

# Efficient & Reliable Hybrid DFT Calculations with ADMM

**Sanliang Ling and Ben Slater**

Email: [S.Ling@ucl.ac.uk](mailto:S.Ling@ucl.ac.uk)

Department of Chemistry  
University College London

**Second Annual CP2K-UK Users Meeting, London, 6th February 2015**

# Hybrid DFT Calculations with CP2K

- ADMM: Auxiliary Density Matrix Methods for Hartree-Fock Exchange Calculations
- Total energy as a functional of the electron density

$$E[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho] + \int v(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}$$

- Exchange-correlation energy with a hybrid functional

$$E_{xc}[\rho] = \alpha E_x^{\text{HFX}}[\{\psi_i\}] + (1 - \alpha) E_x^{\text{DFT}}[\rho] + E_c^{\text{DFT}}[\rho]$$

# ADMM in CP2K

- Hartree-Fock exchange energy

$$E_x^{\text{HFX}}[P] = -\frac{1}{2} \sum_{\lambda\sigma\mu\nu} P^{\mu\sigma} P^{\nu\lambda} (\mu\nu|\lambda\sigma) \longrightarrow \text{scales as } N^4$$

$$P^{\mu\nu} = \sum_i C^{ui} C^{vi} \Leftrightarrow P = CC^T$$

$$(\mu\nu|\lambda\sigma) = \int \int \phi_\mu(\mathbf{r}_1) \phi_\nu(\mathbf{r}_1) g(|\mathbf{r}_2 - \mathbf{r}_1|) \phi_\lambda(\mathbf{r}_2) \phi_\sigma(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$


- Introducing auxiliary density matrix  $\hat{P} \approx P$

$$\begin{aligned} E_x^{\text{HFX}}[P] &= E_x^{\text{HFX}}[\hat{P}] + (E_x^{\text{HFX}}[P] - E_x^{\text{HFX}}[\hat{P}]) \\ &\approx E_x^{\text{HFX}}[\hat{P}] + (E_x^{\text{DFT}}[P] - E_x^{\text{DFT}}[\hat{P}]) \end{aligned}$$

- 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)  **exponents taken from 6-31G\*\* (unoptimised)**
- 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

