ALMOs in CP2K

Rustam Z. Khaliullin

McGill University

Overarching goals

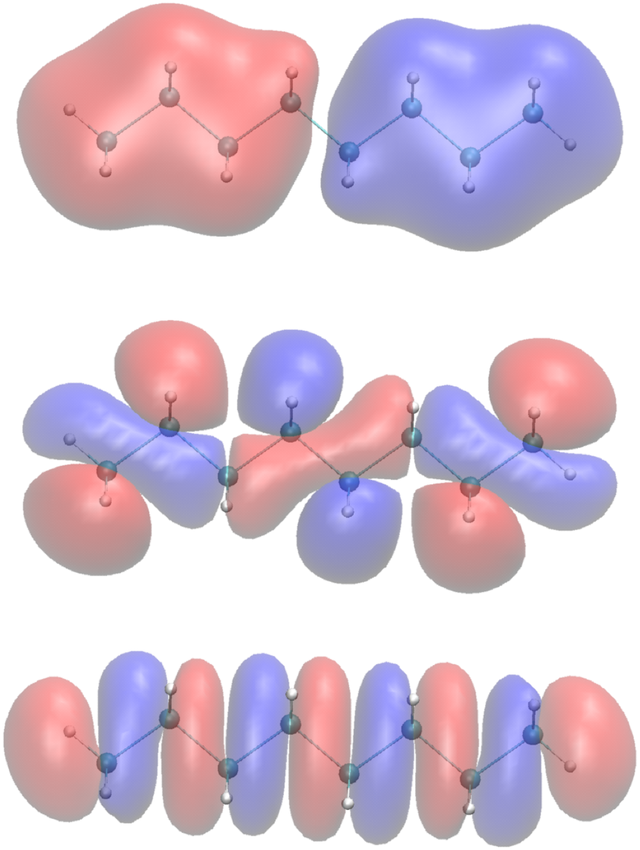
- Use **absolutely localized molecular orbitals (ALMOs)** to gain (**A**) **computational** and (**B**) **physical** advantage in simulations.
  A. Extend length- and time-scales accessible to electronic structure methods and *ab initio* molecular dynamics (linear-scaling techniques),
  B. Provide deeper physical insight into the nature of chemical bonding between atoms in materials and molecules (energy decomposition analysis techniques).

Outline

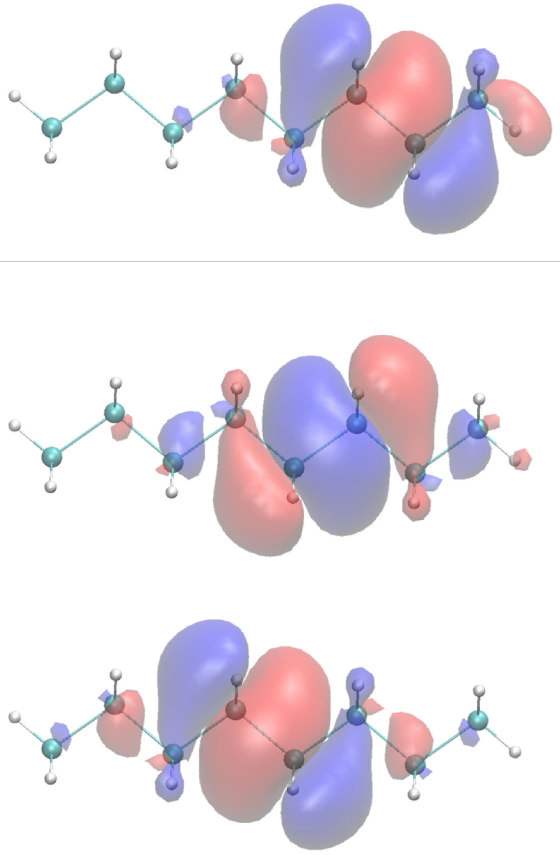
1. What are ALMOs? Ideas and terminology.
2. ALMOs for computational advantage
   - Computational speed without compromising accuracy
   - Energy (static)
     - Weakly interacting systems – molecular and ionic materials (2013)
     - Strongly interacting atoms – finite-gap materials (2018)
   - Forces (molecular dynamics)
3. ALMOs for physical advantage
   - Energy decomposition analysis (EDA) and charge-transfer analysis (CTA)
   - Devalent molecular dynamics

What are ALMOs?

Canonical MOs



Localized MOs

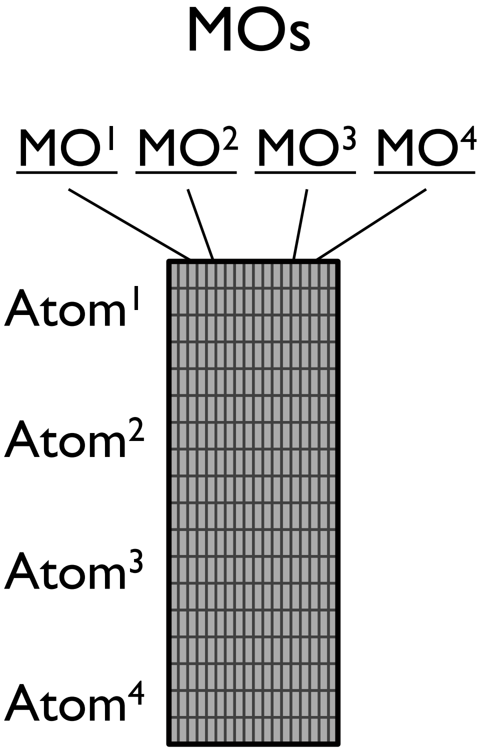


Canonical MOs

- Canonical MOs tend to delocalize over all atoms even in large systems.

All of O(N^2) elements of the MO matrix are significant

⇒ **No linear scaling!**



MOs

MO^1 MO^2 MO^3 MO^4

Atom^1

Atom^2

Atom^3

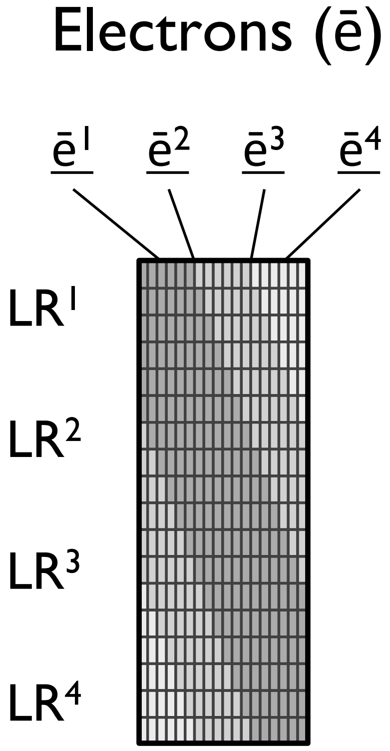
Atom^4

Localized MOs

- Traditional localization of MOs does not help because small but non-negligible **orthogonalization** tails extend to very large distances.

Although some LMO elements are smaller all O(N^2) of them are still significant

⇒ **No linear scaling!**

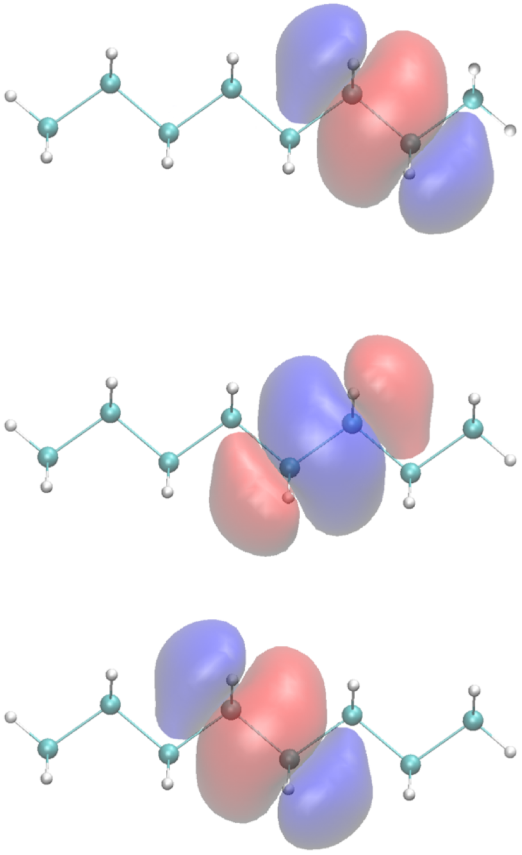


Main idea

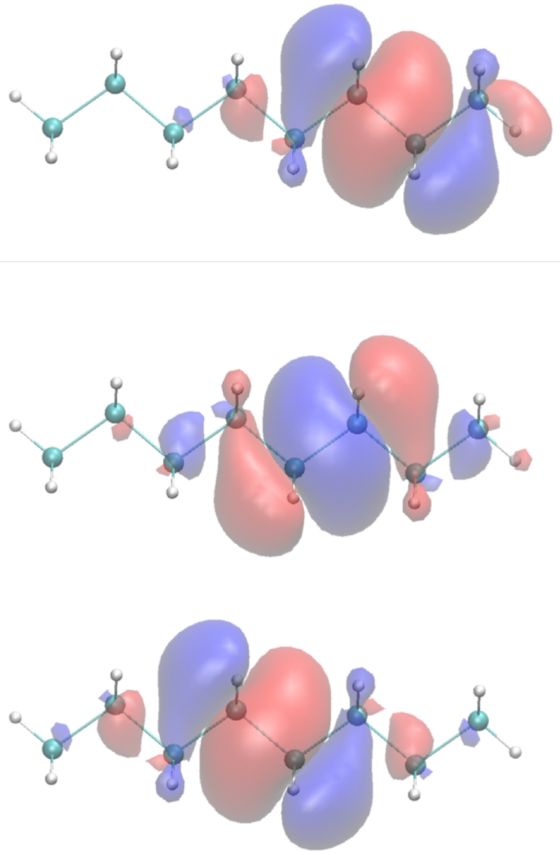
- If an ē can be well-represented with a localized MO why not enforce this locality further by explicitly setting small MO coefficients to zero?
- The result of this operation is an **absolutely** localized MO.

ALMOs

Absolutely localized MOs

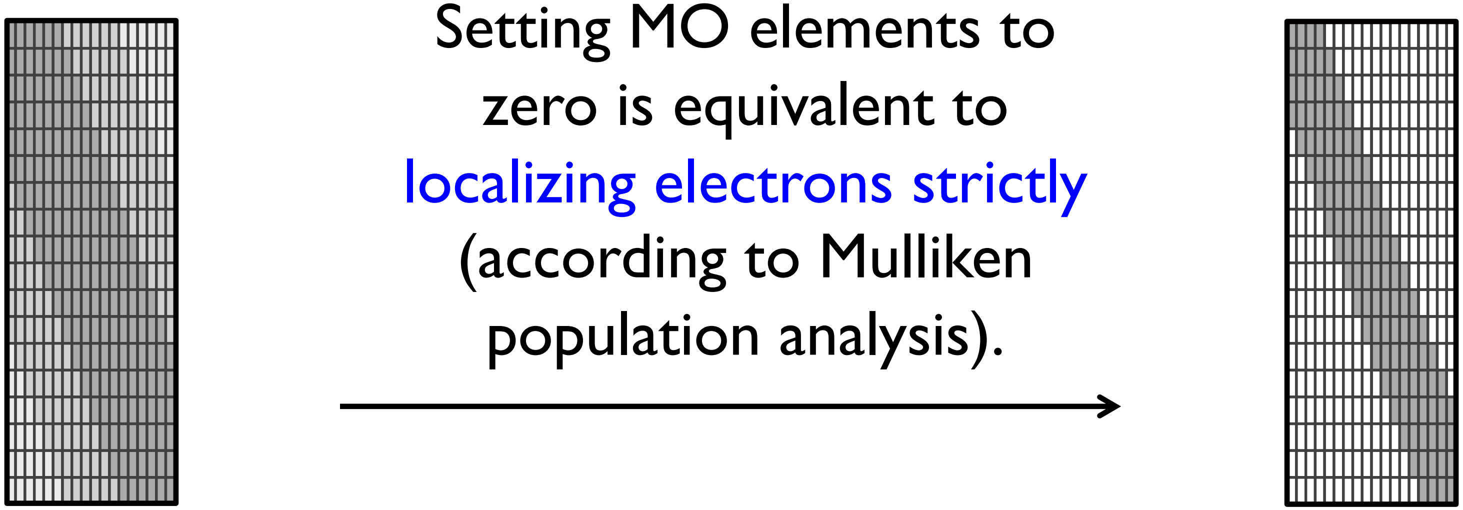


Localized MOs



ALMOs = sparsity = linear scaling

- Guess what MO coefficients can be set to zero and minimize the energy wrt retained non-zero coefficients.
- Use only local variables and design linear scaling algorithms.



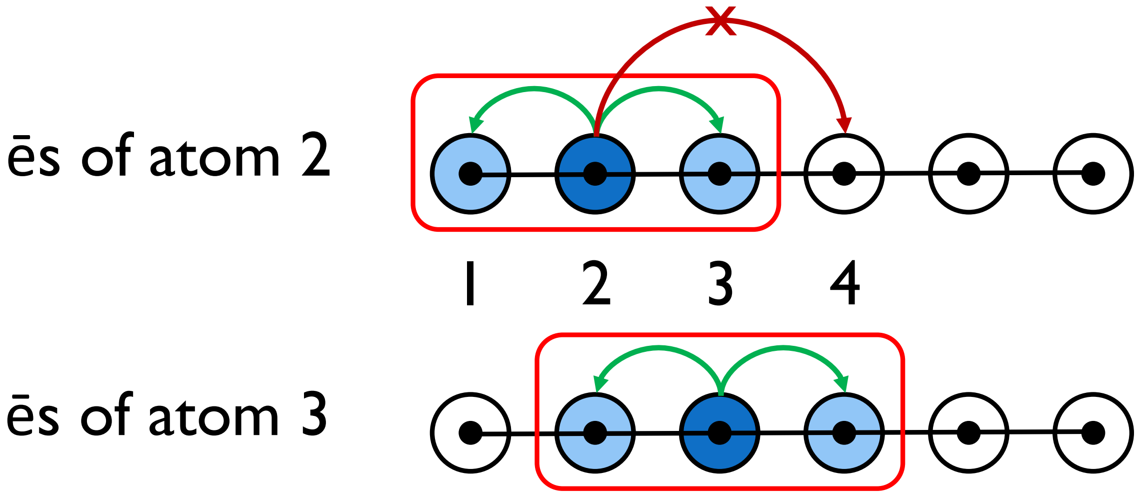
Setting MO elements to zero is equivalent to localizing electrons strictly (according to Mulliken population analysis).

Localized MOs

Absolutely localized MOs

A priori black-box localization

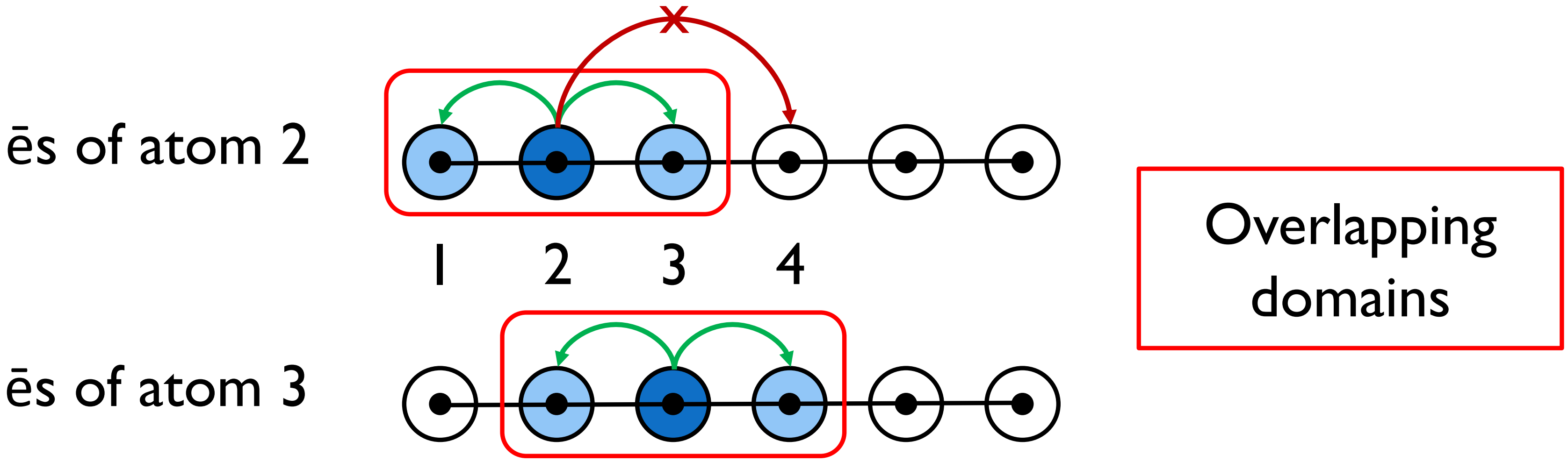
- ***Assume:*** an ē in a system has its own localization center – atom or molecule – and a pre-selected localization radius.
  - Electrons are allowed to delocalize **only** over nearby centers, which we call localization domains. This is an approximation.
  - Localization radius is a single parameter that is tuned for the **best accuracy-performance** compromise.



Overlapping domains

Is the ALMO approximation valid?

- Restricting electrons **switches off only** the donor-acceptor (i.e. covalent) component of interactions between distant domains.
- Other physical interactions such as long-range electrostatics, exchange, polarization, van der Waals are **included.**
- Excluded interactions are **short-range;** it is expected that the approximation will work for all systems, except metals.



ēs of atom 2

1 2 3 4

ēs of atom 3

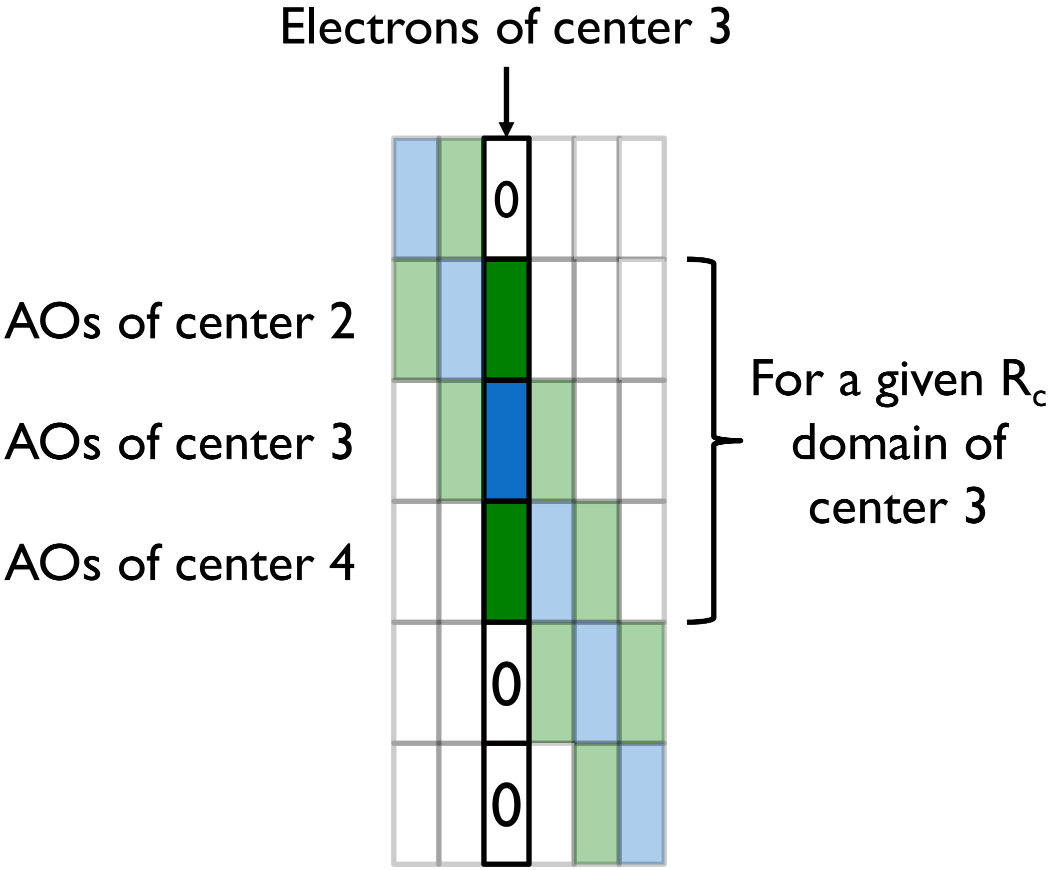
Overlapping domains

Important terminology

- **Localization center** is a compact region in the 3D space.
  - Centers (aka **fragments**) are introduced to define partitioning of the system.
  - The system is partitioned so that its (a) atoms, (b) basis functions, and (c) electrons are logically (not physically) assigned to only one localization center.
- **Localization domain of a center** is a set of all centers within radius R_c including the original center.
  - Domains are introduced to define the structure of the ALMO coefficient matrix: electrons logically assigned to center X are allowed to delocalize **only** over the domain of center X.

ALMO coefficient matrix

- Constraint: electrons assigned to a center are localized only on its domain.
- Result: ALMO matrix is extremely sparse. No. of electronic DOFs grows linearly with no. of atoms and stays small even for large basis sets.



Electrons of center 3

AOs of center 2

AOs of center 3

AOs of center 4

For a given R_c domain of center 3

ALMO vs partitioning methods

- ALMO approach is more accurate than typical partitioning methods.
  - Typical partitioning methods: minimize energy as a functional of small density matrices (DM) on domains. DM of the total system is never computed.

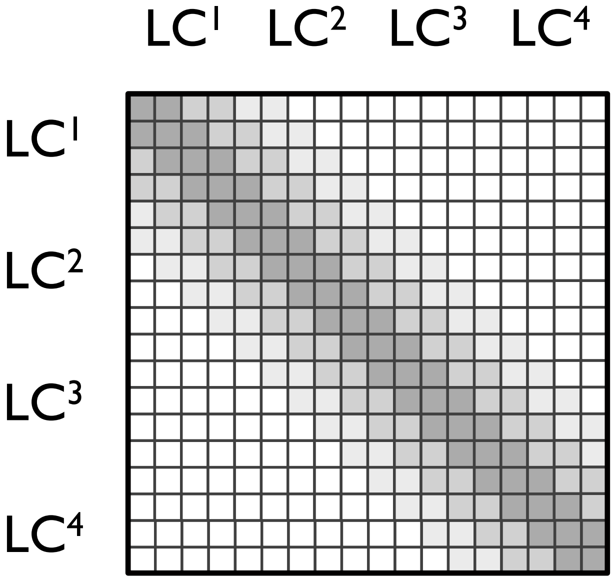
vs

  - ALMO: minimize energy of an approximate but physical DM of the total system. No boundary effects.

