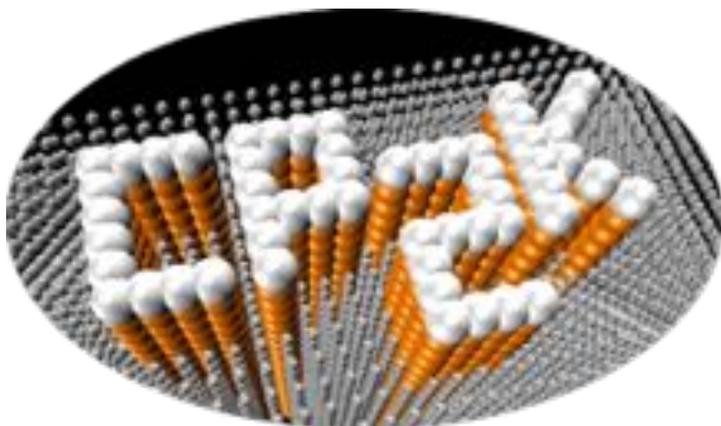


Some spectroscopic tools

Marcella Iannuzzi

Department of Chemistry, University of Zürich



<http://www.cp2k.org>

Electron Density: Cube File

Valence density on regular grids

$$n(\mathbf{r}) = \sum_{\mu\nu} P_{\mu\nu} \varphi_{\mu}(\mathbf{r}) \varphi_{\nu}(\mathbf{r}) \rightarrow \sum_{\mu\nu} P_{\mu\nu} \bar{\varphi}_{\mu\nu}(\mathbf{R}) = n(\mathbf{R})$$

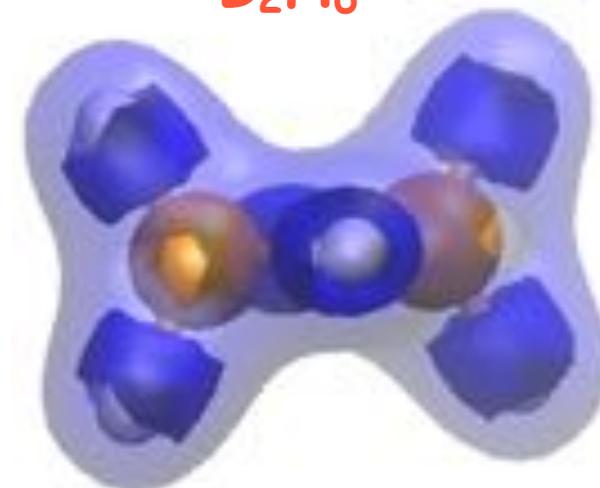
Cutoff might be too small for high resolution close to the nuclei (all electrons)

$$\psi_i(\mathbf{r}) = \sum_{\mu} C_{\mu i} \varphi_{\mu}(\mathbf{r}) \rightarrow \sum_{\mu} C_{\mu i} \bar{\varphi}_{\mu}(\mathbf{R}) = \psi_i(\mathbf{R})$$

-Quickstep-
TOTAL DENSITY

8	0.000000	0.000000	0.000000		
54	0.349949	0.000000	0.000000		
54	0.000000	0.349949	0.000000		
63	0.000000	0.000000	0.362827		
5	0.000000	9.448631	9.448631	11.338357	
5	0.000000	9.448631	9.448631	14.683172	
1	0.000000	11.322313	9.448631	13.010846	
1	0.000000	7.574948	9.448631	13.010846	
1	0.000000	9.448631	11.416848	15.778669	
1	0.000000	9.448631	7.480413	15.778669	
1	0.000000	9.448631	7.480413	10.242860	
1	0.000000	9.448631	11.416848	10.242860	
0.16324E-08	0.14425E-08	0.13016E-08	0.12075E-08	0.11584E-08	0.11533E-08
0.11920E-08	0.12755E-08	0.14051E-08	0.15832E-08	0.18123E-08	0.20955E-08
0.24355E-08	0.28348E-08	0.32950E-08	0.38170E-08	0.44000E-08	0.50422E-08
0.57400E-08	0.64880E-08	0.72795E-08	0.81060E-08	0.89579E-08	0.98243E-08

B₂H₆



Spin Density

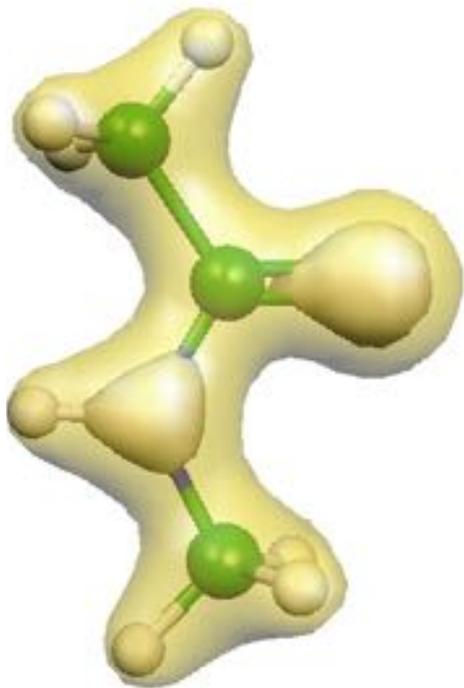
Spin polarized DFT calculations:

$$n^{(\alpha)}(\mathbf{r}) = \sum_{\mu\nu} P_{\mu\nu}^{(\alpha)} \varphi_{\mu}(\mathbf{r}) \varphi_{\nu}(\mathbf{r}) \quad n^{(\beta)}(\mathbf{r}) = \sum_{\mu\nu} P_{\mu\nu}^{(\beta)} \varphi_{\mu}(\mathbf{r}) \varphi_{\nu}(\mathbf{r})$$

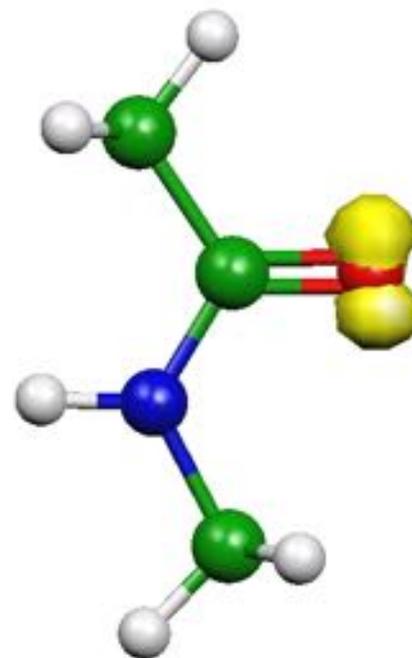
$$\Delta n_{\text{spin}}(\mathbf{r}) = n^{(\alpha)}(\mathbf{r}) - n^{(\beta)}(\mathbf{r}) \rightarrow \Delta n_{\text{spin}}(\mathbf{R})$$



