University of Southampton

Introduction to ONETEP

Chris-Kriton Skylaris

Outline

UNIVERSITY OF Southampton
School of Chemistry

- Density matrix reformulation of DFT
- Localised function representation of density matrix
- Linear-scaling with localised functions
- Linear-scaling with large basis set accuracy
  - NGWFs, density kernel
  - Plane waves and psinc basis set
  - FFT box
  - Parallel scaling
- Compilation and hardware requirements
- Running a simple calculation
- Functionality available
- Examples of ONETEP applications

Density Functional Theory (DFT)

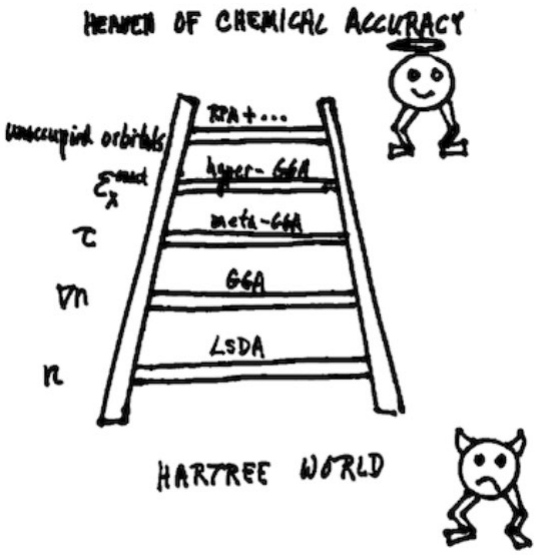
$$E[n] = \sum_i \int \psi_i^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2\right) \psi_i(\mathbf{r}) d\mathbf{r} + E_{\text{ext}}[n] + E_{\text{Coul}}[n] + E_{xc}[n]$$

$$\int V_{ext}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}$$

$$\frac{1}{2} \int \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

A hierarchy of approximations for $E_{xc}[n]$ are available ("Jacob's ladder")

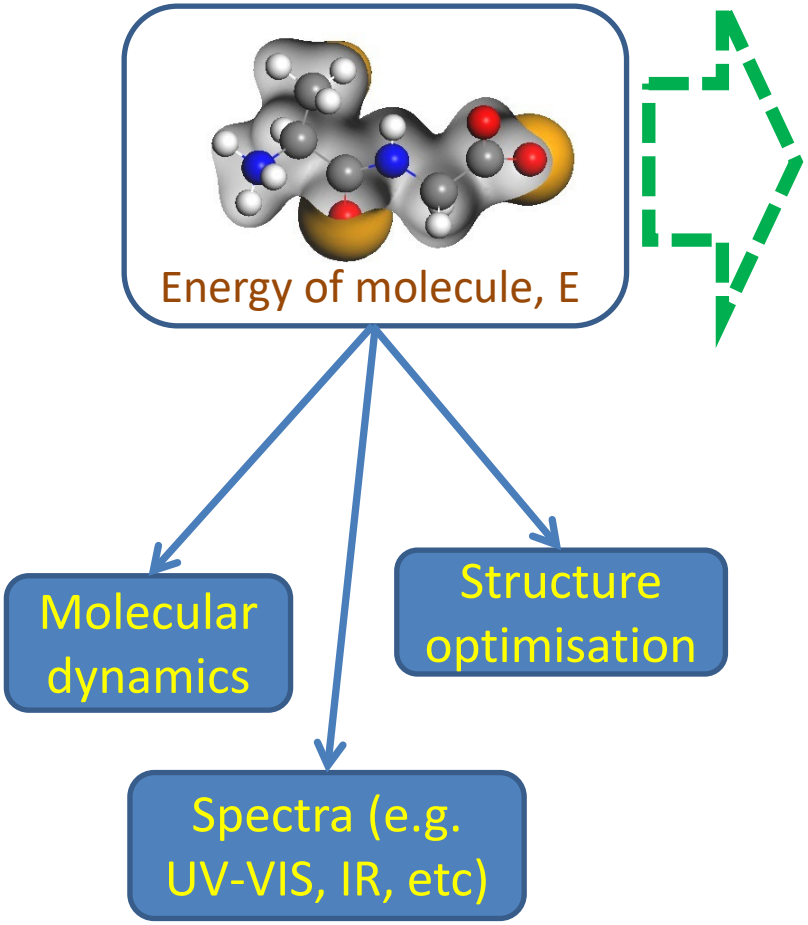
- Local density approximation (LDA): e.g. VWN or CAPZ correlation
- Generalised Gradient Approximations (GGA): e.g. BLYP, PW91, PBE
- Meta-GGAs: e.g. B95,B98,ISM,KCIS,PKZB,TPSS,VSXC
- Hybrid (including exact exchange): e.g. B3LYP, B1PW91, B1LYP, B1B95, mPW1PW91, PBE1PBE



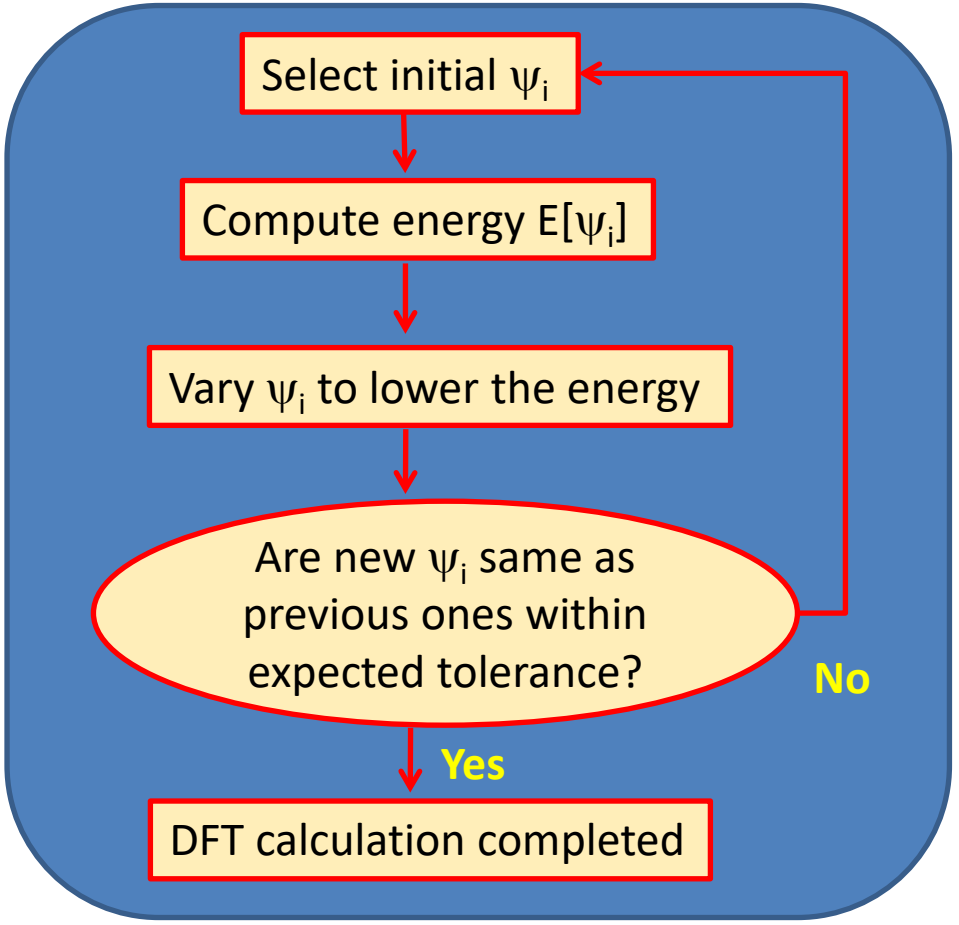
From Perdew, J. et. al. *J. Chem. Theory Comput.* **2009**, *5*, 902.

DFT simulations

Molecular simulations



DFT energy of a molecule $E[\psi_i]$



Computational bottlenecks in DFT

Non-interacting electrons

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v_{\text{eff}}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

Density of interacting electrons

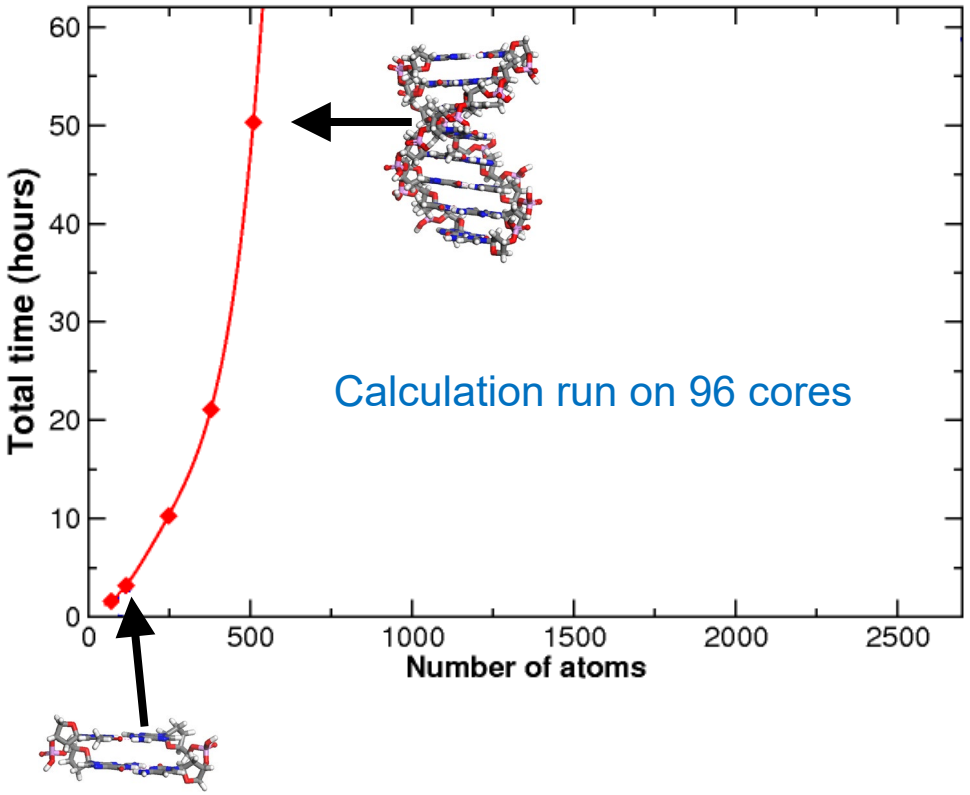
$$n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2$$

Minimise energy w.r.t.: Molecular Orbitals $\{\psi_i\}$

$O(N^3)$ Computational bottlenecks

- Solving eigenvalue problem / imposing MO orthogonality $\langle\psi_i|\psi_j\rangle = \delta_{ij}$
- Building the Hamiltonian matrix

Computational cost of DFT: cubic-scaling



- Not suitable for biomolecules/nanostructures with **thousands of atoms**
- A **linear-scaling reformulation of DFT** is needed

