Introduction to ONETEP

Chris-Kriton Skylaris

Outline

- 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

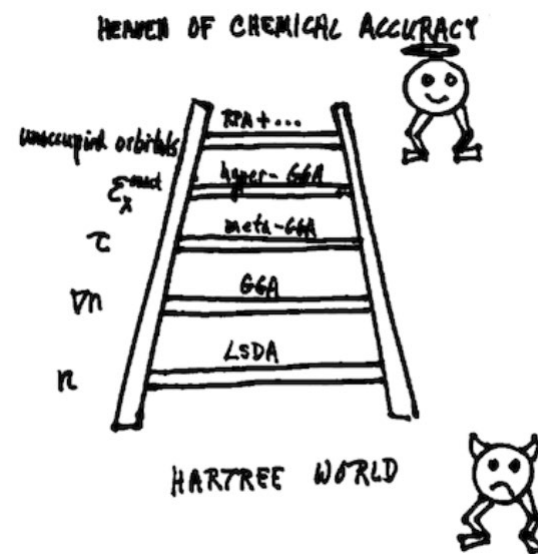- Examples of ONETEP applications

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")
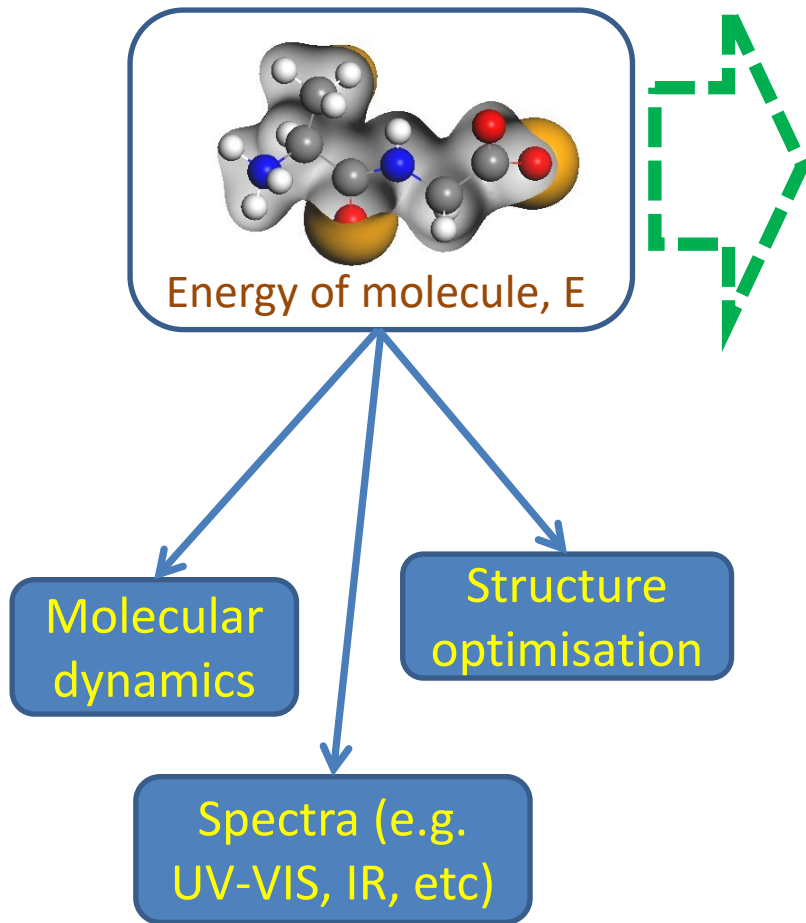
- Local density approximation (LDA): e.g. VWN or CAPZ correlation

- Generalised Gradient Approximations (GGA): e.g. BLYP, PW91, PBE

- Meta-GGAs: e.g. B95,B98,ISM,KCIS,PKZB,TPSS,VSXC

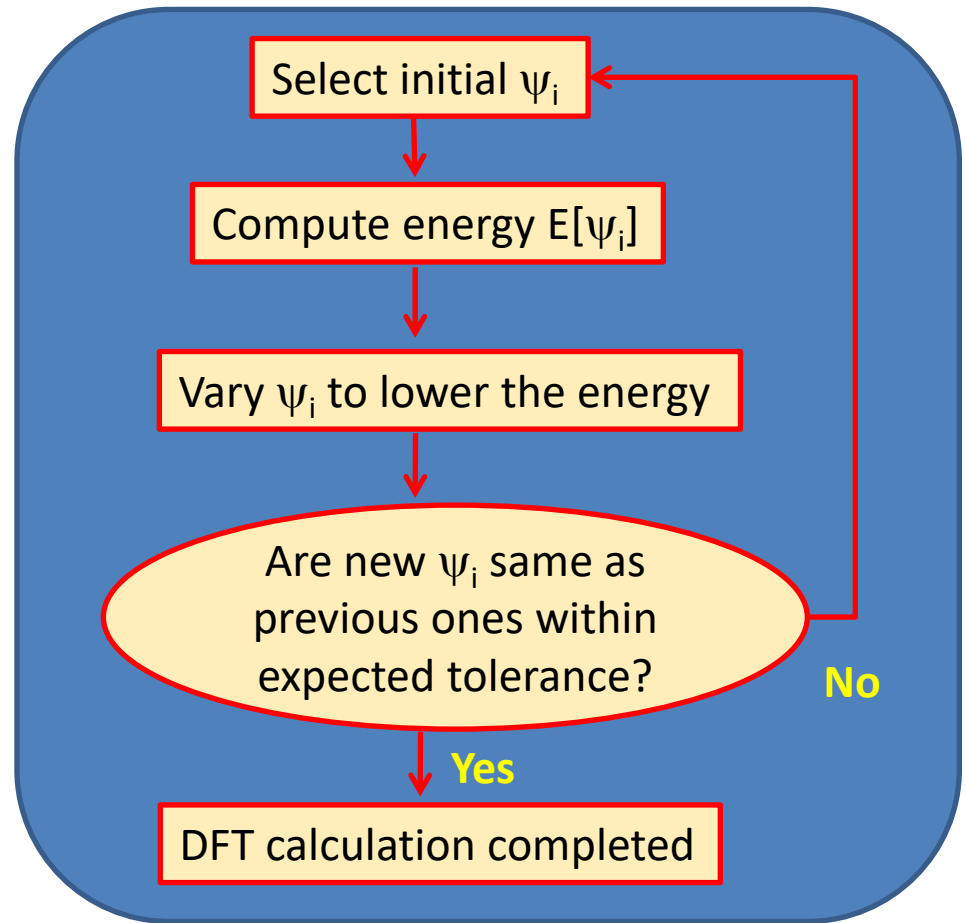- Hybrid (including exact exchange): e.g. B3LYP, B1PW91, B1LYP, B1B95, mPW1PW91, PBE1PBE

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

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DFT simulations

Molecular simulations

Energy of molecule, E

Molecular dynamics

Structure optimisation

Spectra (e.g. UV-VIS, IR, etc)

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

Select initial ψ_i

Compute energy $E[\psi_i]$

Vary ψ_i to lower the energy

Are new ψ_i same as previous ones within expected tolerance?