<b>1A</b>																	<b>8A</b>	
1 <b>H</b> 1s <sup>1</sup>	<b>2A</b>												<b>3A</b>	<b>4A</b>	<b>5A</b>	<b>6A</b>	<b>7A</b>	2 <b>He</b> 1s <sup>2</sup>
3 <b>Li</b> 1s <sup>2</sup> 2s <sup>1</sup>	4 <b>Be</b> 1s <sup>2</sup> 2s <sup>2</sup>											5 <b>B</b> 1s <sup>2</sup> 2s <sup>2</sup> p <sup>1</sup>	6 <b>C</b> 1s <sup>2</sup> 2s <sup>2</sup> p <sup>2</sup>	7 <b>N</b> 1s <sup>2</sup> 2s <sup>2</sup> p <sup>3</sup>	8 <b>O</b> 1s <sup>2</sup> 2s <sup>2</sup> p <sup>4</sup>	9 <b>F</b> 1s <sup>2</sup> 2s <sup>2</sup> p <sup>5</sup>	10 <b>Ne</b> 1s <sup>2</sup> 2s <sup>2</sup> p <sup>6</sup>	
11 <b>Na</b> [Ne]3s <sup>1</sup>	12 <b>Mg</b> [Ne]3s <sup>2</sup>											13 <b>Al</b> [Ne]3s <sup>2</sup> p <sup>1</sup>	14 <b>Si</b> [Ne]3s <sup>2</sup> p <sup>2</sup>	15 <b>P</b> [Ne]3s <sup>2</sup> p <sup>3</sup>	16 <b>S</b> [Ne]3s <sup>2</sup> p <sup>4</sup>	17 <b>Cl</b> [Ne]3s <sup>2</sup> p <sup>5</sup>	18 <b>Ar</b> [Ne]3s <sup>2</sup> p <sup>6</sup>	
		<b>3B</b>	<b>4B</b>	<b>5B</b>	<b>6B</b>	<b>7B</b>	<b>8B</b>		<b>1B</b>	<b>2B</b>								
19 <b>K</b> [Ar]4s <sup>1</sup>	20 <b>Ca</b> [Ar]4s <sup>2</sup>	21 <b>Sc</b> [Ar]3d <sup>1</sup> 4s <sup>2</sup>	22 <b>Ti</b> [Ar]3d <sup>2</sup> 4s <sup>2</sup>	23 <b>V</b> [Ar]3d <sup>3</sup> 4s <sup>2</sup>	24 <b>Cr</b> [Ar]3d <sup>5</sup> 4s <sup>1</sup>	25 <b>Mn</b> [Ar]3d <sup>5</sup> 4s <sup>2</sup>	26 <b>Fe</b> [Ar]3d <sup>6</sup> 4s <sup>2</sup>	27 <b>Co</b> [Ar]3d <sup>7</sup> 4s <sup>2</sup>	28 <b>Ni</b> [Ar]3d <sup>8</sup> 4s <sup>2</sup>	29 <b>Cu</b> [Ar]3d <sup>10</sup> 4s <sup>1</sup>	30 <b>Zn</b> [Ar]3d <sup>10</sup> 4s <sup>2</sup>	31 <b>Ga</b> [Ar]3d <sup>10</sup> 4s <sup>2</sup> p <sup>1</sup>	32 <b>Ge</b> [Ar]3d <sup>10</sup> 4s <sup>2</sup> p <sup>2</sup>	33 <b>As</b> [Ar]3d <sup>10</sup> 4s <sup>2</sup> p <sup>3</sup>	34 <b>Se</b> [Ar]3d <sup>10</sup> 4s <sup>2</sup> p <sup>4</sup>	35 <b>Br</b> [Ar]3d <sup>10</sup> 4s <sup>2</sup> p <sup>5</sup>	36 <b>Kr</b> [Ar]3d <sup>10</sup> 4s <sup>2</sup> p <sup>6</sup>	
37 <b>Rb</b> [Kr]5s <sup>1</sup>	38 <b>Sr</b> [Kr]5s <sup>2</sup>	39 <b>Y</b> [Kr]4d <sup>1</sup> 5s <sup>2</sup>	40 <b>Zr</b> [Kr]4d <sup>2</sup> 5s <sup>2</sup>	41 <b>Nb</b> [Kr]4d <sup>4</sup> 5s <sup>1</sup>	42 <b>Mo</b> [Kr]4d <sup>5</sup> 5s <sup>1</sup>	43 <b>Tc</b> [Kr]4d <sup>5</sup> 5s <sup>2</sup>	44 <b>Ru</b> [Kr]4d <sup>7</sup> 5s <sup>1</sup>	45 <b>Rh</b> [Kr]4d <sup>8</sup> 5s <sup>1</sup>	46 <b>Pd</b> [Kr]4d <sup>10</sup>	47 <b>Ag</b> [Kr]4d <sup>10</sup> 5s <sup>1</sup>	48 <b>Cd</b> [Kr]4d <sup>10</sup> 5s <sup>2</sup>	49 <b>In</b> [Kr]4d <sup>10</sup> 5s <sup>2</sup> p <sup>1</sup>	50 <b>Sn</b> [Kr]4d <sup>10</sup> 5s <sup>2</sup> p <sup>2</sup>	51 <b>Sb</b> [Kr]4d <sup>10</sup> 5s <sup>2</sup> p <sup>3</sup>	52 <b>Te</b> [Kr]4d <sup>10</sup> 5s <sup>2</sup> p <sup>4</sup>	53 <b>I</b> [Kr]4d <sup>10</sup> 5s <sup>2</sup> p <sup>5</sup>	54 <b>Xe</b> [Kr]4d <sup>10</sup> 5s <sup>2</sup> p <sup>6</sup>	
