

Hartree-Fock exchange with localized orbitals for fast and efficient calculations with Quantum ESPRESSO

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Hybrid functional are very popular due to their accuracy and predictive capabilities. However implementation with plane wave based methods is computationally heavy.

TARGET

A fast method for the evaluation of Fock exchange with plane waves

OUTLINE

- Exchange with localized orbitals
- Computational performances
- Accuracy of the method on realistic systems

We want to solve a set of Kohn-Sham equations

$$\hat{f}\psi_k(\mathbf{r}) = \varepsilon_k\psi_k(\mathbf{r}) \quad k = 1, 2, \dots, N$$

...where in the Fock operator there is also the exact Hartree-Fock exchange contribution (Hybrid functionals)

$$\hat{f} = -\frac{1}{2}\nabla^2 + \hat{V}_{ext} + \hat{V}_{Hxc}[n] + \hat{V}_X[\gamma]$$

$$\gamma(\mathbf{r}, \mathbf{r}') = \sum_i^N \psi_i(\mathbf{r})\psi_i^*(\mathbf{r}')$$

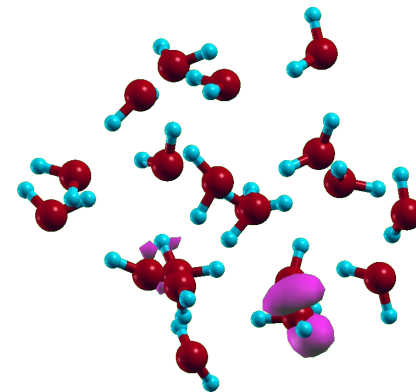
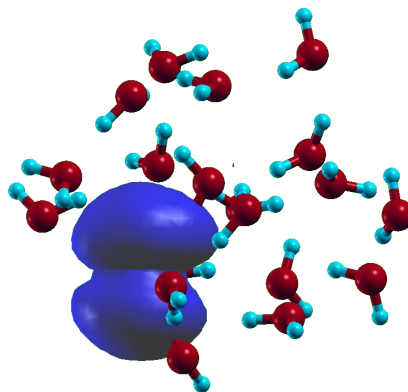
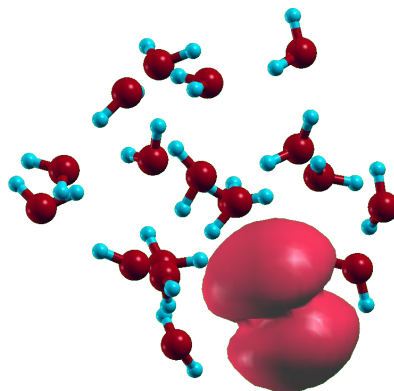
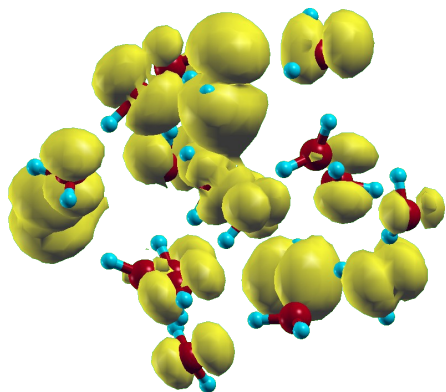
The Exchange potential
has to be computed
along the SCF

$$\hat{V}\psi_j(\mathbf{r}) = e^2 \sum_i^N \psi_i(\mathbf{r}) \int d\mathbf{r}' \frac{\psi_i^*(\mathbf{r}')\psi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

PROOF OF CONCEPT

the exchange integrals vanish for vanishing products of orbitals

$$\hat{V}\psi_j(\mathbf{r}) = e^2 \sum_i^N \psi_i(\mathbf{r}) \int d\mathbf{r}' \frac{\psi_i^*(\mathbf{r}')\psi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$



EFFICIENT ALGORITHM

- A fast and efficient localization
- Projection of the exchange operator on the localized basis set compatible with the ACE method
- An efficient and safe truncation criterion

