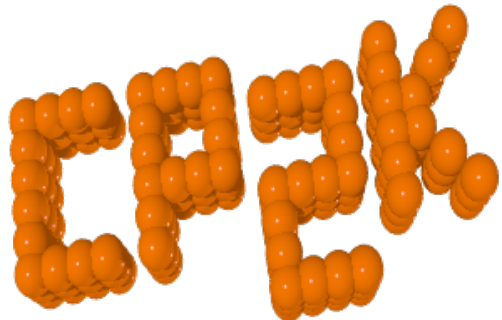# Density Functional Theory and X-ray Absorption Spectroscopy

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1st CONEXS Summer School

Newcastle University

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Summary

- Elementary quantum mechanics
- Motivation: why DFT?
- Density Functional Theory
  - Hohenberg-Kohn theorems
  - The Kohn-Sham approach
  - DFT in practice
- Absorption Spectroscopy
  - ΔSCF method
  - Transition Potential
  - XAS in practice
  - Absorption spectra of H_2O

Elementary quantum mechanics

We want to be able to obtain properties of many-body systems (aka solve Schrödinger equation)

$$i\,\frac{\partial}{\partial t}\Psi = \hat{H}\,\Psi$$

$$\hat{H} = -\frac{1}{2}\sum_{i}^{N}\nabla_i^2 + \frac{1}{2}\sum_{i}^{N}\sum_{j\neq i}^{N}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i}^{N}\sum_{A}^{M}\frac{Z_A}{\mathbf{r}_{iA}}$$

$$-\frac{1}{2}\sum_{A}^{M}\frac{\nabla_A^2}{M_A} + \sum_{A}^{M}\sum_{B\neq A}^{M}\frac{Z_A Z_B}{\mathbf{R}_{AB}}$$

Elementary quantum mechanics

Since the $M_A \gg m_e$, we can assume the electrons move much faster than the nuclei, i.e. the nuclei are fixed (Born-Oppenheimer approximation).

$$\hat{H} = -\frac{1}{2}\sum_i^N \nabla_i^2 + \frac{1}{2}\sum_i^N\sum_{j\neq i}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_i^N\sum_A^M \frac{Z_A}{\mathbf{r}_{iA}}$$

$$= \hat{T} + \hat{V}_{ee} + \hat{V}_{Ne}$$

$$\boxed{\hat{H}\,\Psi_i(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = E_i\,\Psi_i(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)}$$

Elementary quantum mechanics

- Variational principle: the energy computed from a "trial" wavefunction Ψ is an upper bound to the true ground-state energy E_0.

$$E_0 \leq \langle \Psi | \hat{H} | \Psi \rangle$$

Full minimization of E with respect to all allowed N-electron wavefunctions will give the true ground-state.

$$E_0[\Psi_0] = \min_{\Psi} E[\Psi] = \min_{\Psi} \langle \Psi | \hat{T} + \hat{V}_{ee} + \hat{V}_{Ne} | \Psi \rangle$$

Motivation: why DFT?

- it includes all electronic effects (kinetic, Coulomb, exchange and correlation);

- it can be applied to atoms, molecules and solids;

- it can be used for very large systems (thousands of atoms);

- it predicts numerous molecular properties, as molecular structures, ionization energies, electric and magnetic properties etc;

- knowing the wavefunction is not necessary: saves computational time.
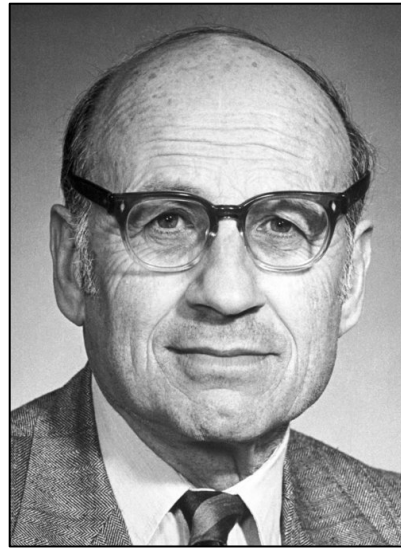
Motivation: why DFT?

- Number of publications with 'DFT' in the title or abstract
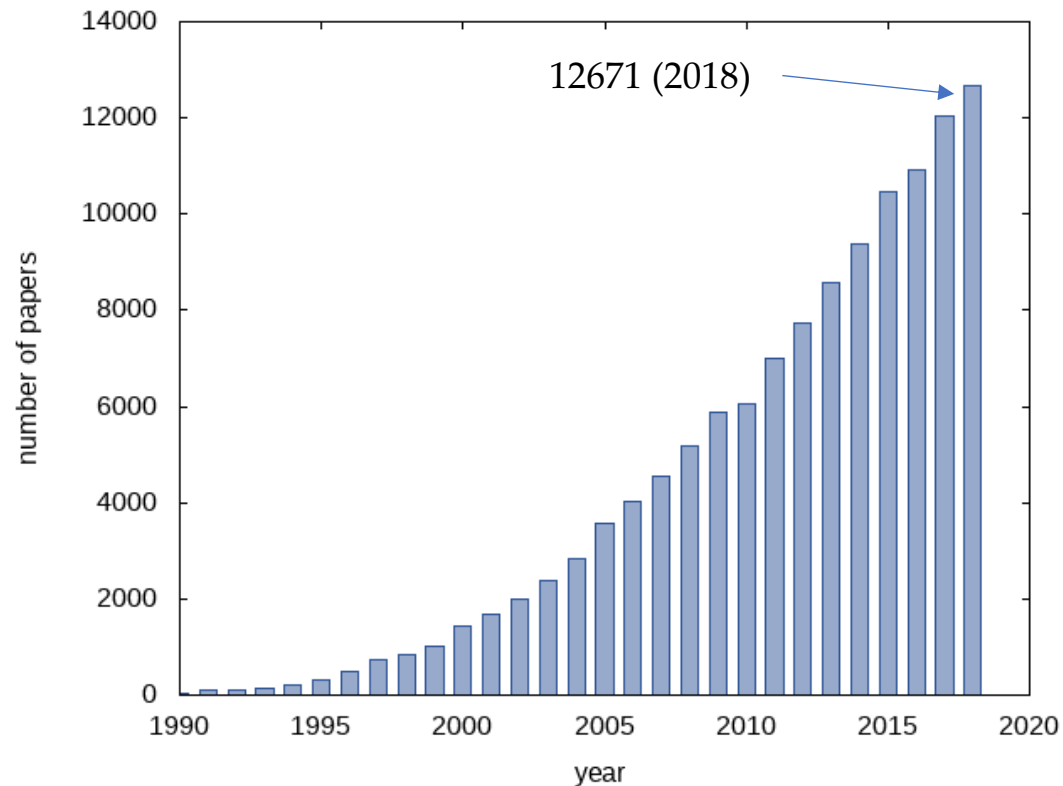
- until 27th of August, 8803 have been published in 2019 (around 1100 papers/month).

Density Functional Theory

Theory developed by Pierre Hohenberg, Walter Kohn and Lu Sham.

Nobel prize in Chemistry in 1998 to W. Kohn

P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
W. Kohn and L. Sham, Phys Rev. **140**, A1133 (1965).

Density Functional Theory

Goal: formulate DFT as an <u>exact</u> theory of many-body systems. It applies to any system of interacting particles in an external potential $V_{ext}(\mathbf{r})$.

$$\hat{H} = -\frac{1}{2}\sum_i^N \nabla_i^2 + \frac{1}{2}\sum_i^N\sum_{j\neq i}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i^N V_{ext}(\mathbf{r}_i)$$

$$\hat{H}\,\Psi_i(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = E_i\,\Psi_i(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$$

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problem: wavefunctions!

Density Functional Theory

What is the problem with wavefunctions?

- even though they are used as a central quantity in wavefunction approaches, they cannot be measured experimentally;
- calculations are time consuming;
- the wavefunction depends on 3N variables

Density Functional Theory

Solution: reduce the 3N-dimensional problem to a 3-dimensional one.

$$n(\mathbf{r}) = \int d\mathbf{r}_1 \, d\mathbf{r}_2 \, \ldots \, d\mathbf{r}_N \, \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \, \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$$

- it integrates to the total number of electrons $\int d\mathbf{r} \, n(\mathbf{r}) = N$
- it vanishes at infinity $n(\mathbf{r} \to \infty) = 0$
- it can be measured experimentally

Hohenberg-Kohn theorems

Inhomogeneous Electron Gas*

P. Hohenberg†

École Normale Superieure, Paris, France

AND

W. Kohn‡

École Normale Superieure, Paris, France and Faculté des Sciences, Orsay, France
and
University of California at San Diego, La Jolla, California

(Received 18 June 1964)

This paper deals with the ground state of an interacting electron gas in an external potential $v(\mathbf{r})$. It is proved that there exists a universal functional of the density, $F[n(\mathbf{r})]$, independent of $v(\mathbf{r})$, such that the expression $E \equiv \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})]$ has as its minimum value the correct ground-state energy associated with $v(\mathbf{r})$. The functional $F[n(\mathbf{r})]$ is then discussed for two situations: (1) $n(\mathbf{r}) = n_0 + \tilde{n}(\mathbf{r})$, $\tilde{n}/n_0 \ll 1$, and (2) $n(\mathbf{r}) = \varphi(\mathbf{r}/r_0)$ with φ arbitrary and $r_0 \to \infty$. In both cases F can be expressed entirely in terms of the correlation energy and linear and higher order electronic polarizabilities of a uniform electron gas. This approach also sheds some light on generalized Thomas-Fermi methods and their limitations. Some new extensions of these methods are presented.

Hohenberg-Kohn theorems

Theorem I: $V_{ext}(\mathbf{r})$ is determined uniquely by the ground-state electronic density $n_0(\mathbf{r})$.

$$V_{ext}(\{\mathbf{r}\}) \overset{\mathrm{HK}}{\Longleftarrow} n_0(\{\mathbf{r}\})$$

$$\Downarrow \qquad\qquad \Uparrow$$

$$\Psi_i(\{\mathbf{r}\}) \;\Rightarrow\; \Psi_0(\{\mathbf{r}\})$$

Theorem II: The ground-state energy can be obtained variationally: the density that minimizes the total energy is the exact ground-state density.

$$E_0[n_0(\mathbf{r})] = \min_{n}(T[n] + E_{ee}[n] + E_{ext}[n])$$

R. R. Martin, Electronic Structure, Basic Theory and Practical Methods (Cambridge University Press, 2004).

Hohenberg-Kohn theorems

- Corollary I: with V_{ext} determined, the Hamiltonian of the system is fully determined. Then it follows that the wavefunctions for all states are also known, and therefore all the properties of the system are completely determined by the ground-state density $n_0(\mathbf{r})$.

$$E_{HK}[n] = \underline{T[n] + E_{int}} + \int d\mathbf{r}\, n(\mathbf{r})\, V_{ext}(\mathbf{r})$$

$$\equiv \underline{F_{HK}[n]} + \int d\mathbf{r}\, n(\mathbf{r})\, V_{ext}(\mathbf{r})$$

universal!

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Hohenberg-Kohn theorems

Theorem I: $V_{ext}(\mathbf{r})$ is determined uniquely by the ground-state electronic density $n_0(\mathbf{r})$

- Hohenberg and Kohn reformulated the interacting many-body problem, but did not solve it;
- the functional F_{HK} is, in principle, unknown;
- HK theory is exact (it has no approximations), but it cannot be used to solve problems (impractical).