55 <b>Cs</b> [Xe]6s <sup>1</sup>	56 <b>Ba</b> [Xe]6s <sup>2</sup>	57-71 Lanthanides		72 <b>Hf</b> [Xe]4f <sup>14</sup> 5d <sup>2</sup> 6s <sup>2</sup>	73 <b>Ta</b> [Xe]4f <sup>14</sup> 5d <sup>3</sup> 6s <sup>2</sup>	74 <b>W</b> [Xe]4f <sup>14</sup> 5d <sup>4</sup> 6s <sup>2</sup>	75 <b>Re</b> [Xe]4f <sup>14</sup> 5d <sup>5</sup> 6s <sup>2</sup>	76 <b>Os</b> [Xe]4f <sup>14</sup> 5d <sup>6</sup> 6s <sup>2</sup>	77 <b>Ir</b> [Xe]4f <sup>14</sup> 5d <sup>7</sup> 6s <sup>2</sup>	78 <b>Pt</b> [Xe]4f <sup>14</sup> 5d <sup>9</sup> 6s <sup>1</sup>	79 <b>Au</b> [Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>1</sup>	80 <b>Hg</b> [Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup>	81 <b>Tl</b> [Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> p <sup>1</sup>	82 <b>Pb</b> [Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> p <sup>2</sup>	83 <b>Bi</b> [Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> p <sup>3</sup>	84 <b>Po</b> [Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> p <sup>4</sup>	85 <b>At</b> [Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> p <sup>5</sup>	86 <b>Rn</b> [Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> p <sup>6</sup>
87 <b>Fr</b> [Rn]7s <sup>1</sup>	88 <b>Ra</b> [Rn]7s <sup>2</sup>	89-103 Actinides		104 <b>Rf</b> [Rn]5f <sup>14</sup> 6d <sup>2</sup> 7s <sup>2</sup>	105 <b>Db</b> [Rn]5f <sup>14</sup> 6d <sup>3</sup> 7s <sup>2</sup>	106 <b>Sg</b> [Rn]5f <sup>14</sup> 6d <sup>4</sup> 7s <sup>2</sup>	107 <b>Bh</b> [Rn]5f <sup>14</sup> 6d <sup>5</sup> 7s <sup>2</sup>	108 <b>Hs</b> [Rn]5f <sup>14</sup> 6d <sup>6</sup> 7s <sup>2</sup>	109 <b>Mt</b> [Rn]5f <sup>14</sup> 6d <sup>7</sup> 7s <sup>2</sup>	110 <b>Ds</b> [Rn]5f <sup>14</sup> 6d <sup>9</sup> 7s <sup>1</sup>	111 <b>Rg</b> [Rn]5f <sup>14</sup> 6d <sup>10</sup> 7s <sup>1</sup>	112 <b>Cn</b> [Rn]5f <sup>14</sup> 6d <sup>10</sup> 7s <sup>2</sup>	113 <b>Uut</b> [Rn]5f <sup>14</sup> 6d <sup>10</sup> 7s <sup>2</sup> p <sup>1</sup>	114 <b>F1</b> [Rn]5f <sup>14</sup> 6d <sup>10</sup> 7s <sup>2</sup> p <sup>2</sup>	115 <b>Uup</b> [Rn]5f <sup>14</sup> 6d <sup>10</sup> 7s <sup>2</sup> p <sup>3</sup>	116 <b>Lv</b> [Rn]5f <sup>14</sup> 6d <sup>10</sup> 7s <sup>2</sup> p <sup>4</sup>	117 <b>Uus</b> [Rn]5f <sup>14</sup> 6d <sup>10</sup> 7s <sup>2</sup> p <sup>5</sup>	118 <b>Uuo</b> [Rn]5f <sup>14</sup> 6d <sup>10</sup> 7s <sup>2</sup> p <sup>6</sup>