Why not optimize density matrix?

- After all, density matrix (DM) is *naturally* sparse: the number of significant DM elements grows linearly with the number of atoms.

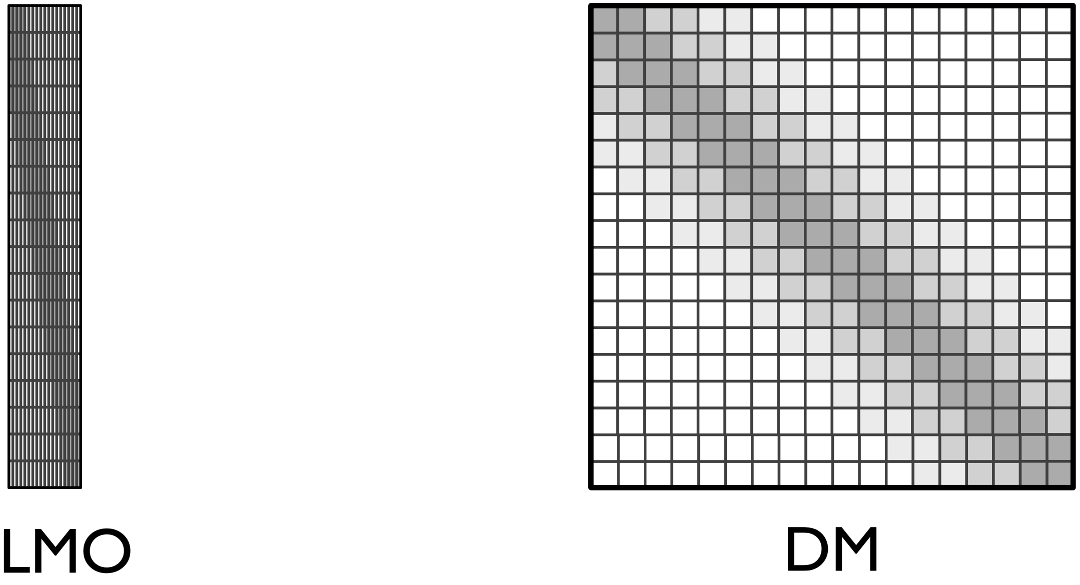
Two distant
localization centers
do NOT contribute
⇒ O(N)



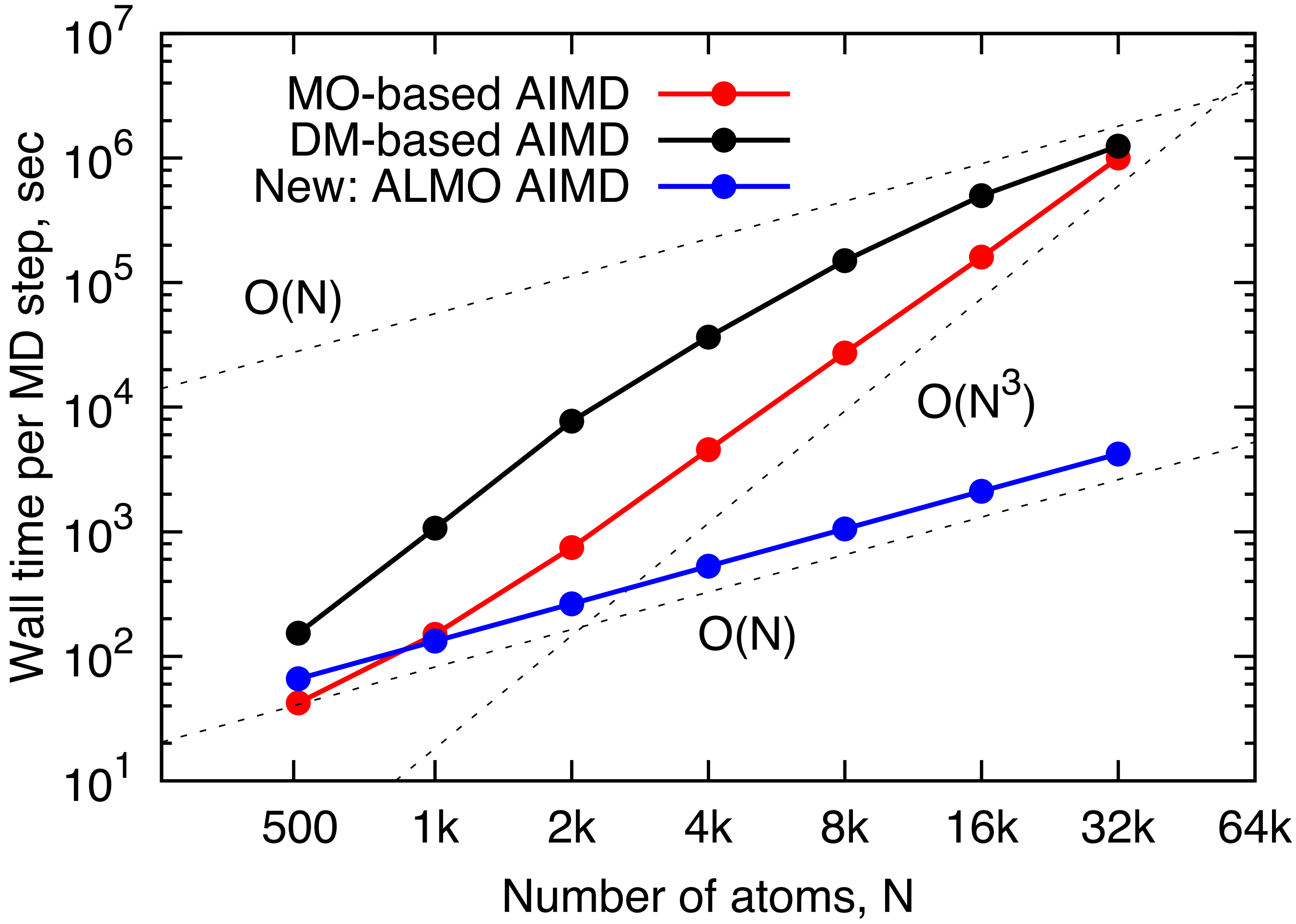
Localization centers (LC)

DM vs ALMO

- MO matrix is smaller: 10 times even for moderate basis sets.
- ALMO elements are independent, DM elements are not.
- For these reasons, the cost of ALMO-based calculations can potentially be substantially lower.



Typical timing curves



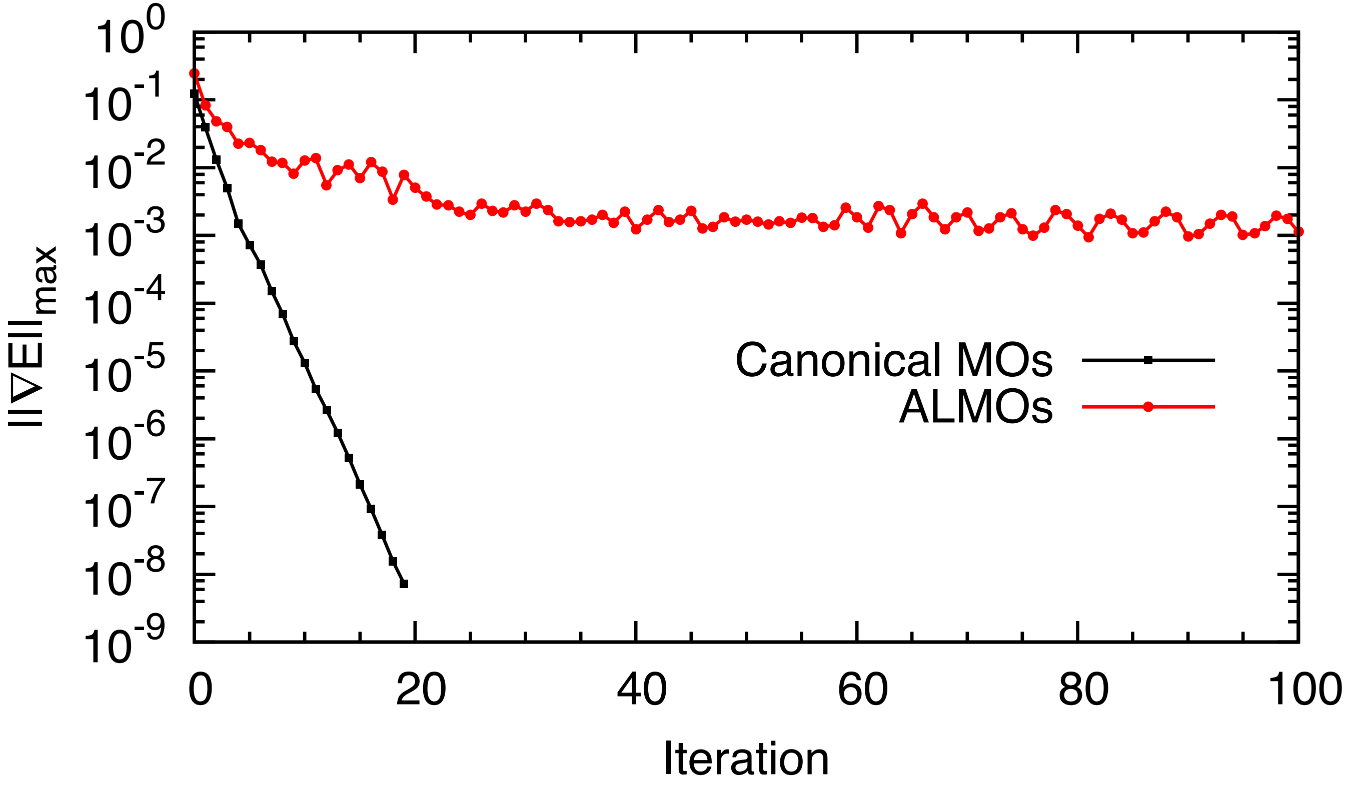
Brief history of the approach

- The idea of enforcing electron locality dates back to the beginning of the Gaussian-based quantum chemistry:
  - Extremely/strictly localized MOs
  - Nonorthogonal localized MOs (NOLMOs)
  - MOs on compact support
  - Nonorthogonal Wannier functions
- How to call them? My list of preferred names:
  - Hermann Stoll, 1980: absolutely localized MOs (ALMOs)
  - Generalized or eXtended ALMOs (XALMOs)

Brief history of the approach

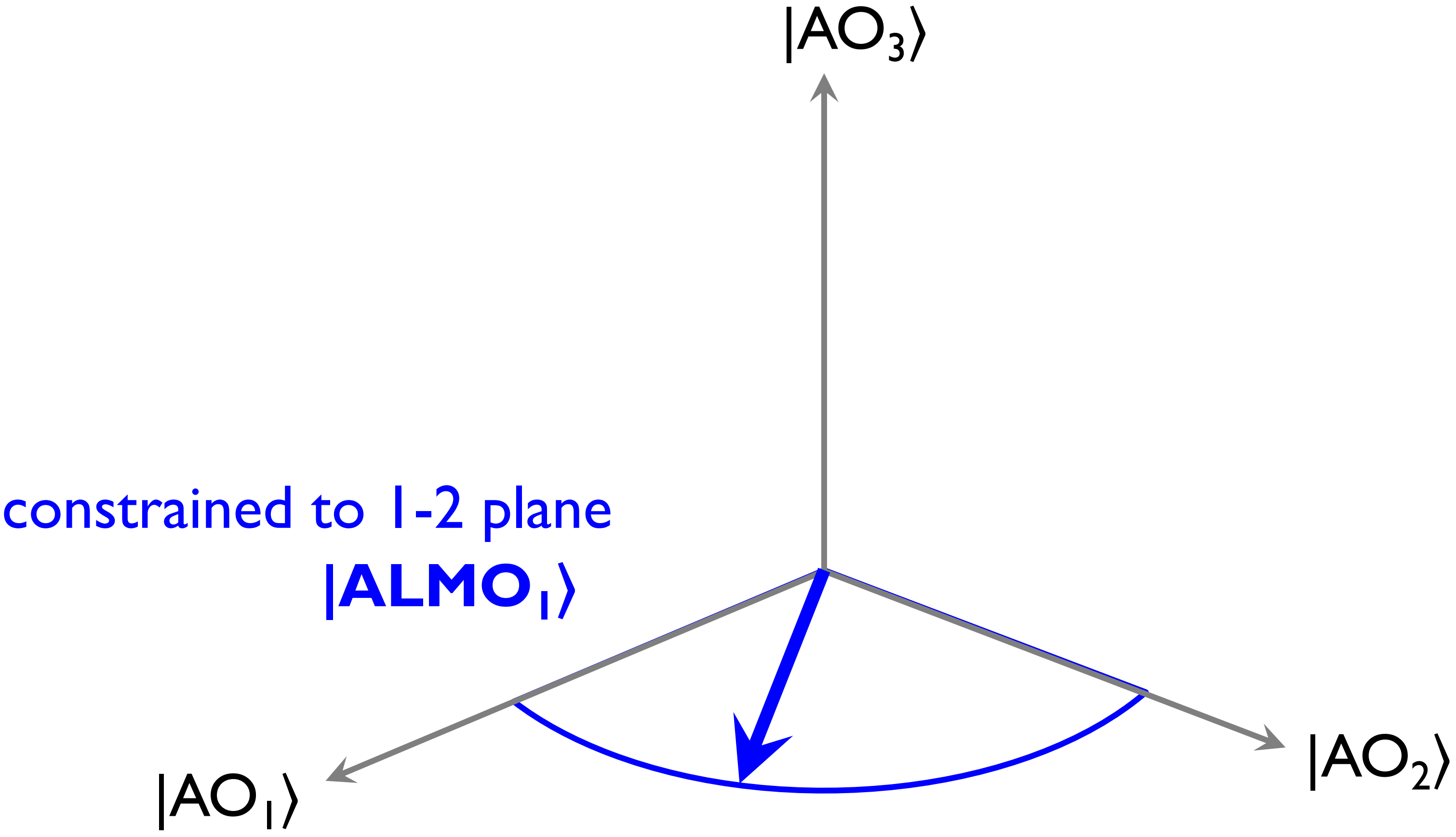
- Despite significant progress and numerous efforts an efficient O(N) algorithm for MO-based DFT does not yet exist.
  - 1991-1995: Roberto Car, Michele Parrinello, Giulia Galli
  - 1993-1995: Richard Martin, Matthew Grumbach
  - 2004-2006: Francois Gygi, Jean-Luc Fattebert
  - 90s-present: Weitao Yang
- **Major problem (Goedecker, review 1999):** the progress has been hindered by the inherently difficult convergence of the optimization of localized orbitals.

Convergence problem



- Even for the simple case of water molecules, the direct optimization of ALMOs is extremely slow, essentially non-convergent.

