CP2K : GAPW & Spectroscopy

Marcella Iannuzzi

University of Zurich

University of Zurich UZH

Basis Set Representation

KS matrix formulation when the wavefunction is expanded into a basis

System size $\{N_{el}, M\}$, **P** [MxM], **C** [MxN]

$$\psi_i(\mathbf{r}) = \sum_\alpha C_{\alpha i}\phi_\alpha(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_i \sum_{\alpha\beta} f_i C_{\alpha i} C_{\beta i}\phi_\alpha(\mathbf{r})\phi_\beta(\mathbf{r}) = \sum_{\alpha\beta} P_{\alpha\beta}\phi_\alpha(\mathbf{r})\phi_\beta(\mathbf{r})$$

$$\mathbf{P} = \mathbf{PSP}$$

Variational principle
Constrained minimisation problem

KS total energy

$$E[\{\psi_i\}] = T[\{\psi_i\}] + E^{\mathrm{ext}}[n] + E^{\mathrm{H}}[n] + E^{\mathrm{XC}}[n] + E^{II}$$

Matrix formulation of the KS equations

$$\mathbf{K}(C)\mathbf{C} = \mathbf{T}(C) + \mathbf{V}_{\mathrm{ext}}(C) + \mathbf{E}^{\mathrm{H}}(C) + \mathbf{E}^{\mathrm{xc}}(C) = \mathbf{SC}\varepsilon$$

Classes of Basis Sets

☀ Extended basis sets, **PW** : condensed matter

☀ Localised basis sets centred at atomic positions, **GTO**

Idea of GPW: auxiliary basis set to represent the density

☀ Mixed (GTO+PW) to take best of two worlds, **GPW**

☀ Augmented basis set, **GAPW**: separated hard and soft density domains

GPW Ingredients

linear scaling KS matrix computation for GTO

☀ Gaussian basis sets (many terms analytic)

$$\psi_i(\mathbf{r}) = \sum_\alpha C_{\alpha i}\phi_\alpha(\mathbf{r}) \qquad \phi_\alpha(\mathbf{r}) = \sum_m d_{m\alpha}g_m(\mathbf{r}) \qquad g_m(\mathbf{r}) = x^{m_x}y^{m_y}z^{m_z}e^{-\alpha_m r^2}$$

☀ Pseudo potentials

☀ Plane waves auxiliary basis for Coulomb integrals

☀ Regular grids and FFT for the density

☀ Sparse matrices (KS and P)

☀ Efficient screening

G. Lippert et al, Molecular Physics, 92, 477, 1997

J. VandeVondele et al, Comp. Phys. Comm.,167 (2), 103, 2005

Basis Set library

GTH_BASIS_SETS ; BASIS_MOLOPT ; EMSL_BASIS_SETS

O 6-31Gx 6-31G*

O SZV-MOLOPT-GTH SZV-MOLOPT-GTH-q6

O DZVP-GTH

O DZVP-MOLOPT-GTH DZVP-MOLOPT-GTH-q6

O 6-31Gxx 6-31G**

O TZVP-MOLOPT-GTH TZVP-MOLOPT-GTH-q6

O 6-311++G3df3pd   6-311++G(3df,3pd)
9
1 0 0 6 1
  8588.50000000   0.00189515
  1297.23000000   0.01438590
  299.29600000   0.07073200
  87.37710000   0.24000100
  25.67890000   0.59479700
  3.74004000   0.28080200
1 0 1 3 1 1
  42.11750000   0.11388900   0.03651140
                      0.92081100   0.23715300
                     -0.00327447   0.81970200
                      0.90566100   1.00000000   1.00000000
                      1.00000000   1.00000000
  5.16000000   1.00000000
1 2 2 1 1
  1.29200000   1.00000000

GTO in CP2K

✳ The repository contains several GTO libraries

cp2k/data/

ALL_BASIS_SETS	**BASIS_RI_cc–TZ**	GTH_POTENTIALS	dftd3.dat
ALL_POTENTIALS	**BASIS_SET**	**HFX_BASIS**	nm12_parameters.xml
BASIS_ADMM	**BASIS_ZIJLSTRA**	HF_POTENTIALS	rVV10_kernel_table.dat
BASIS_ADMM_MOLOPT	DFTB	MM_POTENTIAL	t_c_g.dat
BASIS_LRIGPW_AUXMOLOPT	ECP_POTENTIALS	NLCC_POTENTIALS	t_sh_p_s_c.dat
BASIS_MOLOPT	**EMSL_BASIS_SETS**	POTENTIAL	vdW_kernel_table.dat
BASIS_MOLOPT_UCL	GTH_BASIS_SETS	README	

Tools for the optimisation of GTO basis sets are available in cp2k, based on atomic and molecular electronic structure calculations

Generate GTO basis set

```
&ATOM
  ELEMENT Ru
  RUN_TYPE BASIS_OPTIMIZATION
  ELECTRON_CONFIGURATION  CORE 4d7 5s1
  CORE [Kr]
  MAX_ANGULAR_MOMENTUM 2
  &METHOD
    METHOD_TYPE  KOHN-SHAM
    &XC
      &XC_FUNCTIONAL
        &PBE
        &END
      &END XC_FUNCTIONAL
    &END XC
  &END METHOD
  &OPTIMIZATION
    EPS_SCF 1.e-8
  &END OPTIMIZATION
  &PP_BASIS
   NUM_GTO  6 6 6
   S_EXPONENTS 3.73260 1.83419 0.80906 0.34515
0.13836 0.04967
   P_EXPONENTS 3.73260 1.83419 0.80906 0.34515
0.13836 0.04967
   D_EXPONENTS 3.73260 1.83419 0.80906 0.34515
0.13836 0.04967
    EPS_EIGENVALUE 1.E-14
  &END PP_BASIS
```

```
&POTENTIAL
  PSEUDO_TYPE GTH
  &GTH_POTENTIAL
  1    0    7
    0.61211332  1  5.04489332
  3
    0.6421504 2 4.625563 -1.8033490
                          2.32811359
    0.6793665 2 3.233952 -2.42101064
                          2.86457842
    0.3805972 2 -15.5316  13.58045054
                          -15.39878349
  &END GTH_POTENTIAL
  CONFINEMENT   0.5  20.00  4.5
&END POTENTIAL
&POWELL
  ACCURACY   1.e-8
  STEP_SIZE  1.0
&END POWELL
&END ATOM
```

GTH PP for O: 6 val. el.

```
&ATOM

  ELEMENT O
  RUN_TYPE  PSEUDOPOTENTIAL_OPTIMIZATION

  ELECTRON_CONFIGURATION  [He] 2s2 2p4
  CORE [He]
  MAX_ANGULAR_MOMENTUM 2

  COULOMB_INTEGRALS ANALYTIC
  EXCHANGE_INTEGRALS ANALYTIC

  &METHOD
    METHOD_TYPE  KOHN-SHAM
    RELATIVISTIC DKH(2)
    &XC
      &XC_FUNCTIONAL PBE0
      &END XC_FUNCTIONAL
    &END XC
  &END METHOD
  &OPTIMIZATION
    EPS_SCF 1.e-10
  &END
  &PRINT
    &BASIS_SET
    &END
  &END
```

```
  &AE_BASIS
    BASIS_TYPE GEOMETRICAL_GTO
  &END AE_BASIS
  &PP_BASIS
    BASIS_TYPE GEOMETRICAL_GTO
  &END PP_BASIS
  &POTENTIAL
    PSEUDO_TYPE GTH
    &GTH_POTENTIAL
    2    4
    0.24455430  2 -16.66721480 2.48731132
    2
    0.22095592  1  18.33745811
    0.21133247  0
    &END GTH_POTENTIAL
  &END POTENTIAL

  &POWELL
    ACCURACY   1.e-10
    STEP_SIZE  0.5
    WEIGHT_PSIR0 0.1
  &END

&END ATOM
```

8

GTH_POTENTIALS

$$N_{\mathrm{el}}(s) \qquad N_{\mathrm{el}}(p) \qquad N_{\mathrm{el}}(d) \qquad ...$$

$$r_{\mathrm{loc}}^{\mathrm{PP}} \qquad N_C \qquad C_1^{\mathrm{PP}} \quad ... \quad C_{N_C}^{\mathrm{PP}}$$

$$N_p$$

$$r_1 \qquad n_{\mathrm{nl}}^1 \qquad \{h_{ij}^1\}_{ij=1...n^1}$$

$$r_2 \qquad n^2 \qquad \{h_{ij}^2\}_{ij=1...n^2}$$

Few parameters

```
C GTH-BLYP-q4
  2   2
  0.33806609   2   -9.13626871    1.42925956
  2
  0.30232223   1    9.66551228
  0.28637912   0
#
N GTH-BLYP-q5
  2   3
  0.28287094   2  -12.73646720    1.95107926
  2
  0.25523449   1   13.67893172
  0.24313253   0
```

```
#
#
Al GTH-PBE-q3
  2   1
  0.45000000   1   -7.55476126
  2
  0.48743529   2    6.95993832   -1.88883584
                                  2.43847659
  0.56218949   1    1.86529857
```

$$
\begin{aligned}
E^{\text{el}}[n] \quad = \quad & \sum_{\mu\nu} P_{\mu\nu} \left\langle \varphi_\mu \left| -\frac{1}{2}\nabla^2 + V_{\text{loc}}^{\text{SR}} + V_{\text{nl}} \right| \varphi_\nu \right\rangle \\
+ \quad & 2\pi\Omega \sum_{\mathbf{G}} \frac{\tilde{n}_{\text{tot}}^*(\mathbf{G})\tilde{n}_{\text{tot}}(\mathbf{G})}{\mathbf{G}^2} + \sum_{\mathbf{R}} \tilde{n}(\mathbf{R})V^{\text{XC}}(\mathbf{R}) \\
= \quad & \sum_{\mu\nu} P_{\mu\nu} \left(\left\langle \varphi_\mu \left| -\frac{1}{2}\nabla^2 + V^{\text{ext}} \right| \varphi_\nu \right\rangle + \sum_{\mathbf{R}} V_{\mu\nu}^{\text{HXC}}(\mathbf{R})\varphi'_{\mu\nu}(\mathbf{R}) \right)
\end{aligned}
$$

Linear scaling KS matrix construction

CP2K DFT input

```
&FORCE_EVAL
 METHOD Quickstep

 &DFT
    BASIS_SET_FILE_NAME   GTH_BASIS_SETS
    POTENTIAL_FILE_NAME GTH_POTENTIALS
    LSD F
    MULTIPLICITY 1
    CHARGE 0
    &MGRID
       CUTOFF 300
       REL_CUTOFF 50
    &END MGRID
    &QS
      EPS_DEFAULT 1.0E-10
    &END QS
    &SCF
      MAX_SCF     50
      EPS_SCF     2.00E-06
      SCF_GUESS   ATOMIC
    &END SCF
    &XC
      &XC_FUNCTIONAL
        &PBE
        &END PBE
      &END XC_FUNCTIONAL
```

```
      &XC_GRID
         XC_DERIV SPLINE2_smooth
         XC_SMOOTH_RHO NN10
      &END XC_GRID
    &END XC
 &END DFT

 &SUBSYS
   &CELL
      PERIODIC XYZ
      ABC 8. 8. 8.
   &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
   &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
 &END SUBSYS
&END FORCE_EVAL
```

Hard and Soft Densities
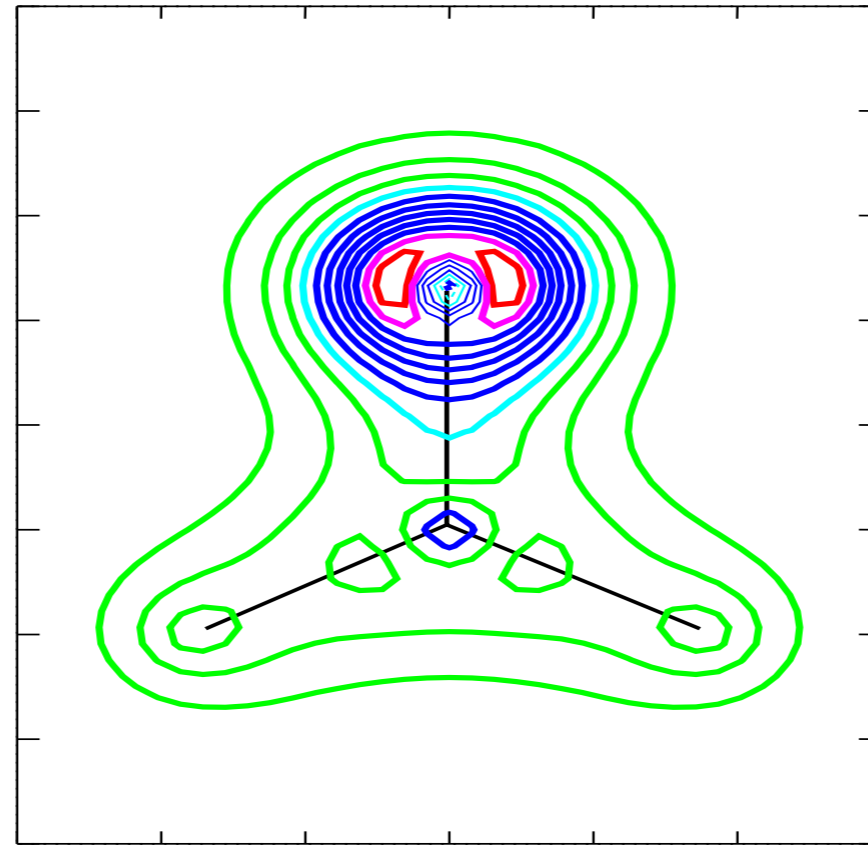
Formaldehyde

⚙ Pseudopotential ⇨ frozen core

⚙ Augmented PW ⇨ separate regions (matching at edges)
LAPW, LMTO (OK Andersen, PRB **12**, 3060 (1975)

⚙ Dual representation ⇨ localized orbitals and PW
PAW (PE Bloechl, PRB, **50**, 17953 (1994))

$$n(\mathbf{r}) = \sum_{\mu\nu} P_{\mu\nu} \varphi_\mu(\mathbf{r}) \varphi_\nu(\mathbf{r})$$
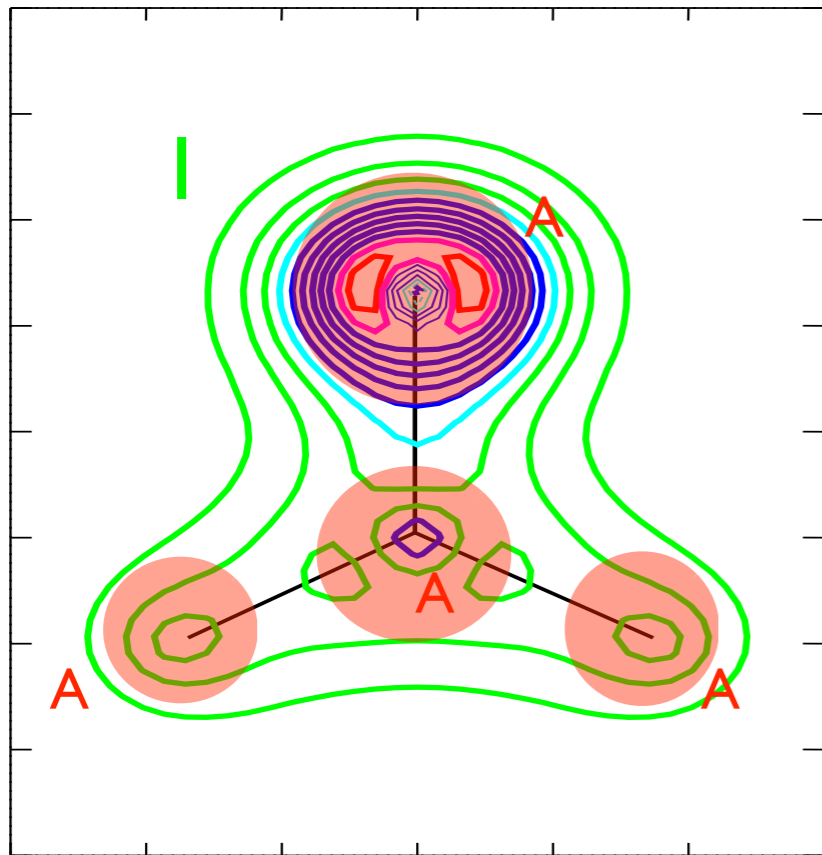
$$n = \tilde{n} + \sum_A n_A - \sum_A \tilde{n}_A$$

$$\left. \begin{array}{ccc} n(\mathbf{r}) & - & \tilde{n}(\mathbf{r}) = 0 \\ n_A(\mathbf{r}) & - & \tilde{n}_A(\mathbf{r}) = 0 \end{array} \right\} \quad \mathbf{r} \in I$$

$$\left. \begin{array}{ccc} n(\mathbf{r}) & - & n_A(\mathbf{r}) = 0 \\ \tilde{n}(\mathbf{r}) & - & \tilde{n}_A(\mathbf{r}) = 0 \end{array} \right\} \quad \mathbf{r} \in A$$

$$n_A(\mathbf{r}) = \sum_{\mu\nu} P_{\mu\nu} \chi_\mu^A \chi_\nu^A \qquad \tilde{n}(\mathbf{r}) = \sum_{\mu\nu} P_{\mu\nu} \tilde{\varphi}_\mu \tilde{\varphi}_\nu \rightarrow \sum_{\mathbf{G}} \hat{n}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{R}}$$

Gaussian Augmented Plane Waves

$$n_A(\mathbf{r}) = \sum_{\mu\nu} P_{\mu\nu} \chi_\mu^A \chi_\nu^A$$

X$_\mu$ projection of φ$_\mu$ in Ω_A
through atom-dependent d'

$$\chi_\mu = \sum_\alpha d_{\mu\alpha}'^A \ g_\alpha(\mathbf{r})$$

A **μ**

ν

μ ν

overlap in **A**

projector basis (same size)

$$\{p_\alpha\} \qquad \lambda_\alpha = k^\alpha \lambda_{min} \qquad \langle p_\alpha | \varphi_\mu \rangle = \sum_\beta d_{\mu\beta}'^A \langle p_\alpha | g_\beta \rangle$$

$$n_A(\mathbf{r}) = \sum_{\alpha\beta} \left[\sum_{\mu\nu} P_{\mu\nu} d_{\mu\alpha}'^A d_{\nu\beta}'^A \right] g_\alpha(\mathbf{r}) g_\beta(\mathbf{r}) = \sum_{\alpha\beta} P_{\alpha\beta}'^A \ g_\alpha(\mathbf{r}) g_\beta(\mathbf{r})$$
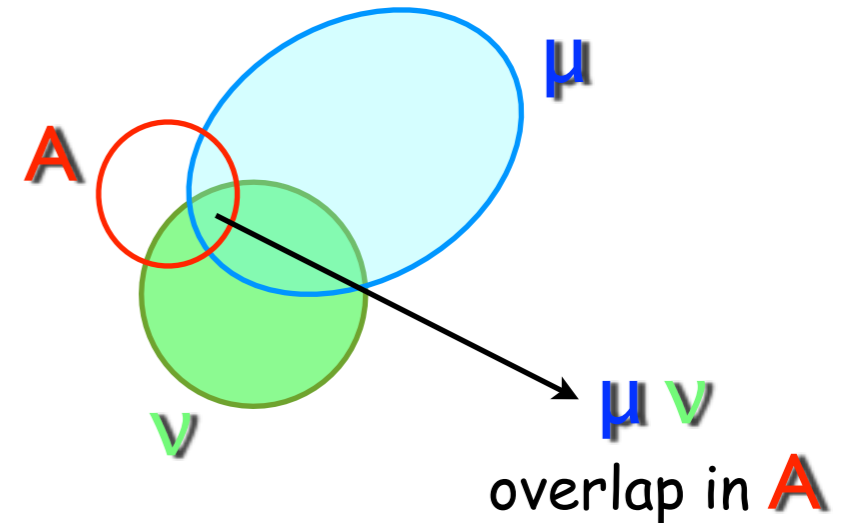
Density Dependent Terms: XC

Semi-local functionals like local density approximation, generalised gradient approximation or meta-functionals

Gradient: $\quad \nabla n(\mathbf{r}) = \nabla \tilde{n}(\mathbf{r}) + \sum_A \nabla n_A(\mathbf{r}) - \sum_A \nabla \tilde{n}_A(\mathbf{r})$

$$E[n] = \int V_{loc}(\mathbf{r})n(\mathbf{r}) = \int \left\{ \tilde{V}_{loc}(\mathbf{r}) + \sum_A V_{loc}^A(\mathbf{r}) + \sum_A \tilde{V}_{loc}^A(\mathbf{r}) \right\}$$

$$\times \quad \left\{ \tilde{n}(\mathbf{r}) + \sum_A n_A(\mathbf{r}) - \sum_A \tilde{n}_A(\mathbf{r}) \right\} d\mathbf{r}$$

(A)
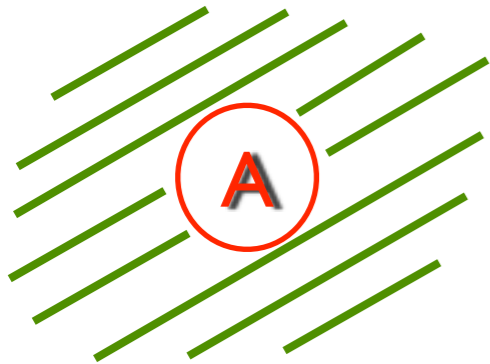
$$= \int \left\{ \tilde{V}_{loc}(\mathbf{r})\tilde{n}(\mathbf{r}) + \sum_A V_{loc}^A(\mathbf{r})n_A(\mathbf{r}) - \sum_A \tilde{V}_{loc}^A(\mathbf{r})\tilde{n}_A(\mathbf{r}) \right\}$$

Density Dependent Terms: ES

Non local Coulomb operator

$$\mathbf{n^0(r)} = \sum_A \mathbf{n_A^0(r)} = \sum_A \left\{ \sum_L Q_A^L \, g_A^L(\mathbf{r}) \right\}$$