$n(\mathbf{R})$

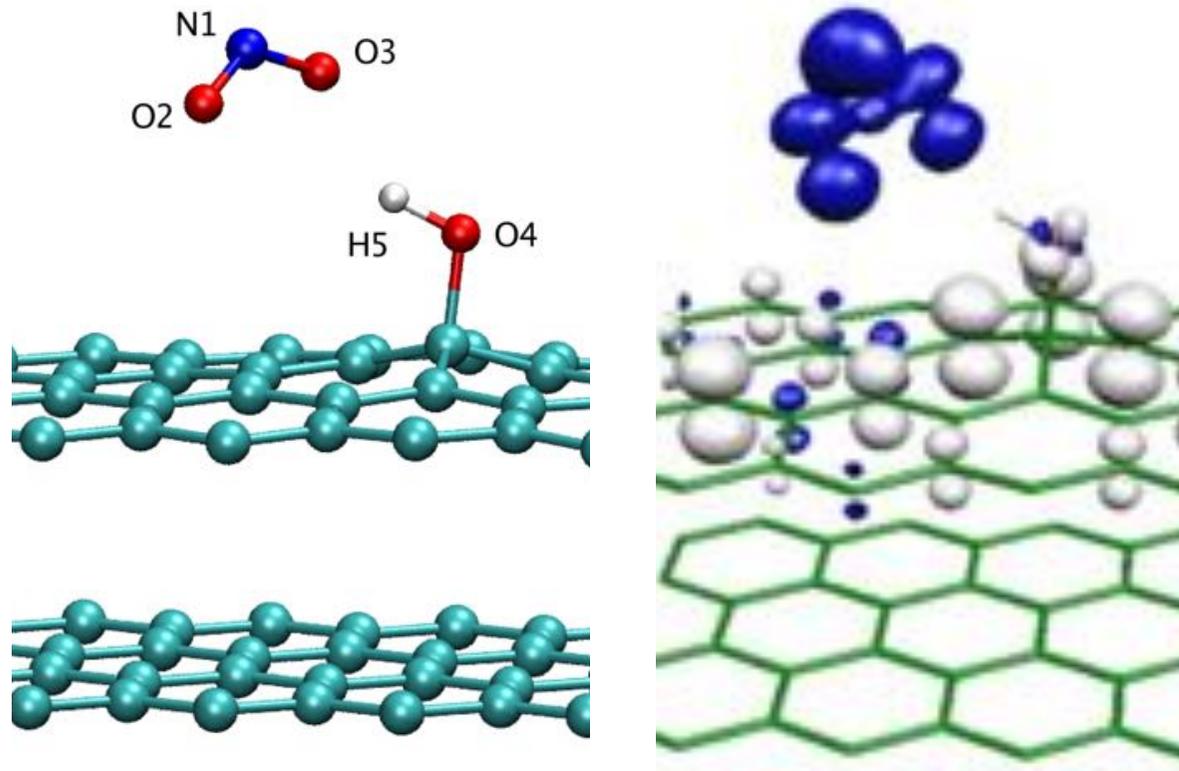


$\Delta n_{\text{spin}}(\mathbf{R})$



Not Localized Spin Density

Dissociation of HNO_3 catalysed by graphite



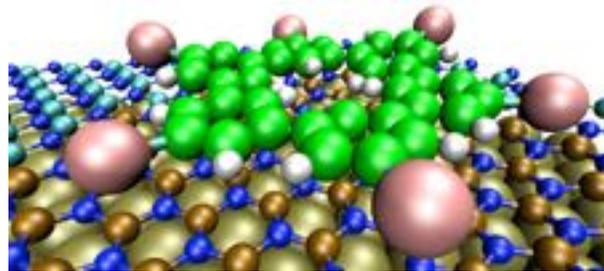
Density Difference

Changes in the electronic density due to interactions, e.g., molecule adsorbed on substrate

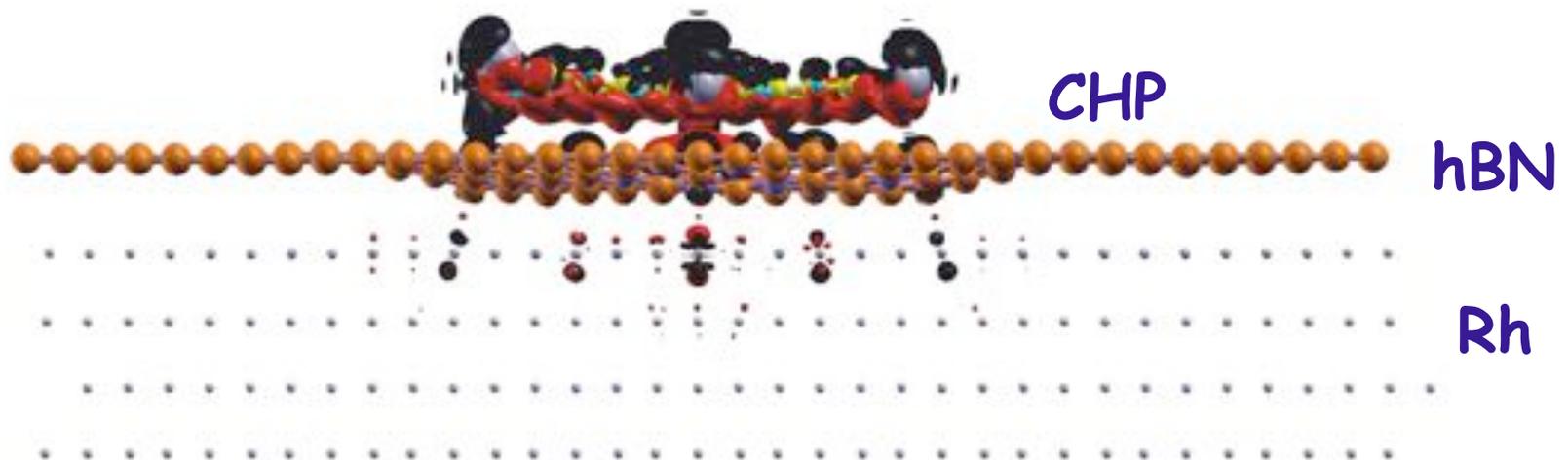
$$E_{\text{ads}} = E_{\text{tot}} - (E_{\text{sub}}^{\circ} + E_{\text{mol}}^{\circ})$$

$$E_{\text{int}} = E_{\text{tot}} - (E_{\text{sub}}^f + E_{\text{mol}}^f)$$

CHP on hBN/Rh (5 eV)



$$\Delta n_{\text{int}}(\mathbf{r}) = n_{\text{tot}}(\mathbf{r}) - (n_{\text{sub}}^f(\mathbf{r}) + n_{\text{mol}}^f(\mathbf{r}))$$



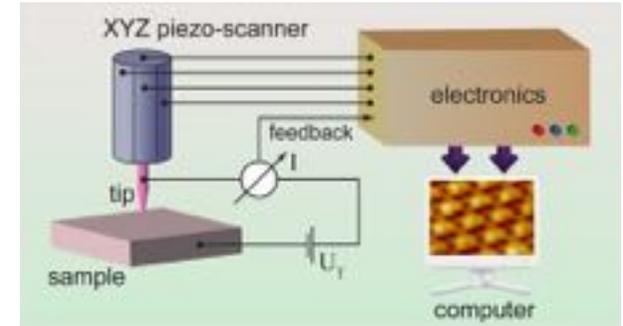
STM images

Tersoff-Hamann approximation to mimic the iso-current topography

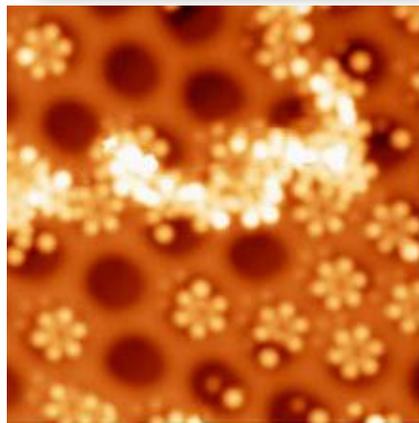
$$n_b(\mathbf{r}) = \sum_{i: \varepsilon_i \in [E_f - V_b : E_f]} \left[\sum_{\mu\nu} C_{\mu i}^* C_{\nu i} \varphi_{\mu}(\mathbf{r}) \varphi_{\nu}(\mathbf{r}) \right] \rightarrow n_b(\mathbf{R})$$

Find height at constant energy projected density

$$z : n_b(X, Y, z) e^{-2kR_0 \sqrt{\Phi(X, Y, z)}}$$

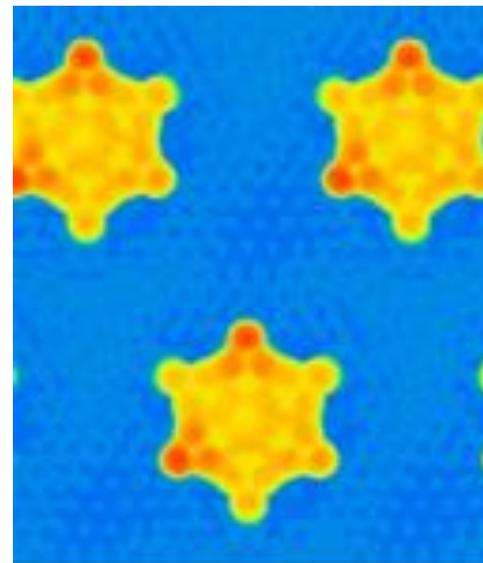
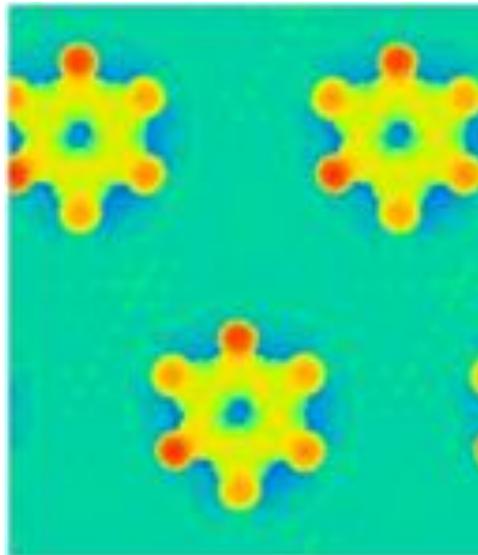


V_b = -1310 mV

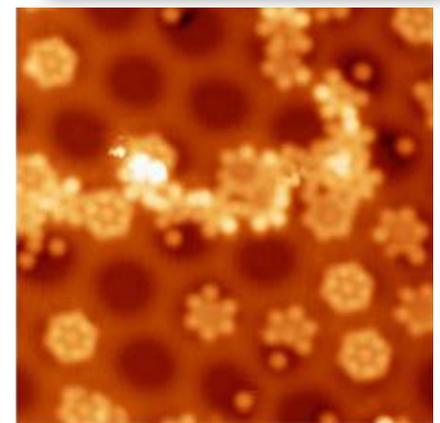


occupied states

CHP on hBN/Rh (5 eV)