The origin of the problem



$|AO_3\rangle$

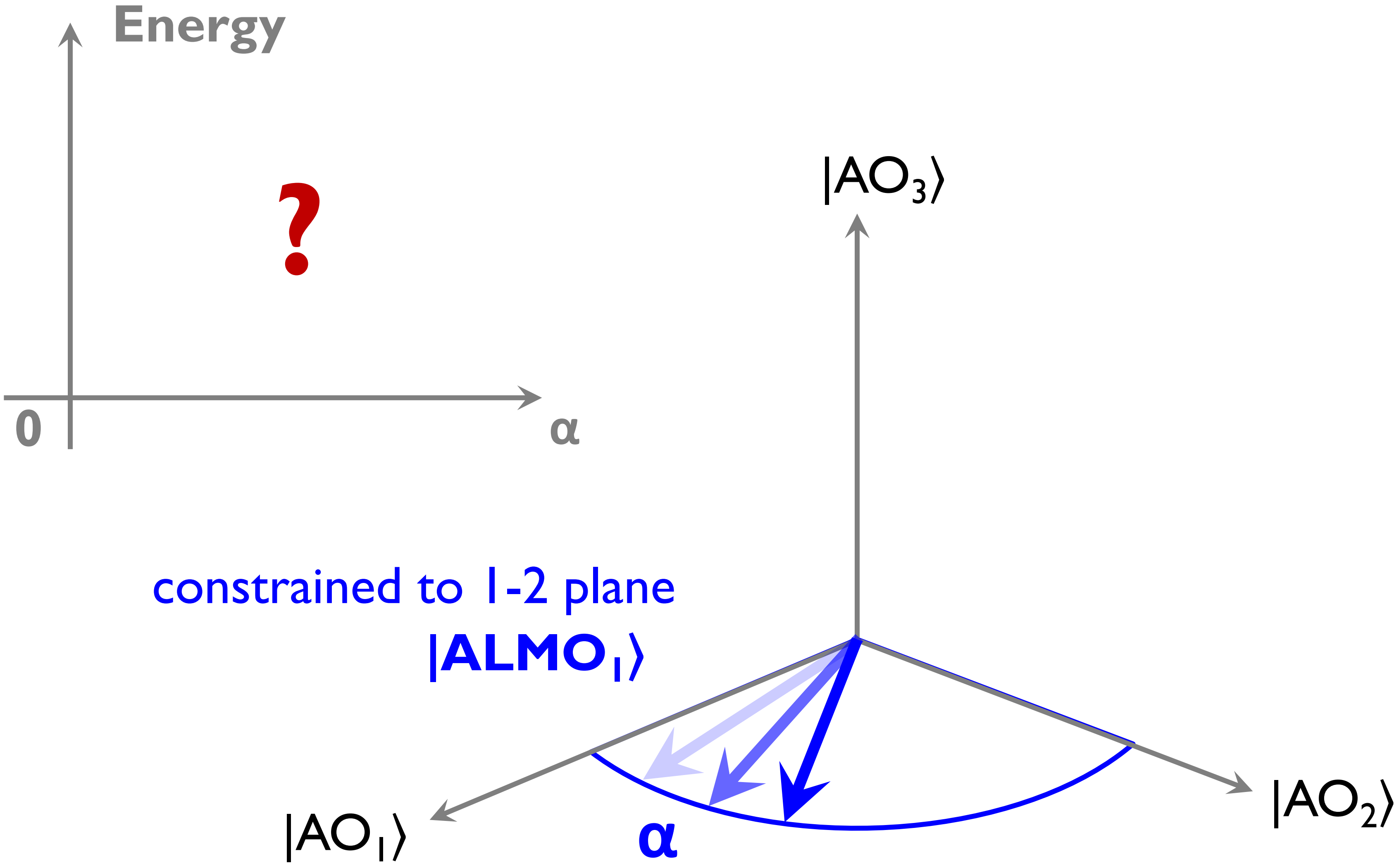
constrained to 1-2 plane

$|ALMO_1\rangle$

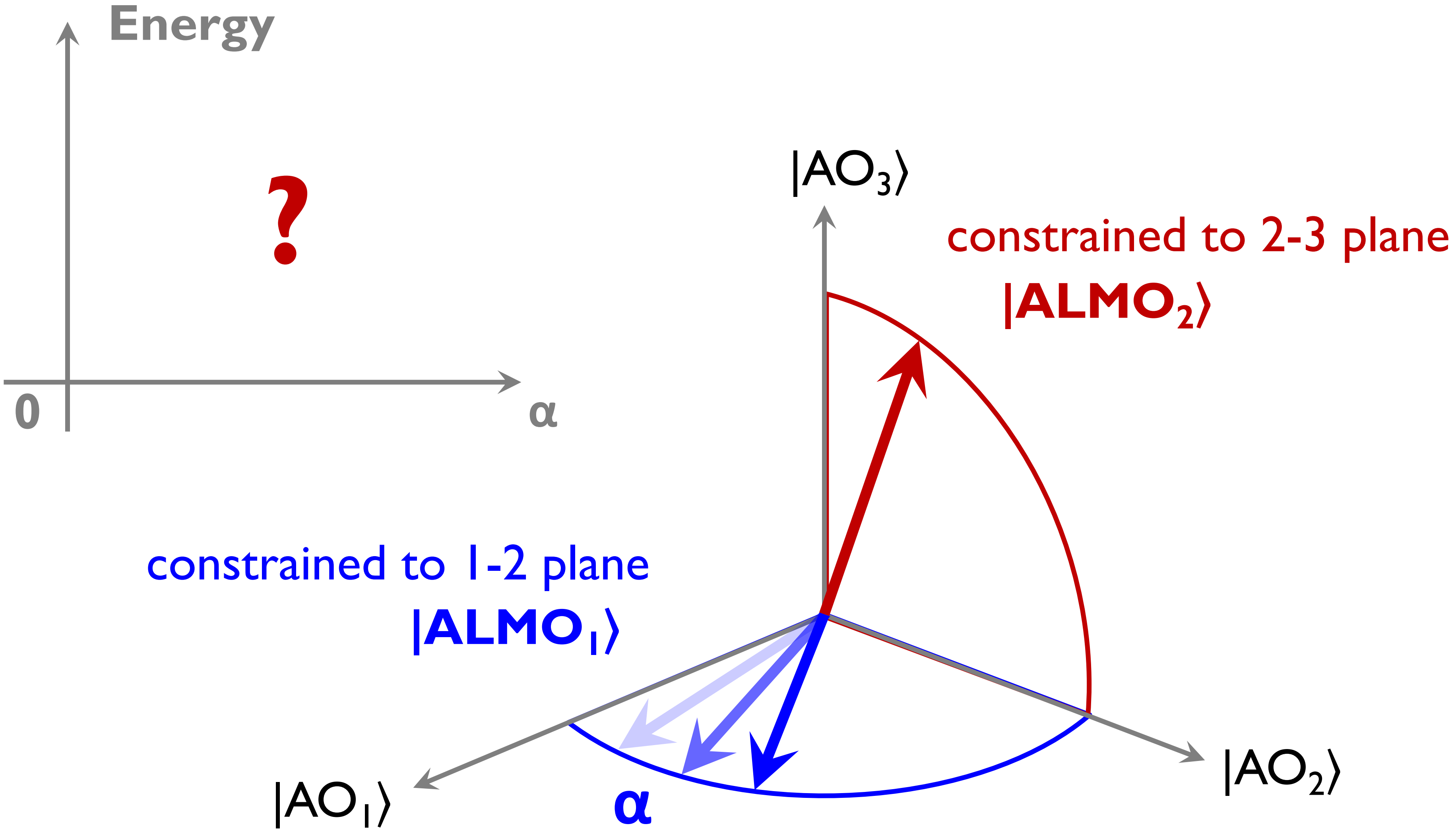
$|AO_1\rangle$

$|AO_2\rangle$

The origin of the problem



The origin of the problem



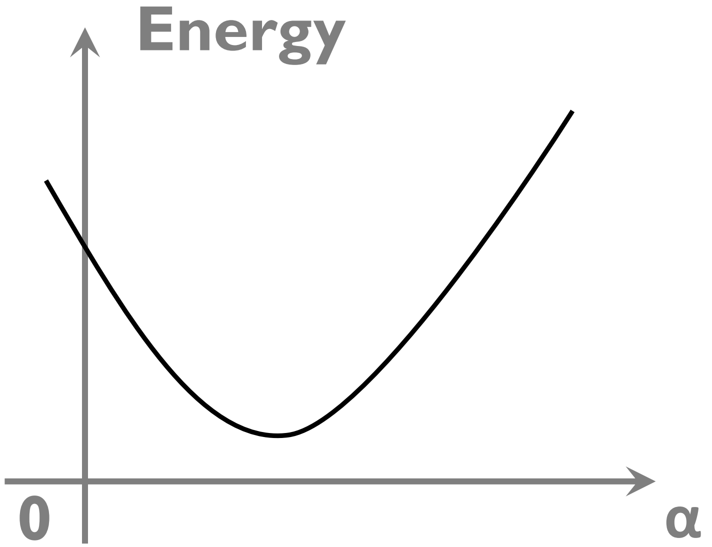
constrained to 2-3 plane

$|ALMO_2\rangle$

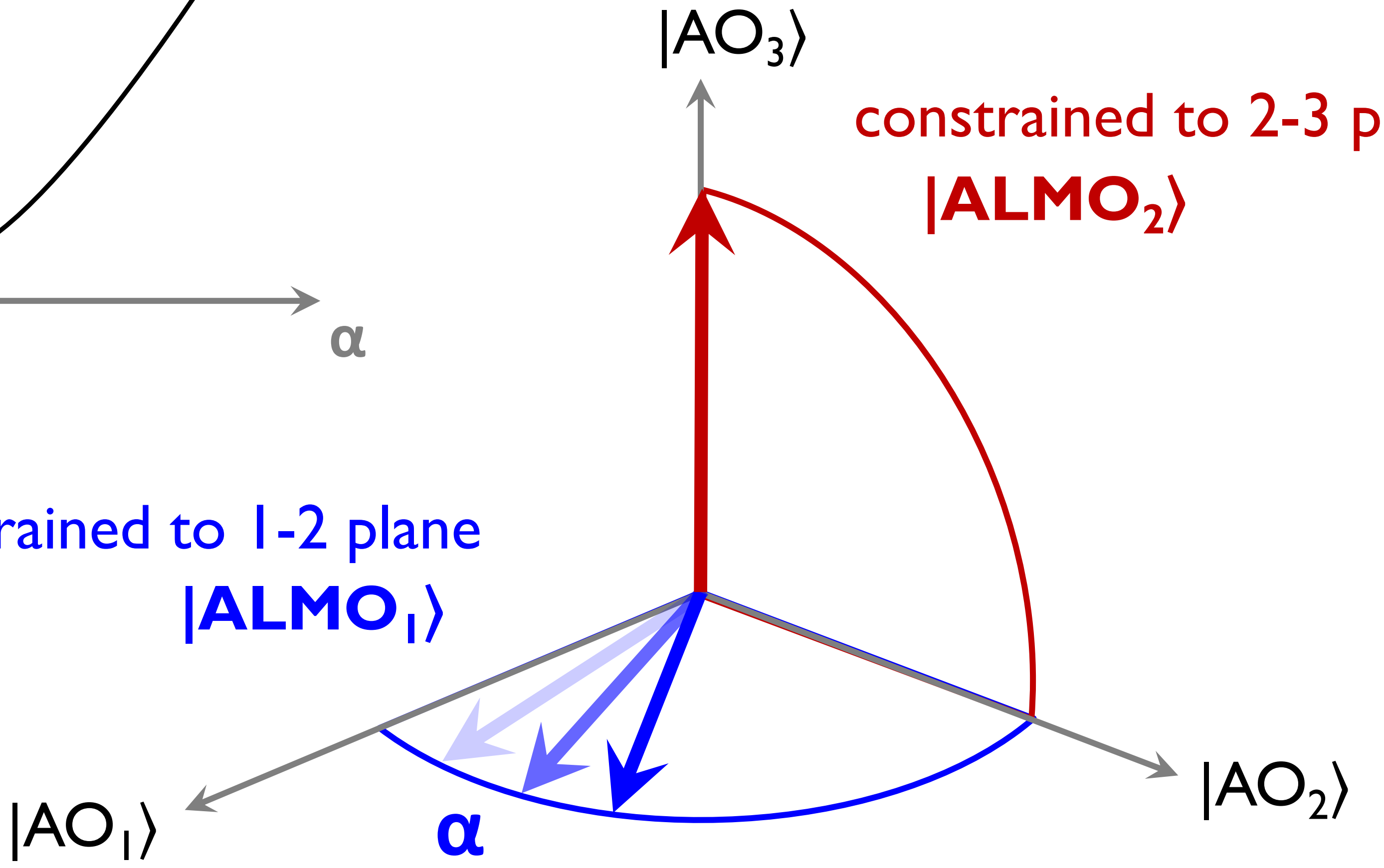
constrained to 1-2 plane

$|ALMO_1\rangle$

The origin of the problem



For $|\mathrm{ALMO}_1\rangle$ this is occupied-virtual mixing



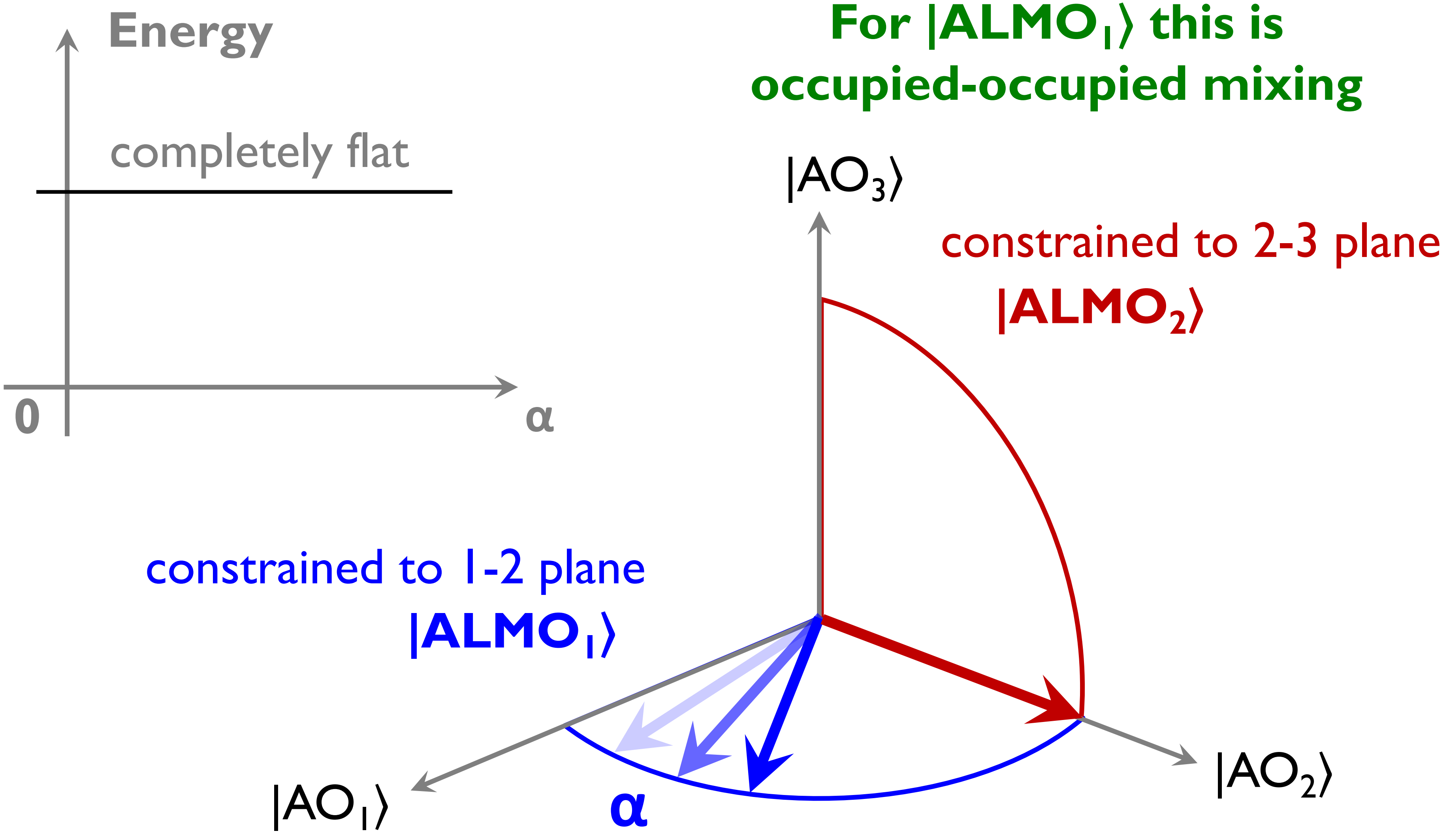
constrained to 2-3 plane

$|\mathrm{ALMO}_2\rangle$

constrained to 1-2 plane

$|\mathrm{ALMO}_1\rangle$

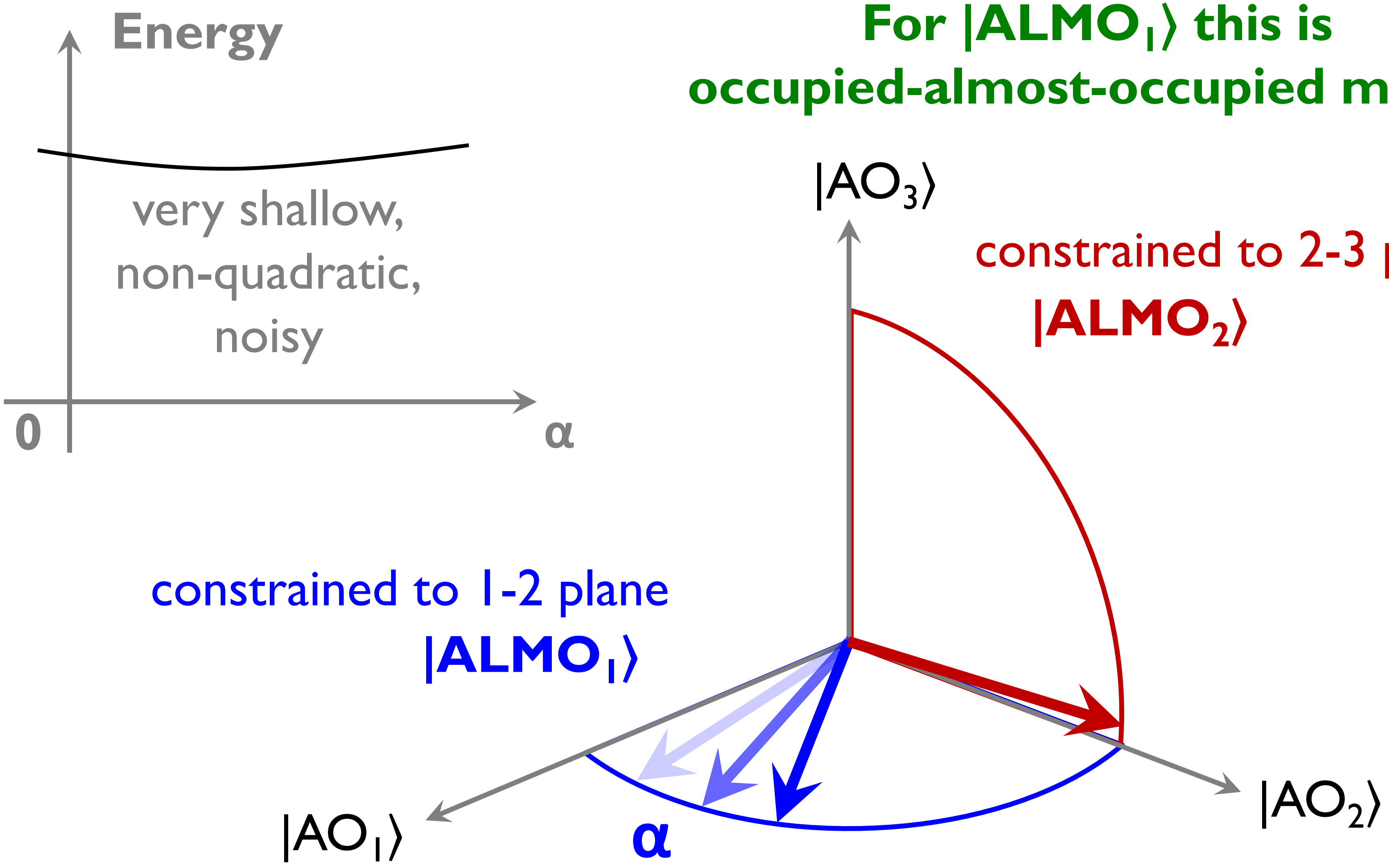
The root of the problem



For |ALMO$_1$⟩ this is occupied-occupied mixing

The root of the problem

For |ALMO$_1$⟩ this is
occupied-almost-occupied mixing

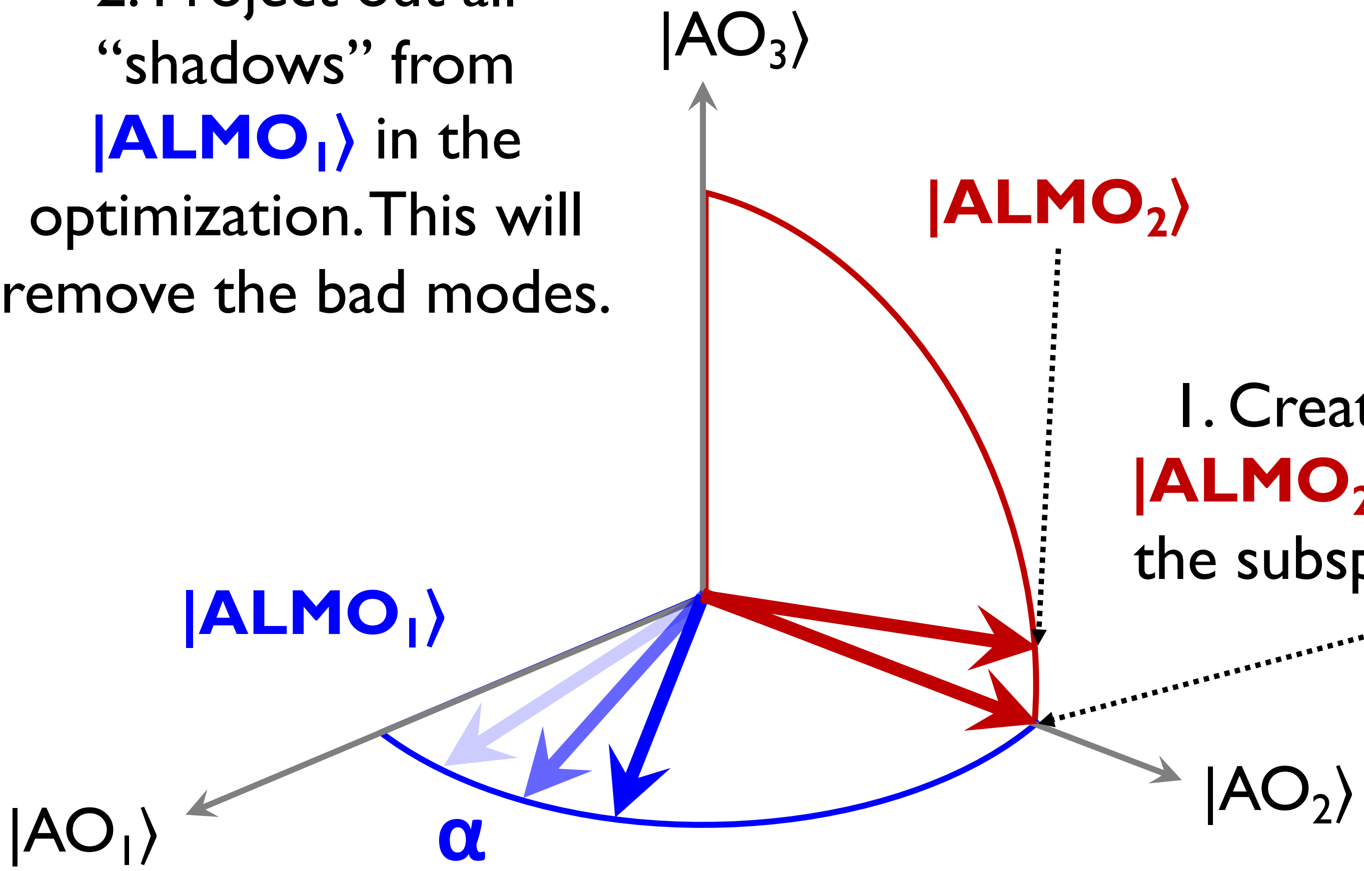


very shallow,
non-quadratic,
noisy

constrained to 2-3 plane
|ALMO$_2$⟩

constrained to 1-2 plane
|ALMO$_1$⟩

Solution: basic idea

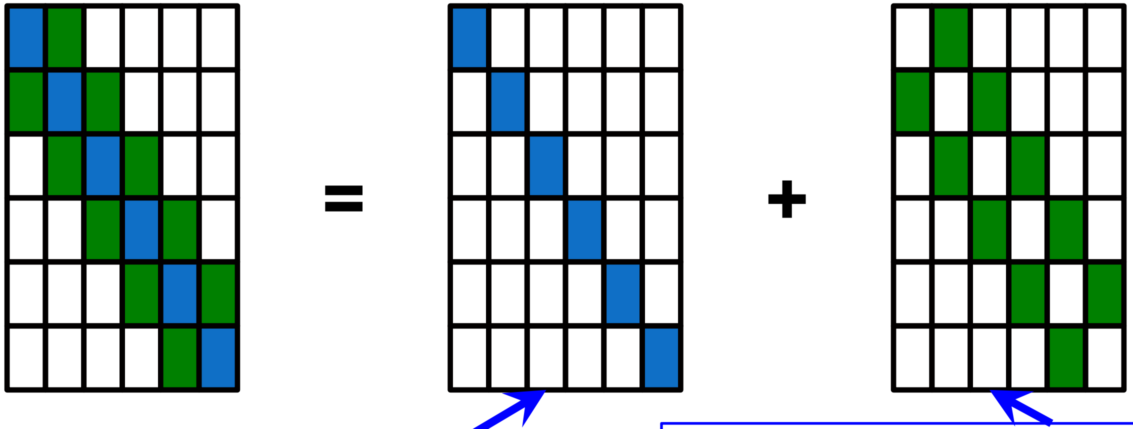


2. Project out all "shadows" from **$|ALMO_1\rangle$** in the optimization. This will remove the bad modes.

1. Create a "shadow" of **$|ALMO_2\rangle$** fully localized in the subspace of **$|ALMO_1\rangle$**

2013 solution

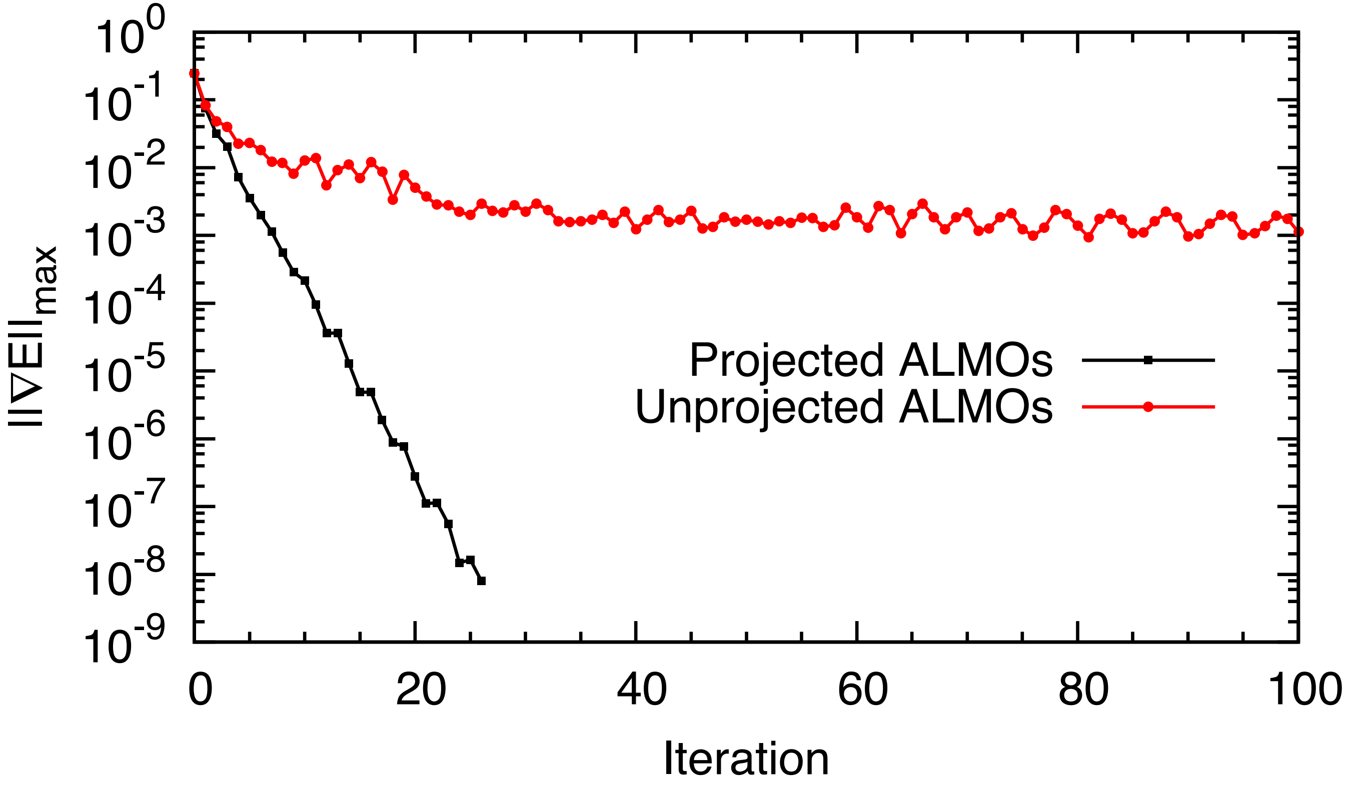
- Our 2013 solution: use block-diagonal ALMOs as "shadows".
- Construct a **new two-term trial form** for ALMOs and perform optimization in two steps:



Step 1:
Optimize variationally

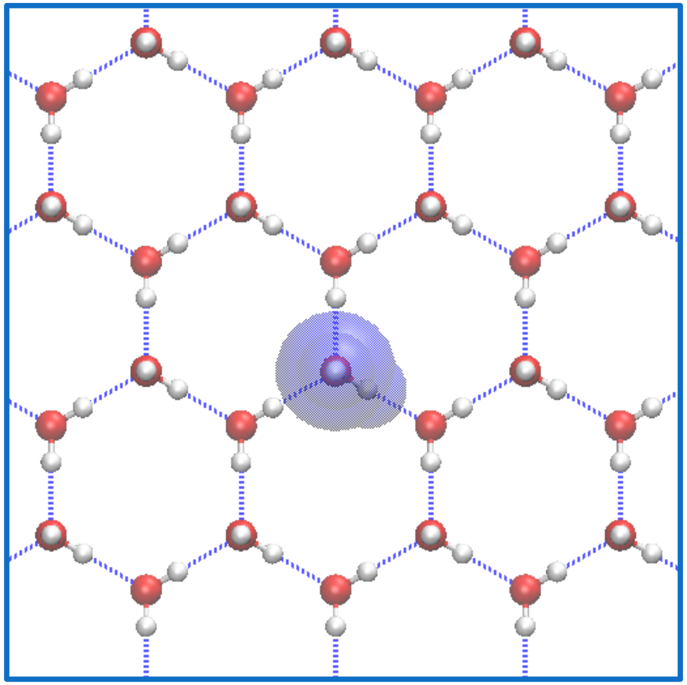
Step 2:
Use the 1st term to remove shallow modes!
Optimize delocalization amplitudes variationally

Convergence

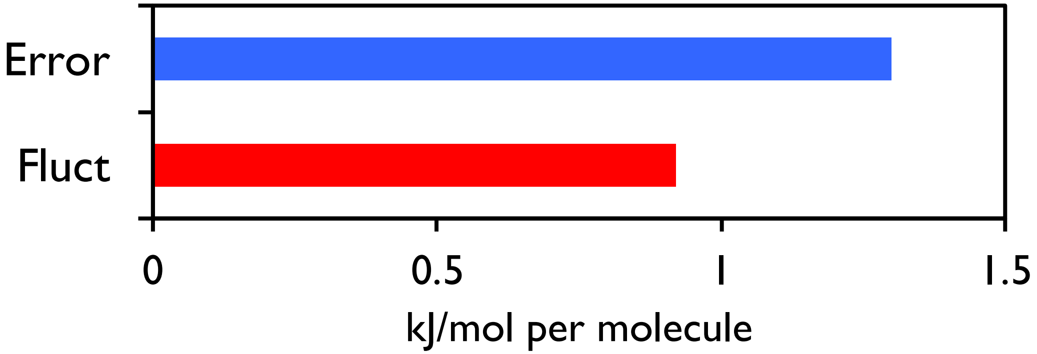


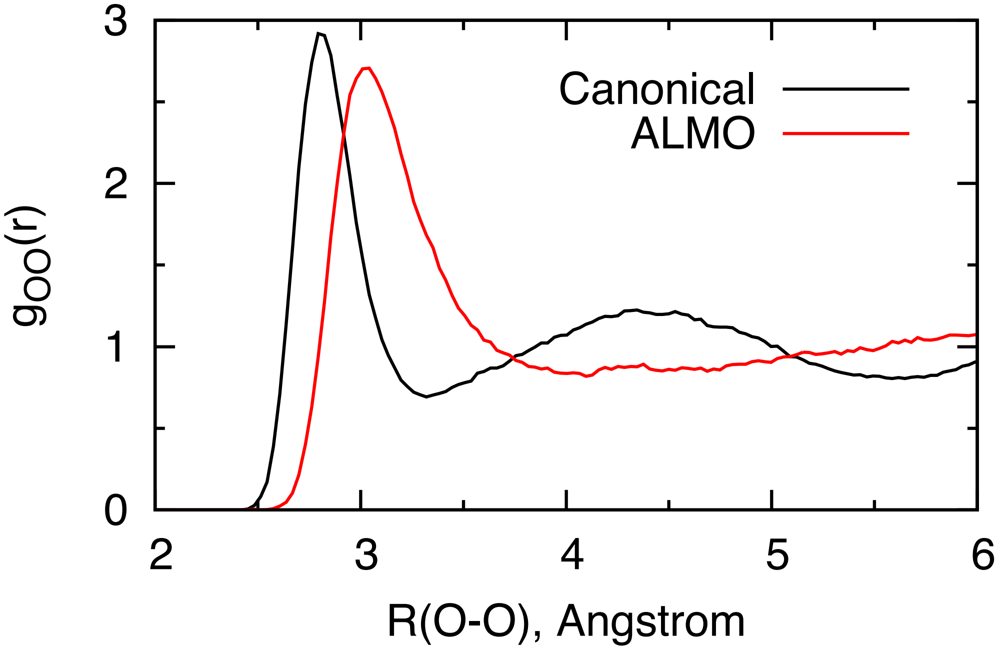
- For molecular systems, the two-stage variational procedure exhibits fast and stable convergence and represents a way to practical applications of the orbital-based linear scaling DFT.

Accuracy: liquid water

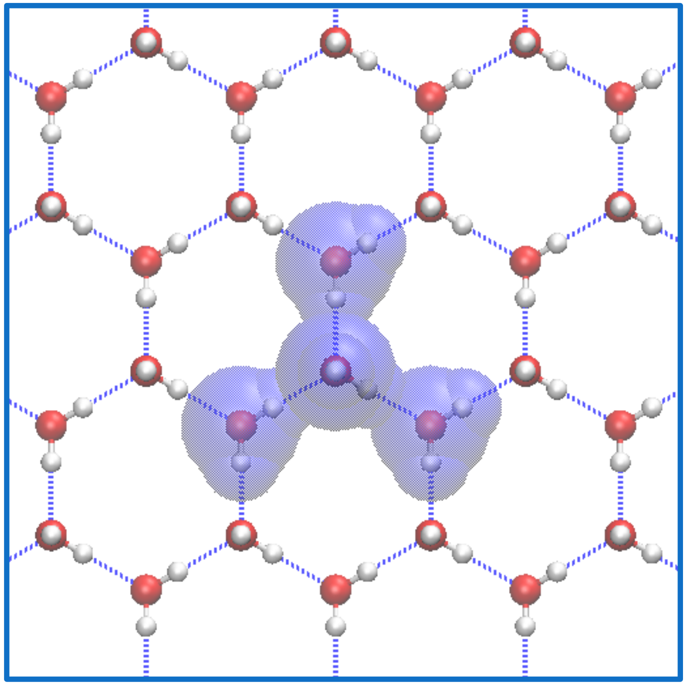


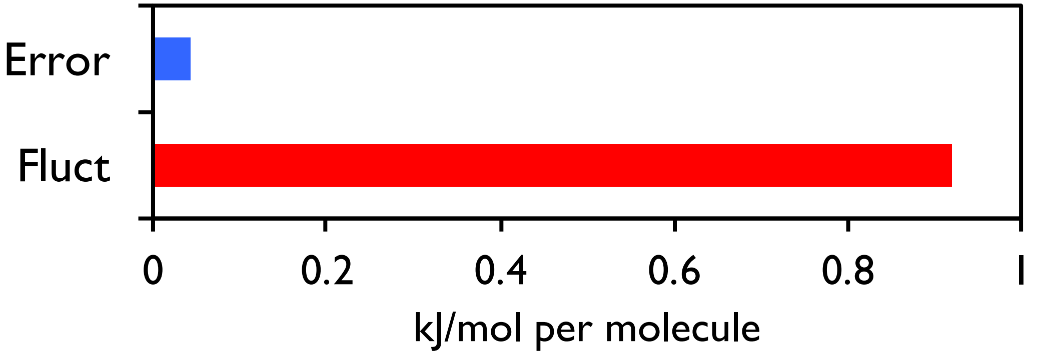
$R_{cutoff} = 0$,
Electrons are restricted to their molecules



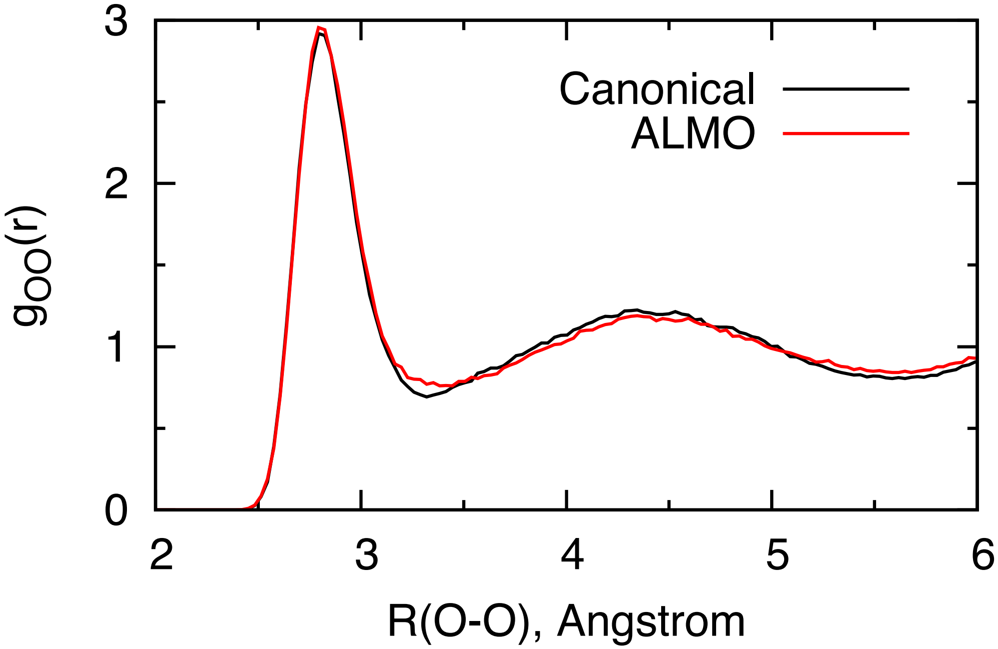


Accuracy: liquid water

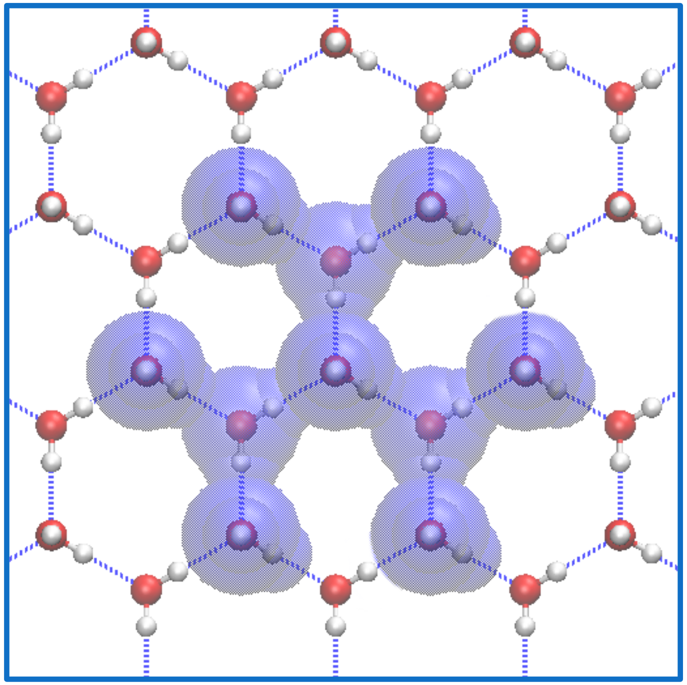


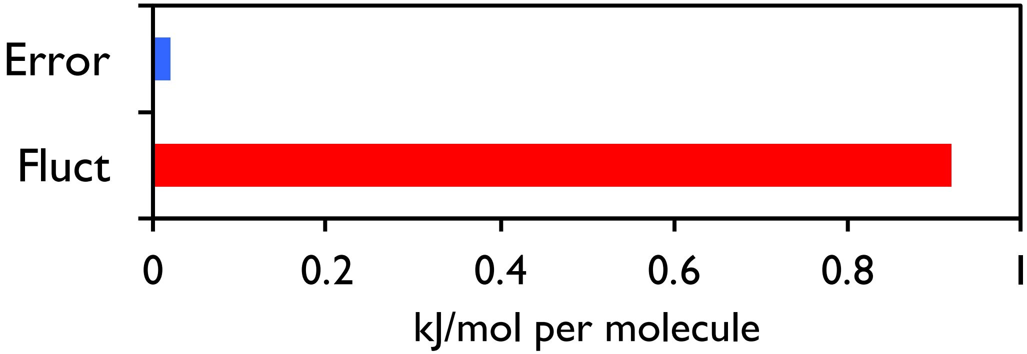


R_{cutoff} = 1.2 vdW
⟨Neighb.⟩ = 5.5 mols
Electrons are restricted
to the first coord. shell

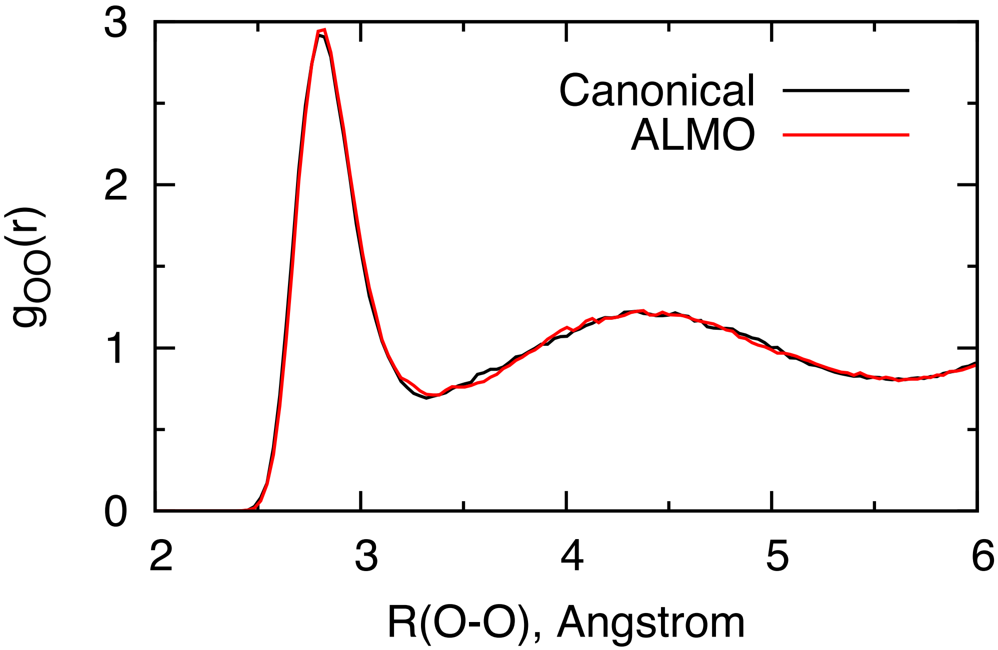


Accuracy: liquid water

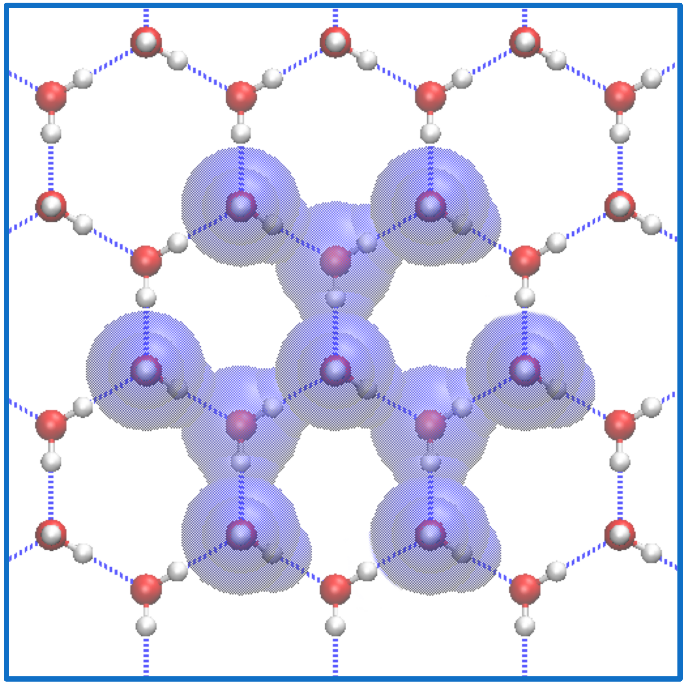


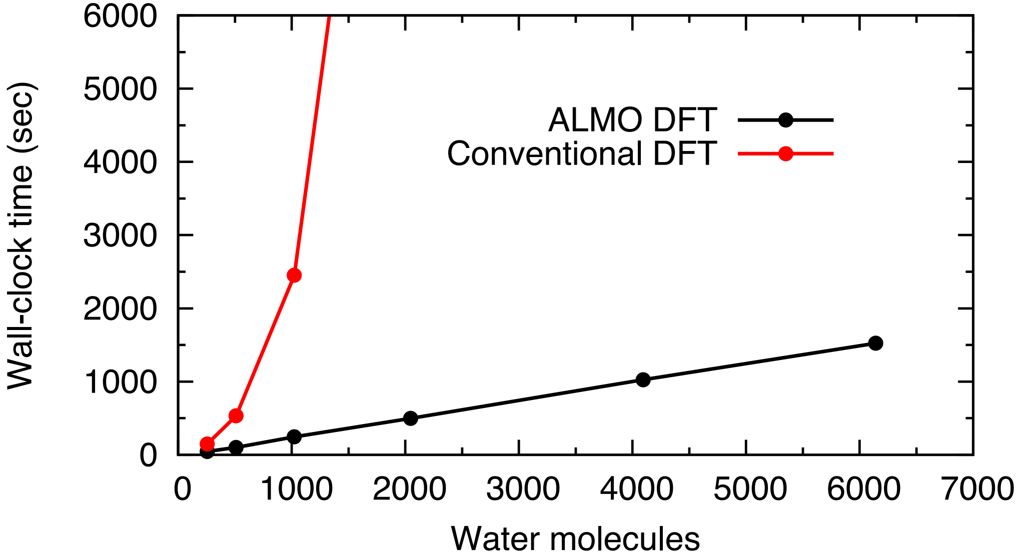


R_{cutoff} = 1.6 vdW
⟨Neighb.⟩ = 13.2 mols
Electrons are restricted
to two coord. shell