Theorem II: ...ally: the density th... ...ensity.

$$E_0[n_0(\mathbf{r})] = \min_n (T[n] + E_{ee}[n] + E_{ext}[n])$$

R. R. Martin, Electronic Structure, Basic Theory and Practical Methods (Cambridge University Press , 2004).

The Kohn-Sham approach

Self-Consistent Equations Including Exchange and Correlation Effects*

W. KOHN AND L. J. SHAM

University of California, San Diego, La Jolla, California

(Received 21 June 1965)

From a theory of Hohenberg and Kohn, approximation methods for treating an inhomogeneous system of interacting electrons are developed. These methods are exact for systems of slowly varying or high density. For the ground state, they lead to self-consistent equations analogous to the Hartree and Hartree-Fock equations, respectively. In these equations the exchange and correlation portions of the chemical potential of a uniform electron gas appear as additional effective potentials. (The exchange portion of our effective potential differs from that due to Slater by a factor of $\frac{2}{3}$.) Electronic systems at finite temperatures and in magnetic fields are also treated by similar methods. An appendix deals with a further correction for systems with short-wavelength density oscillations.

The Kohn-Sham approach

- Replace the original interacting many-body system with an auxiliary one of non-interacting particles.
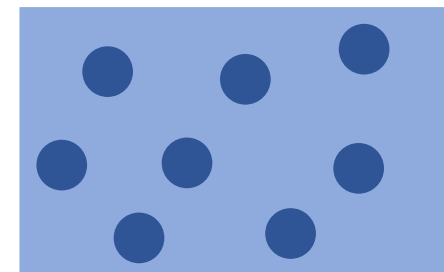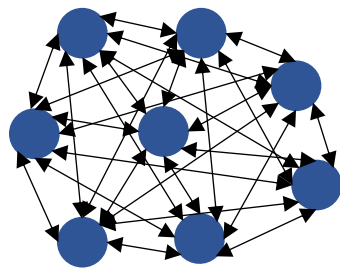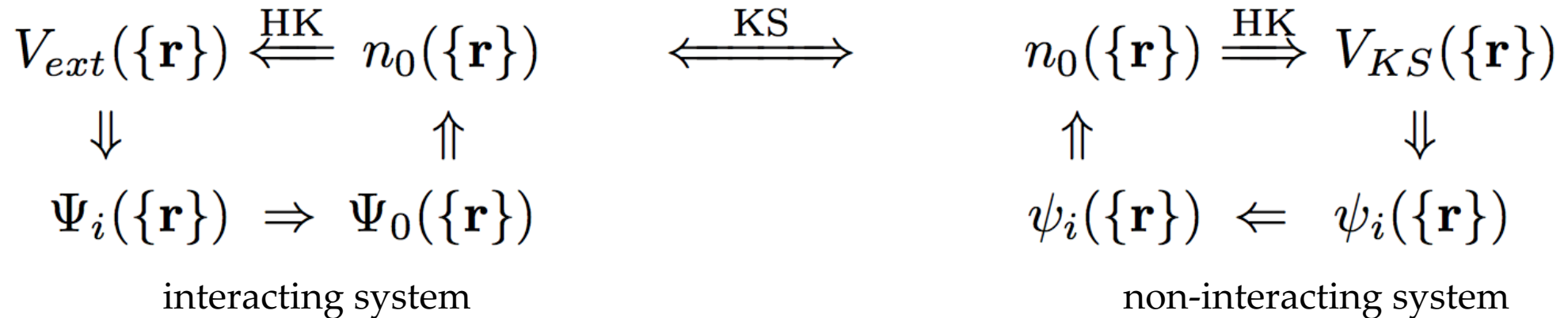
Assumptions:

1. the GS density of the <u>interacting system</u> is equal to the GS density of some <u>auxiliary non-interacting system</u> (exactly soluble);

2. the auxiliary Hamiltonian is chosen to have usual kinetic energy operator and an effective local potential acting on the electrons.

$$\hat{H}_{aux} = -\frac{1}{2}\nabla^2 + V_{eff}(\mathbf{r})$$

The Kohn-Sham approach

In principle, the solution of the non-interacting system determines all properties of the original problem.

$$V_{ext}(\{\mathbf{r}\}) \overset{\text{HK}}{\Longleftarrow} n_0(\{\mathbf{r}\}) \qquad \overset{\text{KS}}{\Longleftrightarrow} \qquad n_0(\{\mathbf{r}\}) \overset{\text{HK}}{\Longrightarrow} V_{KS}(\{\mathbf{r}\})$$

$$\Downarrow \qquad\qquad \Uparrow \qquad\qquad\qquad\qquad\qquad \Uparrow \qquad\qquad \Downarrow$$

$$\Psi_i(\{\mathbf{r}\}) \Rightarrow \Psi_0(\{\mathbf{r}\}) \qquad\qquad\qquad \psi_i(\{\mathbf{r}\}) \Leftarrow \psi_i(\{\mathbf{r}\})$$

interacting system

non-interacting system

R. R. Martin, Electronic Structure, Basic Theory and Practical Methods (Cambridge University Press, 2004).

The Kohn-Sham energy functional

- In the Kohn-Sham approach, the total energy can be decomposed as (rewriting HK GS energy functional)

$$E[n(\mathbf{r})] = T_0[n] + \int d\mathbf{r} \, V_{ext}(\mathbf{r}) \, n(\mathbf{r}) + E_{Hartree}[n] + E_{xc}[n]$$

$$n(\mathbf{r}) = \sum_i^N |\psi_i(\mathbf{r})|^2 \qquad \text{density of the auxiliary system}$$

$$E_{Hartree}[n] = \frac{1}{2} \int d\mathbf{r} \, d\mathbf{r}' \, \frac{n(\mathbf{r}) \, n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \qquad \text{classical Coulomb energy}$$

$$E_{xc}[n] = \int d\mathbf{r} \, n(\mathbf{r}) \, \varepsilon[n(\mathbf{r})] \qquad \text{exchange and correlation}$$

The Kohn-Sham equations

Using the energy functional, it is possible to write Schrödinger-like eigenvalue equations

$$\left(H_{KS} - \varepsilon_i\right)\psi_i(\mathbf{r}) = 0$$

where the ε_i are the eigenvalues, and H_{KS} is the effective Hamiltonian, given by

$$H_{KS}(\mathbf{r}) = -\frac{1}{2}\nabla^2 + V_{KS}(\mathbf{r})$$

$$V_{KS}(\mathbf{r}) = V_{ext}(\mathbf{r}) + V_{Hartree}(\mathbf{r}) + V_{xc}(\mathbf{r})$$

$$\varepsilon_i = \frac{\mathrm{d}E_{total}}{\mathrm{d}n_i}$$

$$= \int \mathrm{d}\mathbf{r}\, \frac{\mathrm{d}E_{total}}{\mathrm{d}\mathbf{r}} \frac{\mathrm{d}n(\mathbf{r})}{\mathrm{d}n_i}$$

DFT in practice: XC functionals

- Local density approximation - LDA

$$E_{xc}^{LDA}[n] = \int \mathrm{d}\mathbf{r}\, n(\mathbf{r})\, \varepsilon_{xc}^{HEG}(n(\mathbf{r}))$$
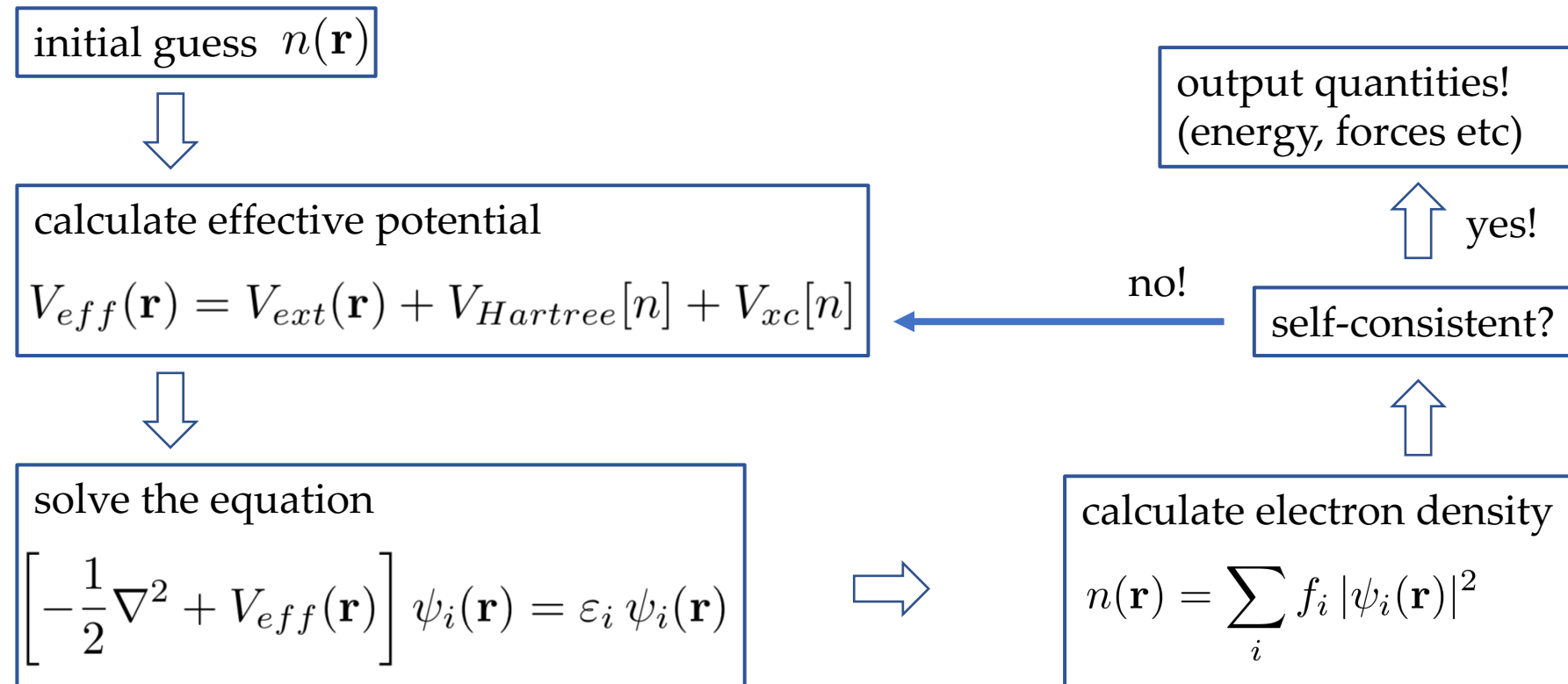
- Generalized gradient approximation - GGA

$$E_{xc}^{GGA}[n] = \int \mathrm{d}\mathbf{r}\, n(\mathbf{r})\, \varepsilon_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r}))$$

- Hybrid functionals

$$E_{xc}^{hyb}[n] = a\, E_x^{DFT} + b\, E_x^{HF} + c\, E_c^{DFT}$$

DFT in practice: Solving the Kohn-Sham equations

This equations have to be solved subject to the constraint that the effective potential $V_{eff}(\mathbf{r})$ and the density n($\mathbf{r}$) are consistent.

initial guess $n(\mathbf{r})$

⇩

calculate effective potential

$$V_{eff}(\mathbf{r}) = V_{ext}(\mathbf{r}) + V_{Hartree}[n] + V_{xc}[n]$$

⇩

solve the equation

$$\left[-\frac{1}{2}\nabla^2 + V_{eff}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i\, \psi_i(\mathbf{r})$$

⟹

calculate electron density

$$n(\mathbf{r}) = \sum_i f_i\, |\psi_i(\mathbf{r})|^2$$

⇧

self-consistent?

no! ⟵

yes! ⇧

output quantities!
(energy, forces etc)

DFT in practice: Basis set

- it refers to the set of one-particle functions used to build molecular orbitals;

- usually the functions that compose the basis set are centered on atoms;

- calculations are usually performed using a finite set of basis functions (finite basis set);

- basis set can also be composed of plane waves (cp2k applies this for GPW and GAPW methods).
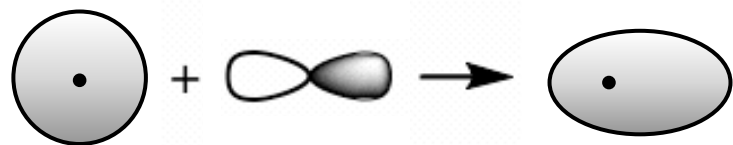
DFT in practice: Basis set

- it refers to the set of one-particle functions used to build molecular orbitals;

- usually   toms;

- calculat   functions (finite b

   GPW (gaussian plane wave approach): mixed approach in which both gaussian functions and plane waves are used to represent the electron density.

