UNIVERSITY OF Southampton
School of Chemistry

Multiple Accuracy Approach and Pulay Forces in ONETEP

Álvaro Ruiz Serrano

ONETEP Spring School

April 2010

ONETEP

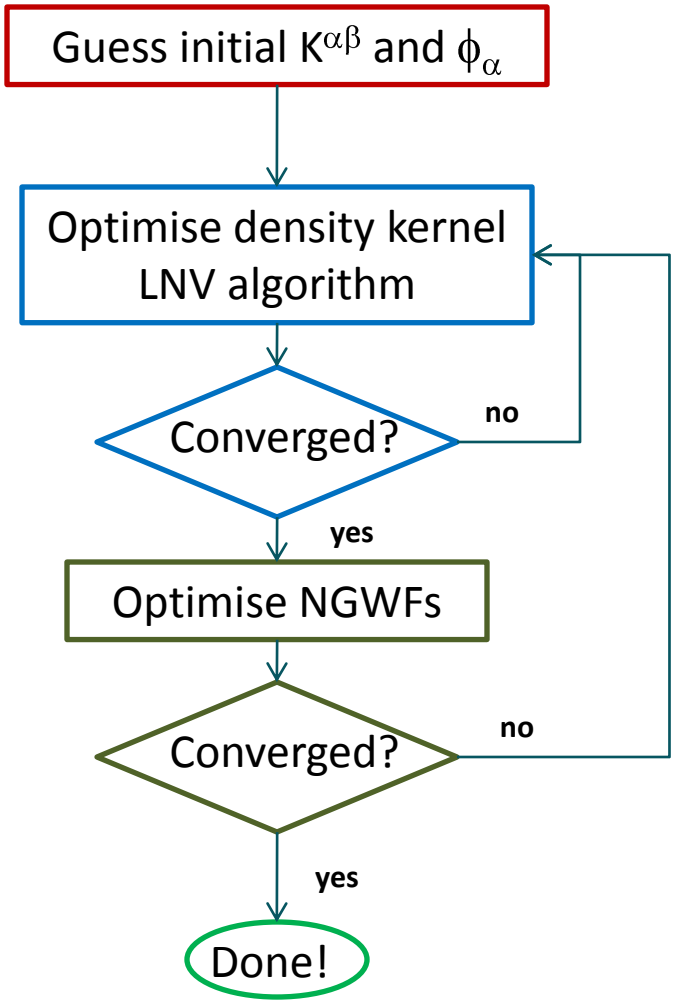
Density matrix DFT:

$$E = E[\rho]$$

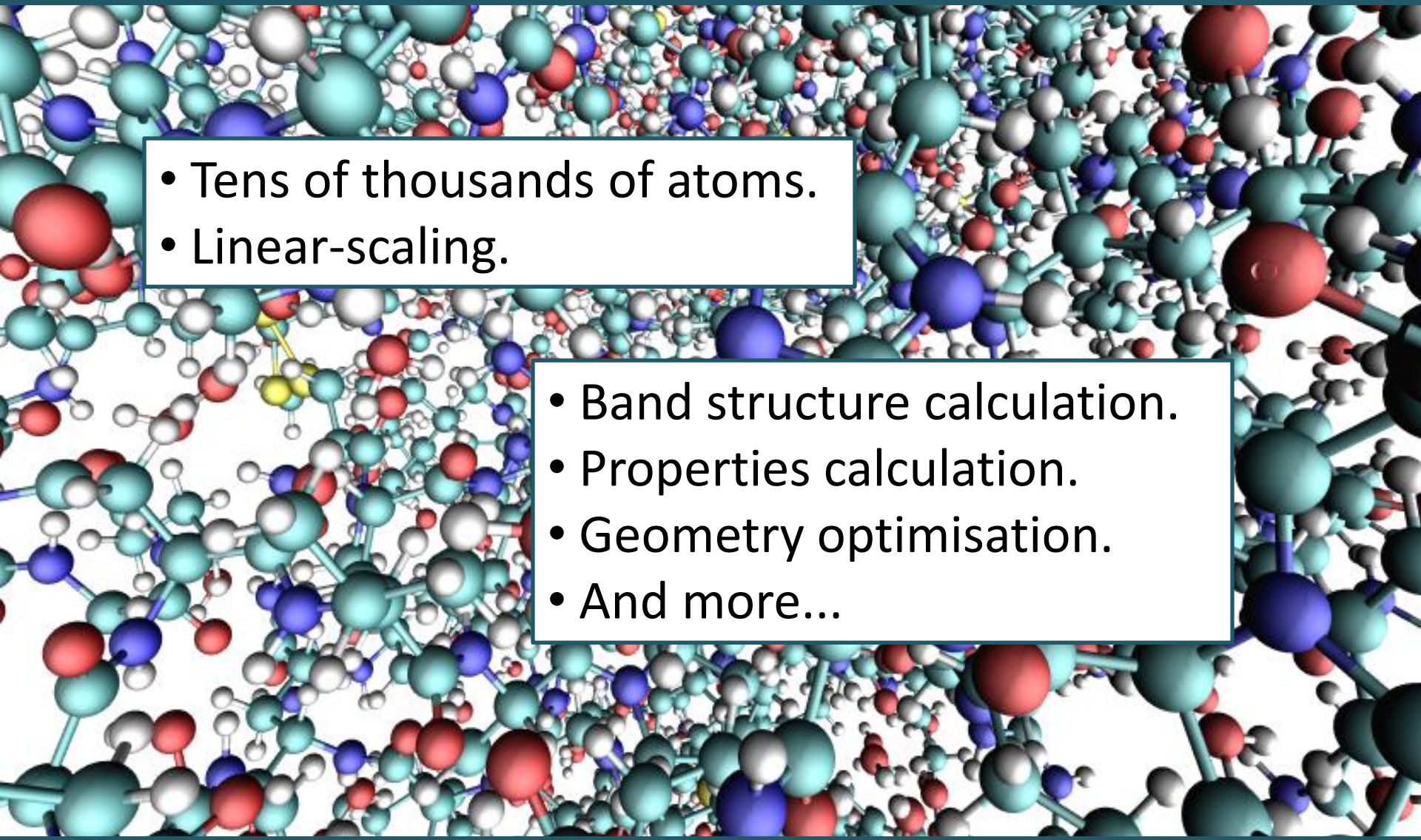
$$\rho(\vec{r},\vec{r}') = \sum_{\alpha\beta} \phi_\alpha(\vec{r}) K^{\alpha\beta} \phi_\beta(\vec{r}')$$