No

Yes

DFT calculation completed

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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

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

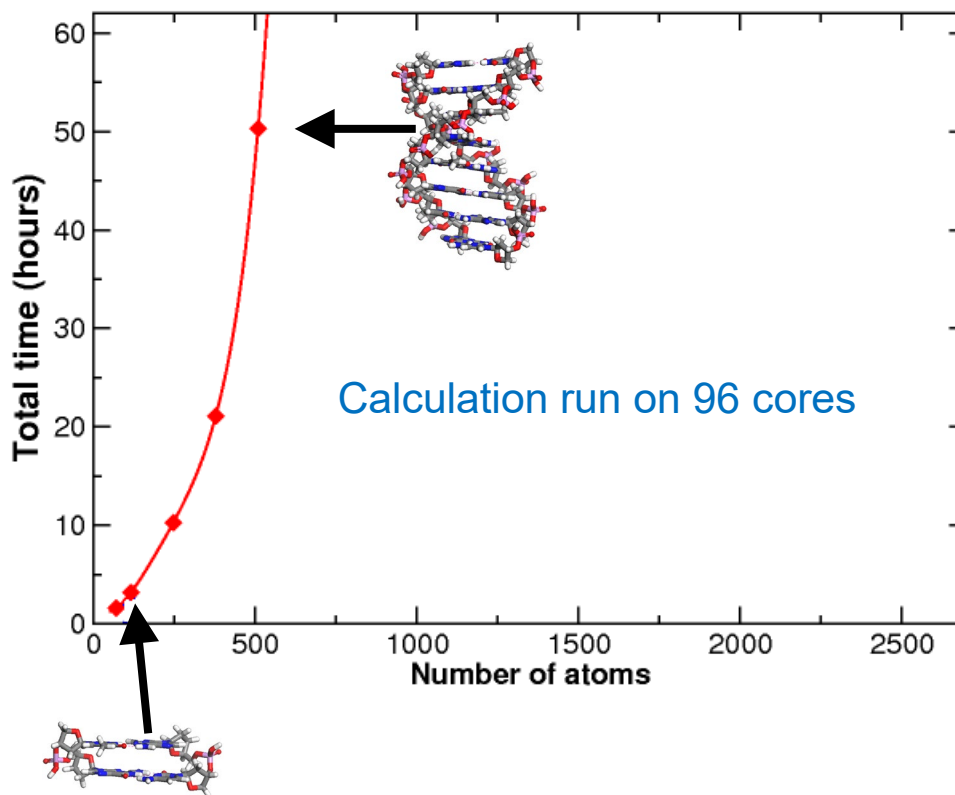Minimise energy w.r.t.:

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

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Computational cost of DFT: cubic-scaling

Calculation run on 96 cores

- Not suitable for biomolecules/nanostructures with **thousands of atoms**

- A **linear-scaling reformulation of DFT** is needed

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Linear-scaling DFT

- **Physical principle**

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

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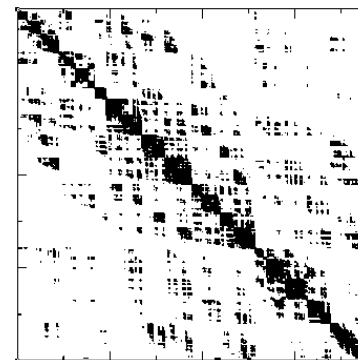
- **Linear-scaling approaches**

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

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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

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

Density

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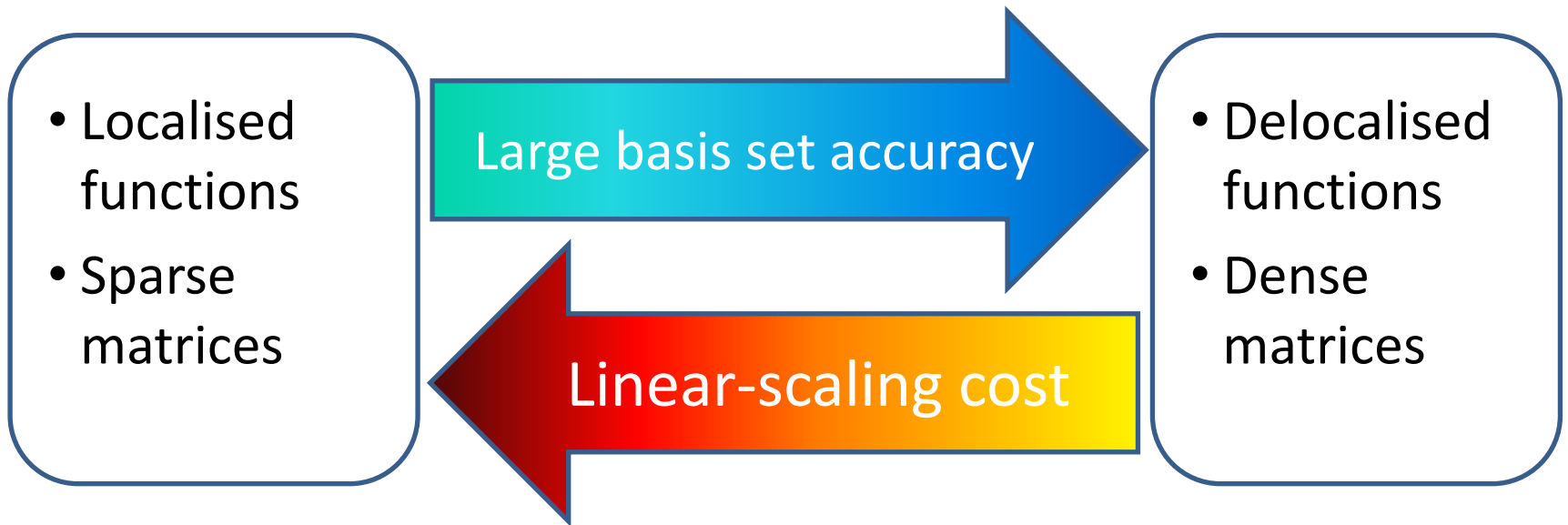
Molecular orbitals

Localised orbitals

DFT energy with density matrix

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

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Linear-scaling DFT in practice

Conflicting requirements

- Localised functions
- Sparse matrices

Large basis set accuracy →

← Linear-scaling cost

- Delocalised functions
- Dense matrices

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

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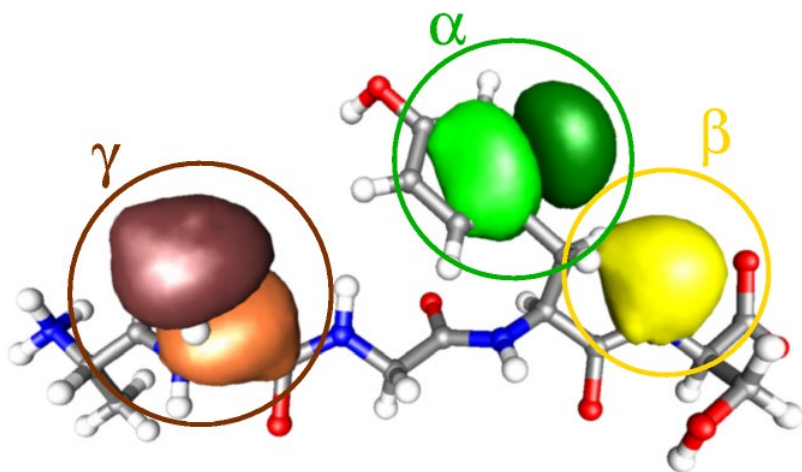
$$\rho(\mathbf{r}, \mathbf{r}') = \sum_{\alpha\beta} \phi_\alpha(\mathbf{r}) K^{\alpha\beta} \phi_\beta(\mathbf{r}')$$

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).

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Linear-scaling with near-complete basis set accuracy
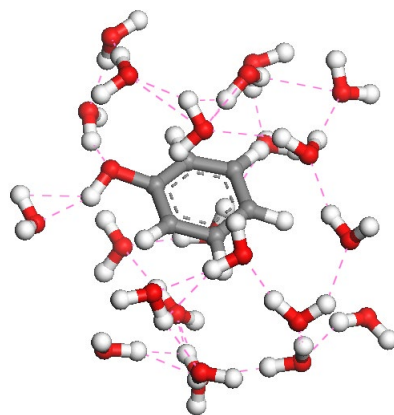
Example: binding energy calculation

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).