Limited availability of ADMM basis sets

# ADMM basis sets for transition metals

1A		2A										3A					4A	5A	6A	7A	8A
1 H $1s^1$																					2 He $1s^2$
3 Li $1s^2 2s^1$	4 Be $1s^2 2s^2$											5 B $1s^2 2s^2 2p^1$	6 C $1s^2 2s^2 2p^2$	7 N $1s^2 2s^2 2p^3$	8 O $1s^2 2s^2 2p^4$	9 F $1s^2 2s^2 2p^5$	10 Ne $1s^2 2s^2 2p^6$				
11 Na [Ne] $3s^1$	12 Mg [Ne] $3s^2$											13 Al [Ne] $3s^2 3p^1$	14 Si [Ne] $3s^2 3p^2$	15 P [Ne] $3s^2 3p^3$	16 S [Ne] $3s^2 3p^4$	17 Cl [Ne] $3s^2 3p^5$	18 Ar [Ne] $3s^2 3p^6$				
19 K [Ar] $4s^1$	20 Ca [Ar] $4s^2$	21 Sc [Ar] $3d^1 4s^2$	22 Ti [Ar] $3d^2 4s^2$	23 V [Ar] $3d^3 4s^2$	24 Cr [Ar] $3d^5 4s^1$	25 Mn [Ar] $3d^5 4s^2$	26 Fe [Ar] $3d^6 4s^2$	27 Co [Ar] $3d^7 4s^2$	28 Ni [Ar] $3d^8 4s^2$	29 Cu [Ar] $3d^{10} 4s^1$	30 Zn [Ar] $3d^{10} 4s^2$	31 Ga [Ar] $3d^{10} 4s^2 4p^1$	32 Ge [Ar] $3d^{10} 4s^2 4p^2$	33 As [Ar] $3d^{10} 4s^2 4p^3$	34 Se [Ar] $3d^{10} 4s^2 4p^4$	35 Br [Ar] $3d^{10} 4s^2 4p^5$	36 Kr [Ar] $3d^{10} 4s^2 4p^6$				
37 Rb [Kr] $5s^1$	38 Sr [Kr] $5s^2$	39 Y [Kr] $4d^1 5s^2$	40 Zr [Kr] $4d^2 5s^2$	41 Nb [Kr] $4d^4 5s^1$	42 Mo [Kr] $4d^5 5s^1$	43 Tc [Kr] $4d^5 5s^2$	44 Ru [Kr] $4d^7 5s^1$	45 Rh [Kr] $4d^8 5s^1$	46 Pd [Kr] $4d^{10}$	47 Ag [Kr] $4d^{10} 5s^1$	48 Cd [Kr] $4d^{10} 5s^2$	49 In [Kr] $4d^{10} 5s^2 4p^1$	50 Sn [Kr] $4d^{10} 5s^2 4p^2$	51 Sb [Kr] $4d^{10} 5s^2 4p^3$	52 Te [Kr] $4d^{10} 5s^2 4p^4$	53 I [Kr] $4d^{10} 5s^2 4p^5$	54 Xe [Kr] $4d^{10} 5s^2 4p^6$				
55 Cs [Xe] $6s^1$	56 Ba [Xe] $6s^2$	57-71 Lanthanides	72 Hf [Xe] $4f^{14} 5d^2 6s^2$	73 Ta [Xe] $4f^{14} 5d^3 6s^2$	74 W [Xe] $4f^{14} 5d^4 6s^2$	75 Re [Xe] $4f^{14} 5d^5 6s^1$	76 Os [Xe] $4f^{14} 5d^6 6s^2$	77 Ir [Xe] $4f^{14} 5d^7 6s^2$	78 Pt [Xe] $4f^{14} 5d^9 6s^1$	79 Au [Xe] $4f^{14} 5d^{10} 6s^1$	80 Hg [Xe] $4f^{14} 5d^{10} 6s^2$	81 Tl [Xe] $4f^{14} 5d^{10} 6s^2 6p^1$	82 Pb [Xe] $4f^{14} 5d^{10} 6s^2 6p^2$	83 Bi [Xe] $4f^{14} 5d^{10} 6s^2 6p^3$	84 Po [Xe] $4f^{14} 5d^{10} 6s^2 6p^4$	85 At [Xe] $4f^{14} 5d^{10} 6s^2 6p^5$	86 Rn [Xe] $4f^{14} 5d^{10} 6s^2 6p^6$				
87 Fr [Rn] $7s^1$	88 Ra [Rn] $7s^2$	89-103 Actinides	104 Rf [Rn] $5f^{14} 6d^2 7s^2$	105 Db [Rn] $5f^{14} 6d^3 7s^2$	106 Sg [Rn] $5f^{14} 6d^4 7s^2$	107 Bh [Rn] $5f^{14} 6d^5 7s^2$	108 Hs [Rn] $5f^{14} 6d^6 7s^2$	109 Mt [Rn] $5f^{14} 6d^7 7s^2$	110 Ds [Rn] $5f^{14} 6d^9 7s^1$	111 Rg [Rn] $5f^{14} 6d^{10} 7s^1$	112 Cn [Rn] $5f^{14} 6d^{10} 7s^2$	113 Uut [Rn] $5f^{14} 6d^{10} 7s^2 7p^1$	114 Fl [Rn] $5f^{14} 6d^{10} 7s^2 7p^2$	115 Uup [Rn] $5f^{14} 6d^{10} 7s^2 7p^3$	116 Lv [Rn] $5f^{14} 6d^{10} 7s^2 7p^4$	117 Uus [Rn] $5f^{14} 6d^{10} 7s^2 7p^5$	118 Uuo [Rn] $5f^{14} 6d^{10} 7s^2 7p^6$				

