-PDOS in $\text{NH}_3(\text{aq})$

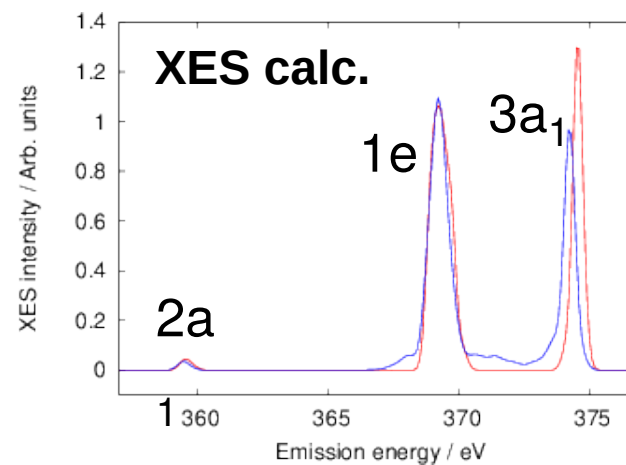
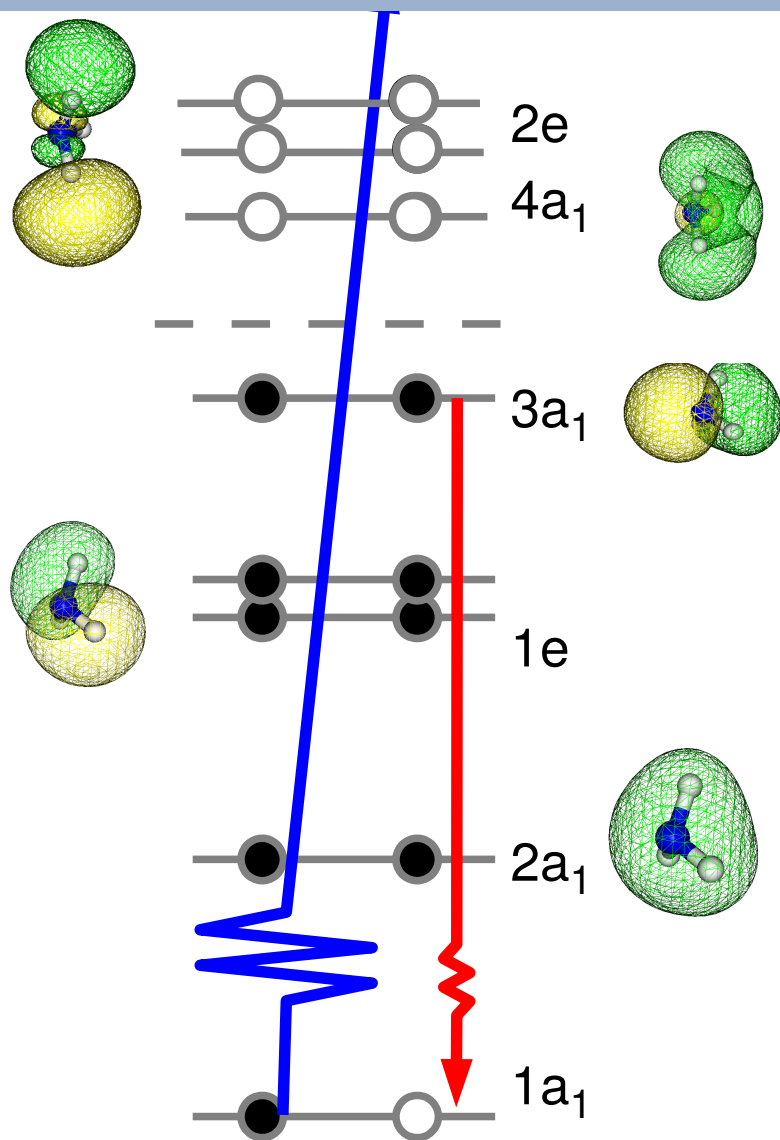
Aqueous ammonia:
Energy mismatch in orbital mixing



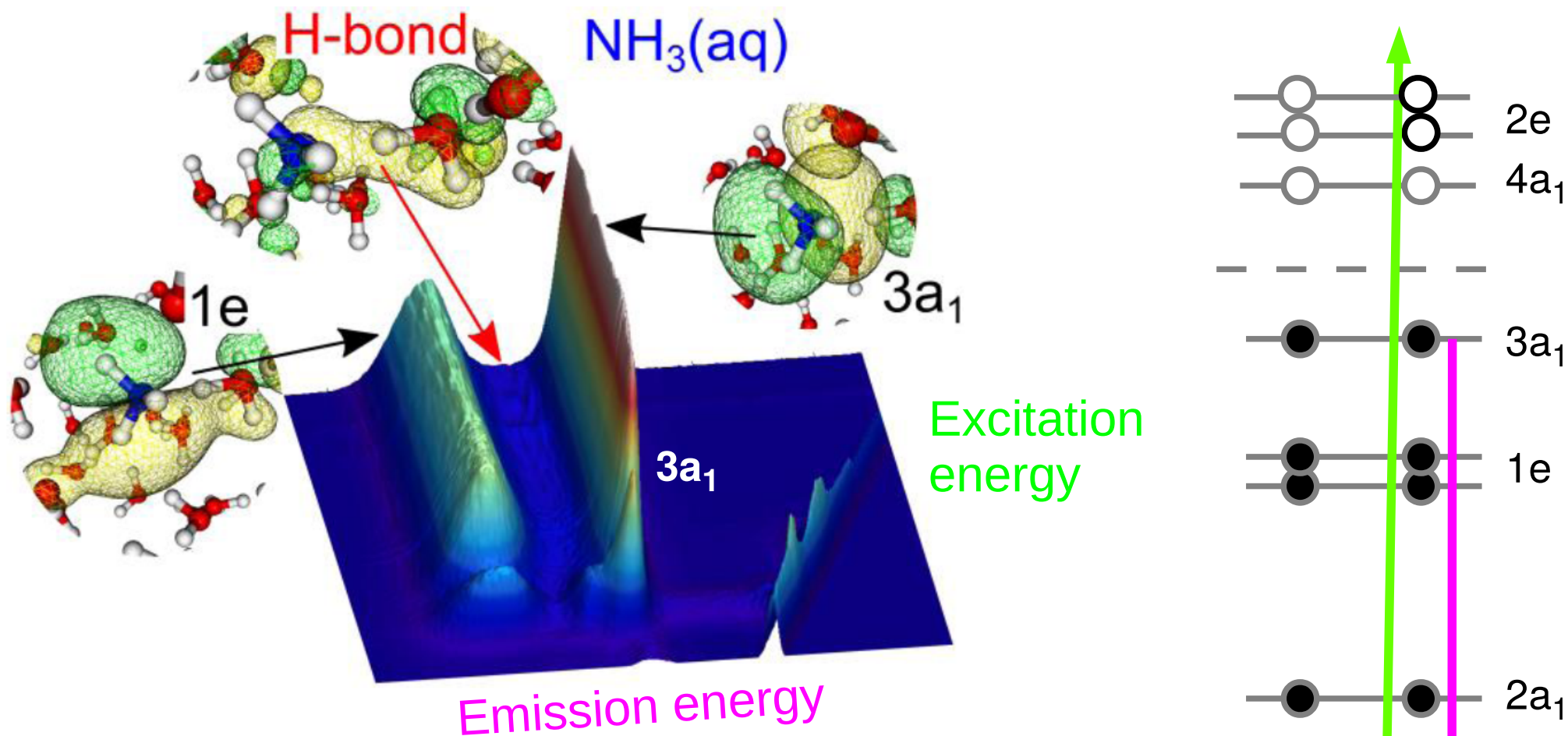
O PDOS would dominate in valence XPS

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

Electronic structure of $\text{NH}_3(\text{g})$ and $\text{NH}_3(\text{aq})$



X-ray emission spectroscopy of $\text{NH}_3(\text{g})$ and $\text{NH}_3(\text{aq})$



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
- The optimal method might vary between systems

```
&FORCE_EVAL
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...