- basis se   for GPW and GAPW methods).

DFT in practice: Basis set – polarization functions

- adds flexibility: allow orbitals to change shape (being polarized);
- important for reproducing chemical bonding;
- should be included when correlation effects are important;
- high angular momentum polarization functions ($d, f, g...$) are important for heavy atoms;
- be aware: adding these functions to your basis set is costly!

an s orbital polarized by a p-type orbital
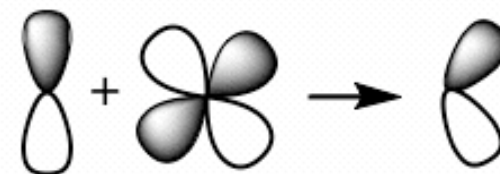
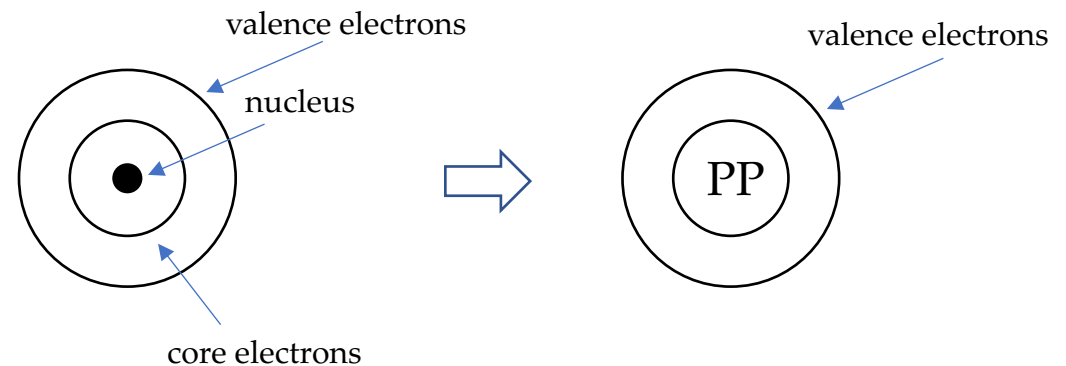a p orbital polarized by a d-type orbital

DFT in practice: Basis set – diffuse functions

- gaussians have small exponents and decay slowly with the distance from the nucleus;

- are necessary for the correct description of anions, Rydberg states and weak bonds (e.g. hydrogen bonds) – systems with extended electronic density.

$$g(r) \propto e^{-\zeta\, r^2}$$

$\zeta = 5.0$
$\zeta = 0.5$
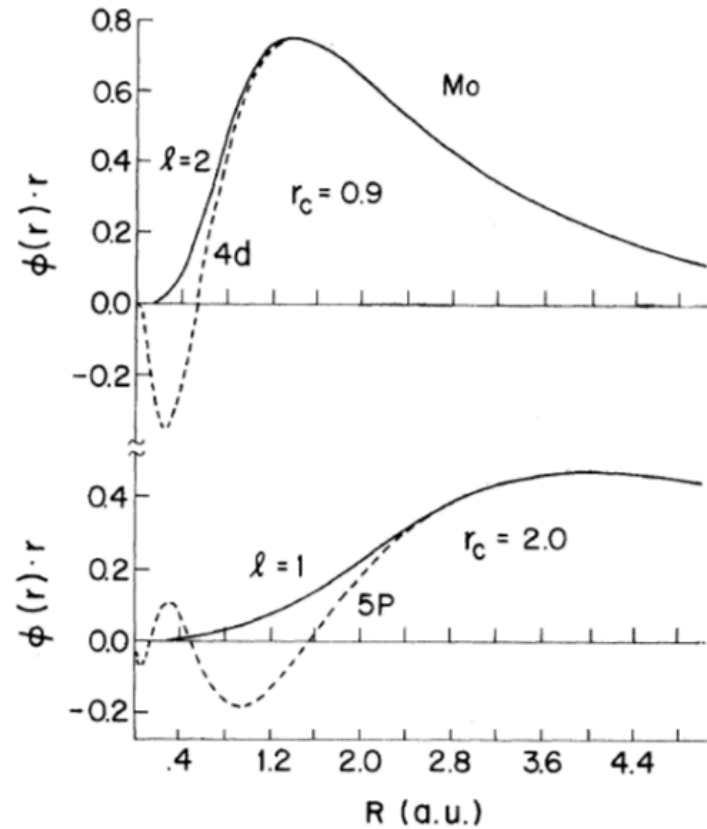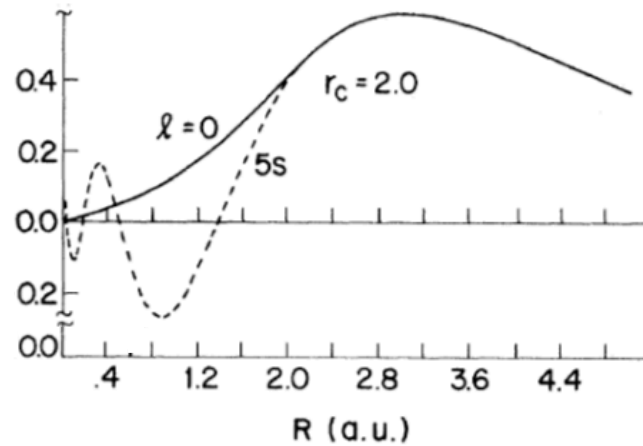$\zeta = 0.05$

r (arbitrary units)
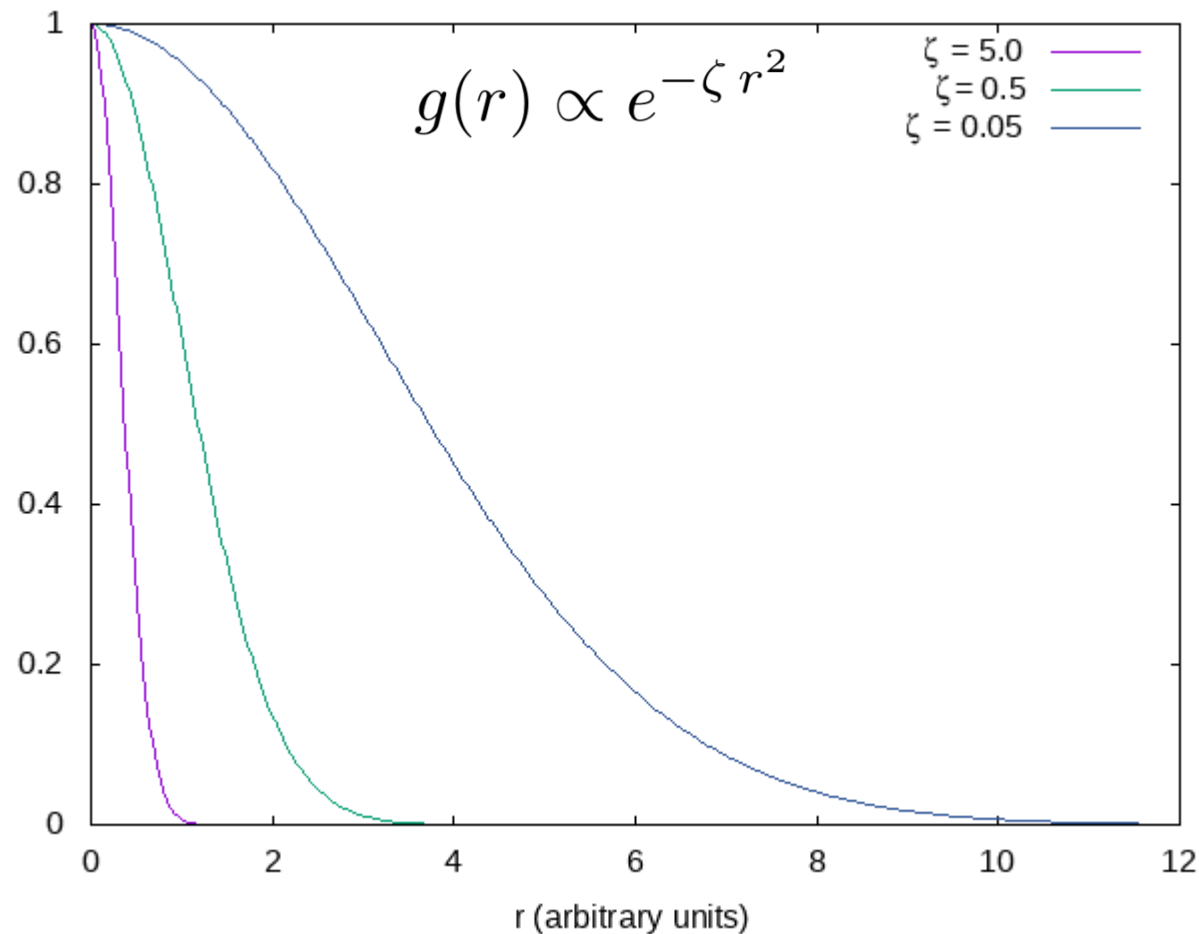
DFT in practice: Pseudopotentials (PP)

- effective core potentials replace core electrons with an effective potential which is added to the Hamiltonian;

- very useful for transition metals;

- reduce the cost of calculations, since it reduces the number of the electrons;

- pseudo-wavefunctions are much smoother in the core region than the all-electron functions;

- can include relativistic effects.

valence electrons

nucleus

core electrons

PP

valence electrons

DFT in practice Pseudopotentials (PP)

- effective ~~~~~~~~~~~~~~~~~~~ ive potential which

- very u~~~~~~~

- reduce ~~~~~~~~~~~~~~~~~~ nber of the electro~~~~

- pseud~~~~~~~~~~~~~~~~~~~~~~~~~ than the all-electro~~~~

- can in~~~~

valence electrons

core electrons

D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).