Compensation charge
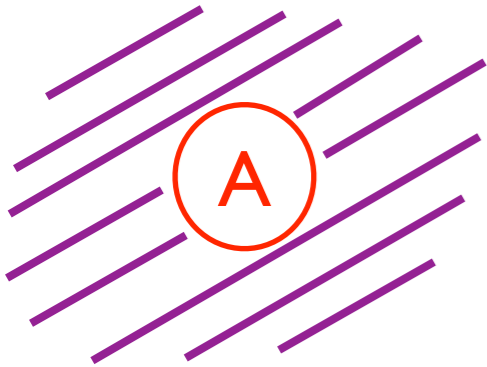
Same multipole expansion as the local densities
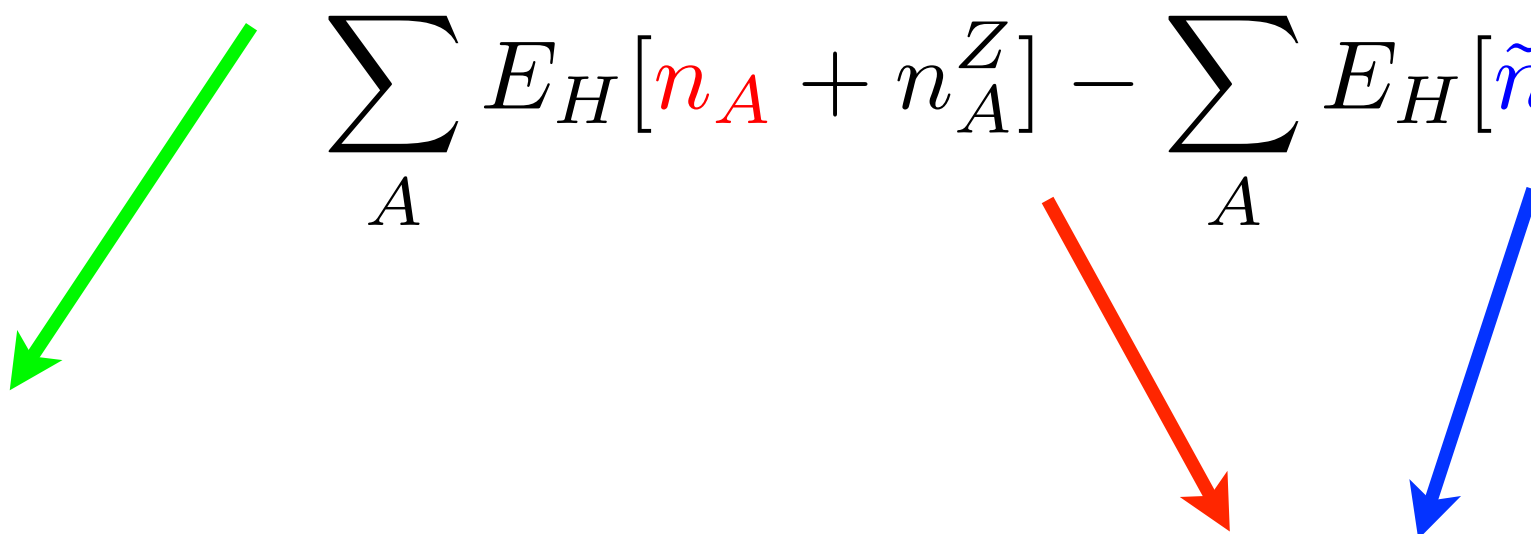
$$\mathcal{Q}_A^L = \int \left\{ n_A(\mathbf{r}) - \tilde{n}_A(\mathbf{r}) + n_A^Z(\mathbf{r}) \right\} r^l \mathcal{Y}_{lm}(\theta\phi) r^2 dr \sin(\theta) d\theta d\phi$$

$$V[\tilde{n} + \mathbf{n^0}] + \sum_A V[n_A + n_A^Z] - \sum_A V[\tilde{n}_A + \mathbf{n_A^0}]$$

Interstitial region
Atomic region

GAPW Functionals

$$E_{xc}[n] = E_{xc}[\tilde{n}] + \sum_A E_{xc}[n_A] - \sum_A E_{xc}[\tilde{n}_A]$$

$$E_H[n + n^Z] = E_H[\tilde{n} + \mathbf{n^0}] +$$

$$\sum_A E_H[n_A + n_A^Z] - \sum_A E_H[\tilde{n}_A + \mathbf{n^0}]$$

**on global grids
via collocation + FFT**

**Analytic integrals
Local Spherical Grids**

Lippert et al., Theor. Chem. Acc. 103, 124 (1999);
Krack et al, PCCP, **2**, 2105 (2000)

Iannuzzi, Chassaing, Hutter, Chimia (2005);
VandeVondele , Iannuzzi, Hutter, CSCM2005 proceedings

17

Integrals on Atom Centered Grids

Separation into radial and angular contributions

$$n_A(\mathbf{r}) = \sum_{\alpha\beta} P^A_{\alpha\beta} \, r^{l_\alpha} e^{-\alpha_\alpha r^2} \mathcal{Y}_{l_\alpha m_\alpha}(\theta,\phi) \, r^{l_\beta} e^{-\alpha_\beta r^2} \mathcal{Y}_{l_\beta m_\beta}(\theta,\phi)$$

$$= \sum_{\alpha\beta} \left[P^A_{\alpha\beta} \, r^{l_\alpha + l_\beta} e^{-(\alpha_\alpha + \alpha_\beta)r^2} \sum_{LM} C(\alpha,\beta,L,M)\mathcal{Y}_{LM}(\theta,\phi) \right]$$

$$= \sum_{LM} \left[\sum_{\alpha\beta} n^{(r)}_{\alpha\beta}(r) \, C(\alpha,\beta,L,M) \right] \mathcal{Y}_{LM}(\theta,\phi)$$

Clebsch-Gordon expansion

$$\langle \alpha | V^A_{\text{XC}} | \beta \rangle \qquad \langle \alpha | V^A_{\text{H}} | \beta \rangle \qquad \text{integrated numerically on spherical grids}$$

Radial : Gauss-Chebyshev quadrature
Angular : Lebedev quadrature

GAPW Input

&DFT

...

```
&QS
  EXTRAPOLATION ASPC
  EXTRAPOLATION_ORDER 4
  EPS_DEFAULT 1.0E-12
  METHOD GAPW
  EPS_DEFAULT 1.0E-12
  QUADRATURE   GC_LOG
  EPSFIT       1.E-4
  EPSISO       1.0E-12
  EPSRHO0      1.E-8
  LMAXN0       4
  LMAXN1       6
  ALPHA0_H     10
&END QS
```

&END DFT

&SUBSYS

...

```
&KIND O
  BASIS_SET DZVP-MOLOPT-GTH-q6
  POTENTIAL GTH-BLYP-q6
  LEBEDEV_GRID 80
  RADIAL_GRID 200
&END KIND
&KIND O1
  ELEMENT O
#  BASIS_SET 6-311++G2d2p
  BASIS_SET 6-311G**
  POTENTIAL ALL
  LEBEDEV_GRID 80
  RADIAL_GRID 200
&END KIND
```

&END SUBSYS

All-electron Calculations:CP2K vs G03
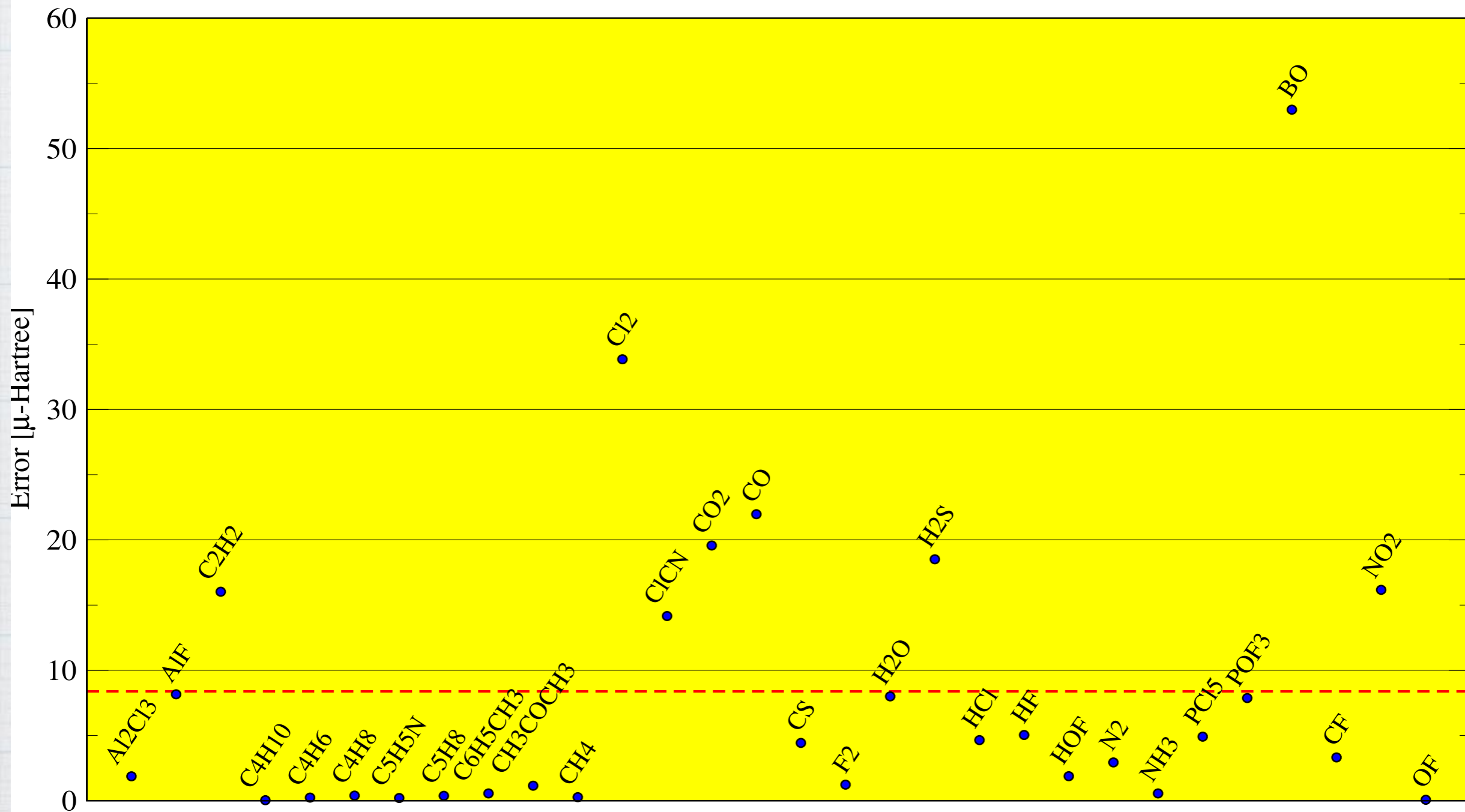
Energy Functional Minimisation

$$C^* = \arg\min_C \left\{ E(C) \; : \; C^T S C = 1 \right\}$$

- Standard: Diagonalisation + mixing (DIIS, Pulay, J. Comput. Chem. 3, 556,(1982); iterative diag. Kresse G. et al, PRB, 54(16), 11169, (1996))

- Direct optimisation: Orbital rotations (maximally localised Wannier functions)

- Linear scaling methods: Efficiency depends on sparsity of P (S. Goedecker, Rev. Mod. Phys. 71, 1085,(1999))

$$\mathbf{P}(\mathbf{r}, \mathbf{r}') \propto e^{-c\sqrt{E_{\mathrm{gap}}}|\mathbf{r}-\mathbf{r}'|}$$

$$\mathbf{P}_{\mu\nu} = \sum_{pq} \mathbf{S}_{\mu p}^{-1} \mathbf{S}_{q\nu}^{-1} \iint \varphi_p(\mathbf{r}) \mathbf{P}(\mathbf{r}, \mathbf{r}\prime) \varphi_q(\mathbf{r}') \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'$$
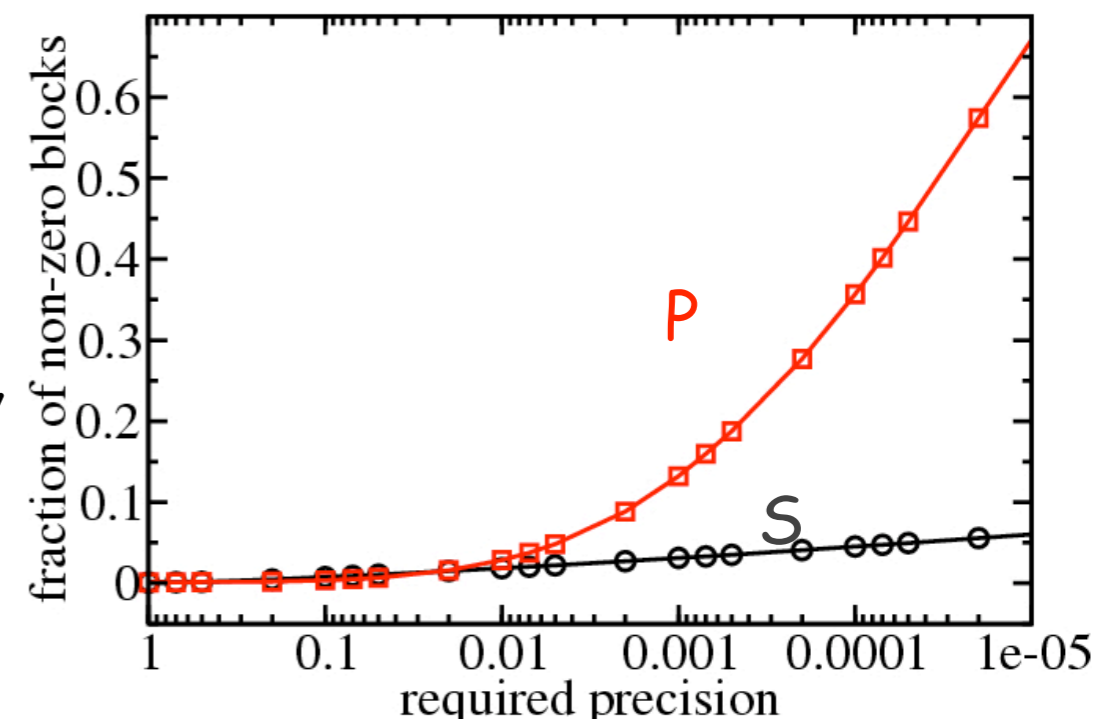
Refined preconditioner, most effective during MD of large systems with well conditioned basis sets
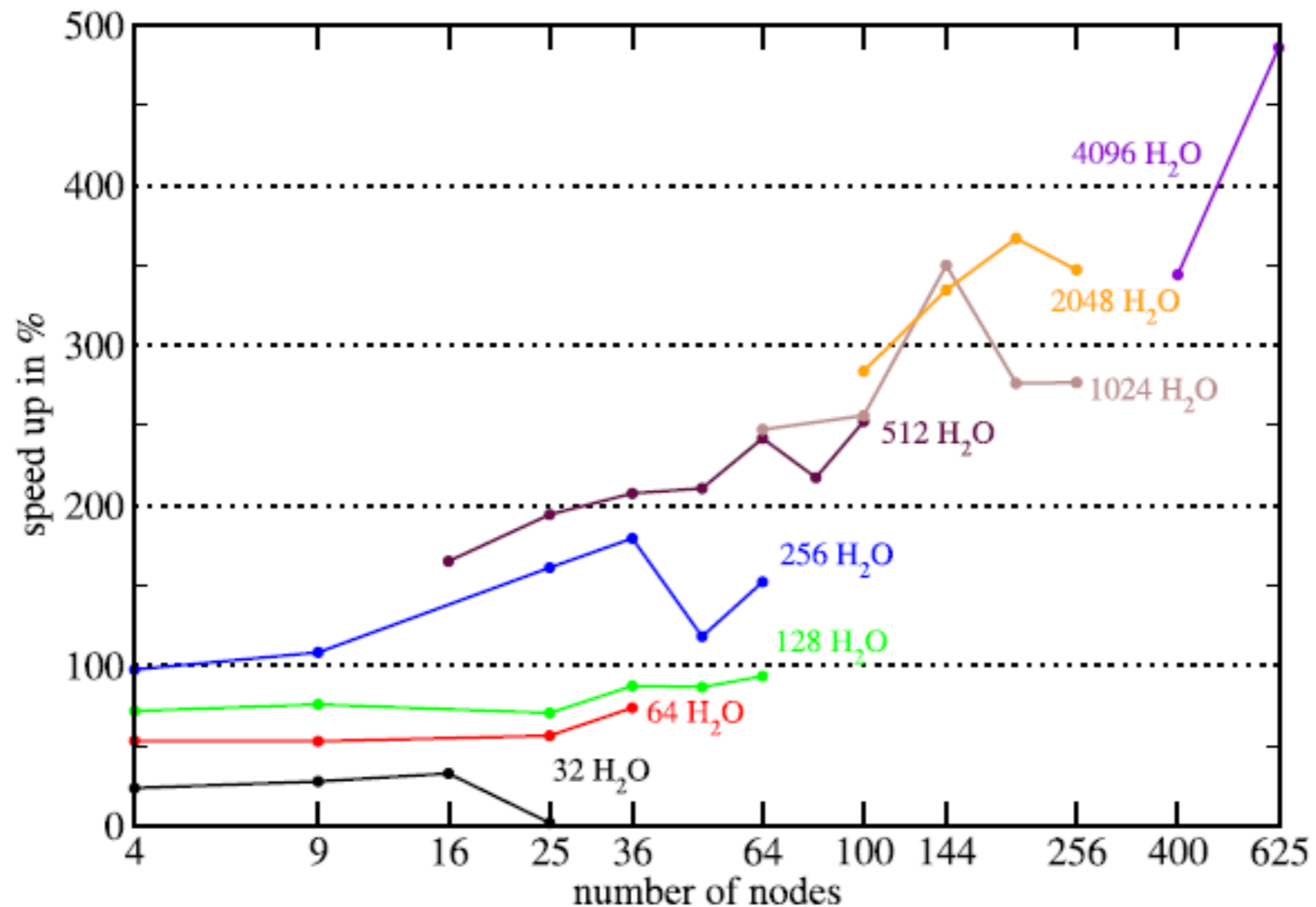
on Daint (XC30)

3844 nodes

(8 cores + 1 GPU)

Schiffmann, VandeVondele, JCP 142 244117 (2015)

OT input

```
&SCF
  EPS_SCF      1.01E-07
  &OUTER_SCF
    MAX_SCF 20
    EPS_SCF      1.01E-07
  &END OUTER_SCF
  SCF_GUESS RESTART
  MAX_SCF 20
  &OT
    MINIMIZER DIIS
    PRECONDITIONER FULL_ALL
  &END OT
&END SCF
```

Metallic Electronic Structure

$$E_{\text{band}} = \sum_n \frac{1}{\Omega_{\text{BZ}}} \int_{\text{BZ}} \varepsilon_{n\mathbf{k}} \Theta(\varepsilon_{n\mathbf{k}} - E_f) d^3\mathbf{k} \quad \rightarrow \quad \sum_n \sum_k w_{\mathbf{k}} \varepsilon_{n\mathbf{k}} \Theta(\varepsilon_{n\mathbf{k}} - E_f) d^3\mathbf{k}$$

Rh band structure
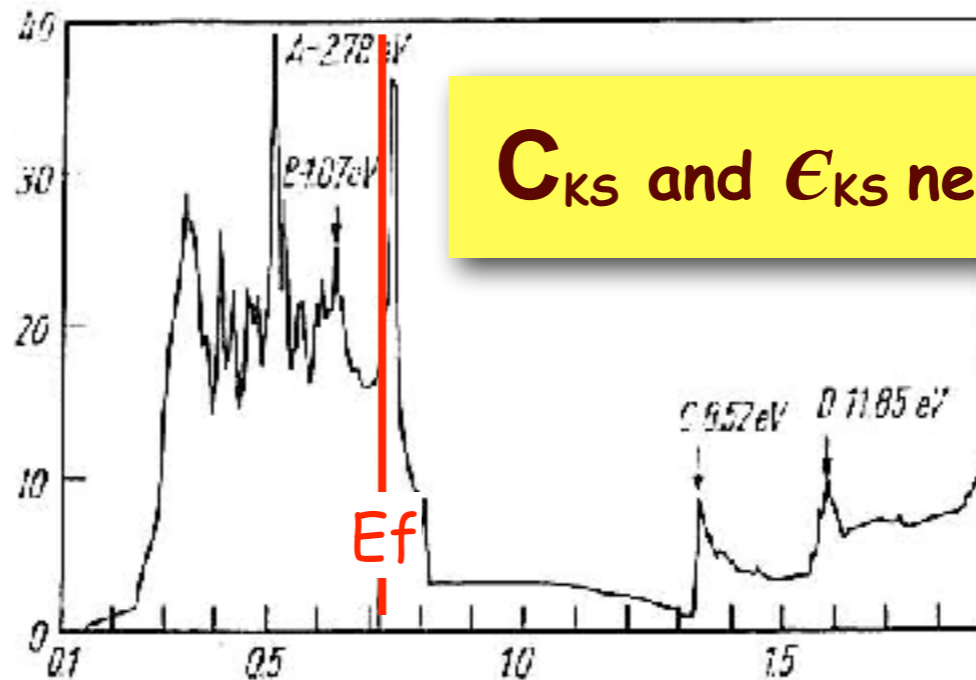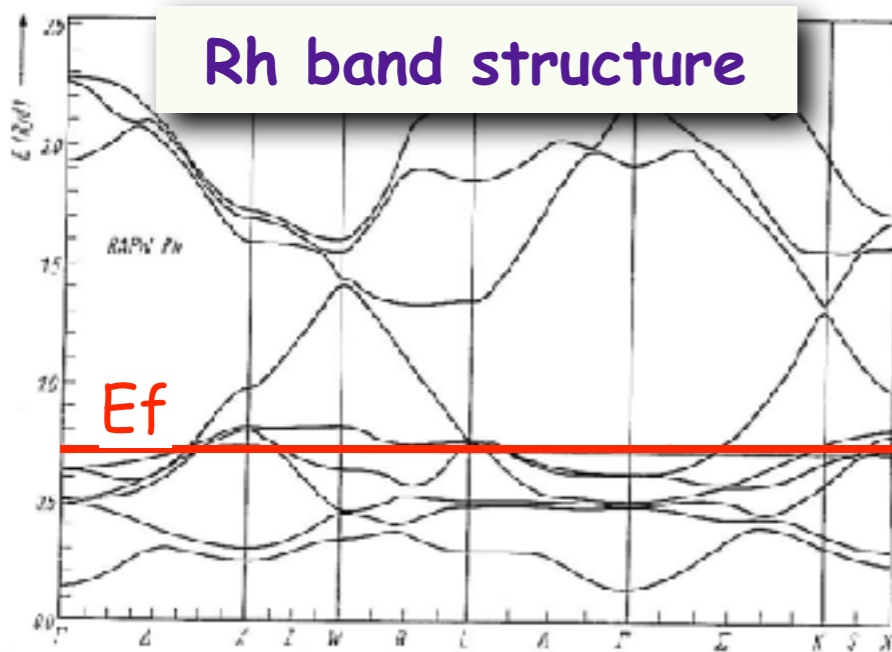
C_{KS} and ϵ_{KS} needed

charge sloshing and exceedingly slow convergence

✳ Wavefunction must be orthogonal to unoccupied bands close in energy

✳ Discontinuous occupancies generate instability (large variations in n(r))

✳ Integration over k-points and iterative diagonalisation schemes

Smearing

Step function replaced by smooth-varying function (incl. unocc)

$$f_n\left(\frac{\varepsilon_n - E_f}{kT}\right) = \frac{1}{\exp\left(\frac{\varepsilon_n - E_f}{k_\mathrm{B}T}\right) + 1}$$