Linear-scaling DFT

- Physical principle

Nearsightedness of electronic matter
W. Kohn, *Phys. Rev. Lett.* **76**, 3168 (1996)

In molecules with non-zero band gap, the density matrix decays exponentially

$$\rho(\mathbf{r},\mathbf{r}') \sim e^{-\gamma|\mathbf{r}-\mathbf{r}'|} \to 0 \quad \text{as} \quad |\mathbf{r}-\mathbf{r}'| \to \infty$$

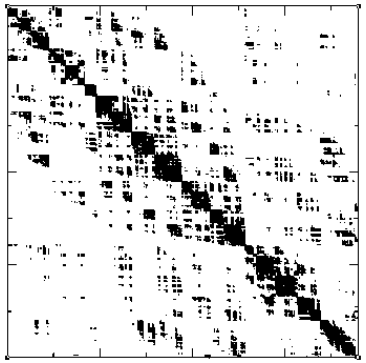
- Linear-scaling approaches

Truncate exponential "tail"

$$\rho(\mathbf{r},\mathbf{r}') = 0 \quad \text{when} \quad |\mathbf{r}-\mathbf{r}'| > r_{\text{cut}}$$

- Practical implementation

- Localised orbitals
- No diagonalisation
- Energy minimisation
- Sparse matrices and algorithms – O(N) memory and CPU cost



Density matrix DFT: energy expression

DFT energy with molecular orbitals

$$E_{\mathrm{DFT}} = \sum_i f_i \int \psi_i^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2\right) \psi_i(\mathbf{r}) d\mathbf{r} + \int V_{ext}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int\int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}[n]$$

Density matrix

$$\rho(\mathbf{r},\mathbf{r}') = \sum_n f_n \psi_n(\mathbf{r}) \psi_n^*(\mathbf{r}') = \sum_{\alpha,\beta} \phi_\alpha(\mathbf{r})\, K^{\alpha\beta}\, \phi_\beta^*(\mathbf{r}')$$

Molecular orbitals

Localised orbitals

Density

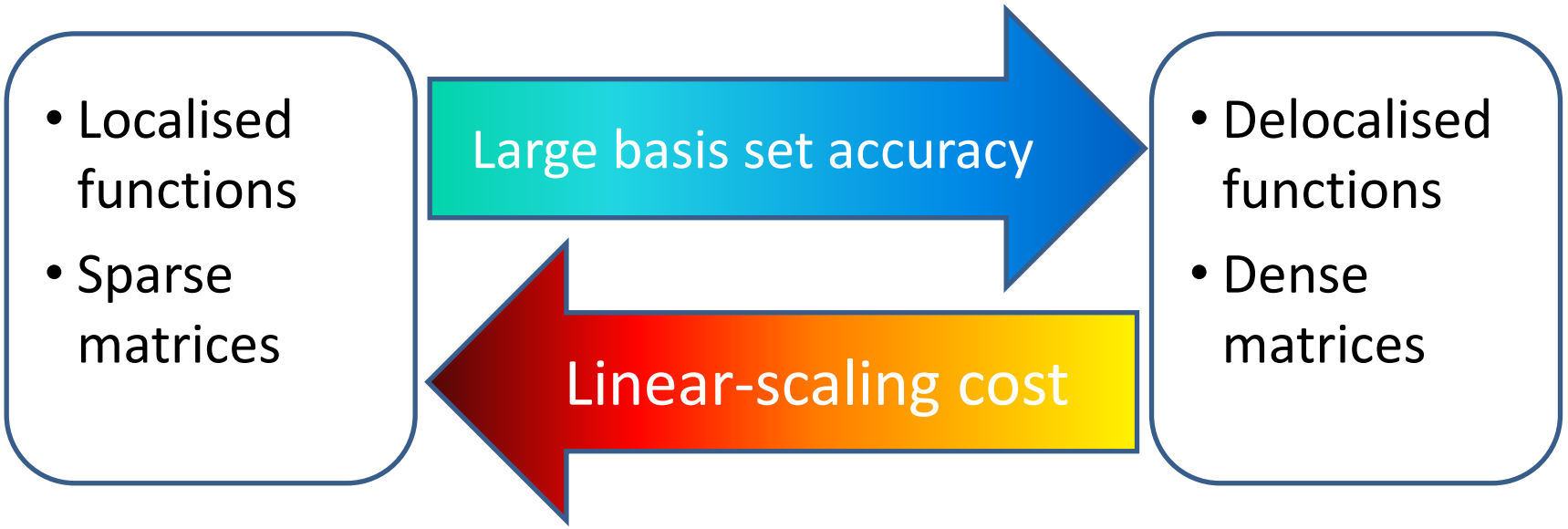
$$n(\mathbf{r}) = \rho(\mathbf{r},\mathbf{r})$$

DFT energy with density matrix

$$E_{\mathrm{DFT}} = -\sum_{\alpha,\beta} K^{\alpha\beta} \int \phi_\beta^*(\mathbf{r}) \frac{1}{2}\nabla^2 \phi_\alpha(\mathbf{r}) d\mathbf{r} + \int V_{\mathrm{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int\int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}[n]$$

Linear-scaling DFT in practice

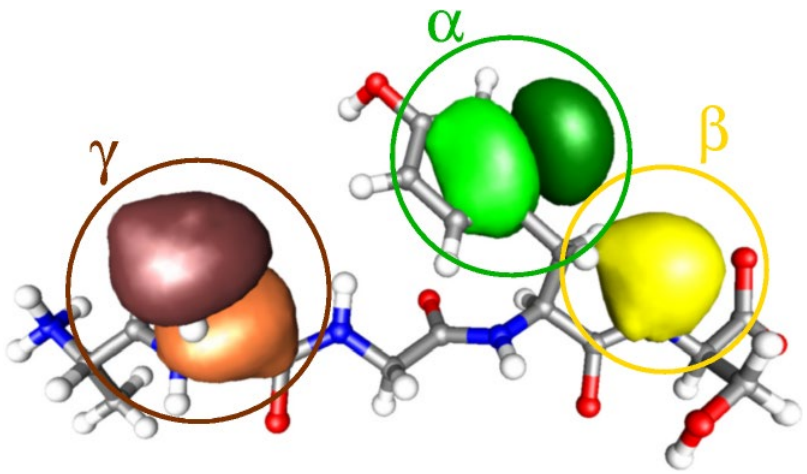
Conflicting requirements



How can we have linear-scaling cost with “cubic-scaling accuracy” ?

The ONETEP linear-scaling approach

- Use a minimal number of $\{\phi_\alpha\}$
- Optimise both **K** and $\{\phi_\alpha\}$
- Aim is to have linear-scaling DFT with large basis set accuracy



$$\rho(\mathbf{r},\mathbf{r}') = \sum_{\alpha\beta} \phi_\alpha(\mathbf{r}) K^{\alpha\beta} \phi_\beta(\mathbf{r}')$$

Non-orthogonal Generalised Wannier Functions (**NGWFs**)

Density kernel

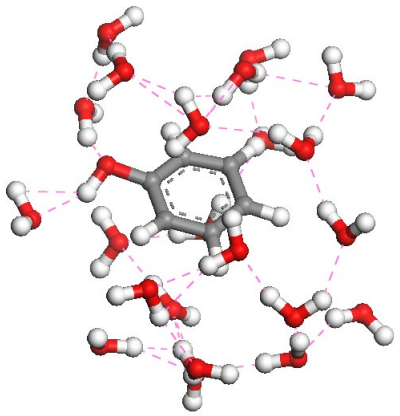
- NGWFs confined to spherical regions
- Density kernel **K** sparse by truncation

C.-K. Skylaris, A. A. Mostofi, P. D. Haynes, O. Dieguez, M. C. Payne, *Phys. Rev. B* **66**, 035119 (2002).

C.-K. Skylaris, P. D. Haynes, A. A. Mostofi and M. C. Payne, *J. Chem. Phys.* **122**, 084119 (2005).

C.-K. Skylaris, P. D. Haynes, A. A. Mostofi and M. C. Payne, *Phys. Stat. Sol. (b)* **243**, 973 (2006).

Linear-scaling with near-complete basis set accuracy



Example: binding energy calculation

ONETEP linear-scaling DFT

NGWF radii (Å)	# NGWFs	BE (kcal/mol)
2.9	166	**-11.93**
3.2	166	**-12.86**
3.7	166	**-8.25**
4.2	166	**-7.06**
4.8	166	**-7.04**

Cubic-scaling DFT

Basis set	# AOs	BE + BSSE (kcal/mol)
3-21G	361	**-12.55**
6-31G*	535	**-8.95**
6-311++G**	1017	**-7.39**
cc-pVTZ	1765	**-7.04**

C.-K. Skylaris, O. Dieguez, P. D. Haynes and M. C. Payne, *Phys. Rev. B* **66**, 073103 (2002).

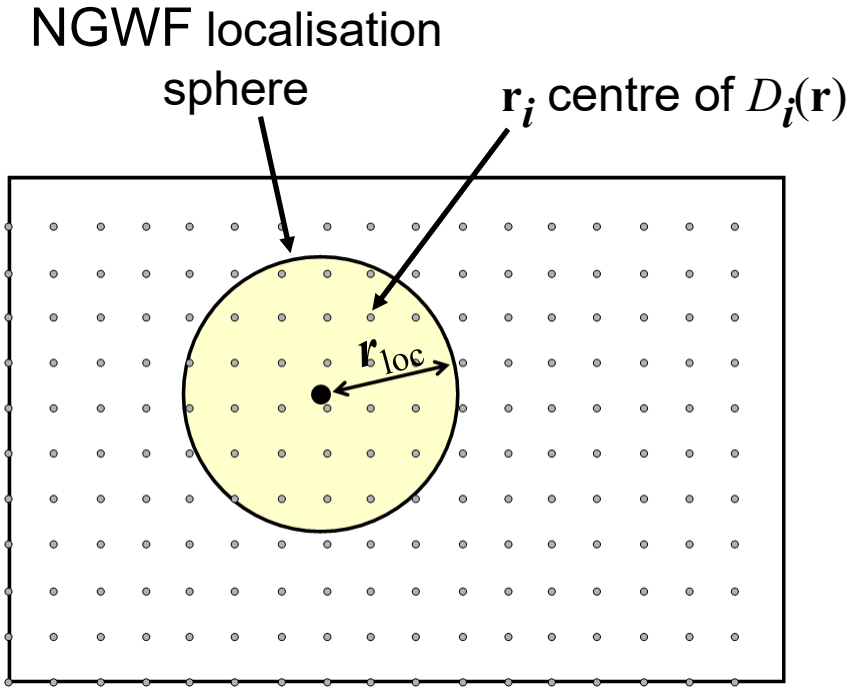
P. D. Haynes, C.-K. Skylaris, A. A. Mostofi and M. C. Payne, *Chem. Phys. Lett.* **422** 345 (2006).