**ADMM basis sets will be released in mid-2015!**

(Email: [S.Ling@ucl.ac.uk](mailto: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](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 (files can be found in $CP2K/cp2k/data)
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

# Which functional to use?

- **PBE0-TC-LRC**

$$E_{xc}^{PBE0-TC-LRC} = aE_x^{HF,TC}(R_C) + aE_x^{PBE,LRC}(R_C) \\ + (1-a)E_x^{PBE} + E_c^{PBE}$$

J. Chem. Theory Comput., 5, 3010 (2009)

- **HSE06**

$$E_{xc}^{HSE06} = aE_x^{HF,SR}(\omega) + (1-a)E_x^{PBE,SR}(\omega) \\ + E_x^{PBE,LR}(\omega) + E_c^{PBE}$$

J. Chem. Phys., 125, 224106 (2006)

# Input Structure: PBE0 vs. HSE06

&XC

```

&XC_FUNCTIONAL
  &PBE
    SCALE_X 0.75
    SCALE_C 1.0
  &END PBE
  &PBE_HOLE_T_C_LR
    CUTOFF_RADIUS 2.0
    SCALE_X 0.25
  &END PBE_HOLE_T_C_LR
&END XC_FUNCTIONAL
&HF
  &SCREENING
    EPS_SCHWARZ 1.0E-6
    SCREEN_ON_INITIAL_P FALSE
  &END SCREENING
  &INTERACTION_POTENTIAL
    POTENTIAL_TYPE TRUNCATED
    CUTOFF_RADIUS 2.0
    T_C_G_DATA ./t_c_g.dat
  &END INTERACTION_POTENTIAL
  &MEMORY
    MAX_MEMORY 2400
    EPS_STORAGE_SCALING 0.1
  &END MEMORY
  FRACTION 0.25
&END HF
&END XC

```

**PBE0-TC-LRC**

&XC

```

&XC_FUNCTIONAL
  &PBE
    SCALE_X 0.0
    SCALE_C 1.0
  &END PBE
  &XWPBE
    SCALE_X -0.25
    SCALE_X0 1.0
    OMEGA 0.11
  &END XWPBE
&END XC_FUNCTIONAL
&HF
  &SCREENING
    EPS_SCHWARZ 1.0E-6
    SCREEN_ON_INITIAL_P FALSE
  &END SCREENING
  &INTERACTION_POTENTIAL
    POTENTIAL_TYPE SHORTRANGE
    OMEGA 0.11
  &END INTERACTION_POTENTIAL
  &MEMORY
    MAX_MEMORY 2400
    EPS_STORAGE_SCALING 0.1
  &END MEMORY
  FRACTION 0.25
&END HF
&END XC