DFT in practice: cp2k input file

```
&GLOBAL
  PROJECT name_project
  RUN_TYPE ENERGY
  PRINT_LEVEL LOW
&END GLOBAL

&FORCE_EVAL
  METHOD Quickstep

  &DFT
    BASIS_SET_FILE_NAME  GTH_BASIS_SET    !
    POTENTIAL_FILE_NAME  GTH_POTENTIALS
    UKS .FALSE.

    &MGRID
      NGRIDS 4
      CUTOFF 300
      REL_CUTOFF 60
    &END MGRID

    &QS
      EPS_DEFAULT 1.0E-10
    &END QS

    &SCF
      SCF_GUESS ATOMIC
      EPS_SCF 1.0E-6
      MAX_SCF 300
    &END SCF
```

```
    &XC
      &XC_FUNCTIONAL PBE
      &END XC_FUNCTIONAL
    &END XC
  &END DFT

  &SUBSYS
    &KIND H
      BASIS_SET DZVP-GTH-PBE      !
      POTENTIAL GTH-PBE-q1
    &END KIND

    &KIND O
      BASIS_SET DZVP-GTH-PBE      !
      POTENTIAL GTH-PBE-q6
    &END KIND

    &CELL
      PERIODIC XYZ
      ABC 5.430697500 5.430697500 5.430697500
    &END CELL

    &COORD
      O  0.000000  0.000000 -0.065587
      H  0.000000 -0.757136  0.520545
      H  0.000000  0.757136  0.520545
    &END COORD
  &END SUBSYS

&END FORCE_EVAL
```
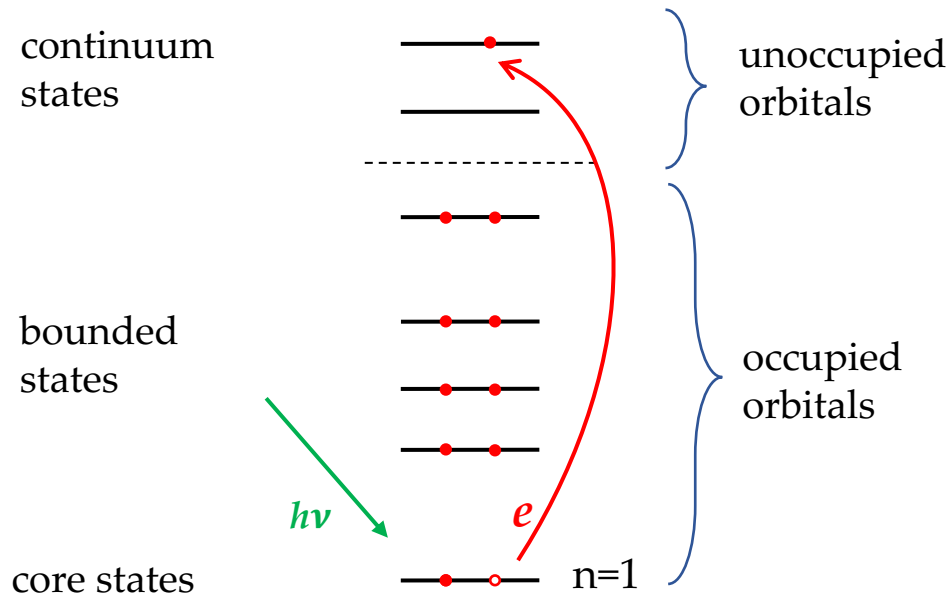
! check cp2k files for different options!

Absorption spectroscopy

Static absorption

- absorption probes unoccupied states;
- transitions satisfy dipole transition rules;
- element-specific technique;
- local-bonding sensitive;
- final state includes a core hole and an excited electron.

Absorption spectroscopy

The interaction between an spinless electron and an electromagnetic field (incoming radiation) can be described using the Hamiltonian

$$\hat{H}_{electron-field}(\hat{\mathbf{R}}, \hat{\mathbf{P}}, t) = \frac{1}{2m} \left[\hat{\mathbf{P}} + \frac{e}{c} \mathbf{A}(\hat{\mathbf{R}}, t) \right]^2$$

where the vector potential is defined as

$$\mathbf{A}(\mathbf{r}, t) = \mathbf{A}_0 \cos(\mathbf{k} \cdot \mathbf{r} - \omega t)$$

Rewriting $\hat{H}_{electron\text{-}field}$, it is possible to identify the interaction Hamiltonian, which contains the terms describing both emission and absorption processes

$$\hat{H}_{int}(\hat{\mathbf{R}}, \hat{\mathbf{P}}, t) = \frac{e}{2mc} \left[\underbrace{(\mathbf{A}_0 \cdot \hat{\mathbf{P}}) \, e^{i\,\mathbf{k}\cdot\hat{\mathbf{R}}} e^{-i\,\omega t}}_{\text{absorption}} + \underbrace{(\mathbf{A}_0 \cdot \hat{\mathbf{P}}) \, e^{-i\,\mathbf{k}\cdot\hat{\mathbf{R}}} e^{i\,\omega t}}_{\text{emission}} \right]$$

Absorption spectroscopy

Considering only the absorption term, the transition probability between a initial state i and a final state f can be written as

$$P_{i \to f} = \frac{2\pi}{\hbar} \left(\frac{e}{2mc} \right)^2 \left| \langle \psi_f | (\mathbf{A}_0 \cdot \hat{\mathbf{P}}) \, e^{i\,\mathbf{k} \cdot \hat{\mathbf{R}}} \, | \psi_i \rangle \right|^2 \delta(E_f - E_i - \hbar\omega)$$

For X-ray energies below ~10keV, it is possible to rewrite the expression above, making use of the dipole approximation, as

$$P_{i \to f} = \frac{2\pi}{\hbar} \left(\frac{e}{2mc} \right)^2 \left| \langle \psi_f | (\mathbf{A}_0 \cdot \hat{\mathbf{P}}) \, | \psi_i \rangle \right|^2 \delta(E_f - E_i - \hbar\omega)$$

F. M. F. de Groot and A. Kotani, Core Level Spectroscopy of Solids, Advances in Condensed Matter Science (CRC Press, 2008).

Absorption spectroscopy

Considerin[...]   [...]een a initial
state i and [...]

For X-ray [...]   [...]sion above,
making use[...]

> ## Electric dipole approximation
>
> As a starting point, it is possible to expand an exponential function in a power series.
>
> For an incoming radiation with energy below ~10keV, $\left| k \cdot \hat{R} \right| <$ 10^{-2}. Since the transition probability is proportional to the matrix element squared, the exponential function can be approximated to the zeroth-order term of the power series:
>
> $$e^{i\,\mathbf{k}\cdot\hat{\mathbf{R}}} = 1 + i\,\mathbf{k}\cdot\hat{\mathbf{R}} + \dots$$
> $$\approx 1$$

F. M. F. de Groot and A. Kotani, Core Level Spectroscopy of Solids, Advances in Condensed Matter Science (CRC Press, 2008).

Absorption spectroscopy

Considering only the absorption term, the transition probability between a initial state i and a final state f can be written as

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Absorption spectroscopy

The matrix element can be calculated using either the velocity or the length representation of the momentum operator (writing $\mathbf{A}_0 = A_0\,\hat{\epsilon}$)

$$P_{i \to f} \propto \left| \langle \psi_f | \, \hat{\epsilon} \cdot \hat{\mathbf{p}} \, | \psi_i \rangle \right|^2 \qquad\qquad P_{i \to f} \propto (E_f - E_i) \left| \langle \psi_f | \, \hat{\epsilon} \cdot \hat{\mathbf{r}} \, | \psi_i \rangle \right|^2$$

ΔSCF method

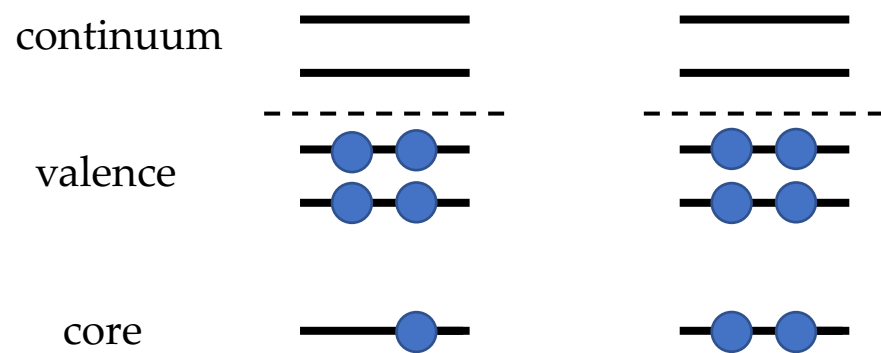- Transition energies can be calculated employing different occupations of Kohn-Sham orbitals.

$$IP_i \neq -\varepsilon_i \qquad \Delta E(1s \to \pi^*) \neq \varepsilon_{\pi^*} - \varepsilon_{1s}$$

ΔSCF method

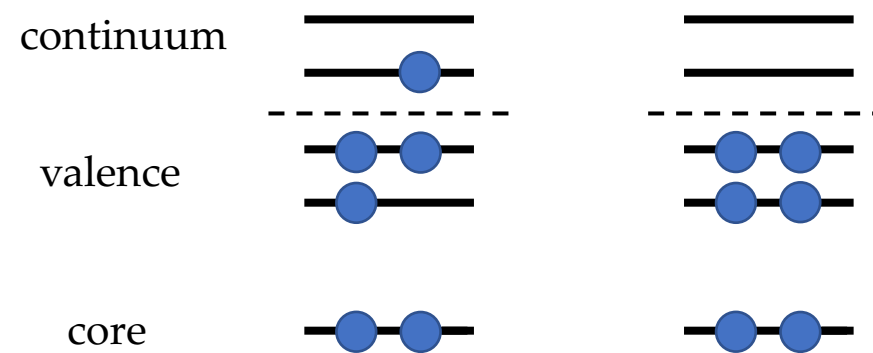- Transition energies can be calculated employing different occupations of Kohn-Sham orbitals.

$$IP_i \neq -\varepsilon_i \qquad \Delta E(1s \to \pi^*) \neq \varepsilon_{\pi^*} - \varepsilon_{1s}$$

$$IP_{i=1} = \widetilde{E}(0_1, 1_2, \dots, 1_N, \dots, 0_s, \dots)$$
$$- \widetilde{E}(1_1, 1_2, \dots, 1_N, \dots, 0_s, \dots)$$

$$\Delta E(i \to r) = \widetilde{E}(1_1, 1_2, \dots, 0_i, \dots, 1_N, \dots, 1_r, \dots)$$
$$- \widetilde{E}(1_1, 1_2, \dots, 1_i, \dots, 1_N, \dots, 0_r, \dots)$$

continuum

valence

core

ΔSCF method

• Transition energies can be calculated employing different occupations of Kohn-Sh...

$$IP_i \neq -\varepsilon$$

- ΔSCF is state-specific: excited states need to be calculated one by one;
- numerically not stable, since it is the difference between two different SCF calculations;
- the method only gives excited states that are well described by a single determinant;
- collapses for high excited states;
- excited states from different calculations are not orthogonal.

$$IP_{i=1} = \widetilde{E}(0 \quad \quad \quad 1_N, \ldots, 1_r, \ldots)$$
$$- \widetilde{E}(1_1 \quad \quad \quad 1_N, \ldots, 0_r, \ldots)$$

continuum

valence

core

continuum

valence

core

N. Ferré, M. Filatov, and M. Huix-Rotllant, Density-Functional Methods for Excited States (Springer, 2016).
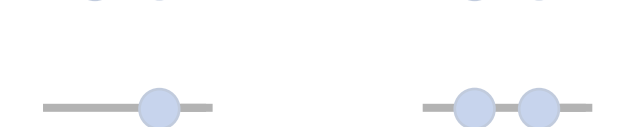
Transition Potential

- Calculation of the excitation energies from the solution of the KS equations, using a modified core potential on the absorbing atom, which reproduces the relaxation of the orbitals induced by the promotion of the core electron.

$$IP_{1s} \approx -\left.\frac{\partial E_0(n_{1s})}{\partial n_{1s}}\right|_{n_{1s}=1/2} = \varepsilon_{1s}\left(1/2\right)$$