Psinc basis set

- Real linear combinations of plane waves
- Highly localised
- Orthogonal

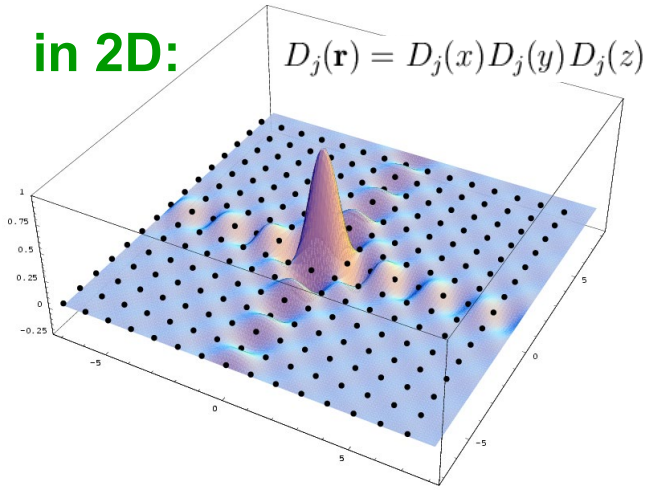
$$D_j(\mathbf{r}) = \frac{1}{N} \sum_{\mathbf{G}}^{\mathbf{G}_{\max}} e^{i\mathbf{G}\cdot(\mathbf{r}-\mathbf{r}_j)}$$

$$\phi_\alpha(\mathbf{r}) = \sum_{i \in \mathrm{LR}_\alpha} D_i(\mathbf{r})\, C_{i,\alpha}$$



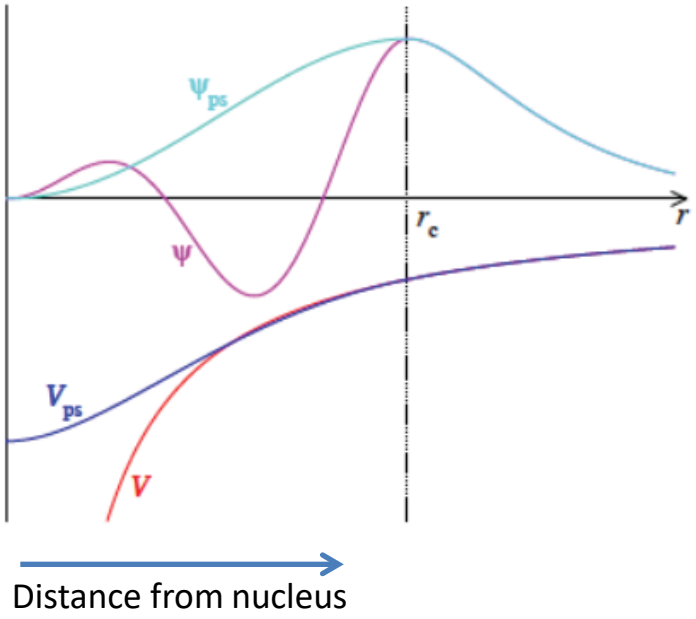
in 2D:

$$D_j(\mathbf{r}) = D_j(x) D_j(y) D_j(z)$$



- A. A. Mostofi, P. D. Haynes, C.-K. Skylaris and M. C. Payne, *J. Chem. Phys.* **119**, 8842 (2003)
- D. Baye and P. H. Heenen, *J. Phys. A: Math. Gen.* **19**, 2041 (1986)

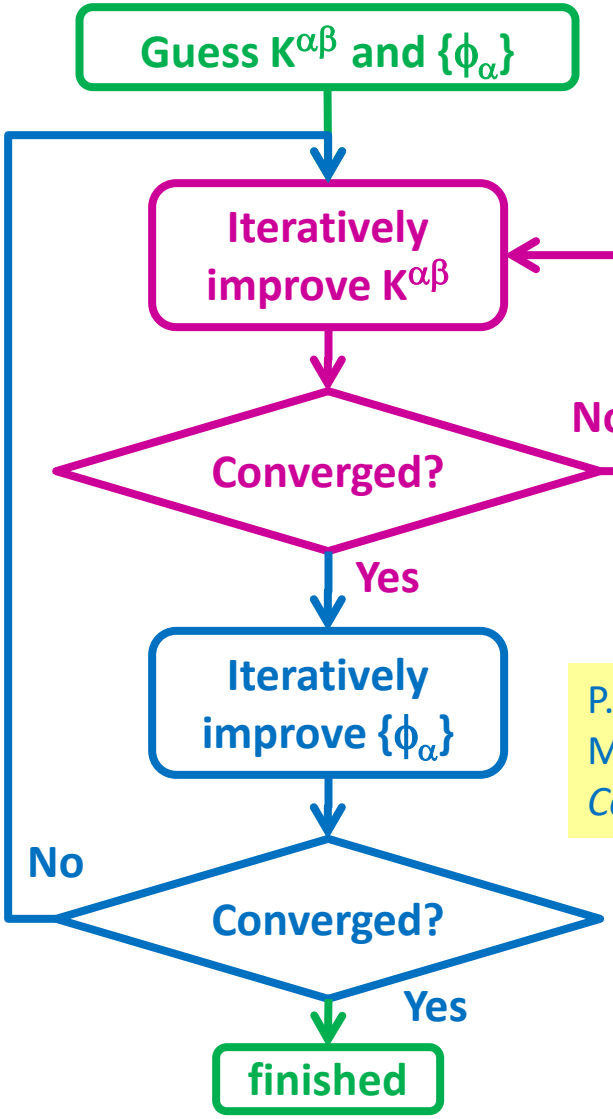
Pseudopotentials



- Replace the strong Coulomb nuclear potential V by a much weaker *pseudopotential* V_{ps} which mimics the effect of the core electrons
- Only keep the valence electrons, in smooth valence wave functions Ψ_{ps} without oscillations in the core region
- Eliminating the 1/r singularity at the nucleus and the rapid oscillations of the valence wavefunctions near it make it possible to use a plane wave basis set and converge with a reasonable kinetic energy cut-off
- Even hydrogen atoms (obviously, no core electrons) have pseudopotentials in plane wave calculations!

- Beyond the core radius r_c, the V_{ps} and Ψ_{ps} match the all-electron calculation
- Determining r_c, as well as which electrons to remove as "core" and which to keep as "valence" is an art and requires experience
- Small r_c leads to "hard" pseudopotentials which are more transferable but require more plane waves (higher E_{max}) and therefore more computational effort
- There are several recipes for generating pseudopotentials and libraries of these are publicly available, see for example http://opium.sourceforge.net/ and http://www.sas.upenn.edu/rappegroup/research/pseudo-potential-gga.html
- Before selecting a pseudopotential it is crucial to test it thoroughly, ideally against all-electron calculations

Energy optimisation in ONETEP



$$E = E[\mathbf{K}, \{\phi_\alpha\}]$$

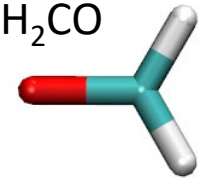
- **Outer loop:** Optimise total (interacting) energy *E* w.r.t. to **K** and $\{\phi_\alpha\}$

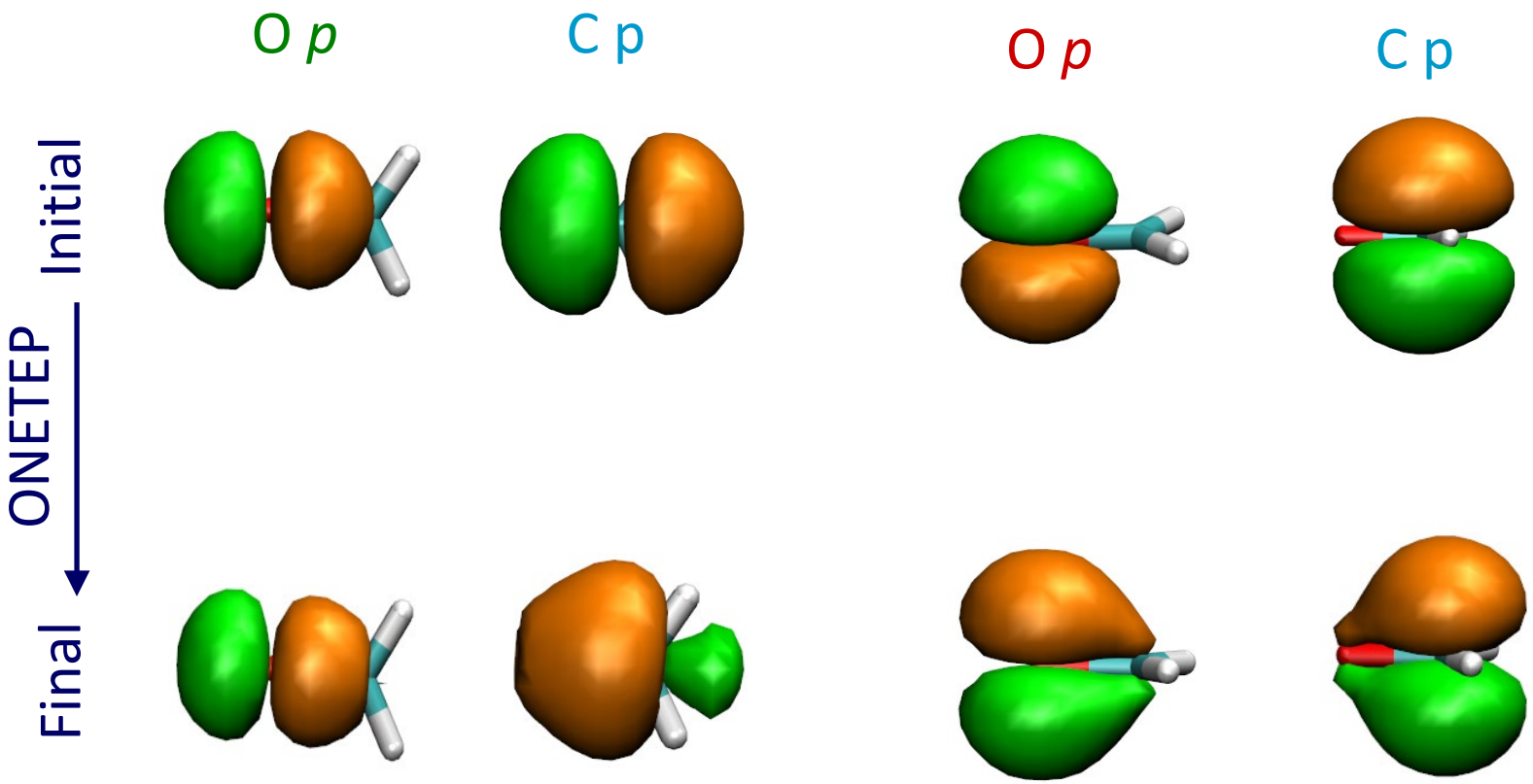
- **Inner loop**: Optimise total (interacting) energy *E* w.r.t **K** for fixed $\{\phi_\alpha\}$ while imposing **idempotency** and **normalisation**