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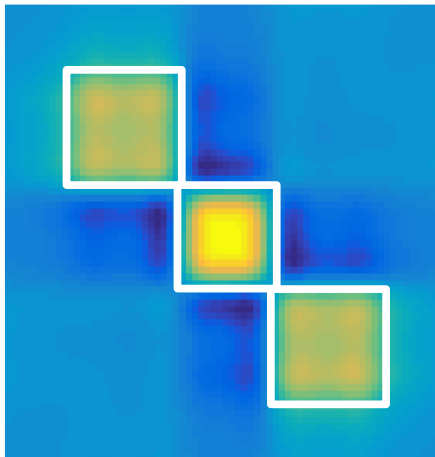
$$\Psi_{ki} = \psi_i(\mathbf{r}_k) \quad i = 1, \dots, N \quad k = 1, \dots, N_R$$

$$\mathbf{W} = \Psi \cdot \mathbf{U}$$

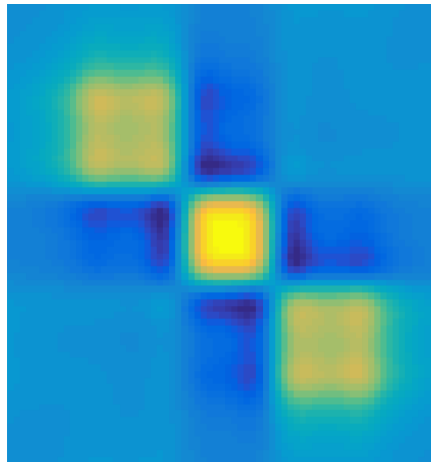
\mathbf{U} is computed from the QRCP of Ψ

An efficient
implementation of the
SCDM method

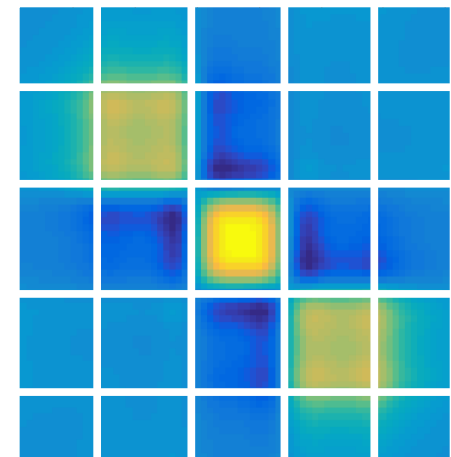
Prescreening
+
broadcast



Scalar code



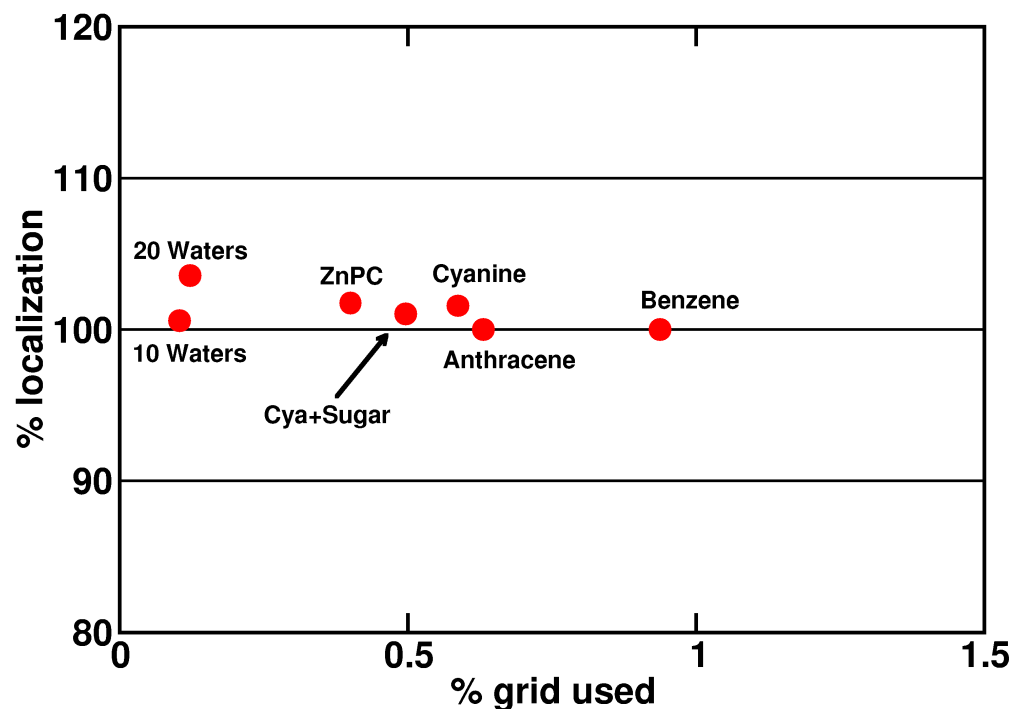
Distributed QRCP with a
SCALAPACK
implementation