V_b = +1480 mV



unoccupied states

Position operator for isolated systems

One body operator

$$\hat{X} = \sum_{i=1}^N x_i$$

Expectation value

$$\langle X \rangle = \langle \Psi | \hat{X} | \Psi \rangle = \int x n(x) dx$$

Gauge invariance

$$\langle X \rangle_R = \langle \Psi | \hat{X} + R | \Psi \rangle = \langle X \rangle_0 + R \int n(x) dx = \langle X \rangle_0 + RZ$$

Position Operator with PBC

Expectation value of the position operator

$$\hat{\mathbf{R}} = \sum_i \hat{\mathbf{r}}_i \quad \langle \mathbf{R} \rangle = \langle \Psi | \hat{\mathbf{R}} | \Psi \rangle = \int \mathbf{r} n(\mathbf{r}) d\mathbf{r} \quad (3D)$$

Wavefunctions are periodic, result of an operator has also to be periodic

$$\Psi(\mathbf{r}) = \Psi(\mathbf{r} + \mathbf{L}) \quad \hat{\mathbf{R}}\Psi(\mathbf{r}) \neq (\hat{\mathbf{R}} + \mathbf{L})\Psi(\mathbf{r} + \mathbf{L})$$

Many-body periodic position operator (1D)

$$\langle X \rangle = \frac{L}{2\pi} \text{Im} \ln \langle \Psi | e^{i\frac{2\pi}{L}\hat{X}} | \Psi \rangle$$

Berry Phase

Electronic polarisation

$$P_{\text{el}} = \lim_{L \rightarrow \infty} \frac{e}{2\pi} \text{Im} \ln \langle \Psi | e^{i\frac{2\pi}{L}\hat{X}} | \Psi \rangle$$

Resta, R. (1998). Quantum-Mechanical Position Operator in Extended Systems. *Physical Review Letters*, **80**(9), 1800–1803. and more by R. Resta

Polarisation

Many-body wavefunction (Bloch orbitals)

$$|\Psi\rangle = A \prod_i \prod_s \psi_{q_s, i}(\mathbf{r})$$

New set of Bloch orbitals

$$\tilde{\psi}_{q_s, m}(x) = e^{-i \frac{2\pi}{L} x} \psi_{q_s, m}(x) \quad \frac{2\pi}{L} = G_1$$

Expectation value from overlap of determinants = determinants of overlap of orbitals

$$\langle X \rangle = -\frac{L}{2\pi} \text{Im} \ln \langle \Psi | \tilde{\Psi} \rangle = -\frac{L}{2\pi} \text{Im} \ln \det S$$

$$S_{ij}^\alpha = \int \psi_i(\mathbf{r}) e^{i \mathbf{G}_{\alpha 1} \cdot \mathbf{r}} \psi_j(\mathbf{r}) d\mathbf{r}$$

$$P^\alpha = \frac{2e}{\mathbf{G}_{\alpha 1}} \text{Im} \ln [\det \mathbf{S}^\alpha]$$

Localised Orbitals

* Boys spread of the orbitals through a 2-el operator $\Omega = \sum_i \langle \psi_i \psi_i | (\mathbf{r}_1 - \mathbf{r}_2)^2 | \psi_i \psi_i \rangle$

* With PBC, localize equivalent to minimize

$$\Omega = \frac{1}{2\pi} \sum_s \sum_i \omega_s (1 - (|z_{si}|^2)) \quad z_{si} = \int d\mathbf{r} e^{i\mathbf{k}_s \cdot \mathbf{r}} |\psi_i(\mathbf{r})|^2$$

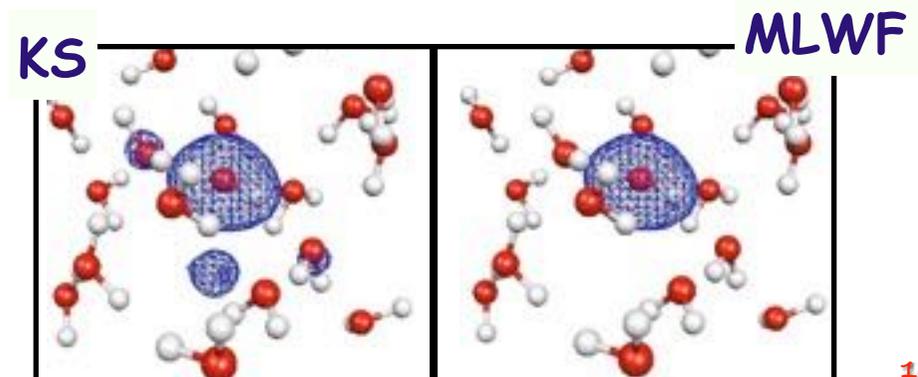
* Find the unitary transformation

$$\tilde{\psi}_i(\mathbf{r}) = \sum_j U_{ij} \psi_j(\mathbf{r}) \quad \frac{\partial \Omega}{\partial U_{ij}} = 0$$

* Iterative procedure (parallel Jacobi rotations)

* Centre of the charge distribution of the rotated orbital

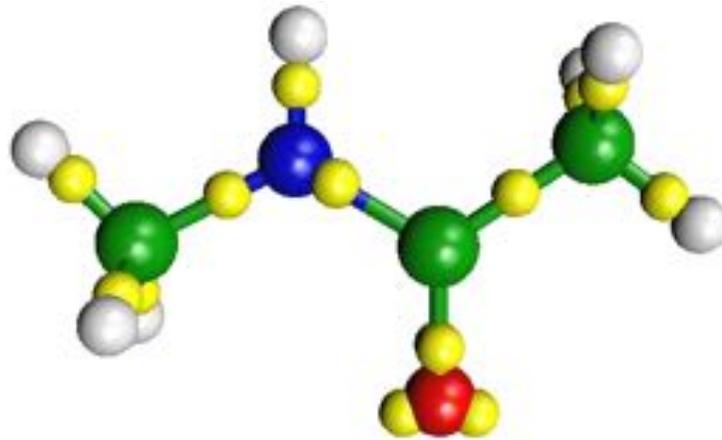
$$\langle r_{si} \rangle = \frac{L_s}{2\pi} \text{Im} \ln z_{si}$$



Wannier Centers (3D)

For a generalised 3D box \mathbf{h} , for each maximally localised Wannier orbital

$$z_{si} = \frac{1}{\text{deth } \mathbf{h}} \int d\mathbf{r} e^{i\mathbf{k}_s \cdot \mathbf{r}} |\psi_i(\mathbf{r})|^2 \quad \mathbf{r}_{si} = - \sum_t \frac{\mathbf{h}_{st}}{2\pi} \text{Im} \ln z_{ti}$$



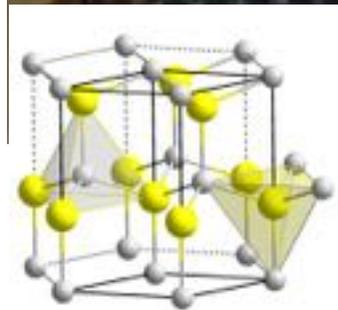
Molecular dipole moment from Wannier centres

$$\mu_s^W = e \sum_i \mathbf{r}_{si} = -e \sum_i \sum_t \frac{\mathbf{h}_{st}}{2\pi} \text{Im} \ln z_{ti} = -e \sum_t \frac{\mathbf{h}_{st}}{2\pi} \text{Im} \ln \prod_i z_{ti}$$

IR spectra from dipole moment autocorrelation function

$$\alpha(\omega) = \frac{4\pi \omega \tanh(\beta\hbar\omega/2)}{\hbar n(\omega) cV} \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle P(t) \cdot P(0) \rangle$$

