Inner projection methods for fast and efficient Hartree-Fock exchange evaluation with plane waves

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Overview

1. [Exact exchange in PWscf](#)

2. [The ACE method](#)

3. [The SCDM approach](#)

EEX in PWscf

For a molecular system composed by N electrons distributed in N occupied molecular orbitals $\{\varphi_i\}$, we want to solve a set of Kohn-Sham equations for NMO molecular orbitals

$$\hat{f}_k\left[\{\varphi_i\}\right]|\varphi_k\rangle = \varepsilon_k|\varphi_k\rangle \qquad k = 1, 2, ..., NMO$$

The Fock operator is defined (in atomic units) as

$$\hat{f}_k(\vec{r}) = -\frac{1}{2}\nabla^2 + \hat{V}_{\text{ext}}(\vec{r}) + \hat{V}_{\text{H}}[n(\vec{r})] + \hat{V}_{\text{xc}}[n(\vec{r})] + \hat{V}_{\text{X}}[\{\varphi_i\}]$$

The particular choice of $\hat{V}_{\text{xc}}[n(\vec{r}\,')]$ accounts for all the different types of exchange-correlation functionals, while the empirical coefficients weighting the exact exchange part have been included in the operators.

EEX in PWscf

The exchange operator can be defined by means of its action on a generic function φ_k

$$\hat{V}_X \left| \varphi_k \right> = (\hat{V}_X \varphi_k)(\vec{r}) = - \sum_i^N \varphi_i(\vec{r}) \int d\vec{r}' \frac{\varphi_i(\vec{r}')\varphi_k(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

and is evaluated as

- $\varphi_k(\vec{G}) \rightarrow \varphi_k(\vec{r})$
- $\rho_{ik}(\vec{r}) = \varphi_i(\vec{r}) \cdot \varphi_k(\vec{r})$
- $\rho_{ik}(\vec{r}) \rightarrow \rho_{ik}(\vec{G})$
- $v_{ik}(\vec{G}) = \sum \rho_{ik}(\vec{G})/G^2$
- $v_{ik}(\vec{G}) \rightarrow v_{ik}(\vec{r})$
- $(V_X \varphi_k)(\vec{r}) = \sum \varphi_i(\vec{r}) \cdot v_{ik}(\vec{r})$
- $(V_X \varphi_k)(\vec{r}) \rightarrow (V_X \varphi_k)(\vec{G})$

EEX in PWscf

Double-loop algorithm

Pure DFT
Outer loop: Do n = 1, ...
$\{\psi_i^{(n)}\}$

$$\hat{V}_X \, |\psi_k^{(n)}\rangle = -\sum_i^N \psi_i^{(n)}(\vec{r}) \int d\vec{r}\,' \frac{\psi_i^{(n)}(\vec{r}\,')\psi_k^{(n)}(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}$$

$\{\psi_i^{(n)}\} \rightarrow \{\varphi_i^{(n,m=0)}\}$

Inner loop: Do m = 1, ...

$$\hat{V}_X \, |\varphi_k^{(n,m)}\rangle = -\sum_i^N \psi_i^{(n)}(\vec{r}) \int d\vec{r}\,' \frac{\psi_i^{(n)}(\vec{r}\,')\varphi_k^{(n,m)}(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}$$

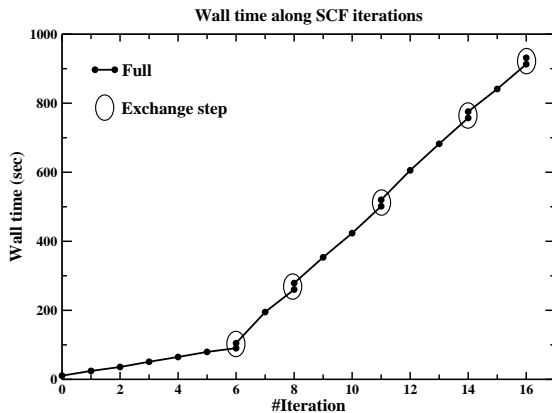Diagonalization $\rightarrow \{\varphi_i^{(n,m+1)}\}$
Check Convergence on $\{\varphi_i^{(n,m+1)}\}$ at fixed $\{\psi_i^{(n)}\}$
End Inner loop
$\{\varphi_i^{(n,m+1)}\} \rightarrow \{\psi_i^{(n+1)}\}$ and check convergence
End Outer loop

In order to speed-up the convergence a double-loop algorithm is used.