- Minimise the energy with respect to:
  - Density kernel.
  - NGWFs.

- Solve Kohn – Sham equations.
- Self-consistent method.
- Plane wave accuracy.
- Parallel code.



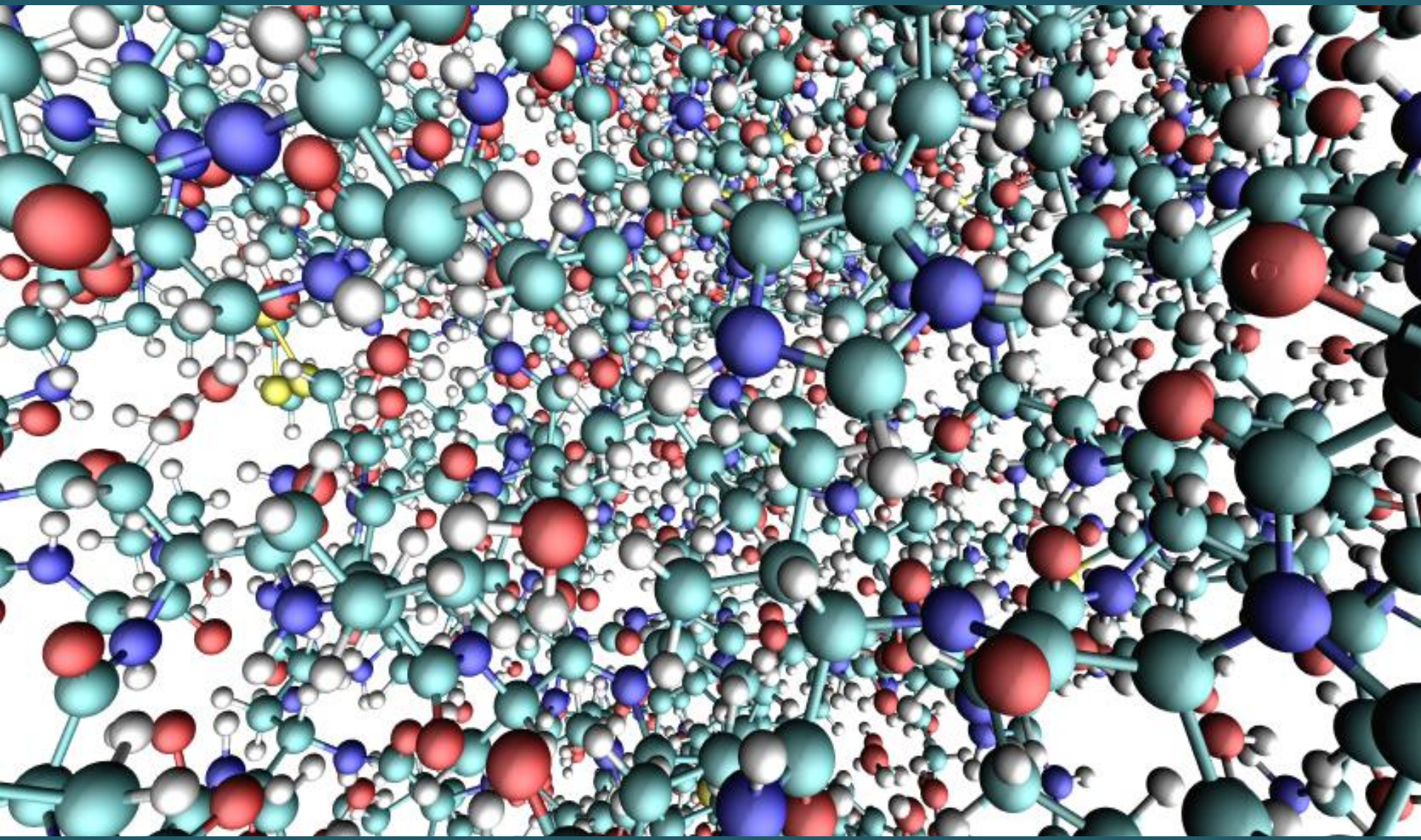
ONETEP



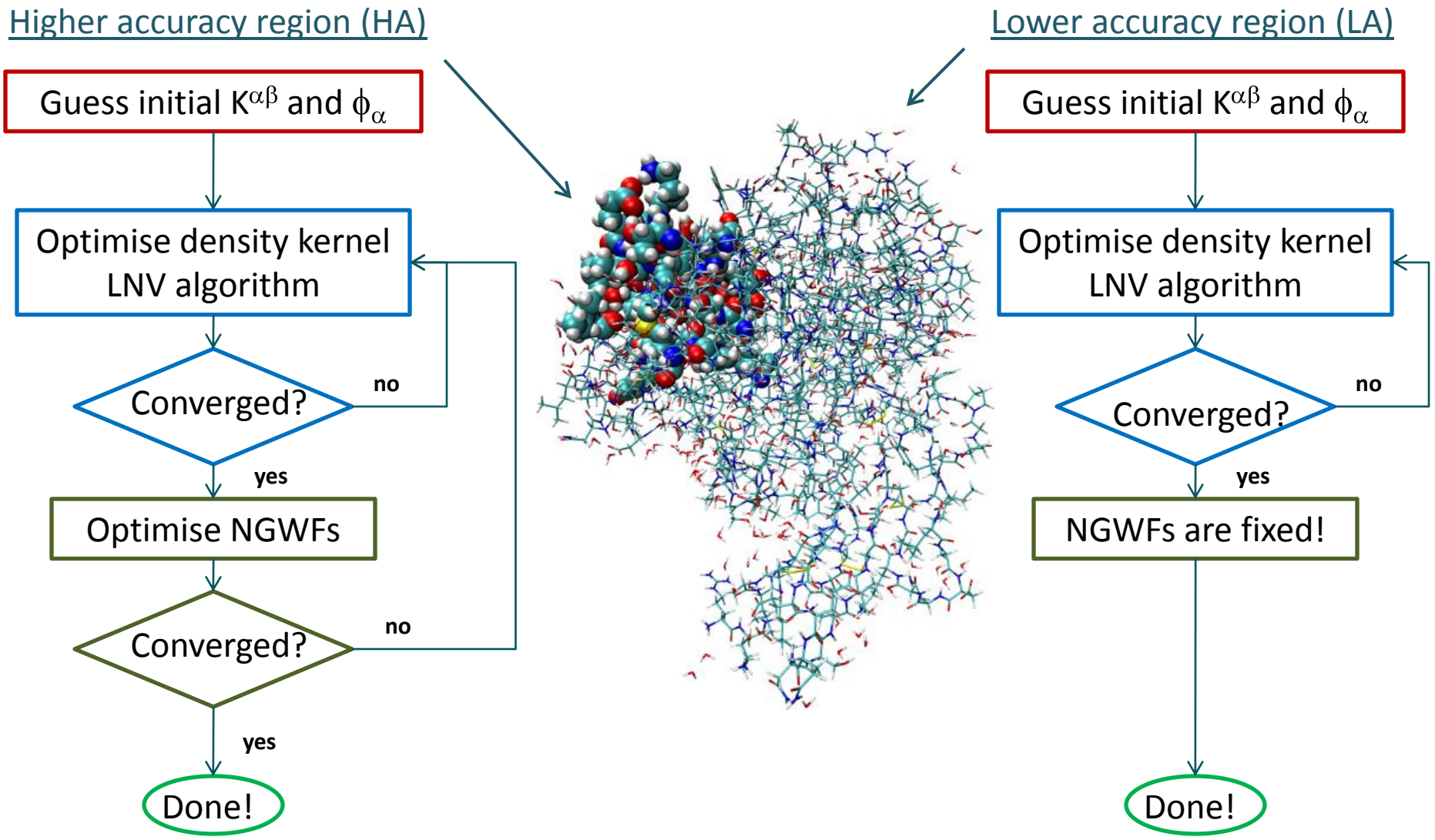
- Tens of thousands of atoms.
- Linear-scaling.