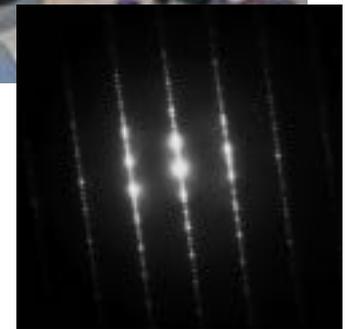
Materials Science Research



theoretical model



sample

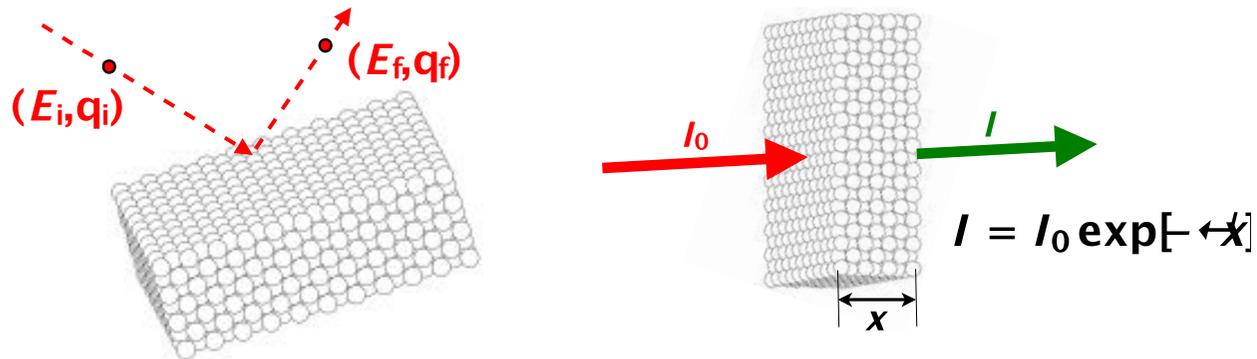


measurement

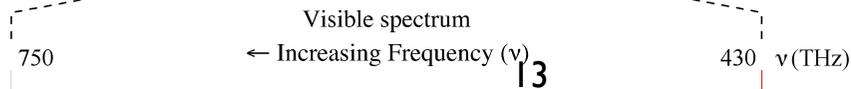
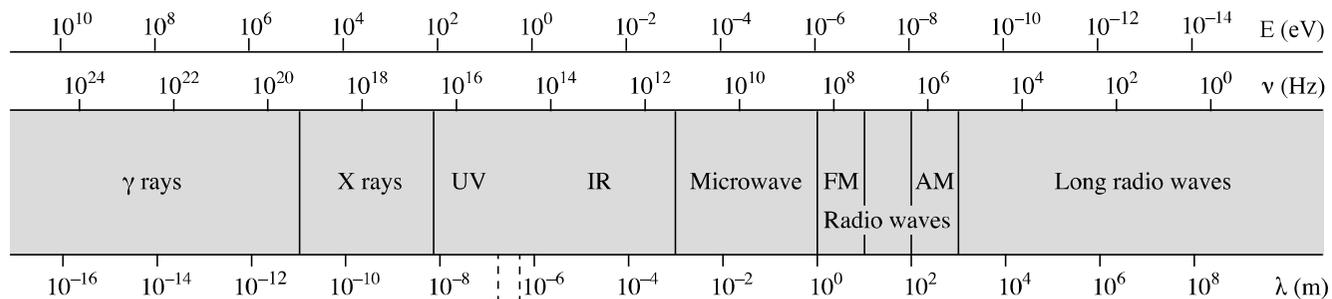
interpretation

Spectroscopies

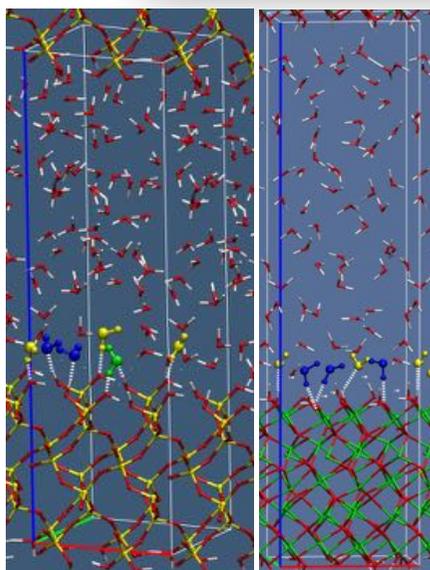
methods to study the properties of matter (atoms, molecules, solids) by investigating its interactions with particles (photons, electrons, neutrons, ions)



Electromagnetic Spectrum

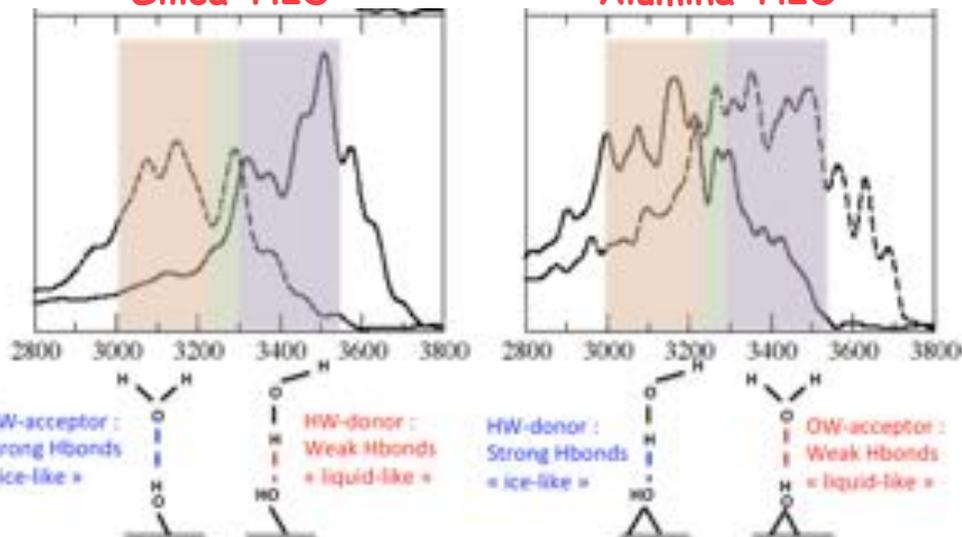


Various Spectroscopic Methods



Silica-H₂O

Alumina-H₂O

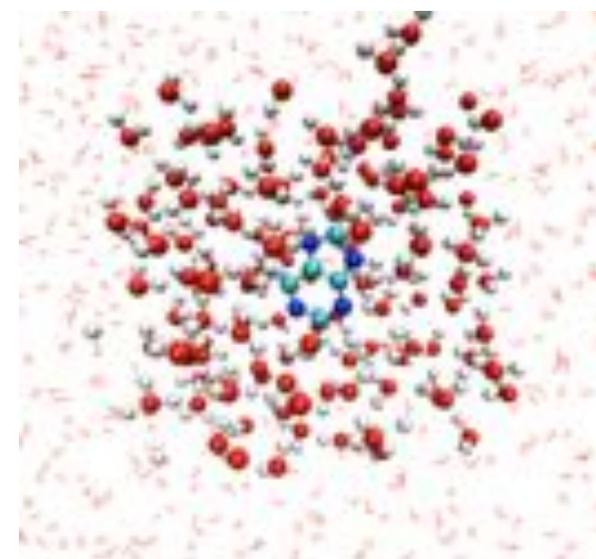


Vibrational spectroscopy

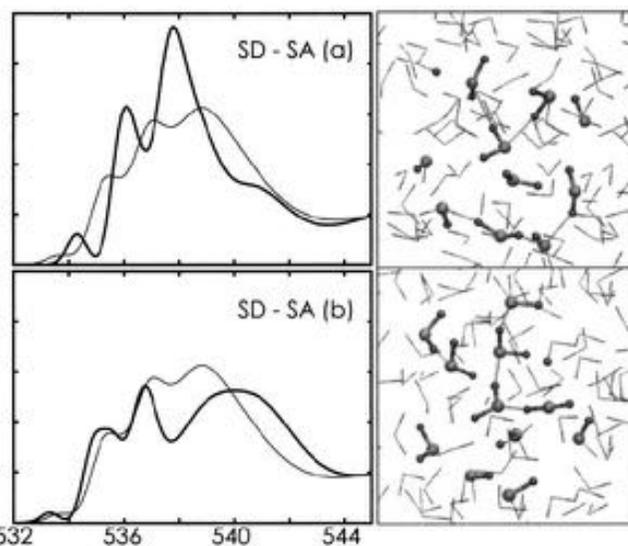
Silica-H₂O Alumina-H₂O

Gaigeot, M.-P. et al (2012). *J Phys Cond Matt*, 24, 124106.

NMR/EPR



Hydrated Adenine: QM/MM NMR



XANES

Iannuzzi, M. M. (2008) *JCP*, 128, 204506.