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Psinc basis set

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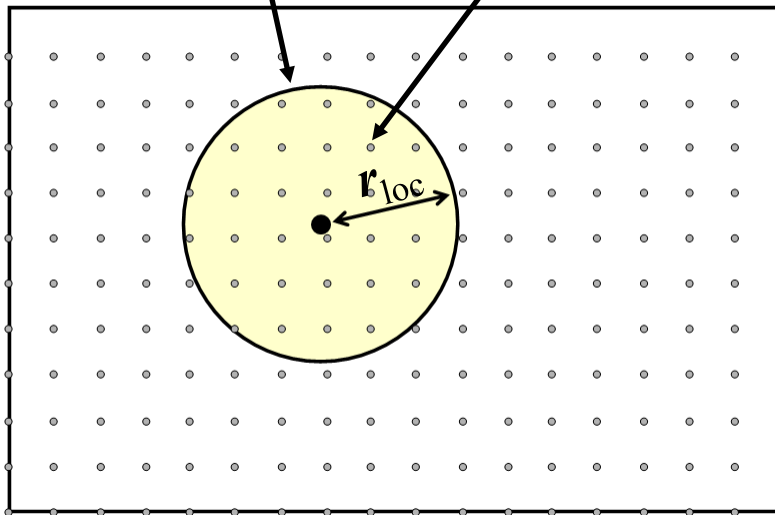- Highly localised
- Orthogonal

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

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

NGWF localisation sphere

$\mathbf{r}_i$ centre of $D_i(\mathbf{r})$

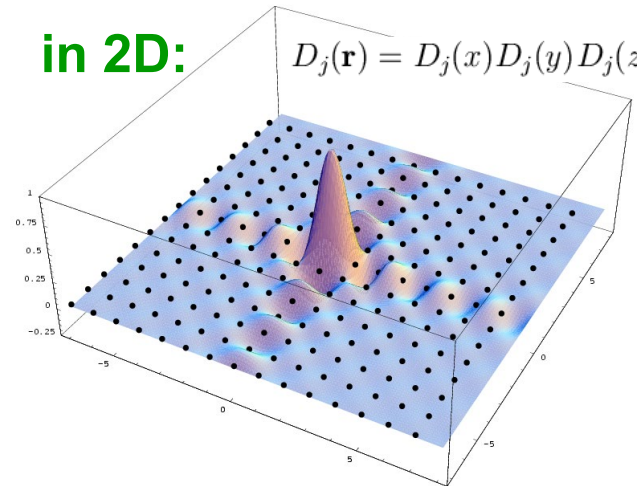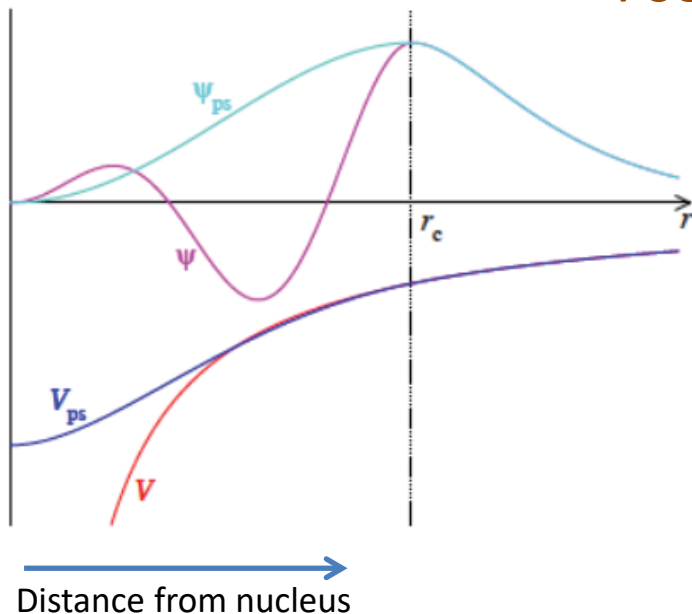$\mathbf{r}_{\mathrm{loc}}$

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)

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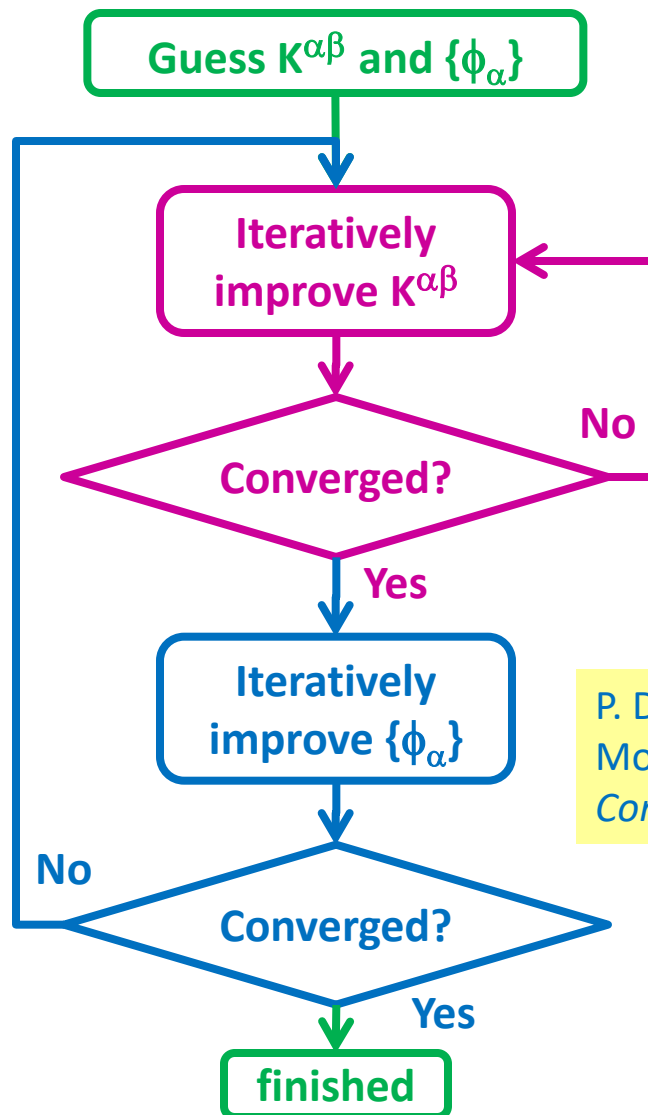
Pseudopotentials

Distance from nucleus

- 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

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Energy optimisation in ONETEP

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

Guess $K^{\alpha\beta}$ and $\{\phi_\alpha\}$

Iteratively improve $K^{\alpha\beta}$

Converged? — No

Yes

Iteratively improve $\{\phi_\alpha\}$

Converged? — No

Yes

finished

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

- **Inner loop:** Optimise total (interacting) energy E w.r.t $\mathbf{K}$ 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)