The prescreening is done by choosing the grid points where the norm of the density is greater than **scdmden** threshold, and the norm of the gradient is lower than **scdmgrd** threshold.

$$\text{DenThr} = \text{scdmden} \cdot \langle n \rangle$$

$$\text{GrdThr} = \text{scdmgrd} \cdot \langle \nabla n \rangle$$



	Spread Before	Spread after	Grid	Used
Cya + Sugar (52)	12.73	4.71	729000	393
Water (711)	38.52	0.74	11390625	2898
Si (1005)	175.16	2.35	1728000	3024
TiO ₂ (246)	38.39	1.00	10077696	6449

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$$\hat{W} |\psi_i\rangle = \sum_{pq}^{N_P} \hat{V} |w_p\rangle \cdot (\mathbf{M}^{-1})_{pq} \cdot \langle w_q | \hat{V} | \psi_i \rangle$$

$$\hat{V} \psi_j(\mathbf{r}) = e^2 \sum_i^N \psi_i(\mathbf{r}) \int d\mathbf{r}' \frac{\psi_i^*(\mathbf{r}') \psi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$\hat{V} w_j(\mathbf{r}) = e^2 \sum_i^N w_i(\mathbf{r}) \int d\mathbf{r}' \frac{w_i^*(\mathbf{r}') w_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Using the ACE formalism, the exchange potential on the canonical KS orbitals, can be computed from the exchange potential on localized orbitals:

L-ACE

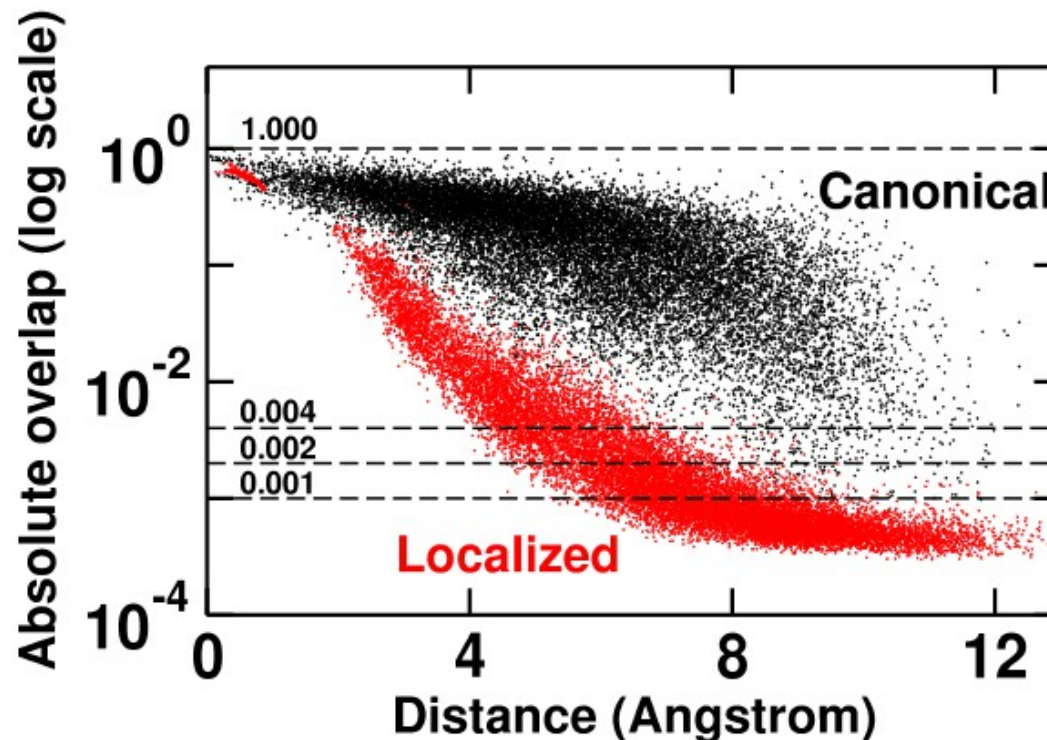
EFFICIENT ALGORITHM

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$$\hat{V} w_j(\mathbf{r}) = e^2 \sum_i^N w_i(\mathbf{r}) \int d\mathbf{r}' \frac{w_i^*(\mathbf{r}') w_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$S_{ij} = \int d\mathbf{r} |w_i(\mathbf{r})| \cdot |w_j(\mathbf{r})| < S_{thr}$$

The electrostatic integrals
can be neglected
whenever the absolute
overlap integral is lower
than **localization_thr**



```
&system
```

```
ibrav=6,
```

```
celldm(1)=47.075876,
```

```
celldm(3)=0.600000,
```

```
nat=86, ntyp=3,
```

```
nbnd = 132
```

[occ + virt]

```
ecutwfc = 80.0,
```

```
ecutfock = 160.0,
```

[ge ecutwfc]

```
ecutrho = 320.0,
```

```
input_dft='pbe0'
```

```
nspin = 2
```

