KS matrix formulation when the wavefunction is expanded into a basis

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

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

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

\[ P = \text{PSP} \]

KS total energy

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

Matrix formulation of the KS equations

\[ \textbf{K}(C)C = \textbf{T}(C) + \textbf{V}_{\text{ext}}(C) + \textbf{E}^H(C) + \textbf{E}^{xc}(C) = \text{SC}\varepsilon \]
Classes of Basis Sets

- Extended basis sets, \textbf{PW} : condensed matter
- Localised basis sets centred at atomic positions, \textbf{GTO}

\textbf{Idea of GPW:} auxiliary basis set to represent the density

- Mixed (GTO+PW) to take best of two worlds, \textbf{GPW}
- Augmented basis set, \textbf{GAPW}: separated hard and soft density domains
GPW Ingredients

linear scaling KS matrix computation for GTO

- Gaussian basis sets (many terms analytic)
  \[ \psi_i(r) = \sum_{\alpha} C_{\alpha i} \phi_\alpha(r) \]
  \[ \phi_\alpha(r) = \sum_{m} d_{m \alpha} g_m(r) \]
  \[ g_m(r) = x^m_x y^m_y z^m_z e^{-\alpha_m r^2} \]

- 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

<table>
<thead>
<tr>
<th>Basis Set</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>O 6-31G*</td>
<td>GTH SZV-MOLOPT-GTH-q6</td>
</tr>
<tr>
<td>O 6-31G**</td>
<td>GTH BASIS_SETS ; BASIS_MOLOPT ; EMSL_BASIS_SETS</td>
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#### O 6-31Gx 6-31G**

<table>
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<tr>
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<td>O 6-31Gx 6-31G**</td>
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#### O GTH

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#### O 6-311++G3df3pd 6-311++G(3df,3pd)

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<td>O 6-311++G3df3pd 6-311++G(3df,3pd)</td>
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1. **Basis Set library**
2. **GTH_BASIS_SETS ; BASIS_MOLOPT ; EMSL_BASIS_SETS**
3. **O 6-31G**
   - **GTH**
   - **GTH SZV-MOLOPT-GTH-q6**
4. **O 6-31G**
   - **O 6-31G**
   - **O 6-31G**
   - **O 6-31G**
5. **O 6-311++G3df3pd 6-311++G(3df,3pd)**
   - **O 6-311++G3df3pd 6-311++G(3df,3pd)**
   - **O 6-311++G3df3pd 6-311++G(3df,3pd)**
   - **O 6-311++G3df3pd 6-311++G(3df,3pd)**

---

### Additional Information

- **Basis Set library** provides various options for basis sets, including GTH and 6-31G**.
- **GTH_BASIS_SETS** includes options like **GTH BASIS_SETS ; BASIS_MOLOPT ; EMSL_BASIS_SETS**.
- **O 6-31G** offers options such as **GTH SZV-MOLOPT-GTH-q6**.
- **O 6-31G** is used when more detailed and flexible basis sets are needed. For example, **O 6-31G** can be specified with different basis sets like **O 6-31G**.
- **O 6-311++G3df3pd 6-311++G(3df,3pd)** is another advanced basis set that can be selected when even more precision is required.

---

### Conclusion

By selecting the appropriate basis set, users can achieve better accuracy in their calculations and simulations, which is crucial in fields such as quantum chemistry and materials science.
The repository contains several GTO libraries

cp2k/data/

<table>
<thead>
<tr>
<th>ALL_BASIS_SETS</th>
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<th>BASIS_SET</th>
<th>BASIS_ZI JLSTRA</th>
<th>BASIS_MOLOPT</th>
<th>BASIS_MOLOPT_UCL</th>
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<tr>
<td>ALL_POTENTIALS</td>
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<td>HF_POTENTIALS</td>
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</tbody>
</table>

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
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&POTENTIAL
  PSEUDO_TYPE GTH
  &GTH_POTENTIAL
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    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
&ATOM

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

COULOMB_INTEGRALS ANALYTIC
EXCHANGE_INTEGRALS ANALYTIC

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  RELATIVISTIC DKH(2)
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    &XC_FUNCTIONAL PBE0
    &END XC_FUNCTIONAL
  &END XC
&END METHOD

&OPTIMIZATION
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  &END
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  &GTH_POTENTIAL
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    2
    0.22095592  1 18.33745811
    0.21133247  0
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&END POTENTIAL

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

&END ATOM
### GTH_POTENTIALS

\[
\begin{align*}
N_{\text{el}}(s) & \quad N_{\text{el}}(p) & \quad N_{\text{el}}(d) & \quad \ldots \\
r_{\text{loc}}^{P\text{P}} & \quad N_C & \quad C_1^{P\text{P}} & \quad \ldots & \quad C_{N_C}^{P\text{P}} \\
N_p & \\
r_1 & \quad n_{nl}^1 & \quad \{h_{ij}^1\}_{ij=1\ldots n^1} \\
r_2 & \quad n^2 & \quad \{h_{ij}^2\}_{ij=1\ldots n^2}
\end{align*}
\]