Performance: liquid water



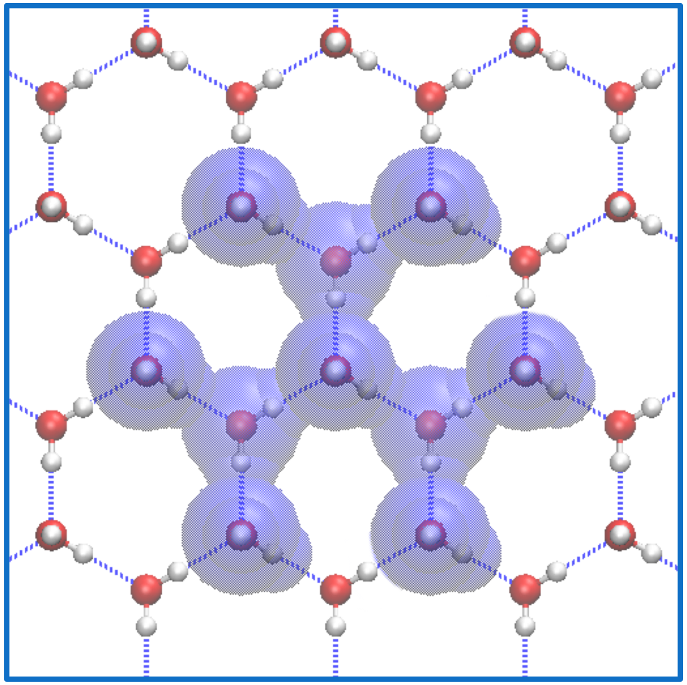


R_{cutoff} = 1.6 vdW

⟨Neighb.⟩ = 13 mols

Electrons are restricted to two coord. shell

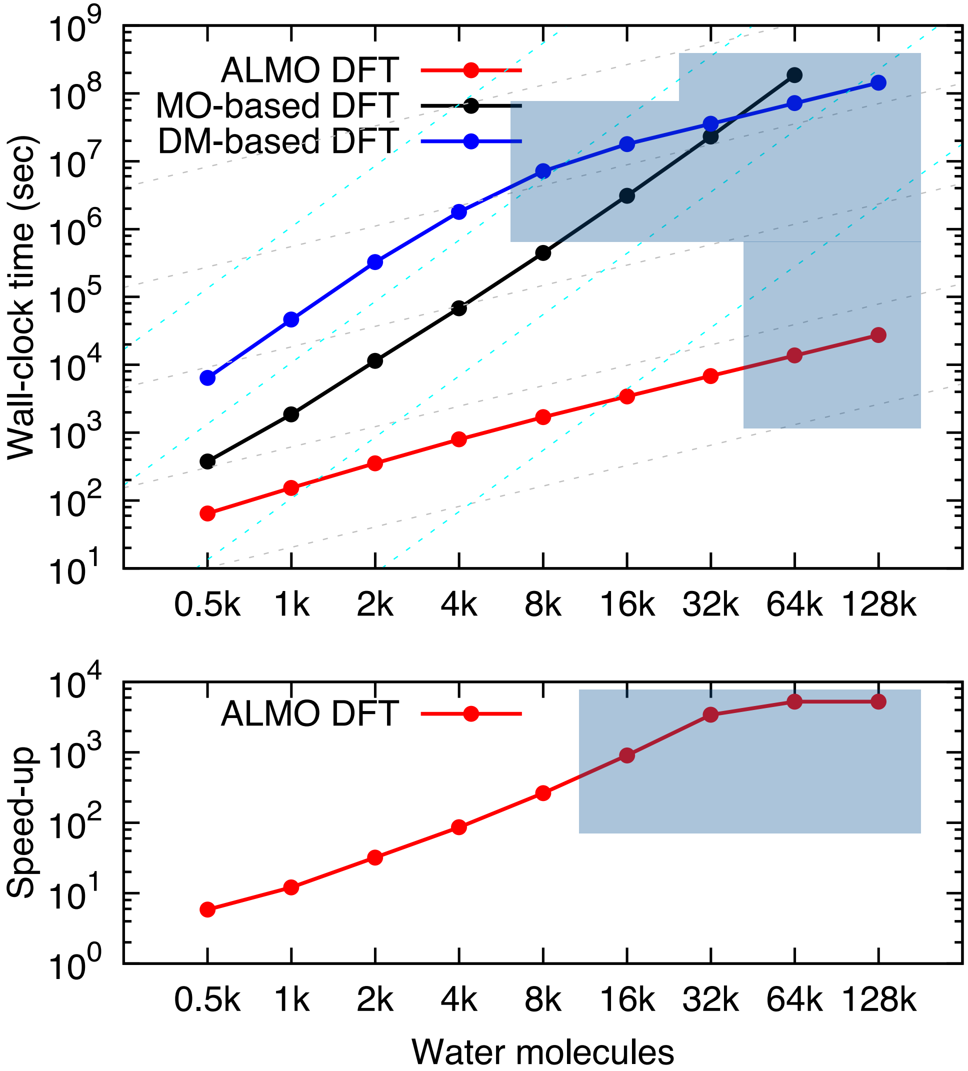
Performance: liquid water



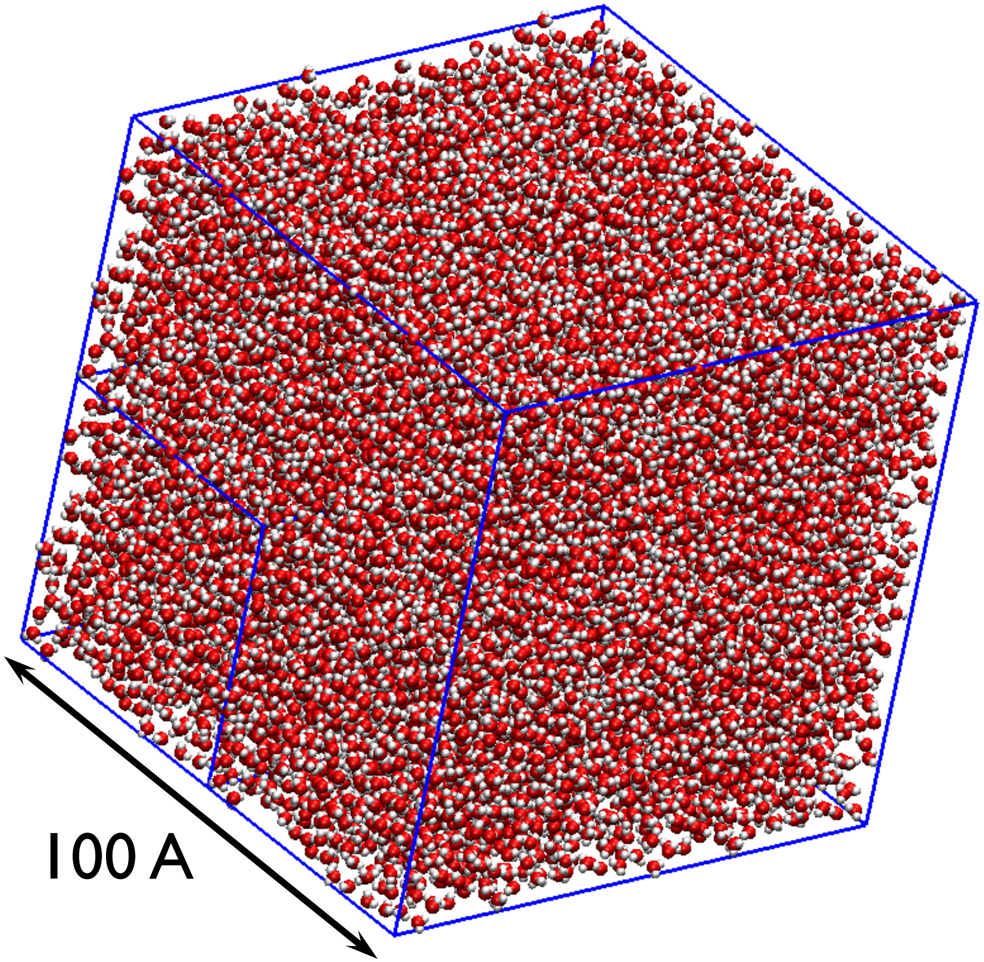
R_{cutoff} = 1.6 vdW

⟨Neighb.⟩ = 13 mols

Electrons are restricted to two coord. shell



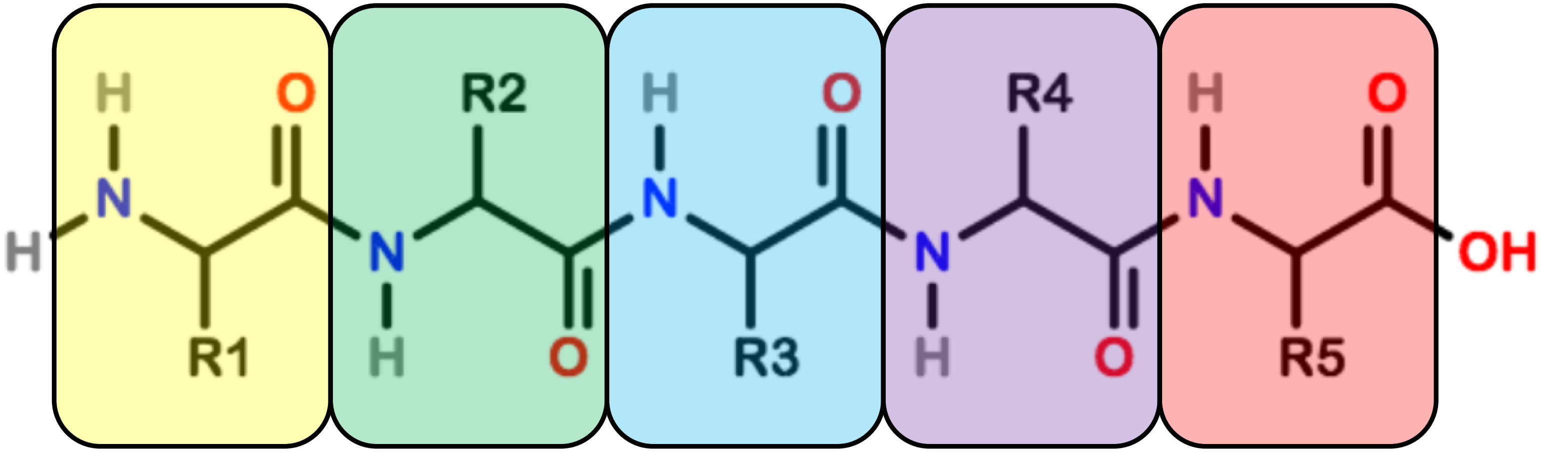
Example of a static system



- 32k H_2O molecules
- BLYP/TZV2P
- 10^4 snapshots
- Not a toy problem: long-range behavior of the electron density is the key to interpreting X-ray scattering data and resolving an "iceberg" model controversy

Peptide domains in proteins

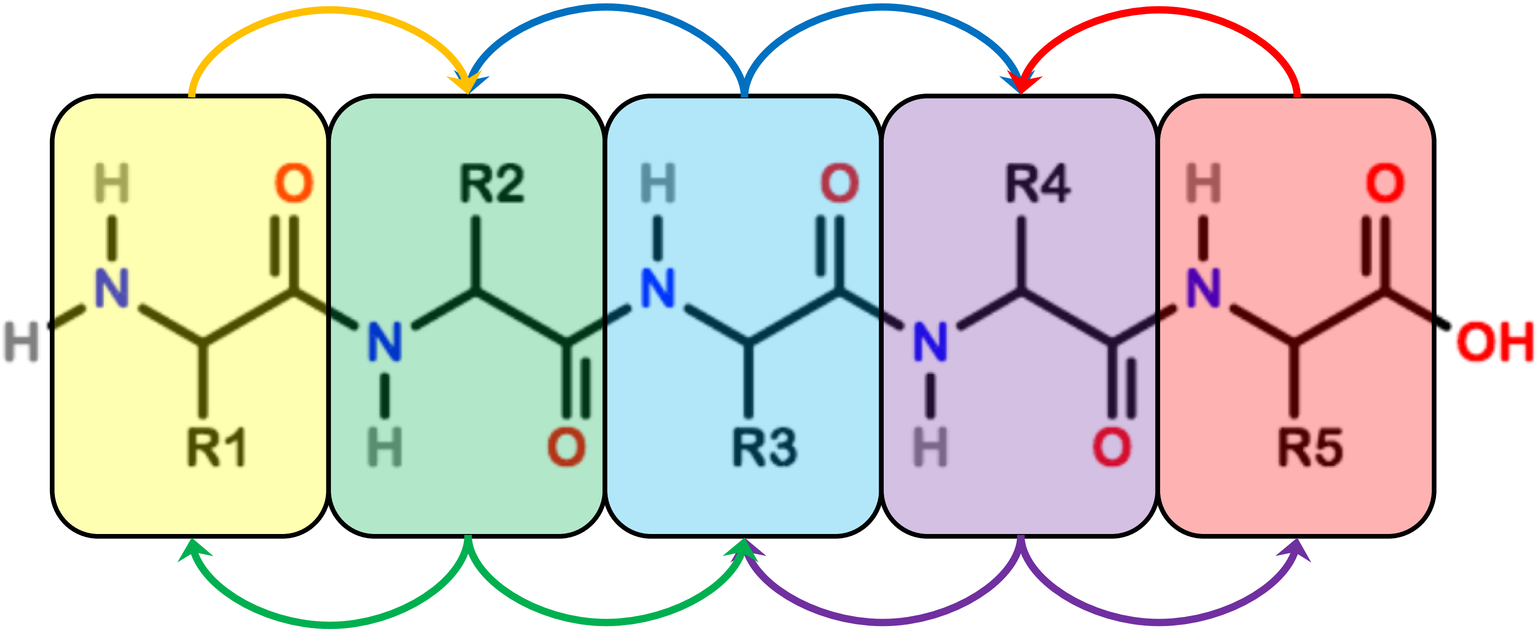
- Fragment borders break strong covalent bonds
- Electrons delocalize only over spatially close centers



Localization centers

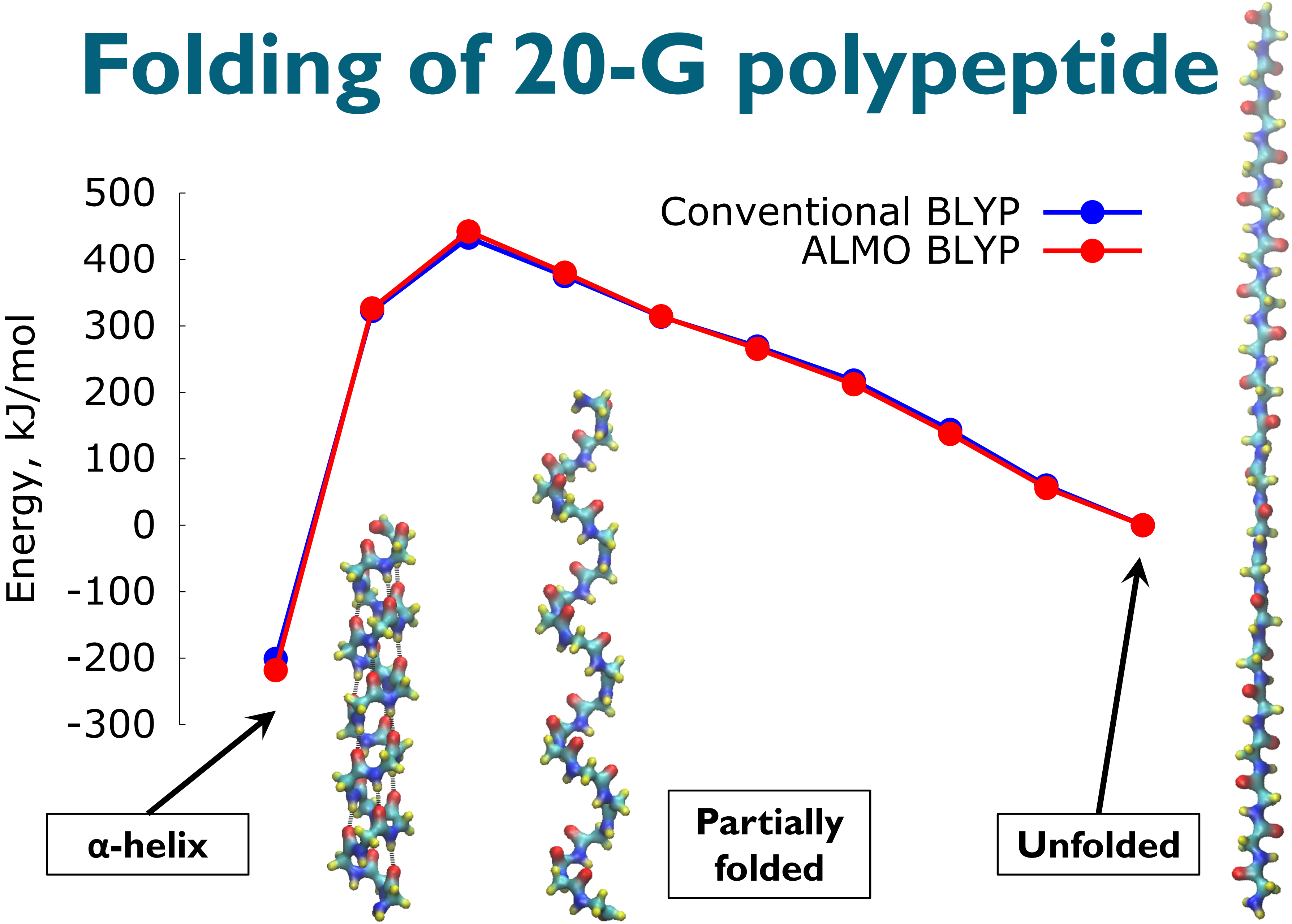
Peptide domains in proteins

- Domain borders break strong covalent bonds
- Electrons delocalize only over spatially close domains



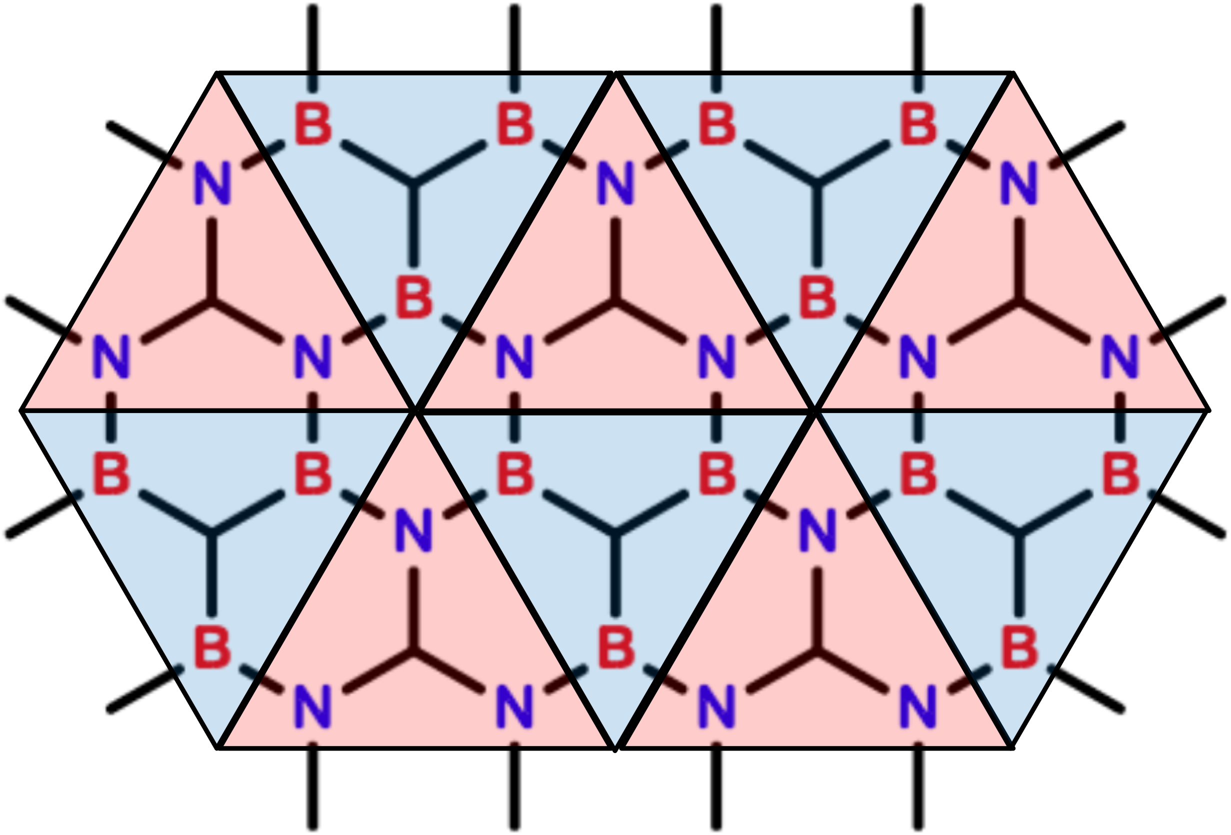
Error in absolute energies is less than 1kJ/mol per fragment!

Folding of 20-G polypeptide



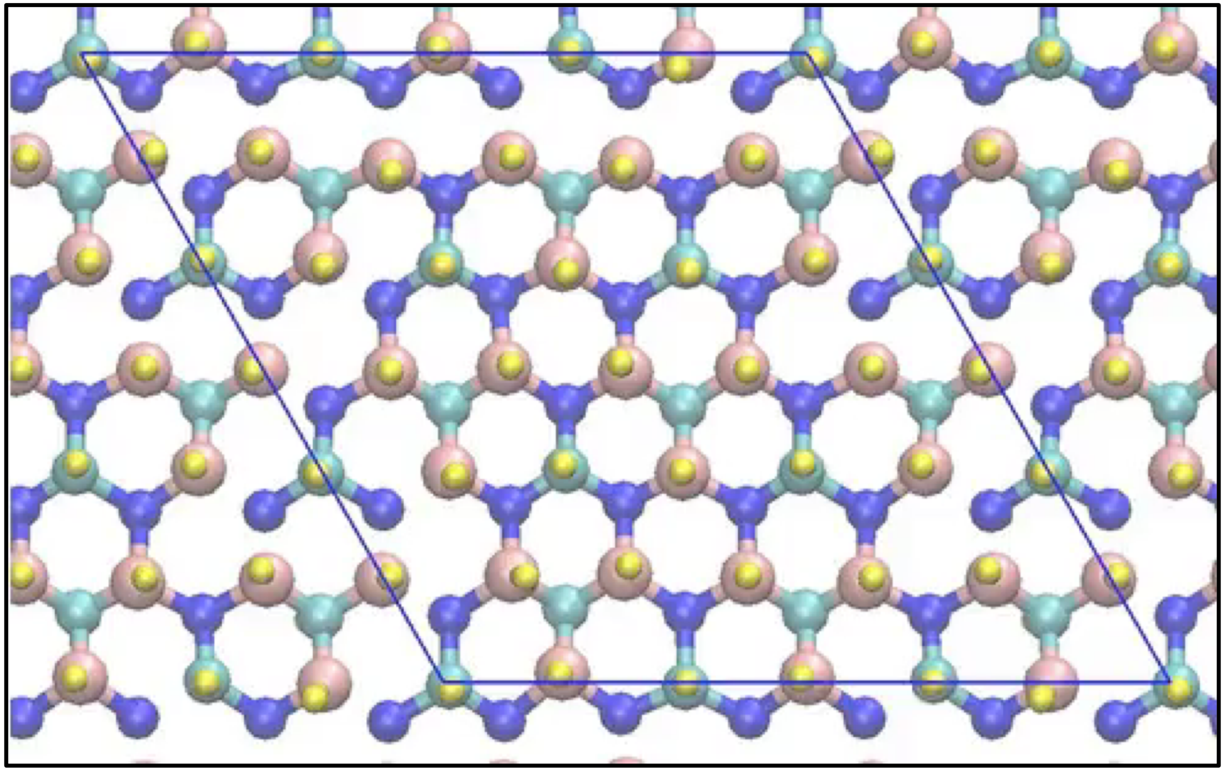
Layered $C_2B_3N_3H_6$

- Isoelectronic to graphane (hydrogen atoms not shown)



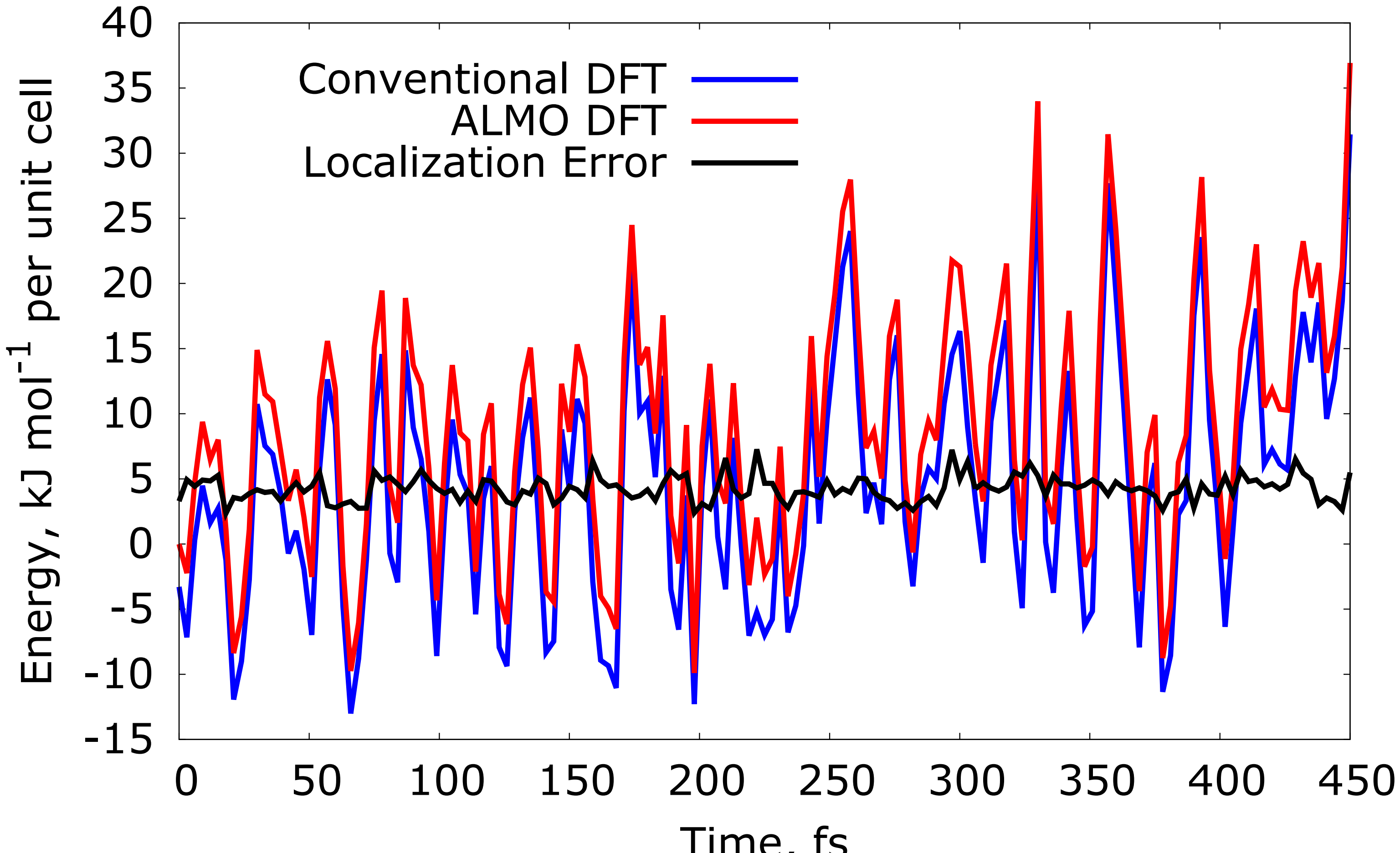
Configuration sampling

- Conventional (non-ALMO) AIMD at 1000K generates a set of configurations with significantly distorted bonds.