P. D. Haynes, C.-K. Skylaris, A. A. Mostofi and M. C. Payne, *J. Phys. Condens*. Matter **20**, 294207 (2008)

NGWF optimisation

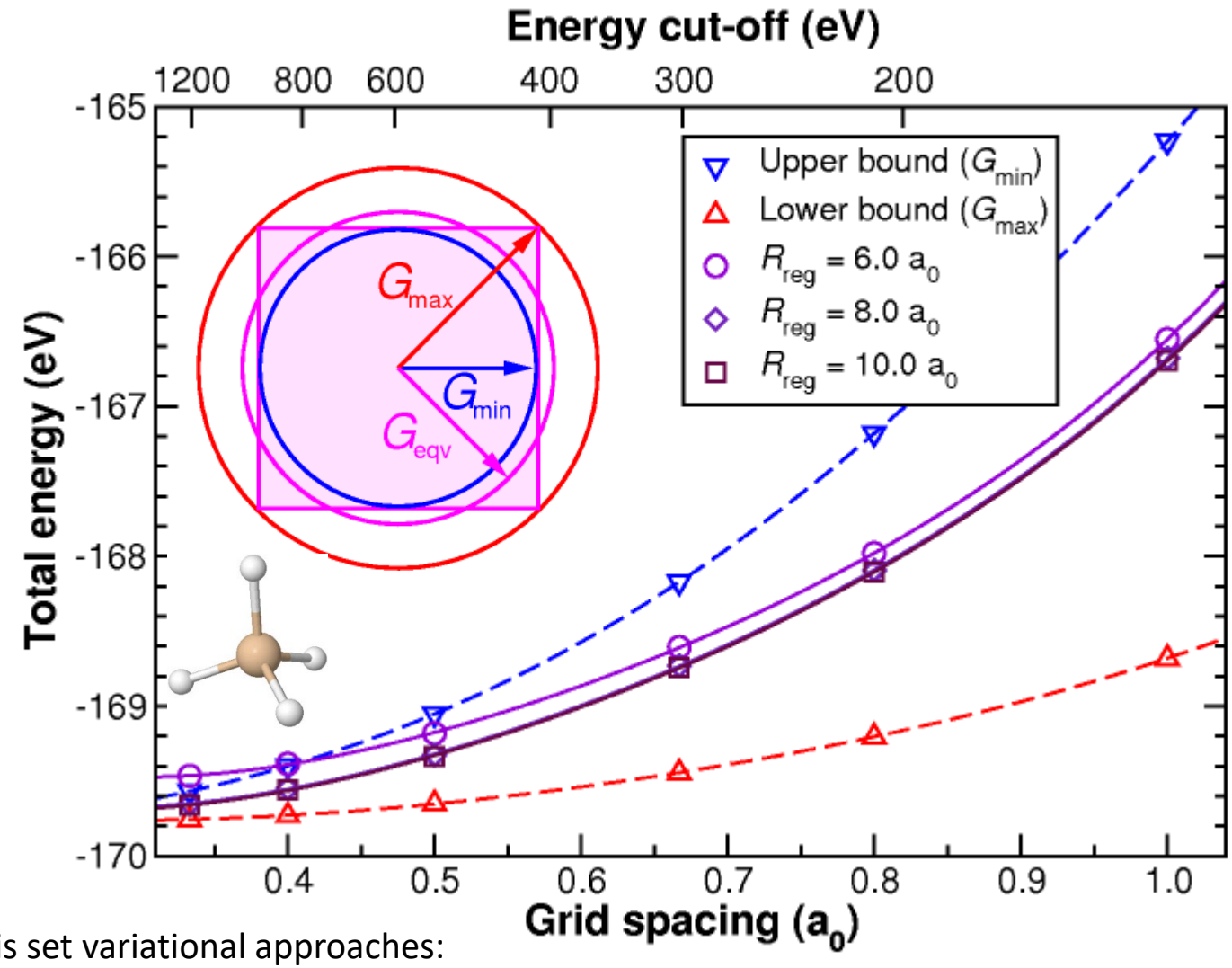
formaldehyde, H_2CO





UNIVERSITY OF Southampton
School of Chemistry

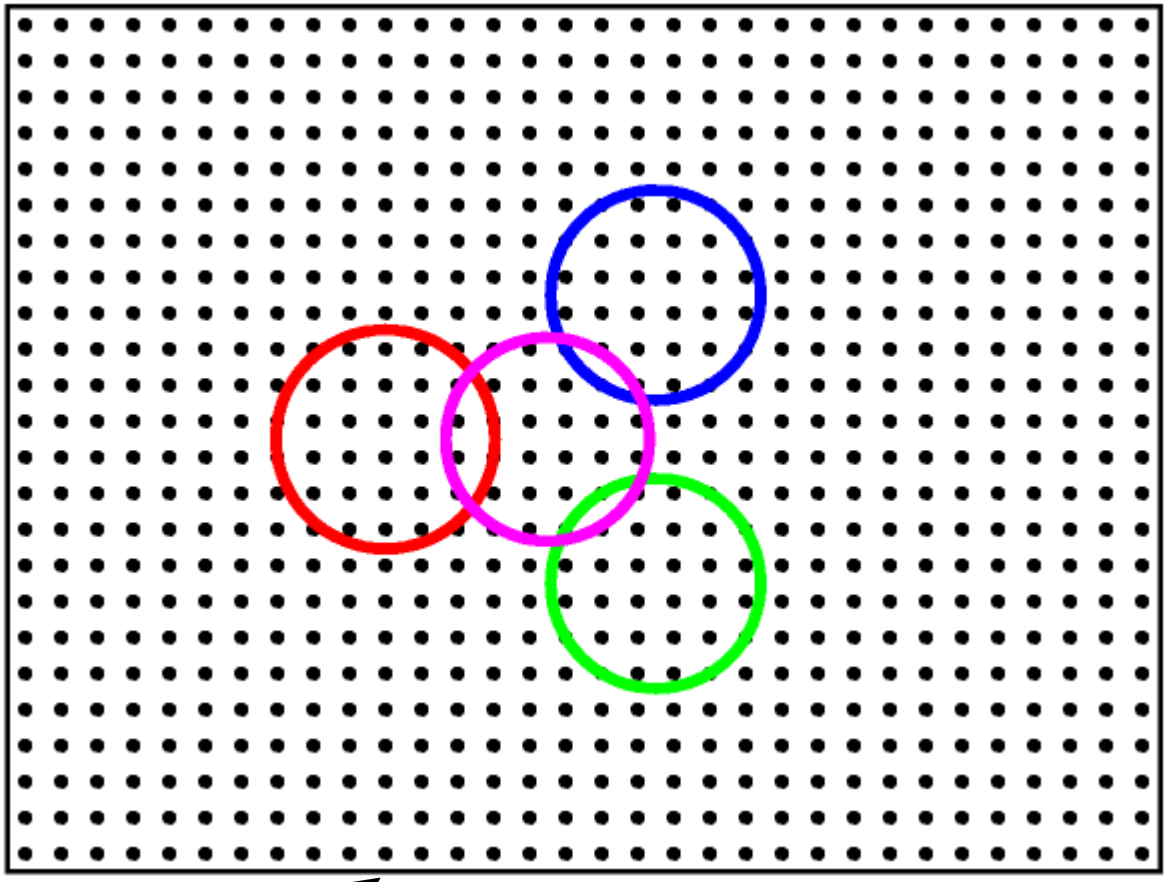
Psinc basis energy cut-off



Basis set variational approaches:

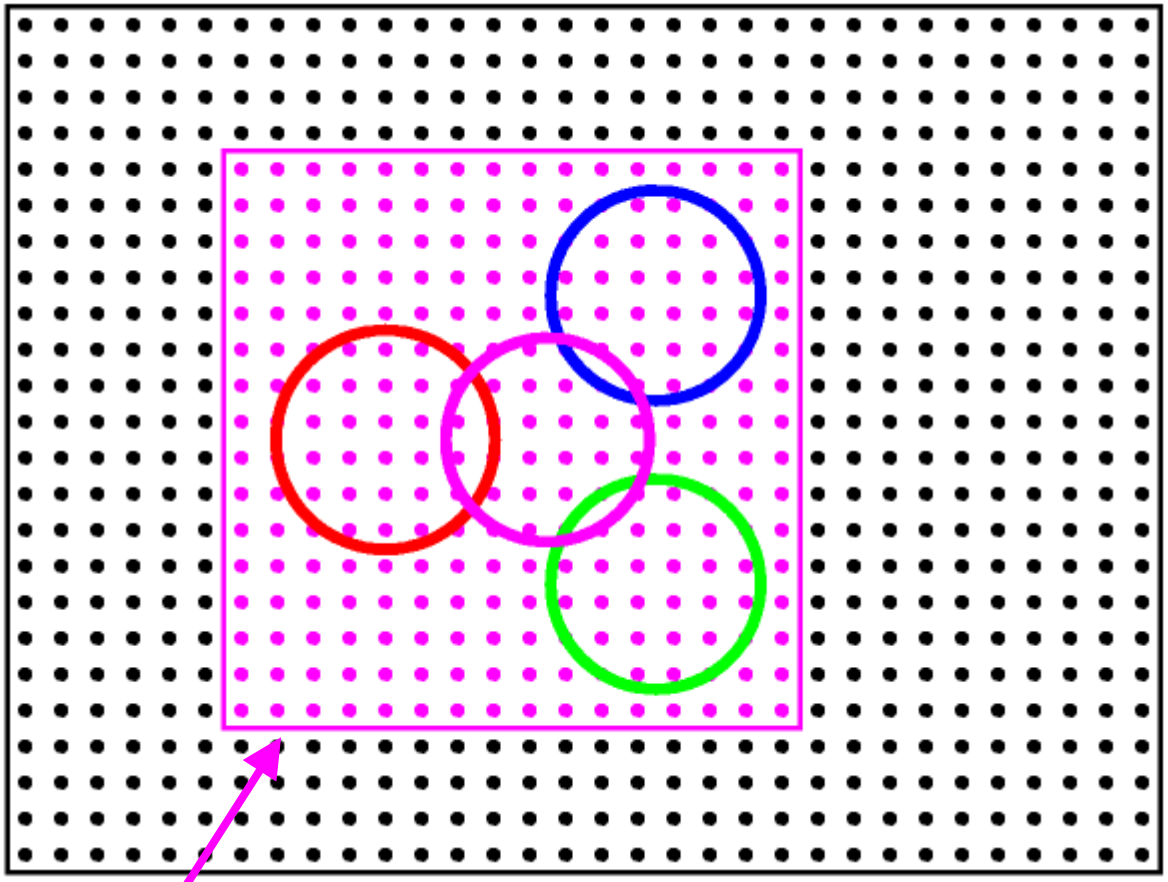
C.-K. Skylaris, O. Dieguez, P. Haynes and M. C. Payne, *Phys. Rev. B* **66**, 073103 (2002).