Fermi-Dirac

E no longer variational with respect to fn
Mermin functional: minimise the free energy

$$F(T) = E - \sum_n k_B T S(f_n) \qquad S(f_n) = -[f_n \ln f_n + (1 - f_n)\ln(1 - f_n)]$$

Any smooth operator that allows accurate S(f$_n$) to recover the T=0 result

Mixing in G-space

Charge sloshing instabilities: small G, degenerate states, long-range n(r) oscillations

$$n^{\text{new}} = \sum_i \alpha_i n_i^{\text{inp}}$$

Residual $\quad \mathcal{R}[n^{\text{inp}}] = n^{\text{out}}[n^{\text{inp}}] - n^{\text{inp}}$

$$\left[\mathbf{J}^{-1}\right]^m |\Delta \mathcal{R}_m\rangle = -|\Delta n_m\rangle \quad \text{minimise the residual}$$

Kerker : damping oscillations at small G $\qquad \left[\mathbf{J}^{-1}\right]^1 = w(G) = \dfrac{|G|^2}{|G|^2 + \beta}$

Trial density mixed with previous densities and residuals

$$n_{m+1}^{\text{inp}} = n_m^{\text{inp}} + \mathbf{G}^I \mathcal{R}[n_m^{\text{inp}}] + \sum_{i=1}^{m-1} \alpha_i \left(\Delta n_i + \mathbf{G}^I \Delta \mathcal{R}_i\right)$$

Iterative Improvement of the the n(r)

Input density matrix

$$\mathbf{P}^{\mathrm{in}}_{\alpha\beta} \to n^{\mathrm{in}}(\mathbf{r})$$

Update of KS Hamiltonian

diagonalization plus iterative refinement $\quad \mathbf{C}_n \; \varepsilon_n$

Calculation of Fermi energy and occupations $E_f \; f_n$

New density matrix

$$\mathbf{P}^{\mathrm{out}}_{\alpha\beta} \to n^{\mathrm{out}}(\mathbf{r})$$

Check convergence

$$\max\left\{\mathbf{P}^{\mathrm{out}}_{\alpha\beta} - \mathbf{P}^{\mathrm{in}}_{\alpha\beta}\right\}$$

Density mixing

$$n^{\mathrm{out}} \; n^{\mathrm{in}} \; n^{\mathrm{h}} \; \ldots \to n^{\mathrm{new}}$$

$$\mathbf{P}^{\mathrm{out}}_{\alpha\beta} \; n^{\mathrm{new}}(\mathbf{r})$$

density
Build KS
other
Eigensolver
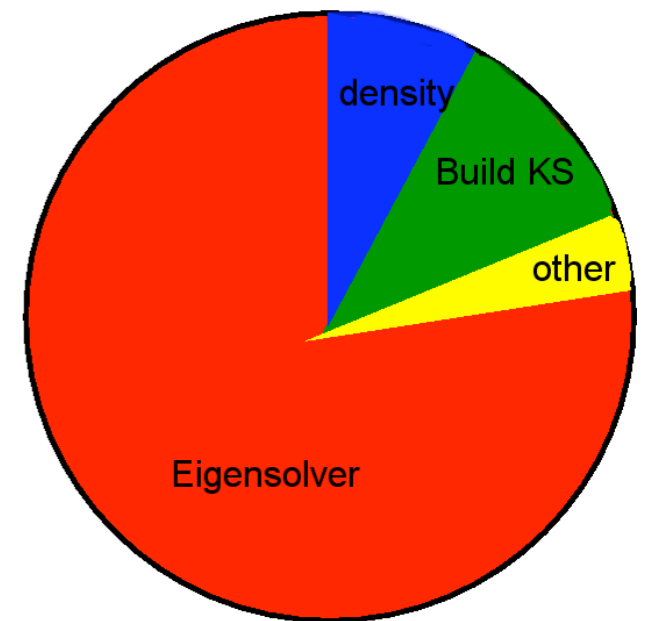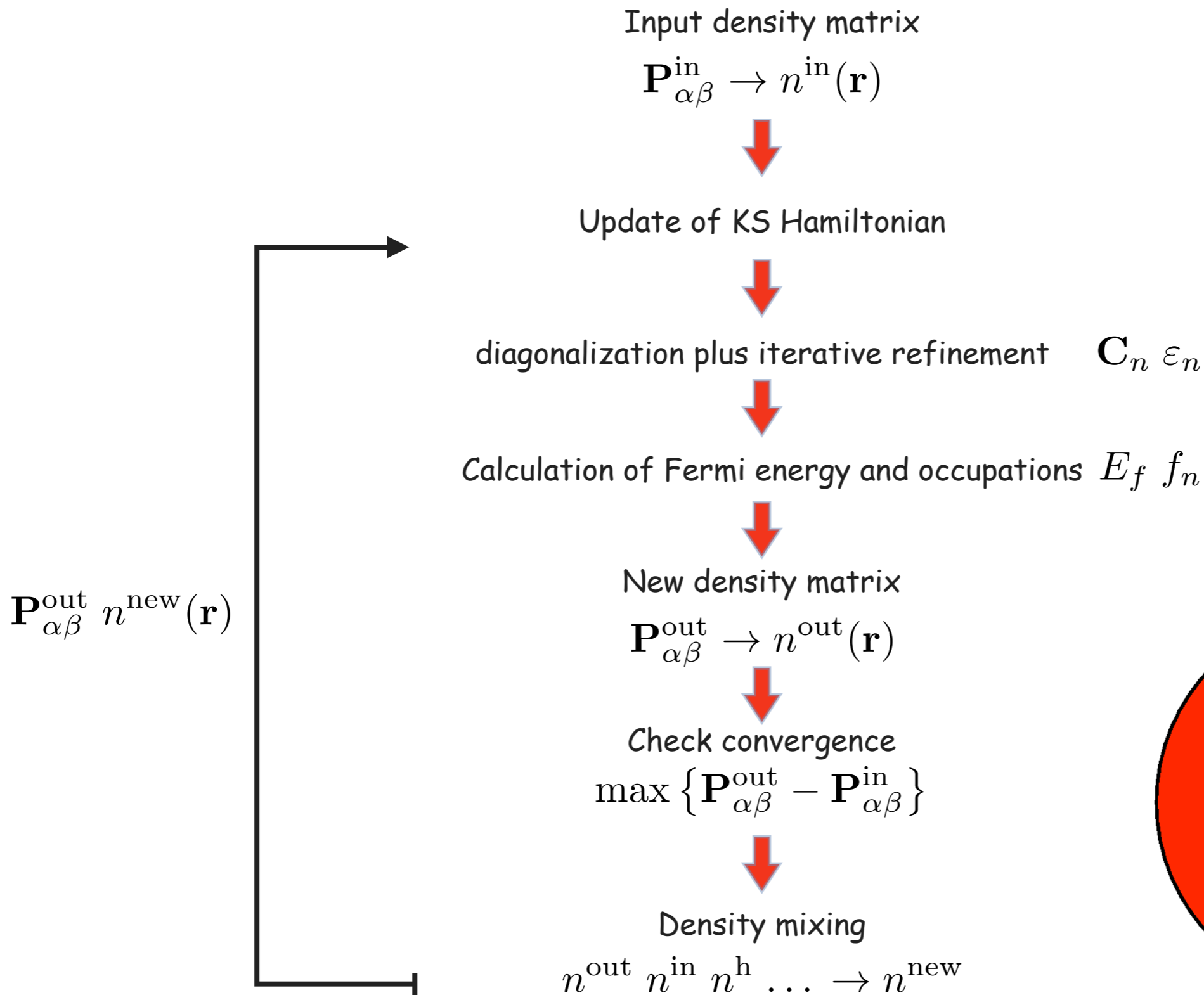
Rhodium: Bulk and Surface

Bulk: 4x4x4

Surface: 6x6 7 layers

Basis	PP	a_0 [Å]	B[GPa]	E_s[eV/Å^2]	W_f[eV]
3s2p2df	17e	3.80	258.3	0.186	5.11
2s2p2df	9e	3.83	242.6	0.172	5.14
2sp2d	9e	3.85	230.2	0.167	5.20
spd	9e	3.87	224.4	0.164	5.15

Rh(111) d-projected LDOS

Q17 — DZVP

Q9 — DZVP, SZVP, SZV

$E-Ef$ [eV]

Diaz, et al. Theo Chem Acc (2013).

ScaLAPACK for diagonlisation

$$A \longrightarrow T \longrightarrow (\lambda, q_T) \longrightarrow q_A$$

reduction to tridiagonal form   compute eigenvalues and –vectors of T   transform eigenvectors

1003 atoms
3410 MOS
27069 BSf

Polyalanine peptide
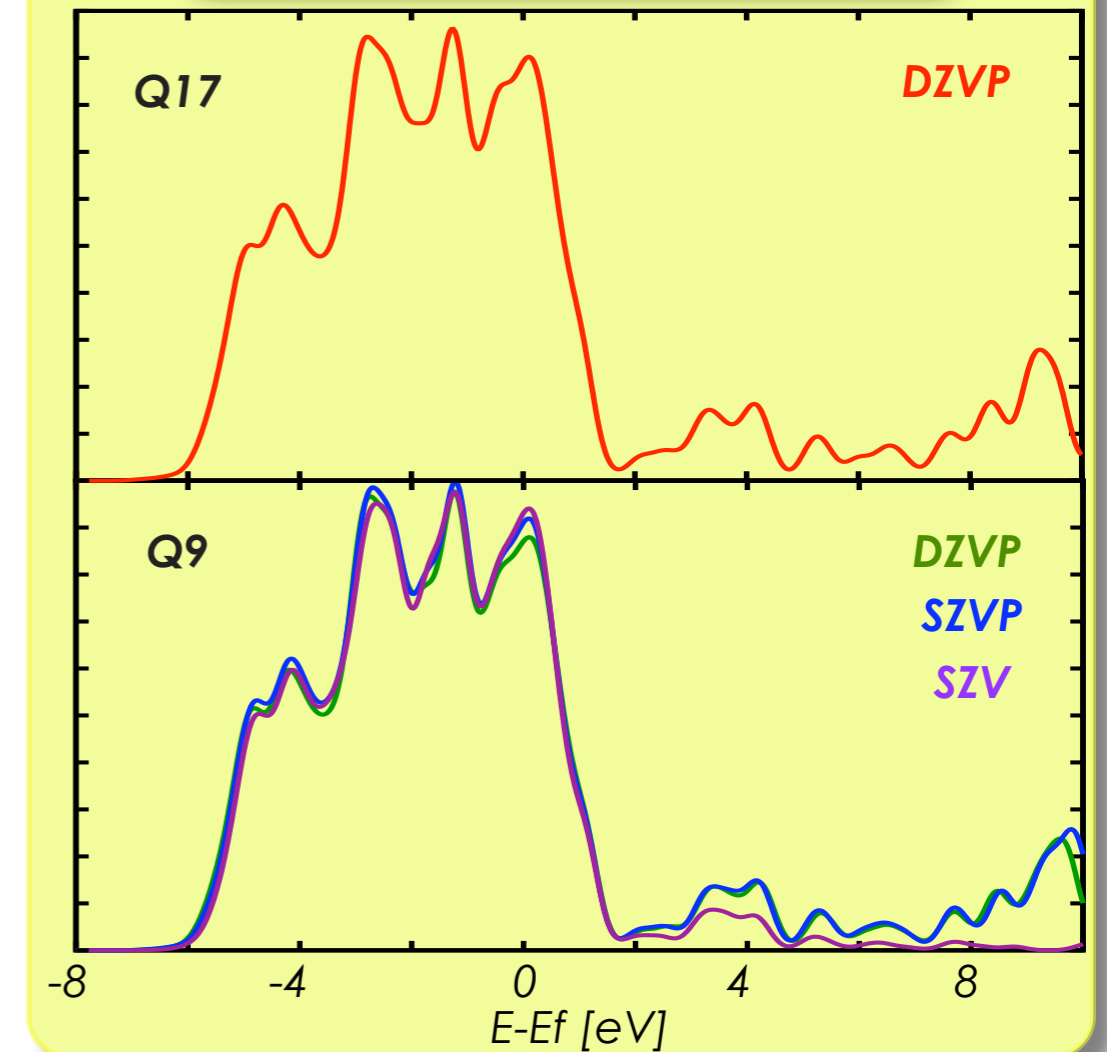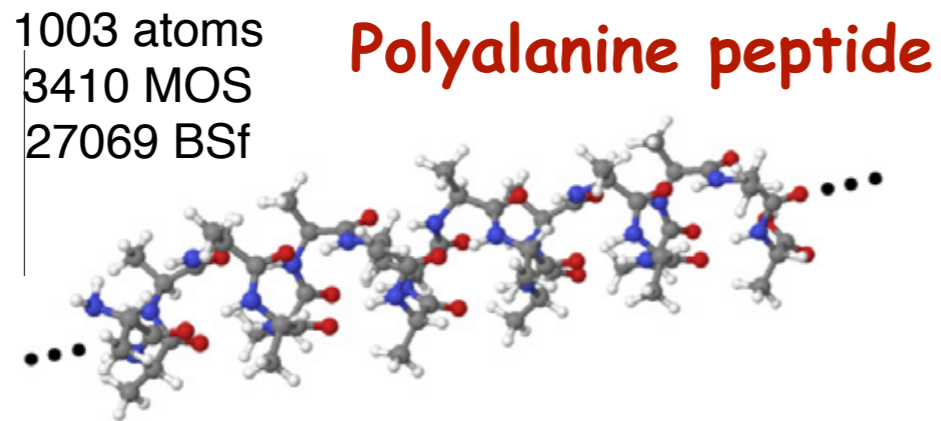
pdsyevd (ESSL) on IBM BGP
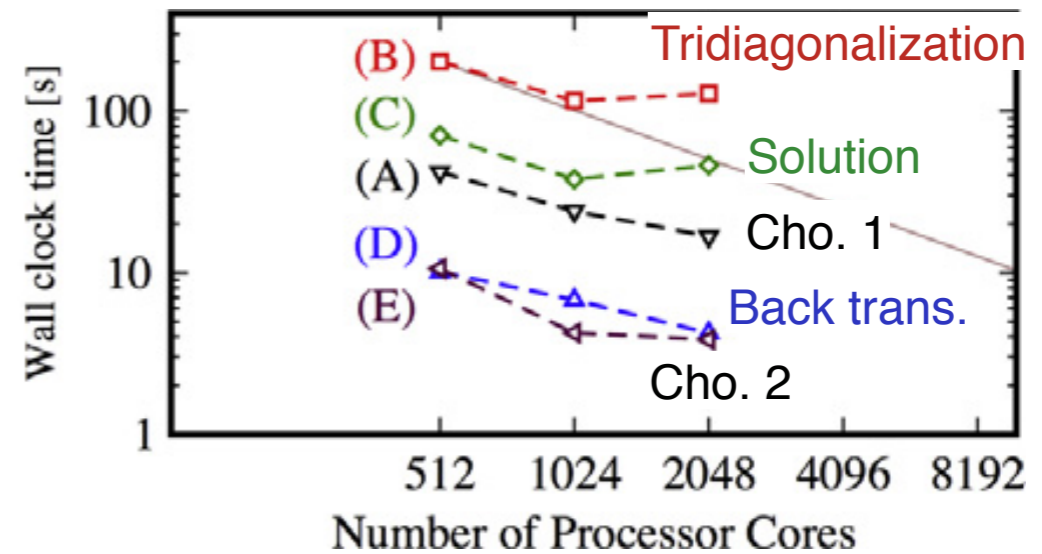
576 Cu, nao=14400, Nelect.=6336, k of eigen-pairs=3768

nprocs	syevd	syevr	Cholesky
32	106 (49%)	72 (40%)	38 (21%)
64	69 (46%)	48 (37%)	34 (26%)
128	41 (41%)	29 (34%)	23 (28%)
256	35 (41%)	26 (34%)	24 (32%)

Syevd: D&C
Syevr: MRRR

time × SCF, on CRAY XE6

>70% in eigenvalue solver

poor scaling

29

ELPA (http://elpa.rzg.mpg.de)

Improved efficiency by a two-step transformation and back transformation

better scaling
complex
mainly BLAS 3

B

better scaling
complex
"cheap"

higher per−node perf
better scaling
complex
partial

q_B

complex
partial

band form by
blocked
orthogonal
transformations

A → **T** → (λ, q_T) → q_A

reduction to
tridiagonal form

compute
eigenvalues and
−vectors of T

transform
eigenvectors
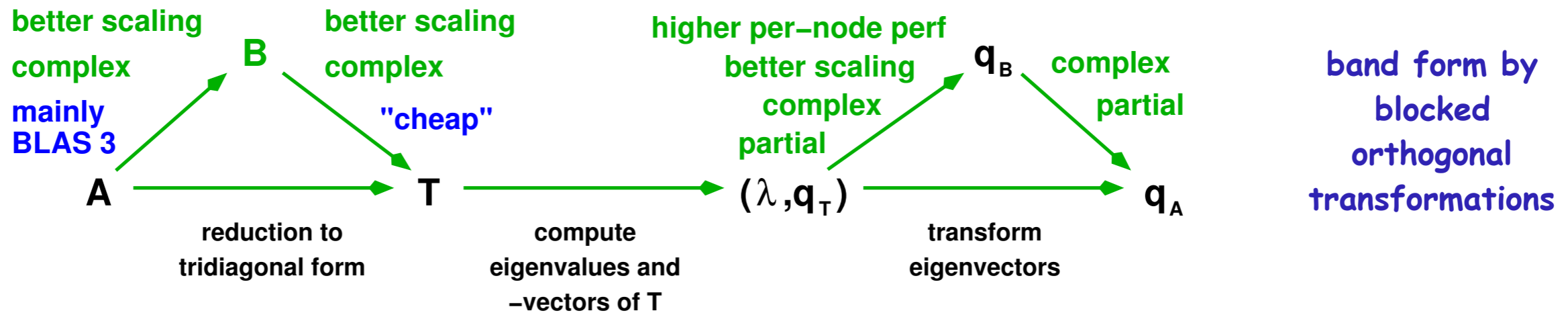
N atom= 2116; Nel = 16928;
nmo = 10964; nao = 31740

CRAY XE6

N atom= 480; Nel = 6000;
nmo = 7400; nao = 14240

BG-P

All - syevd
All - syevr
All - ELPA
Diag - syevd
Diag - syevr
Diag - ELPA

Total time for 12 SCF
1000

Number of cores
500 1000 1500 2000 2500 3000

All - syevd
All - ELPA
Diag - syevd
Diag - ELPA

10000
1000

500 1000 1500 2000 2500 3000 3500 4000 4500
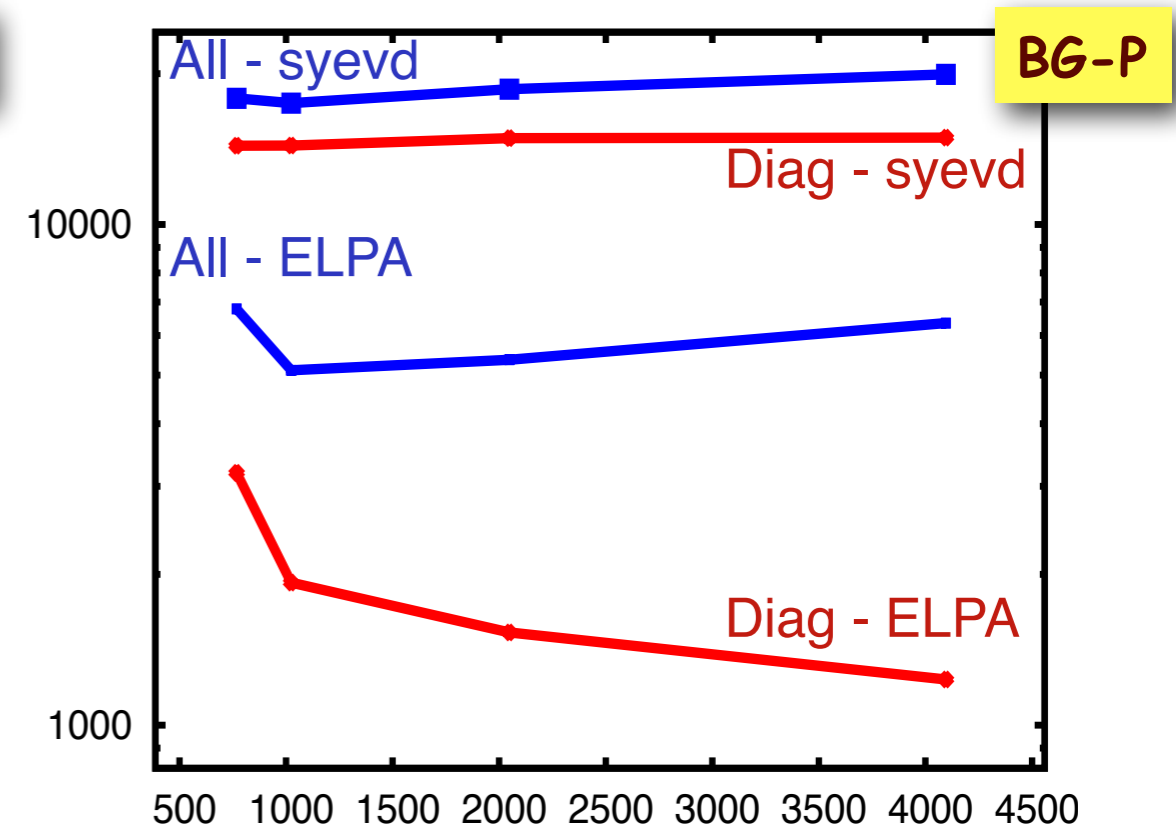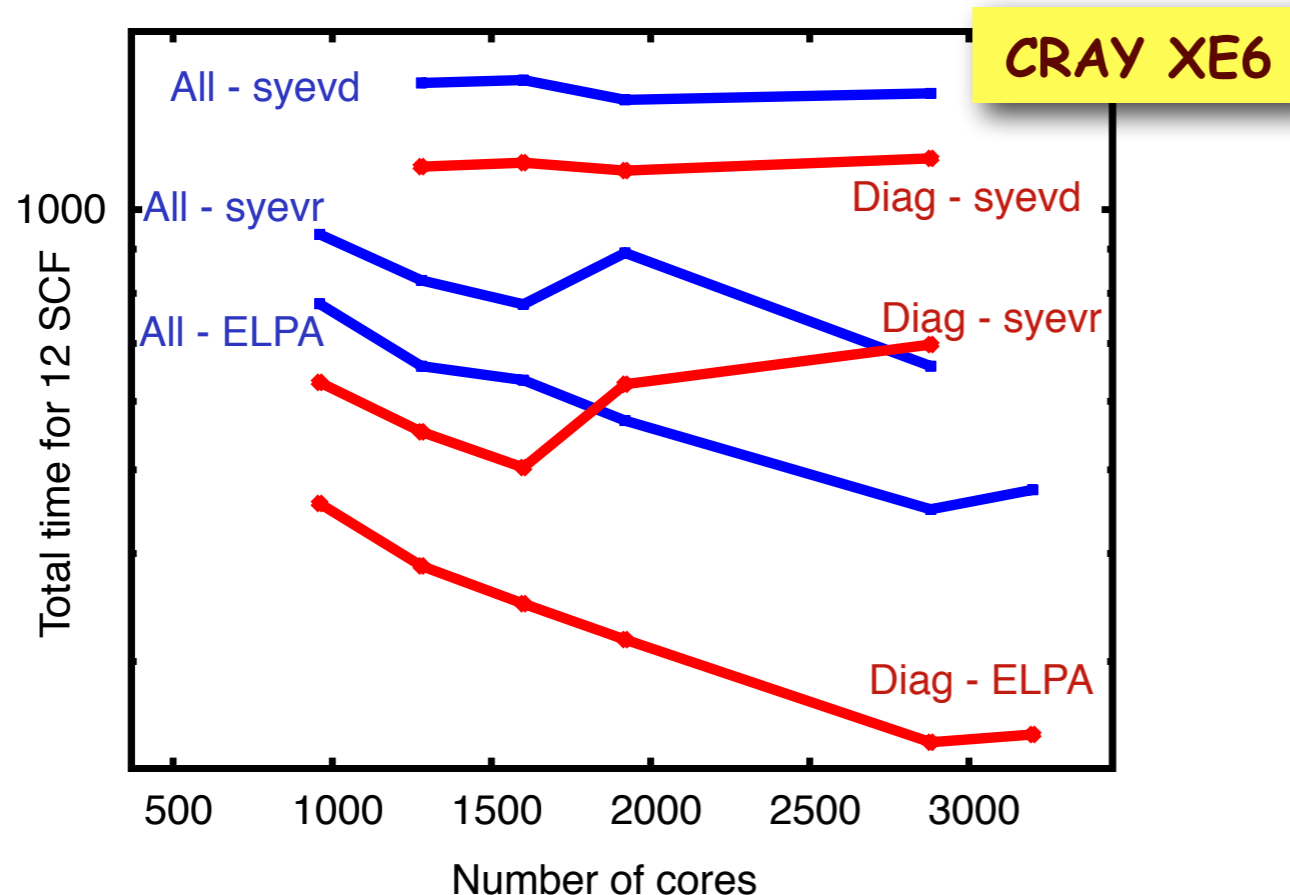
Large metallic systems