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NGWF optimisation

formaldehyde, H_2CO

O *p*   C p   O *p*   C p

Initial

ONETEP

Final

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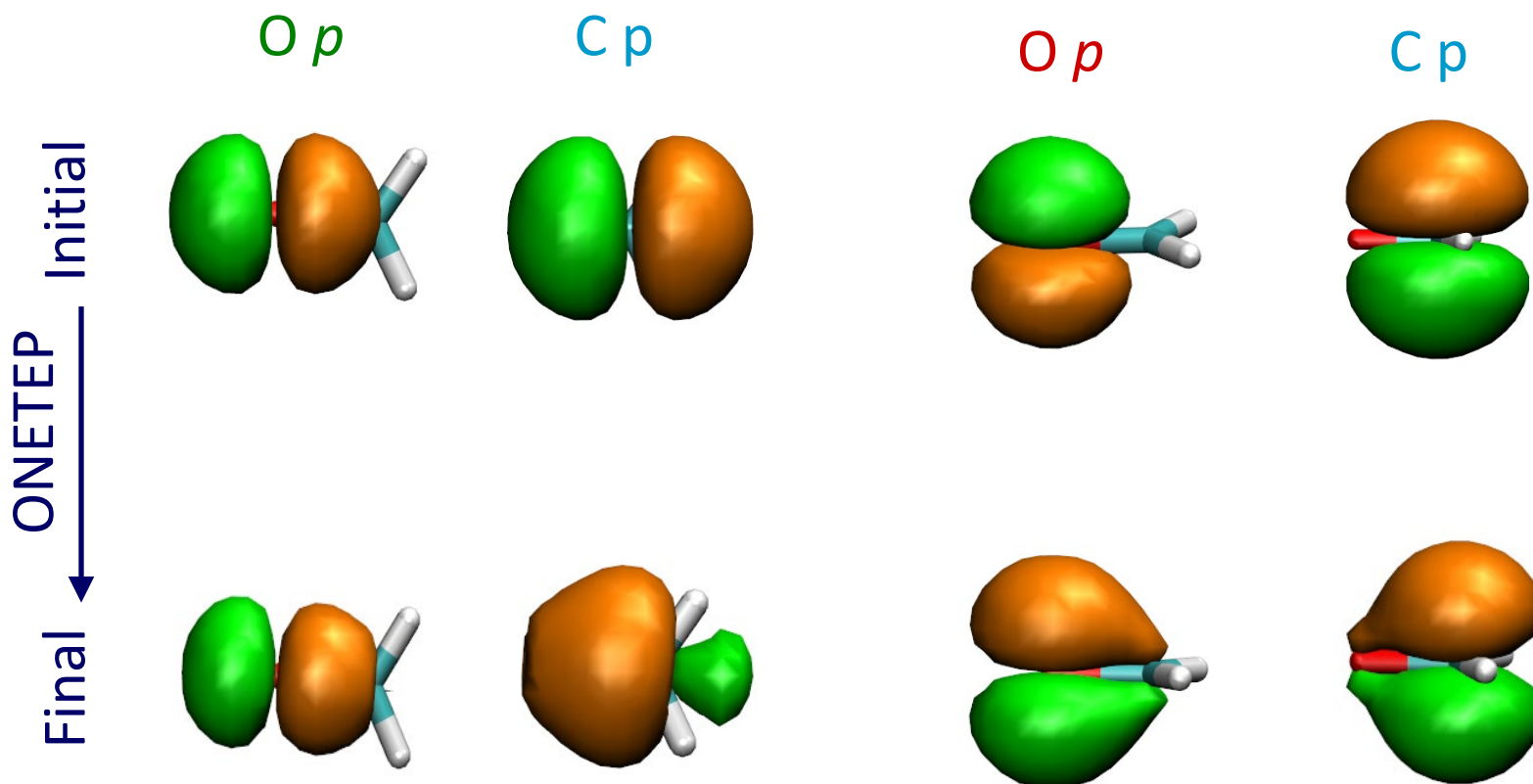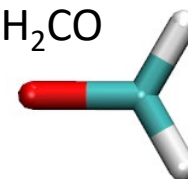
Psinc basis energy cut-off
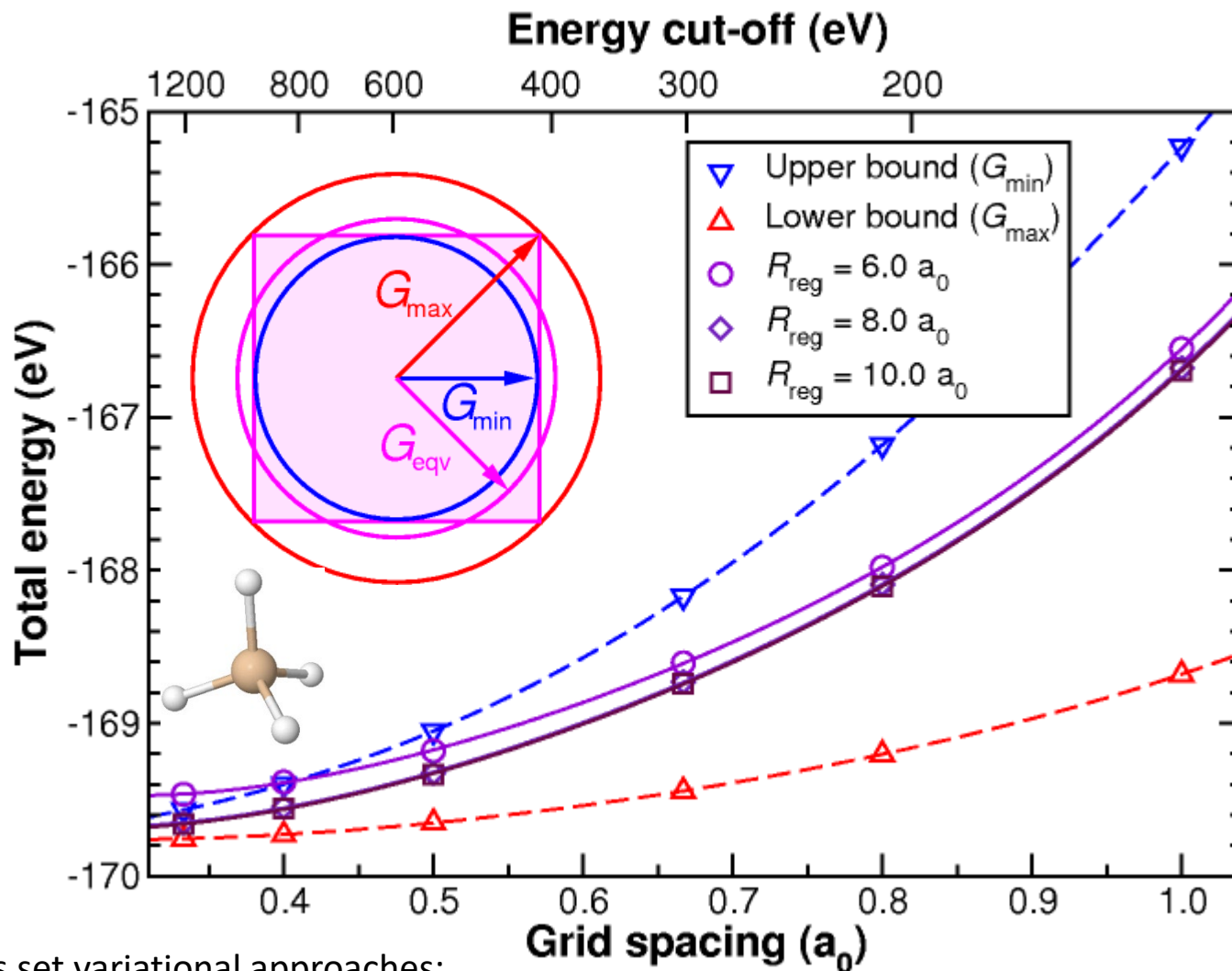
Basis set variational approaches:

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

FFT box technique

simulation cell

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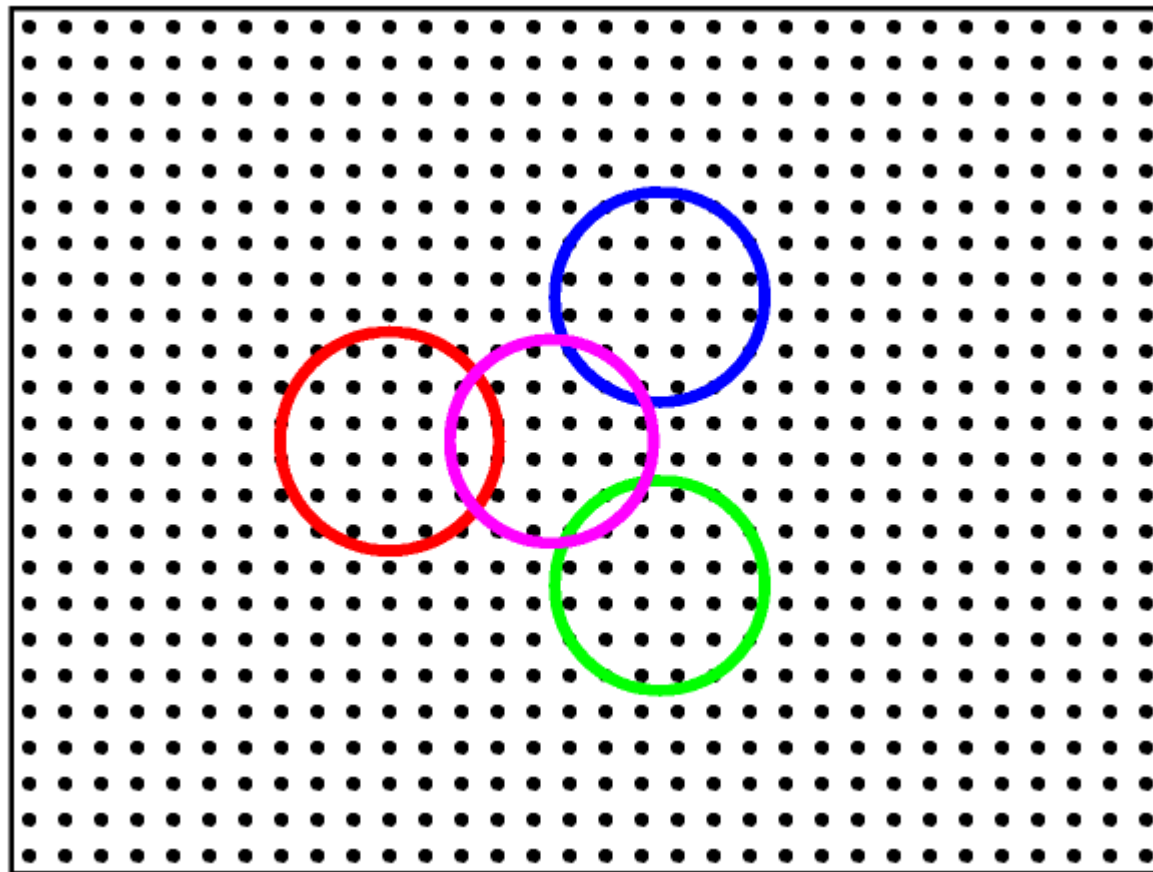
FFT box technique
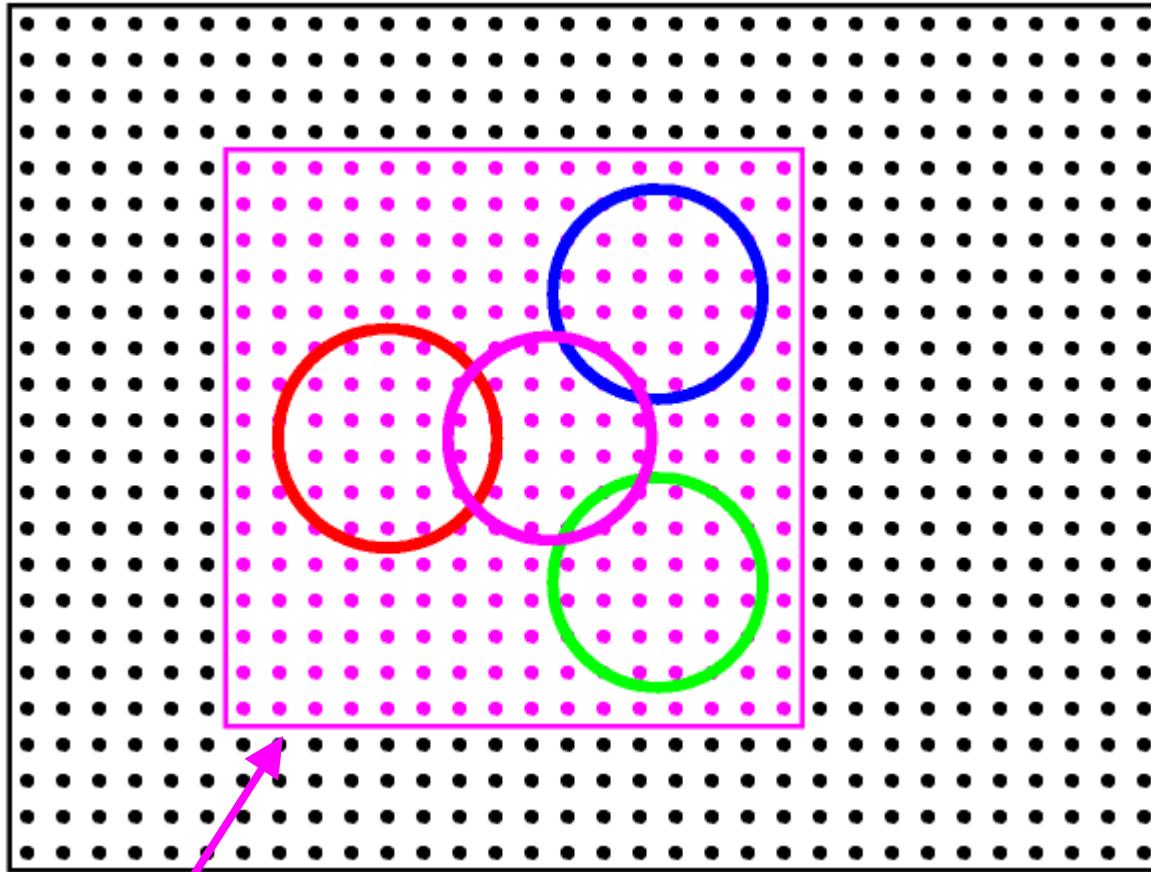
FFT box

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)

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Linear-scaling with the number of atoms
Example: ONETEP calculations on amyloid fibril proteins

Run on 960 cores

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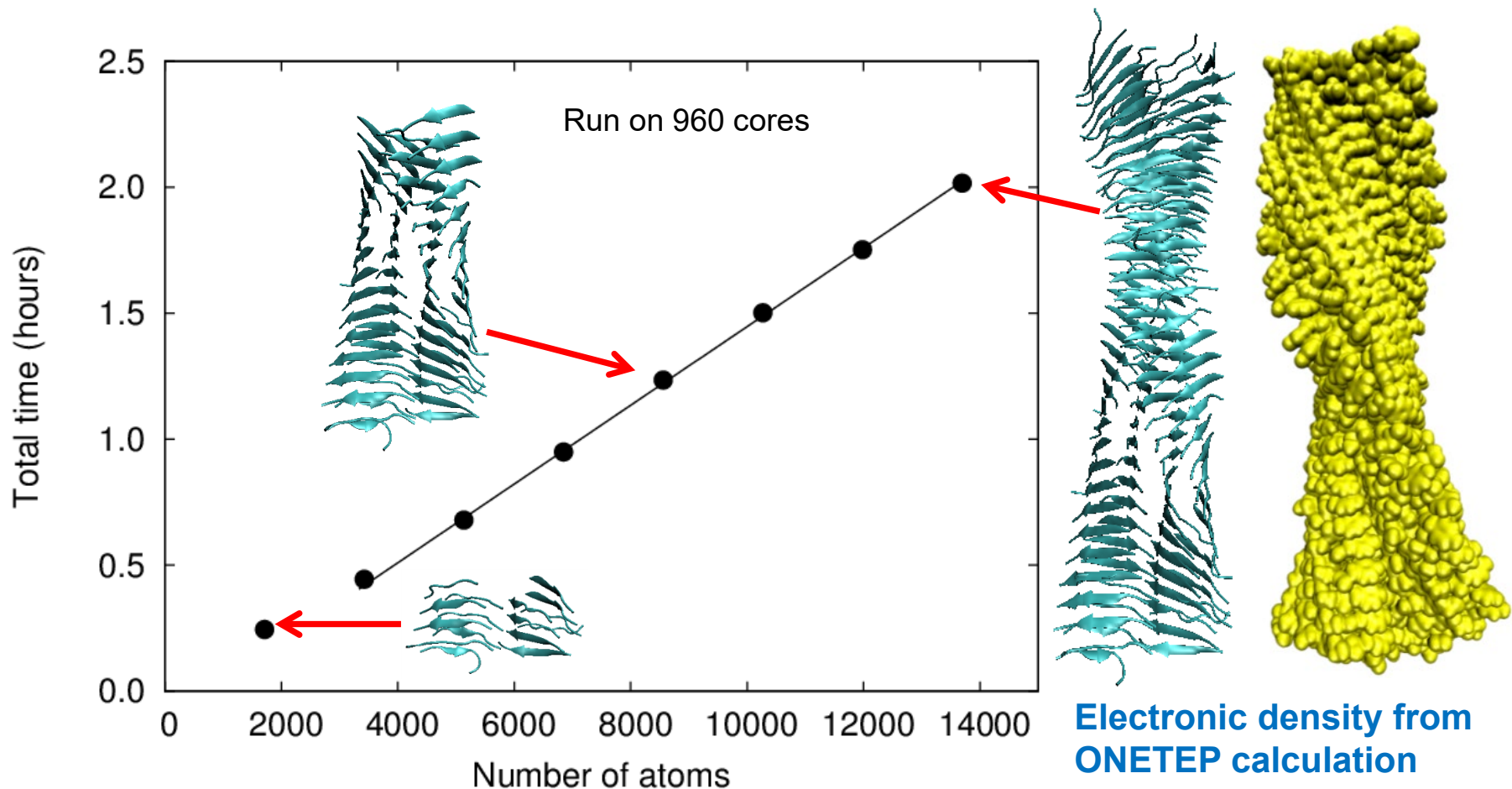
Structures of the amyloid fibril kindly provided by the authors of
*J. T. Berryman, S. E. Radford and S. A. Harris, Biophysical Journal, **97** 1 (2009)*