Weber, V. V., et al (2009). *JCP*, 131, 014106

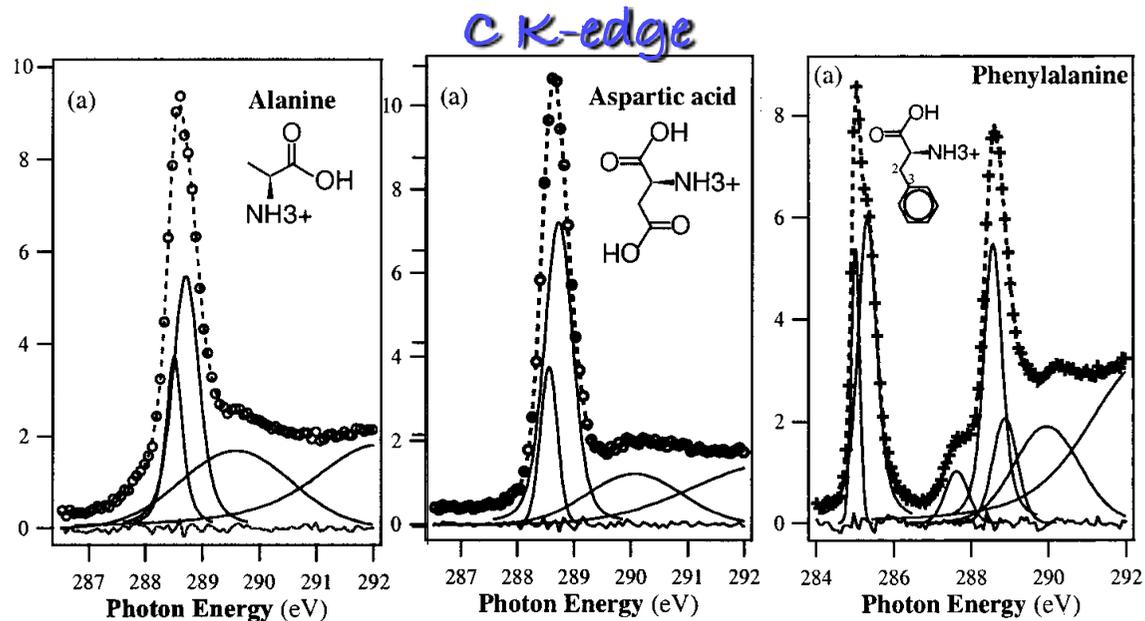
X-ray absorption Fine Structure

- * 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
- * Challenging interpretation of the spectra
- * Central role of theoretical approach
 - charge transfer
 - nature of bonding
 - hybridization
 - chemical environment

X-ray Absorption Simulations

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

XAS
of amino-acid
series



Kaznacheyev et al,
JPC A, 106, 3153 (2002)

Computational spectroscopy (inner-shell, NMR, ..) often requires
approaches beyond cluster model or PP approximation:

Efficient scheme for AE in condensed matter
AE linear response theory

Core-hole Creation and Decay

XES/NEXAFS local probes for electronic and geometric properties

Unoccupied levels, symmetry resolved

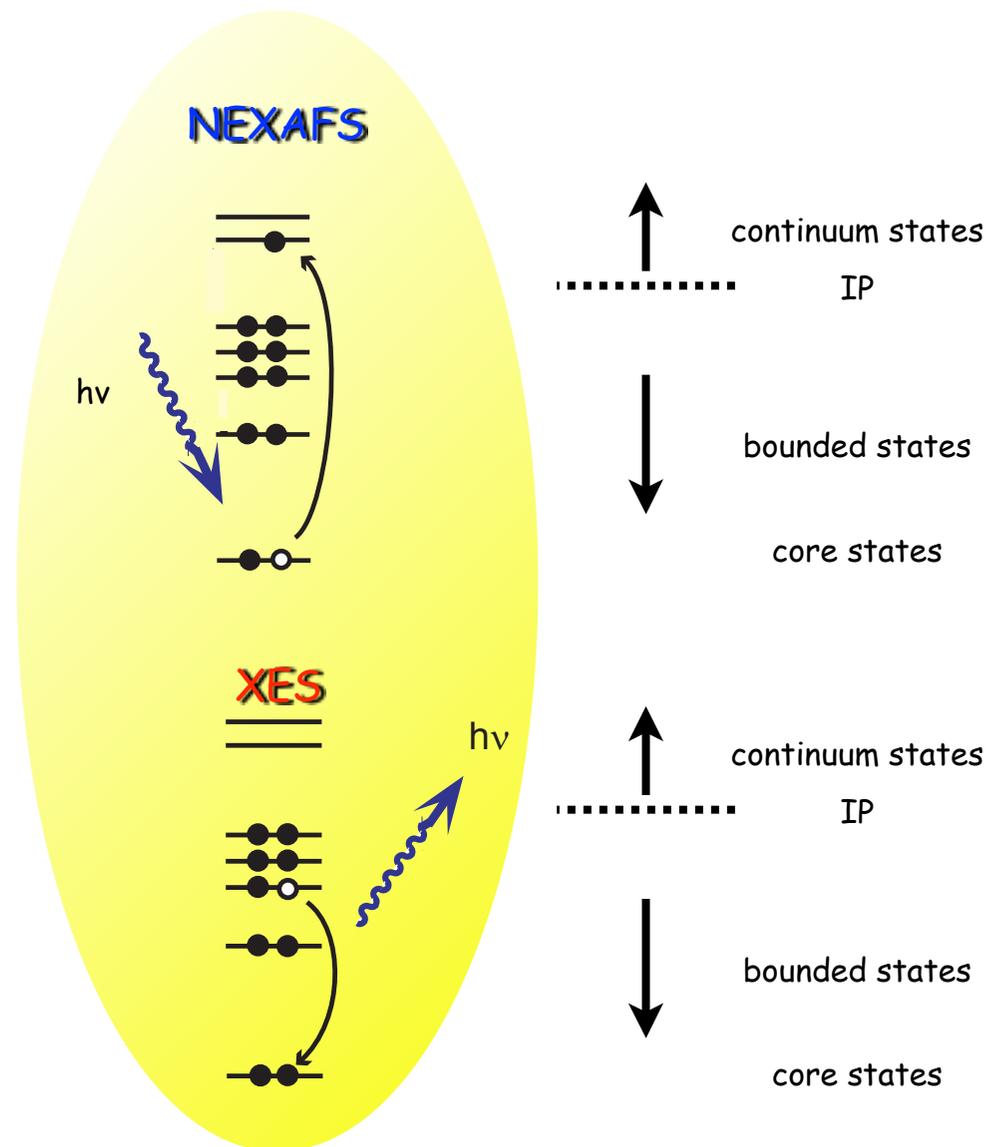
One step process
Final state: core-hole

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)

$$V(t) = \frac{e}{mc} \mathbf{A} \cdot \mathbf{p}$$

- * 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) $kr_s = \frac{2\pi}{\lambda} r_s \ll 1$

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

- * Equivalent operators

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

length form

Δ SCF

* Ground state KS virtual orbitals

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

* Parametric SCF solution

$$\tilde{E}[n(\{f_i\})] \quad n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2$$

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

* Numerically not stable : difference between 2 SCF calculations

* Higher excited states states (collapse)

* Not orthogonal MOs sets

$$P_{if} \propto |\langle f | \mathbf{e} \cdot \mathbf{p} | i \rangle|^2 \rho_i(E)$$

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 $\partial E / \partial f$: balance between initial and final state contributions

- * One calculation for each excitation

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

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 ΔSCF

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

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

- * 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

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

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

* Half Core Hole or Full Core Hole (LSD)