- Band structure calculation.
- Properties calculation.
- Geometry optimisation.
- And more...

ONETEP



Multiple Accuracy Approach

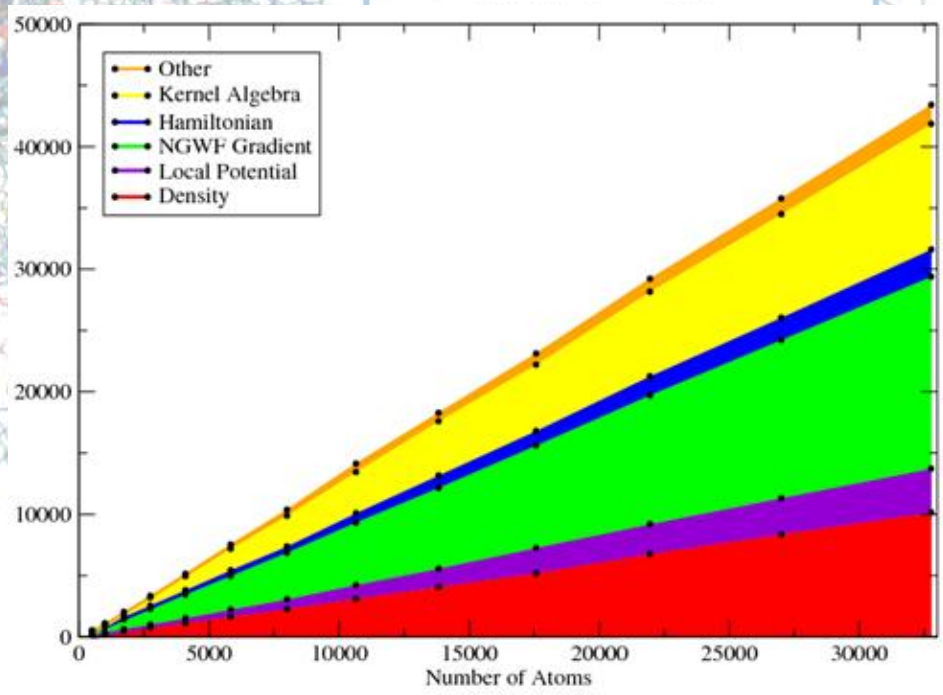


Multiple Accuracy Approach

Why?

- In several systems high accuracy is only needed in a certain part.
  - Protein – ligand systems, for example.

- It saves time.
  - Less NGWF gradients to calculate.
  - Less work per iteration.
- Larger systems could be simulated.
  - Hundreds of thousands.
- It is linear-scaling.