FFT box technique



simulation cell

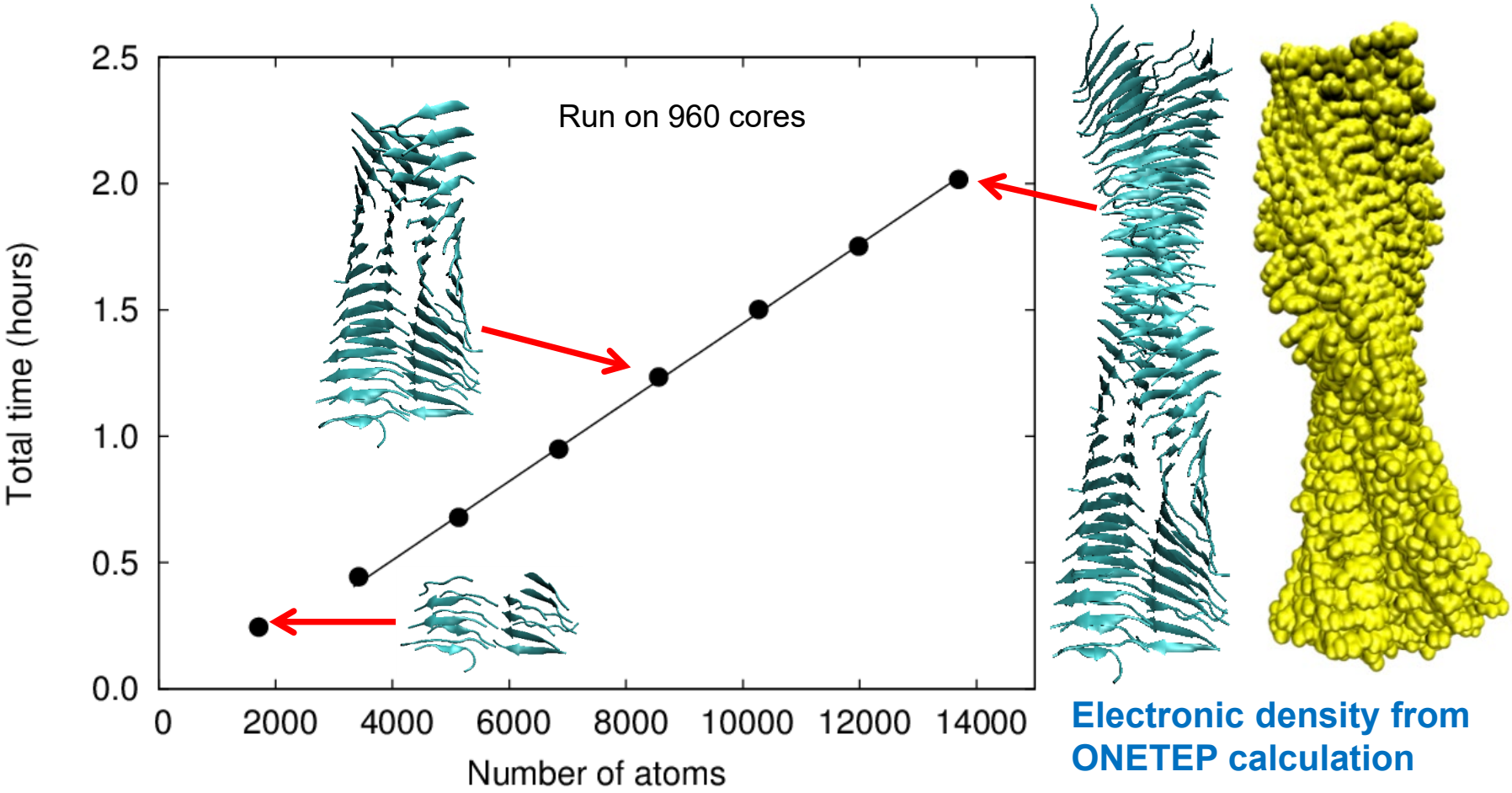
FFT box technique



C.-K. Skylaris, A. A. Mostofi, P. D. Haynes, C. J. Pickard & M. C. Payne, *Comp. Phys. Comm.* **140**, 315 (2001)
A. A. Mostofi, C.-K. Skylaris, P. D. Haynes & M. C. Payne, *Comp. Phys. Comm.* **147**, 788 (2002)

Linear-scaling with the number of atoms

Example: ONETEP calculations on amyloid fibril proteins

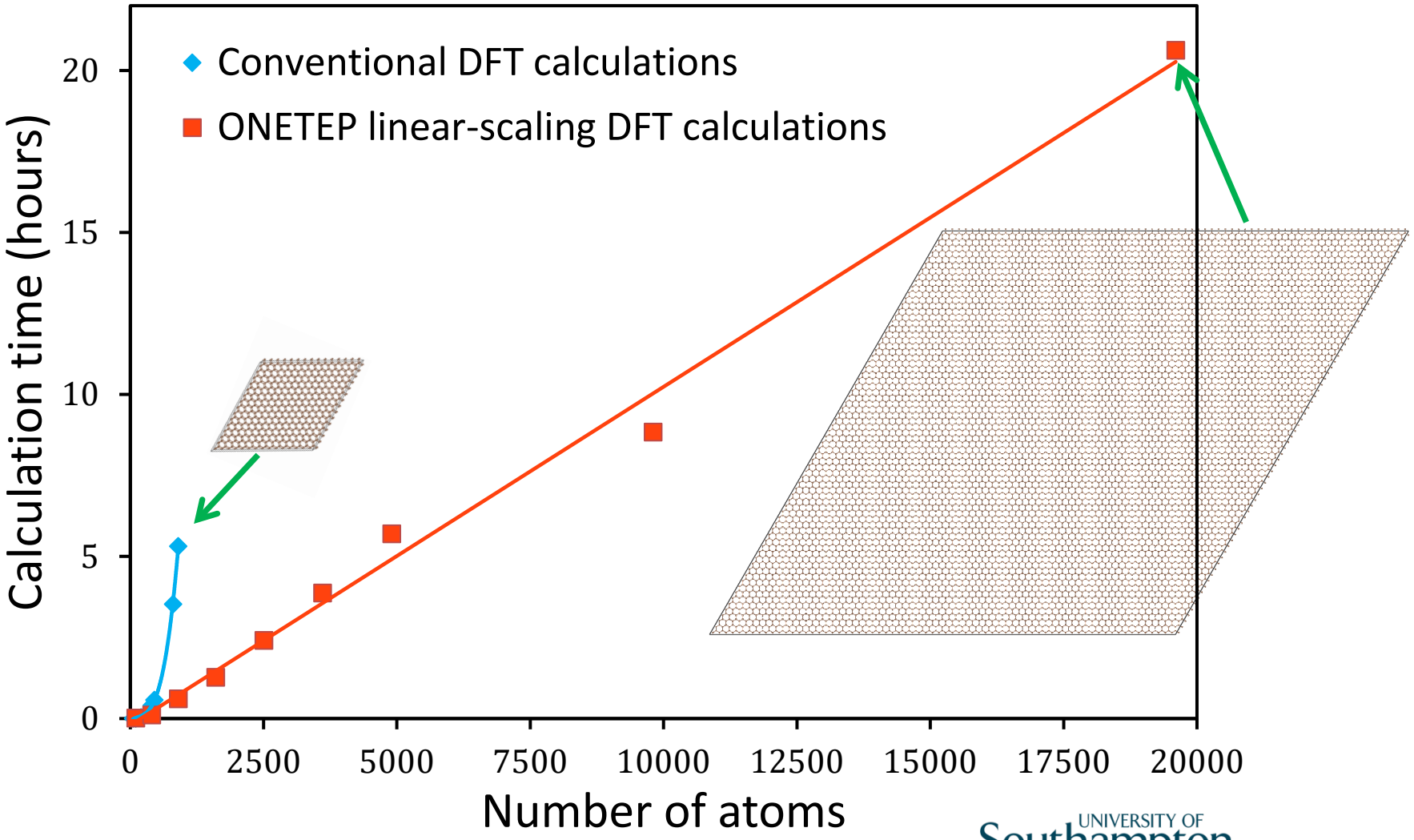


Structures of the amyloid fibril kindly provided by the authors of
J. T. Berryman, S. E. Radford and S. A. Harris, Biophysical Journal, ***97*** *1 (2009)*

Linear-scaling with the number of atoms

Example: ONETEP calculations on graphite segments

Calculations run on 160 2.0 GHz Intel Skylake cores (4 nodes, with 2x20 cores per node) with 192 GB per node



Compiling ONETEP

Simple multi-platform build system, needs:

- Fortran 2003/2008 compiler
- BLAS and LAPACK (or SCALAPACK) numerical libraries
- FFT library: vendor-supplied or FFTw
  - www.fftw.org
- MPI library for parallel version
- OpenMP

Running ONETEP

- Parallel computer
  - Minimum 1 GB per processor (core)
  - Typically distribute 10-100 atoms per processor
  - Cross-over >100 atoms

- Prepare input file: free format
  - Documentation at www.onetep.org

- Supply pseudopotential files (`.recpot` format)

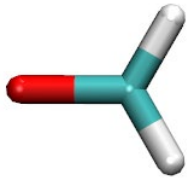
- We suggest that instead of running ONETEP directly, you run the **onetep_launcher** script which sets up correctly the runtime environment and does important checks

Input file

- Keywords of different types:
  - Integer
  - Boolean
  - String
  - Real
  - Physical (real + unit)
  - Block data e.g. atomic positions, delimited by **`%block`** and **`%endblock`**
- Atomic units by default (hartree and bohr)

