Multiple Accuracy Approach and Pulay Forces in ONETEP

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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.

---

Guess initial \( K^{\alpha \beta} \) and \( \phi_{\alpha} \)

Optimise density kernel

LNV algorithm

Converged?

no

Optimise NGWFs

Converged?

no

yes

Done!
ONETEP

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

- Band structure calculation.
- Properties calculation.
- Geometry optimisation.
- And more...
Multiple Accuracy Approach

Higher accuracy region (HA)

- Guess initial $K^{\alpha\beta}$ and $\phi_{\alpha}$
- Optimise density kernel LNV algorithm
- Converged?
  - yes: Optimise NGWFs
  - no: Converged?
    - yes: Done!
    - no: Optimise density kernel LNV algorithm

Lower accuracy region (LA)

- Guess initial $K^{\alpha\beta}$ and $\phi_{\alpha}$
- Optimise density kernel LNV algorithm
- Converged?
  - yes: NGWFs are fixed!
  - no: Converged?
    - yes: Done!
    - no: Optimise NGWFs
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.

Multiple Accuracy Approach

Why?

• And it is all quantum!
Multiple Accuracy Approach

How?

Read input data

Initialise elements array

Density kernel optimisation

Check elements%dkn_only value

Calculate gradient with respect to NGWFs on this atom

Calculate RMS

Converged?

Calculate search direction and update NGWFs

PPDs will be zero for frozen NGWFs

Contributions to RMS only from optimised NGWFs

Search direction only includes optimised NGWFs, others keep frozen

Next NGWF iteration

Exit

If species is in %block_dkn_only then elements%dkn_only = .true.
Else elements%dkn_only = .false.
End if
Multiple Accuracy Approach

Results

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

\[
Q = 3LHL - 2LSLHL - 2LHLSL
\]

\[
K = 3SLS - 2LSLSL
\]

• Convergence problems to be solved.
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.
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”).

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.

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

Appear if the basis set moves with the atoms.

What about \[ \int d\vec{r} \left( \frac{\delta E}{\delta \phi_\alpha(\vec{r})} \right) \frac{\partial \phi_\alpha(\vec{r})}{\partial x_A} \]?
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:

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

- Zero if NGWFs are optimised
- Psincs do not move with the atoms
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?

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

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

\[
\frac{\partial \phi_\alpha(\vec{r})}{\partial x_A} = \sum_{\vec{G}} G_{cutoff}^{-1} \exp \left( -i\vec{G}(\vec{r}-\vec{R}_A) \right) - i G_x \phi(\vec{G}) \exp \left( -i\vec{G}(\vec{r}) \right)
\]
How to calculate Pulay forces?

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

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

\[ \frac{\partial \phi_\alpha(\vec{r})}{\partial x_A} = \sum_{\tilde{G}} \tilde{G}_{\text{cutoff}} \hat{G} e^{-i\tilde{G} (\vec{r} - \vec{R}_A)} \]

The derivative of the NGWFs with respect to the atomic positions has to be implemented in ONETEP.
### Multiple Accuracy Approach – Pulay Forces

#### Calculated derivative of the overlap matrix

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#### Finite differences: derivative of the overlap matrix

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We have the two ingredients…

... Pulay forces coming soon...
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.
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Any questions?