[new]

```
tot_magnetization = 2.0d0
```

```
ace=.true.
```

[default]

```
localization_thr = 0.004
```

```
scdmden = 1.0
```

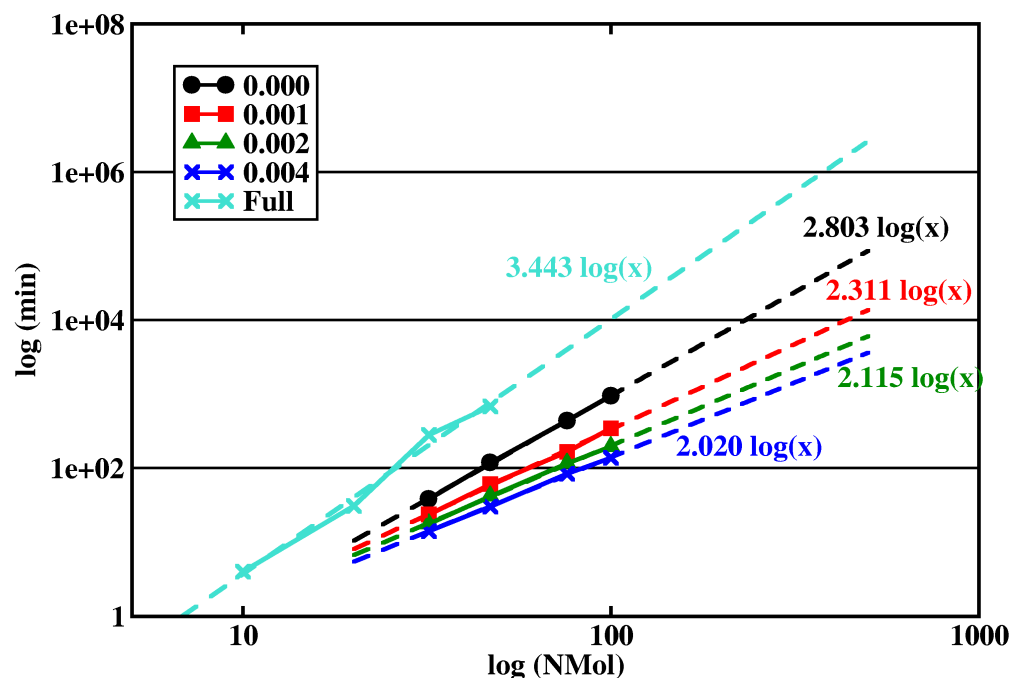
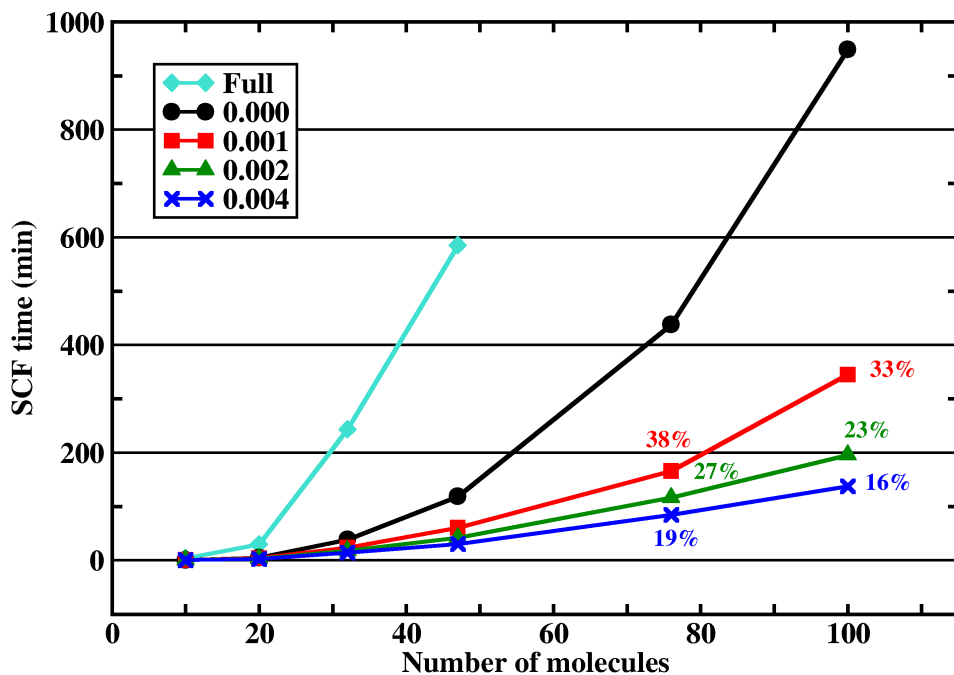
```
scdmgrd = 10.0
```

```
/
```