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
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↓

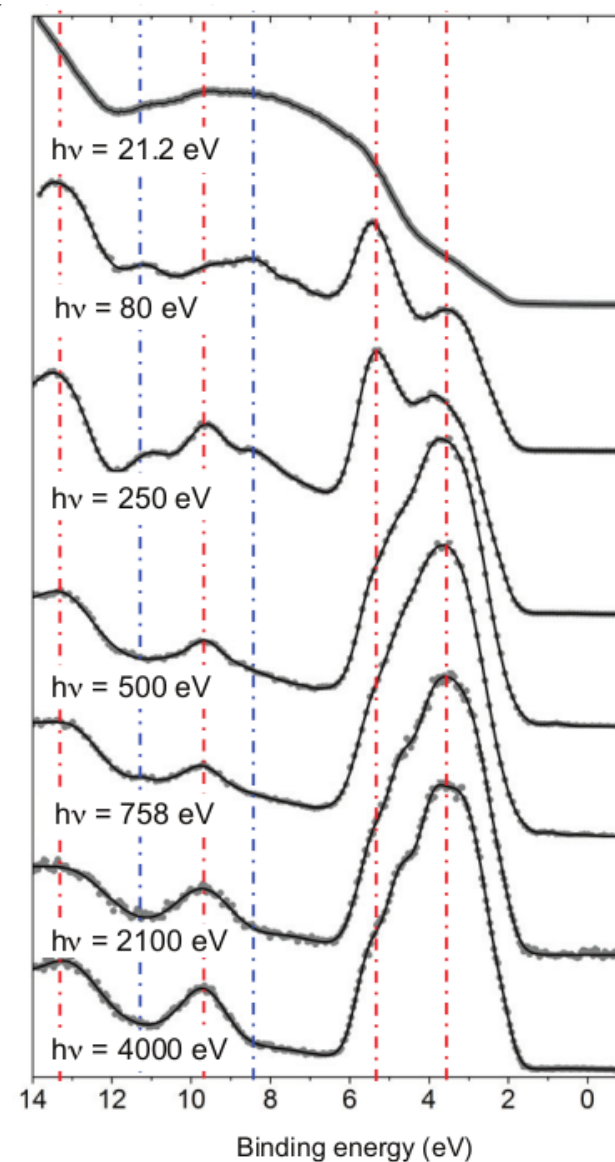
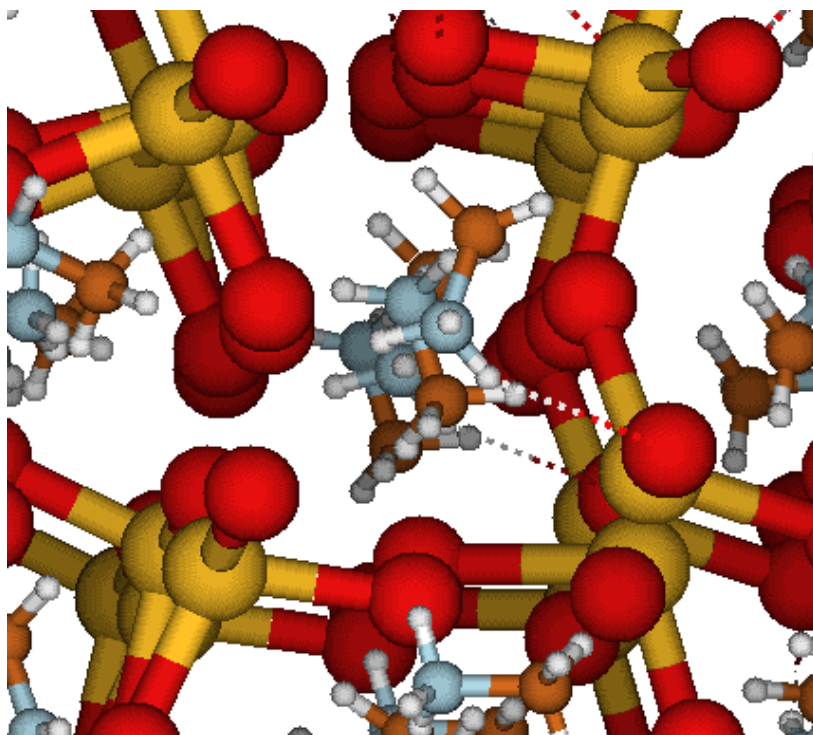
METHOD	TP_FLEX
XAS_CORE	1.0