hBN/Rh(111) Nanomesh
13x13 hBN on 12x12 Rh slab
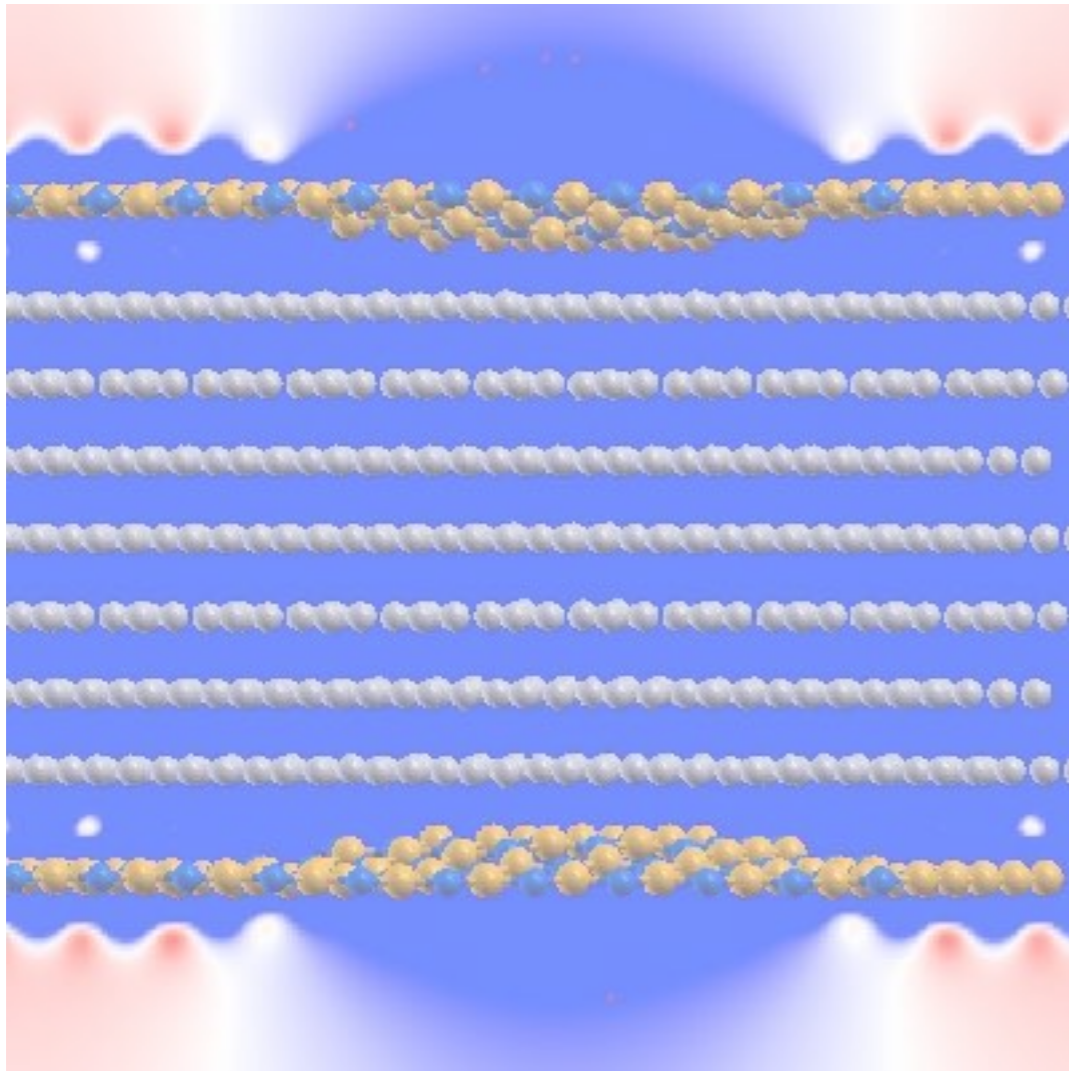
graph./Ru(0001) Superstructure
25x25 g on 23x23 Ru
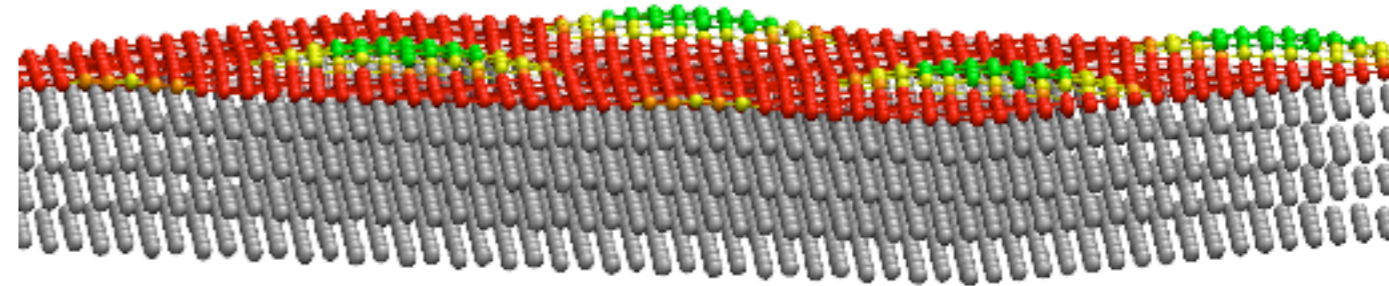
2116 Ru atoms (8 valence el.) + 1250 C atoms,
Nel=21928, Nao=47990 ;

~ several days per structure optimisation

Slab 12x12 Rh(111) slab, a_0=3.801 Å, 1 layer hBN 13x13
4L: 576Rh + 169BN: Nao=19370 ; Nel=11144
7L: 1008Rh + 338BN: Nao=34996 ; Nel=19840

Structure opt. > 300 iterations => 1÷2 weeks on 512 cores

Iannuzzi et al., PRB (2013)
Cun, Iannuzzi et al, Nano Letter (2013)

```
&SCF
  SCF_GUESS ATOMIC
  MAX_SCF   50
  EPS_SCF 1.0e-7
  EPS_DIIS 1.0e-7
 &SMEAR
    METHOD FERMI_DIRAC
    ELECTRONIC_TEMPERATURE   500.
  &END SMEAR
  &MIXING
      METHOD BROYDEN_MIXING
      ALPHA   0.6
      BETA    1.0
      NBROYDEN 15
  &END MIXING
  ADDED_MOS   20 20
&END SCF
```

```
&XC
  &XC_FUNCTIONAL PBE
  &END
  &vdW_POTENTIAL
    DISPERSION_FUNCTIONAL PAIR_POTENTIAL
    &PAIR_POTENTIAL
        TYPE DFTD3
        PARAMETER_FILE_NAME dftd3.dat
        REFERENCE_FUNCTIONAL PBE
    &END PAIR_POTENTIAL
  &END vdW_POTENTIAL
&END XC
```

Experiment	2.46	1.42	2.7059	9.09		2.18	
12on11 DZ PBE D3	2.469	1.425	2.681	7.907	9.16115	2.18	3.69
12on11 DZ PBE rVV10	2.468	1.425	2.677	7.807	9.19794	2.18	3.61
12on11 DZ BEEF	2.456	1.418	2.703	9.138	9.63944	2.23	3.77
12on11 DZ optB88 DRSLL	2.467	1.424	2.690	8.290	9.23473	2.24	3.69
12on11 DZ optPBE rVV10	2.468	1.425	2.668	7.496	9.19794	2.16	3.55
12on11 TZ PBE rVV10	2.468	1.425	2.677	7.807	9.19794	2.18	3.61
25on23 DZ PBE rVV10	2.468	1.425	2.677	7.807	9.19794	2.18	3.55
25on23 DZ revPBE D2	2.471	1.426	2.672	7.52	9.08756	2.21	3.22

Method	h_{min} (Å)	Δh (Å)
LEEM[5]	1.5 ± 0.1	-
LEED[18]	2.1 ± 0.2	1.5 ± 0.2
SXRD[21]	-	0.82 ± 0.15
HAS[19]	-	0.17 ± 0.03

Issues: **binding distance**

corrugation

height distribution
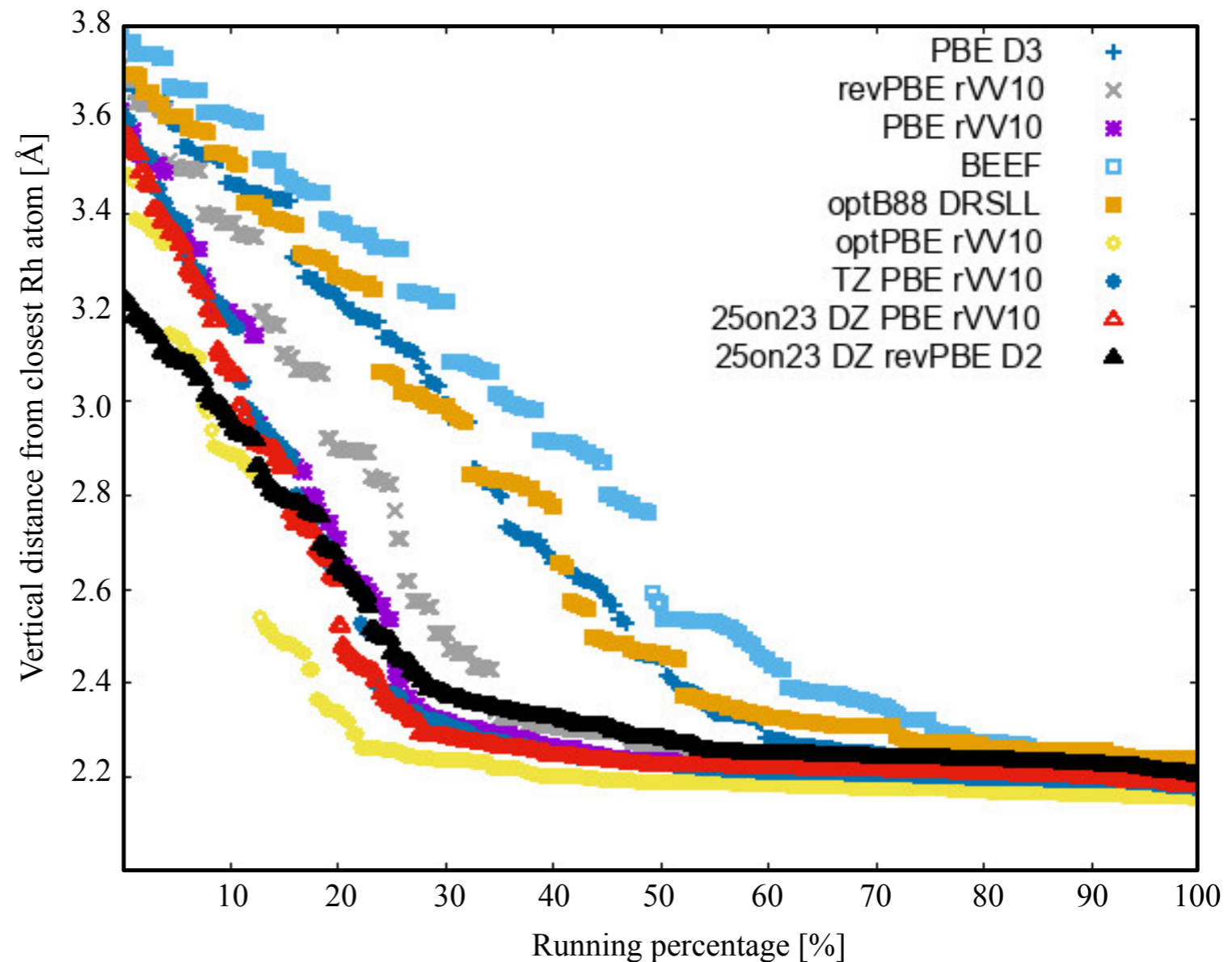
Gaussian-fitted line shape
Two distinguished C1s components
valley/hill boundary not clearly distinguished

PBE+rVV10

C 1s

hv = 330 eV
surf. sensitive

Photoemission Intensity [a. u.]

Ru 3d$_{5/2}$

Ru 3d$_{3/2}$

C2

C1

Binding Energy [eV]
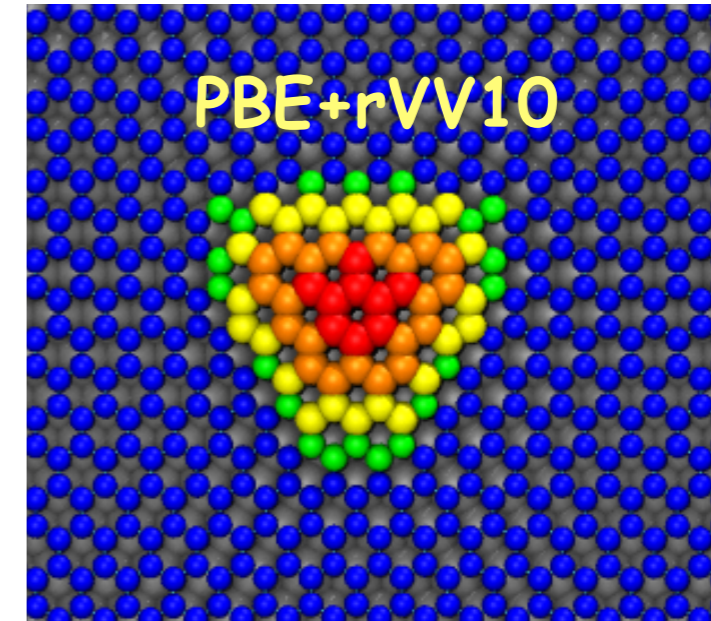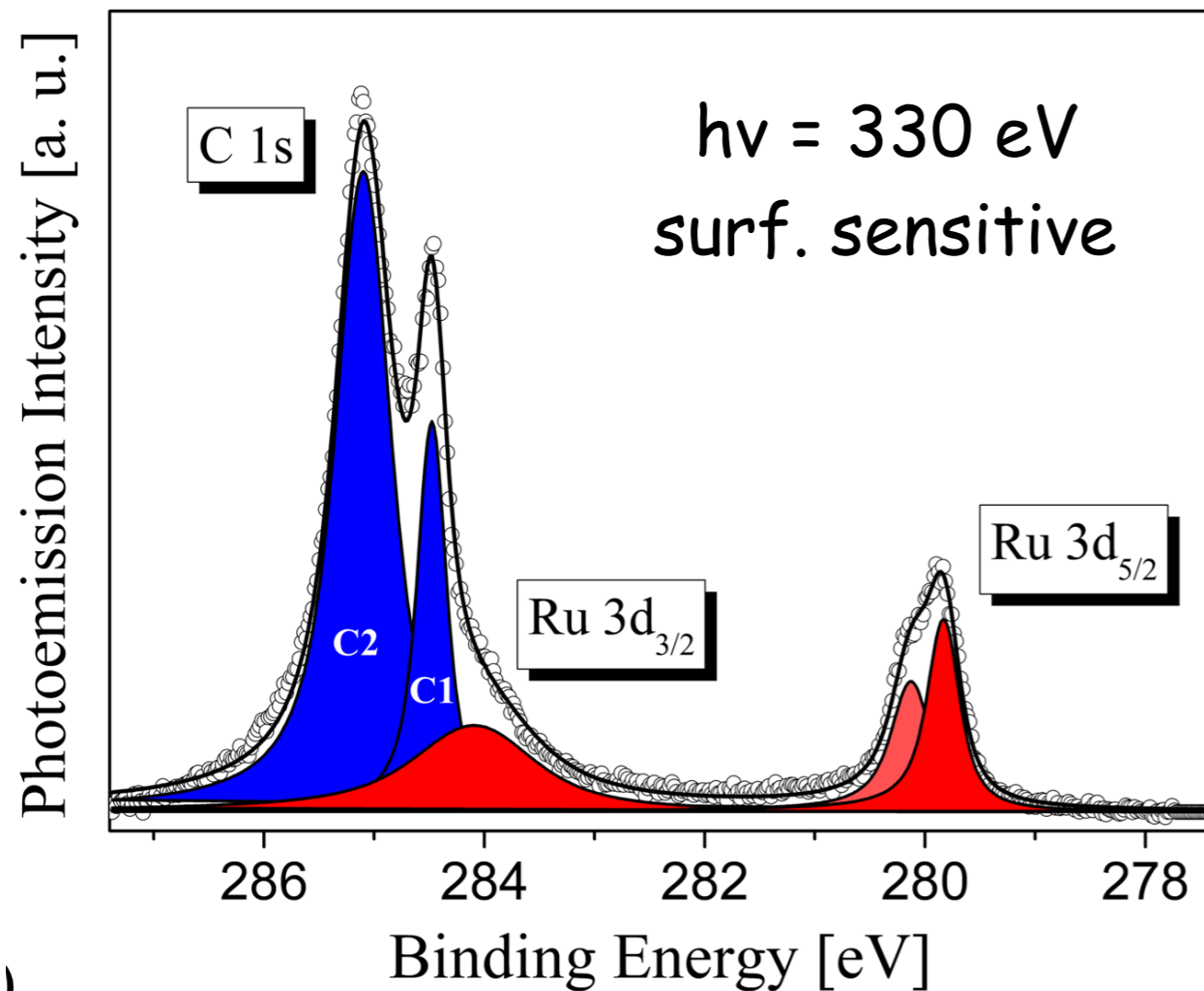
continuous distribution valley-to-hill

Local DOS [a. u.]

