Efficient & Reliable Hybrid DFT Calculations with ADMM

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Hybrid DFT Calculations with CP2K

- ADMM: Auxiliary Density Matrix Methods for Hartree-Fock Exchange Calculations
- Total energy as a functional of the electron density
  \[ E[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho] + \int v(r) \rho(r) \, dr \]
- Exchange-correlation energy with a hybrid functional
  \[ E_{xc}[\rho] = \alpha E_x^{HFX}[\{\psi_i\}] + (1 - \alpha) E_x^{DFT}[\rho] + E_c^{DFT}[\rho] \]
ADMM in CP2K

• Hartree-Fock exchange energy

\[ E_{x}^{HFX}[P] = -\frac{1}{2} \sum_{\lambda \sigma \mu \nu} P^{\mu \sigma} P^{\nu \lambda} (\mu \nu | \lambda \sigma) \]

\[ P^{\mu \nu} = \sum_{i} C^{\mu i} C^{\nu i} \iff P = CC^{T} \]

\[ (\mu \nu | \lambda \sigma) = \int \int \phi_{\mu}(r_{1}) \phi_{\nu}(r_{1}) g(|r_{2} - r_{1}|) \phi_{\lambda}(r_{2}) \phi_{\sigma}(r_{2}) \, dr_{1} \, dr_{2} \]

• Introducing auxiliary density matrix \( \hat{P} \approx P \)

\[ E_{x}^{HFX}[P] = E_{x}^{HFX}[\hat{P}] + (E_{x}^{HFX}[P] - E_{x}^{HFX}[\hat{P}]) \]

\[ \approx E_{x}^{HFX}[\hat{P}] + (E_{x}^{DFT}[P] - E_{x}^{DFT}[\hat{P}]) \]

• How to construct auxiliary basis set?
  – smaller in size (i.e. less number of basis functions)
  – more rapidly decaying (i.e. bigger Gaussian exponents)
ADMM in CP2K

Choice of auxiliary basis set for ADMM

- FIT3: three Gaussian exponents for each valence orbital
- cFIT3: a contraction of FIT3 (i.e. fixed linear combinations of Gaussian functions)
- pFIT3: FIT3 + polarization functions (i.e. higher angular momentum functions)
- cpFIT3: cFIT3 + polarization functions
- aug-FIT3, aug-cFIT3, aug-pFIT3, aug-cpFIT3: augmented with a “diffuse” function (i.e. smaller Gaussian exponents)
- FIT3 as trial ADMM basis

ADMM in CP2K

Limited availability of ADMM basis sets

(see $CP2K/cp2k/data/BASIS_ADMM)
ADMM basis sets for transition metals

ADMM basis sets will be released in mid-2015!

(Email: S.Ling@ucl.ac.uk)
ADMM basis sets for transition metals

Uncontracted basis sets

- FIT10: $4s + 3p + 3d$
- FIT11: $4s + 3p + 3d + 1d$ → recommended for solids
- FIT12: $4s + 3p + 4d + 1d$
- FIT13: $4s + 4p + 4d + 1d$

Contracted basis sets (double-$\zeta$ quality)

- cFIT10 / cFIT11 / cFIT12 / cFIT13

All exponents were optimised, including the polarisation function
Some general suggestions

- Always check the convergence of CUTOFF (see http://www.cp2k.org/howto:converging_cutoff).
- Always check the convergence of properties (e.g. lattice parameters, band gaps) with respect to supercell sizes.
- Always start from pre-converged GGA (e.g. PBE) wavefunction and geometry.
- Always check the convergence of primary and ADMM basis sets (start from a small basis and gradually increase the size).
- ADMM has only been implemented for use with GPW.
Work Flow

1. Convergence test (primary basis, CUTOFF, supercell, etc)

2. GGA optimisation with selected primary basis

3. Name GGA wave function file for use with ADMM

4. Construct ADMM input with auxiliary basis (e.g. FIT3)

5. Run calculations and check convergence of ADMM basis
Input Structure: GGA/PBE

&DFT

...  
BASIS_SET_FILE_NAME ./BASIS_MOLOPT  (file can be found in $CP2K/cp2k/data)
...
&XC

&XC_FUNCTIONAL PBE
&END XC_FUNCTIONAL
&END XC
...
&END DFT
&SUBSYS

&KIND Si

BASIS_SET DZVP-MOLOPT-SR-GTH
POTENTIAL GTH-PBE-q4
&END KIND
&END SUBSYS
Input Structure: ADMM

&DFT

... 
BASIS_SET_FILE_NAME ./BASIS_MOLOPT
BASIS_SET_FILE_NAME ./BASIS_ADMM
WFN_RESTART_FILE_NAME ${project}-RESTART.wfn
&SCF

SCF_GUESS RESTART
... 
&END SCF
&AUXILIARY_DENSITY_MATRIX_METHOD
METHOD BASIS_PROJECTION
ADMM_PURIFICATION_METHOD MO_DIAG
&END AUXILIARY_DENSITY_MATRIX_METHOD
...
&XC
... 
&END XC
&END DFT
&SUBSYS

&KIND Si 
BASIS_SET DZVP-MOLOPT-SR-GTH
AUX_FIT_BASIS_SET cFIT3
POTENTIAL GTH-PBE-q4 
&END KIND
&END SUBSYS

(files can be found in $CP2K/cp2k/data)
Which functional to use?