---

**C GTH-BLYP-q4**

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**N GTH-BLYP-q5**

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**Al GTH-PBE-q3**

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<td>0.56218949</td>
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---

*Roughly 20 parameters*
\[ E^{\text{el}}[n] = \sum_{\mu \nu} P_{\mu \nu} \left\langle \varphi_\mu \left| -\frac{1}{2} \nabla^2 + V_{\text{loc}} + V_{\text{nl}} \right| \varphi_\nu \right\rangle \]

\[ + \ 2\pi \Omega \sum_G \frac{\tilde{n}_{\text{tot}}^*(G) \tilde{n}_{\text{tot}}(G)}{G^2} + \sum_R \tilde{n}(R) V^{\text{XC}}(R) \]

\[ = \sum_{\mu \nu} P_{\mu \nu} \left( \left\langle \varphi_\mu \left| -\frac{1}{2} \nabla^2 + V^{\text{ext}} \right| \varphi_\nu \right\rangle + \sum_R V^{\text{HXC}}_{\mu \nu}(R) \varphi'_\mu(R) \right) \]

**Linear scaling KS matrix construction**
&FORCE_EVAL
  METHOD Quickstep

&DFT
  BASIS_SET_FILE_NAME GTH_BASIS_SETS
  POTENTIAL_FILE_NAME GTH_POTENTIALS
  LSD F
  MULTIPLICITY 1
  CHARGE 0
&DGRID
  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.
  &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

- Pseudopotential $\Rightarrow$ frozen core
- Augmented PW $\Rightarrow$ separate regions (matching at edges)
  LAPW, LMTO (OK Andersen, PRB 12, 3060 (1975))
- Dual representation $\Rightarrow$ localized orbitals and PW
  PAW (PE Bloechl, PRB, 50, 17953 (1994))
Partitioning of the Density

\[ n(r) = \sum_{\mu\nu} P_{\mu\nu} \varphi_{\mu}(r) \varphi_{\nu}(r) \]

\[ n = \tilde{n} + \sum_{A} n_{A} - \sum_{A} \tilde{n}_{A} \]

\[ \begin{cases} n(r) - \tilde{n}(r) = 0 & \text{for } r \in I \\ n_{A}(r) - \tilde{n}_{A}(r) = 0 & \text{for } r \in A \end{cases} \]

\[ n_{A}(r) = \sum_{\mu\nu} P_{\mu\nu} \chi_{\mu}^{A} \chi_{\nu}^{A} \]

\[ \tilde{n}(r) = \sum_{\mu\nu} P_{\mu\nu} \tilde{\varphi}_{\mu} \tilde{\varphi}_{\nu} \rightarrow \sum_{G} \hat{n}(G) e^{iG \cdot R} \]

Gaussian Augmented Plane Waves
Local Densities

\[ n_A(r) = \sum_{\mu \nu} P_{\mu \nu} \chi^{A}_\mu \chi^{A}_\nu \]

\( \chi_\mu \) projection of \( \varphi_\mu \) in \( \Omega_A \)
through atom-dependent \( d' \)

\[ \chi_\mu = \sum_\alpha d'_{\mu \alpha} g_\alpha(r) \]

projector basis (same size)

\( \{ p_\alpha \} \)

\( \lambda_\alpha = k^\alpha \lambda_{\text{min}} \)

\[ \langle p_\alpha | \varphi_\mu \rangle = \sum_\beta d'_{\mu \beta} \langle p_\alpha | g_\beta \rangle \]

\[ n_A(r) = \sum_{\alpha \beta} \left[ \sum_{\mu \nu} P_{\mu \nu} d'_{\mu \alpha} d'_{\nu \beta} \right] \]

\[ g_\alpha(r) g_\beta(r) = \sum_{\alpha \beta} P'_{\alpha \beta} g_\alpha(r) g_\beta(r) \]
Density Dependent Terms: XC

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

\[ \nabla n(\mathbf{r}) = \nabla \tilde{n}(\mathbf{r}) + \sum_A \nabla n_A(\mathbf{r}) - \sum_A \nabla \tilde{n}_A(\mathbf{r}) \]

\[ E[n] = \int V_{\text{loc}}(\mathbf{r}) n(\mathbf{r}) = \int \left\{ \tilde{V}_{\text{loc}}(\mathbf{r}) + \sum_A V^A_{\text{loc}}(\mathbf{r}) + \sum_A \tilde{V}^A_{\text{loc}}(\mathbf{r}) \right\} \times \left\{ \tilde{n}(\mathbf{r}) + \sum_A n_A(\mathbf{r}) - \sum_A \tilde{n}_A(\mathbf{r}) \right\} d\mathbf{r} \]

\[ = \int \left\{ \tilde{V}_{\text{loc}}(\mathbf{r}) \tilde{n}(\mathbf{r}) + \sum_A V^A_{\text{loc}}(\mathbf{r}) n_A(\mathbf{r}) - \sum_A \tilde{V}^A_{\text{loc}}(\mathbf{r}) \tilde{n}_A(\mathbf{r}) \right\} \]
Density Dependent Terms: ES