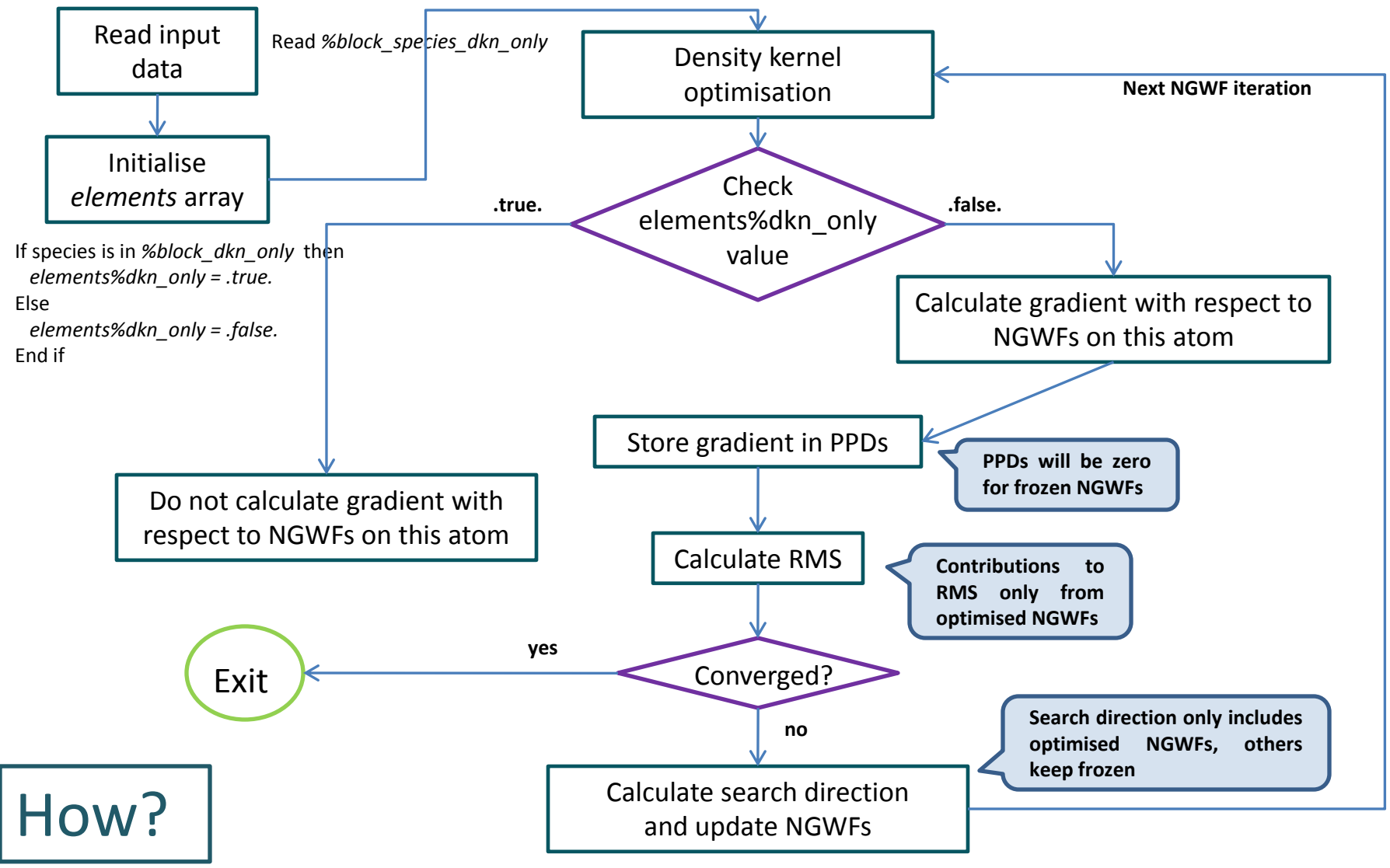
[1] Hine, Haynes, Mostofi, Skylaris and Payne. Comput. Phys. Commun. 180 (2009).

Multiple Accuracy Approach

Why?

- And it is all quantum!