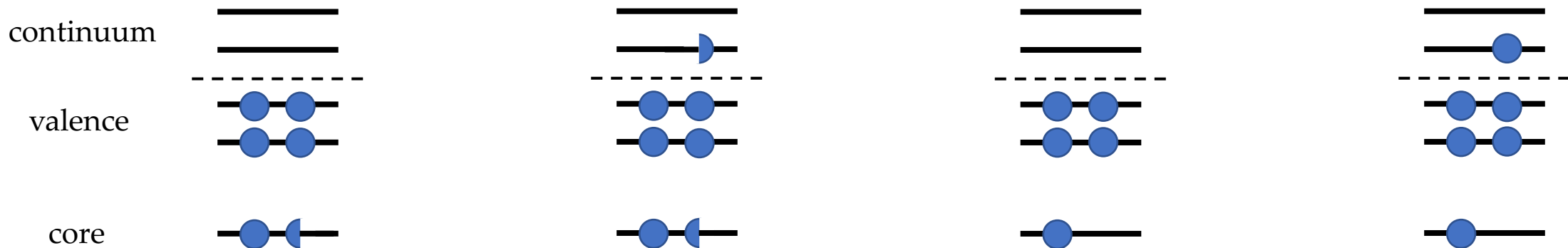- In this approach both initial and final states are taken from the same wavefunction.

$$\Delta E(1s \to f) = \varepsilon_f^{TP} - \varepsilon_{1s}^{TP}$$

$$I_{1s \to f} = \frac{2}{3}\,\omega_{1s \to f}\,|\langle\psi_{1s}|\,\boldsymbol{\mu}\,|\psi_f\rangle|^2$$

L. Triguero, L. G. M. Pettersson, and H. Ågren, Phys. Rev. B **58**, 8097 (1998).

Transition Potential - the core hole

- After the excitation, the electron is assumed to be immediately delocalized in the conduction band, so its actual final state is not relevant in the determination of the spectra.

- The hole left by the electron (core hole) is the focus of this approach.

- The core hole formed at the 1s level can be modeled through a modified pseudopotential.

L. Triguero, L. G. M. Pettersson, and H. Ågren, Phys. Rev. B **58**, 8097 (1998).
M. Cavaleri, M. Odelius, A. Nilsson, and L. Pettersson, J. Chem. Phys. **121**, 10065 (2004).

Transition Potential - the core hole

Transition Potential - the core hole

continuum

valence

core

HCH
- half core hole
- half of an electron is removed from the core
- system has charge +1/2

LUMO
- system has no charge

core
- system has charge +1

XFCH
- excited full core hole
- one electron is assigned to the LUMO
- system has no charge

- HCH tends to underestimate near-edge intensities and overemphasize the resonances at higher energies;
- FCH excessively shifts balance towards the final state, which might overestimate near-edge intensities;
- XHCH and XFCH are an attempt to restore balance between initial and final state contributions.

initial state

final state

M. Iannuzzi and J. Hutter, Phys. Chem. Chem. Phys. **9**, 1599 (2007).
B. Hetényi, F. D. Angelis, P. Giannozzi, and R. Car, J. Phys. Chem. B **120**, 8632 (2004).
D. Prendergast and G. Galli, Phys. Rev. Lett **96**, 215502 (2006).
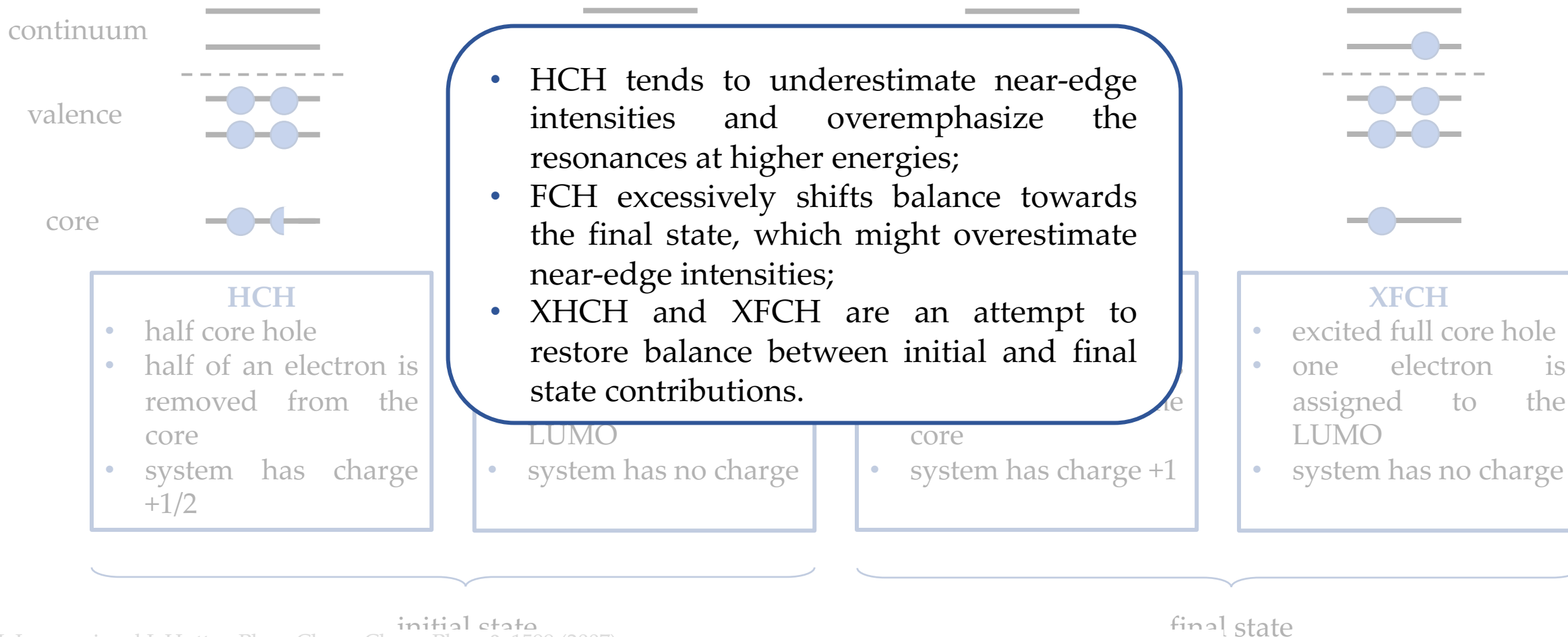
XAS in practice

1. Optimize geometry or use the experimental one;

2. Compute the absorption spectrum (oscillator strengths) using the Transition Potential method;

3. Align the spectrum according to the first transition energy obtained with the ΔSCF method;

4. Convolute the spectrum using gaussian functions with different width depending on the energy region.

M. Iannuzzi and J. Hutter, Phys. Chem. Chem. Phys. **9**, 1599 (2007).
M. Cavalleri, M. Odelius, A. Nilsson, and L. Pettersson, J. Chem. Phys. **121**, 10065 (2004).

XAS in practice: cp2k input file
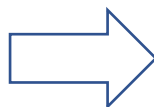
XAS in practice: cp2k input file

```
&SUBSYS
  &KIND H
    BASIS_SET DZVP-GTH-PBE
    POTENTIAL GTH-PBE-q1
  &END KIND

  &KIND O
    BASIS_SET DZVP-GTH-PBE
    POTENTIAL GTH-PBE-q6
  &END KIND

  &CELL
    PERIODIC XYZ
    ABC 5.430697500 5.430697500 5.430697500
  &END CELL

  &COORD
    O  0.000000  0.000000 -0.065587
    H  0.000000 -0.757136  0.520545
    H  0.000000  0.757136  0.520545
  &END COORD
&END SUBSYS
```

```
&SUBSYS
  &KIND H
    BASIS_SET DZVP-GTH-PBE
    POTENTIAL GTH-PBE-q1
  &END KIND

  &KIND O
    BASIS_SET DZVP-GTH-PBE
    POTENTIAL GTH-PBE-q6
  &END KIND

  &KIND O2
    ELEMENT O
    BASIS_SET DZVP-ALL
    POTENTIAL ALL
  &END KIND
  ...
&END SUBSYS
```

do not forget to change the name of the absorbing atom in the &COORD section/file!

XAS in practice: cp2k input file

- &XAS subsection should be added inside the &DFT subsection

```
&XAS                                             &PRINT
  RESTART F                                        &PROGRAM_RUN_INFO
  METHOD TP_HH ! half core hole                    &END PROGRAM_RUN_INFO
  DIPOLE_FORM VELOCITY
  STATE_TYPE 1s                                    &RESTART
  ! ATOMS_LIST indicates the indexes of the atoms to be excited  FILENAME ./name_file
  ! In order to include atoms from N to M use the syntax N..M       &EACH
  ATOMS_LIST 1..32                                   XAS_SCF 15
  ! ADDED_MOS indicates the number of virtual KS orbitals        &END EACH
  ! to compute the XAS                               ADD_LAST NUMERIC
  ADDED_MOS 10                                     &END RESTART
                                                   &XAS_SPECTRUM
  &SCF                                                FILENAME ./name_file
    EPS_SCF 1.0E-5                                 &END XAS_SPECTRUM
    MAX_SCF 200                                    &XES_SPECTRUM
                                                     FILENAME ./name_file
    &MIXING                                        &END XES_SPECTRUM
      METHOD BROYDEN_MIXING                      &END PRINT
      ALPHA 0.6                                 &END XAS
    &END MIXING
  &END SCF

  &LOCALIZE
  &END
```

XAS in practice: spectrum output file

```
Absorption spectrum for atom      1, index of excited core MO is      1, # of lines      10
   6      539.85006691     -0.05640206      0.43440389     -0.20522584      0.23400558    0.00000
   7      541.88798367      0.23643946      0.31879735      0.61291126      0.53319558    0.00000
   8      558.28821127     -0.11412717     -0.14615174     -0.29552089      0.12171794    0.00000
   9      558.91556968      0.12323985     -0.96780780      0.45225697      1.15637637    0.00000
  10      559.42319544     -1.11139441      0.04728497      0.40443734      1.40100297    0.00000
  11      561.72591964      0.05772737     -0.44849613      0.21013242      0.24863686    0.00000
  12      564.37023648      0.36756128      0.49435463      0.95250506      1.28675368    0.00000
  13      573.37372369     -0.02355321      0.18335237     -0.08598825      0.04156682    0.00000
  14      583.07153898      0.00054334     -0.00421800      0.00197214      0.00002198    0.00000
  15      583.41557986     -0.00004733     -0.00006394      0.00006007      0.00000001    0.00000
```