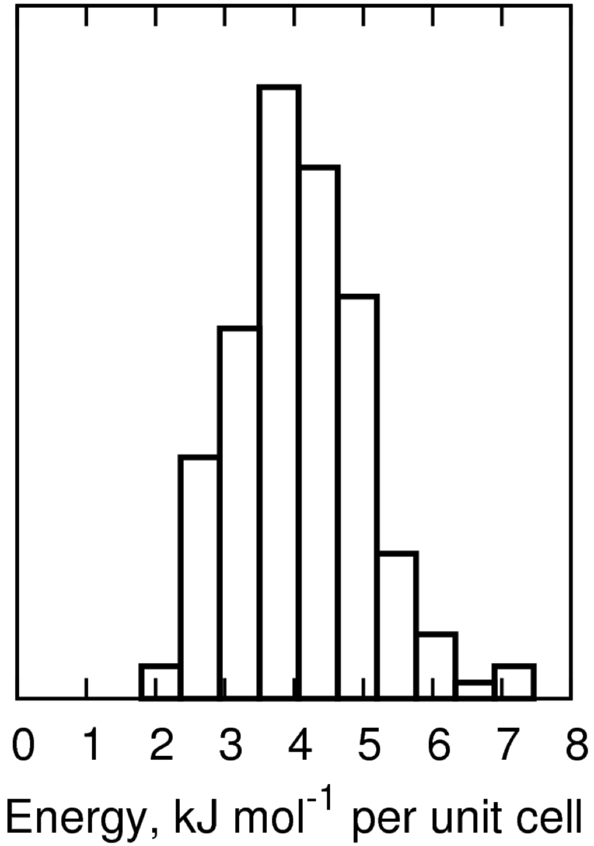


$C_2B_3N_3H_6$: error analysis

ALMO calculations at the PBE/DZVP level



$C_2B_3N_3H_6$: error analysis



- The constant shift is 4 kJ/mol
  - **Small** compared to the total binding energy of ~220 kJ/mol
- The RMS error is 0.9 kJ/mol
  - **Small** compared to 9.1 kJ/mol fluctuations in energy
- The error can be further decreased by increasing the localization radius

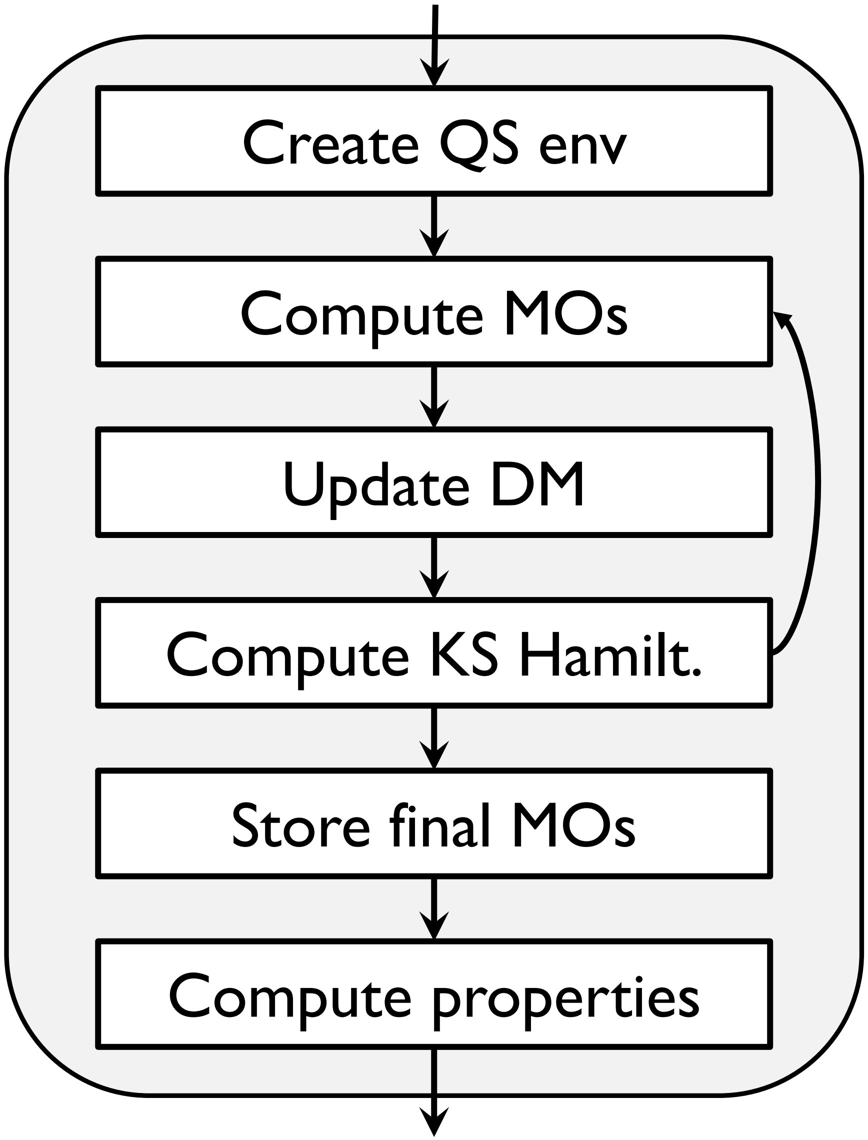
Implementation

- The algorithm is not embarrassingly parallel
- Two parallel libraries deal with sparse matrices (~32k compute cores tested): DBCSR and a home-made library for overlapping domains in domain_submatrix_*.F
- **Features:**
  - Early-offset linear-scaling behavior even for 3D systems
  - Works extremely well with large (diffuse) basis sets
  - Massively parallel code (30k cores tested, 1k routine)
- Freely available as a part of the CP2K package

www.cp2k.org

ALMO integration into CP2K

The SCF loop in CP2K
is replaced with the
ALMO SCF loop



Create QS env

Compute MOs

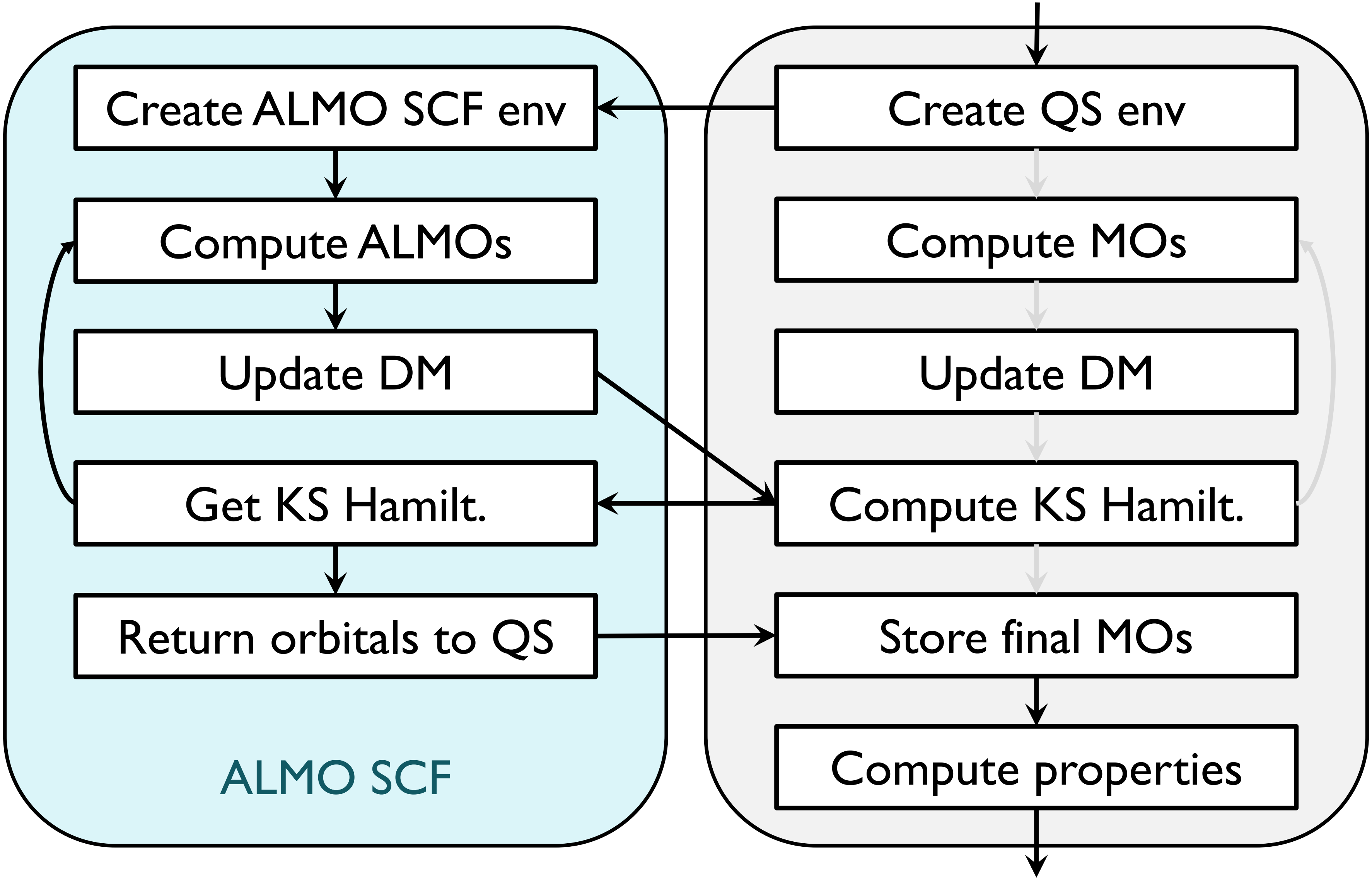
Update DM

Compute KS Hamilt.

Store final MOs

Compute properties

ALMO integration into CP2K



Create ALMO SCF env

Compute ALMOs

Update DM

Get KS Hamilt.

Return orbitals to QS

ALMO SCF

Create QS env

Compute MOs

Update DM

Compute KS Hamilt.

Store final MOs

Compute properties

Basic ALMO job in CP2K

1. Set up a regular DFT energy calculation.
2. Assign atoms, basis set functions, and electrons to localization centers.
3. Specify electron localization radius (radii) to create electron localization domains.
4. Exert control over the job using ALMO keywords. Most of them are in &ALMO_SCF, which replaces the traditional &SCF.

Step 2. Localization centers

A. Assign atoms to localization centers.
   - To take advantage of the existing functionality we chose to use a CP2K data structure called "molecule" to represent a center.
   - The first step in ALMO calculations is to specify "molecules".
   - Creating one-atom "molecules" allows to achieve atomic partitioning.

B. Assign Gaussian basis set orbitals to localization centers.
   - Trivial (GTOs have natural centers) and is done automatically.

C. Assign electrons to localization centers.
   - It is assumed that all electrons of a neutral atom belong to its center.
   - This default behavior can be changed by adding (removing) electrons to (from) atoms.

Step 2A. Assign atoms to centers

```
# Example of molecular partitioning: a
subset of atoms with the same molecular
label is analyzed for connectivity and split
into molecules

&FORCE_EVAL
  &SUBSYS

    &COORD
      O     1.528     1.706     3.914   WATER
      H     1.629     1.272     4.787   WATER
      H     2.042     2.530     4.077   WATER
      O     1.649     0.986     1.108   WATER
      H     1.585     1.181     2.064   WATER
      H     0.689     0.878     0.808   WATER
    &END COORD

  &END SUBSYS
&END FORCE_EVAL
```

- ALMO code relies on the existing and powerful CP2K infrastructure to define molecules:
  - 5th columns in the &COORD to create molecular labels explicitly
  - &GENERATE to connect atoms into molecules
  - Connectivity input file
  - Combination of the above

Step 2A. Assign atoms to centers

```
# Example of atomic partitioning: low
BONDPARM_FACTOR prevents atoms from being
combined into water molecules


&FORCE_EVAL
  &SUBSYS

    &TOPOLOGY
      &GENERATE
        BONDLENGTH_MAX 1.0
        BONDPARM COVALENT
        BONDPARM_FACTOR 0.3
      &END GENERATE
    &END TOPOLOGY

    &COORD
      O     1.528    1.706    3.914
      H     1.629    1.272    4.787
      H     2.042    2.530    4.077
      O     1.649    0.986    1.108
      H     1.585    1.181    2.064
      H     0.689    0.878    0.808
    &END COORD

  &END SUBSYS
&END FORCE_EVAL
```

- ALMO code relies on the existing and powerful CP2K infrastructure to define molecules:
  - 5th columns in the &COORD to create molecular labels explicitly
  - &GENERATE to connect atoms into molecules
  - Connectivity input file
  - Combination of the above

Step 2C. Assign ē to centers

```
# Remove one ē from 1s orbitals of H to
define H+ centers. Add two ēs to 2p orbitals
of O to get O2- centers

  &SUBSYS
    &KIND H
      …
      &BS
        &ALPHA
          NEL -1
          L    0
          N    1
        &END
      &END
    &END KIND

    &KIND O
      …
      &BS
        &ALPHA
          NEL +2
          L    1
          N    2
        &END
      &END
    &END KIND
  &END SUBSYS
```

- Closed-shell centers only!
- All ēs of a neutral atom are assumed to belong to its center.
- Ēs can be added (removed) to (from) using the &BS section.
- The ALMO guess is consistent with &BS.
- &ALPHA and &BETA copies in &BS should be the same for closed-shell calculations to avoid warnings.

Step 3. Define domains

```
# Currently a single cutoff threshold
XALMO_R_CUTOFF_FACTOR is used to define
neighbor lists for all centers. Units are
element-specific vdW radii.

&FORCE_EVAL
  &DFT
    &ALMO_SCF
      XALMO_R_CUTOFF_FACTOR      1.3
    &END ALMO_SCF
  &END DFT
&END FORCE_EVAL
```

- *Reminder*: electrons of a center are allowed to delocalize only over nearby centers called localization domain.
- Each domain is thus specified by creating a neighbor list for each center.
- Centers A and B are neighbors if there is a pair of atoms i_A and j_B within distance D

  $D = R_c \, (R_{vdW}(i_A) + R_{vdW}(j_B))$
- R_c = xalmo_r_cutoff_factor

Step 4. ALMO keywords

```
&DFT

  &QS
    ALMO_SCF T
  &END QS

  &ALMO_SCF
    EPS_FILTER                  1.0E-8
    ALMO_ALGORITHM              DIAG
    DELOCALIZE_METHOD           XALMO_SCF
    XALMO_R_CUTOFF_FACTOR       1.4

    &ALMO_OPTIMIZER_DIIS
      MAX_ITER                  50
      EPS_ERROR                 1.0E-6
    &END ALMO_OPTIMIZER_DIIS

    &XALMO_OPTIMIZER_PCG
      MAX_ITER_OUTER_LOOP       5
      MAX_ITER                  50
      EPS_ERROR                 1.0E-6
    &END XALMO_OPTIMIZER_PCG
  &END ALMO_SCF

&END DFT
```

- Set ALMO_SCF to TRUE to pass the control over SCF from &SCF to &ALMO_SCF
- EPS_FILTER controls how sparse ALMO matrices are
- 1st SCF stage is controlled by ALMO_ALGORITHM
- 2nd SCF stage is controlled by DELOCALIZE_METHOD
-

Step 4. ALMO keywords

```
&DFT

   &QS
     ALMO_SCF T
   &END QS

   &ALMO_SCF
     EPS_FILTER                   1.0E-8
     ALMO_ALGORITHM               DIAG
     DELOCALIZE_METHOD            XALMO_SCF
     XALMO_R_CUTOFF_FACTOR        1.4

     &ALMO_OPTIMIZER_DIIS
       MAX_ITER                   50
       EPS_ERROR                  1.0E-6
     &END ALMO_OPTIMIZER_DIIS

     &XALMO_OPTIMIZER_PCG
       MAX_ITER_OUTER_LOOP        5
       MAX_ITER                   50
       EPS_ERROR                  1.0E-6
     &END XALMO_OPTIMIZER_PCG
   &END ALMO_SCF

 &END DFT
```

- *1st SCF stage (optimization of the block-diagonal ALMOs):*
- ALMO_ALGORITHM can be set either to DIAG or PCG
- This determines whether &ALMO_OPTIMIZER_DIIS or &ALMO_OPTIMIZER_PCG is used
- Two main keywords in both optimizers are MAX_ITER and EPS_ERROR
- The final energy in the 1st stage is independent of what optimizer is employed

Step 4. ALMO keywords

```
&DFT

   &QS
     ALMO_SCF T
   &END QS

   &ALMO_SCF
     EPS_FILTER                 1.0E-8
     ALMO_ALGORITHM             DIAG
     DELOCALIZE_METHOD          XALMO_SCF
     XALMO_R_CUTOFF_FACTOR      1.4

     &ALMO_OPTIMIZER_DIIS
       MAX_ITER                 50
       EPS_ERROR                1.0E-6
     &END ALMO_OPTIMIZER_DIIS

     &XALMO_OPTIMIZER_PCG
       MAX_ITER_OUTER_LOOP      5
       MAX_ITER                 50
       EPS_ERROR                1.0E-6
     &END XALMO_OPTIMIZER_PCG
   &END ALMO_SCF

 &END DFT
```

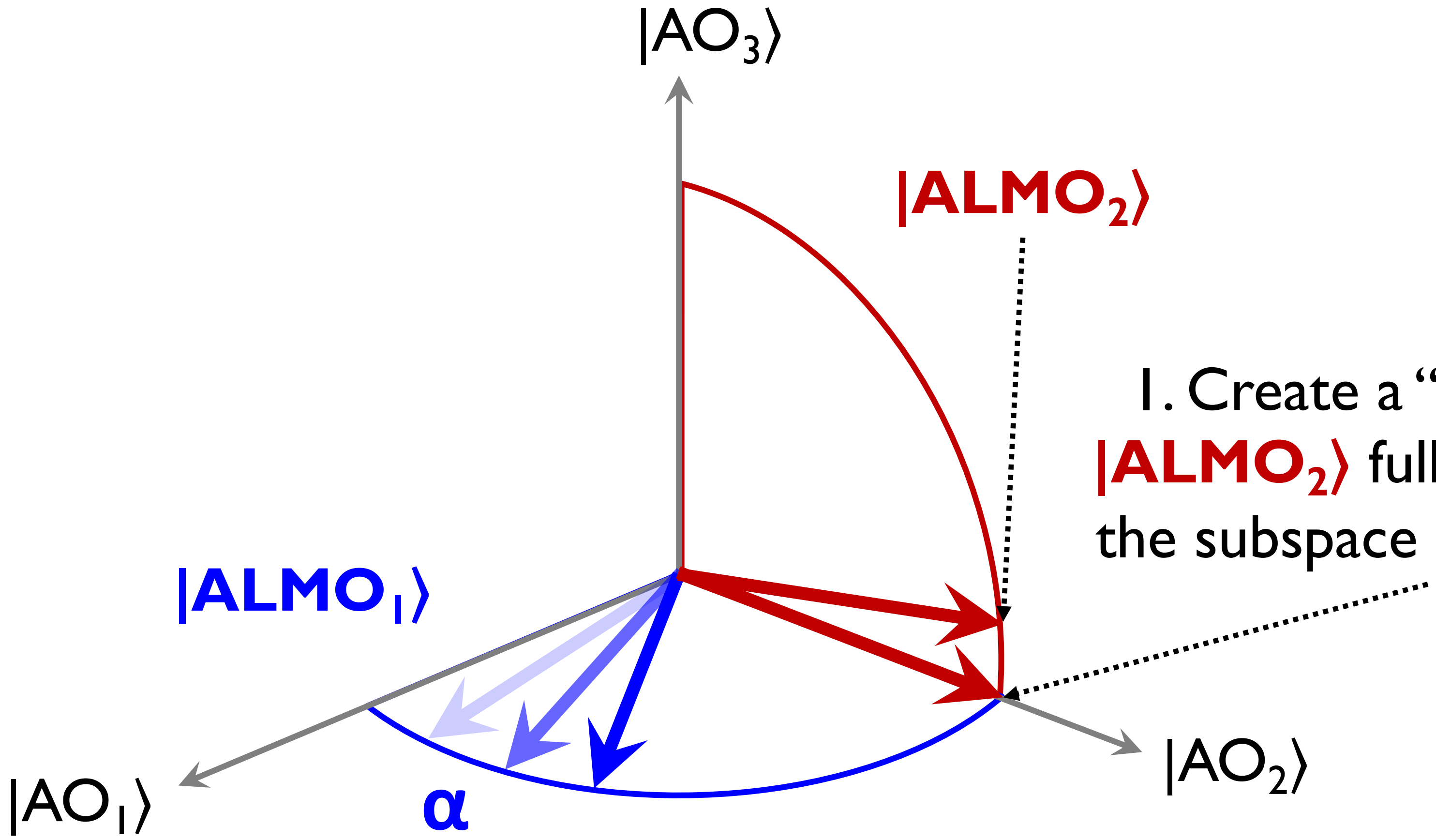
- *2nd SCF stage (optimization of eXtended ALMOs = XALMOs):*
- DELOCALIZE_METHOD determines the level of approximation and the accuracy of the final result
- Unless XALMO_1DIAG, &XALMO_OPTIMIZER_PCG controls the optimization
- If convergence is slow use the outer loop to restart the PCG optimizer: conjugation is reset, preconditioner is recalculated

Limitations of the 2013 solution

- Block-diagonal ALMOs are good “shadows” as long as they are close to the final optimal orbitals.
- This is true only if there is no substantial electron delocalization (i.e. covalent bonds) between LCs.
- That is why the 2013 two-stage method works well only for molecular or ionic systems.