• **PBE0-TC-LRC**

$$E_{xc}^{PBE0-TC-LRC} = aE_{x}^{HF,TC}(R_C) + aE_{x}^{PBE,LRC}(R_C)$$

$$+ (1 - a)E_{x}^{PBE} + E_{c}^{PBE}$$


• **HSE06**

$$E_{xc}^{HSE06} = aE_{x}^{HF,SR}(\omega) + (1 - a)E_{x}^{PBE,SR}(\omega)$$

$$+ E_{x}^{PBE,LR}(\omega) + E_{c}^{PBE}$$

Input Structure: PBE0 vs. HSE06

**PBE0-TC-LRC**

(t_c_g.dat can be found in $CP2K/cp2k/data)

**HSE06**

(see examples in $CP2K/cp2k/tests/QS/regtest-admm-1/2/3/4)
Example: Diamond Band Gap

<table>
<thead>
<tr>
<th>Method</th>
<th>Number of Integrals</th>
<th>Gap [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE (PBS)</td>
<td></td>
<td>4.17</td>
</tr>
<tr>
<td>PBE (ABS)</td>
<td></td>
<td>4.37</td>
</tr>
<tr>
<td>PBE0 (PBS)</td>
<td>40 787 850 778 591</td>
<td>6.07</td>
</tr>
<tr>
<td>PBE0 (ABS)</td>
<td>23 561 509 497</td>
<td>6.25</td>
</tr>
<tr>
<td>PBE0 ADMM1</td>
<td>24 816 897 009</td>
<td>6.03</td>
</tr>
<tr>
<td>PBE0 ADMM2</td>
<td>24 795 460 638</td>
<td>6.02</td>
</tr>
</tbody>
</table>

3x3x3 supercell
# Example: Bulk Silicon

<table>
<thead>
<tr>
<th>Cutoff radius (Å)</th>
<th>Band gap (eV)</th>
<th>Integrals</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.16&lt;sup&gt;a&lt;/sup&gt;</td>
<td>77799946176</td>
</tr>
<tr>
<td>4</td>
<td>1.54&lt;sup&gt;a&lt;/sup&gt;</td>
<td>154325979000</td>
</tr>
<tr>
<td>6</td>
<td>1.71&lt;sup&gt;a&lt;/sup&gt;</td>
<td>265868148312</td>
</tr>
<tr>
<td>8</td>
<td>1.78&lt;sup&gt;a&lt;/sup&gt;</td>
<td>422457823080</td>
</tr>
</tbody>
</table>

PBE0-TC-LRC with cFIT3 ADMM basis, 3x3x3 supercell, 216 atoms

- Cutoff radius: \( R_C \leq \frac{L}{2} \)

<table>
<thead>
<tr>
<th>ADMM basis</th>
<th>Band gap (eV)</th>
<th>Integrals</th>
</tr>
</thead>
<tbody>
<tr>
<td>cFIT3</td>
<td>1.78&lt;sup&gt;a&lt;/sup&gt;</td>
<td>422457823080</td>
</tr>
<tr>
<td>FIT3</td>
<td>1.80&lt;sup&gt;a&lt;/sup&gt;</td>
<td>424426850352</td>
</tr>
<tr>
<td>pFIT3</td>
<td>1.98&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1447428361680</td>
</tr>
<tr>
<td>Ref. (VASP)</td>
<td>1.93&lt;sup&gt;b&lt;/sup&gt; (indirect)</td>
<td></td>
</tr>
</tbody>
</table>

PBE0-TC-LRC with 8 Å cutoff radius, 3x3x3 supercell, 216 atoms

- Polarisation function is important for covalent solids!

<sup>a</sup> Ling & Slater, unpublished; <sup>b</sup> J. Chem. Phys. 124, 154709 (2006)
Example: excess electrons in TiO$_2$

\[ E_{\text{pol}} = E_{\text{loc}(N+1)} - E_{\text{deloc}(N+1)} \]

at 298 K, \( kT = \sim 0.03 \) eV
Example: Li doped ZSM-5

- Widely used nanoporous zeolite catalyst
- $\text{Si}_{1-x}\text{O}_2\text{Al}_x\text{Li}_x$
- 289 atoms in the unit cell
- 95 Si (dark blue), 1 Al (green), Li (light blue)
- 12 symmetry distinct positions for the Al and 48 distinct positions for the Li cation
- $2 \times 2 \times 1.3$nm cell
- TZV2P primary basis/ PBE

Open question in zeolite science – what determines where the Al is found in this material?
Important, because Al is associated with acidity and catalytic activity
Example: Li doped ZSM-5

- Preference for two lattice sites at PBE and hybrid PBE0 level of theory
- 1 energy evaluation with full hybrid ~2 hours on 480 cores (ARCHER)
- ADMM (CFIT), full geometry optimisation in 6 hours on 480 cores (ARCHER) – 1936 energy evaluations, 293 optimisation steps!
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