3.40 Å < h < 3.60 Å
3.10 Å < h < 3.40 Å
2.70 Å < h < 3.10 Å
2.40 Å < h < 2.70 Å
h < 2.40 Å

Binding Energy [eV]
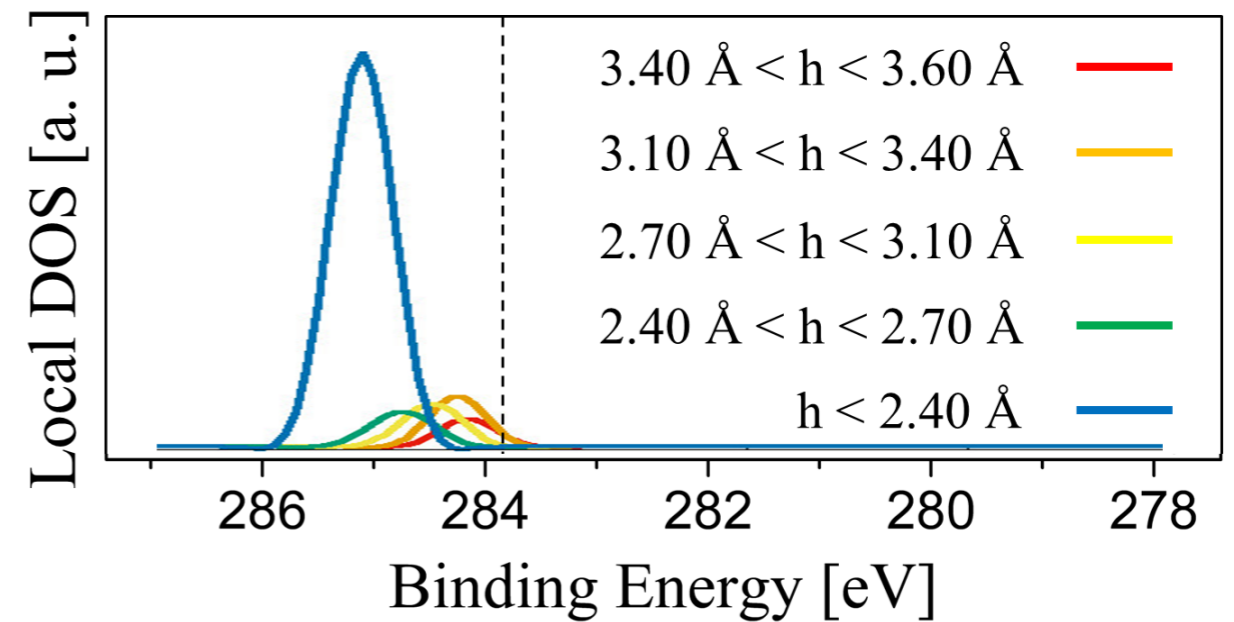
Free standing graphene @ 283.8 eV

Exploit spatial modulation of XSW field (interference) by scanning through the Bragg condition:
spatial resolution and chemical sensitivity

$$Y(\Omega) = 1 + R + 2C\sqrt{R}\, f_H \cos\left(\nu - 2\pi P_H\right)$$
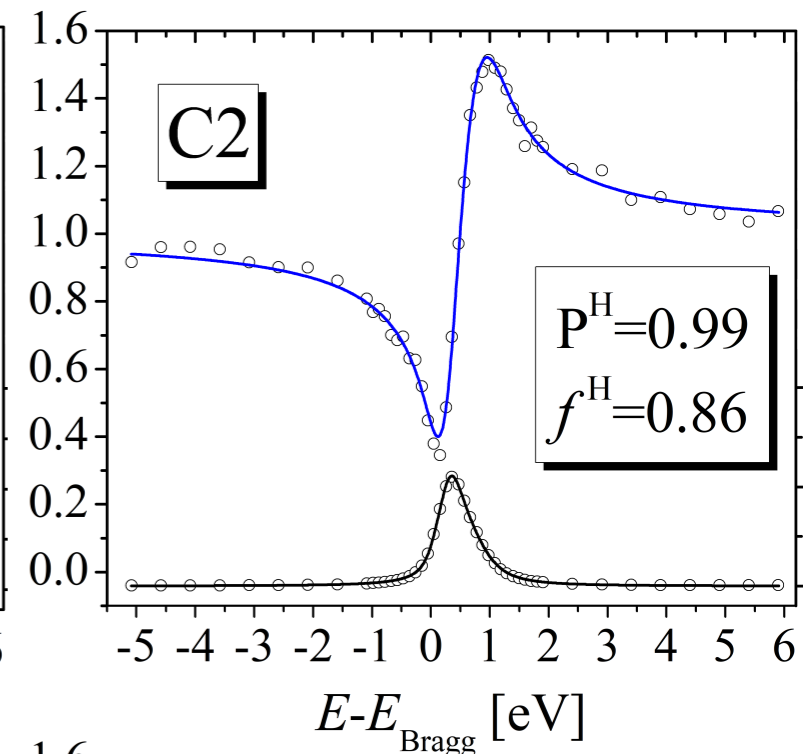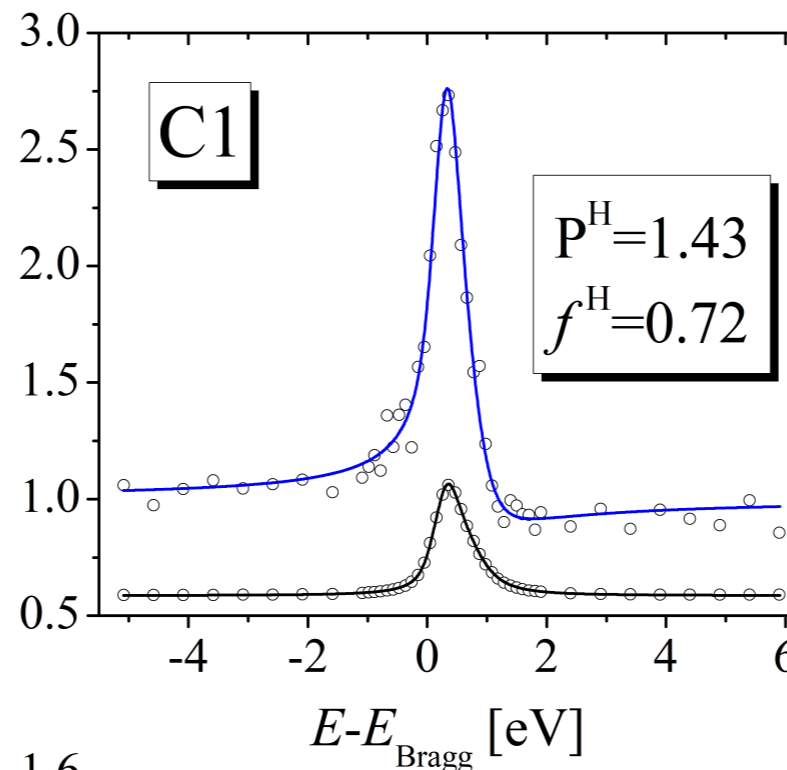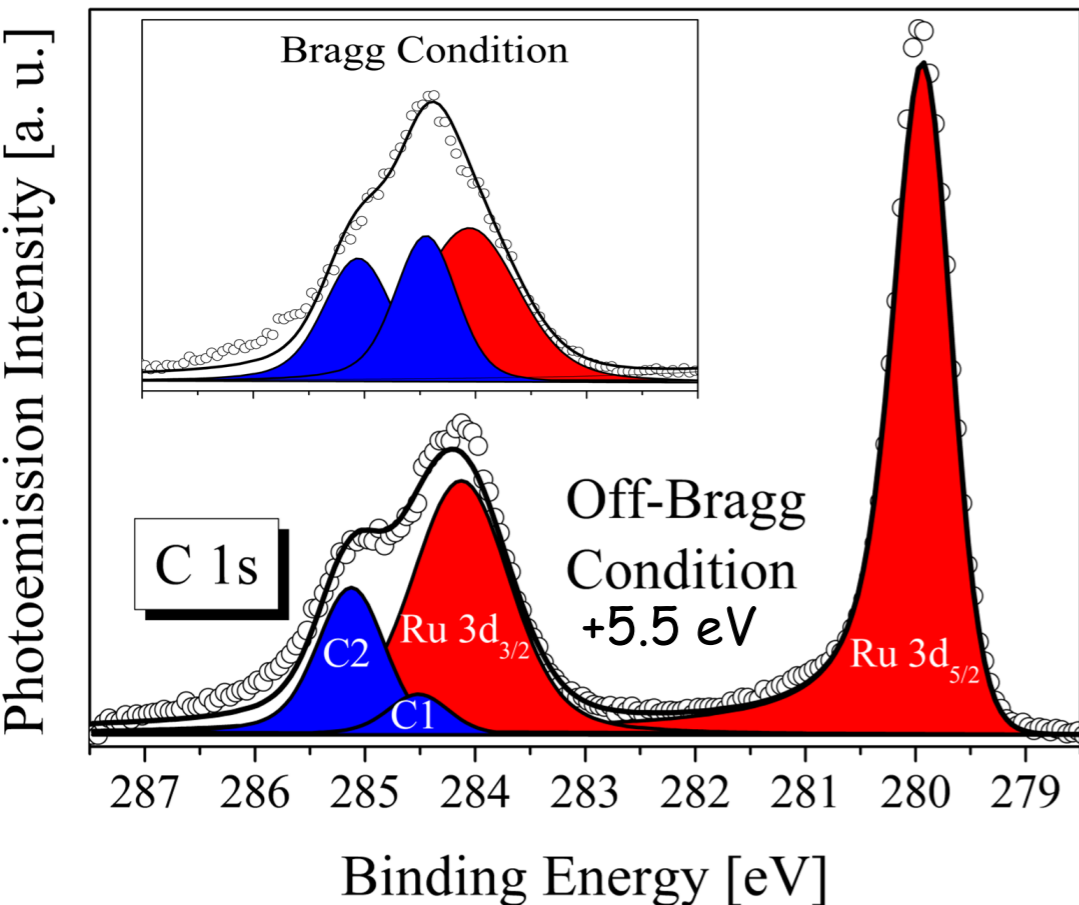
$$\langle h \rangle = P_H \times d_{\text{Ru}(0002)}$$

	valleys				hills		
	P_{C2}^H	f_{C2}^H	h_{valley} (Å)	$h_{\min}$ (Å)	P_{C1}^H	f_{C1}^H	Δh (Å)
XSW	0.99 ± 0.01	0.86 ± 0.02	2.12 ± 0.03		1.43 ± 0.02	0.72 ± 0.02	
DFT	1.01	0.94	2.17	2.06	1.43	0.73	1.47

Silva, Iannuzzi et al., JPC C (2018)

Theoretical Spectroscopy

Computed Spectrum

Experimental Spectrum

Interaction potential V(R_{at})

ok?

Forces F(R_{at})

MD

Energy minimization

?

Conformation { R_{at}}

Xray diffraction: S(q)

$$E_{\mathrm{kin}} = \hbar\nu - E_{\mathrm{bind}} + E_r - \Phi$$
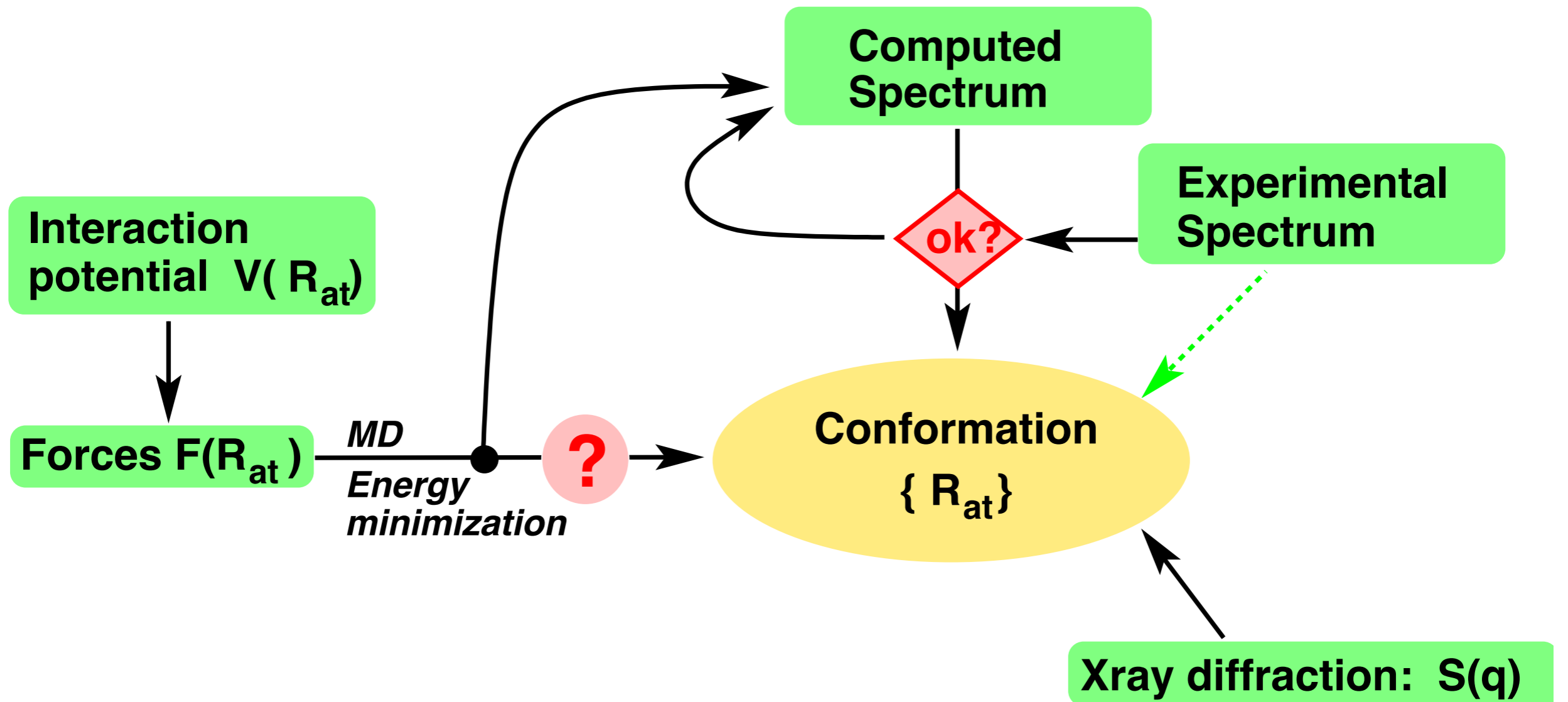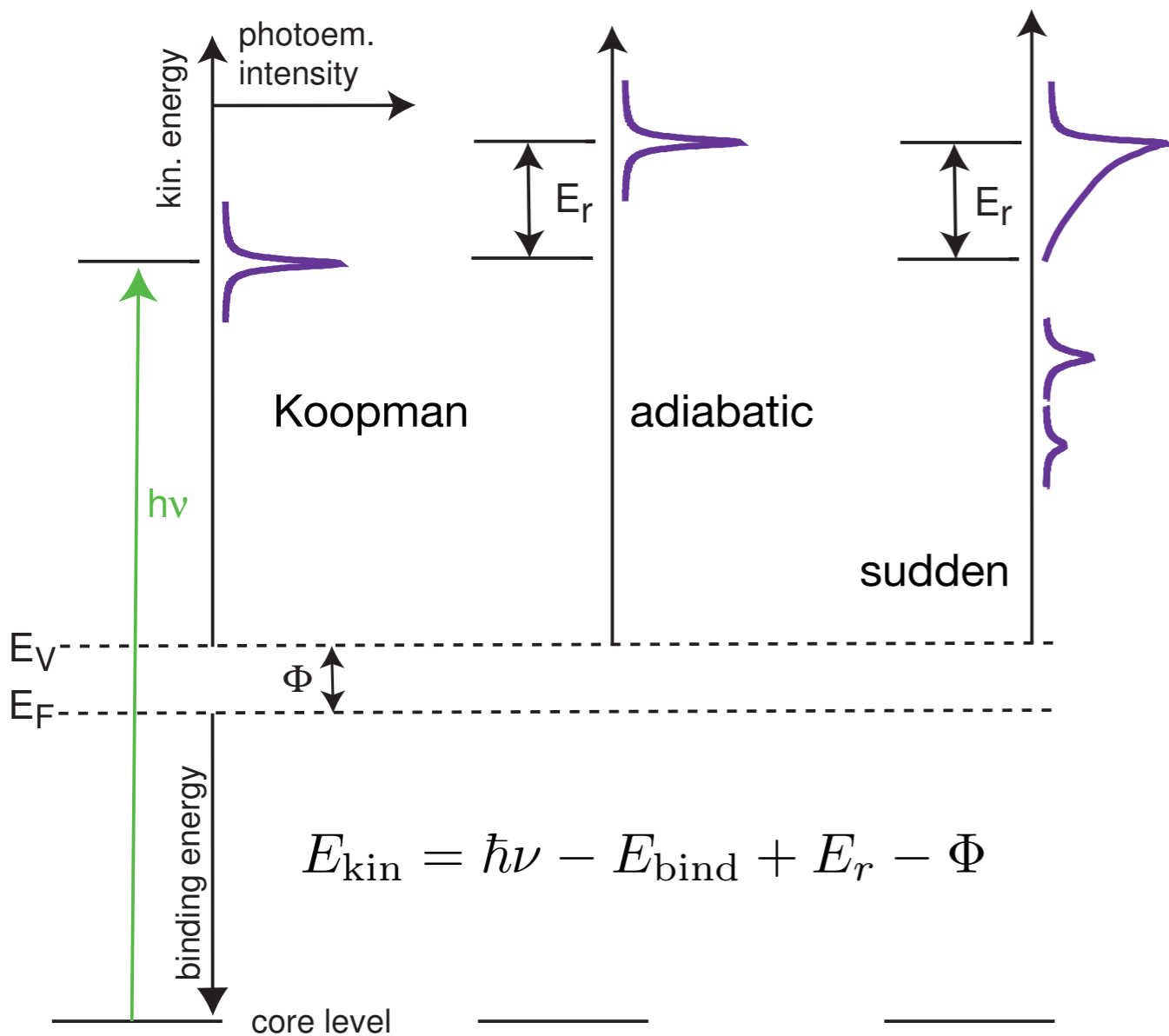
* Consider possible excited states @ higher level of theory

* ΔSCF takes into account the relaxation

* Transition operator method, according to Slater's transition state idea

$$E(\lambda) = \sum_k \lambda^k E_k = E(0) + \lambda E_1 + \frac{1}{2}\lambda^2 E_2 + \ldots$$

Slater Transition State

Emptying the state (occupation): energy change as finite difference

$$\Delta E = E(1) - E(0) = E_1 + E_2 + E_3 + ...$$

$$F(\lambda) = \frac{\partial E}{\partial \lambda} = E_1 + 2\lambda E_2 + 3\lambda^2 E_3 + ...$$

$$-\varepsilon_k = F(\frac{1}{2}) = E_1 + E_2 + \frac{3}{4}E_3 + ... \qquad \text{Error in E3}$$

Janak's theorem: KS energy computed with the modified Hamiltonian

$$\mathcal{H}(f_k = 1/2)$$

X-ray Absorption Fine Structure

✱ Characterization of materials by synchrotron radiation

✱ X-ray spectra connect to the core-electron excited states (role of core hole)

✱ Element specific probe:

- electronic structure in situ

- time resolution (fs)

- no long range order required

- imaging

Interpretation of experiment,
structures refinement (signal assignment),
understanding of physical-chemical properties of materials

✱ Challenging interpretation of the spectra

✱ Central role of theoretical approach

- charge transfer

- nature of bonding

- hybridization

- chemical environment
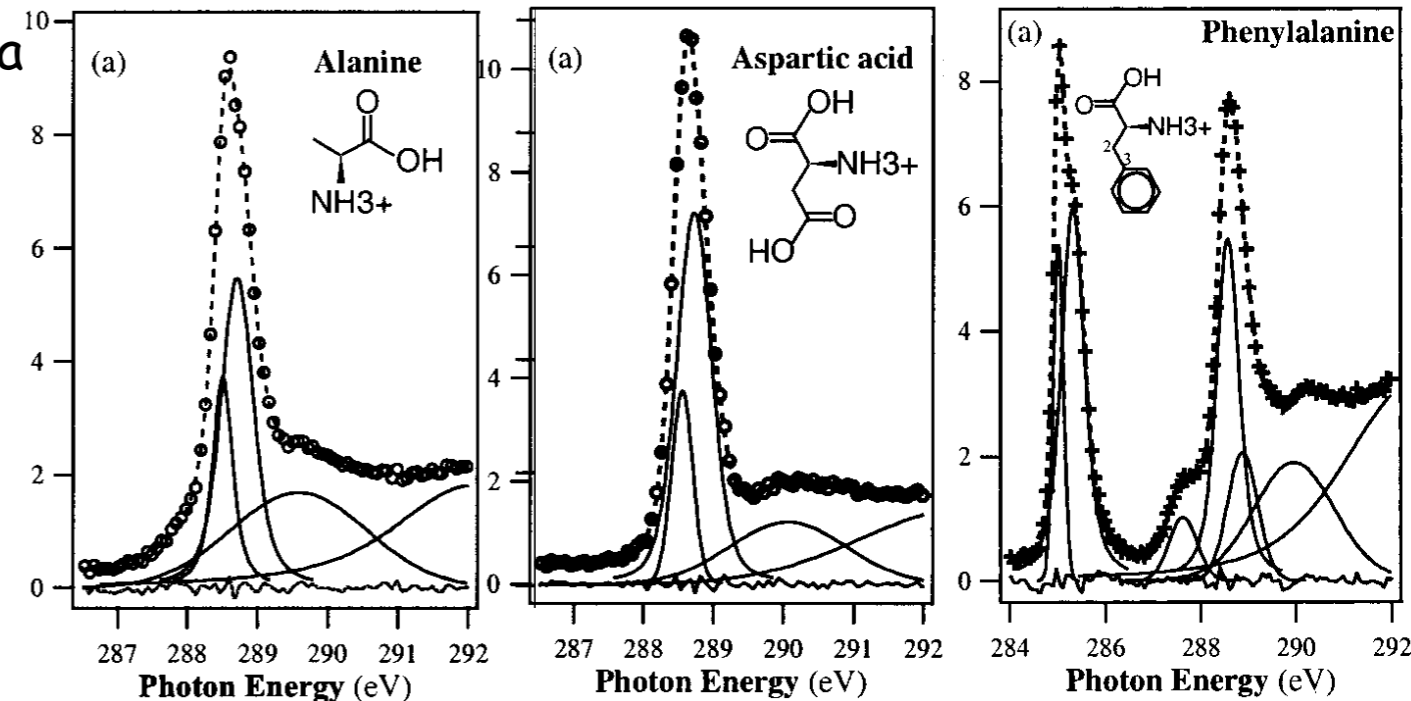
C K-edge for different amino acids

Core Hole Creation and Decay

XES/NEXAFS local probes for electronic and geometric properties

Unoccupied levels, symmetry resolved

One step process
Finale state: core-hole

Instantaneous configuration in dynamic systems

Occupied orbitals

Two step process
Final state : valence-hole

Binding of adsorbed molecules
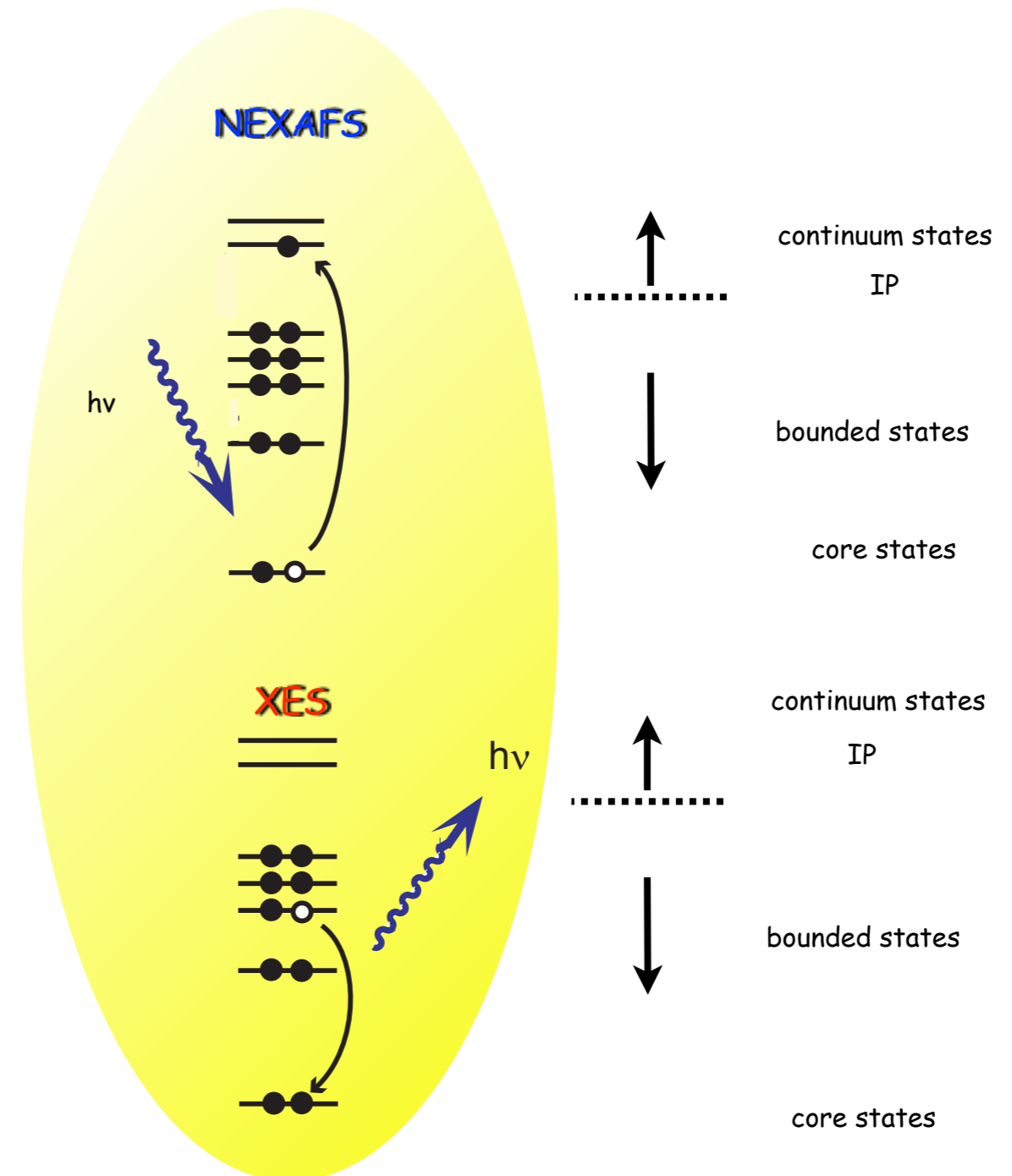
Interaction X-ray with matter