```

**HSE06**

# Example: Diamond Band Gap

method	number of integrals	gap [eV]
PBE (PBS)		4.17
PBE (ABS)		4.37
PBE0 (PBS)	40 787 850 778 591	6.07
PBE0 (ABS)	23 561 509 497	6.25
PBE0 ADMM1	24 816 897 009	6.03
PBE0 ADMM2	24 795 460 638	6.02

**3x3x3 supercell**

# Example: Bulk Silicon

Cutoff radius (Å)	Band gap (eV)	Integrals
2	1.16 <sup>a</sup>	77799946176
4	1.54 <sup>a</sup>	154325979000
6	1.71 <sup>a</sup>	265868148312
8	1.78 <sup>a</sup>	422457823080

Cutoff radius

$$R_C \leq \frac{L}{2}$$

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

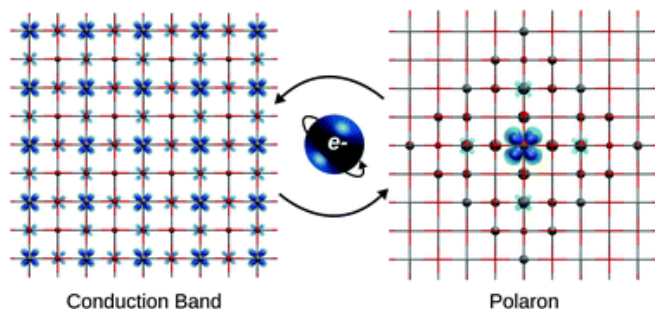
ADMM basis	Band gap (eV)	Integrals
cFIT3	1.78 <sup>a</sup>	422457823080
FIT3	1.80 <sup>a</sup>	424426850352
pFIT3	1.98 <sup>a</sup>	1447428361680
Ref. (VASP)	1.93 <sup>b</sup> (indirect)	

Polarisation function is important for covalent solids!

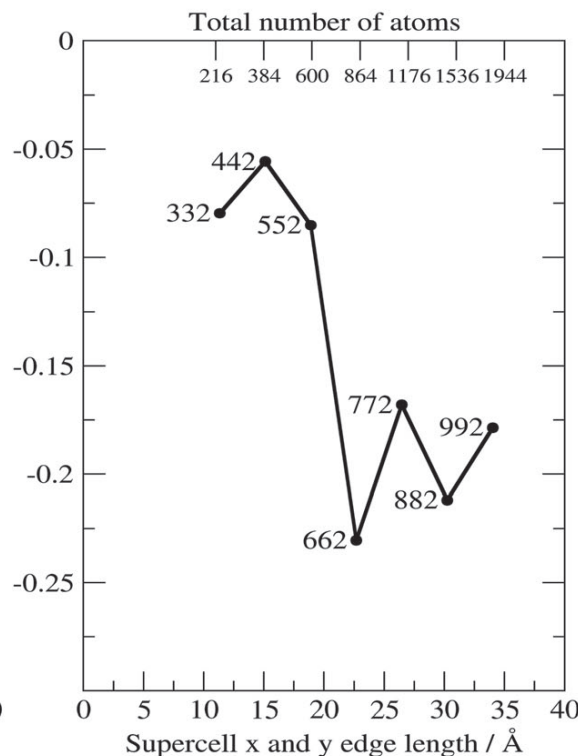
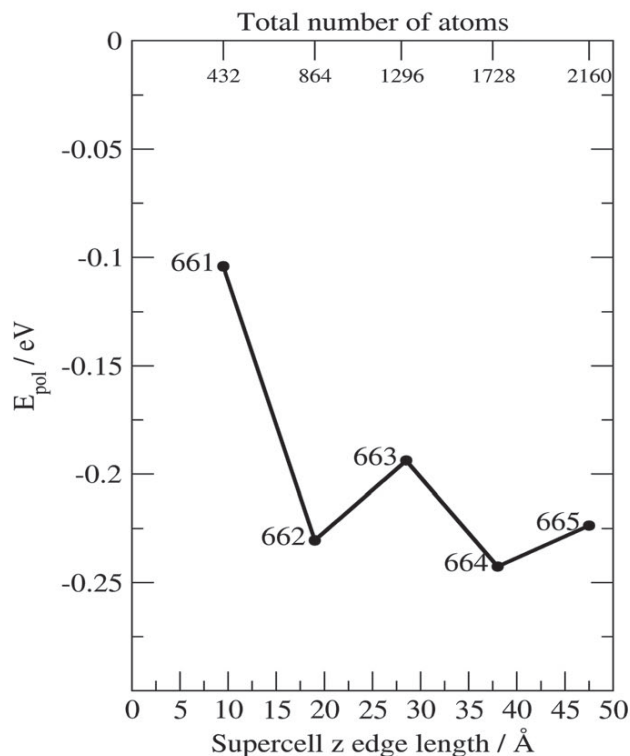
PBE0-TC-LRC with 8 Å cutoff radius, 3x3x3 supercell, 216 atoms