Non local Coulomb operator

\[ n^0(r) = \sum_A n^0_A(r) = \sum_A \left\{ \sum_L Q^L_A \, g^L_A(r) \right\} \]

Same multipole expansion as the local densities

\[ Q^L_A = \int \{ n_A(r) - \tilde{n}_A(r) + n^Z_A(r) \} \, Y_{lm}(\theta\phi) r^2 \, dr \sin(\theta) \, d\theta \, d\phi \]

\[ V[\tilde{n} + n^0] + \sum_A V[n_A + n^Z_A] - \sum_A V[\tilde{n}_A + n^0_A] \]

Interstitial region

Atomic region

Compensation charge
GAPW Functionals

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

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

on global grids via collocation + FFT

Local Spherical Grids

Analytic integrals

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
Separation into radial and angular contributions

\[ n_A(r) = \sum_{\alpha \beta} P_{\alpha \beta}^{A} r^{l_{\alpha}} e^{-\alpha_{\alpha} r^2} \mathcal{Y}_{\alpha m_{\alpha}}(\theta, \phi) r^{l_{\beta}} e^{-\alpha_{\beta} r^2} \mathcal{Y}_{\beta m_{\beta}}(\theta, \phi) \]

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

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

\[ \langle \alpha | V_{XC}^{A} | \beta \rangle \quad \langle \alpha | V_{H}^{A} | \beta \rangle \quad \text{integrated numerically on spherical grids} \]

Radial: Gauss-Chebyshev quadrature

Angular: Lebedev quadrature
&DFT  ...

&QS
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EXTRAPOLATION_ORDER 4
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METHOD GAPW
EPS_DEFAULT 1.0E-12
QUADRATURE GC_LOG
EPSFIT 1.0E-12
EPSISO 1.0E-12
EPSRH00 1.0E-8
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LMAXN1 6
ALPHA0_H 10
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POTENTIAL GTH-BLYP-q6
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RADIAL_GRID 200
&END KIND

&KIND 01
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RADIAL_GRID 200
&END KIND

&END DFT

&SUBSYS  ...

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POTENTIAL GTH-BLYP-q6
LEBEDEV_GRID 80
RADIAL_GRID 200
&END KIND

&KIND 01
ELEMENT 0
# 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

\[ C^* = \arg \min_C \{ E(C) : C^T SC = 1 \} \]


- 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))

\[
P(r, r') \propto e^{-c \sqrt{E_{\text{gap}} |r-r'|}}
\]

\[
P_{\mu\nu} = \sum_{pq} S_{\mu p}^{-1} S_{q \nu}^{-1} \int \int \varphi_p(r) P(r, r') \varphi_q(r') dr dr'
\]
Refined preconditioner, most effective during MD of large systems with well conditioned basis sets

Schiffmann, VandeVondele, JCP 142 244117 (2015)
&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

\[ E_{\text{band}} = \sum_{n} \frac{1}{\Omega_{\text{BZ}}} \int_{\text{BZ}} \varepsilon_{n \mathbf{k}} \Theta(\varepsilon_{n \mathbf{k}} - E_f) d^{3} \mathbf{k} \rightarrow \sum_{n} \sum_{k} w_{k} \varepsilon_{n \mathbf{k}} \Theta(\varepsilon_{n \mathbf{k}} - E_f) d^{3} \mathbf{k} \]

Rh band structure

\[ C_{KS} \text{ and } \varepsilon_{KS} \text{ needed} \]

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

\[ f_n \left( \frac{\varepsilon_n - E_f}{kT} \right) = \frac{1}{\exp\left( \frac{\varepsilon_n - E_f}{k_B T} \right) + 1} \]

Fermi-Dirac

\[ E \text{ no longer variational with respect to } f_n \]

Mermin functional: minimise the free energy

\[ F(T) = E - \sum_{n} k_B T S(f_n) \quad S(f_n) = -\left[ f_n \ln f_n + (1 - f_n) \ln(1 - f_n) \right] \]

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

\[ n^{\text{new}} = \sum_i \alpha_i n^{\text{inp}}_i \]

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

\[
\begin{bmatrix} J^{-1} \end{bmatrix}^m |\Delta \mathcal{R}_m\rangle = -|\Delta n_m\rangle \quad \text{minimise the residual}
\]