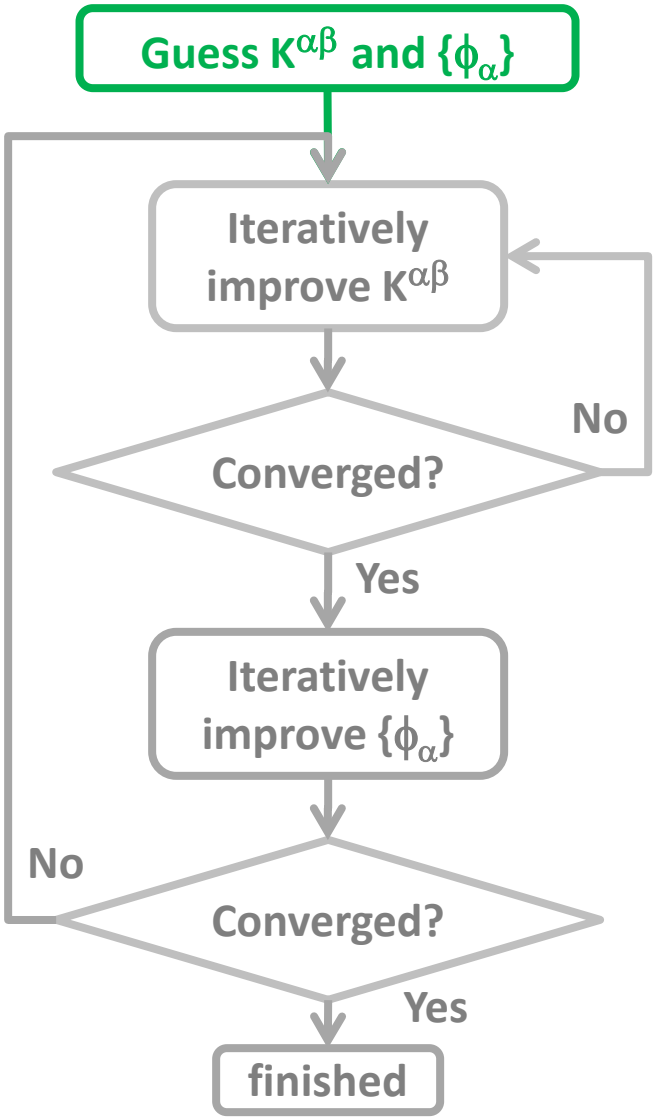
Example input file: formaldehyde

```
! Example input file for the ONETEP program
! Formaldehyde molecule

cutoff_energy 600 eV

%block   lattice_cart
  48.00     0.00     0.00
   0.00    48.00     0.00
   0.00     0.00    48.00
%endblock  lattice_cart

%block  positions_abs
O     24.887507   23.896975   22.647313
C     27.731659   23.667449   22.643306
H     28.655157   21.721170   22.637547
H     28.955467   25.440371   22.646039
%endblock  positions_abs

%block species
O    O    8    4    6.5
C    C    6    4    6.5
H    H    1    1    6.5
%endblock species

%block species_pot
O    oxygen.recpot
C    carbon.recpot
H    hydrogen.recpot
%endblock species_pot
```



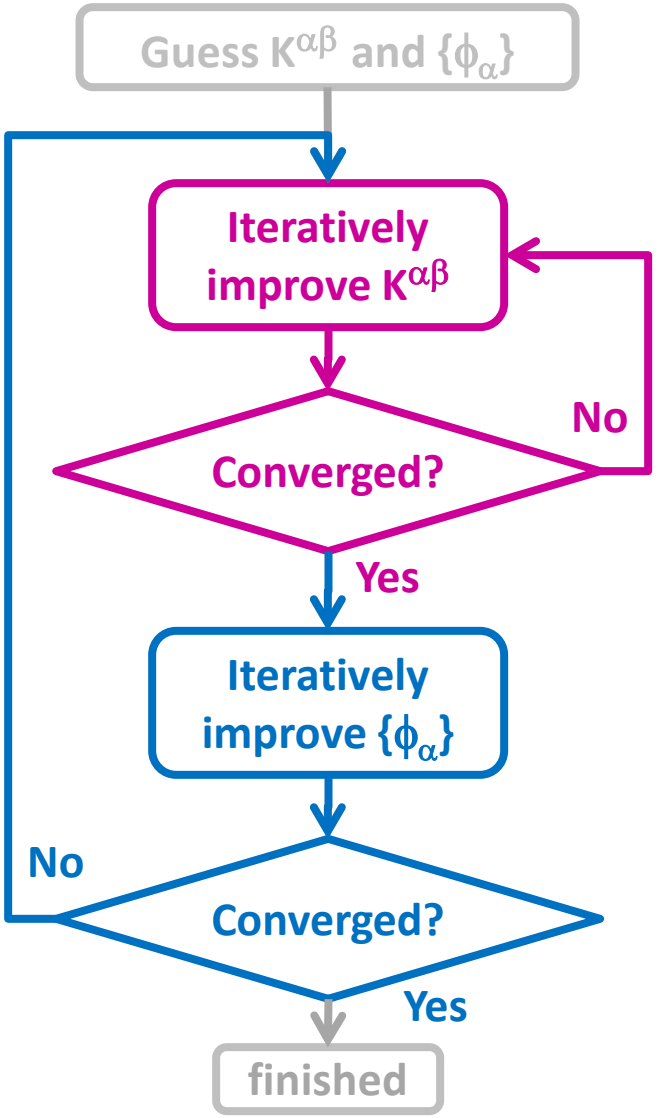
ONETEP calculation outline

- Initialisation phase:
  - Construct initial NGWFs (STOs or PAOs)
  - Construct initial charge density (atomic superposition) and effective potential
  - Construct initial Hamiltonian
  - Obtain initial density kernel using iterative approach



ONETEP calculation outline continued

- Main optimisation phase:
  - Combination of nested self-consistent loops
  - Outer loop optimises the NGWFs (density kernel fixed)
  - Inner loop optimises the density kernel (NGWFs fixed) using Density Matrix Minimisation approaches



Example output file: formaldehyde

```
+-------------------------------------------------------------+
|                                                             |
|        ####### #     # ####### ####### ####### ######      |
|        #     # ##    # #          #    #       #     #     |
|        #     # # #   # #          #    #       #     #     |
|        #     # #  #  # #####      #    #####   ######      |
|        #     # #   # # #          #    #       #           |
|        #     # #    ## #          #    #       #           |
|        ####### #     # #######    #    ####### #           |
|                                                             |
|        Linear-Scaling Ab Initio Total Energy Program        |
|                                                             |
|          Release for academic collaborators of ODG          |
|                                          Version 6.1.15.7   |
|                                                             |
+-------------------------------------------------------------+
|                                                             |
|  Authors:                                                   |
|  Jacek Dziedzic, Peter D. Haynes, Nicholas D. M. Hine,      |
|  Arash A. Mostofi, Mike C. Payne and Chris-Kriton Skylaris  |
|                                                             |
|  Contributors:                                              |
|  J. Aarons, L. Andrinopoulos, P. W. Avraam, R. A. Bell,     |
|  A. Bhandari, G. A. Bramley, R. J. Charlton, S. J. Clark,   |
|  R. J. Clements, G. C. Constantinescu, F. Corsetti,         |
|  N. Corsini, O. Dieguez, S. M. M. Dubois, K. K. B. Duff,    |
|  J. M. Escartin, A. Greco, H. Helal, Q. O. Hill, L. P. Lee, |
|  J.-H. Li, E. B. Linscott, G. Moynihan, D. D. O`Regan,      |
|  O. K. Okan, M. J. S. Phipps, C. J. Pickard,                |
|  J. C. A. Prentice, M. I. J. Probert, L. E. Ratcliff,       |
|  M. Robinson, A. Ruiz Serrano, J. S. Spencer, E. W. Tait,   |
|  G. Teobaldi, D. Turban, V. Vitale, K. A. Wilkinson,        |
|  C. Weber, J. C. Womack, N. Yeung and T. J. Zuehlsdorff     |
|                                                             |
|                                  Copyright (c) 2004-2023    |
|                                                             |
```

- Parallel strategy, calculation parameters

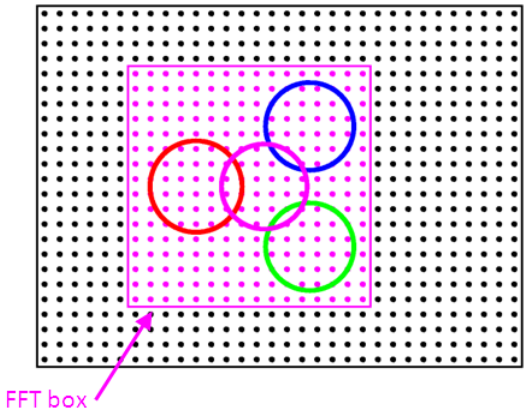
```
Job started: 09-01-2023 11:33 (-0000)

Reading parameters from file "h2co_2-threads.dat" ..... done

If your calculation crashes here, before "Checking processes and threads..."
is displayed, then your stack size is insufficient.
If so, use "ulimit -s unlimited" at runtime.
You can disable this check with "check_stack_size F".

Checking processes and threads...
      Default threads: 2
   Running with 2 MPI processes.
   There are 2 MPI processes running on the same node as the root process.
   Each MPI process is using:
               2 threads for simulation cell FFTs.
               2 threads for parallel FFT box operations.
               2 threads for loops over batched FFT box operations.
               2 threads in other parallel regions.
... done

Basic input checks..... done

Reading geometry and species blocks from file "h2co_2-threads.dat" ...
  <species_atomic_set> block not found: NGWF initialisation set to SOLVE
... done


-------------------------------------------------------------------------------
---------------------------------- INPUT FILE ---------------------------------
-------------------------------------------------------------------------------

cutoff_energy 600 eV
```

Input file parameters for OMP threads

```
threads_max 2
threads_per_fftbox 2
threads_num_fftboxes 2
threads_per_cellfft 2
```

Example output file: formaldehyde

```
------------------------- Atom counting information -------------------------
Symbol     Natoms     Nngwfs     Nprojs
  O           1          4          1
  C           1          4          1
  H           2          2          0
.......    ......     ......     ......
Totals:       4         10          2
-----------------------------------------------------------------------------

============================== PSINC grid sizes =============================
                       Simulation cell:   84 x  84 x  84
                               FFT-box:   75 x  75 x  75
                                   PPD:    6 x   6 x   1
Grid space d1=  0.571428571429a0 (KE cutoff=  23.26377Eh = 633.03940eV)
Grid space d2=  0.571428571429a0 (KE cutoff=  23.26377Eh = 633.03940eV)
Grid space d3=  0.571428571429a0 (KE cutoff=  23.26377Eh = 633.03940eV)
=============================================================================
```



- Simulation cell, FFT box, grid spacing

Example output file: formaldehyde

- NGWF initialisation to pseudo-atomic orbitals (PAOs)

```
Atom SCF Calculation for O  : Z (AE atom) =   8 : Z (PS atom) =   6
Config String:
Orbitals (num,occ):  2     2.00 4.00
Orbitals   (num,l):  2        0    1
Atom SCF converged after  33 iterations to a total energy of    -15.71589674

Atom SCF Calculation for C  : Z (AE atom) =   6 : Z (PS atom) =   4
Config String:
Orbitals (num,occ):  2     2.00 2.00
Orbitals   (num,l):  2        0    1
Atom SCF converged after  33 iterations to a total energy of     -5.33577996

Atom SCF Calculation for H  : Z (AE atom) =   1 : Z (PS atom) =   1
Config String:
Orbitals (num,occ):  1     1.00
Orbitals   (num,l):  1        0
Atom SCF converged after  30 iterations to a total energy of     -0.43623914
NGWF initialisation ..... done
```