EEX in PWscf

Wall time along SCF iterations

Example: Ethylene,
1 CPU, 100 Ry,
converged to 10^{-7} Ry

Pure DFT: 6
Outer loop: 5
Inner loop: 2, 3, 3, 2
Tot. calls: 32

The ACE method

$$\hat{V}'_X = -\, \hat{V}_X \, |\psi\rangle \, \langle\psi| \hat{V}_X |\psi\rangle^{-1} \, \langle\psi| \, \hat{V}_X$$
$$= -\, \hat{V}_X \, |\psi\rangle \, \mathbf{M}^{-1} \, \langle\psi| \, \hat{V}_X$$
$$= -\, \hat{V}_X \, |\psi\rangle \, \mathbf{L}^{-T} \mathbf{L}^{-1} \, \langle\psi| \, \hat{V}_X$$
$$= -\, |\xi\rangle \, \langle\xi|$$

where the exchange matrix $(\mathbf{M})_{ij} = \langle\psi_i| \hat{V}_X |\psi_j\rangle$ has been factorized (Cholesky) as proposed in Ref.[Lin, 2016]

$$|\xi\rangle = \hat{V}_X \, |\psi\rangle \, \mathbf{L}^{-T}$$

The expectation value over the set $\{\psi\}$ is identical

$$\langle\psi| - V'_X |\psi\rangle = \langle\psi| \hat{V}_X |\psi\rangle \, \langle\psi| \hat{V}_X |\psi\rangle^{-1} \, \langle\psi| \hat{V}_X |\psi\rangle = \langle\psi| V_X |\psi\rangle$$

The ACE method

Double-loop algorithm

Pure DFT
Outer loop: Do n = 1, ...
$\{\psi_i^{(n)}\}$

$$\hat{V}_X \, |\psi_k^{(n)}\rangle = - \sum_i^N \psi_i^{(n)}(\vec{r}) \int d\vec{r}\,' \frac{\psi_i^{(n)}(\vec{r}\,')\psi_k^{(n)}(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}$$

$$\langle \psi^{(n)} | \hat{V}_X | \psi^{(n)} \rangle = \mathbf{M} = \mathbf{L}^{-T} \mathbf{L}^{-1}$$

$$|\xi^{(n)}\rangle = \hat{V}_X \, |\psi\rangle \, \mathbf{L}^{-T}$$

Inner loop: Do m = 1, ...

$$\hat{V}_X' \, |\varphi_k^{(n,m)}\rangle = - \sum_i |\xi_i^{(n)}\rangle \, \langle \xi_i^{(n)} | \varphi_k^{(n,m)} \rangle$$

Diagonalization $\rightarrow \{\varphi_i^{(n,m+1)}\}$
Check Convergence on $\{\varphi_i^{(n,m+1)}\}$ at fixed $\{\xi_i^{(n)}\}$
End Inner loop
$\{\varphi_i^{(n,m+1)}\} \rightarrow \{\psi_i^{(n+1)}\}$ and check convergence
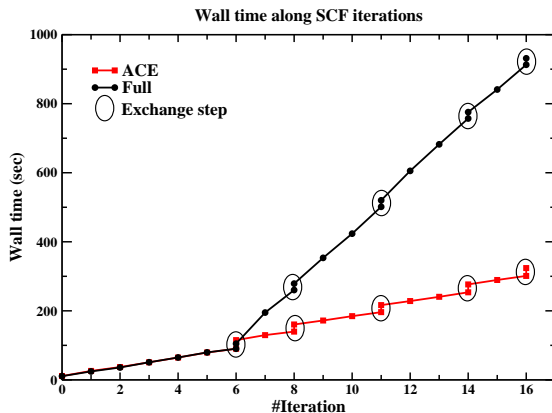**End Outer loop**

Only in the outer loop I have to evaluate the exchange integrals, while in the inner loop the evaluation of the exchange potential and energy just requires scalar products:

$$\hat{V}_X \, |\varphi_j\rangle = - |\xi\rangle \, \langle \xi | \varphi_j \rangle$$

$$\langle \varphi_i | \hat{V}_X | \varphi_j \rangle = - \langle \varphi_i | \xi \rangle \, \langle \xi | \varphi_j \rangle$$

$$E_X = \frac{1}{2} \sum_i \langle \varphi_i | \xi \rangle \, \langle \xi | \varphi_i \rangle$$

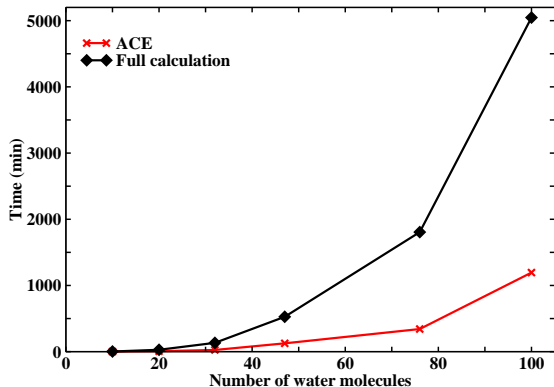# The ACE method

Wall time along SCF iterations

With the ACE method the cost of the inner iterations is analogous to the cost of a pure DFT method.