transition energies

index of the virtual KS state

transition probabilities
projected onto X, Y and Z

norm of the transition
probability

XAS in practice: spectrum output file

```
Absorption spectrum for atom     1, index of excited core MO is     1, # of lines     10
   6    539.85006691      -0.05640206      0.43440389     -0.20522584     0.23400558    0.00000
   7    541.88798367       0.23643946      0.31879735      0.61291126     0.53319558    0.00000
   8    558.28821127      -0.11412717     -0.14615174     -0.29552089     0.12171794    0.00000
   9    558.91556968       0.12323985     -0.96780780      0.45225697     1.15637637    0.00000
  10    559.42319544      -1.11139441      0.04728497      0.40443734     1.40100297    0.00000
  11    561.72591964       0.05772737     -0.44849613      0.21013242     0.24863686    0.00000
  12    564.37023648       0.36756128      0.49435463      0.95250506     1.28675368    0.00000
  13    573.37372369      -0.02355321      0.18335237     -0.08598825     0.04156682    0.00000
  14    583.07153898       0.00054334     -0.00421800      0.00197214     0.00002198    0.00000
  15    583.41557986      -0.00004733     -0.00006394      0.00006007     0.00000001    0.00000
```
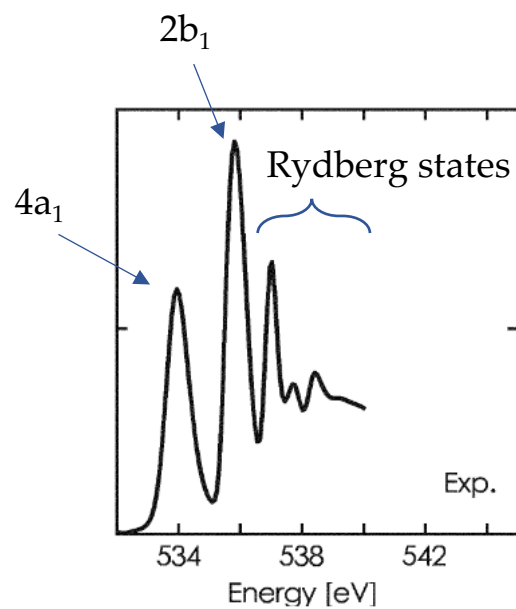
transition energies

index of the virtual KS state

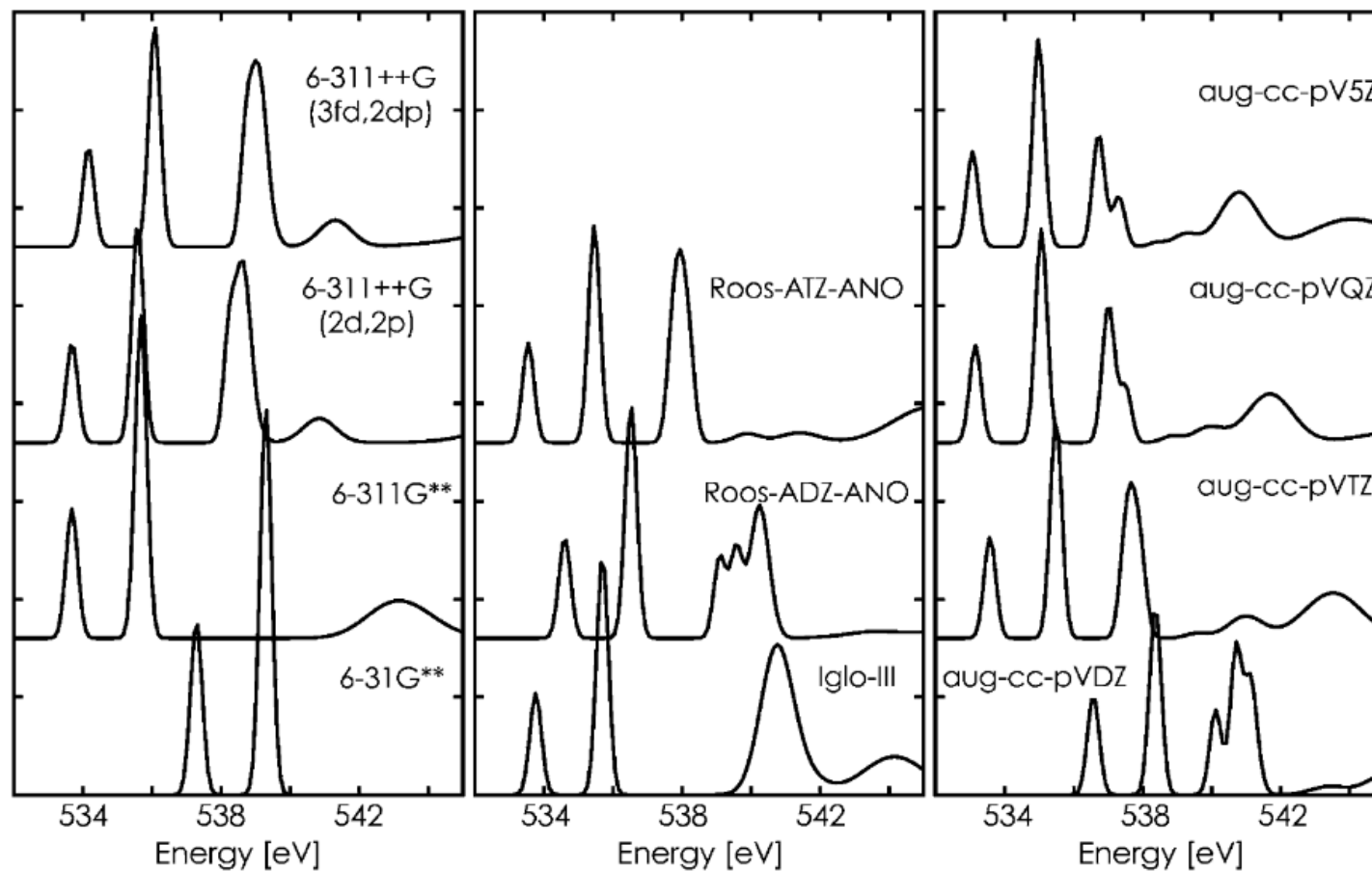transition probabilities
projected onto X, Y and Z

norm of the transition
probability (oscillator strength)
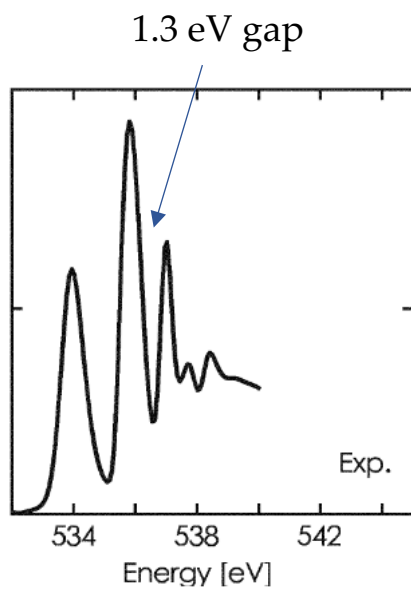
Absorption spectra of H$_2$O - O K-edge

2b$_1$

4a$_1$

Rydberg states

Exp.

liquid water

calculated using BLYP XC functional and HCH potential

6-311++G (3fd,2dp)

6-311++G (2d,2p)

6-311G**

6-31G**

Roos-ATZ-ANO

Roos-ADZ-ANO

Iglo-III

aug-cc-pV5Z

aug-cc-pVQZ

aug-cc-pVTZ

aug-cc-pVDZ

gas-phase water

M. Iannuzzi and J. Hutter, Phys. Chem. Chem. Phys. **9**, 1599 (2007).
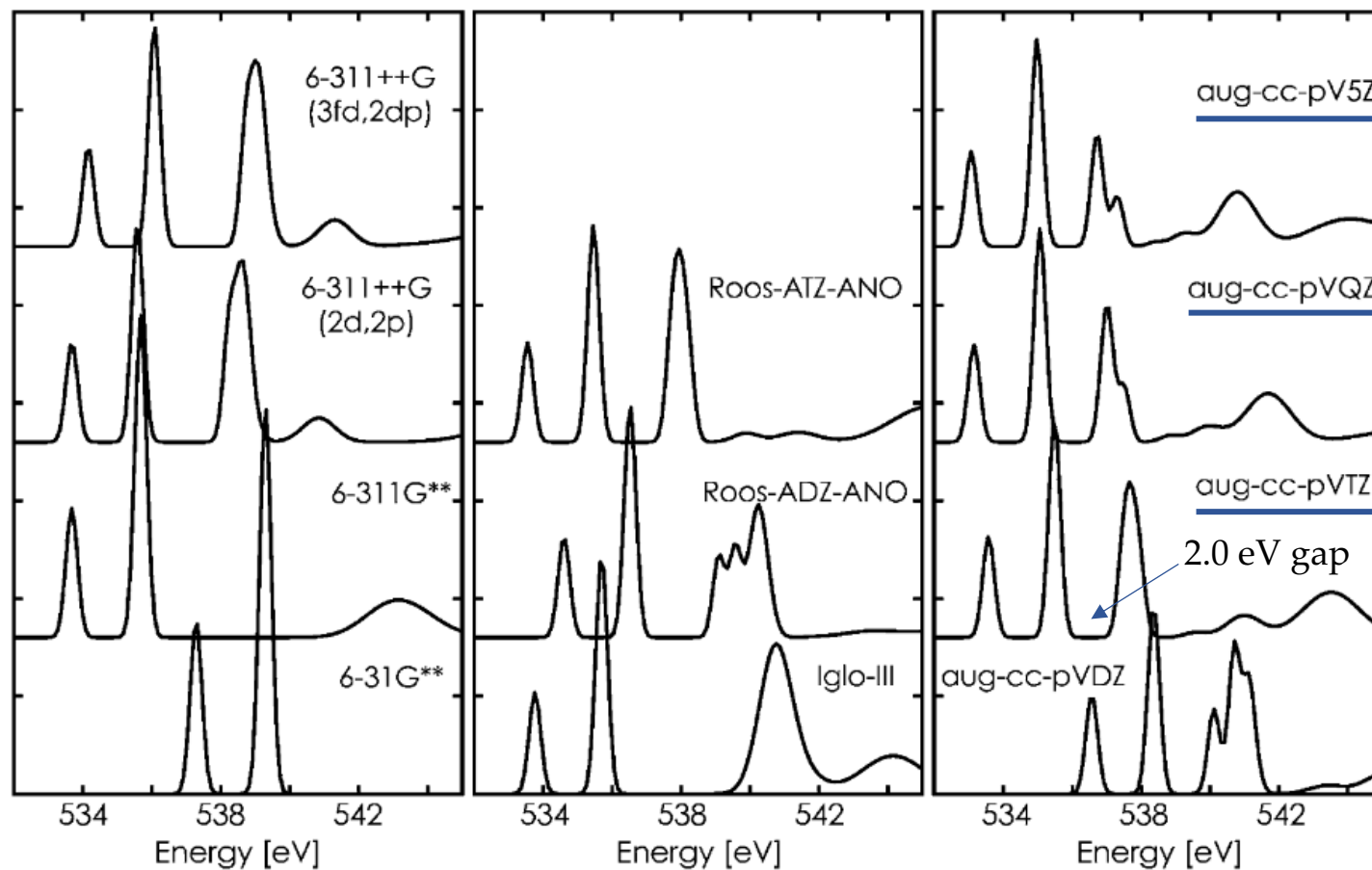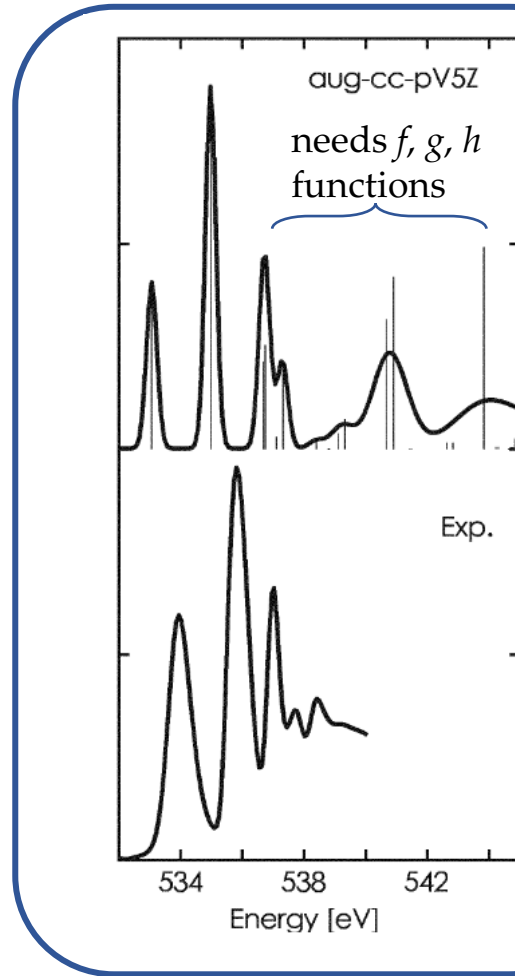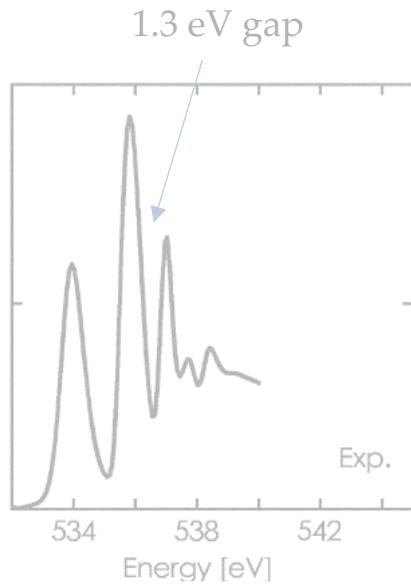S. Myneni *et al.*, J. Phys.: Condens. Matter **14**, 213 (2002).