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

* SCF with modified occupation numbers

* Oscillator strengths in the velocity form

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

Input XAS

&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 1

ATOMS_LIST 1

ADDED_MOS 1000

&LOCALIZE

&END

&PRINT

&PROGRAM_RUN_INFO

&END

&RESTART

FILENAME ./hch_dim_p12_ud

&EACH

XAS_SCF 15

&END

ADD_LAST NUMERIC

&END

&XAS_SPECTRUM

FILENAME ./hch_dim_p12_ud

&END

&XES_SPECTRUM

FILENAME ./hch_dim_p12_ud

&END

&END

&END XAS

Broadening and Shift

Convolution using Gaussian functions with adapted width

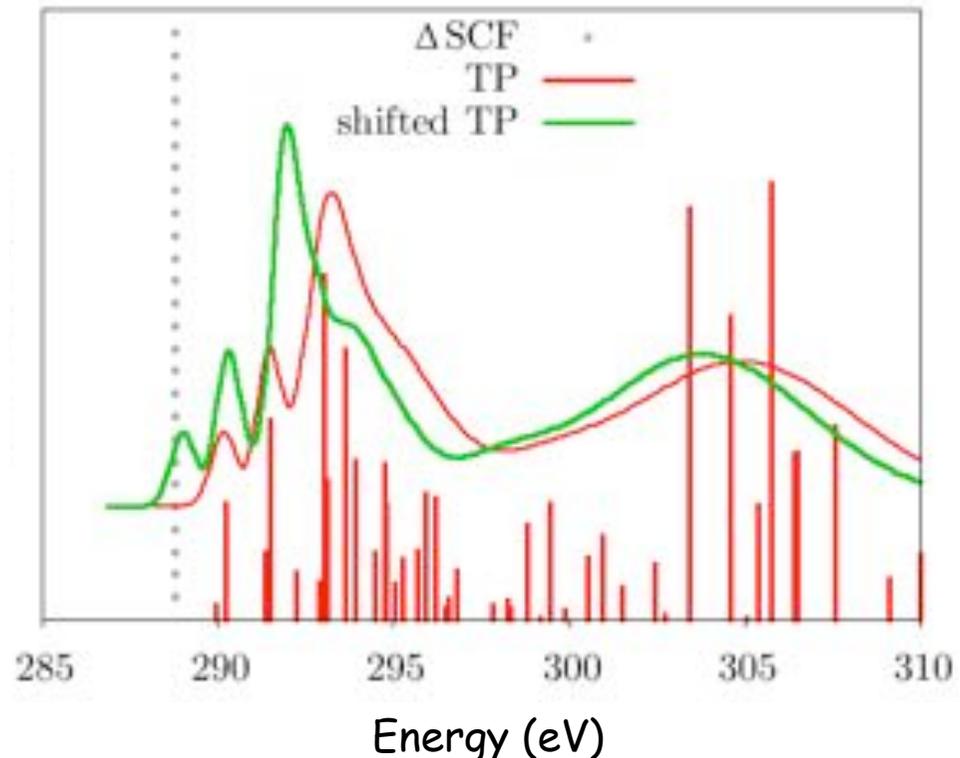
$$f(x) = I_{SL} \frac{1}{\sigma\sqrt{2\pi}} e^{-(x-x_{SL})^2/(2\sigma^2)}$$

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

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

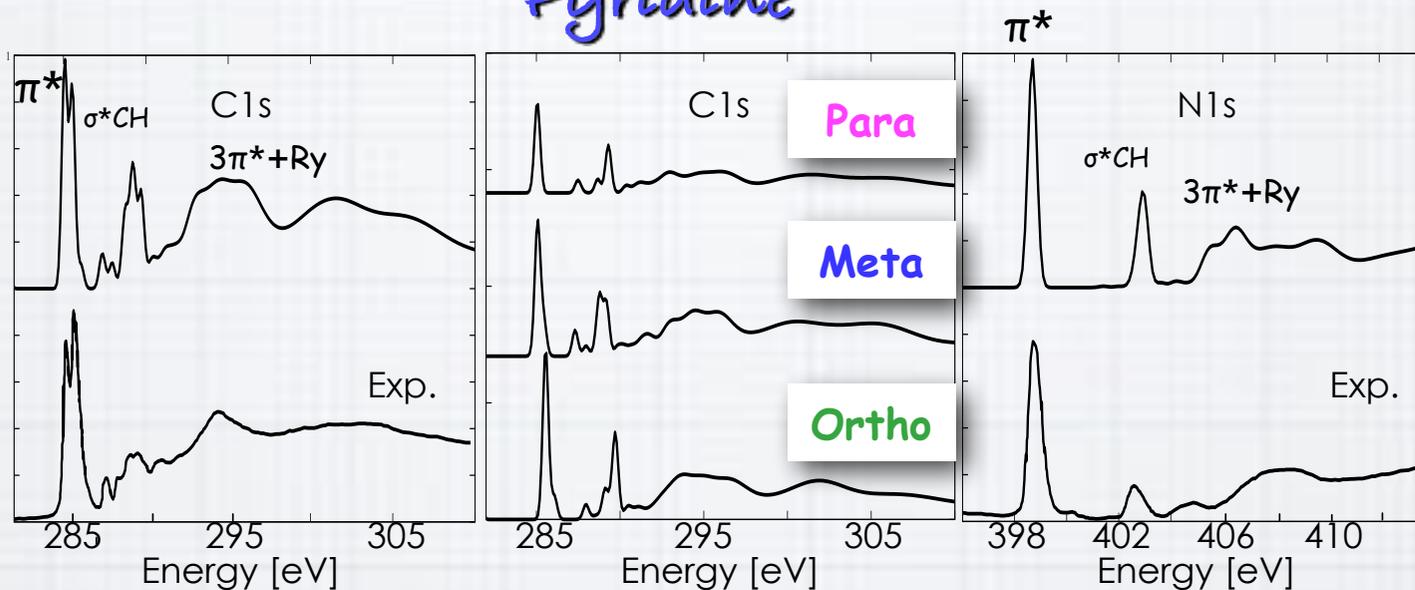
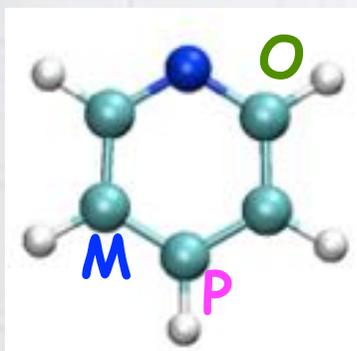
$$\sigma_{\max} = 8 \text{ eV}$$

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

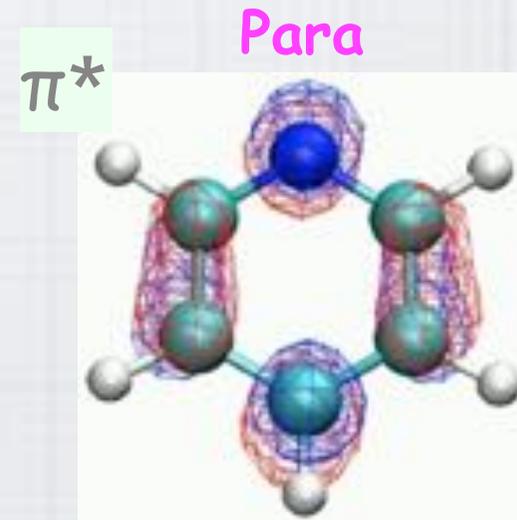
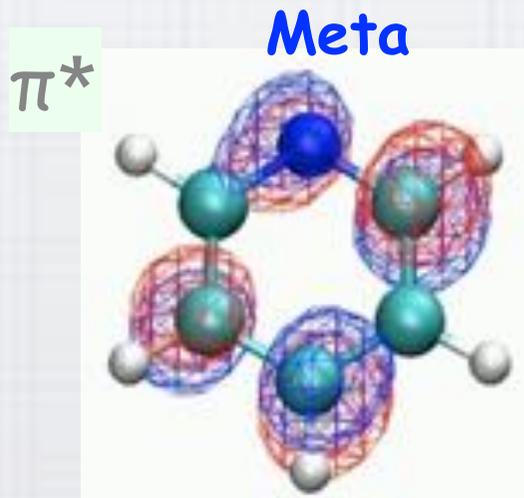