Setup: 80 CPU, 4 GB x core

Test: Water clusters (up to **300 atoms**) at B3LYP/80/320/320 Ry

Computational SCF times

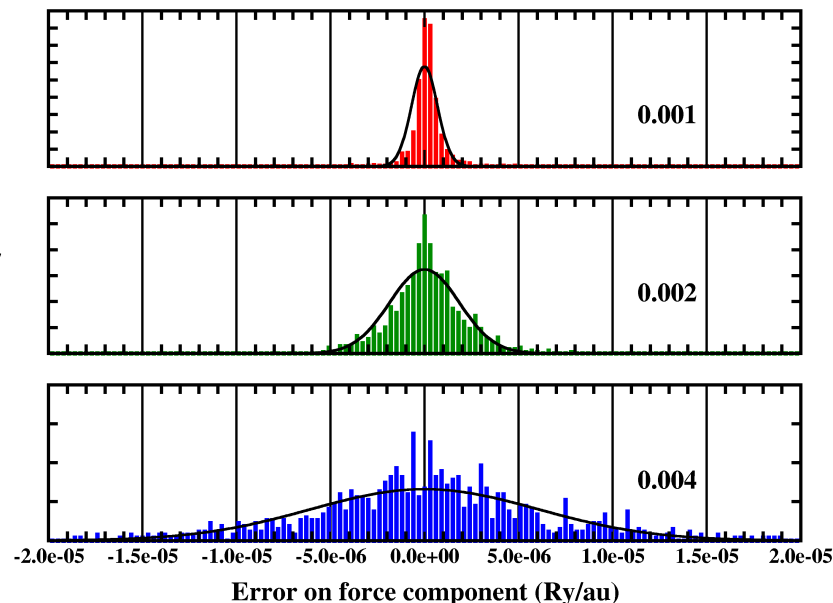


Scaling with respect to the system size: the exponent is 3.5 for Full, 2.8 for ACE and drops to 2.0 using L-ACE(0.004)

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Error distribution of the force
components for the
100 molecules water cluster

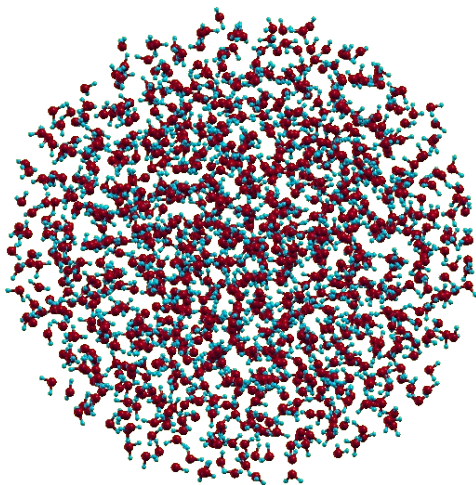


MAE of binding and HOMO energies

	ΔBE (kcal/mol)	$\Delta HOMO$ (eV)
ACE	0	0
L-ACE(0.001)	0.0002	0.0000
L-ACE(0.002)	0.0012	0.0000
L-ACE(0.004)	0.0040	0.0001
BLYP	0.4015	1.3834

Setup: 576 CPU, 118 GB x 16 nodes

Test: Water clusters (up to **711 atoms**) at B3LYP/80/320/320 Ry



ACE

>24h (approx 25h)

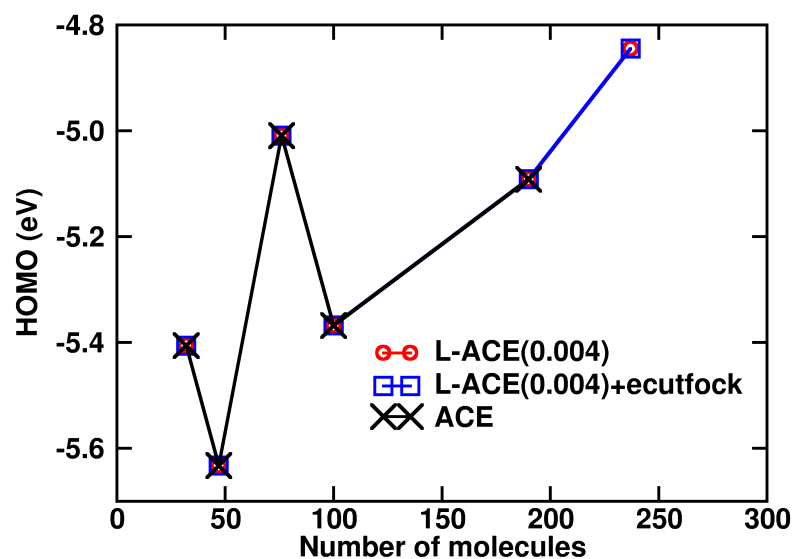
L-ACE(0.004)