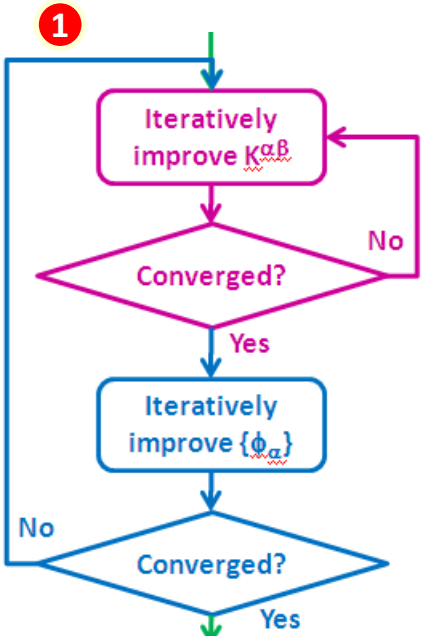
Example output file: formaldehyde

- Initialise and refine density kernel

```
Up spin density kernel initialisation ...... done

Writing density kernel to file "h2co.dkn" ... done

>>> Optimising kernel for current NGWFs:
   iter   |      energy (Eh)       | rms gradient |  commutator  |   dE (Eh)
    1        -2.230601586111E+01     5.3808E-02     4.4840E-02
    2        -2.233073648394E+01     3.8281E-02     3.1901E-02    -2.4721E-02
    3        -2.235530086009E+01     1.1889E-02     9.9074E-03    -2.4564E-02
    4        -2.235864046835E+01     6.8691E-03     5.7242E-03    -3.3396E-03
    5        -2.235945547230E+01     3.9727E-03     3.3106E-03    -8.1500E-04
Finished density kernel iterations (   5)

Writing density kernel to file "h2co.dkn" ... done


>>> Density kernel optimised for the current NGWF basis:
     ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
     Total energy                =  -2.23594554723032E+01  Eh
     Estimated bandgap           =   5.4645E-02  Eh
     RMS occupancy error         =   5.0205E-13
     [H,K] commutator            =   3.3106E-03
     Occupancy bounds            = [  0.000:  1.000]
     ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
```

Example output file: formaldehyde

- SCF iterations



1

```
################################################################################
########################### NGWF CG iteration  003 ############################
################################################################################

>>> Checking for convergence of NGWFs:   NOT CONVERGED
  ================================================================================
         NGWF RMS gradient =  5.2368E-04 >  2.0000E-06  | above tolerance
  ================================================================================

>>> Improving NGWFs using line search:
  ================================================================================
   Predicted total energy    =      -2.26058828338753E+01 Eh
   Predicted gain in energy  =      -6.90722410908862E-03 Eh
  ================================================================================

Writing NGWFs to file "h2co.tightbox_ngwfs"....  done

>>> Optimising kernel for current NGWFs:
   iter   |       energy (Eh)        | rms gradient |  commutator  |   dE (Eh)
    1        -2.260585039399E+01     4.3060E-03     3.5884E-03
    2        -2.260614202529E+01     8.8690E-04     7.3908E-04    -2.9163E-04
    3        -2.260616377801E+01     2.2375E-04     1.8646E-04    -2.1753E-05
    4        -2.260616700389E+01     5.2027E-05     4.3355E-05    -3.2259E-06
    5        -2.260616709879E+01     1.7239E-05     1.4365E-05    -9.4900E-08
Finished density kernel iterations (   5)

Writing density kernel to file "h2co.dkn" ... done


>>> Density kernel optimised for the current NGWF basis:
     ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
     Total energy                =  -2.26061670987944E+01  Eh
     Estimated bandgap           =   7.1917E-02  Eh
     RMS occupancy error         =   8.2047E-14
     [H,K] commutator            =   1.4365E-05
     Occupancy bounds            = [  0.000:  1.000]
     ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~


################################################################################
########################### NGWF CG iteration  004 ############################
################################################################################
```

Example output file: formaldehyde

- End of SCF calculation

```
>>> Checking for convergence of NGWFs:
            ..........................................................
            |         *** NGWF optimisation converged ***            |
            | RMS NGWF gradient =    0.00000126658643                |
            | Criteria satisfied:                                    |
            | -> RMS NGWF gradient lower than set threshold.         |
            ==========================================================

================================================================================
            ---------------- ENERGY COMPONENTS (Eh) ----------------
            | Kinetic                     :       14.91662629423981 |
            | Pseudopotential (local)     :      -75.55456193656947 |
            | Pseudo (non-coul chg cor)   :        0.00000000000000
            | Pseudopotential (non-local):        3.08867264674192 |
            | Hartree                     :       29.55304098295274 |
            | Exchange-correlation        :       -5.51703677107650 |
            | Ewald                       :       10.90369328705708 |
            | Total                       :      -22.60956549665441 |
            ----------------------------------------------------------
            Integrated density          :       11.99999999999941
================================================================================


                          <<<<< CALCULATION SUMMARY >>>>>
|ITER|     RMS GRADIENT    |      TOTAL ENERGY     |    step    |      Epredicted
   0     0.00339284991963    -22.35945547230321    0.578496    -22.56473206954799
   1     0.00109819484603    -22.56842090396507    0.774264    -22.59768874673372
   2     0.00052368029265    -22.59897560976616    0.779737    -22.60588283387525
   3     0.00030645887473    -22.60616709879438    0.778478    -22.60852120360797
   4     0.00017075786499    -22.60861681158951    0.618320    -22.60917256889675
   5     0.00010955112072    -22.60917385344275    0.827718    -22.60948077698849
   6     0.00006504197690    -22.60948592159049    0.577777    -22.60956236994081
   7     0.00000603288289    -22.60956529599148   -0.003358    -22.60956529222391
   8     0.00000662328177    -22.60956547322916    0.099059    -22.60956549599337
   9     0.00000126658643    -22.60956549665442   <-- CG
```

Summary of Functionality

Total energies

- Different exchange-correlation functionals:
  - LDA (Ceperley-Alder-Perdew-Zunger, Vosko-Wilk-Nusair, PW92)
  - GGA (PW91, PBE, revPBE, RPBE, BLYP, XLYP, WC)
  - Non-local exchange-correlation functionals for dispersion (e.g. Langreth and Lundqvist, VV10)
  - Meta-GGAs, e.g. PKZB, B97m-v
  - Hartree-Fock exchange and hybrid functionals, B3LYP, PBE0
- Spin polarisation
- DFT+D (empirical dispersion)
- DFT+U
- Charge-constrained DFT
- Finite temperature DFT for metallic systems (Ensemble DFT, AQUA-FOE)
- Embedding (e.g. mGGA in LDA), using EMFT
- DFTB (GFN0 available, GFN1 and GFN2 to follow)

Summary of Functionality

Excited states

- Conduction NGWFs
- LR-TDDFT
- LR-TDDFT with the Tamm-Dancoff approximation (TDA)

Boundary conditions and embedding

- Periodic boundary conditions
- Open boundary conditions (Cut-off Coulomb, Martyna-Tuckerman or real-space open boundaries)
- Solvent and electrolyte models
- Electrostatic embedding

Core electrons

- Norm conserving pseudopotentials
- Projector Augmented wave (PAW) approach (all electron)

Summary of Functionality

Atomic forces and stresses

- Geometry optimisation
- Transition state search
- *Ab initio* molecular dynamics
- Simulation cell relaxation

Visualisation

- NGWFs
- Molecular Orbitals
- Density and potentials
- Electron Localisation Function (ELF)

Atomic orbital basis set option

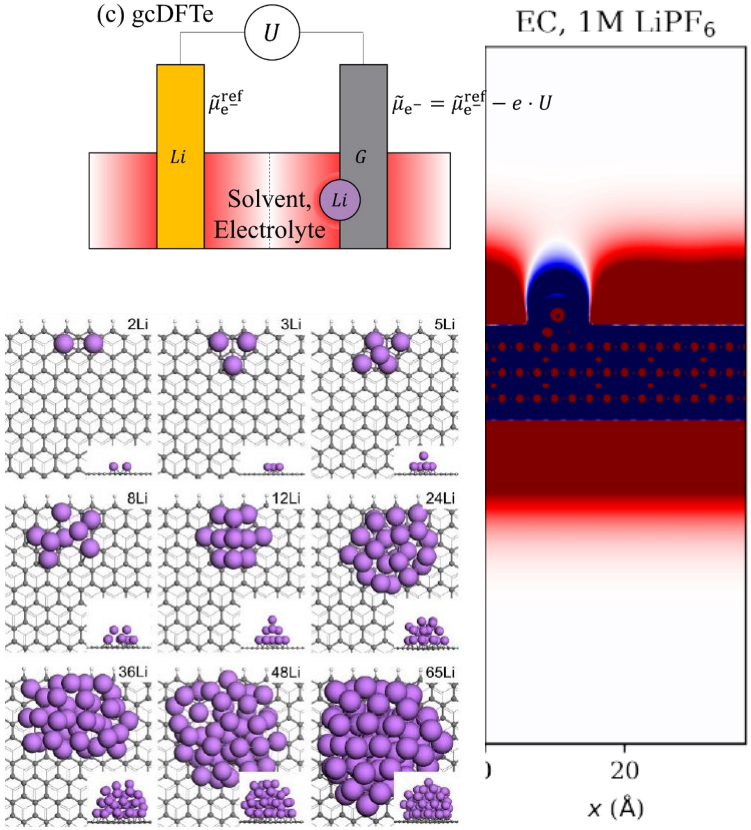
- Instead of NGWFs construct and use SZ, SZP, DZ, DZP, etc atomic orbital basis sets

Summary of Functionality

Electronic properties

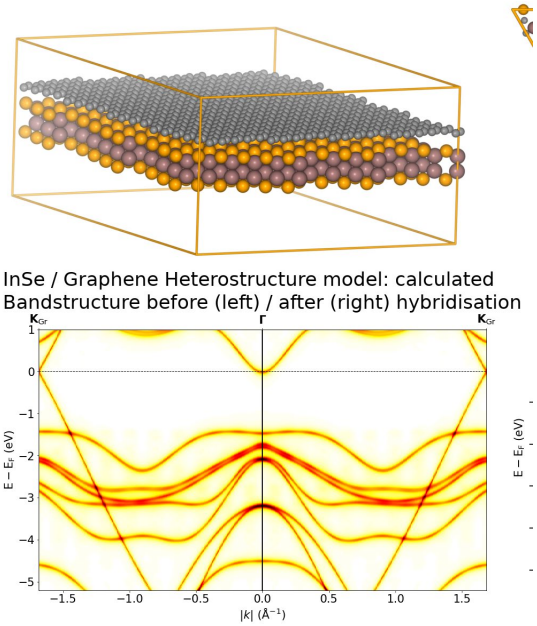
- Density of states (DOS), local DOS, projected DOS
- Atomic charges (Mulliken, IH, Density derived electrostatic and chemical (DDEC))
- Dipoles and higher moments
- Optimisation of separate NGWF set for accurate conduction bands and optical absorption spectra
- Natural Bond Orbital (NBO) analysis (Natural Atomic Orbitals in ONETEP and interface to NBO5.9 program)
- Energy Decomposition Analysis (EDA)
- Electron transport
- Distributed multipole analysis

Simulations in electrolyte and voltage to predict degradation mechanisms in Li-ion batteries



J. Mater. Chem. A **10** 11426 (2022)

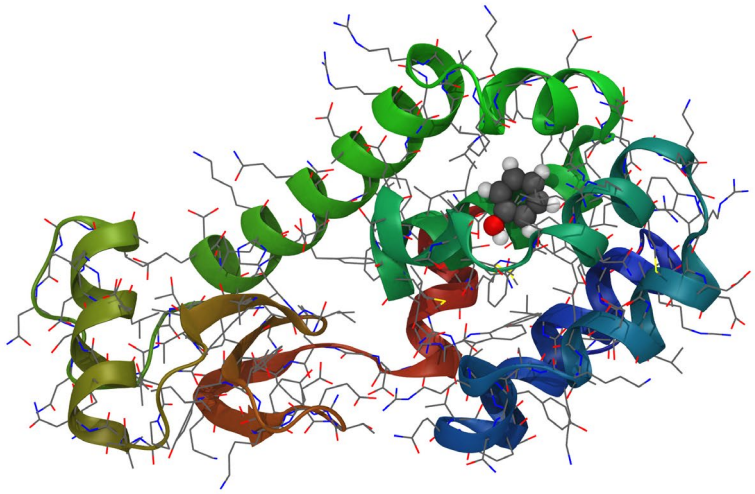
2-D heterostructures with "impossible" electronic and mechanical properties



ONETEP was required as the cell necessary to keep the strain low for a misaligned heterostructure is very large.