✳ Interaction with an electromagnetic field (incoming radiation)

$$\mathbf{A}(\mathbf{r}, t) = A_0 \ \mathbf{e} \ \cos(\mathbf{k} \cdot \mathbf{r} - \omega t)$$

✳ Linear perturbation term (time dependent perturbations) $V(t) = \dfrac{e}{mc}\mathbf{A} \cdot \mathbf{p}$

✳ Induced transition: probability according to **Fermi golden rule**

$$P_{if} = \frac{\pi e^2}{2\hbar m^2 c^2} A_0^2 |\langle f|e^{i\mathbf{k}\cdot\mathbf{r}} \mathbf{e} \cdot \mathbf{p}|i\rangle|^2 \rho_i(E)$$

✳ Long wavelength (UV, soft x-rays) $kr_s = \dfrac{2\pi}{\lambda} r_s \ll 1$

$$P_{if} \propto |\langle f| \ \hat{e} \cdot \hat{p} \ |i\rangle|^2 \qquad \text{**velocity form**}$$

✳ Equivalent operators

$$\hat{p} = -i\hbar\nabla = \frac{im}{\hbar}[\hat{H}, \hat{r}] \qquad P_{if} \propto (E_f - E_i) |\langle f| \ \hat{\mu} \ |i\rangle|^2 \qquad \text{**length form**}$$

Δ SCF

✳ Ground state KS virtual orbitals

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

✳ Parametric SCF solution $\qquad \tilde{E}[n(\{f_i\})] \qquad n(\mathbf{r}) = \sum_i f_i \ |\psi_i(\mathbf{r})|^2$

$$
\begin{aligned}
IP_{i=1} &= \tilde{E}(0_1, 1_2.., 1_N, ...0_r...) \ - \tilde{E}(1_1, 1_2.., 1_N, ..., 0_r, ...) \\
\Delta E(i \to r) &= \tilde{E}(1_1, 1_2..., 0_i, ..., 1_N, ..., 1_r, ...) \ - \tilde{E}(1_1, 1_2..., 1_i, ...1_N..., 0_r, ...)
\end{aligned}
$$

✳ Numerically not stable : difference between 2 SCF calculations

✳ Higher excited states states (collapse)

✳ Not orthogonal MOs sets $\qquad P_{if} \propto |\langle f|\mathbf{e} \cdot \mathbf{p}|i\rangle|^2 \rho_i(E)$

The Transition Potential Method

Independent-Particle Approach

✳ Direct calculation of the excitation energies from the solution of KS equation with a modified core potential on the absorbing atom

$$IP_i = \int_1^0 df_i \frac{\partial \tilde{E}(\{f_j\})}{\partial f_i} \simeq \left(\frac{\partial \tilde{E}(\{f_j\})}{\partial f_i} \right)_{f_i = \frac{1}{2}} = \varepsilon_i \left(\frac{1}{2} \right)$$

✳ Relaxation effects up to second order in ∂E/∂f : balance between initial and final state contributions

✳ One calculation for each excitation

$$\hbar \omega_{if} = \varepsilon_f^T - \varepsilon_i^T \qquad I_{if} = \frac{2}{3} \omega_{if} |\langle \psi_i^T | \bar{\mu} | \psi_f^T \rangle|^2$$

Errors/Corrections

* Single particle picture (hole/electron correlation)

* Basis sets flexible to relaxation to describe Rydberg states;
  Double basis set approach [19s,19p,19d]

* Using TP: error due to higher order contributions to the core
  relaxation energy

* Energy corrections based on Δ SCF

$$\Delta IP = \varepsilon_{1s}^T \left(\frac{1}{2}\right) - IP_{\Delta SCF}$$

$$\Delta (1s \rightarrow \pi^*) = \left(\varepsilon_{\pi*} - \varepsilon_{1s}^T \left(\frac{1}{2}\right)\right) - \Delta E_{\Delta SCF}$$

* Relativistic correction as rigid, species-dependent translation

The Core Hole

The actual location of the excited electron in the final state has a relative small effect on relaxation of the orbitals

The focus is set on the core hole

HCH	XHCH	FCH	XFCH
HCH half core hole system charged +1/2 contribution from the initial state	**XHCH** half core hole half 1st excited state neutral system contribution from the initial state	**FCH** full core hole system charged +1 dominated by the final state	**XFCH** full core hole full 1st excited state neutral system contribution by the final state

Only one SCF calculation per core hole for the entire spectrum

AE-TP in Condensed Matter

✱ Ground state SCF and localization of the occupied orbitals

✱ Character of the Core states

$$\tilde{\psi}_i(\mathbf{r}) = \sum_\mu \tilde{C}_{\mu i} \varphi_\mu(\mathbf{r}) \qquad \stackrel{O_{1s},n}{\Longrightarrow} \qquad Max_i \ \left\{ \left\langle \tilde{\psi}_i^{O_n} | \varphi_{O,1s}^{STO} \right\rangle \right\} \qquad \Longrightarrow \qquad \text{j-th state}$$

✱ Half Core Hole / Full Core Hole / any core occupation (LSD)

$$f_j = \frac{1}{2}, 0$$

✱ SCF with modified occupation numbers

✱ Oscillator strengths in the velocity form

$$I_{if} = |\langle \psi_i^T | \nabla | \psi_f^T \rangle|^2$$

&XAS

```
    &SCF
        EPS_SCF 1.0E-4
        MAX_SCF 200
        &SMEAR ON
            METHOD FERMI_DIRAC
            ELECTRONIC_TEMPERATURE [K] 300
        &END
        &MIXING
            METHOD  BROYDEN_MIXING
            ALPHA 0.1
            BETA 1.5
            NBUFFER 8
        &END MIXING
    &END SCF
    METHOD       TP_HH
    DIPOLE_FORM  VELOCITY
    STATE_TYPE   1s
    STATE_SEARCH 10 # mult. matches
    ATOMS_LIST   1
    ADDED_MOS    1000
    &LOCALIZE
    &END

                              &PRINT
                                &PROGRAM_RUN_INFO
                                &END
                                &RESTART
                                    FILENAME ./root
                                    &EACH
                                      XAS_SCF 15
                                    &END
                                    ADD_LAST NUMERIC
                                &END
                                &XAS_SPECTRUM
                                  FILENAME ./root
                                &END
                                &XES_SPECTRUM
                                  FILENAME ./root
                                &END
                              &END
```

&END XAS

Convolution using Gaussian functions with adapted width

$$f(x) = I_{SL} \frac{1}{\sigma\sqrt{2\pi}} e^{(x-x_{SL})^2/(2\sigma^2)}$$

$$\sigma = \begin{cases} \sigma_{min} & : & \omega_{if} < E_{min} \\ \sigma_{min} + (\omega_{if} - E_{min}) \cdot \frac{\sigma_{max} - \sigma_{min}}{E_{max} - E_{min}} & : & E_{min} < \omega_{if} < E_{max} \\ \sigma_{max} & : & E_{max} < \omega_{if} \end{cases}$$

$$\sigma_{min} = 0.5 eV$$

$$\sigma_{max} = 8\ eV$$

$$E_{max} - E_{min} \approx 20\ eV$$

Energy (eV)
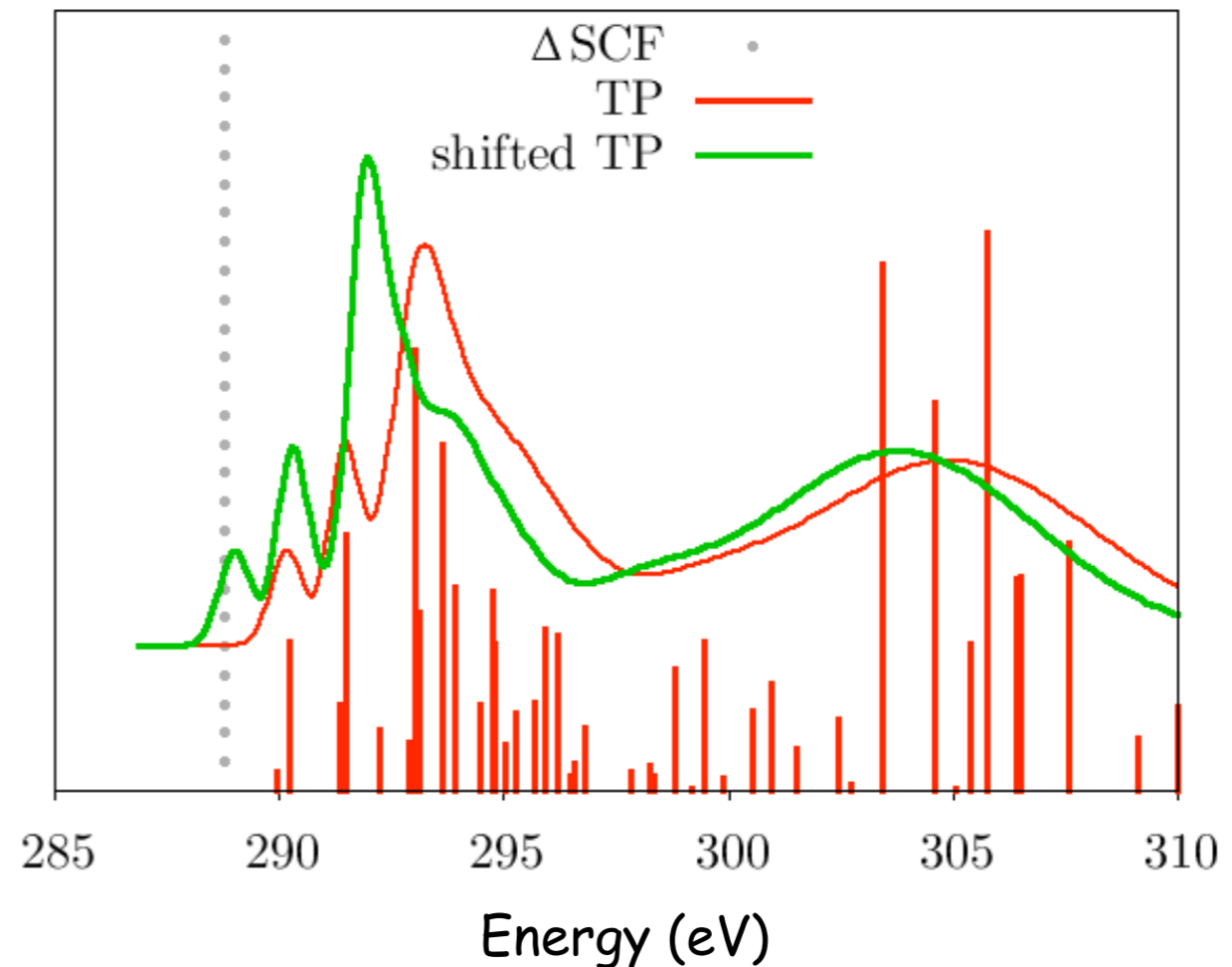
NEXAFS for Hexagonal Ice

Hexagonal Ice

128H2O
6-311G(dp)

Exp.

Energy (eV)
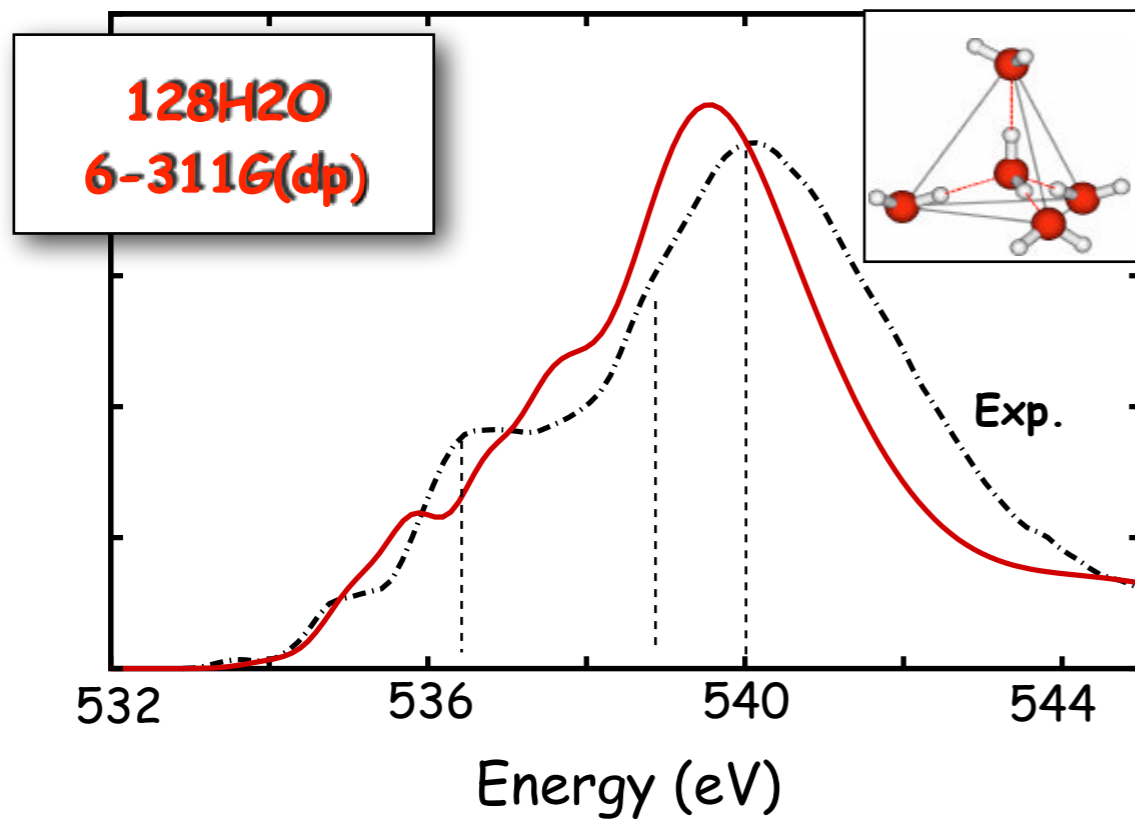
Exp: gas phase vs Ice

Energy (eV)
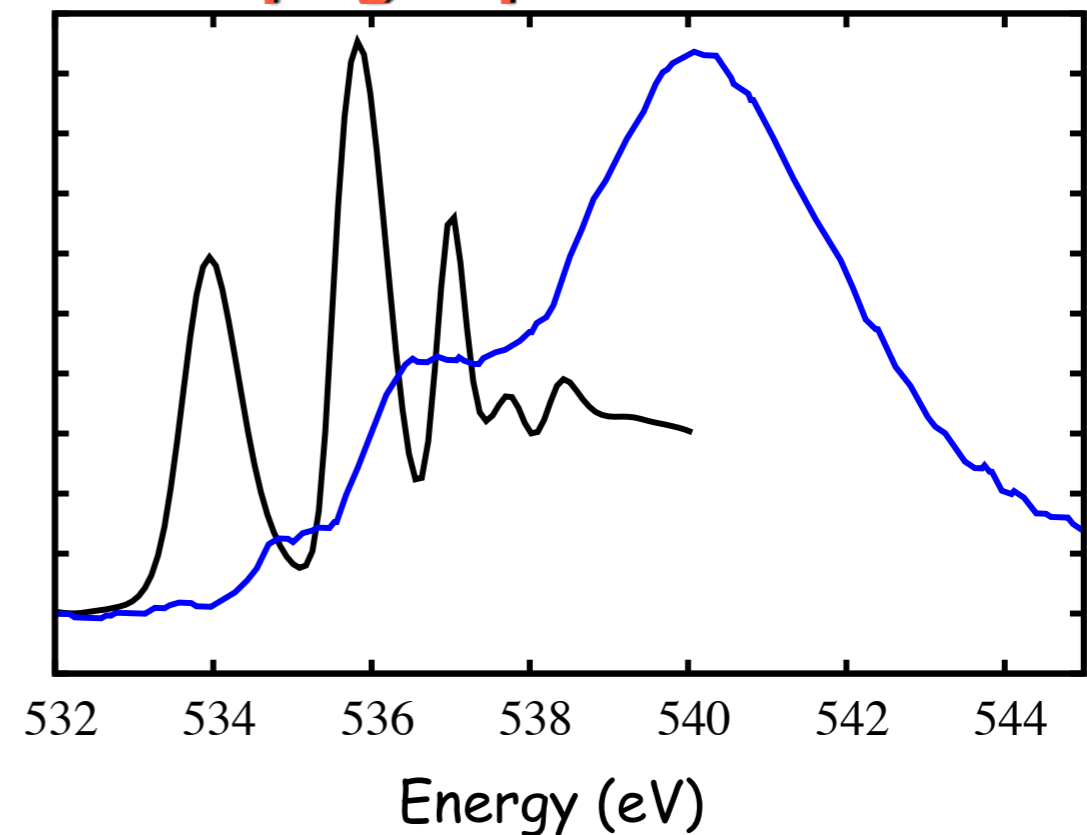
- All O **donating** and **accepting** 2 h-bonds

- Charge redistribution (no antibonding OH)

- Large post-edge band (emptied lone-pairs)

Exp. Ice : Nilsson et al. JCP, **122**, 154505 (2005)
Exp. liquid water : M. Odelius et al., PRB, **73**, 024205 (2006)

Size of the Simulation Cell
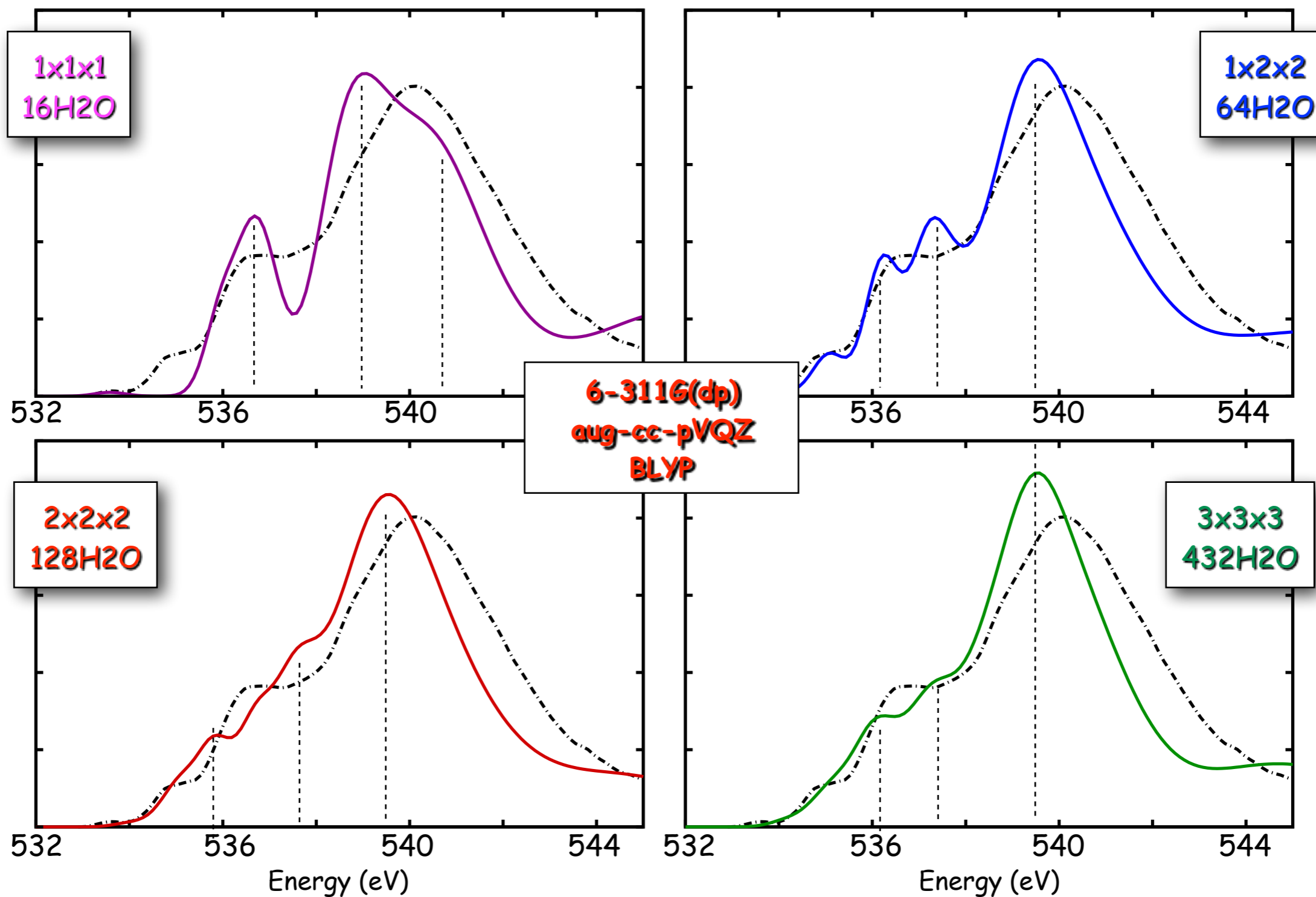
Different Core State Occupation

Not only the **absolute position** but also the **shape** of the spectrum might change

HCH

FCH

XHCH

XFCH

6-311G(dp) + aug-cc-pVZ4 BLYP

Energy (eV)