XAS_TOT_EL	5

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			

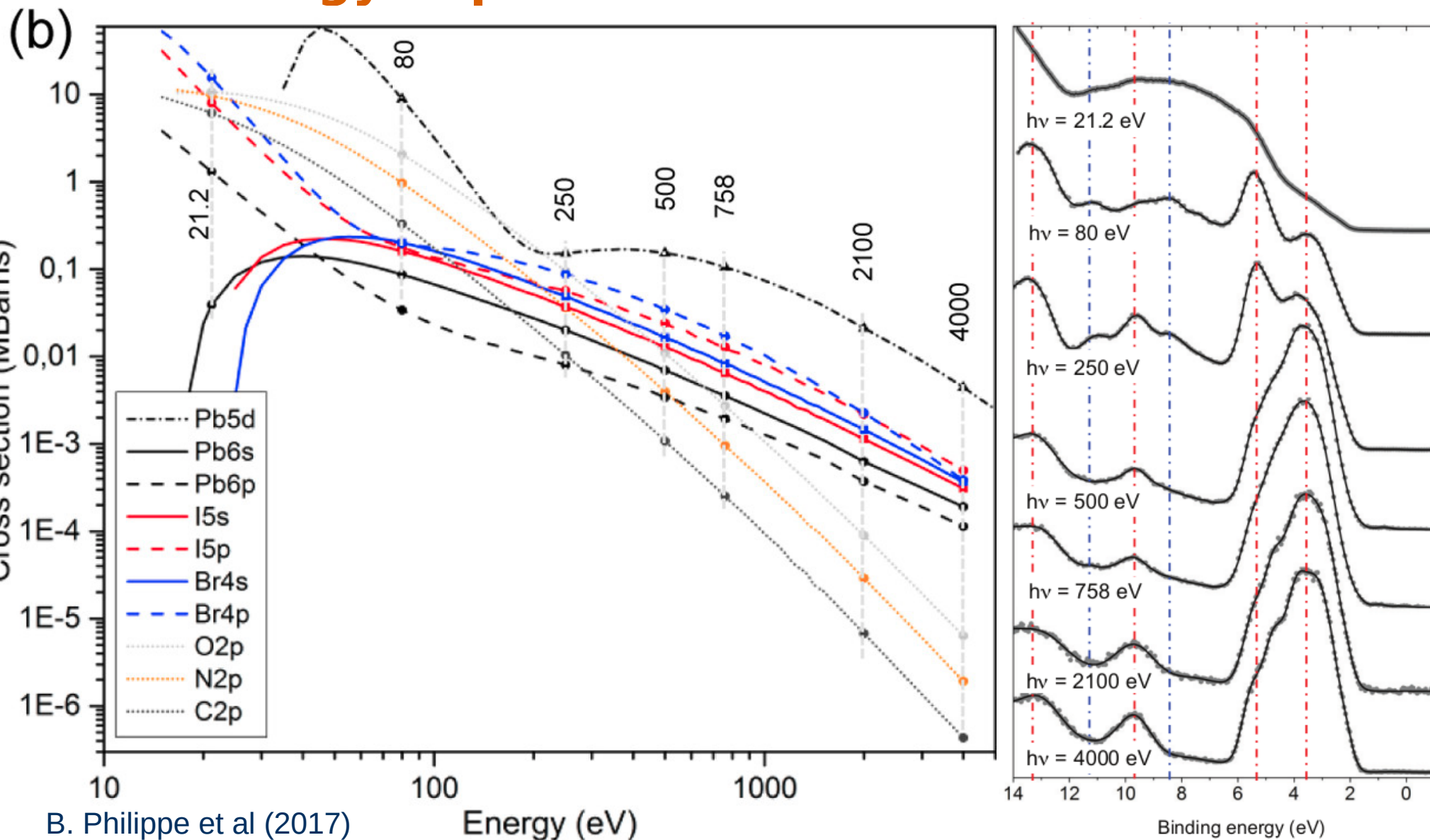
Perovskite solar cells: $\text{PbI}_3\text{CH}_3\text{NH}_3$

Photo-energy dependence in XPS