1h50m

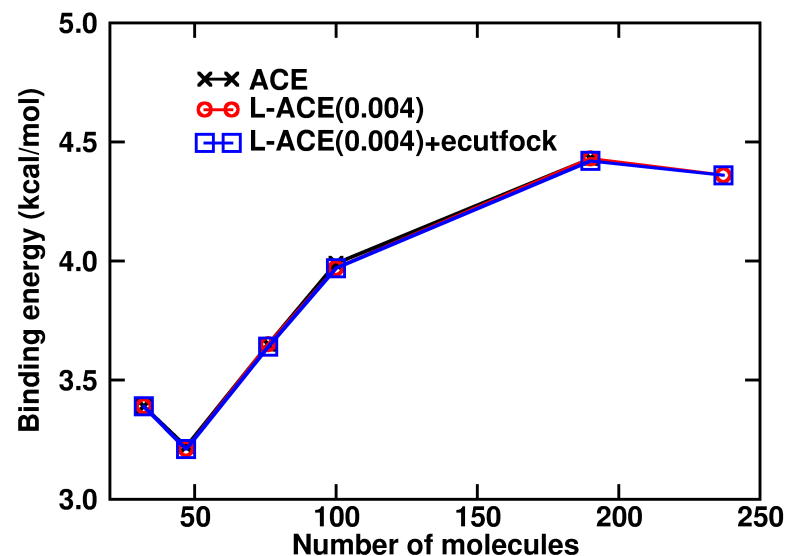
L-ACE(0.004)+ecutfock

1h20m

HOMO energies
Max error: 0.0005 eV

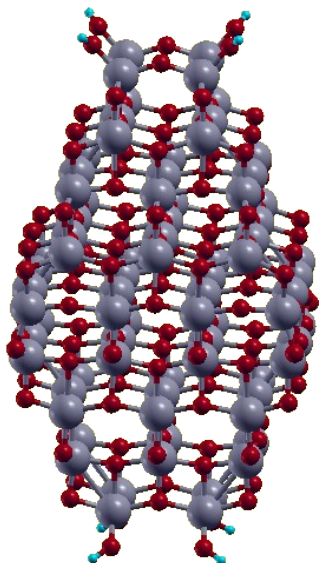


Binding energies per molecule
Max error: 0.02 kcal/mol



Setup: 576 CPU, 118 GB x 16 nodes

Test: TiO₂ clusters (up to **246 atoms**)

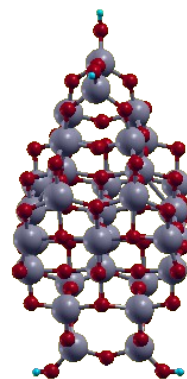


246 atoms

60/120/240 Ry

ACE 11h (*)

L-ACE(0.005) 3h (*)