Absorption spectra of H$_2$O - O K-edge

calculated using BLYP XC functional and HCH potential

1.3 eV gap

liquid water

gas-phase water

6-311++G (3fd,2dp)

6-311++G (2d,2p)

6-311G**

6-31G**

Roos-ATZ-ANO

Roos-ADZ-ANO

Iglo-III

aug-cc-pV5Z

aug-cc-pVQZ

aug-cc-pVTZ

2.0 eV gap

aug-cc-pVDZ

Exp.

M. Iannuzzi and J. Hutter, Phys. Chem. Chem. Phys. **9**, 1599 (2007).
S. Myneni *et al.*, J. Phys.: Condens. Matter **14**, 213 (2002).

Absorption spectra of H$_2$O - O K-edge

1.3 eV gap

liquid water

aug-cc-pV5Z

needs *f*, *g*, *h* functions

Exp.

534 538 542
Energy [eV]

gas-phase water

BLYP XC functional and HCH potential

Roos-ATZ-ANO

Roos-ADZ-ANO

Iglo-III

534 538 542
Energy [eV]

aug-cc-pV5Z

aug-cc-pVQZ

aug-cc-pVTZ

aug-cc-pVDZ

534 538 542
Energy [eV]

M. Iannuzzi and J. Hutter, Phys. Chem. Chem. Phys. **9**, 1599 (2007).
S. Myneni *et al.*, J. Phys.: Condens. Matter **14**, 213 (2002).

Absorption spectra of H_2O - O K-edge

M. Iannuzzi and J. Hutter, Phys. Chem. Chem. Phys. **9**, 1599 (2007).
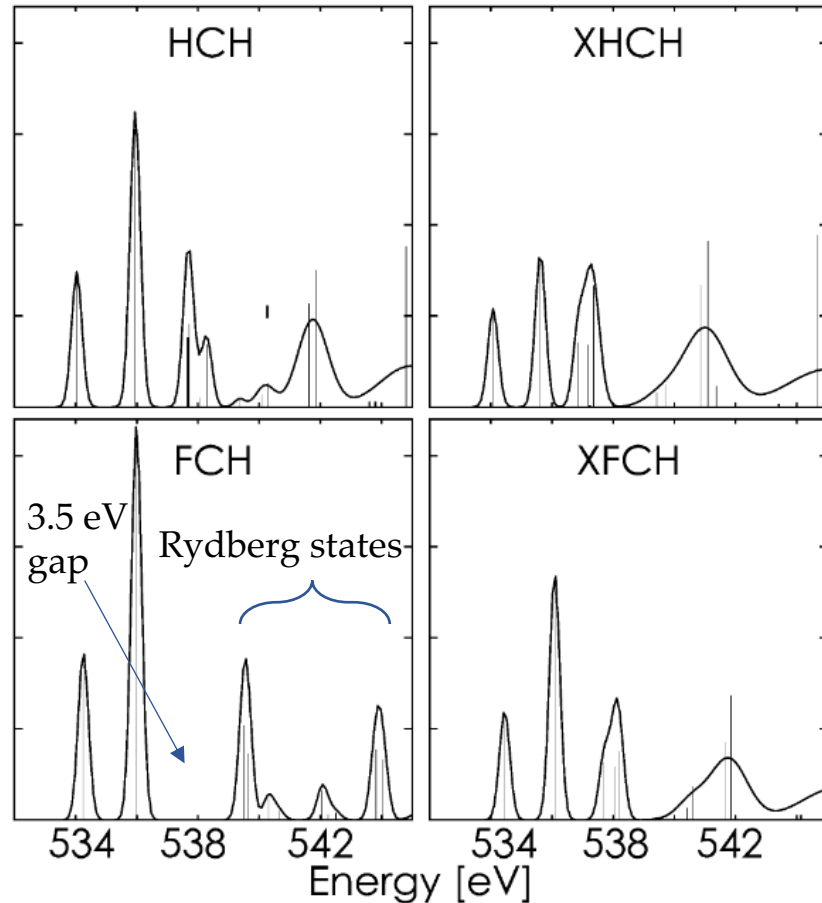
Absorption spectra of H_2O - O K-edge

- FCH
  - contraction of orbitals at lower energies, which favors the overlap with 1s and enhances intensities of pre-edge structures;