**Kerker**: damping oscillations at small $G$ \quad \[
\begin{bmatrix} J^{-1} \end{bmatrix}^1 = w(G) = \frac{|G|^2}{|G|^2 + \beta}
\]

Trial density mixed with previous densities and residuals

\[ n^{\text{inp}}_{m+1} = n^{\text{inp}}_m + G^I \mathcal{R}[n^{\text{inp}}_m] + \sum_{i=1}^{m-1} \alpha_i \left( \Delta n_i + G^I \Delta \mathcal{R}_i \right) \]
Iterative Improvement of the the $n(r)$

- Input density matrix
  \[ P_{\alpha\beta}^{\text{in}} \rightarrow n^{\text{in}}(r) \]

- Update of KS Hamiltonian
  \[ C_n \varepsilon_n \]

- Diagonalization plus iterative refinement

- Calculation of Fermi energy and occupations
  \[ E_f \, f_n \]

- New density matrix
  \[ P_{\alpha\beta}^{\text{out}} \rightarrow n^{\text{out}}(r) \]

- Check convergence
  \[ \max \{ P_{\alpha\beta}^{\text{out}} - P_{\alpha\beta}^{\text{in}} \} \]

- Density mixing
  \[ n_{\text{out}} \, n_{\text{in}} \, n^h \ldots \rightarrow n^{\text{new}} \]
Rhodium: Bulk and Surface

**Bulk: 4x4x4**

**Surface: 6x6 7 layers**

<table>
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<tr>
<th>Basis</th>
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<th>(B) [GPa]</th>
<th>(E_s) [eV/Å²]</th>
<th>(W_f) [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3s2p2df</td>
<td>17e</td>
<td>3.80</td>
<td>258.3</td>
<td>0.186</td>
<td>5.11</td>
</tr>
<tr>
<td>2s2p2df</td>
<td>9e</td>
<td>3.83</td>
<td>242.6</td>
<td>0.172</td>
<td>5.14</td>
</tr>
<tr>
<td>2sp2d</td>
<td>9e</td>
<td>3.85</td>
<td>230.2</td>
<td>0.167</td>
<td>5.20</td>
</tr>
<tr>
<td>spd</td>
<td>9e</td>
<td>3.87</td>
<td>224.4</td>
<td>0.164</td>
<td>5.15</td>
</tr>
</tbody>
</table>

**ScALAPACK for diagonalisation**

A \rightarrow T \rightarrow (\lambda, q_T) \rightarrow q_A

- A → reduction to tridiagonal form
- T → compute eigenvalues and eigenvectors of T
- \((\lambda, q_T)\) → transform eigenvectors

---

**Polyalanine peptide**

1003 atoms
3410 MOS
27069 BSf

---

**pdsyevd (ESSL) on IBM BGP**

- Tridiagonalization
- Solution
- Cho. 1
- Cho. 2
- Back trans.

---

**576 Cu, nao=14400, Nelect.=6336, k of eigen-pairs=3768**

<table>
<thead>
<tr>
<th>nprocs</th>
<th>syevd</th>
<th>syevr</th>
<th>Cholesky</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>106 (49%)</td>
<td>72 (40%)</td>
<td>38 (21%)</td>
</tr>
<tr>
<td>64</td>
<td>69 (46%)</td>
<td>48 (37%)</td>
<td>34 (26%)</td>
</tr>
<tr>
<td>128</td>
<td>41 (41%)</td>
<td>29 (34%)</td>
<td>23 (28%)</td>
</tr>
<tr>
<td>256</td>
<td>35 (41%)</td>
<td>26 (34%)</td>
<td>24 (32%)</td>
</tr>
</tbody>
</table>

**Syevd:** D&C
**Syevr:** MRRR

---

**time x SCF, on CRAY XE6**

- >70% in eigenvalue solver
- poor scaling
Improved efficiency by a two-step transformation and back transformation

The ELPA project

Algorithmic paths for eigenproblems

Improvements with ELPA

Efficient tridiagonalization

Two-step reduction II: banded

<table>
<thead>
<tr>
<th>Reduction to tridiagonal form</th>
<th>Compute eigenvalues and -vectors of $T$</th>
<th>Transform eigenvectors</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>$B$</td>
<td>$q_B$</td>
</tr>
<tr>
<td>$T$</td>
<td>($\lambda, q_T$)</td>
<td>$q_A$</td>
</tr>
</tbody>
</table>
| $q_B$                         | complex partial                        | band form by blocked orthogonal transformations

band form by blocked orthogonal transformations

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

CRAY XE6

<table>
<thead>
<tr>
<th>All - syevd</th>
<th>All - syevr</th>
<th>All - ELPA</th>
<th>Diag - syevd</th>
<th>Diag - syevr</th>
<th>Diag - ELPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>500</td>
<td>1000</td>
<td>1500</td>
<td>2000</td>
<td>2500</td>
<td>3000</td>
</tr>
</tbody>
</table>