Energy (eV)
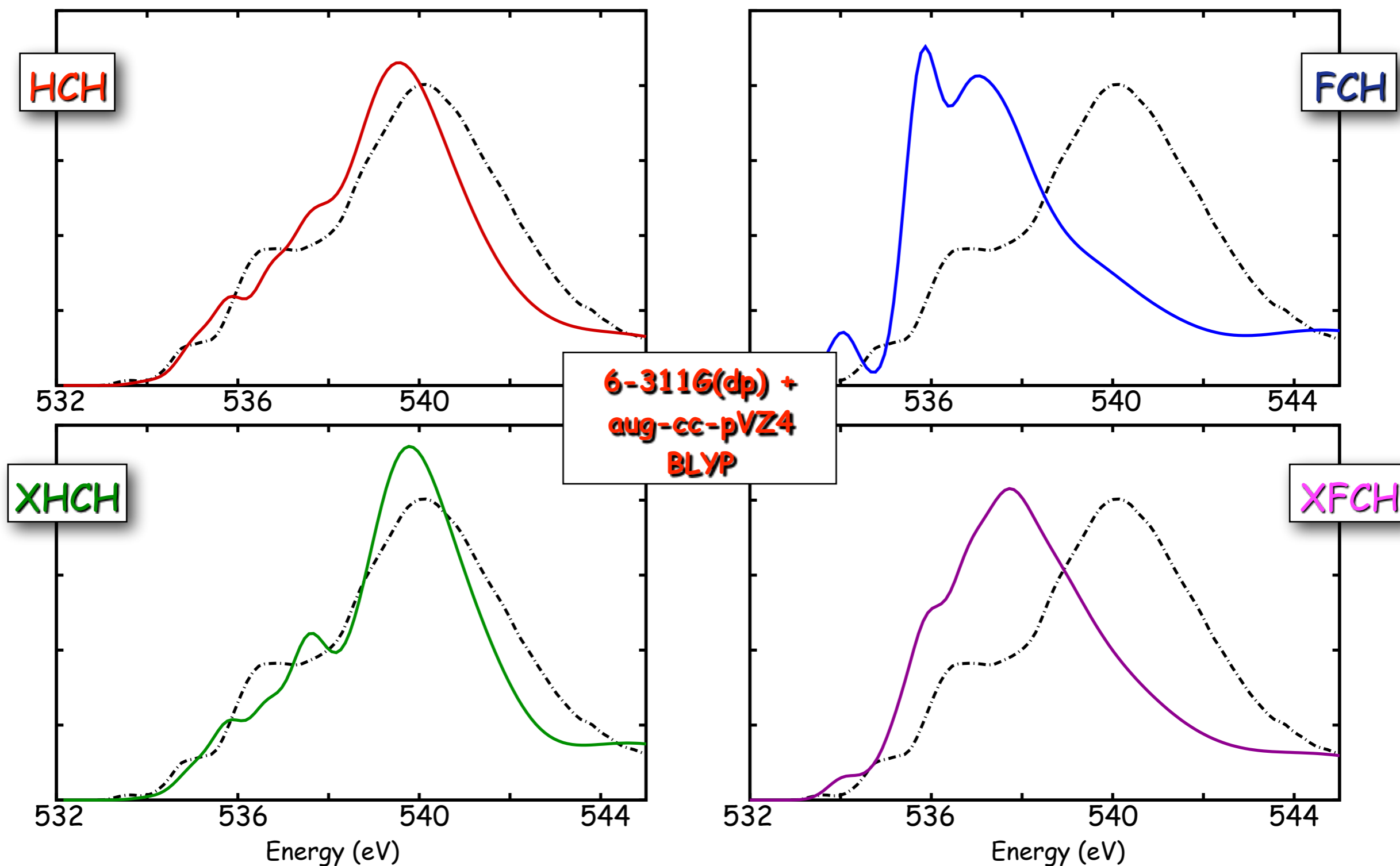
Liquid Water

Sampling over pre-generated trajectories: 20 ps, spectrum every 0.5 ps

XAS 32 H2O 6-31G(dp)
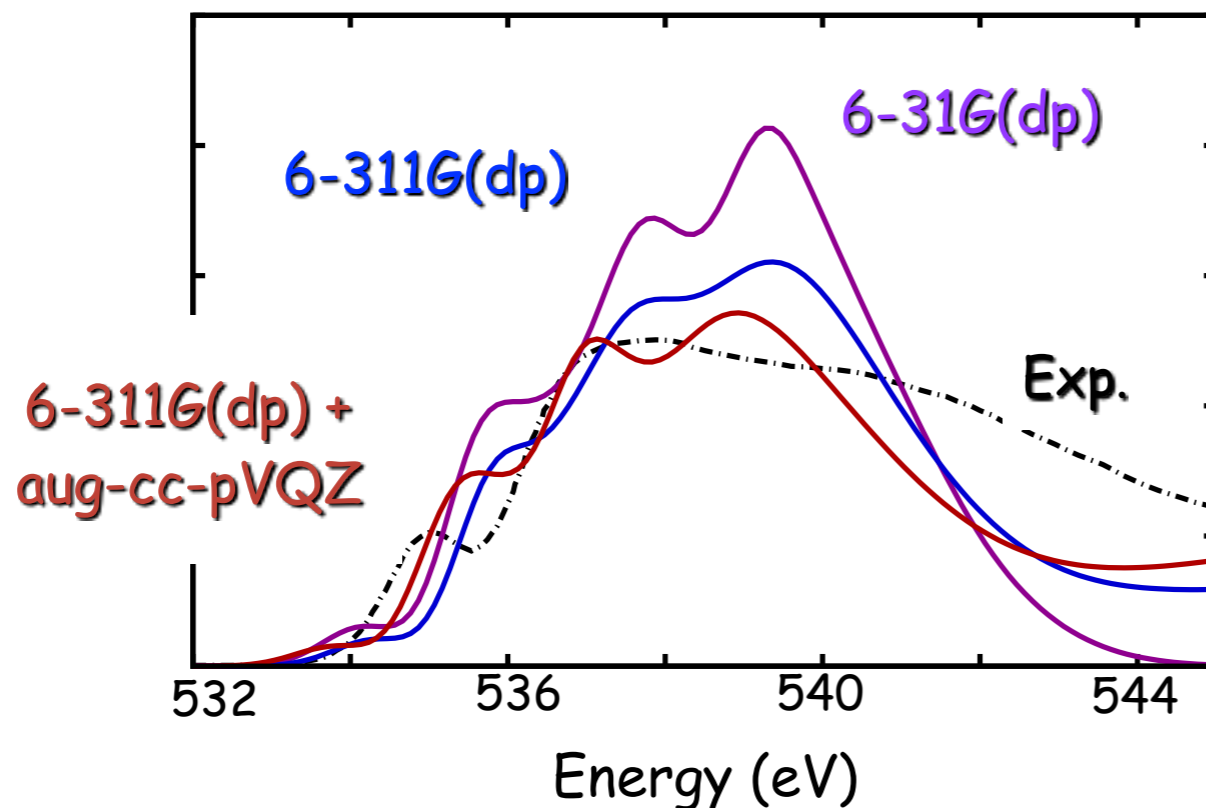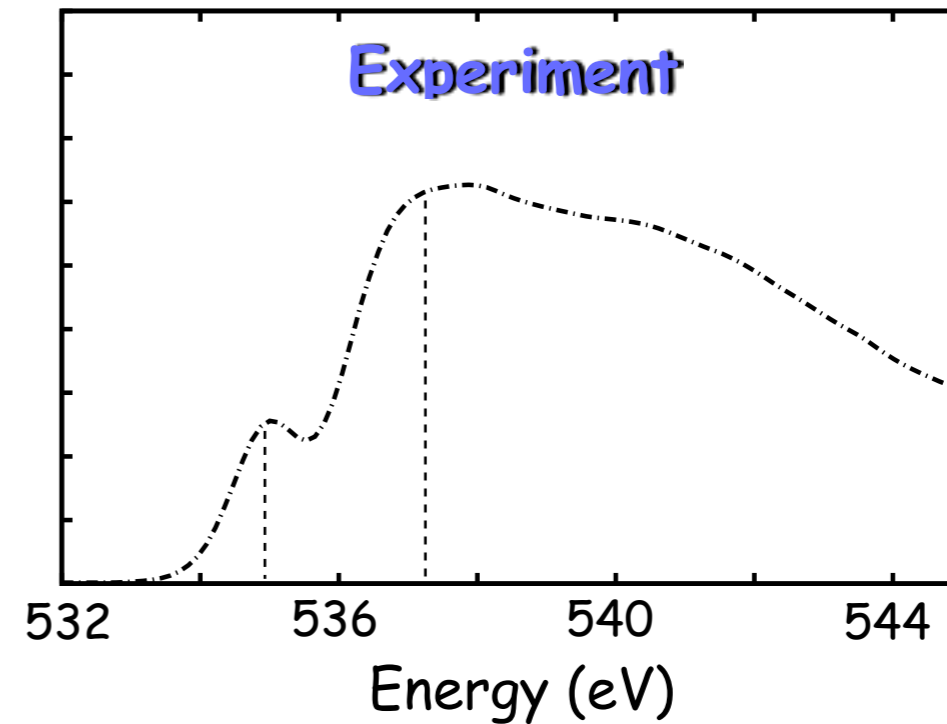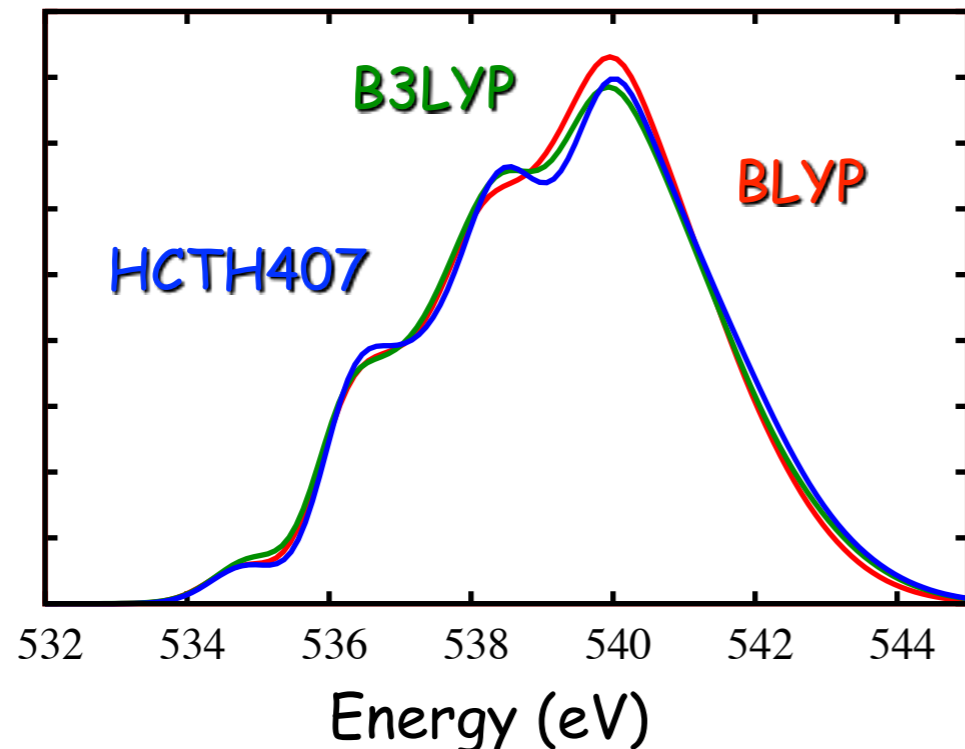
Better relative intensities between Pre-edge and Post-edge by additional flexibility in virtual orbital description around the absorbing atom

Nuclear Magnetic Resonance

Measure of the Larmor precession frequency of the nuclear spin within a magnetic field

$$\omega_{\text{Larmor}} = \frac{d\phi}{dt} = \frac{ge}{2m}B$$

$$\mu = g\frac{e}{2m_p}I$$

$$Torque$$
$$\tau = \mu \times B$$

Quantized nuclear spin

$m_S = +1/2$

$\Delta E = E_{+1/2} - E_{-1/2}$

$m_S = -1/2$

Energy

$B_0 = 0$ $B_0 \neq 0$ Magnetic Field

¹H
¹⁵N
¹⁹F
²⁹S
³¹P

net nuclear spin magnetisation in B
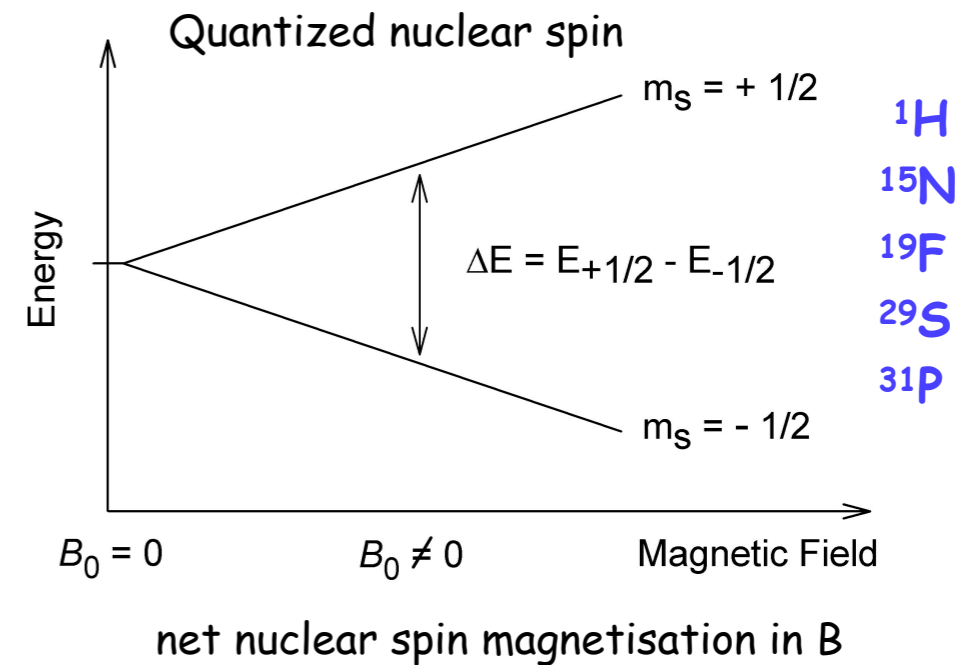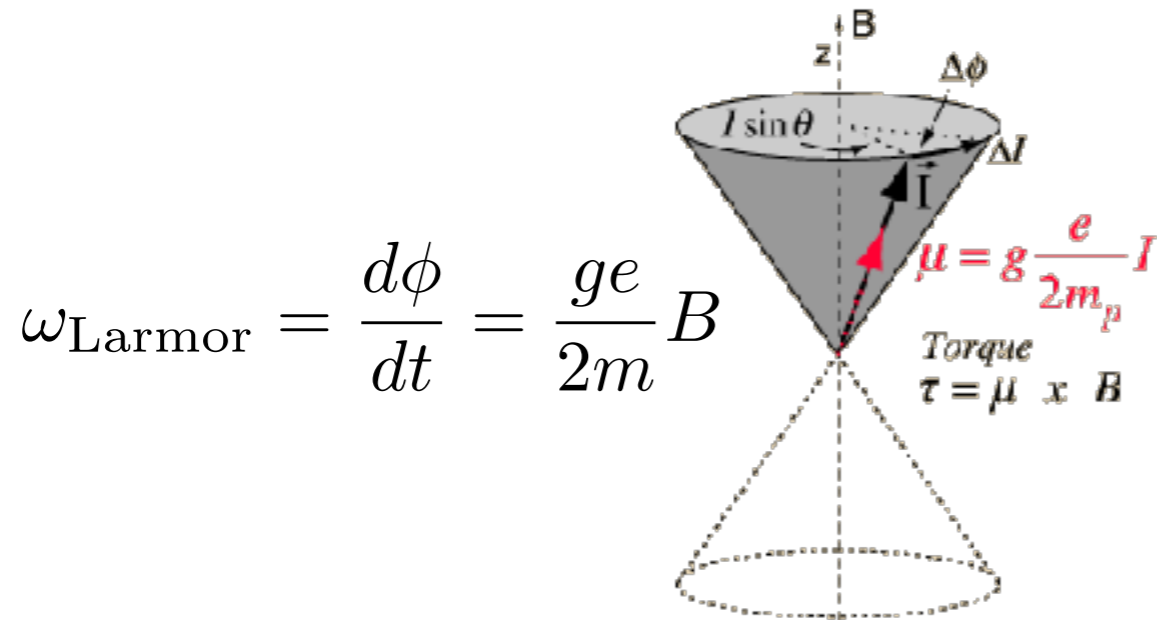
Interaction between **B** and a spin 1/2 nucleus with spin angular momentum $E = -\boldsymbol{\mu} \cdot \mathbf{B}$

$$\hbar\omega = \Delta E = -\gamma\hbar B$$

in diamagnetic materials the **B**ind arises only from the induced orbital currents **j**

$$\mathbf{B} = \mathbf{B}_0 + \mathbf{B}_{\text{ind}} \qquad \mathbf{B}_{\text{ind}} = -\overleftrightarrow{\sigma}_k \mathbf{B}_0$$

Chemical Shielding

m=½

$\hbar\omega$

m=-½

ω

^{13}C spectrum
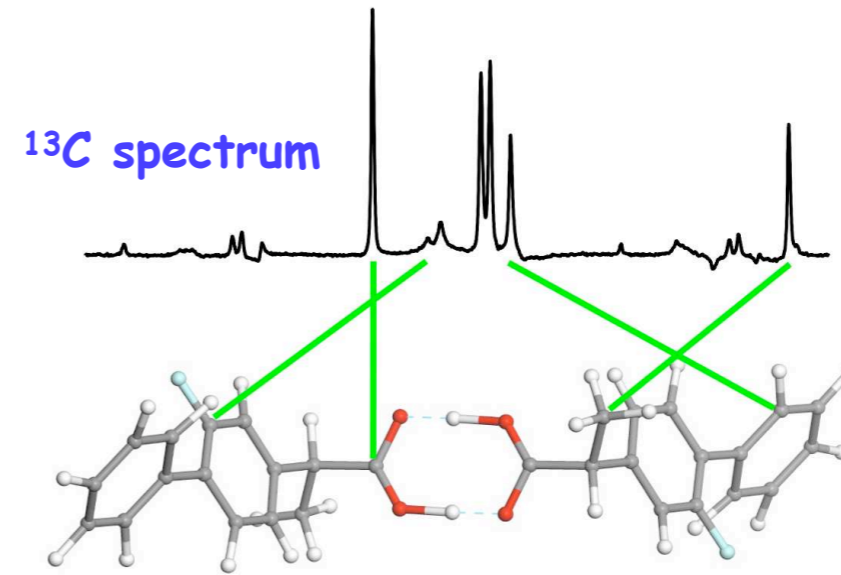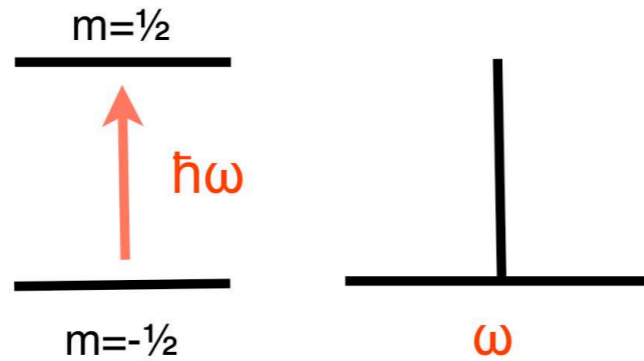
$$\mathbf{B}_{\text{ind}}(\mathbf{r}) = \frac{1}{c}\int d^3r' \mathbf{j}(\mathbf{r}') \times \frac{\mathbf{r}-\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|^3}$$

applied B^0 along x

$$\sigma_{xy}(\mathbf{R}_A) = \frac{1}{c}\int_\Omega \left[\frac{\mathbf{r}-\mathbf{R}_A}{|\mathbf{r}-\mathbf{R}_A|^3} \times \mathbf{j}_x(\mathbf{r})\right]_y d^3r$$

chemical shift w.r.t. reference

$$\delta = \frac{\nu - \nu_{\text{ref}}}{\nu_{\text{ref}}}(\times 10^6) \approx (\sigma_{\text{ref}} - \sigma) \qquad \sigma = \frac{1}{3}\text{Tr}[\overleftrightarrow{\sigma}]$$

Magnetic Field

Representation by means of a vector potential and a Gauge function

$$\mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A}(\mathbf{r}) = \boldsymbol{\nabla} \times [\mathbf{A}(\mathbf{r}) + \boldsymbol{\nabla}\Phi_g(\mathbf{r})]$$

$$\mathbf{A}(\mathbf{r}) = -\frac{1}{2}\mathbf{r} \times \mathbf{B} \qquad\qquad \Phi_g(\mathbf{r}) = \frac{1}{2}\mathbf{r} \cdot \mathbf{R}_b \times \mathbf{B}$$

The Gauge function translates the origin, it does not change the physics, but affects the numerical accuracy

Minimal substitution in the Hamiltonian $\qquad \hat{\mathbf{p}} \rightarrow \hat{\mathbf{p}} - e\mathbf{A}(\hat{\mathbf{r}})$

$$\mathbf{H} = \frac{1}{2m}\left(\mathbf{p} - e\mathbf{A}(\mathbf{r})\right)^2 + \mathcal{V}$$

$$\mathbf{H}^{\text{pert}} = -\frac{e}{m}\hat{\mathbf{p}} \cdot \mathbf{A}(\hat{\mathbf{r}}) + \frac{e^2}{2m}\mathbf{A}(\hat{\mathbf{r}}) \cdot \mathbf{A}(\hat{\mathbf{r}})$$

$\hat{\mathbf{p}} = -i\hbar\boldsymbol{\nabla}$

1st order
imaginary

Density Functional Perturbation Theory

Variational principle at second order in the DFT framework

$$\mathcal{E}_{\text{tot}} = \mathcal{E}_{\text{KS}}^{(0)} + \lambda \mathcal{E}^{\text{pert}}$$

static perturbation

$$E_{\text{tot}} = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + ... \qquad \psi_i = \psi_i^{(0)} + \lambda \psi_i^{(1)} + \lambda^2 \psi_i^{(2)} + ...$$

Expansion to 2nd order and minimisation: **linear response**

$E^{(2)}$ **variational in ψ⁽¹⁾**

$$E^{(2)} = \sum_{ij} \left\langle \psi_i^{(1)} \left| H^{(0)} \delta_{ij} - \langle \psi_j^{(1)} | H^{(0)} | \psi_i^{(0)} \rangle \right| \psi_j^{(1)} \right\rangle + \frac{1}{2} \int \frac{\partial^2 \mathcal{E}_{\text{Hxc}}}{\partial n(\mathbf{r}') \partial n(\mathbf{r})} n^{(1)}(\mathbf{r}) n^{(1)}(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$$

$$+ \sum_i \left[\langle \psi_i^{(1)} | \frac{\partial \mathcal{E}^{\text{pert}}}{\partial \langle \psi_i^{(0)} |} + \frac{\partial \mathcal{E}^{\text{pert}}}{\partial | \psi_i^{(0)} \rangle} | \psi_i^{(1)} \rangle \right]$$

$$H^1 = \hat{\mathbf{p}} \cdot (\hat{\mathbf{r}} - \mathbf{R}_g) \times \mathbf{B} = [(\hat{\mathbf{r}} \times \hat{\mathbf{p}}) - (\mathbf{R}_g \times \hat{\mathbf{p}})] \cdot \mathbf{B}$$

perturbation Hamiltonian

$$-i \sum_{i\nu} \left(H_{\mu\nu}^0 \delta_{ij} - S_{\mu\nu} \langle \psi_i^0 | H | \psi_j^0 \rangle \right) C_{\nu i}^1 = \sum_\nu H_{\mu\nu(j)}^1 C_{\nu j}^0$$