Small Molecules: atomic environment

Pyridine

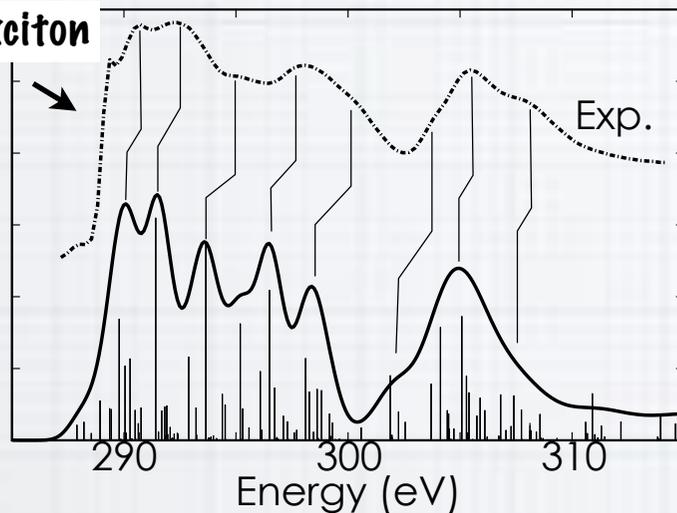


Chemical Shift



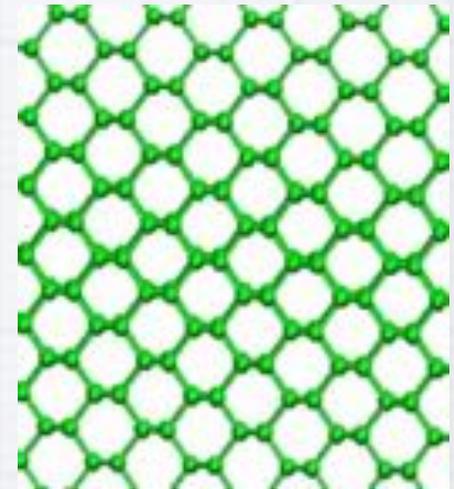
Extended Systems: supercell approach

Core 1s exciton



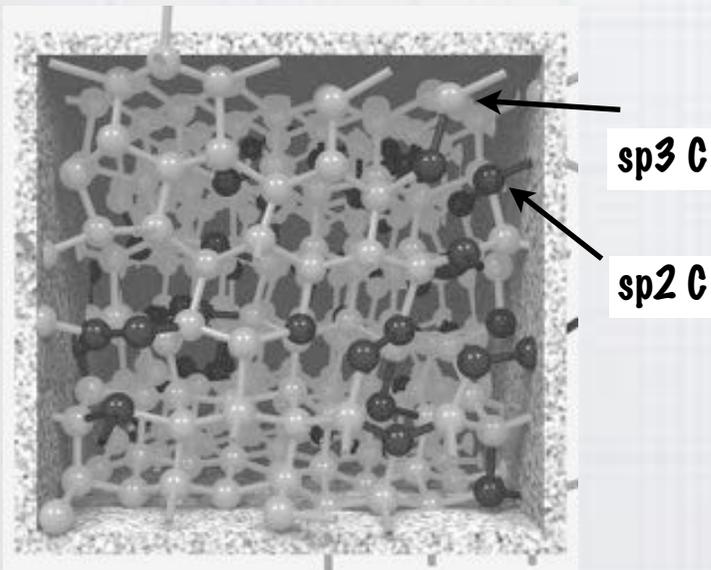
Diamond

512 C atoms
pristine crystal
6-31G(dp)
PBE



Graphite under shock compression

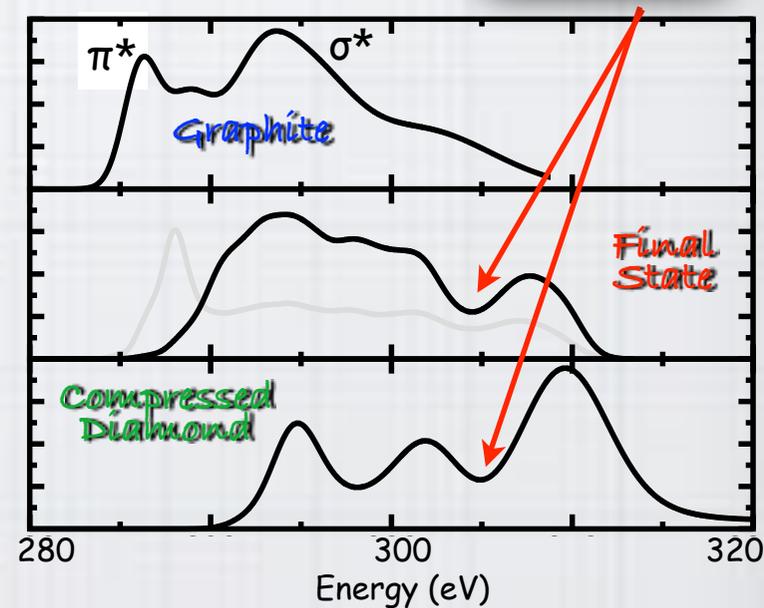
second gap



uniaxial loading
shock 12 km/s (>130GPa)

Martensitic transition
graphite → diamond

high defect
concentration



Magnetic Shielding

Interaction between \mathbf{B} and a spin 1/2 nucleus with spin angular momentum $\hbar\mathbf{I}_k$

$$H = - \sum_k \gamma_k \hbar \mathbf{I}_k (1 + \overleftrightarrow{\sigma}) \mathbf{B}_0$$

in diamagnetic materials the \mathbf{B}_{ind} arises only from the induced orbital currents \mathbf{j}

$$\mathbf{B}_{\text{ind}} = - \overleftrightarrow{\sigma}_k \mathbf{B}_0 \qquad \mathbf{B}_{\text{ind}}(\mathbf{r}) = \frac{1}{c} \int d^3r' \mathbf{j}(\mathbf{r}') \times \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|^3}$$

second derivative of electronic energy

$$\overleftrightarrow{\sigma}_k(\mathbf{R}) = \frac{\partial^2 E}{\partial \mathbf{B} \partial \mathbf{m}_k}$$

chemical shift w.r.t. reference

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

Shielding and g tensors

applied B^0 along x

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

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

spin density

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

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

free el. g value

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

unperturbed kinetic energy

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

induced spin current
effective pot.

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

magnetic field from current

Linear Response

$$-i \sum_{il} \left(H_{kl} \delta_{ij} - S_{kl} \int \psi_i^{(0)}(\mathbf{r}) H(\mathbf{r}) \psi_j^{(0)}(\mathbf{r}) d\mathbf{r}^3 \right) C_{ij}^{(1)} = \sum_l H_{kl(j)}^{(1)} C_{lj}^0$$

The magnetic field \mathbf{B} represented by the vector potential \mathbf{A}

$$\mathbf{A}(\mathbf{r}) = -\frac{1}{2}(\mathbf{r} - \mathbf{R}_g) \times \mathbf{B}_0 \quad \hat{\mathbf{p}} \rightarrow \hat{\mathbf{p}} - e\mathbf{A}(\hat{\mathbf{r}}) \quad \hat{\mathbf{p}} = -i\hbar\nabla$$

First order and second order perturbation terms in the Hamiltonian

$$\mathbf{H}^{\text{pert}} = -\frac{e}{m} \hat{\mathbf{p}} \cdot \mathbf{A}(\hat{\mathbf{r}}) + \frac{e^2}{2m} \mathbf{A}(\hat{\mathbf{r}}) \cdot \mathbf{A}(\hat{\mathbf{r}}) = \mathbf{H}^1 + \mathbf{H}^2$$

First order correction of the electronic ground state

$$\Psi(\mathbf{r}) = \Psi^0(\mathbf{r}) + B\Psi^1(\mathbf{r}) \quad \langle \psi_i^0 | \psi_j^1 \rangle = 0 \quad \forall i, j \quad \text{imaginary response} \\ n^1=0$$

Gauge origin problem

$$\mathbf{j}(\mathbf{r}) = -\frac{e^2}{m} \mathbf{A}(\mathbf{r}) \sum_k |\psi_k^0(\mathbf{r})|^2 - \frac{i\hbar e}{m} \sum_k \langle \psi_k^0 | [\nabla | \mathbf{r} \rangle \langle \mathbf{r} | + | \mathbf{r} \rangle \langle \mathbf{r} | \nabla] | \psi_k^1 \rangle$$

Induced Current

Convergence w.r.t basis set strongly depend on gauge $\mathbf{R}_g = \mathbf{d}(\mathbf{r})$

$$\mathbf{j}(\mathbf{r}) = \sum_k \mathbf{j}_k(\mathbf{r}) = \sum_k \mathbf{j}_k^d(\mathbf{r}) + \mathbf{j}_k^p(\mathbf{r})$$

diamagnetic

paramagnetic

Gauge invariance in molecular and periodic systems

GIAO

$$\mathbf{R}_g = \mathbf{R}_\mu$$

accurate but involved and not efficient

IGLO

$$\mathbf{R}_g = \mathbf{d}_k$$

IGAIM

$$\mathbf{R}_g = \mathbf{R}_I$$

gauge terms on the perturbation functional

no diamagnetic term, computationally convenient, slow

converging with basis set quality

CSGT

$$\mathbf{R}_g = \mathbf{r}$$

Calculation of Induced Currents

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

DFPT

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

dependency on ψ^0

Partitioning of the perturbation operator

$$H_{\mu\nu}^L(j) = -i \langle \mu | (\hat{\mathbf{r}} - \mathbf{d}_j) \times \nabla | \nu \rangle \quad H_{\mu\nu}^P = -i \langle \mu | \nabla | \nu \rangle \quad H_{\mu\nu}^{\Delta_i} = -i (\mathbf{d}_i - \mathbf{d}_j) \times \langle \mu | \nabla | \nu \rangle$$

x-component of linear current density j induced from B^0 applied along y

$$j_{xy}(\mathbf{r}) = -\frac{1}{2c} \sum_i \sum_{\mu\nu} \left[C_{\mu i}^0 \left(C_{\nu i}^{L_y} + (\mathbf{R}_g - \mathbf{d}_i)_x C_{\nu i}^{P_z} - (\mathbf{R}_g - \mathbf{d}_i)_z C_{\nu i}^{P_x} - C_{\nu i}^{\Delta_{iy}} \right) \right. \\ \times \left. ([\nabla_x \varphi_\mu(\mathbf{r})] \varphi_\nu(\mathbf{r}) - \varphi_\mu(\mathbf{r}) [\nabla_x (\varphi_\nu(\mathbf{r}))]) \right] \\ + (\mathbf{r} - \mathbf{R}_g)_z n(\mathbf{r}) \quad \text{diamagnetic}$$

GAPW Chemical Shift

applied B^0 along x

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

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

GAPW
induced
current density

from soft term in reciprocal space

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

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

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

from local terms by integration on spherical grids

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

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 SiH₄

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 Calculated:

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

Localization procedure through Jacobi rotations

*** 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

Write the resulting psi1 in restart file... not implemented yet

NMR Output for SiH₄

Final NMR output

Initialization of the NMR environment

```
NMR|   Shift factor (ppm)                9.863793E-04
NMR| Shift factor gapw (ppm)             5.325134E+01
NMR|   Chi factor (SI)                   1.972757E+01
NMR| Conversion Chi (ppm/cgs)           6.022045E-02
NMR| Conversion Chi to Shift             1.047198E-04
NMR| Shielding tensor computed for  5 atoms
Integrated j_xx(r): G-space= 0.4608768062028217E+00 R-space= 0.4608768062028132E+00
Integrated j_yx(r): G-space= -0.2077039113301925E+01 R-space= -0.2077039113301958E+01
Integrated j_zx(r): G-space= -0.2039298825792812E+01 R-space= -0.2039298825793122E+01
Checksum R-integrated j= 0.2947072888403525E+01
WARNING WARNING WARNING WARNING WARNING WARNING WARNING
chi_analytic: gapw= T
WARNING WARNING WARNING WARNING WARNING WARNING WARNING
Integrated local j_xx(r)= -0.9615000648009942E-06
Integrated local j_yx(r)= -0.4802383200079088E-04
Integrated local j_zx(r)= 0.3935076278575146E-04
```

.....

```
Checksum Chi = 0.6343893866003933E+03
Checksum Shifts = 0.8086834144167068E+03
```

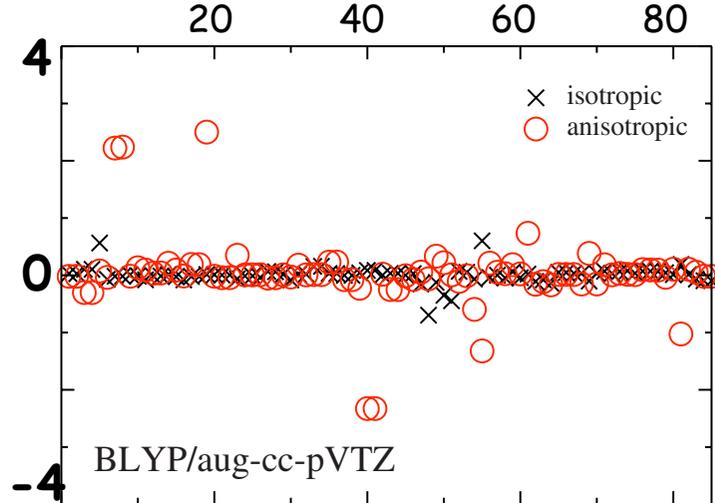
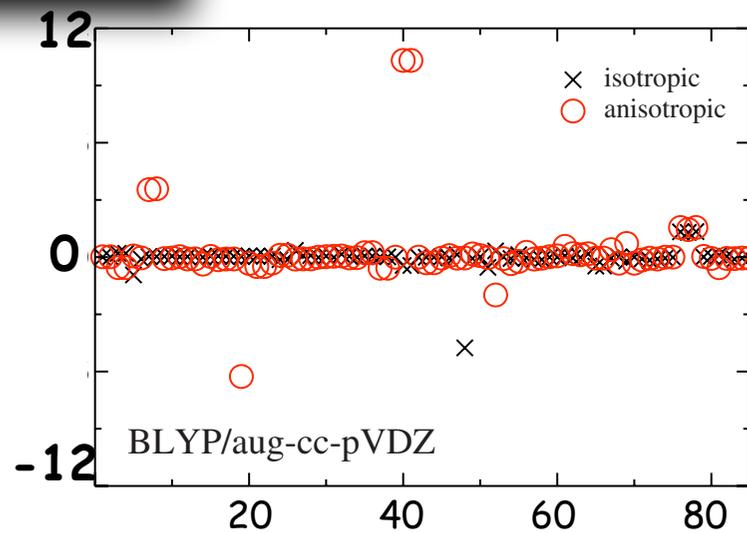
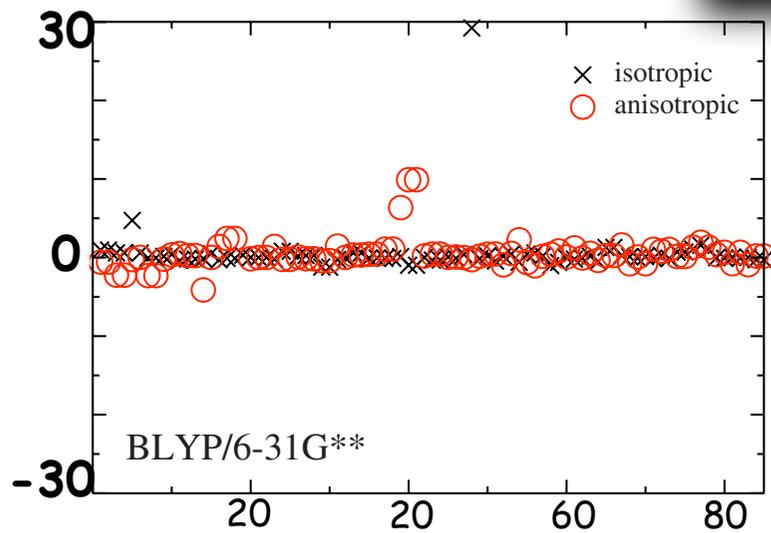
```
=====
ENDED LINRES CALCULATION
=====
```

IGAIM-GAPW

Test set composed of 26 small molecules

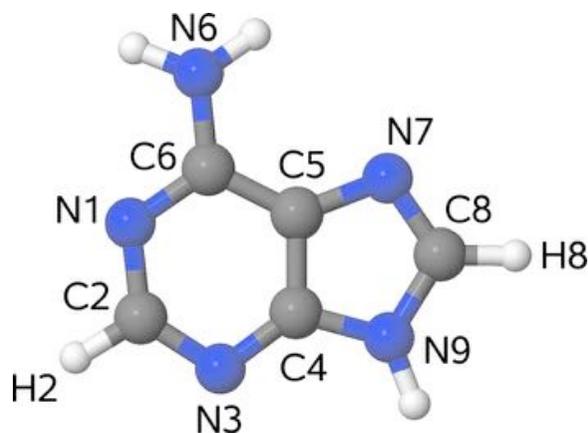
C_2H_2 , CH_2O , CH_3Cl , CH_3F , CH_4 , Cl_2 , CO_2 , F_2 , FCI , H_2O_2 , H_2O , H_2 , H_2S ,
 HCl , HCN , $HCOOH$, HF , HNO_3 , N_2O , N_2 , NH_3 , NO_2 , O_2 , O_3 , PH_3 , SO_2

Relative Error %



Isolated Adenine

Geometry optimized in gas phase : BLYP/6-31G(dp)



	CP2K IGAIM BLYP/cc-p-VQZ	G03 IGAIM BLYP /cc-pVQZ BLYP /aug-cc-pVZ5		CPMD CSGT BLYP/200Ry	
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

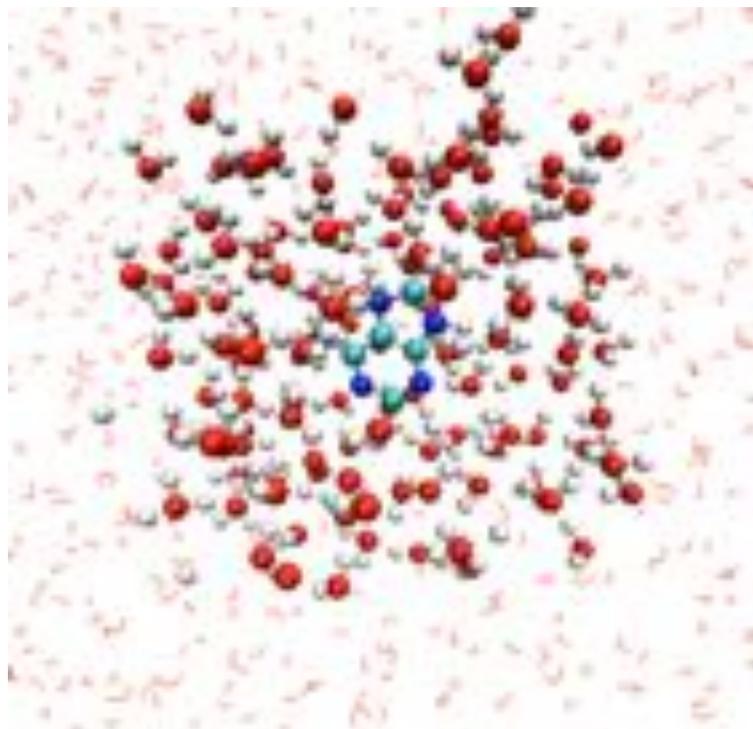
PP correction

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

TMS
MeNO₂
benz.
pyrid.
pyrrol
alidine

Hydrated Adenine

QM/MM with 827 H₂O: snapshot from classical MD



CP2K
IGAIM
BLYP/cc-p-VQZ

	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