M. Iannuzzi and J. Hutter, Phys. Chem. Chem. Phys. **9**, 1599 (2007).
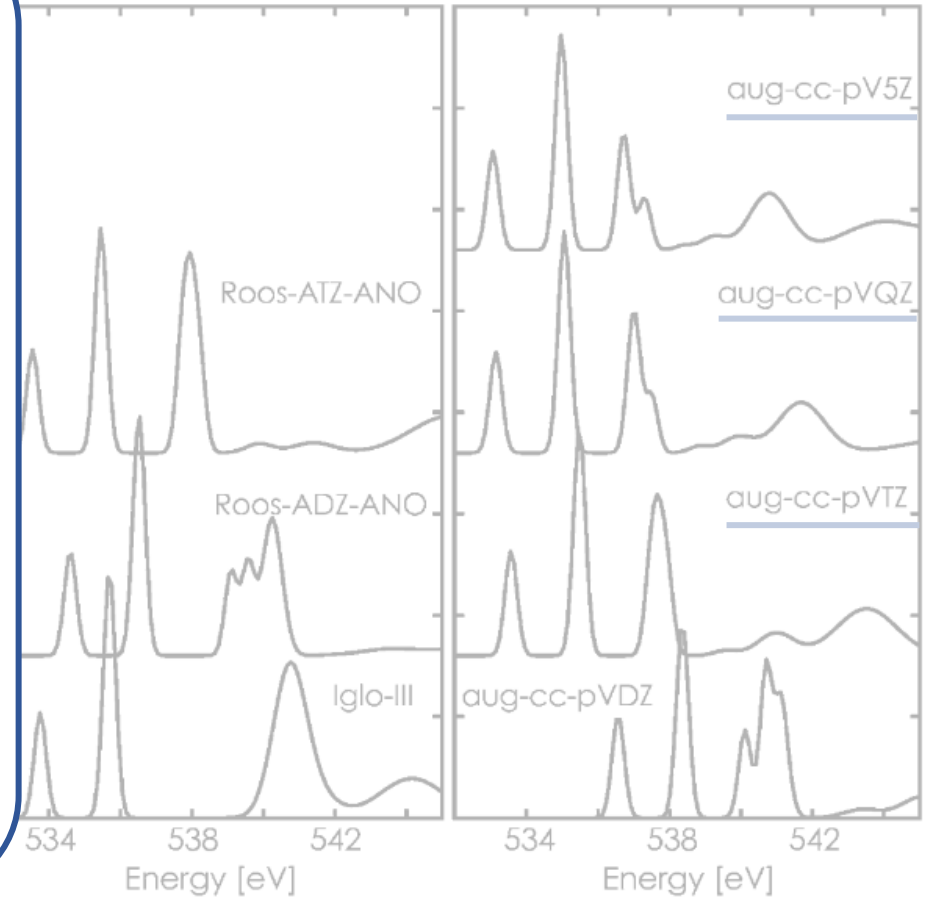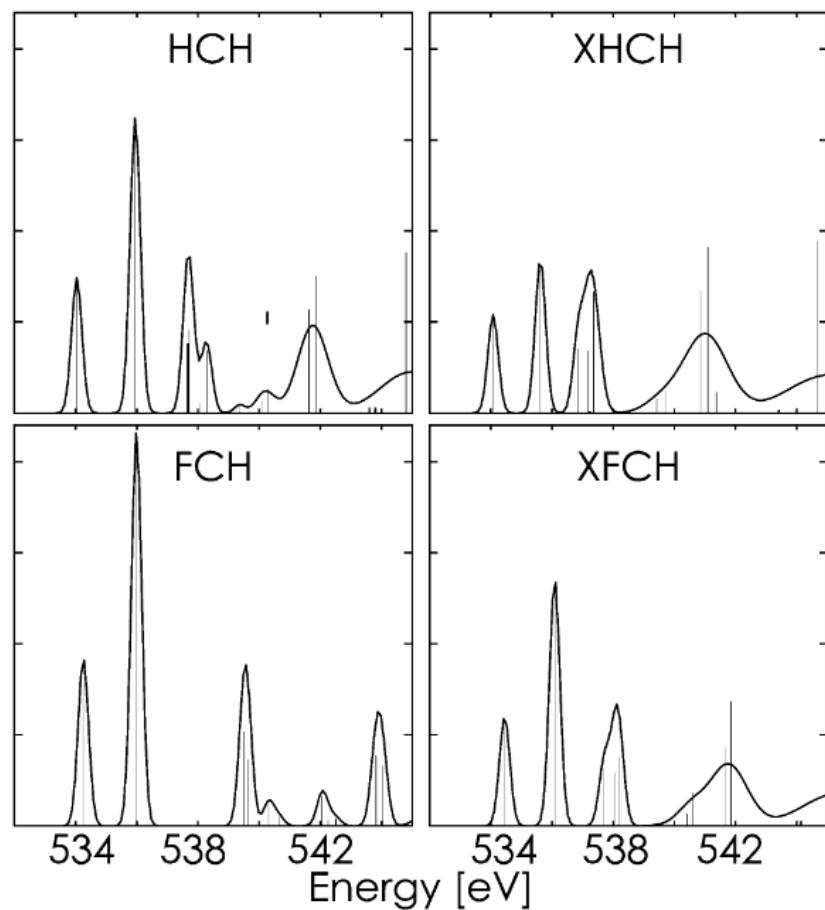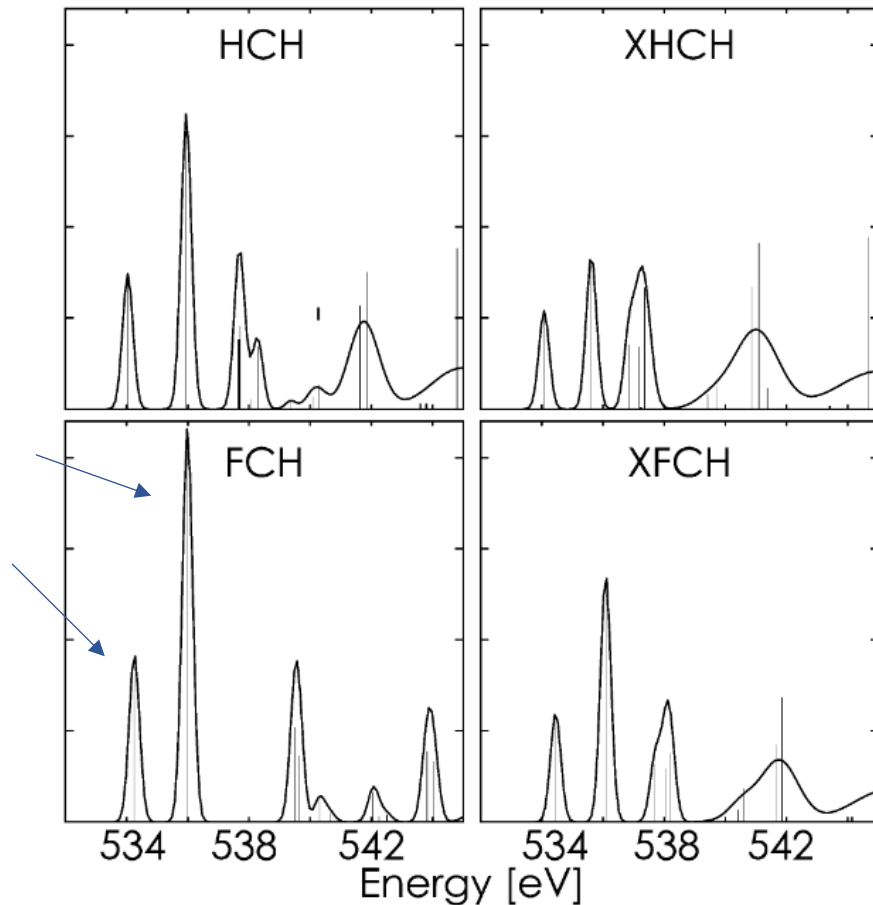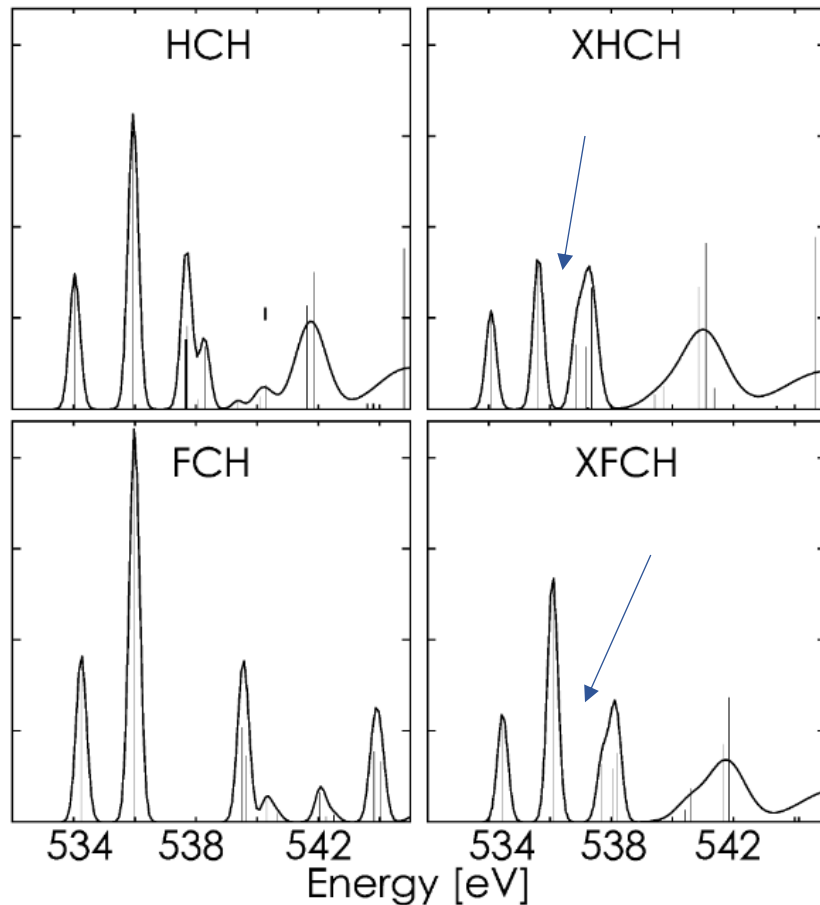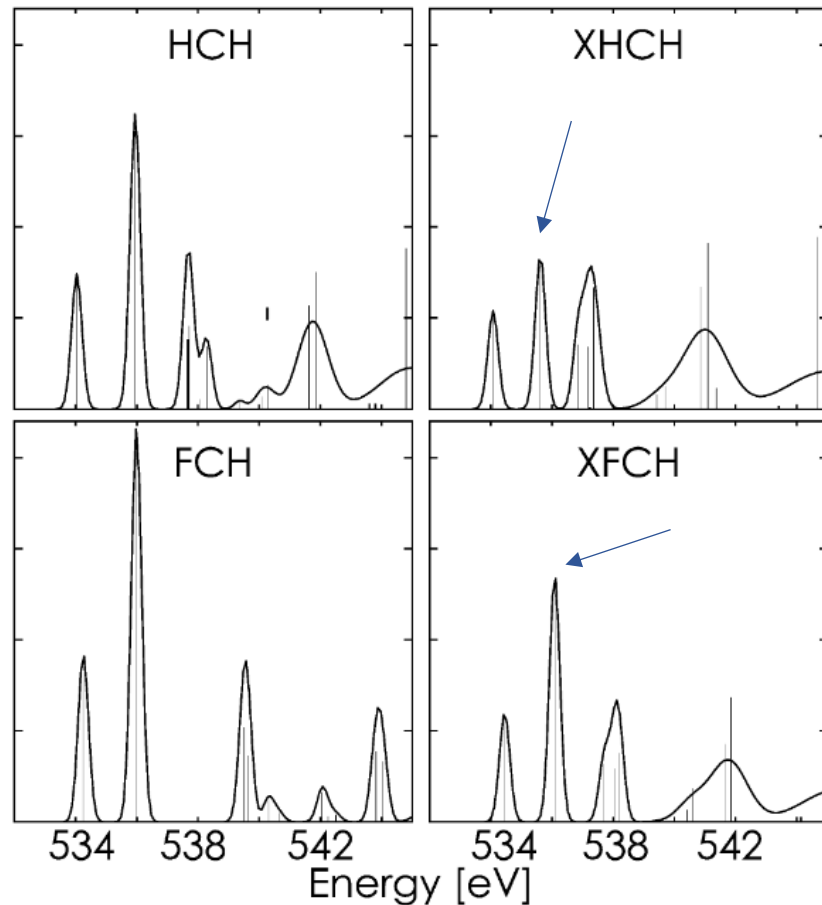
Absorption spectra of H$_2$O - O K-edge

- FCH
  - contraction of orbitals at lower energies, which favors the overlap with 1s and enhances intensities of pre-edge structures;
  - Rydberg states are shifted to higher energies and the gap increases to ~3.5 eV;

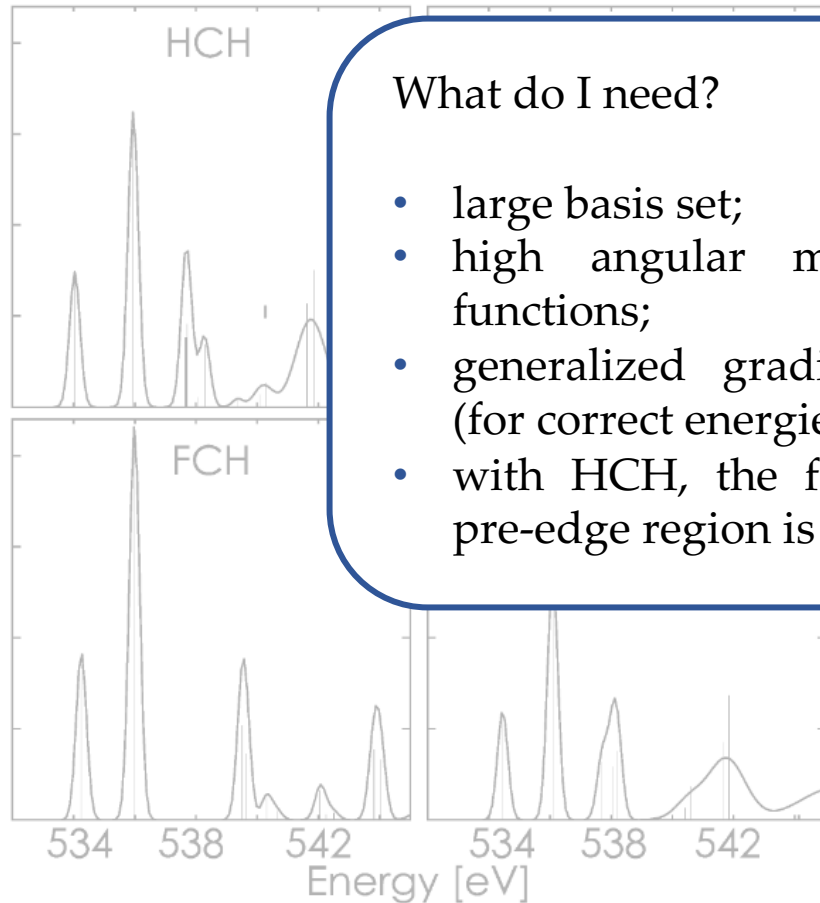M. Iannuzzi and J. Hutter, Phys. Chem. Chem. Phys. **9**, 1599 (2007).

Absorption spectra of H$_2$O - O K-edge

- XHCH and XFCH
  - reduce the gap between the Rydberg states the pre-edge transitions;

M. Iannuzzi and J. Hutter, Phys. Chem. Chem. Phys. **9**, 1599 (2007).

Absorption spectra of H$_2$O - O K-edge

- XHCH and XFCH
  - reduce the gap between the Rydberg states the pre-edge transitions;
  - lower intensity of the second valence peak due to the screening of the core hole.

M. Iannuzzi and J. Hutter, Phys. Chem. Chem. Phys. **9**, 1599 (2007).

Absorption spectra of H₂O - O K-edge

HCH

FCH

p between the Rydberg
edge transitions;
y of the second valence
he screening of the core

What do I need?

- large basis set;
- high angular momentum (*g, h*) basis functions;
- generalized gradient corrected functional (for correct energies in the ΔSCF calculation);
- with HCH, the fine structure beyond the pre-edge region is well reproduced.

534   538   542   534   538   542
Energy [eV]

M. Iannuzzi and J. Hutter, Phys. Chem. Chem. Phys. **9**, 1599 (2007).

References - books

- R. R. Martin, Electronic Structure, Basic Theory and Practical Methods (Cambridge University Press, 2004);

- F. M. F. de Groot and A. Kotani, Core Level Spectroscopy of Solids, Advances in Condensed Matter Science (CRC Press, 2008);

- N. Ferré, M. Filatov, and M. Huix-Rotllant, Density-Functional Methods for Excited States (Springer, 2016);

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- N. Mardirossian and M. Head-Gordon, Mol. Phys. **115**, 2315 (2017).

Thank you!

Questions?