Induced Current Density

Perturbation operator split into three terms

$$H^{L}_{\mu\nu(j)} = -i\langle\mu|(\hat{\mathbf{r}} - \mathbf{d}_j)\times\nabla|\nu\rangle \qquad H^{p}_{\mu\nu} = -i\langle\mu|\nabla|\nu\rangle \qquad H^{\Delta_i}_{\mu\nu j} = -i(\mathbf{d}_i - \mathbf{d}_j)\times\langle\mu|\nabla|\nu\rangle$$

with coefficients $C^{L_x}\ C^{L_y}\ C^{L_z}$, $C^{p_x}\ C^{p_y}\ C^{p_z}$, $C^{\Delta_{ix}}\ C^{\Delta_{iy}}\ C^{\Delta_{iz}}$

x-component of current density j induced by B⁰ applied along y

$$
\begin{aligned}
j_{xy}(\mathbf{r}) =\ & -\frac{1}{2c}\sum_i\sum_{\mu\nu}\Big[C^0_{\mu i}\Big(C^{L_y}_{\nu i} + (\mathbf{R}_g - \mathbf{d}_i)_x C^{p_z}_{\nu i} - (\mathbf{R}_g - \mathbf{d}_i)_z C^{p_x}_{\nu i} - C^{\Delta_{iy}}_{\nu i}\Big)\\
& \times\ ([\nabla_x\varphi_\mu(\mathbf{r})]\varphi_\nu(\mathbf{r}) - \varphi_\mu(\mathbf{r})[\nabla_\mathbf{x}(\varphi_\nu(\mathbf{r}))])]\\
& +\ (\mathbf{r} - \mathbf{R}_g)_z n(\mathbf{r}) \qquad \text{diamagnetic}
\end{aligned}
$$

Gauge invariance in molecular and periodic systems

CSGT $\qquad \mathbf{R}_g = \mathbf{r} \qquad$ computationally convenient, slow converging with basis set quality

IGAIM $\qquad \mathbf{R}_g = \mathbf{R}_I \qquad$ individual gauge for atoms in molecules

Sebastiani, Parrinello, JPC, **105**, 1951 (2001)
Weber, Iannuzzi, Giani, Hutter, Declerck, Waroquier, JCP, **131**, 014106 (2009)

GAPW Chemical Shift

applied B⁰ along x

$$\sigma_{xy}(\mathbf{R}_A) = \frac{1}{c} \int_\Omega \left[\frac{\mathbf{r} - \mathbf{R}_A}{|\mathbf{r} - \mathbf{R}_A|^3} \times \mathbf{j}_x(\mathbf{r}) \right]_y \mathrm{d}^3 r$$

GAPW induced current density

$$\mathbf{j}(\mathbf{r}) = \tilde{\mathbf{j}}(\mathbf{r}) + \sum_A \left(\mathbf{j}_A(\mathbf{r}) - \tilde{\mathbf{j}}_A(\mathbf{r}) \right)$$

from soft term in reciprocal space

$$\tilde{\mathbf{B}}^{\mathrm{ind}}(\mathbf{G} \neq 0) = -\mu_0 i \frac{\mathbf{G}}{|\mathbf{G}|^2} \times \tilde{\mathbf{j}}(\mathbf{G})$$

$$\tilde{\mathbf{B}}^{\mathrm{ind}}(\mathbf{G} = 0) = \kappa \chi \mathbf{B}^{\mathrm{ext}}$$

$$\chi_{xy} = \frac{2\pi}{\Omega} \int \left[\mathbf{r} \times \tilde{\mathbf{j}}_x(\mathbf{r}) \right]_y \mathrm{d}^3 r$$

from local terms by integration on spherical grids

$$\sigma_{xy}^{\mathrm{loc}}(\mathbf{R}_A) = \frac{1}{c} \sum_B \int_{\Omega_B} \left[\frac{\mathbf{r} - \mathbf{R}_A}{|\mathbf{r} - \mathbf{R}_A|^3} \times \left(\mathbf{j}_{xB}(\mathbf{r}) - \tilde{\mathbf{j}}_{xB}(\mathbf{r}) \right) \right]_y \mathrm{d}^3 r$$

NMR Input

Linear Response run-type

```
&GLOBAL
   PROJECT              ${PROJECT_NAME}
   PRINT_LEVEL      LOW
   RUN_TYPE                 LINEAR_RESPONSE
&END GLOBAL
```

Ground State GAPW

```
&DFT
   BASIS_SET_FILE_NAME        EMSL_BASIS_SETS
   POTENTIAL_FILE_NAME        POTENTIAL
   &MGRID
      CUTOFF          300
   &END MGRID
   &QS
      METHOD          GAPW
   &END QS
   &SCF
      &OUTER_SCF
         MAX_SCF       200
      &END OUTER_SCF
      MAX_SCF            20
      EPS_SCF          10E-6
      &OT
         ALGORITHM       IRAC
         PRECONDITIONER  FULL_ALL
      &END OT
   &END SCF
   &XC
      &XC_FUNCTIONAL      BLYP
      &END XC_FUNCTIONAL
   &END XC
&END DFT
```

GAPW kind

```
&KIND N
   LEBEDEV_GRID      100
   RADIAL_GRID       200
   BASIS_SET         aug-cc-pVQZ
   POTENTIAL         ALL
&END KIND
```

NMR Chemical Shift

```
&PROPERTIES
   &LINRES
      &LOCALIZE
      &END
      OPT_METHOD        CG
      LINESEARCH 2PNT
      PRECONDITIONER   FULL_ALL
      MAX_SCF 2000
      &CURRENT
         GAUGE            ATOM
         ORBITAL_CENTER COMMON
      &END CURRENT
      &NMR
         INTERPOLATE_SHIFT T
         &PRINT
            &CHI_TENSOR
            &END CHI_TENSOR
         &END PRINT
      &END
   &END
&END
```

NMR Output for SiH₄

Converged GAPW SCF

```
Total electronic density (r-space):        -11.6551998133        6.3448001867
Total core charge density (r-space):        18.0000000000        0.0000000000

Hard and soft densities (Lebedev):         -67.3124445208      -60.9676446784
Total Rho_soft + Rho1_hard - Rho1_soft (r-space):              -17.9999996557
Total charge density (r-space):                                 0.0000003443
Total Rho_soft + Rho0_soft (g-space):                          0.0000003075

Overlap energy of the core charge distribution:               0.00000011310807
Self energy of the core charge distribution:               -131.30230308020512
Core Hamiltonian energy:                                   -159.90960164160288
Hartree energy:                                              32.53453281991028
Exchange-correlation energy:                                 -5.66831828118873

GAPW| Exc from hard and soft atomic rho1:                    -16.66150292615432
GAPW| local Eh = 1 center integrals:                         -10.87514648571372

outer SCF iter =     2 RMS gradient =   0.35E-05 energy =     -291.8823394818
outer SCF loop converged in   2 iterations or   23 steps


ENERGY| Total FORCE_EVAL ( QS ) energy (a.u.):              -291.882339481846373
```

NMR Output for SiH$_4$

Localization procedure through Jacobi rotations

```
LOCALIZE| The spread relative to a set of orbitals is computed
LOCALIZE| Orbitals to be localized: All the occupied
LOCALIZE| Spread defined by the Berry phase operator
LOCALIZE| The optimal unitary transformation is generated by the Jacobi algorithm


Localization of the ground state orbitals before starting the linear response calculation
        Localization by iterative Jacobi rotation
                    Iteration           Tolerance
                        100           0.2560E-01
                        200           0.1556E-01
                        300           0.6506E-02
                        400           0.1981E-02
                        500           0.8639E-03
                        600           0.3288E-03
            Localization  for spin   1 converged in    698 iterations
      Total Spread (Berry) x,y,z:          1.1135942650    1.1135229959    1.1133052793

  WANNIER CENTERS for spin  1
```

		——————————— Centers ———————————			——————————— Spreads ———————		
state	1	−0.222895	0.146450	0.058049	0.541470	0.000000	0.000000
state	2	0.000107	−0.064397	−0.264849	0.541498	0.000000	0.000000
state	3	0.222716	0.146673	0.058175	0.541470	0.000000	0.000000
state	4	0.000000	0.000121	0.000245	0.140158	0.000000	0.000000
state	5	0.000072	−0.228327	0.149401	0.541477	0.000000	0.000000
state	6	−1.772371	−1.183928	−0.406835	1.888384	0.000000	0.000000
state	7	0.000093	0.608045	2.082470	1.887723	0.000000	0.000000
state	8	0.000211	1.760315	−1.267771	1.887975	0.000000	0.000000
state	9	1.772063	−1.184376	−0.406863	1.888382	0.000000	0.000000

NMR Output for SiH₄

Linear Response Initialization

```
================================================================
                    START LINRES CALCULATION
================================================================
            Properties to be Calulated:

                           NMR Chemical Shift
  LINRES|                                           LOCALIZED PSI0
  LINRES|       Optimization algorithm          Conjugate Gradients
  LINRES|              Line Search                             2pnt
  LINRES|             Preconditioner                       FULL ALL

  LINRES|                 EPS_SCF                           1.0E-05

  LINRES|     Max number of iterations per SCF cycle           2000

  Total energy ground state:                     -291.88233948447117
     -65.49055205     -5.05920132     -3.47810739     -3.47810596
      -3.47809942     -0.48735526     -0.30828056     -0.30810235
      -0.30804975

                  *** Start current Calculation ***

           Initialization of the current environment

  CURRENT| Gauge used ATOM
  CURRENT| Orbital center used COMMON
  CURRENT| Common center   0.000000  0.000000  0.000000
  CURRENT| Calculation of the p and (r-d)xp operators applied to psi0
```

NMR Output for SiH₄

Response calculation for first perturbation operator

*** Self consistent optimization of the response wavefunctions ***

Response to the perturbation operator P_x

| Iter.	Method	Stepsize	G–norm	Convergence	Total energy
10	LR LS	0.99E–01	0.0000000000	0.0323894903	–2.2638501245
20	LR LS	0.12E+00	0.0000000000	0.0077609426	–2.6500765218
30	LR LS	0.48E–01	0.0000000000	0.0077044886	–2.6794773033
40	LR LS	0.15E+00	0.0000000000	0.0050879317	–2.7024052890
50	LR LS	0.60E+00	0.0000000000	0.0074222310	–2.7361724629
60	LR LS	0.55E–01	0.0000000000	0.0036544263	–2.7922066072
70	LR LS	0.68E–01	0.0000000000	0.0027598118	–2.7965811305
80	LR LS	0.90E–01	0.0000000000	0.0011411853	–2.7983145616
90	LR LS	0.11E+00	0.0000000000	0.0008189226	–2.7988545411
100	LR LS	0.72E–01	0.0000000000	0.0005977973	–2.7991253972
110	LR LS	0.73E–01	0.0000000000	0.0003155523	–2.7991931045
120	LR LS	0.64E–01	0.0000000000	0.0002261754	–2.7992267386
130	LR LS	0.76E–01	0.0000000000	0.0000928637	–2.7992365112
140	LR LS	0.62E–01	0.0000000000	0.0000783777	–2.7992406728
150	LR LS	0.94E–01	0.0000000000	0.0000318069	–2.7992417209
160	LR LS	0.90E–01	0.0000000000	0.0000245090	–2.7992422317

The SCF has converged in 167 iterations

Second order energy P_x= –0.2799242338698460E+01
Store the psi1 for the calculation of the response current density

Geometry optimised in gas phase : BLYP/6-31G(dp)
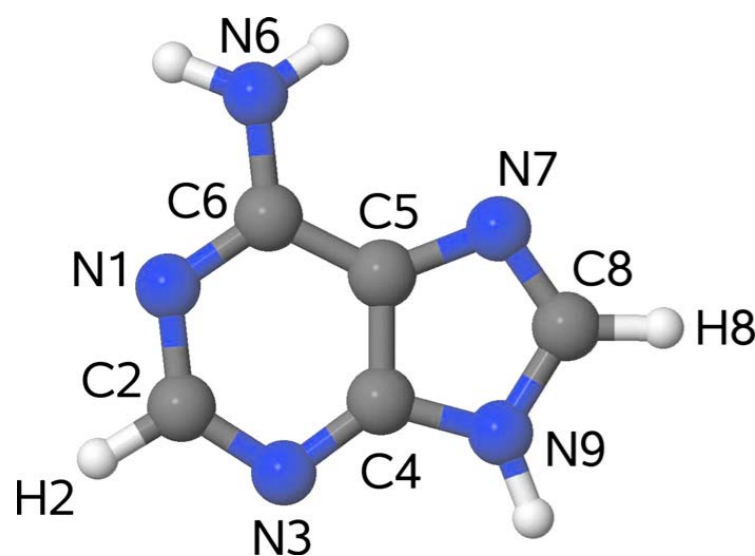
	CP2K IGAIM BLYP/cc-p-VQZ	G03 IGAIM BLYP /cc-pVQZ	G03 IGAIM BLYP /aug-cc-pVZ5	CPMD CSGT BLYP/200Ry	PP corrected
C_2	164	164	166	136	(168)
C_4	159	159	162	130	(161)
C_5	128	128	130	93	(124)
C_6	163	163	165	134	(166)
C_8	141	141	143	115	(146)
H_2	8.4	8.4	8.5	7.4	
H_8	7.5	7.5	7.7	7.0	
N_1	-134	-134	-135	-143	(-118)
N_3	-142	-142	-146	-152	(-127)
N_6	-319	-319	-327	-285	(-332)
N_7	-129	-129	-132	-154	(-129)
N_9	-235	-235	-240	-217	(-240)
C_t	177	177	175	7	
H_t	31.3	31.3	31.3	30.6	
N_n	-159	-159	-166	-299	
C_b			37	-99	
N_{py}			-119	-227	
N_{pr}			77	-79	
N_a			171	-8	

PP corrected
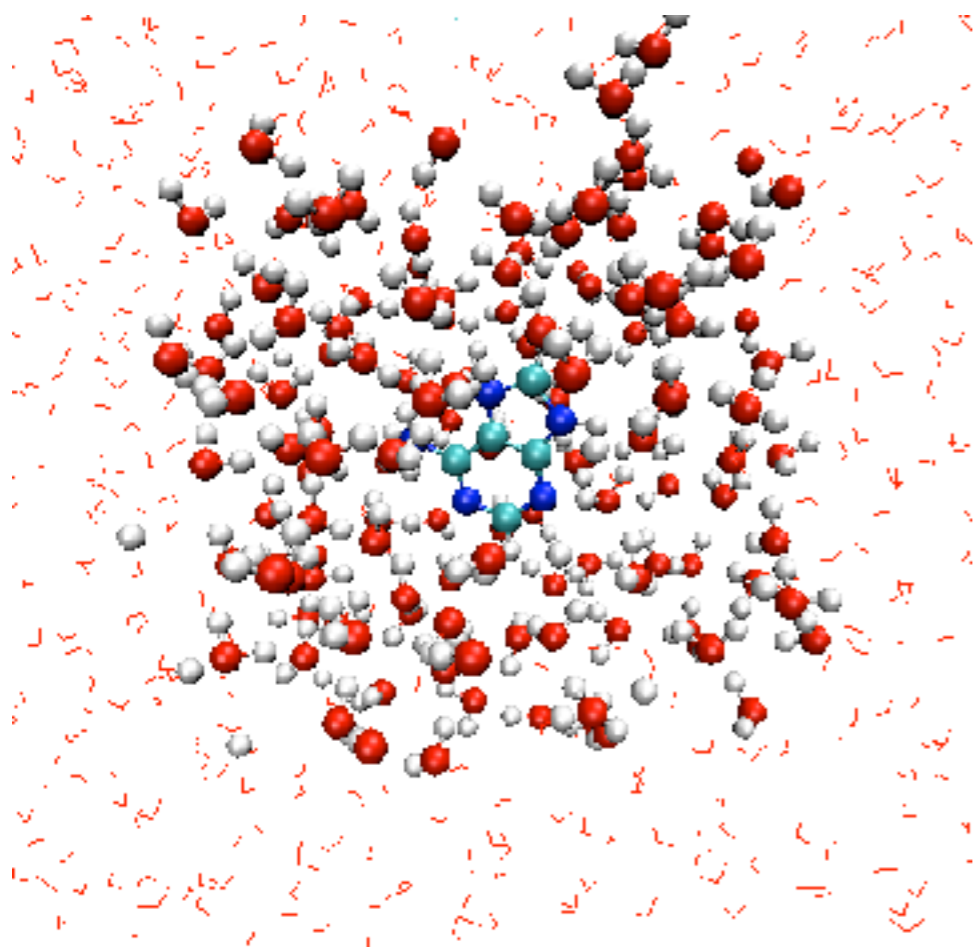
external reference

TMS
MeNO₂
benz.
pyrid.
pyrrol
alinine

PP correction

$$\delta(X) = \sigma(X_{\text{ref}}) - \sigma(X) + \delta(X_{\text{ref}})$$

64

Hydrated Adenine

QM/MM with 827 H2O: snapshot from classical MD

CP2K IGAIM BLYP/cc-p-VQZ			
	ISO	**W0**	**W3**	**W5**

	ISO	W0	W3	W5
C_2	164	164	166	166
C_4	148	148	148	148
C_5	120	120	120	120
C_6	160	160	159	159
C_8	145	152	154	154
H_2	7.8	7.8	7.8	7.9
H_8	7.7	8.3	8.2	8.4
N_1	-115	-129	-128	-125
N_3	-127	-147	-144	-145
N_6	-330	-330	-318	-317
N_7	-121	-144	-147	-149
N_9	-249	-237	-226	-223

QM water for proper description of solute/solvent h-bonds

Electron Paramagnetic Resonance

$$\rho^s(\mathbf{r}) = \rho^\alpha(\mathbf{r}) - \rho^\beta(\mathbf{r})$$

spin density

$$g_{xy} = g_{xy}^{\mathrm{Z}} + \Delta g_{xy}^{\mathrm{ZKE}} + \Delta g_{xy}^{\mathrm{SO}} + \Delta g_{xy}^{\mathrm{SOO}}$$

$$g_{xy}^{\mathrm{Z}} = g_e \delta_{xy}$$

g_e : free el. g value

$$\Delta g_{xy}^{\mathrm{ZKE}} = -\frac{g_e}{c^2}\left(T^\alpha - T^\beta\right)\delta_{xy}$$

T : unperturbed kinetic energy

induced spin current density

$$\Delta g_{xy}^{\mathrm{SO}} = \frac{g_e - 1}{c}\int_{\Omega_C}\left[\mathbf{j}_x^\alpha \times \nabla V_{\mathrm{eff}}^\alpha - \mathbf{j}_x^\beta \times \nabla V_{\mathrm{eff}}^\beta\right]d^3\mathbf{r}$$

V$_{eff}$: effective pot.

$$\Delta g_{xy}^{\mathrm{SOO}} = 2\int_{\Omega_C} B_{xy}^{\mathrm{corr}}(\mathbf{r})\rho^s(\mathbf{r})d^3\mathbf{r}$$

B^{corr} : magnetic field from induced current density
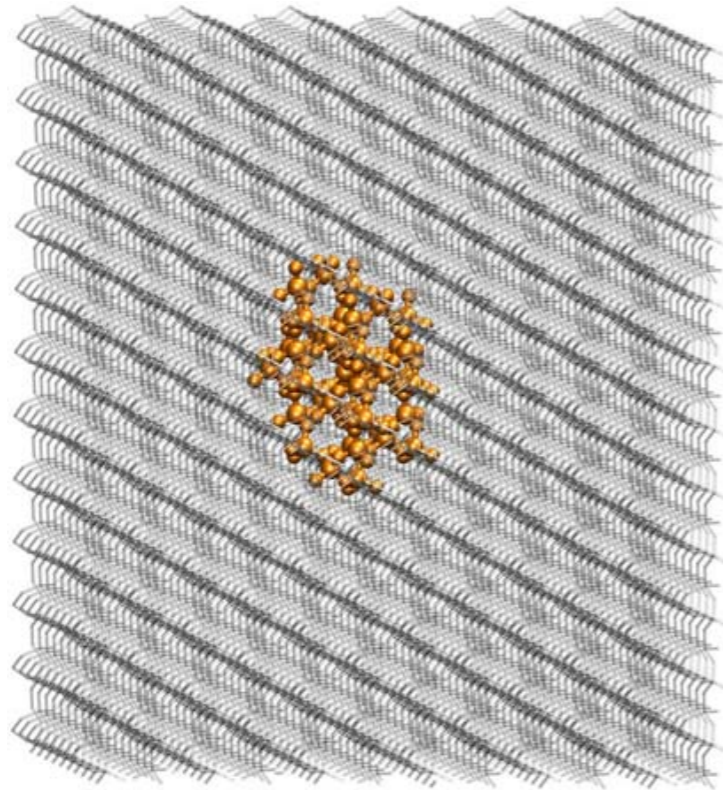
QM/MM: 15000 atoms   159 QM atoms   17 QM AE atoms
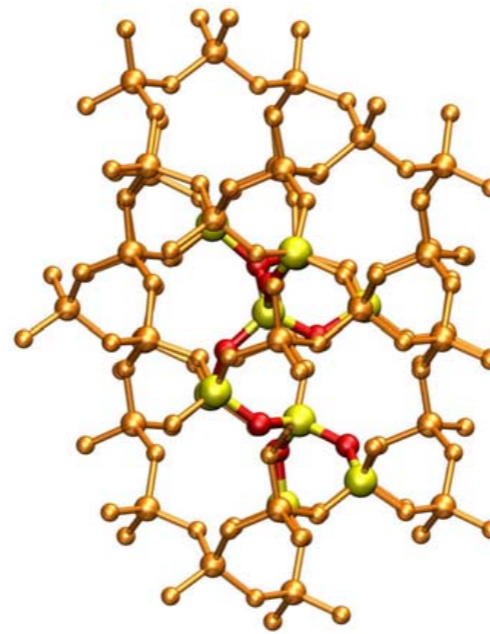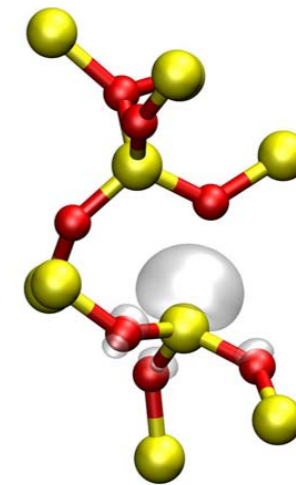
	Expt.			GAPW AE/PSP/MM			GAPW AE/MM		
	Δg_{ii}	θ	φ	Δg_{ii}	θ	φ	Δg_{ii}	θ	φ
Δg_{xx}	-530	$114.5°$	$227.7°$	-561	$108.3°$	$229.6°$	-593	$108.3°$	$230.1°$
Δg_{yy}	-1790	$134.5°$	$344.4°$	-1830	$157.6°$	$372.8°$	-1870	$149.0°$	$353.6°$
Δg_{zz}	-2020	$125.4°$	$118.7°$	-1898	$102.5°$	$135.4°$	-1901	$114.1°$	$131.5°$