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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

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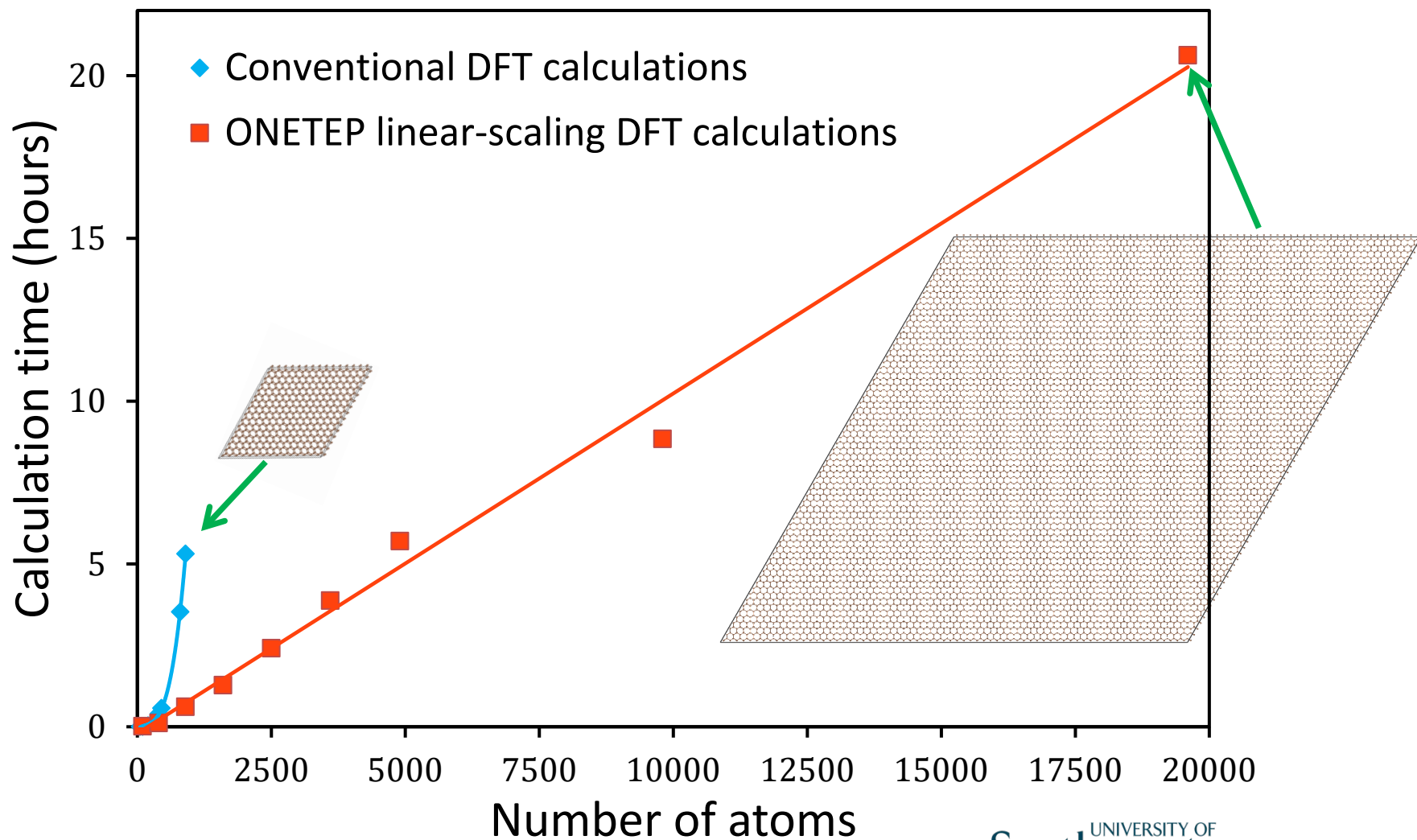
Compiling ONETEP

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

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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

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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)

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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
```

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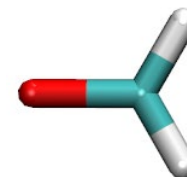
ONETEP calculation outline

- 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

Guess $K^{\alpha\beta}$ and $\{\phi_\alpha\}$

Iteratively improve $K^{\alpha\beta}$

Converged?

No

Yes

Iteratively improve $\{\phi_\alpha\}$

No

Converged?

Yes

finished

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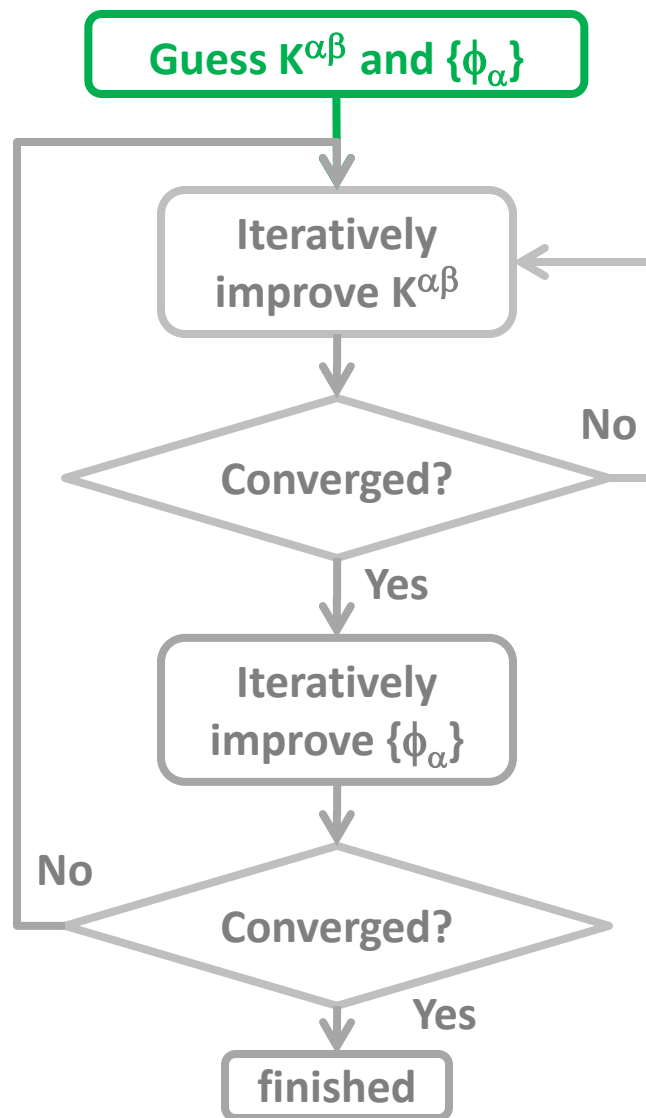
ONETEP calculation outline continued

- 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

Guess $K^{\alpha\beta}$ and $\{\phi_\alpha\}$

Iteratively improve $K^{\alpha\beta}$

Converged?   No

Yes

Iteratively improve $\{\phi_\alpha\}$

No   Converged?   Yes

finished

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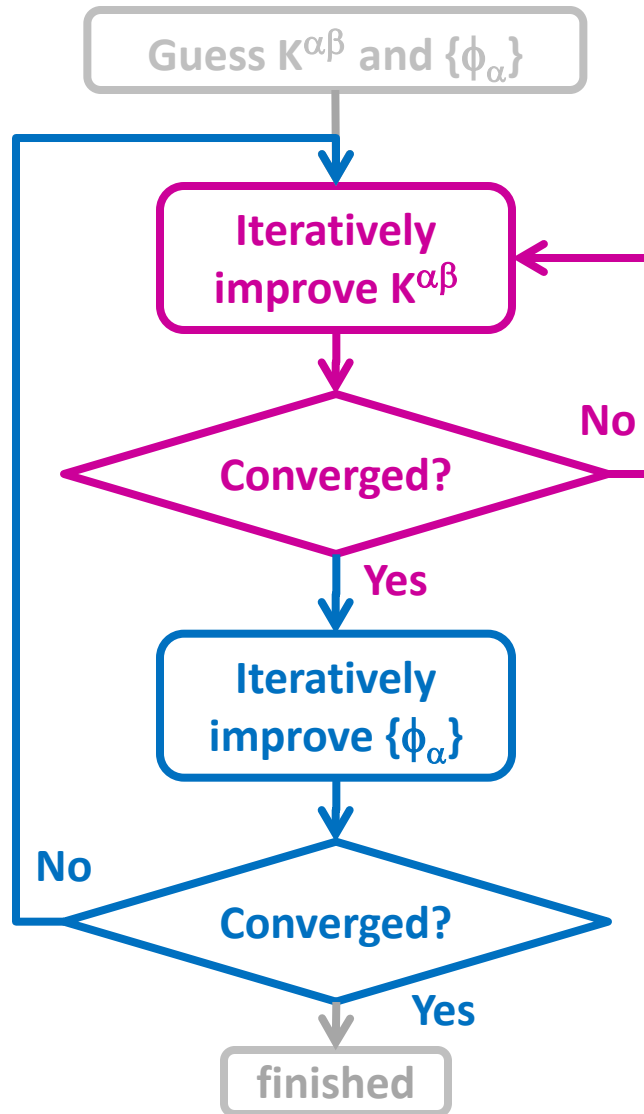
Example output file: formaldehyde