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

BG-P

<table>
<thead>
<tr>
<th>All - syevd</th>
<th>All - ELPA</th>
<th>Diag - syevd</th>
</tr>
</thead>
<tbody>
<tr>
<td>10000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>500</td>
<td>1000</td>
<td>1500</td>
</tr>
</tbody>
</table>
Large metallic systems

hBN/Rh(111) Nanomesh
13x13 hBN on 12x12 Rh slab

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

Slab 12x12 Rh(111) slab, \( a_0 = 3.801 \, \text{Å} \), 1 layer hBN 13x13
4L: 576Rh + 169BN: \( N_{ao} = 19370 \); \( N_{el} = 11144 \)
7L: 1008Rh + 338BN: \( N_{ao} = 34996 \); \( N_{el} = 19840 \)

~ several days per structure optimisation

graph./Ru(0001) Superstructure
25x25 g on 23x23 Ru

2116 Ru atoms (8 valence el.) + 1250 C atoms,
\( N_{el} = 21928 \), \( N_{ao} = 47990 \);

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

&SCF
   SCF_GUESS ATOMIC
   MAX_SCF 50
   EPS_SCF 1.0e-7
   EPS_DIIS 1.0e-7
&END SCF

&MIXING
   METHOD BROYDEN_MIXING
      ALPHA 0.6
      BETA 1.0
      NBROYDEN 15
&END MIXING

&VW
   ADDED_MOS 20 20
&END VDW

&XC
   XC_FUNCTIONAL PBE
&END

&XC_FUNCTIONAL PBE
&END

&VDW
   TYPE DFTD3
   PARAMETER_FILE_NAME dftd3.dat
   REFERENCE_FUNCTIONAL PBE
&END VDW

&END SCF
### Issues:
- binding distance
- corrugation
- height distribution

### Summary of experimental results concerning the structure of gr/Ru(0001)

<table>
<thead>
<tr>
<th>Method</th>
<th>( h_{\text{min}} ) (Å)</th>
<th>( \Delta h ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LEEM(^5)</td>
<td>1.5 ± 0.1</td>
<td>-</td>
</tr>
<tr>
<td>LEED(^18)</td>
<td>2.1 ± 0.2</td>
<td>1.5 ± 0.2</td>
</tr>
<tr>
<td>SXRD(^21)</td>
<td>-</td>
<td>0.82 ± 0.15</td>
</tr>
<tr>
<td>HAS(^19)</td>
<td>-</td>
<td>0.17 ± 0.03</td>
</tr>
</tbody>
</table>

*Table 1:* The findings is a disquieting situation for such a well-studied system.

The strong binding in the valley region is exemplified by the electron scanning tunneling microscopy (STM) image.

Vertical distance from closest Rh atom [Å]

Graphene

Ru slab

<table>
<thead>
<tr>
<th>Running percentage [%]</th>
<th>Vertical distance from closest Rh atom [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>3.89</td>
</tr>
<tr>
<td>20</td>
<td>3.65</td>
</tr>
<tr>
<td>30</td>
<td>3.41</td>
</tr>
<tr>
<td>40</td>
<td>3.17</td>
</tr>
<tr>
<td>50</td>
<td>2.93</td>
</tr>
<tr>
<td>60</td>
<td>2.69</td>
</tr>
<tr>
<td>70</td>
<td>2.45</td>
</tr>
<tr>
<td>80</td>
<td>2.21</td>
</tr>
<tr>
<td>90</td>
<td>1.97</td>
</tr>
<tr>
<td>100</td>
<td>1.73</td>
</tr>
</tbody>
</table>

### Quantification of corrugation-induced effects

The quantification of corrugation-induced effects is crucial for understanding the electronic and mechanical properties of 2D materials. The convolution of topography and electronic or mechanical properties can lead to altered bonding distances and corrugation amplitudes. Additionally, the Debye-Waller factor within the moiré cell can affect the apparent corrugation amplitude.

In summary, the ambiguity of the experimental findings requires the knowledge of the geometric details and the GeO density function. The convolution of topography and electronic or mechanical properties can lead to altered bonding distances and corrugation amplitudes. Additionally, the Debye-Waller factor within the moiré cell can affect the apparent corrugation amplitude.
Figure 2: LEED pattern and C 1s, Ru 3d \(3/2\) and Ru 3d \(5/2\) core-level emission spectrum for gr/Ru(0001). a) LEED pattern for different values of electron energy (inverted contrast). b) Photoemission spectrum with \(h\nu = 330\) eV and emission angle \(\theta = 90^\circ\). Circles: Data points after background subtraction. Colored areas: Fits of the indicated components. Solid black line: Sum of fits. c) DFT calculation of the local density of states (DOS) of C 1s energies, computed separately for atoms at different heights from the surface. The same color code as in Figure 1 has been used. These calculations have been performed using an all electron representation for the C atoms. The binding energy of free-standing graphene is shown as a dashed line. The computed energies have been rigidly shifted to align the first C 1s peak to the experimental one.