Example: Ethylene, 1 CPU, 100 Ry, converged to 10^{-7} Ry

Pure DFT: 6
Outer loop: 5
Inner loop: 2, 3, 3, 2
Tot. calls: 32/5

The ACE method

Time for a complete SCF for a set of clusters composed by different number of water molecules.

The SCDM approach

Double-loop algorithm

Pure DFT
Outer loop: Do n = 1, ...
$\{\psi_i^{(n)}\}$

$$\hat{V}_X \, |\psi_k^{(n)}\rangle = -\sum_i^N \psi_i^{(n)}(\vec{r}) \int d\vec{r}\,' \frac{\psi_i^{(n)}(\vec{r}\,')\psi_k^{(n)}(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}$$

$$\langle\psi^{(n)}|\hat{V}_X|\psi^{(n)}\rangle = \mathbf{M} = \mathbf{L}^{-T}\mathbf{L}^{-1}$$

$$|\xi^{(n)}\rangle = \hat{V}_X \, |\psi\rangle \, \mathbf{L}^{-T}$$

Inner loop: Do m = 1, ...

$$\hat{V}'_X \, |\varphi_k^{(n,m)}\rangle = -\sum_i |\xi_i^{(n)}\rangle \, \langle\xi_i^{(n)}|\varphi_k^{(n,m)}\rangle$$

Diagonalization $\rightarrow \{\varphi_i^{(n,m+1)}\}$
Check Convergence on $\{\varphi_i^{(n,m+1)}\}$ at fixed $\{\xi_i^{(n)}\}$
End Inner loop
$\{\varphi_i^{(n,m+1)}\} \rightarrow \{\psi_i^{(n+1)}\}$ and check convergence
End Outer loop

May I further reduce the computational burden of the evaluation of the exchange integrals in the outer loop?

One promising route could be to localize the molecular orbitals.

The SCDM approach

With the SCDM (Selected Column Density Matrix) approach[Lin, 2015] we have a powerful technique to localize the density matrix using the interpolative decomposition, which is an algebraic, non-iterative method.

$$\rho(\vec{r}, \vec{r}\,') = |\psi\rangle \langle\psi| = |\tilde{\psi}\rangle \langle\tilde{\psi}|$$
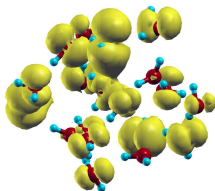
From the *canonical* orbitals, by unitary rotation we can then obtain a set of *localized* orbitals $\{\tilde{\psi}_i\}$, which span the same space and can be used to build the projector.
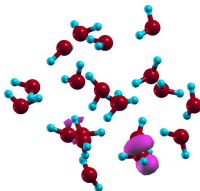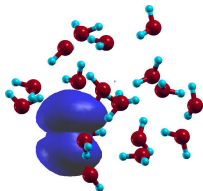
The exchange operator then reads

$$\begin{aligned}
\hat{V}_X' &= -\ \hat{V}_X |\tilde{\psi}\rangle \langle\tilde{\psi}| \hat{V}_X |\tilde{\psi}\rangle^{-1} \langle\tilde{\psi}| \hat{V}_X \\
&= -\ \hat{V}_X |\tilde{\psi}\rangle \, \mathbf{L}^{-T} \mathbf{L}^{-1} \langle\tilde{\psi}| \hat{V}_X \\
&= -\ |\xi\rangle \langle\xi| \\
|\xi\rangle &= \hat{V}_X |\tilde{\psi}\rangle \, \mathbf{L}^{-T}
\end{aligned}$$

The SCDM approach

$$\hat{V}_X |\tilde{\psi}_k\rangle = -\sum_i^N \tilde{\psi}_i(\vec{r}) \int d\vec{r}' \frac{\tilde{\psi}_i(\vec{r}')\tilde{\psi}_k(\vec{r}')}{|\vec{r} - \vec{r}'|}$$
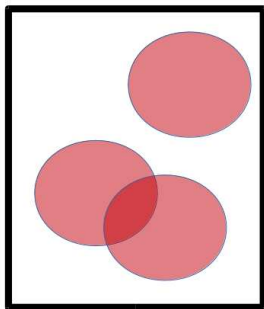

The products between two canonical orbitals are much more delocalized than the product of two localized orbitals, and this can be exploited in order to reduce the cost of the exchange integrals evaluations.
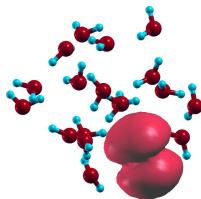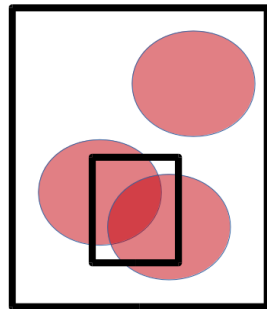
The SCDM approach

Two approaches are under study to cope with the calculation of the integrals of localized functions.