Multiple Accuracy Approach



Multiple Accuracy Approach

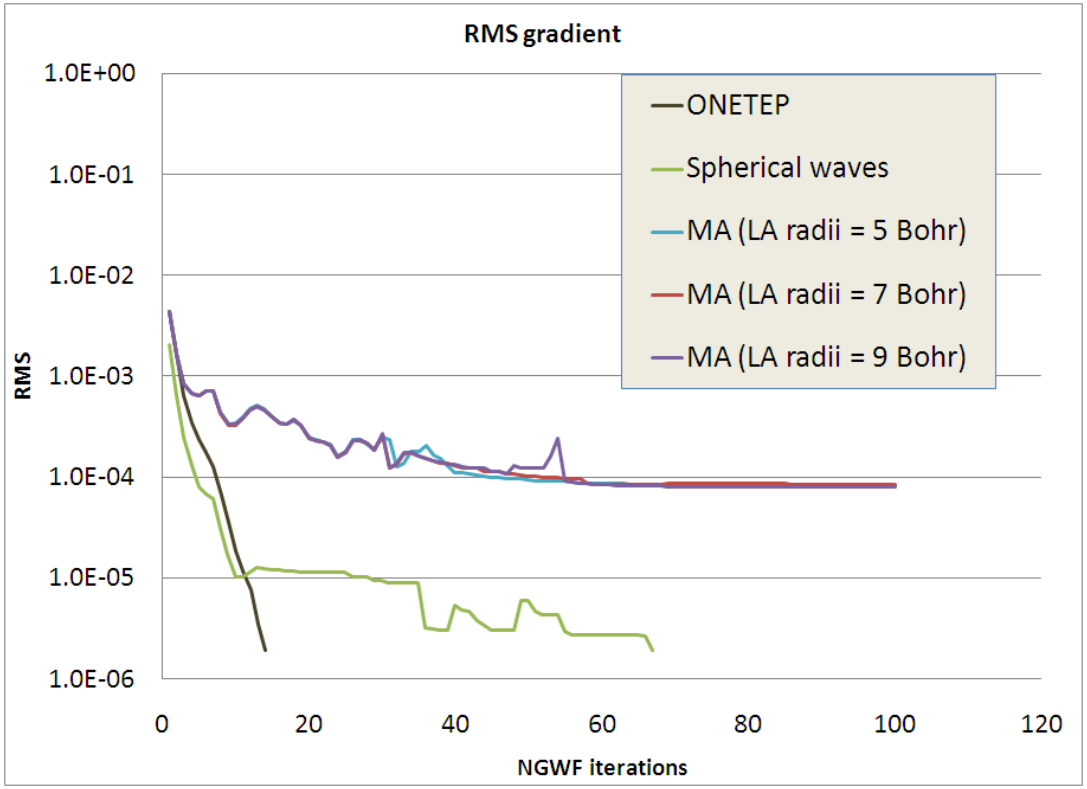
Results

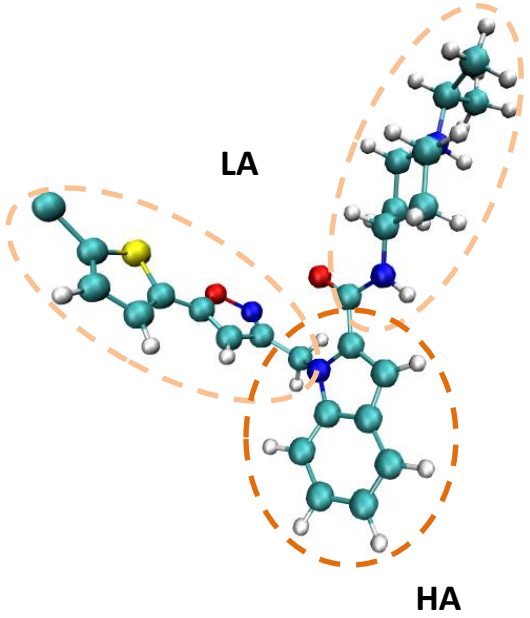
$$\frac{\delta E}{\delta \phi_\alpha(\vec{r})} = 4\left[H(\vec{r})\phi_\beta(\vec{r})K^{\beta\alpha} + \phi_\beta(\vec{r})Q^{\beta\alpha}\right]$$

$$Q = 3LHL - 2LSLHL - 2LHLSL$$

$$K = 3LSL - 2LSLSL$$

- Convergence problems to be solved.





Multiple Accuracy Approach – Pulay Forces

Pulay Forces?

Appear if the basis set moves with the atoms.

- Higher accuracy region, basis set: psinc functions.
- Lower accuracy region, basis set: fixed NGWFs.
  - They move with the atoms.

Pulay forces appear for all the atoms in the lower accuracy region

Pulay forces are necessary for geometry optimisation and MD calculations using the multiple accuracy approach.

Multiple Accuracy Approach – Pulay Forces

Pulay Forces?

Appear if the basis set moves with the atoms.

They will allow to perform Self Consistent Ab-Initio Tight Binding (SC-AITB) calculations in ONETEP [2].

- All the NGWFs are fixed.
- Fast and accurate geometry optimisation calculations in large systems.
- Quantum accuracy (electrons, not “balls”).

[2] Miyazaki, Bowler, Choudry and Gillan. J. Chem. Phys. 121, 13 (2004).

Multiple Accuracy Approach – Pulay Forces

Pulay Forces?

Appear if the basis set moves with the atoms.

$$F_A = -\frac{dE}{dx_A}$$

Multiple Accuracy Approach – Pulay Forces

Pulay Forces?

Appear if the basis set moves with the atoms.

$$-F_A = \frac{dE}{dx_A} = \frac{\partial E}{\partial x_A} + \int d\vec{r} \frac{\delta E}{\delta \phi_\alpha(\vec{r})} \frac{\partial \phi_\alpha(\vec{r})}{\partial x_A} + \frac{\partial E}{\partial K^{\alpha\beta}} \frac{\partial K^{\alpha\beta}}{\partial x_A}$$

Multiple Accuracy Approach – Pulay Forces

Pulay Forces?