- **Works well**: water, NaCl, ionic liquids, TiO_2, peptide bonds
- **Not practical:** CdSe, BN, cubic Si, water with atomic partitioning (e.g. proton transfer)

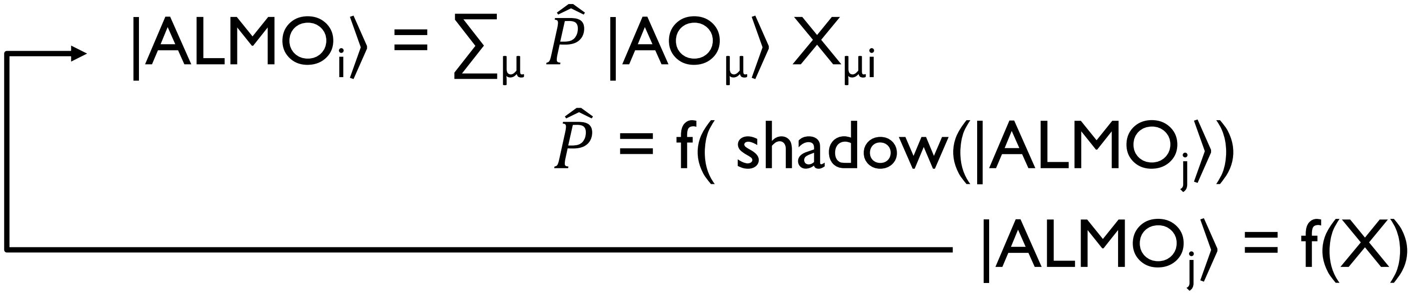
Solution: basic idea



1. Create a "shadow" of **|ALMO₂⟩** fully localized in the subspace of **|ALMO₁⟩**

Other solutions?

- A naïve attempt: update "shadows" to follow ALMOs.



$$|\mathrm{ALMO}_i\rangle = \sum_\mu \hat{P}\,|\mathrm{AO}_\mu\rangle\, X_{\mu i}$$

$$\hat{P} = f(\,\mathrm{shadow}(|\mathrm{ALMO}_j\rangle))$$

$$|\mathrm{ALMO}_j\rangle = f(X)$$

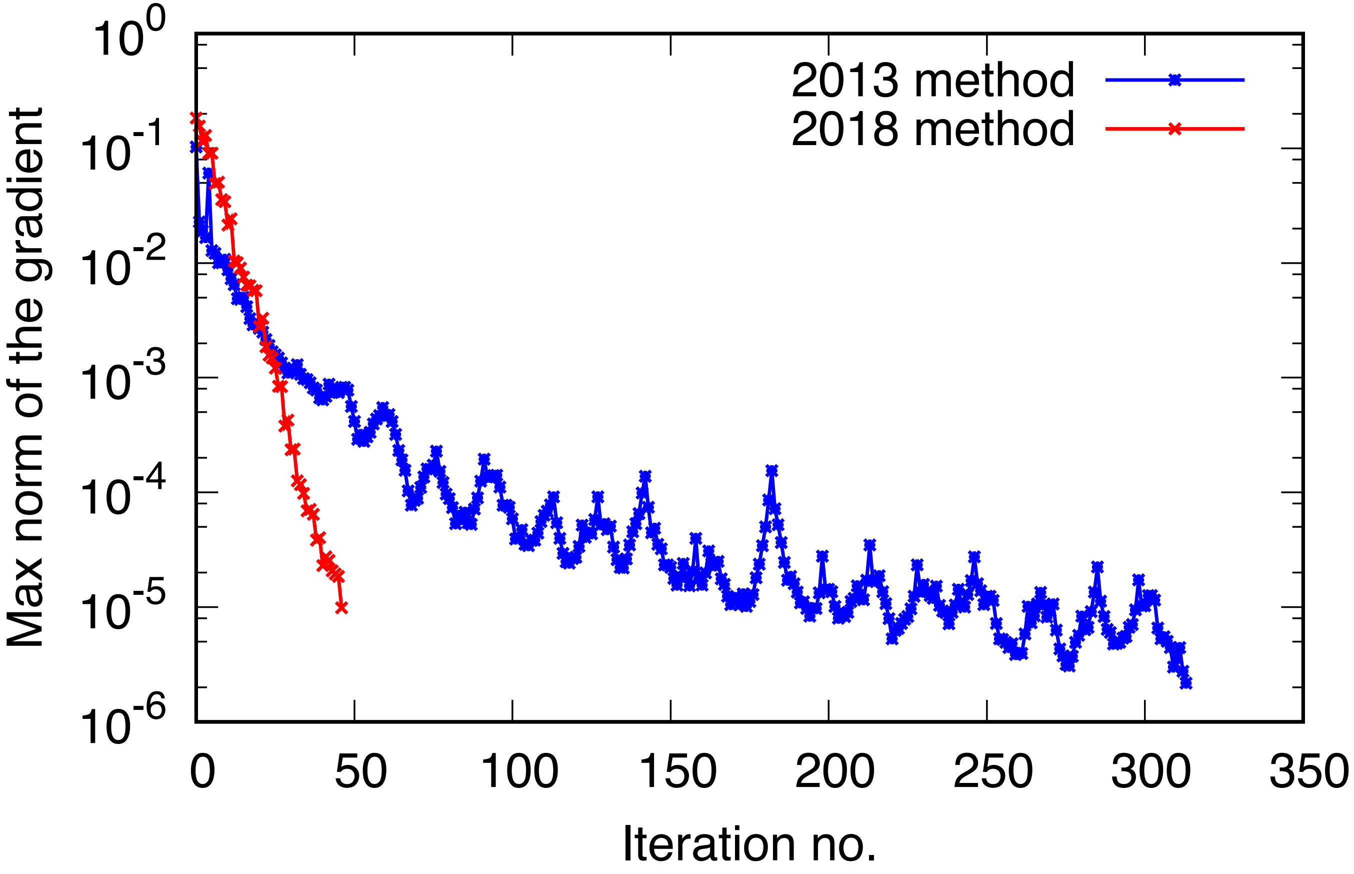
- Trial ALMOs depend on the coefficients **X** "telescopically".
- This approach is way too complicated to be efficient.
- For example, even a simple energy evaluation for fixed **X** becomes an iterative procedure.

2018 solution

- Trial ALMOs are trivial: $|\mathrm{ALMO}_i\rangle = \sum_\mu |\mathrm{AO}_\mu\rangle X_{\mu i}$
- Direct minimization of energy is straightforward and is performed using preconditioned conjugate gradient algorithm*.
- Bad optimization modes are identified "directly" as the eigenvectors of the preconditioner (i.e. approximate Hessian) that have tiny eigenvalues.
- These eigenvectors are projected from the gradient and, as a result, from all search directions.

* Tensorial properties of matrices must be taken into account.

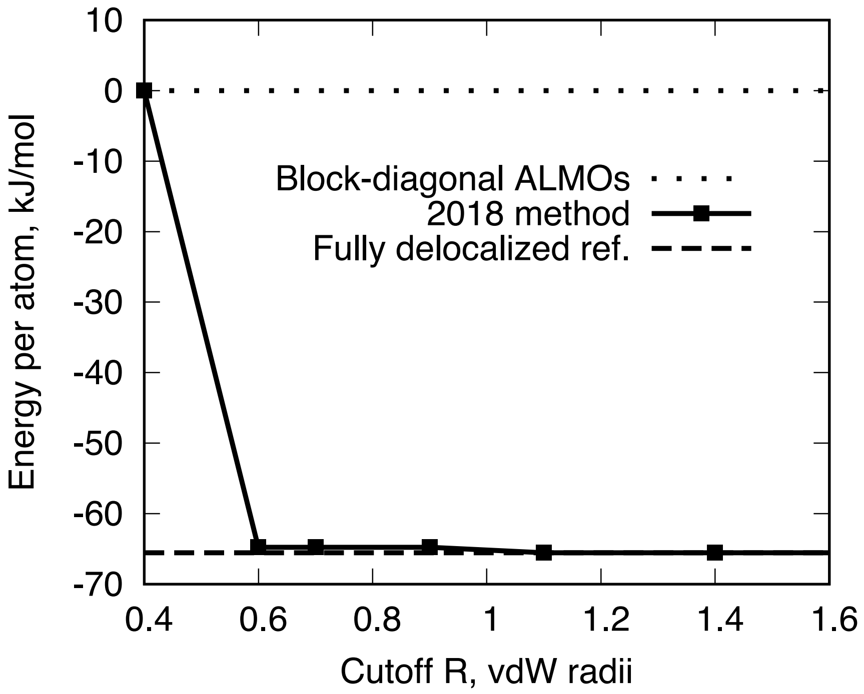
Convergence



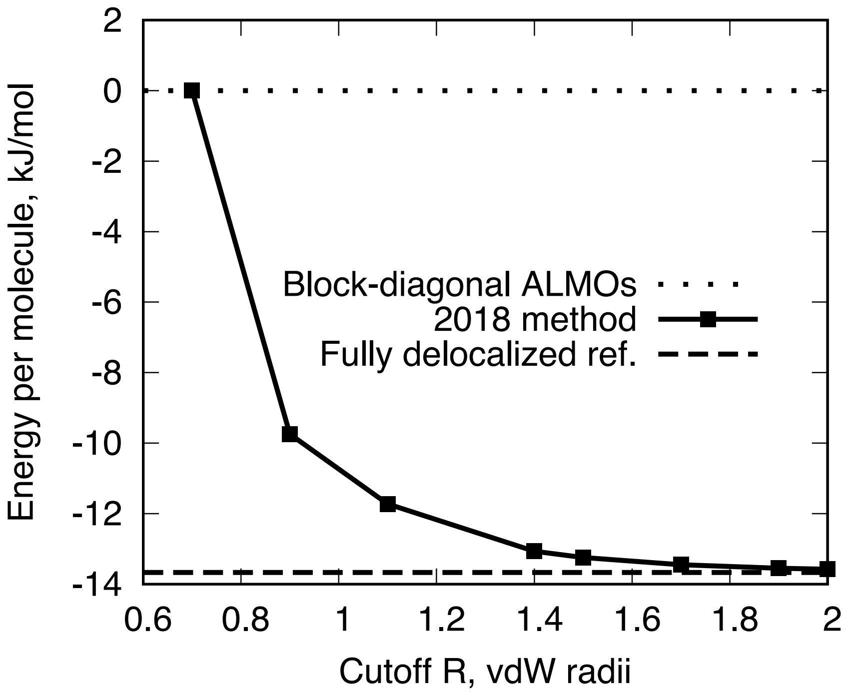
Silicon (cubic diamond lattice), PBE/DZVP, atomic fragments, 4 deloc. neighbors

Accuracy: 2018 method

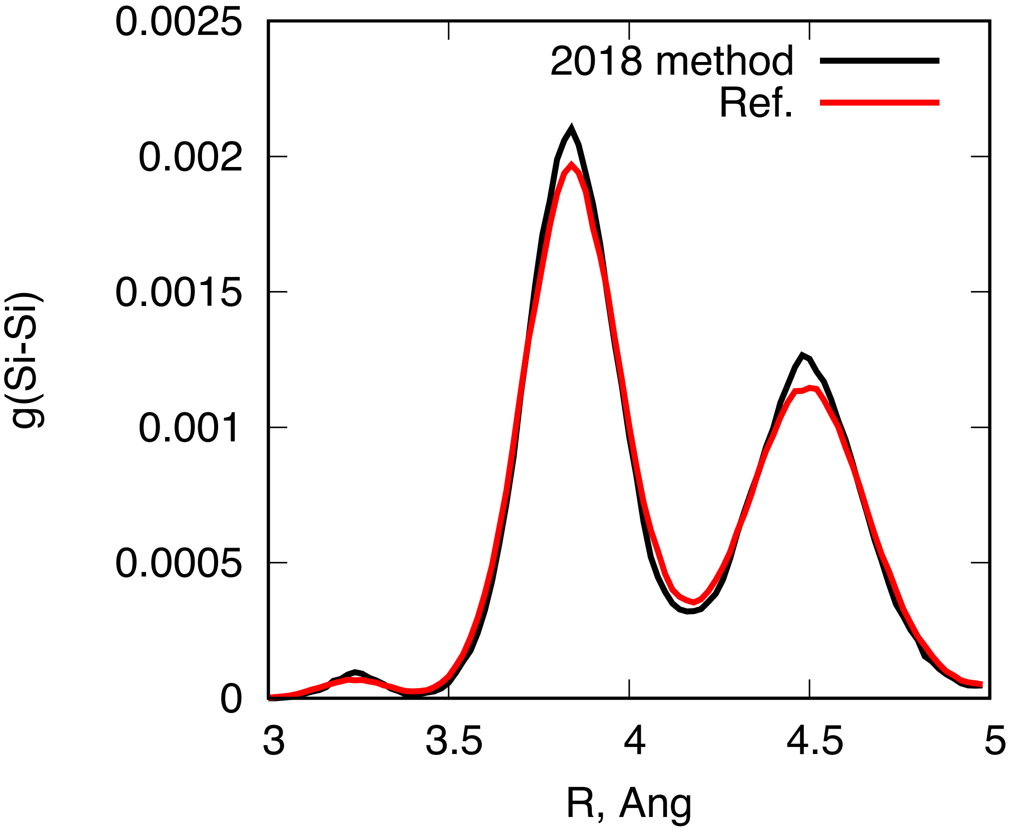
Cubic Si, PBE/DZVP, atomic partitioning

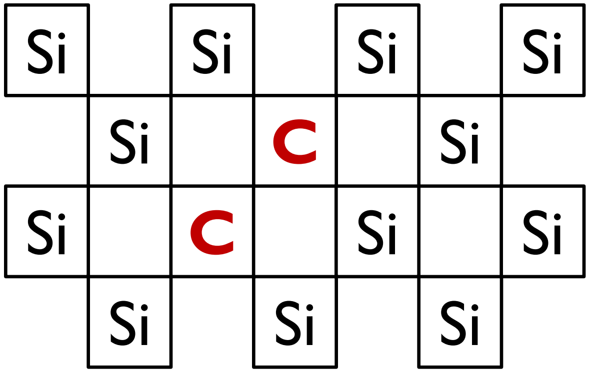


Liquid water, BLYP/TZV2P, atomic partitioning



Cubic Si with a C defect

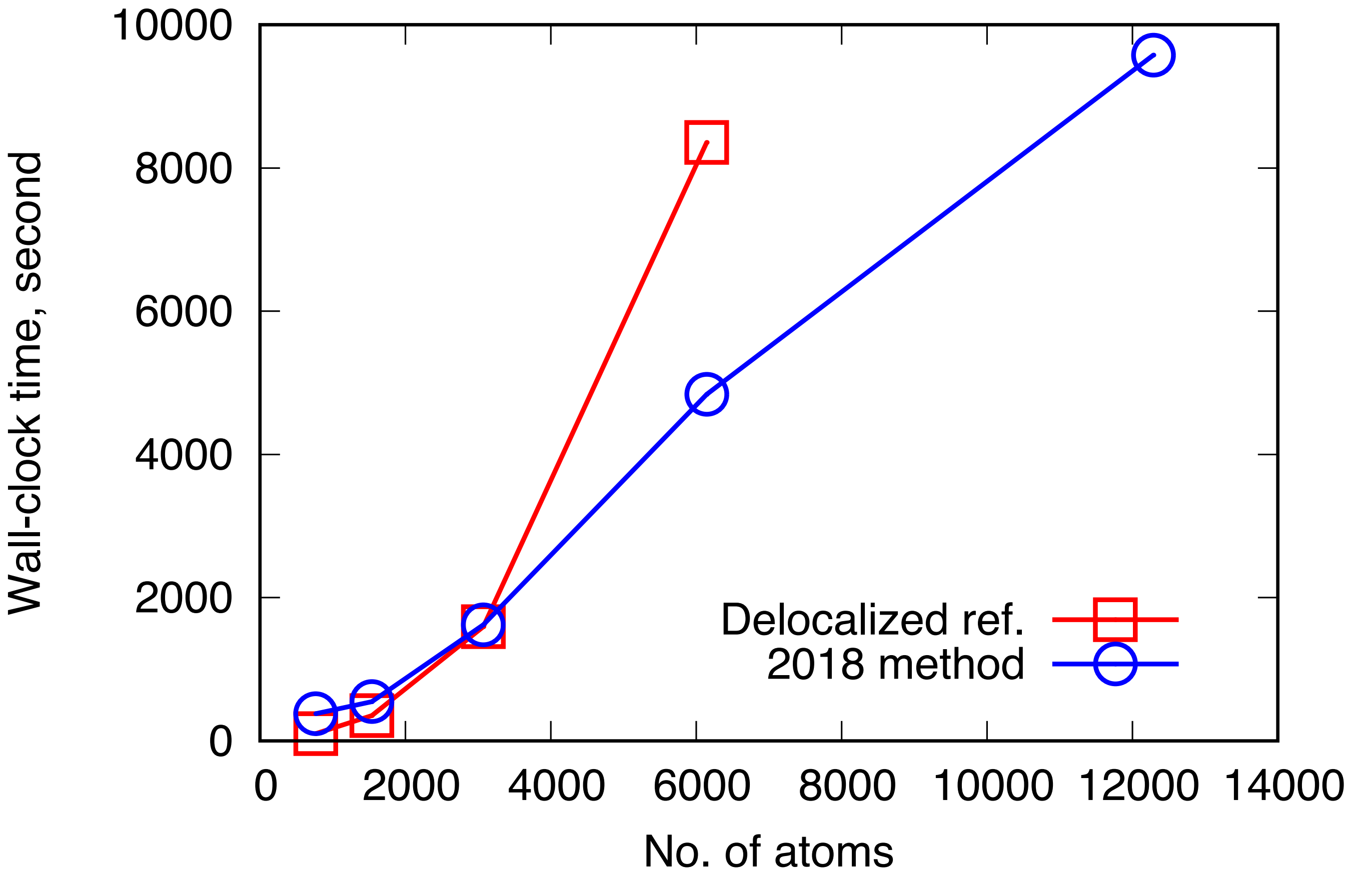




PBE/DZVP, nearest neighbor delocalization,
atomic partitioning

Timing

CdSe, PBE/DZVP, nearest neighbor deloc., atomic partitioning



Weaknesses of 2018 method

- It is important to select "small" eigenvalues properly.
- The "projected" gradient does not correspond to the optimized energy functional. Therefore, the variational principle holds only approximately.

Keywords for the 2018 method

```
&DFT

   &QS
     ALMO_SCF T
   &END QS

   &ALMO_SCF
     XALMO_TRIAL_WF              SIMPLE
     ALMO_ALGORITHM              SKIP
     DELOCALIZE_METHOD           XALMO_SCF
     XALMO_R_CUTOFF_FACTOR       1.4

     &XALMO_OPTIMIZER_PCG
       MAX_ITER_OUTER_LOOP       5
       MAX_ITER                  50
       EPS_ERROR                 1.0E-6
       PRECOND_FILTER_THRESHOLD  0.008
     &END XALMO_OPTIMIZER_PCG

   &END ALMO_SCF

 &END DFT
```

- The 2018 method is requested by setting XALMO_TRIAL_WF to SIMPLE
- Although block-diagonal ALMOs can provide a good initial guess they are not required so there is an option to set ALMO_ALGORITHM to SKIP.
- For strongly interacting atoms, the perturbation theory does not work. Therefore DELOCALIZE_METHOD should be set to XALMO_SCF.
- Eigenvalues smaller than PRECOND_FILTER_THRESHOLD are identified as “bad modes” and ignored.
- The outer loop is often necessary.

From static to dynamic systems

- The challenge of adopting ALMO DFT for molecular dynamics is the slightly nonvariational character of ALMOs:
  - **2013**: the projector defined in the first stage must remain ***fixed*** during the second stage to ensure convergence.
  - **2018**: strictly speaking the energy is always under-optimized.
  - Electron transfer effects can ***suddenly*** become inactive if two neighboring molecules move beyond the localization threshold.
  - The optimization of orbitals is never ***truly*** complete in practice, only up to finite threshold ε_{SCF}
- These errors do not affect the accuracy of static calculations, geometry optimization, and Monte-Carlo simulations. Unfortunately they tend to accumulate in AIMD trajectories leading to non-physical sampling and eventual failure.

Main idea

- Conventional approach is way too slow: solving coupled-perturbed equations, tight SCF convergence, large localization radius.
- Promising two-component recipe:
  - Do a few SCF iterations but do not converge SCF ($\varepsilon_{SCF} = 0.01$ a.u.)
  - Compensate the error by modifying Langevin equation of motion.
- A brief history of key ideas:
  - First mentioned: Krajewski, Parrinello in 2006
  - Formalized: Kuehne, Parrinello, et al. in 2007
  - Rationalized: Dai, Yuan, EPL in 2009
  - Informally known as second generation Car-Parrinello MD.
- Conceptually ALMO AIMD is simpler than CPMD-2.0.