- Skip the integrals involving two bands far enough from each other (a threshold is required).

- Evaluate the integrals on reduced boxes.

A preliminar implementation of the first strategy is available, while the second point is still under study.

The SCDM approach

Double-loop algorithm

Pure DFT
Outer loop: Do n = 1, ...
Localization: $\{\psi_i^{(n)}\} \rightarrow \{\tilde{\psi}_i^{(n)}\}$

$$\hat{V}_X \, |\tilde{\psi}_k^{(n)}\rangle = -\sum_i^N \tilde{\psi}_i^{(n)}(\vec{r}) \int d\vec{r}\,' \frac{\tilde{\psi}_i^{(n)}(\vec{r}\,')\tilde{\psi}_k^{(n)}(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}$$

$$\langle \tilde{\psi}^{(n)} | \hat{V}_X | \tilde{\psi}^{(n)} \rangle = \mathbf{M} = \mathbf{L}^{-T} \mathbf{L}^{-1}$$

$$|\xi^{(n)}\rangle = \hat{V}_X \, |\tilde{\psi}\rangle \, \mathbf{L}^{-T}$$

$$\hat{V}_X \, |\psi_k^{(n)}\rangle = -\sum_i |\xi_i^{(n)}\rangle \, \langle \xi_i^{(n)} | \psi_k^{(n)}\rangle$$

Inner loop: Do m = 1, ...

$$\hat{V}_X' \, |\varphi_k^{(n,m)}\rangle = -\sum_i |\xi_i^{(n)}\rangle \, \langle \xi_i^{(n)} | \varphi_k^{(n,m)}\rangle$$

Diagonalization $\rightarrow \{\varphi_i^{(n,m+1)}\}$
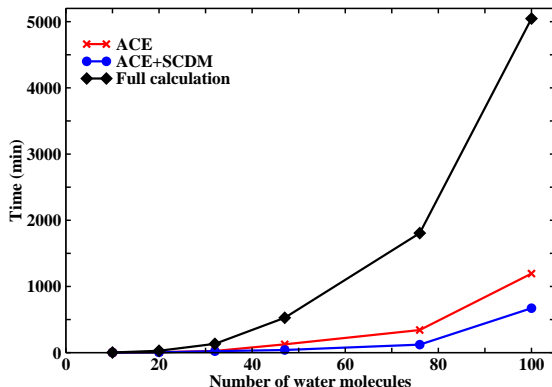Check Convergence on $\{\varphi_i^{(n,m+1)}\}$ at fixed $\{\xi_i^{(n)}\}$
End Inner loop
$\{\varphi_i^{(n,m+1)}\} \rightarrow \{\psi_i^{(n+1)}\}$ and check convergence
End Outer loop

With the localization step the exchange integrals in the outer loop now involve two localized functions.
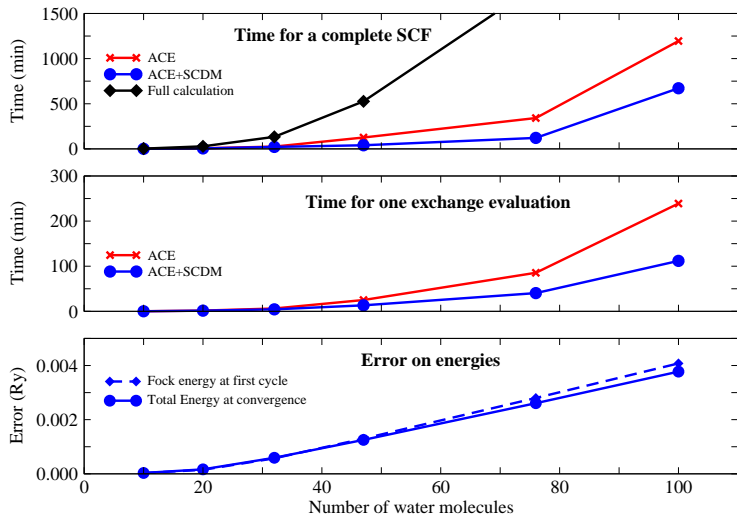
The SCDM approach

Time for a complete SCF for a set of clusters composed by different number of water molecules.

The SCDM approach

Times for a set of clusters composed by different number of water molecules.

References

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IJQC 4, 231.

📄 Lin Lin (2016)
Adaptively Compressed Exchange Operator
JCTC 12, 2242–2249.

📄 Lin Lin (2015)
Compressed Representation of Kohn-Sham Orbitals via Selected Columns of the Density Matrix
JCTC 11, 1463–1469.

The End