```
+-----------------------------------------------------------+
|                                                           |
|     ####### #     # ####### ####### ####### ######        |
|     #      # # ##  # #    #     #    #       #    #        |
|     #      # # # # # #    #     #    #       #     #       |
|     #      # # #  # # #####      #    #####   ######       |
|     #      # #  # # # # #        #    #       #            |
|     #      # #   #  # ## #       #    #       #            |
|     ####### #     #  # #######    #    ####### #           |
|                                                           |
|                                                           |
|     Linear-Scaling Ab Initio Total Energy Program         |
|                                                           |
|        Release for academic collaborators of ODG          |
|                                          Version 7.3.2     |
| Remote: https://github.com/cksdaddy/onetep_cks.git        |
| Local branch: master                                      |
| Commit ID: b4c6aa44c0d7f1571eb406a78225d0ff2140eea1       |
| Date: Fri Aug 23 10:21:36 2024 +0100                      |
| Working tree clean                                        |
|                                                           |
+-----------------------------------------------------------+
|                                                           |
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| and T. J. Zuehlsdorff.                                    |
|                                                           |
|                          Copyright (c) 2004-2024          |
```

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- Parallel strategy, calculation parameters

```
Job started: 28-08-2024 16:49 (+0100)

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 threaded FFT box operations.
                2 threads for loops over batched FFT box operations.
                2 threads in other parallel regions.
    MPI Interface: S1 (use mpi_f08) (-DMPI -DUSE_MPI_F08).
    MPI_ASYNC_PROTECTS_NONBLOCKING: Yes. MPI_SUBARRAYS_SUPPORTED: Yes.
    FFTW Interface: OMP-capable and MODERN. (-DUSE_MODERN_FFTW specified).
    GPU Interface: None.
    GPU FFT Backend: None.
... 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 ------------------------------------
--------------------------------------------------------------------------------
```

Input file parameters for OMP threads
threads_max 2
threads_per_fftbox 2
threads_num_fftboxes 2
threads_per_cellfft 2

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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)
======================================================================
```
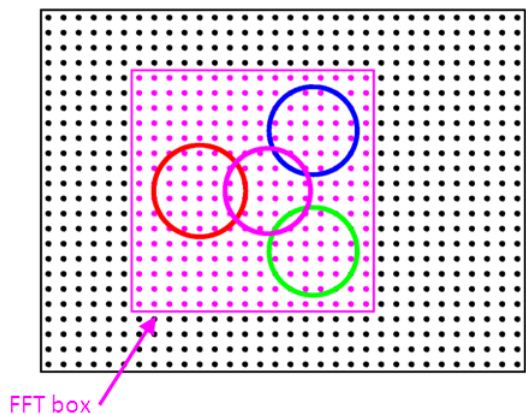

FFT box

• Simulation cell, FFT box, grid spacing

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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
```

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Example output file: formaldehyde

- Initialise and refine density kernel

```
Density kernel initialisation

Writing density kernel to file "h2co_2-threads.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_2-threads.dkn" ... done


>>> Density kernel optimised for the current NGWF basis:
    ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
    Total energy               =   -2.23594554723023E+01   Eh
    Estimated bandgap          =    5.4645E-02   Eh
    RMS occupancy error        =    5.0213E-13
    [H,K] commutator           =    3.3106E-03
    Occupancy bounds           = [  0.000:  1.000]
    ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
```
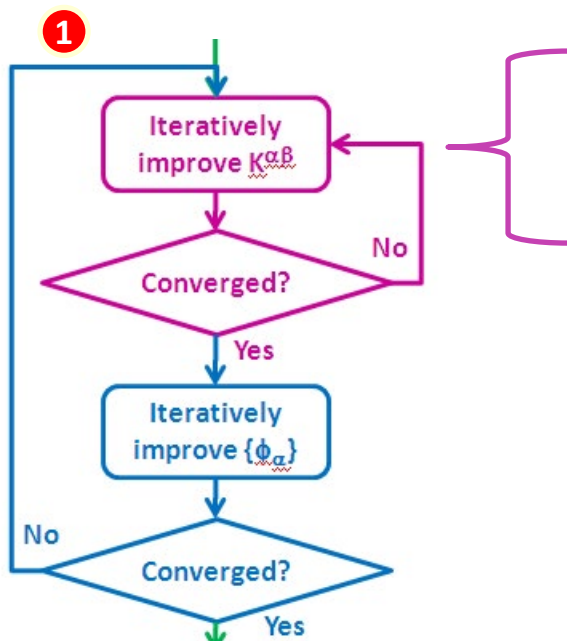
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Example output file: formaldehyde

- SCF iterations

❶
```
################################################################################
######################### 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 ###############################
################################################################################
```

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Example output file: formaldehyde

- End of SCF calculation

```
>>> Checking for convergence of NGWFs:
..................................................
         |        *** NGWF optimisation converged ***     |
         | RMS NGWF gradient =    0.00000126859037         |
         | Criteria satisfied:                             |
         | -> RMS NGWF gradient lower than set threshold.  |
         =================================================


=================================================================================
         --------------- ENERGY COMPONENTS (Eh) ---------------|
         | Kinetic                    :        14.91662617378243 |
         | Pseudopotential (local)    :       -75.55456217635727 |
         | Pseudo (non-coul chg cor)  :         0.00000000000000 |
         | Pseudopotential (non-local):         3.08867294295494 |
         | Hartree                    :        29.55304105253625 |
         | Exchange-correlation       :        -5.51703677662856 |
         | Ewald                      :        10.90369328705708 |
         | Total                      :       -22.60956549665512 |
         -------------------------------------------------------
         Integrated density          :        11.99999999999952
=================================================================================