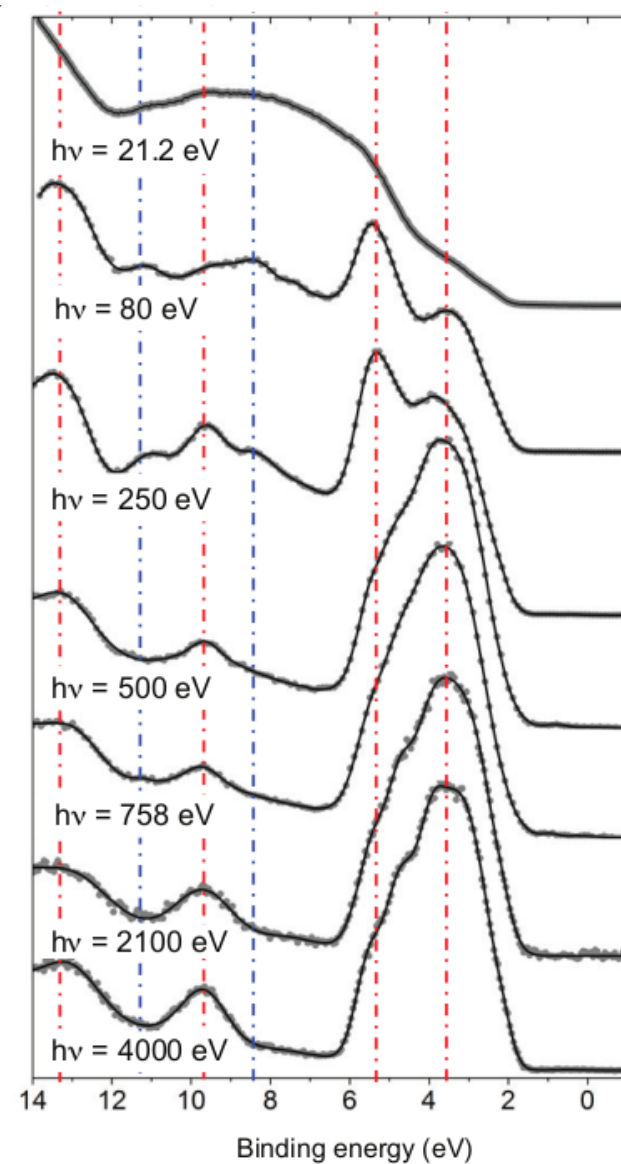
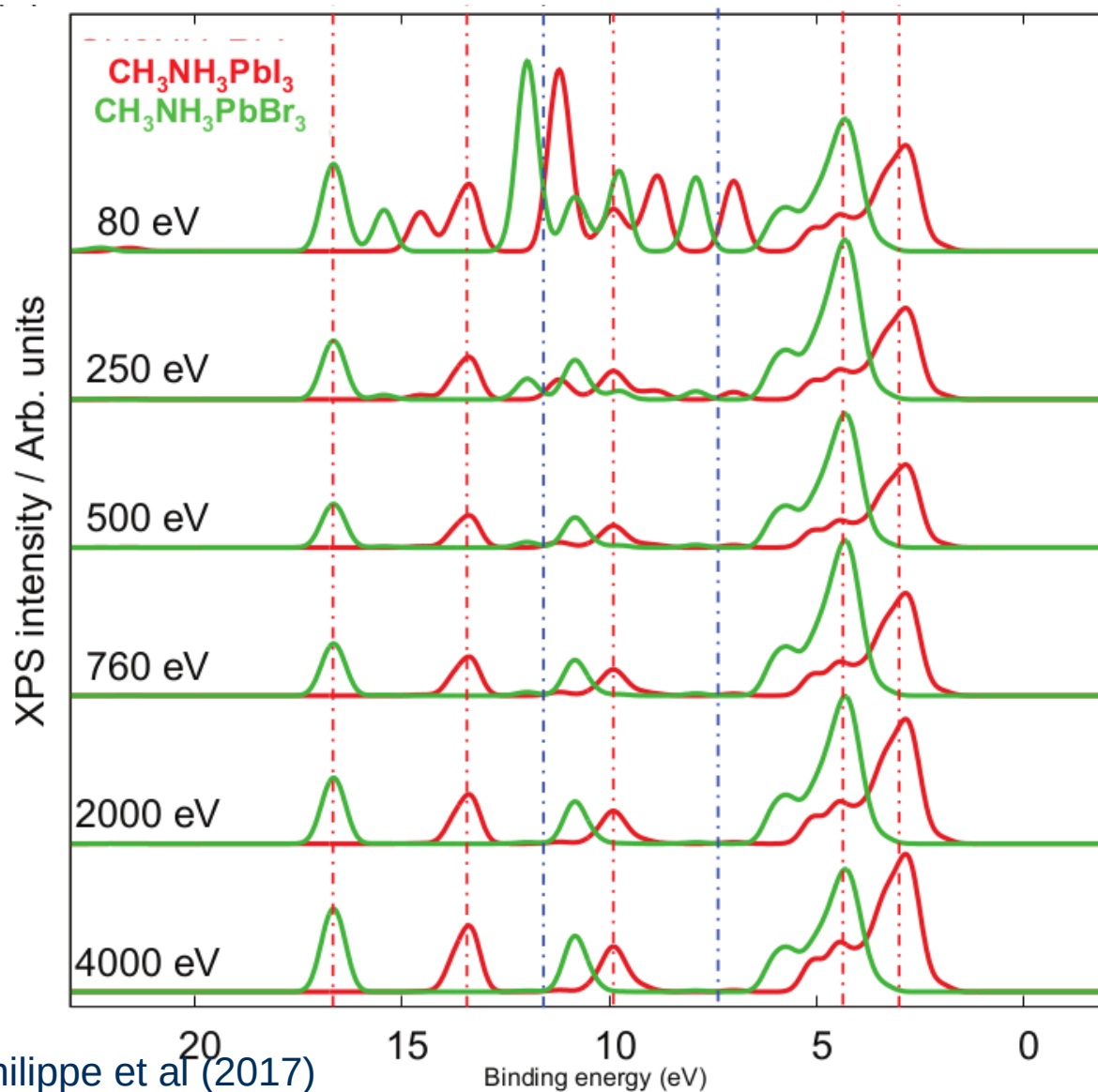
Perovskite solar cells: $\text{PbI}_3\text{CH}_3\text{NH}_3$

Photo-energy dependence in XPS



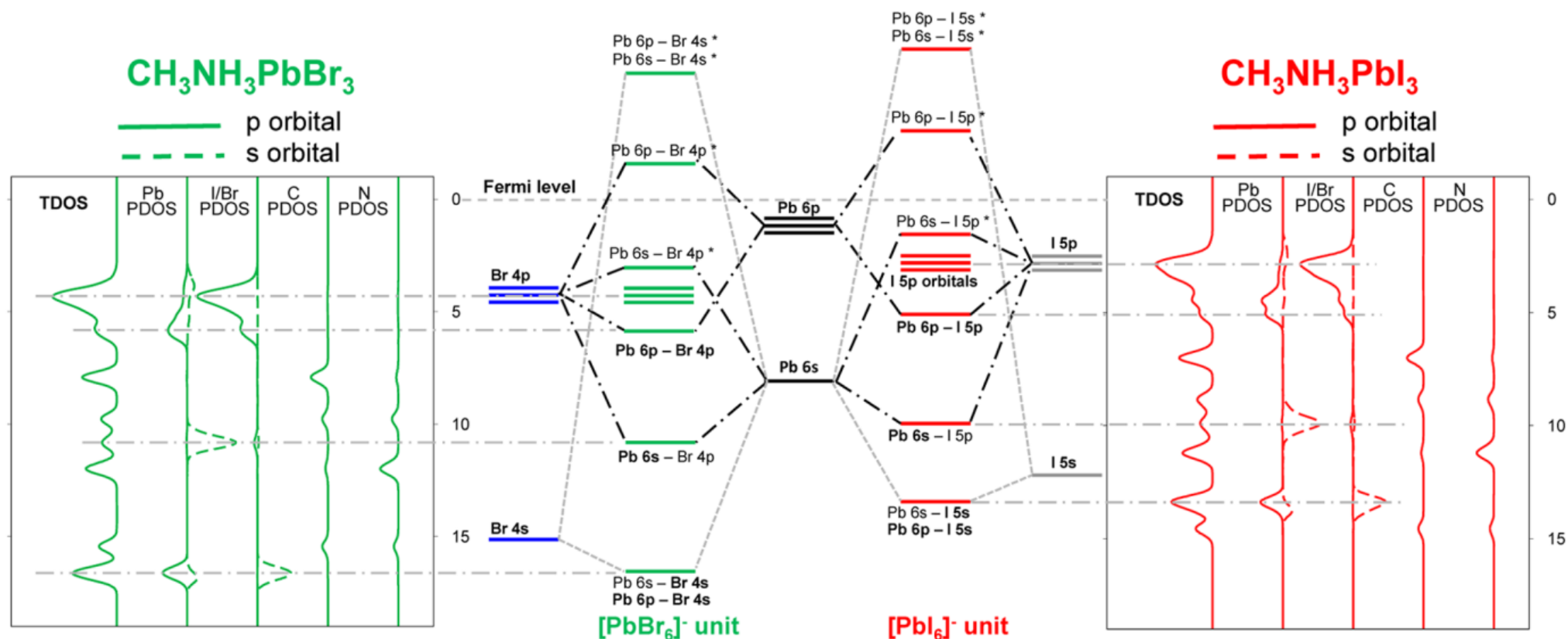
Perovskite solar cells: $\text{PbI}_3\text{CH}_3\text{NH}_3$

Photo-energy dependence in XPS



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

Understanding the valence band from orbitals



Thank you for your attention!

Questions?