<sup>a</sup> Ling & Slater, unpublished; <sup>b</sup> J. Chem. Phys. 124, 154709 (2006)

# Example: excess electrons in $\text{TiO}_2$



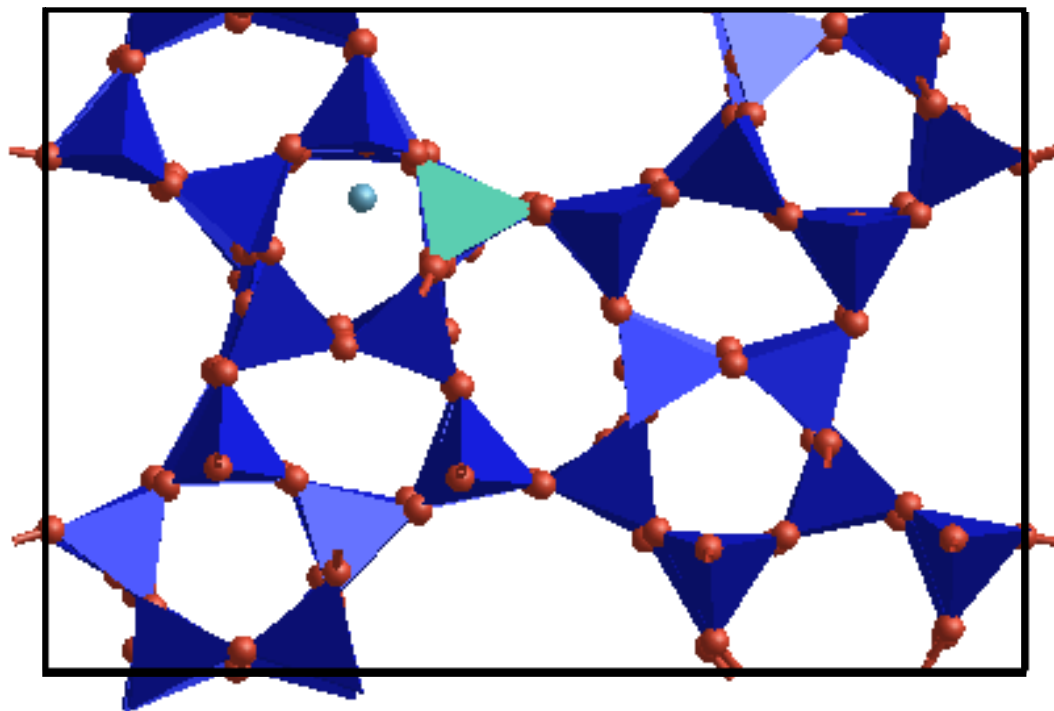
$$E_{\text{pol}} = E_{\text{loc}(N+1)} - E_{\text{deloc}(N+1)}$$