2D Mater. **8** 015016 (2020)

Drug design from quantum mechanical calculations on entire proteins

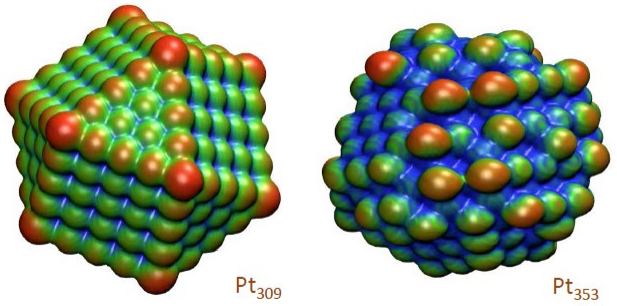


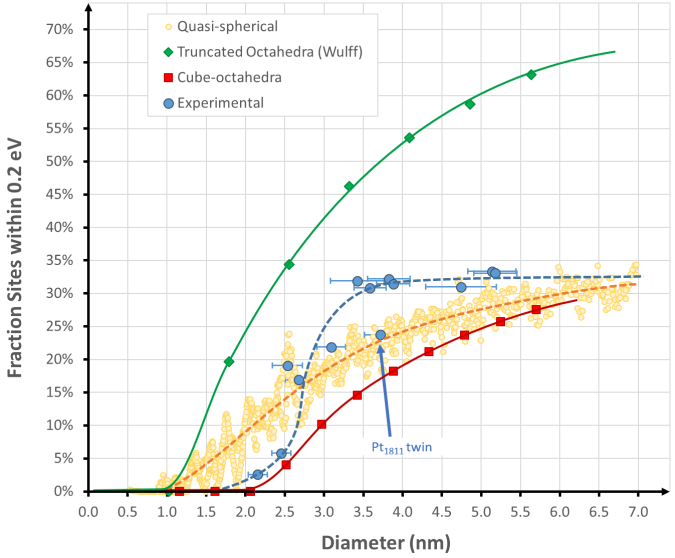
Motivation for full QM:

- Captures more physics (Polarization, Charge transfer Many-body effects)
- Low empiricism
- Transferable

Phys. Chem. Chem. Phys. **23** 9381 (2021)

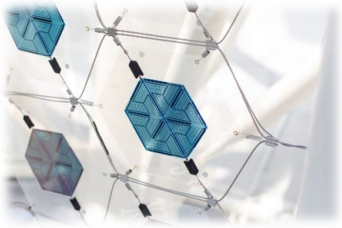
Predicting the catalytic activity of Pt nanoparticles

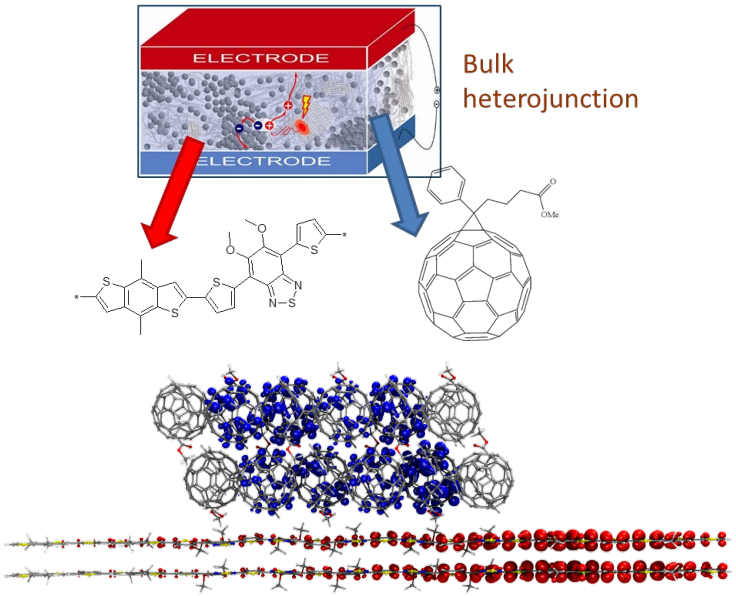




Nano Lett. **17** 4003 (2017)

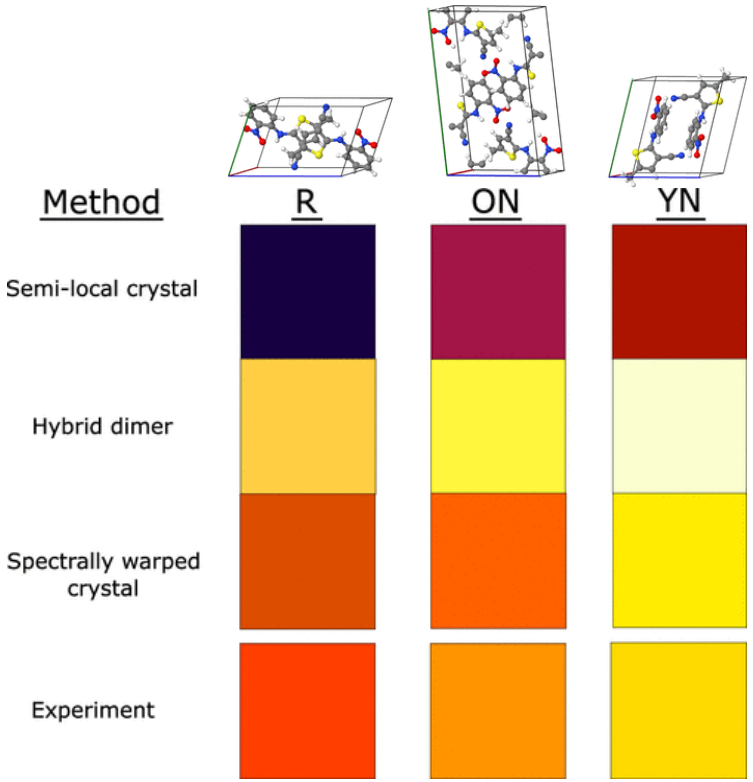
Organic photovoltaics: Linear-scaling Time-Dependent DFT (LS-TDDFT) calculations of excited states





J. Phys. Chem. C **122** 17024 (2018)

Colour prediction from excited state calculations: Including the full crystalline environment to predict experiment



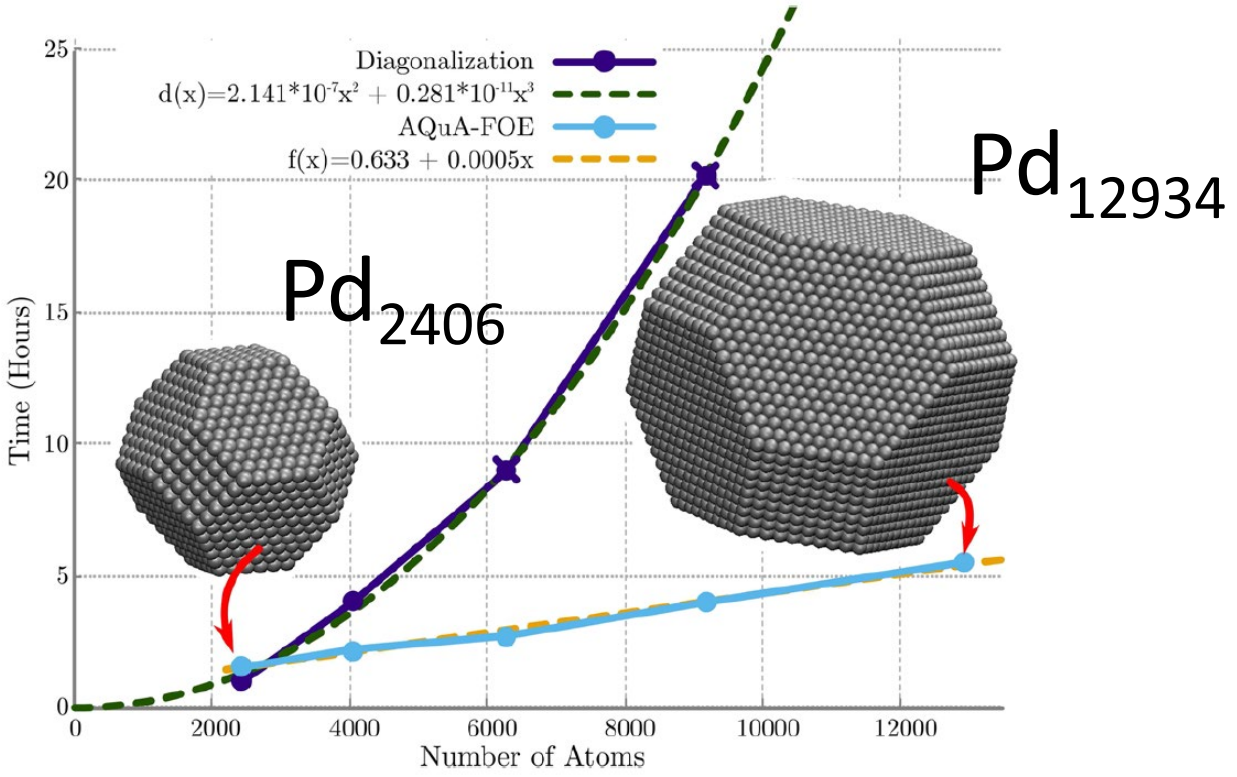
J. Chem. Theory Comput. **17** 5214 (2021)

New linear-scaling method for metallic systems in ONETEP

Annealing and QUenching Algorithm FOE (AQuA-FOE)

J. Aarons and C.-K. Skylaris, *J. Chem. Phys.* **148**, 074107 (2018)

- Construct the density matrix from a polynomial expansion of the Hamiltonian
- Number of terms kept constant by using high electronic temperature and then annealing to the target (low) temperature
- Comparison of AQUA-FOE with EDFT (cubic –scaling diagonalization based calculation)



UNIVERSITY OF Southampton
School of Chemistry

For more information: www.onetep.org