                  <<<<< CALCULATION SUMMARY >>>>>
  |ITER|    RMS GRADIENT    |      TOTAL ENERGY    |   step   |    Epredicted
     0     0.00339284991963     -22.35945547230235    0.578496    -22.56473206956660
     1     0.00109819484620     -22.56842090396639    0.774264    -22.59768874673046
     2     0.00052368029255     -22.59897560976540    0.779737    -22.60588283387591
     3     0.00030645887461     -22.60616709879383    0.778478    -22.60852120360475
     4     0.00017075786505     -22.60861681158946    0.618320    -22.60917256889631
     5     0.00010955112044     -22.60917385344203    0.827718    -22.60948077698768
     6     0.00006504197723     -22.60948592159203    0.577777    -22.60956236994308
     7     0.00000603288450     -22.60956529599250   -0.003358    -22.60956529222493
     8     0.00000662327390     -22.60956547323060    0.099060    -22.60956549599422
     9     0.00000126859037     -22.60956549665513    <-- CG
```

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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)

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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)

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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

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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
- Energy Decomposition Analysis (EDA)
- Electron transport
- Distributed multipole analysis

Interface to ASE

GPU port under development

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Simulations in electrolyte and voltage to predict degradation mechanisms in Li-ion batteries
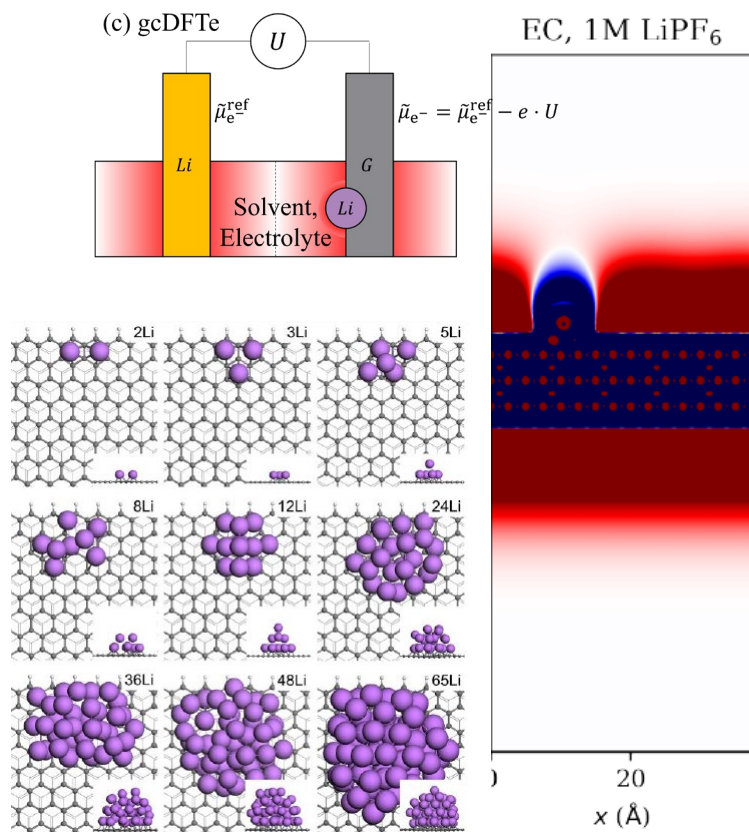
J. Mater. Chem. A **10** 11426 (2022)

2-D heterostructures with "exotic" electronic and mechanical properties
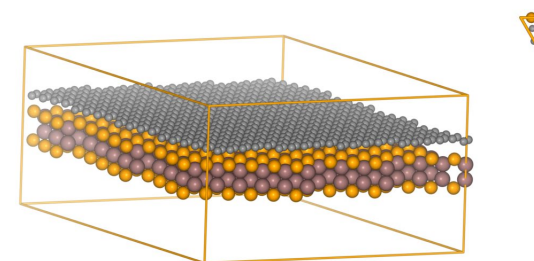
InSe / Graphene Heterostructure model: calculated Bandstructure before (left) / after (right) hybridisation
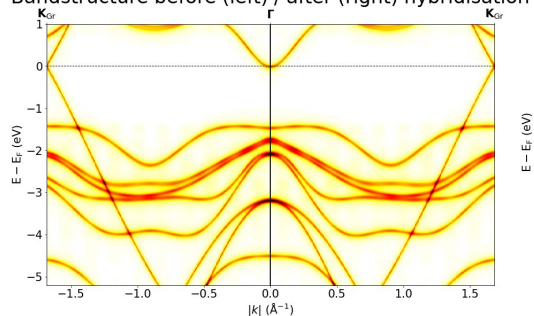
ONETEP was required as the cell necessary to keep the strain low for a misaligned heterostructure is very large.

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

Drug design from quantum mechanical calculations on entire proteins
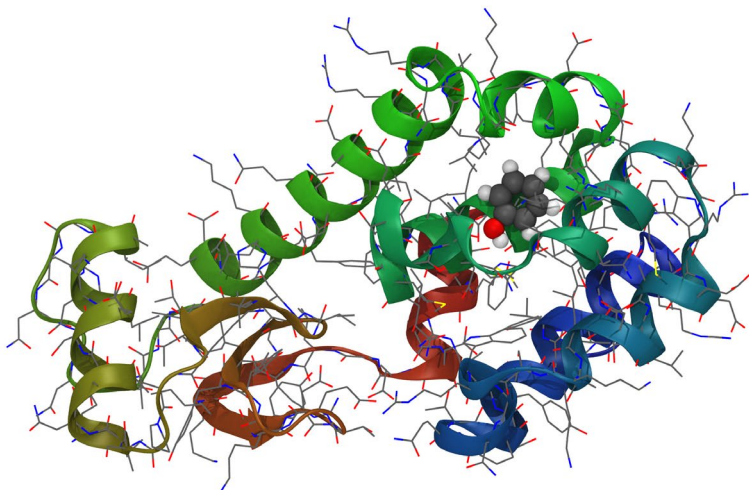
Motivation for full QM:

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

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

Designing new Pd carbide nanoparticle catalysts for selective hydrogenation of acetylene
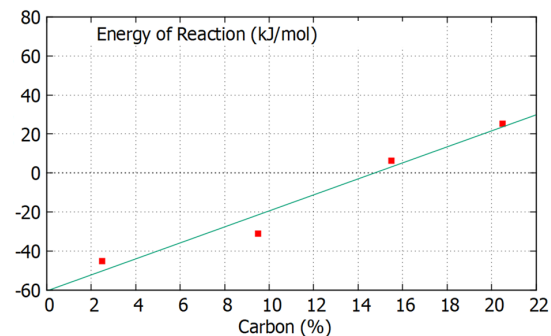
$Pd_{309}C_x$ (13% C)
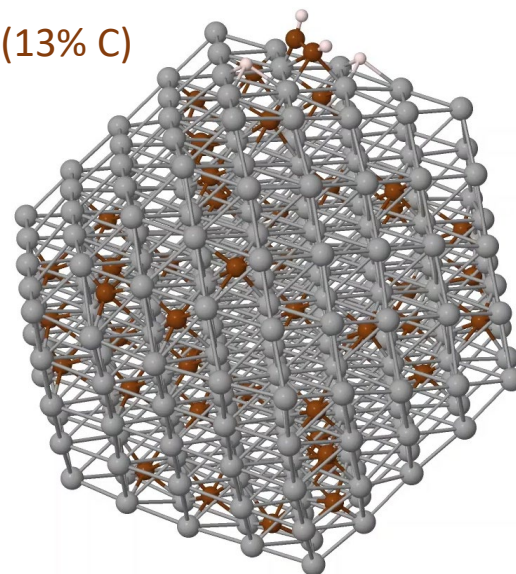
RSC Advances **14** 27799 (2024)

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

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

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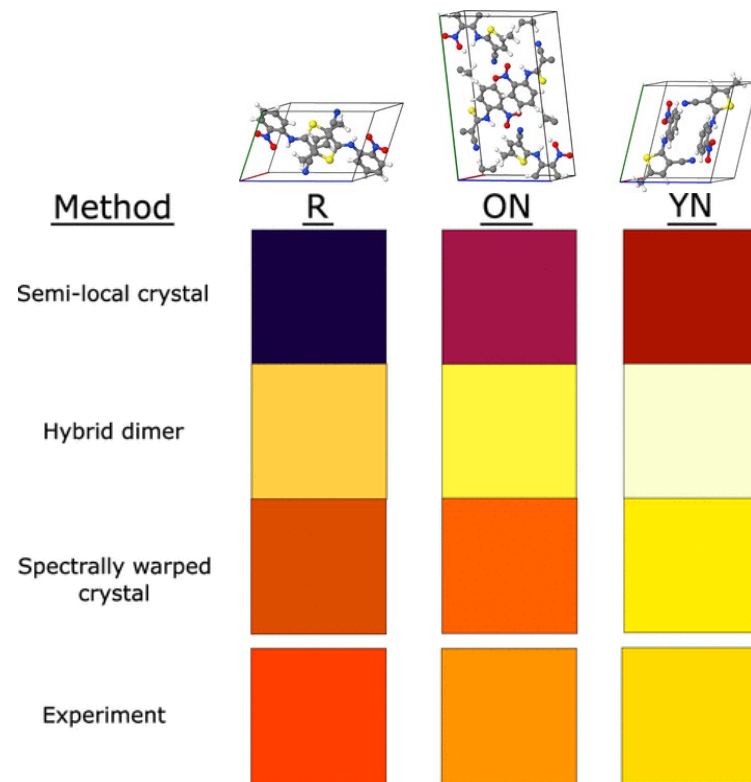
J. Chem. Theory Comput. **17** 5214 (2021)

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

For more information: www.onetep.org

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ONETEP Documentation

7.1

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