Appear if the basis set moves with the atoms.

$$-F_A = \frac{dE}{dx_A} = \frac{\partial E}{\partial x_A} + \int d\vec{r} \frac{\delta E}{\delta \phi_\alpha(\vec{r})} \frac{\partial \phi_\alpha(\vec{r})}{\partial x_A} + \frac{\partial E}{\partial K^{\alpha\beta}} \frac{\partial K^{\alpha\beta}}{\partial x_A}$$

In standard ONETEP:

Forces calculated in standard ONETEP (Pseudopotential only)

Zero if LNV converged

Multiple Accuracy Approach – Pulay Forces

Pulay Forces?

Appear if the basis set moves with the atoms.

What about $\int d\vec{r} \frac{\delta E}{\delta \phi_\alpha(\vec{r})} \frac{\partial \phi_\alpha(\vec{r})}{\partial x_A}$?

Multiple Accuracy Approach – Pulay Forces

Pulay Forces?

Appear if the basis set moves with the atoms.

What about $\int d\vec{r} \frac{\delta E}{\delta \phi_\alpha(\vec{r})} \frac{\partial \phi_\alpha(\vec{r})}{\partial x_A}$?

In standard ONETEP:

$\phi_\alpha(\vec{r}) = \sum_i D_i(\vec{r}) C_i$

$$\int d\vec{r} \frac{\delta E}{\delta \phi_\alpha(\vec{r})} \frac{\partial \phi_\alpha(\vec{r})}{\partial x_A} = \sum_i \frac{\partial E}{\partial C_i} \frac{\partial C_i}{\partial x_A} + \int d\vec{r} \frac{\delta E}{\delta D_i(\vec{r})} \frac{\partial D_i(\vec{r})}{\partial x_A}$$

Multiple Accuracy Approach – Pulay Forces

Pulay Forces?

Appear if the basis set moves with the atoms.

What about $\int d\vec{r} \frac{\delta E}{\delta \phi_\alpha(\vec{r})} \frac{\partial \phi_\alpha(\vec{r})}{\partial x_A}$?

In standard ONETEP:

Zero if NGWFs are optimised

Psincs do not move with the atoms

$$\phi_\alpha(\vec{r}) = \sum_i D_i(\vec{r}) C_i$$

$$\int d\vec{r} \frac{\delta E}{\delta \phi_\alpha(\vec{r})} \frac{\partial \phi_\alpha(\vec{r})}{\partial x_A} = \sum_i \frac{\partial E}{\partial C_i} \frac{\partial C_i}{\partial x_A} + \int d\vec{r} \frac{\delta E}{\delta D_i(\vec{r})} \frac{\partial D_i(\vec{r})}{\partial x_A}$$

Multiple Accuracy Approach – Pulay Forces

Pulay Forces?

Appear if the basis set moves with the atoms.

What about $\int d\vec{r} \frac{\delta E}{\delta \phi_\alpha(\vec{r})} \frac{\partial \phi_\alpha(\vec{r})}{\partial x_A}$?

In multiple accuracy:

$\phi_\alpha(\vec{r}) = \sum_i D_i(\vec{r}) C_i$

NGWFs in LA are not optimised!

$$\int d\vec{r} \frac{\delta E}{\delta \phi_\alpha(\vec{r})} \frac{\partial \phi_\alpha(\vec{r})}{\partial x_A} = \sum_i \frac{\partial E}{\partial C_i} \frac{\partial C_i}{\partial x_A} + \int d\vec{r} \frac{\delta E}{\delta D_i(\vec{r})} \frac{\partial D_i(\vec{r})}{\partial x_A}$$

Multiple Accuracy Approach – Pulay Forces

How to calculate Pulay forces?

$$-F_{Pulay,A} = \int d\vec{r} \frac{\delta E}{\partial \phi_\alpha(\vec{r})} \frac{\partial \phi_\alpha(\vec{r})}{\partial x_A}$$

$$\frac{\delta E}{\delta \phi_\alpha(\vec{r})} = 4\left[H(\vec{r})\phi_\beta(\vec{r})K^{\beta\alpha} + \phi_\beta(\vec{r})Q^{\beta\alpha}\right]$$

$$\frac{\partial \phi_\alpha(\vec{r})}{\partial x_A} = \sum_{\vec{G}}^{\vec{G}_{cutoff}} -iG_x\hat{\phi}(\vec{G})e^{-i\vec{G}(\vec{r}-\vec{R_A})}$$

Multiple Accuracy Approach – Pulay Forces

How to calculate Pulay forces?