The binding energy is approximately flat and bound to Ru. The calculated energy-resolved local density of states (DOS) of C 1s (see Figure 2c) shows that the binding energies depend on the adsorption heights, which correlates well with the splitting observed in the XPS data. It predicts a higher 1s binding energy for a lower-lying carbon atom. The calculated value of binding energy for free-standing graphene is 283.80 eV and it is represented by the vertical dashed line in figure 2c. The measured C 1s binding energies can be therefore attributed to the free standing graphene @ 283.8 eV.
Exploit spatial modulation of XSW field (interference) by scanning through the Bragg condition: spatial resolution and chemical sensitivity

\[
Y(\Omega) = 1 + R + 2C\sqrt{R} f_H \cos (\nu - 2\pi P_H)
\]

<table>
<thead>
<tr>
<th></th>
<th>(P_{C2}^H)</th>
<th>(f_{C2}^H)</th>
<th>(h_{\text{valley}}) (Å)</th>
<th>(h_{\text{min}}) (Å)</th>
<th>(P_{C1}^H)</th>
<th>(f_{C1}^H)</th>
<th>(\Delta h) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XSW</td>
<td>0.99 ± 0.01</td>
<td>0.86 ± 0.02</td>
<td>2.12 ± 0.03</td>
<td></td>
<td>1.43 ± 0.02</td>
<td>0.72 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>DFT</td>
<td>1.01</td>
<td>0.94</td>
<td>2.17</td>
<td>2.06</td>
<td>1.43</td>
<td>0.73</td>
<td>1.47</td>
</tr>
</tbody>
</table>

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

Interaction potential \( V(\mathbf{R}_{\text{at}}) \)

Forces \( \mathbf{F}(\mathbf{R}_{\text{at}}) \)

\( \text{MD} \)

\( \text{Energy minimization} \)

Computed Spectrum

\( \text{ok?} \)

Experimental Spectrum

Conformation \( \{ \mathbf{R}_{\text{at}} \} \)

\( \text{Xray diffraction: } S(q) \)
Core Binding Energies vs XPS

- Consider possible excited states @ higher level of theory
- ΔSCF takes into account the relaxation
- Transition operator method, according to Slater’s transition state idea

\[ \lambda^k E_k = E(0) + \lambda E_1 + \frac{1}{2} \lambda^2 E_2 + \ldots \]
Emptying the state (occupation): energy change as finite difference

\[ \Delta E = E(1) - E(0) = E_1 + E_2 + E_3 + \ldots \]

\[ F(\lambda) = \frac{\partial E}{\partial \lambda} = E_1 + 2\lambda E_2 + 3\lambda^2 E_3 + \ldots \]

\[ -\varepsilon_k = F\left(\frac{1}{2}\right) = E_1 + E_2 + \frac{3}{4} E_3 + \ldots \quad \text{Error in } E_3 \]

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

\[ \mathcal{H}(f_k = 1/2) \]
**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

**Interpretation of experiment,**
structures refinement (signal assignment),
understanding of physical-chemical properties of materials
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)**
  \[ A(r, t) = A_0 \, e \, \cos (k \cdot r - \omega t) \]

- **Linear perturbation term (time dependent perturbations)**
  \[ V(t) = \frac{e}{mc} A \cdot p \]

- **Induced transition: probability according to Fermi golden rule**
  \[ P_{if} = \frac{\pi e^2}{2 \hbar m^2 c^2} A_0^2 |\langle f | e^{i \mathbf{k} \cdot \mathbf{r}} e \cdot p | i \rangle|^2 \rho_i(E) \]

- **Long wavelength (UV, soft x-rays)**
  \[ kr_s = \frac{2\pi}{\lambda} r_s \ll 1 \]

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

- **Equivalent operators**
  \[ \hat{p} = -i\hbar \nabla = \frac{im}{\hbar} [\hat{H}, \hat{r}] \]
  \[ P_{if} \propto (E_f - E_i) |\langle f | \hat{\mu} | i \rangle|^2 \text{ length form} \]
**Ground state KS virtual orbitals**

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

**Parametric SCF solution**

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

\[ IP_{i=1} = \tilde{E}(0_1, 1_2, ..., 1_N, ...0_r, ...) - \tilde{E}(1_1, 1_2, ..., 1_N, ..., 0_r, ...) \]

\[ \Delta E(i \rightarrow r) = \tilde{E}(1_1, 1_2, ..., 0_i, ..., 1_N, ..., 1_r, ...) - \tilde{E}(1_1, 1_2, ..., 1_i, ...1_N, ..., 0_r, ...) \]