at 298 K,  
 $kT = \sim 0.03 \text{ eV}$



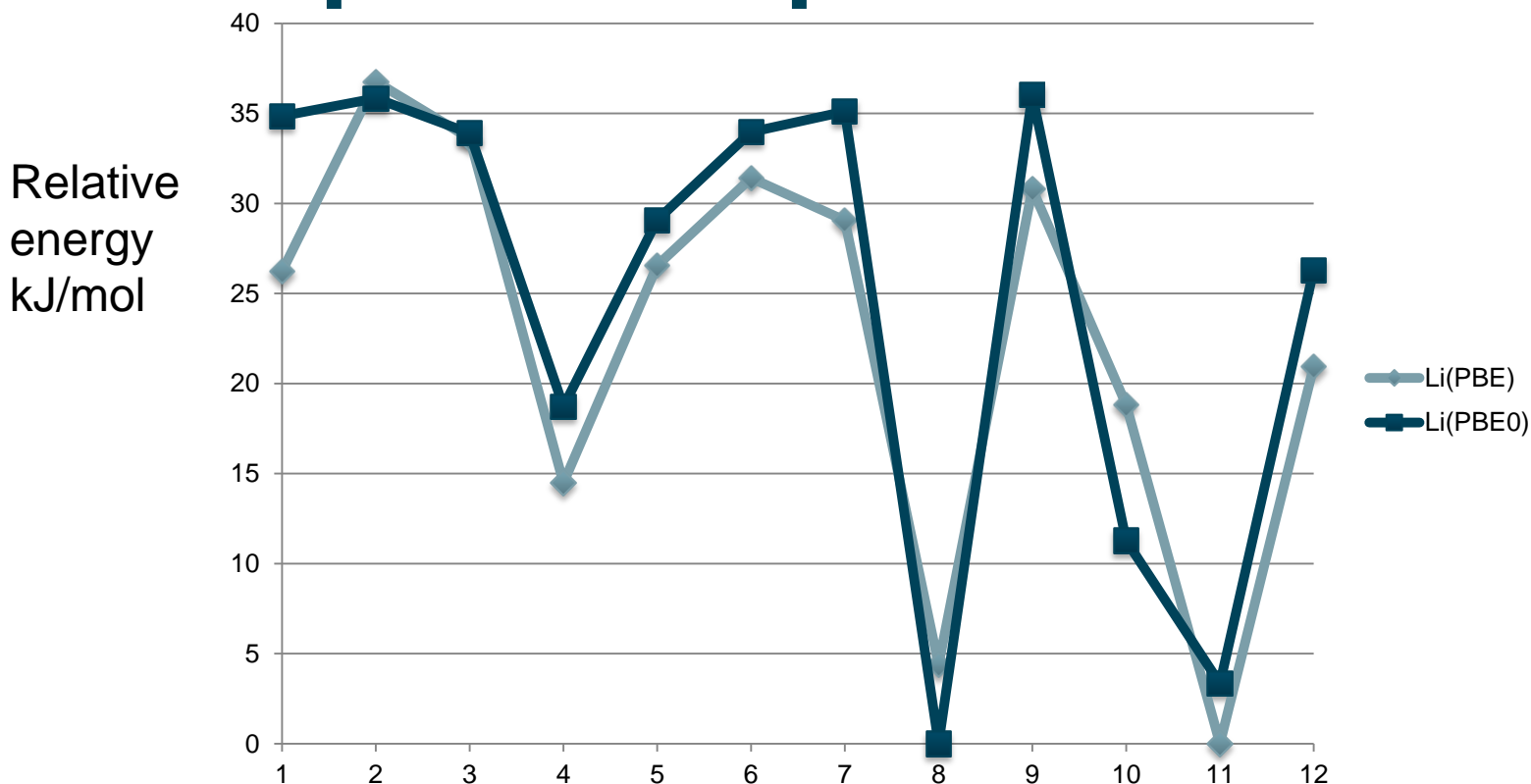
# Example: Li doped ZSM-5



- Widely used nanoporous zeolite catalyst
- $\text{Si}_{1-x}\text{O}_2\text{Al}_x\cdot\text{Li}_x$
- 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 x 2 x 1.3nm 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!

# Acknowledgements

Prof Michiel Sprik

Dr Matt Watkins

Dr Florian Schiffmann

## Funding



EPSRC

Pioneering research  
and skills

## Computing



UK HPC Materials Chemistry Consortium