$$-F_{Pulay,A} = \int d\vec{r} \frac{\delta E}{\partial \phi_\alpha(\vec{r})} \frac{\partial \phi_\alpha(\vec{r})}{\partial x_A}$$

$$\frac{\delta E}{\delta \phi_\alpha(\vec{r})} = 4\left[H(\vec{r})\phi_\beta(\vec{r})K^{\beta\alpha} + \phi_\beta(\vec{r})Q^{\beta\alpha}\right]$$

$$\frac{\partial \phi_\alpha(\vec{r})}{\partial x_A} = \sum_{\vec{G}}^{\vec{G}_{cutoff}} -iG_x\hat{\phi}(\vec{G})e^{-i\vec{G}(\vec{r}-\vec{R_A})}$$

The derivative of the NGWFs with respect to the atomic positions has to be implemented in ONETEP

Multiple Accuracy Approach – Pulay Forces

5 1	H 3 1	C 1 1	C 1 2	C 1 3	C 1 4	H 2 1
00048	−0.07984	−0.11689	0.07597	0.06418	0.12977	−0.02407
.4232	−0.11655	−0.29547	−0.01276	0.01643	0.15770	−0.11691
.2461	0.08810	0.01276	−0.35972	0.00027	−0.00868	−0.07590
7952	0.04807	−0.01643	0.00027	−0.36014	0.01120	−0.06421
.9469	−0.12858	−0.15770	−0.00868	0.01120	−0.44168	−0.12983
0	−0.02396	−0.11655	−0.08811	−0.04807	0.12856	−0.07983
2396	0	0.14235	−0.12462	−0.07953	−0.19469	−0.00048
.1655	−0.14235	0	0	0	0	−0.14385
8811	0.12462	0	0	0	0	−0.12001
4807	0.07953	0	0	0	0	−0.08795
12856	0.19469	0	0	0	0	0.19287
7983	0.00048	0.14385	0.12001	0.08795	−0.19287	0

Calculated derivative of the overlap matrix

5 1	H 3 1	C 1 1	C 1 2	C 1 3	C 1 4	H 2 1
0000	0.00000	−0.11672	0.07603	0.06426	0.13017	0.00000
0000	0.00000	−0.29503	−0.01271	0.01634	0.15848	0.00000
0000	0.00000	0.01267	−0.36095	−0.00077	−0.00851	0.00000
0000	0.00000	−0.01633	−0.00077	−0.36059	0.01102	0.00000
0000	0.00000	−0.15844	−0.00855	0.01103	−0.44205	0.00000
0000	0.00000	−0.11644	−0.08835	−0.04825	0.12920	0.00000
0000	0.00000	0.14199	−0.12393	−0.07921	−0.19663	0.00000
11644	0.14199	0.00000	−0.00000	−0.00000	0.00000	0.14350
08835	−0.12393	−0.00000	0.00002	−0.00001	0.00001	0.11945
04825	−0.07921	−0.00000	−0.00001	0.00001	0.00000	0.08741
.2920	−0.19663	0.00000	0.00001	0.00000	−0.00001	−0.19483
0000	0.00000	0.14350	0.11945	0.08741	−0.19483	0.00000

Finite differences: derivative of the overlap matrix

Multiple Accuracy Approach – Pulay Forces

We have the two ingredients…

… Pulay forces coming soon…

Summary

- The system is divided into two regions:
  - Higher accuracy region: density kernel and NGWFs are optimised.
  - Lower accuracy region: density kernel is optimised, NGWFs are fixed.
- Saves computational time:
  - Energy gradient wrt NGWFs is not calculated in the lower accuracy region.
- All the system is treated in a quantum level – no QM/MM.

- Pulay forces are needed when the NGWFs are fixed.
- The NGWF gradient is needed to calculate Pulay forces.
- It allows SC-AITB calculations in ONETEP.
  - Only one NGWF iteration is necessary.

Future Work

- Improve convergence of the multiple accuracy algorithm.
  - Avoid the influence of the fixed NGWFs on the HA region.
- Perform geometry optimisations.
  - Efficiently calculate Pulay forces.
  - Perform SC-AITB on large systems.

- Implement non self-consistent forces.
- Introduce the Harris – Foulkes scheme.
- Optimise the parallel strategy to be applied for this kind of calculations.
  - Efficiently distribute work load between the processors.
- Apply this new approach to large systems.
  - Large biomolecules like ligand-protein systems or membrane-lipid.
  - Nanomaterials.
- Perform MD simulations using the multiple accuracy scheme.

Acknowledgments

Supervisor
- Dr. Chris-Kriton Skylaris

Group members
- Quintin Hill
- Nicholas Zonias
- Stephen Fox
- Chris Pittock
- Dr. Jacek Dziedzic

iSolutions and Iridis3
HECToR

Any questions?