**Numerically not stable : difference between 2 SCF calculations**

**Higher excited states states (collapse)**

**Not orthogonal MOs sets**

\[ P_{if} \propto |\langle f | e \cdot p | i \rangle|^2 \rho_i(E) \]
Direct calculation of the excitation energies from the solution of KS equation with a modified core potential on the absorbing atom

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

Relaxation effects up to second order in \( \partial \tilde{E}/\partial f \):

balance between initial and final state contributions

One calculation for each excitation

\[ \hbar \omega_{if} = \varepsilon_f^T - \varepsilon_i^T \quad I_{if} = \frac{2}{3} \omega_{if} \left| \langle \psi_i^T | \bar{\mu} | \psi_f^T \rangle \right|^2 \]
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 $\Delta \text{SCF}$

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

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

- Relativistic correction as rigid, species-dependent translation
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.


**Ground state SCF and localization of the occupied orbitals**

**Character of the Core states**

\[ \tilde{\psi}_i(r) = \sum_{\mu} \tilde{C}_{\mu i} \varphi_{\mu}(r) \]

\[ = \max_i \left\{ \langle \tilde{\psi}_i | \phi^{STO}_{1s} \rangle \right\} \rightarrow \text{j-th state} \]

**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**

\[ I_{if} = \left| \langle \psi_i^T | \nabla | \psi_f^T \rangle \right|^2 \]
&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
&END
&END XAS
Convolution using Gaussian functions with adapted width

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

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

\[ \sigma_{\min} = 0.5 \text{eV} \]

\[ \sigma_{\max} = 8 \text{eV} \]

\[ E_{\max} - E_{\min} \approx 20 \text{ eV} \]
**NEXAFS for Hexagonal Ice**

**Hexagonal Ice**

- **128H2O**
- **6-311G(dp)**

**Exp: gas phase vs Ice**

- **Exp.**

![Graph showing energy vs. emission energy for gas phase vs. ice.](image)

- **Energy (eV)**
  - 532
  - 536
  - 540
  - 544

- **Energy (eV)**
  - 532
  - 534
  - 536
  - 538
  - 540
  - 542
  - 544

**Key Findings**

- **All O donating and accepting 2 h-bonds**

- **Charge redistribution (no antibonding OH)**

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

---

Exp. liquid water : M. Odelius et al., PRB, 73, 024205 (2006)
Size of the Simulation Cell

- 1x1x1 16H₂O
- 1x2x2 64H₂O
- 2x2x2 128H₂O
- 3x3x3 432H₂O

Energy (eV)
Not only the absolute position but also the shape of the spectrum might change.
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.
Measure of the Larmor precession frequency of the nuclear spin within a magnetic field

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

Interaction between \( B \) and a spin 1/2 nucleus with spin angular momentum \( E = -\mu \cdot B \)

\[ \hbar \omega = \Delta E = -\gamma \hbar B \]

in diamagnetic materials the \( B_{\text{ind}} \) arises only from the induced orbital currents \( j \)

\[ B = B_0 + B_{\text{ind}} \]

\[ B_{\text{ind}} = -\sigma \times k B_0 \]
Chemical Shielding

Radio frequencies signals from ensemble of sites highly sensitive to atomic structure and dynamics

\[ B_{\text{ind}}(r) = \frac{1}{c} \int d^3 r' j(r') \times \frac{r - r'}{|r - r'|^3} \]

\[ \sigma_{xy}(R_A) = \frac{1}{c} \int_\Omega \frac{r - R_A}{|r - R_A|^3} \times j_x(r) \, d^3 r \]

Chemical shift w.r.t. reference

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

Representation by means of a vector potential and a Gauge function

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

\[ \mathbf{A}(\mathbf{r}) = -\frac{1}{2} \mathbf{r} \times \mathbf{B} \quad \Phi_g(\mathbf{r}) = \frac{1}{2} \mathbf{r} \cdot \mathbf{R}_b \times \mathbf{B} \]

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

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

\[ \mathbf{H} = \frac{1}{2m} (\mathbf{p} - e\mathbf{A}(\mathbf{r}))^2 + \mathbf{V} \]

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

\[ \hat{\mathbf{p}} = -i\hbar \nabla \]

1st order imaginary
Variational principle at second order in the DFT framework

\[ \mathcal{E}_{\text{tot}} = \mathcal{E}_{\text{KS}}^{(0)} + \lambda \mathcal{E}^{\text{pert}} \quad \text{static perturbation} \]

\[ E_{\text{tot}} = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \ldots \]

\[ \psi_i = \psi_i^{(0)} + \lambda \psi_i^{(1)} + \lambda^2 \psi_i^{(2)} + \ldots \]