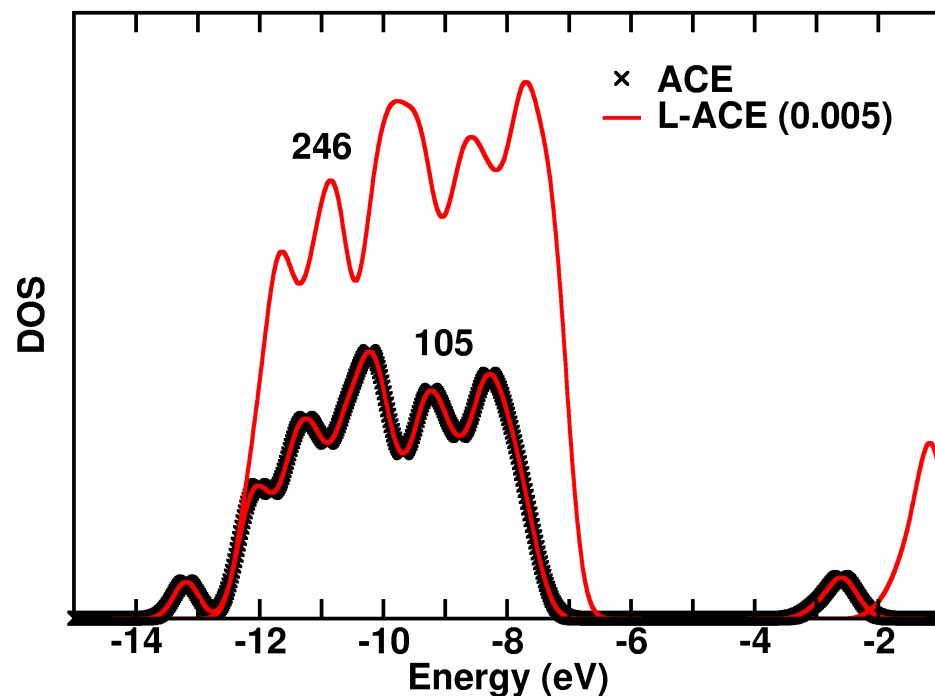
105 atoms

80/160/320 Ry

ACE 6h30m

L-ACE(0.005) 3h50m

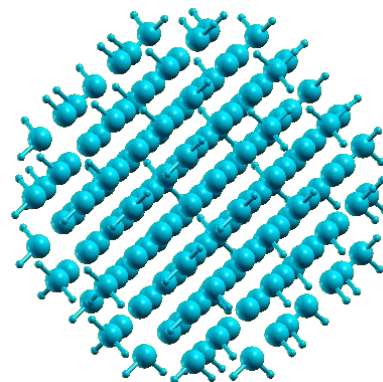
Density of States for the
two clusters using ACE
and L-ACE methods



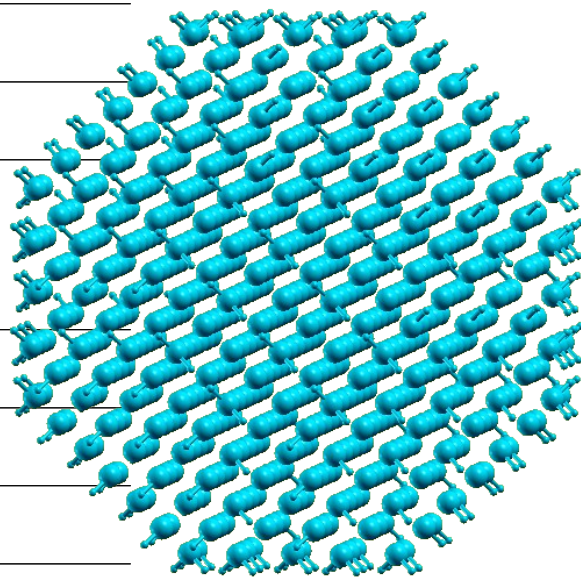
Setup: 576 CPU, 118 GB x 16 nodes

Test: Si clusters (up to **1005 atoms**)

	ACE	L-ACE (0.002)	L-ACE (0.005)
Size	283 atoms (9 Å radius)		
Cutoffs	20/80/80 Ry		
Time	1h24	-	0h53m
Gap (eV)	3.5340	-	3.5329
Tot. force Ry/au	0.325011	-	0.325040



Size	1005 atoms (15 Å radius)		
Cutoffs	15/30/60 Ry		
Time	16h	6h20m	3h48m
Gap (eV)	2.6371	2.6382	2.6390
To.l force Ry/au	0.567834	0.567850	0.567956



PRO

- High accuracy
- Efficiency (both CPU time and memory requirement)
- Suitable for ANY type of computational facilities, from single workstation calculations to large supercomputers

CON

- The method is approximate
- Thresholds need to be tuned

Summary of implementations

	ACE	L-ACE
Gamma only	V	V
Spin polarized	V	V
K-points	V	X
Non collinear spin	V	X
Non cubic cells	V	V
Reduced EXX grids	V	V
Virtual orbitals* (band gaps)	V	V
USPP	V	X

* Compatibility with virtual orbitals:

only the occupied manifold is localized

ov integrals always computed (virtuals assumed completely delocalized)

vv integrals not necessary for ground state SCF

Carnimeo, Baroni, Giannozzi, arXiv:1801.09263 (2018)

Giannozzi *et al.*, *JPCM*, 29, 465901 (2017)

Conclusions and perspectives

- Hybrid functionals for large molecular systems, e.g. **nanoparticles and fragmented clusters**
- Work is in progress for the extension to K-points, in particular for calculations on **large surfaces**.
- Further improvements possible with R-space Poisson solver or FFTs on reduced boxes (e.g. **cp.x**)
- Can be combined with advanced parallelization strategies



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