Expansion to 2nd order and minimisation: linear response

\[ E^{(2)} \] variational in \( \psi^{(1)} \)

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

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

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

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

Perturbation operator split into three terms

\[
H_{\mu\nu}^{\Gamma} = -i\langle \mu | (\hat{r} - d_2) \times \nabla | \nu \rangle \\
H_{\mu\nu}^{P} = -i\langle \mu | \nabla | \nu \rangle \\
H_{\mu\nu}^{\Delta} = -i(d_1 - d_2) \times \langle \mu | \nabla | \nu \rangle
\]

**x-component of current density \( j \) induced by \( B^0 \) applied along \( y \)**

\[
j_{xy}(r) = -\frac{1}{2c} \sum_{i} \sum_{\mu\nu} \left[ C_{\mu i}^{0} \left( C_{\nu i}^{L_Y} + (R_g - d_i)_x C_{\nu i}^{P_x} - (R_g - d_i)_z C_{\nu i}^{P_z} - C_{\nu i}^{\Delta i_y} \right) \right] \\
\times \left( \nabla_x \varphi_{\mu}(r) \varphi_{\nu}(r) - \varphi_{\mu}(r) \nabla_x (\varphi_{\nu}(r)) \right) \\
+ (r - R_g)_y n(r) \text{ diamagnetic}
\]

**Gauge invariance in molecular and periodic systems**

**CSGT** \( R_g = r \) computationally convenient, slow converging with basis set quality

**IGAIM** \( R_g = R_I \) individual gauge for atoms in molecules
applied $B^0$ along $x$

$$\sigma_{xy}(R_A) = \frac{1}{c} \int_{\Omega} \left[ \frac{r - R_A}{|r - R_A|^3} \times j_x(r) \right]_y d^3r$$

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

**GAPW induced current density**

from soft term in reciprocal space

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

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

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

from local terms by integration on spherical grids

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

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
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
**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

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<tr>
<th>Iteration</th>
<th>Tolerance</th>
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<td>500</td>
<td>0.8639E-03</td>
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<tr>
<td>600</td>
<td>0.3288E-03</td>
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</table>

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

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<tr>
<th>state</th>
<th>Centers</th>
<th>Spreads</th>
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<td>0.541470 0.000000 0.000000</td>
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<td>3</td>
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<tr>
<td>4</td>
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</table>
Linear Response Initialization

Properties to be Calculated:

NMR Chemical Shift

LOCALIZED PSI0
Conjugate Gradients
2pnt
FULL ALL

EPS_SCF
1.0E-05

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

Gauge used ATOM
Orbital center used COMMON
Common center 0.000000 0.000000 0.000000
Calculation of the p and (r-d)xp operators applied to psi0
Response calculation for first perturbation operator

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

Response to the perturbation operator P_x

<table>
<thead>
<tr>
<th>Iter.</th>
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<th>Stepsize</th>
<th>G-norm</th>
<th>Convergence</th>
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</table>

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
Isolated Adenine

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

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

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Hydrated Adenine

QM/MM with 827 H2O: snapshot from classical MD

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</table>

CP2K
IGAIM
BLYP/cc-p-VQZ

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

\[ \rho^s(r) = \rho^\alpha(r) - \rho^\beta(r) \]

spin density

\[ g_{xy} = g^Z_{xy} + \Delta g^{ZKE}_{xy} + \Delta g^{SO}_{xy} + \Delta g^{SOO}_{xy} \]

\[ g^Z_{xy} = g_e \delta_{xy} \]

g_e : free el. g value

\[ \Delta g^{ZKE}_{xy} = -\frac{g_e}{c^2} (T^\alpha - T^\beta) \delta_{xy} \]

T : unperturbed kinetic energy

\[ \Delta g^{SO}_{xy} = \frac{g_e - 1}{c} \int_{\Omega_C} \left[ j_x^\alpha \times \nabla V_{\text{eff}}^\alpha - j_x^\beta \times \nabla V_{\text{eff}}^\beta \right] d^3r \]

induced spin current density

\[ \Delta g^{SOO}_{xy} = 2 \int_{\Omega_C} B^{\text{corr}}_{xy}(r) \rho^s(r) d^3r \]

B^{\text{corr}} : magnetic field from induced current density
### O vacancy in α-quartz: g-tensor

#### QM/MM: 15000 atoms

![Diagram of QM/MM: 15000 atoms](image)

#### 159 QM atoms

![Diagram of 159 QM atoms](image)

#### 17 QM AE atoms

![Diagram of 17 QM AE atoms](image)

<table>
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<th>GAPW AE/MM</th>
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<td>$\Delta g_{ii}$</td>
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