ALMO AIMD

- Use the Langevin equation instead of the Newton equation:

$$m_i \ddot{r}_{i\alpha} = f_{i\alpha}^{\mathrm{SCF}} - \gamma_L m_i \dot{r}_{i\alpha} + R_{i\alpha}^{\gamma_L}(t)$$

Retarding force

Stochastic force

$$\langle R_{i\alpha}^{\gamma_L}(t) \rangle = 0,$$
$$\langle R_{i\alpha}^{\gamma_L}(t) R_{j\beta}^{\gamma_L}(t') \rangle = 2 k_B T \gamma_L m_i \delta_{ij} \delta_{\alpha\beta} \delta(t - t')$$

Assumption: $f_{i\alpha}^{\mathrm{SCF}} = f_{i\alpha}^{\mathrm{APP}} + R_{i\alpha}^{\Delta}(t)$

$$m_i \ddot{r}_{i\alpha} = f_{i\alpha}^{\mathrm{APP}} - \gamma_L m_i \dot{r}_{i\alpha} + R_{i\alpha}^{\gamma_L}(t) + R_{i\alpha}^{\Delta}(t)$$

ALMO AIMD

- The traditional and modified re-balanced Langevin equations

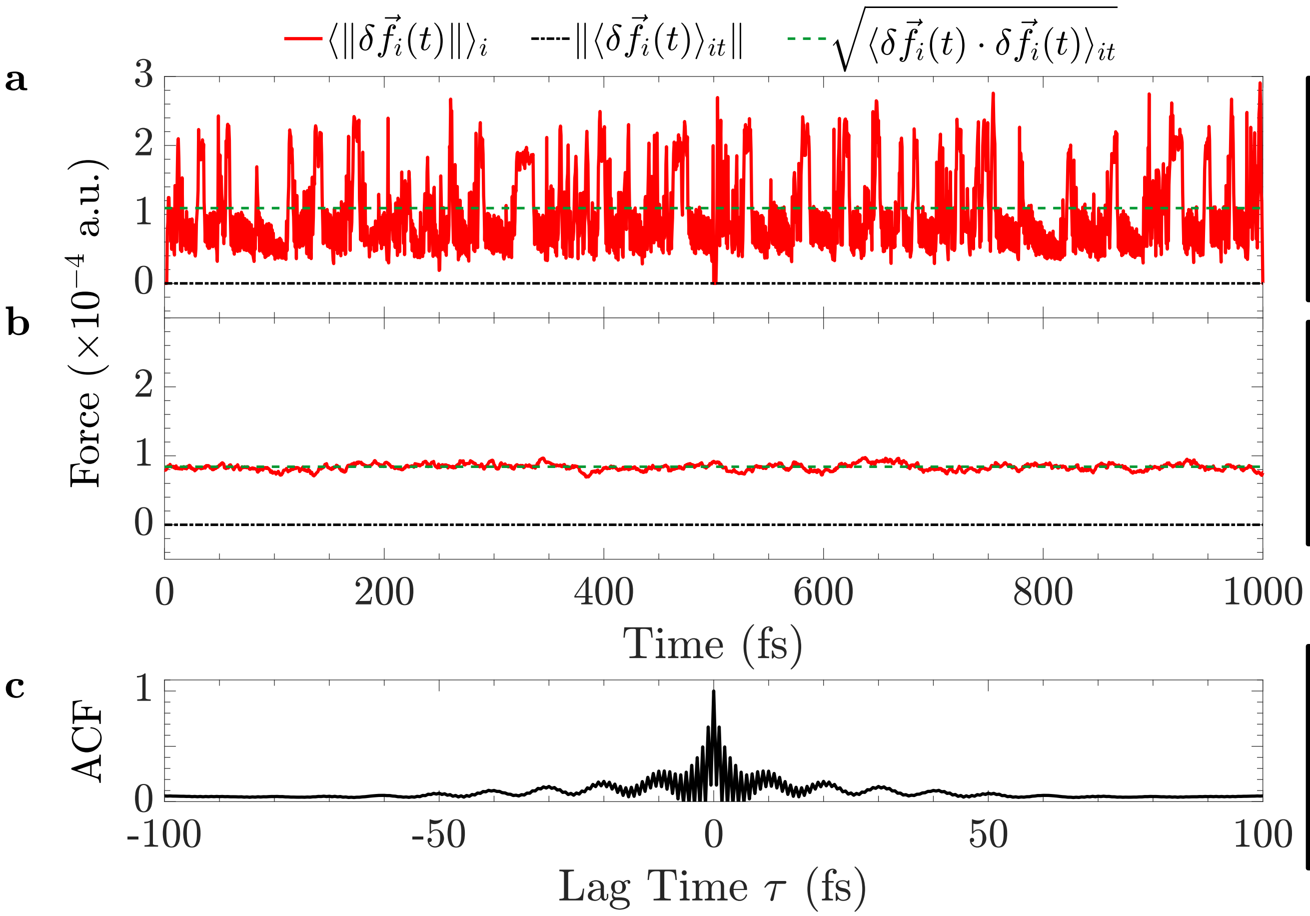
$$m_i \ddot{r}_{i\alpha} = \boxed{f_{i\alpha}^{\mathrm{SCF}}} - \gamma_L m_i \dot{r}_{i\alpha} + R_{i\alpha}^{\gamma_L}(t)$$

$$m_i \ddot{r}_{i\alpha} = \boxed{f_{i\alpha}^{\mathrm{APP}}} - \gamma_L m_i \dot{r}_{i\alpha} + R_{i\alpha}^{\gamma_L}(t) \boxed{+ R_{i\alpha}^{\Delta}(t)}$$

- If the error resembles white noise it can be “compensated” by using a slightly modified Langevin equation.
- How “strong” is the added stochastic term? In other words, what is the value of Δ?

Assessing the error

Liquid water, BLYP/TZV2P, 2013 method, ⟨Neig⟩≈13



$\varepsilon_{SCF}=10^{-2}$

$\varepsilon_{SCF}=10^{-6}$
(converged)

Autocorrelation
of the error

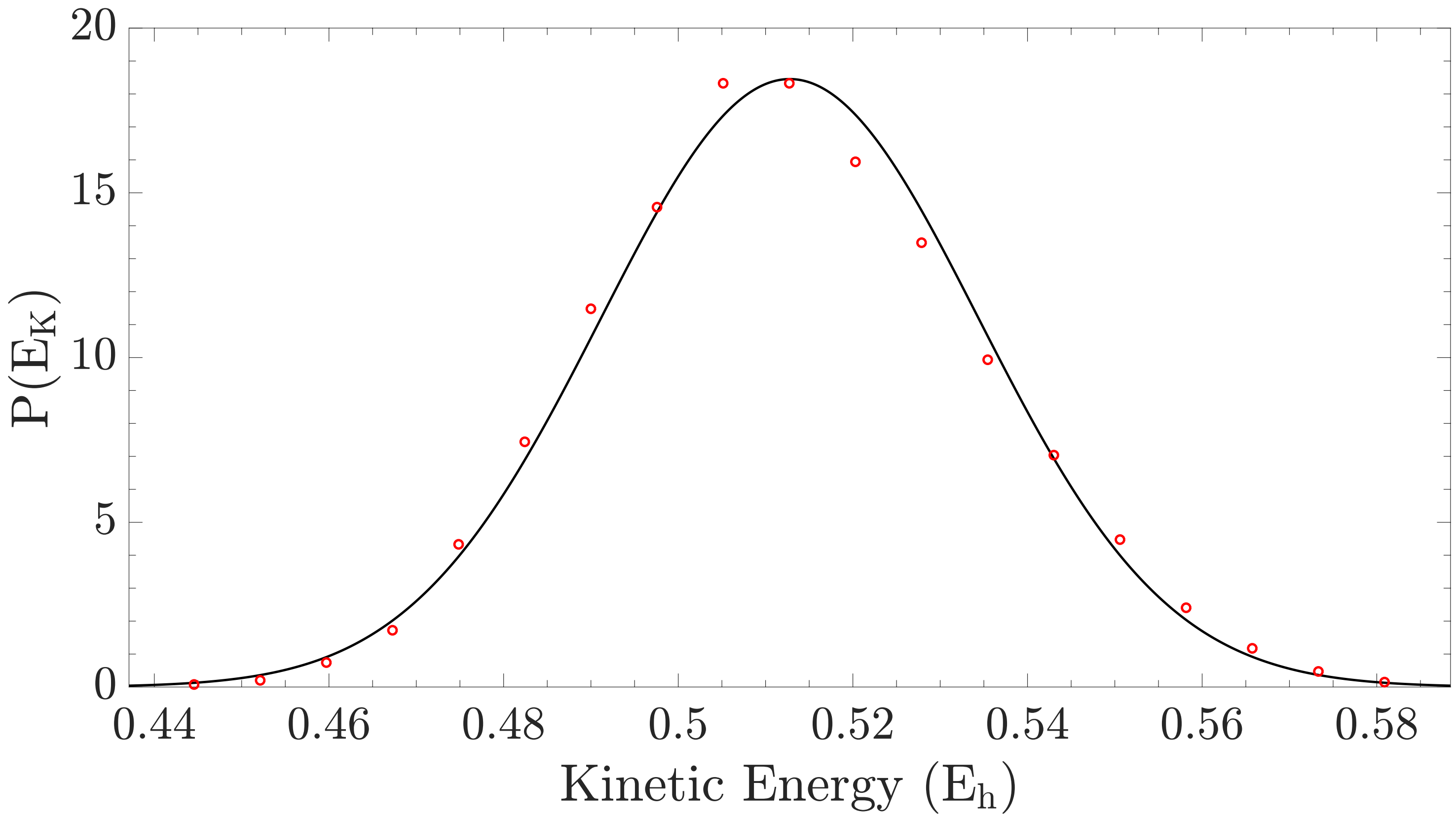
How to calculate Δ

1. Estimate the order of magnitude of Δ by integrating the autocorrelation function.
2. Fine-tune Δ value to reproduce stable dynamics with the correct Maxwell-Boltzmann distribution.

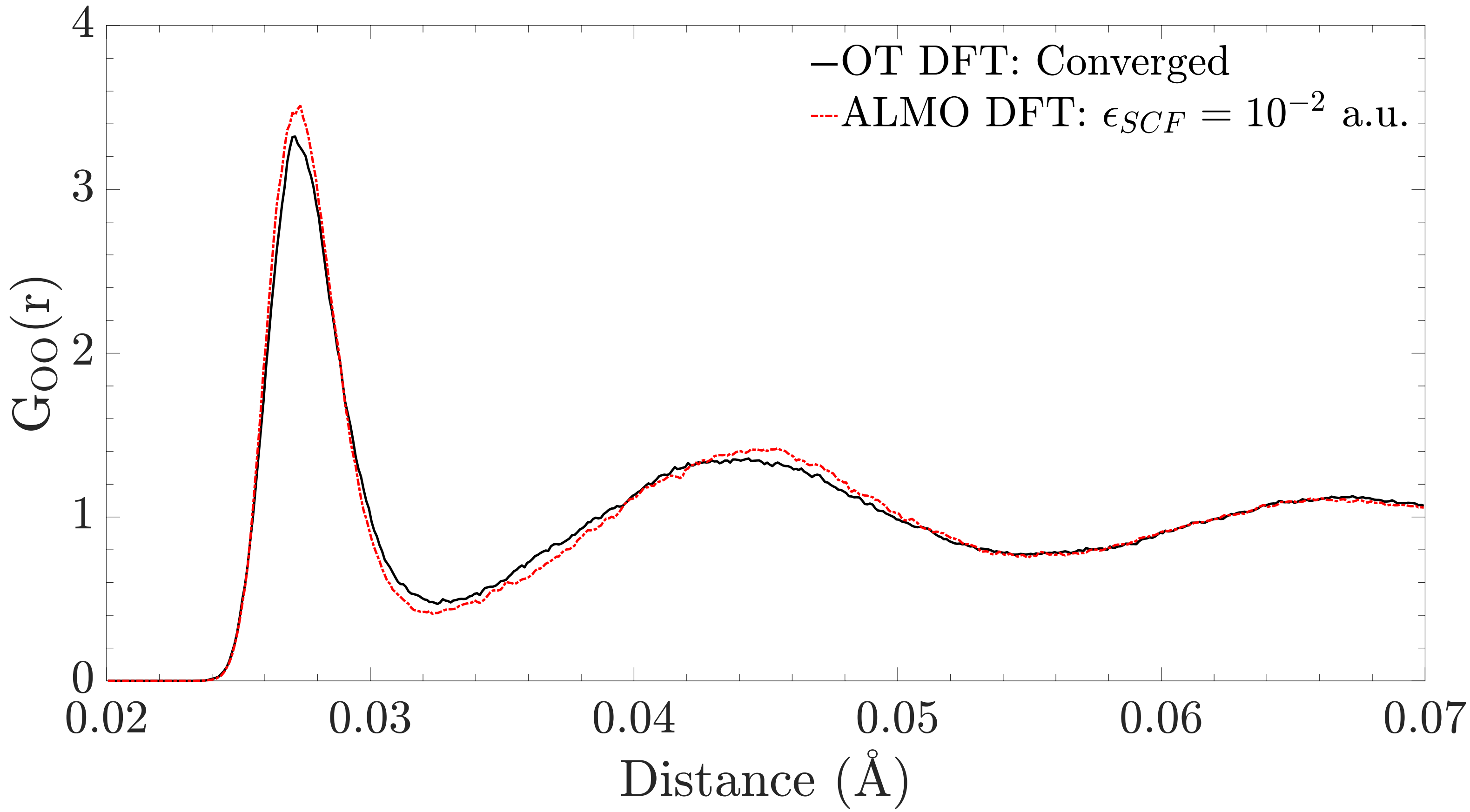
Result: it seems to work!

- Once Δ is tuned AIMD is stable and reproduces MB distribution.

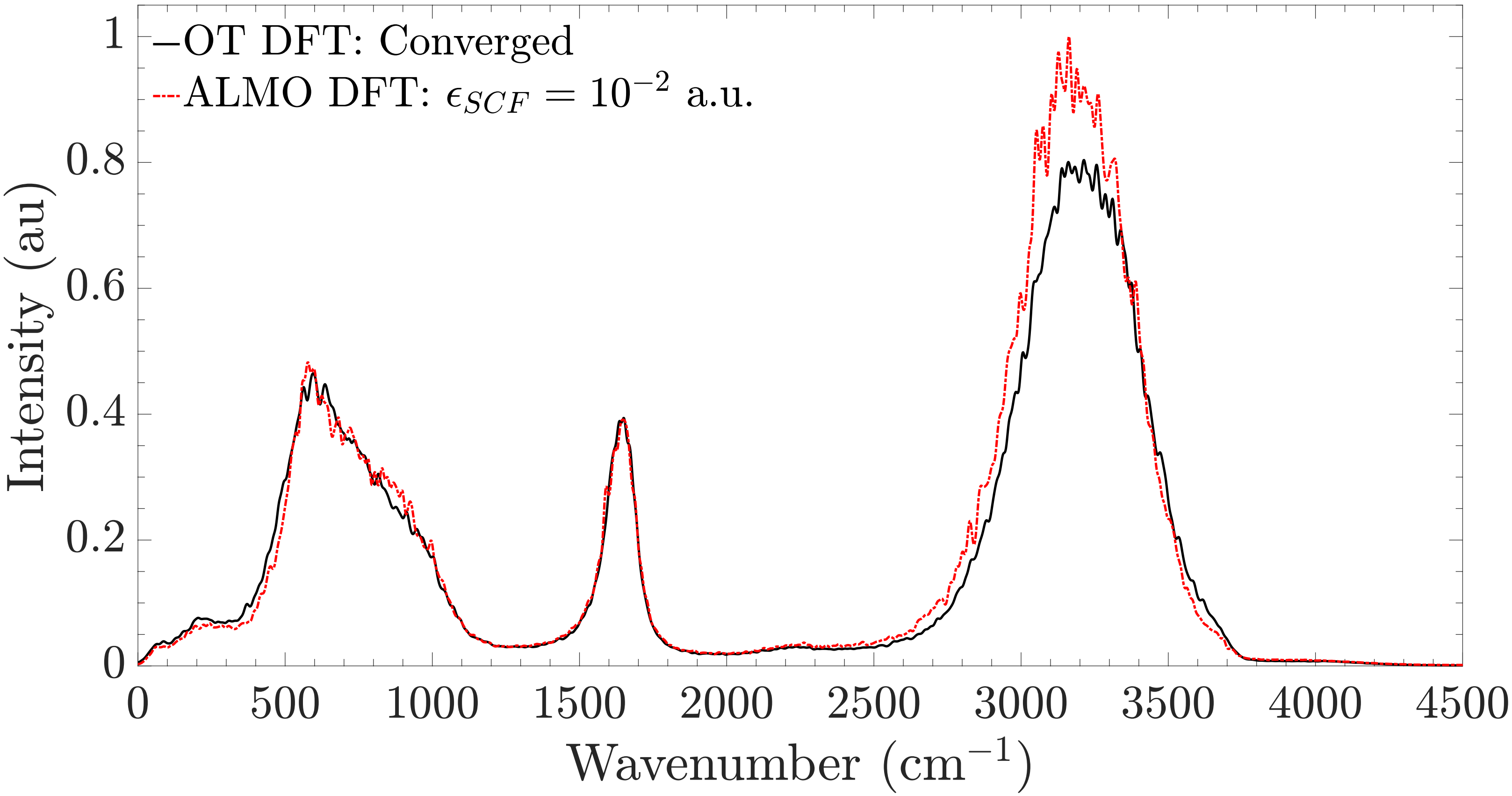
Liquid water, BLYP/TZV2P, ⟨Neig⟩≈13, $\gamma_L = 10^{-3}$ fs^{-1} and $\Delta = 6 \cdot 10^{-5}$ fs^{-1}



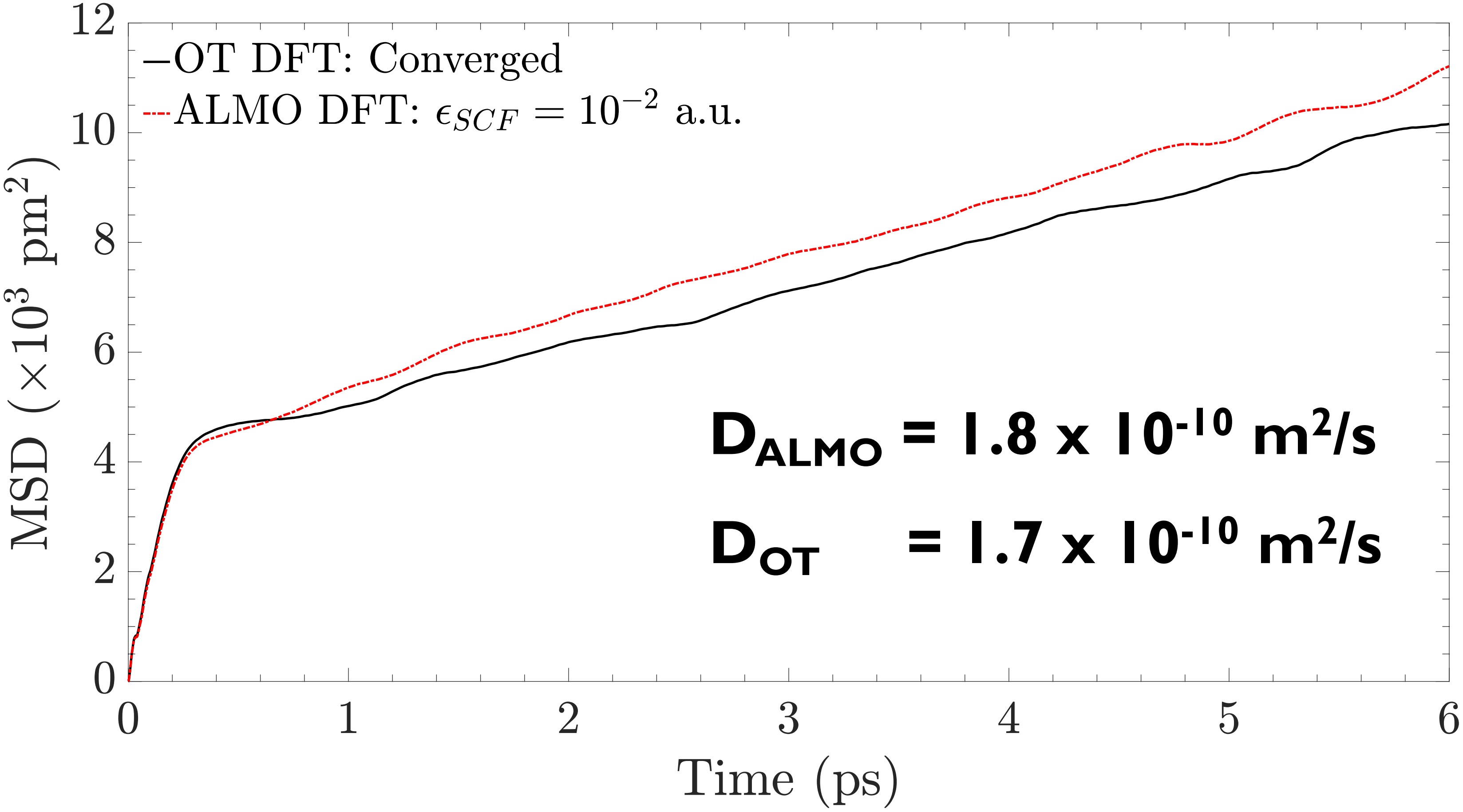
RDF of liquid water



IR spectrum of liquid water



Self-diffusion of liquid water

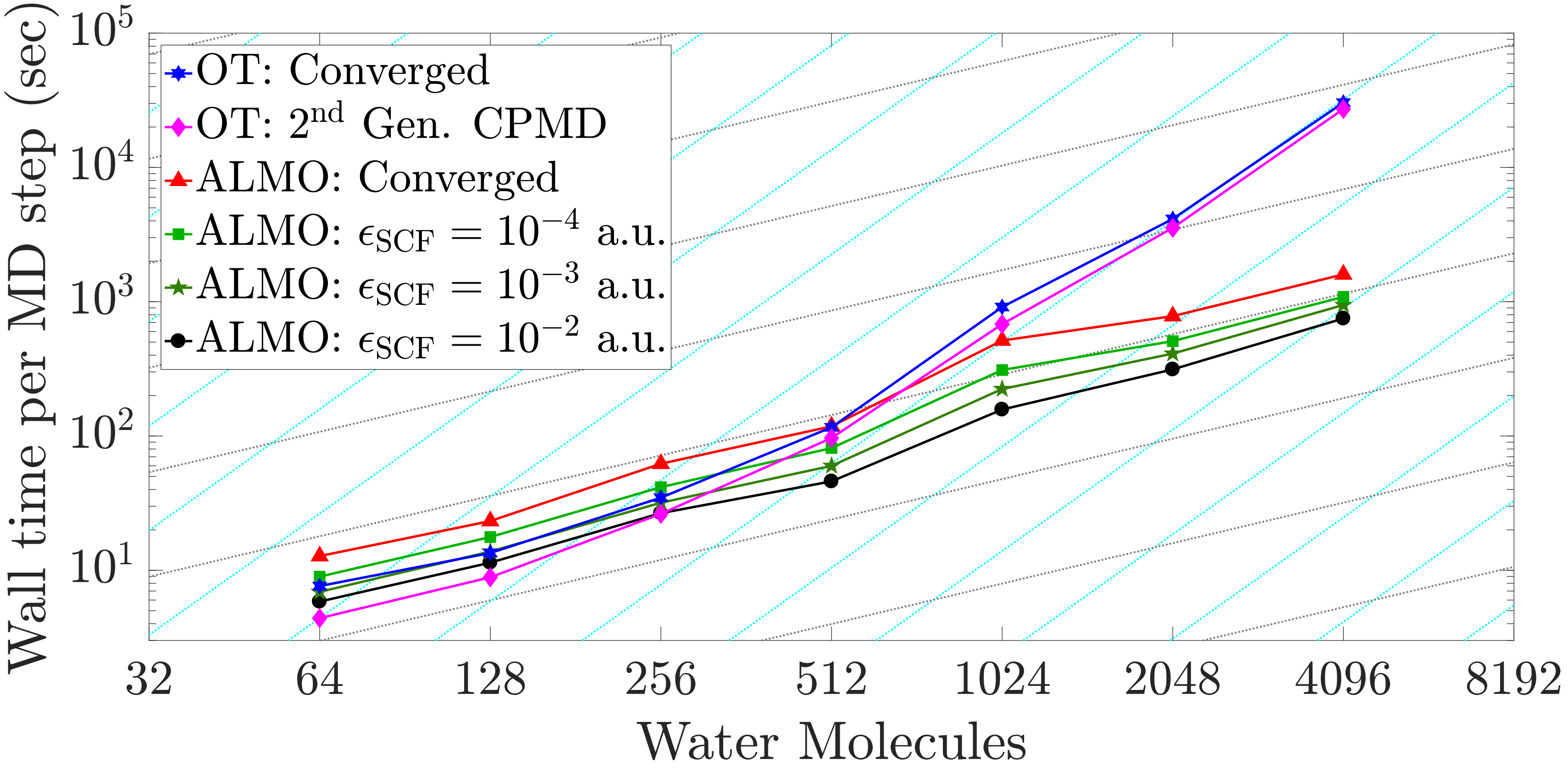


D_{ALMO} = 1.8 x 10^{-10} m^2/s

D_{OT} = 1.7 x 10^{-10} m^2/s

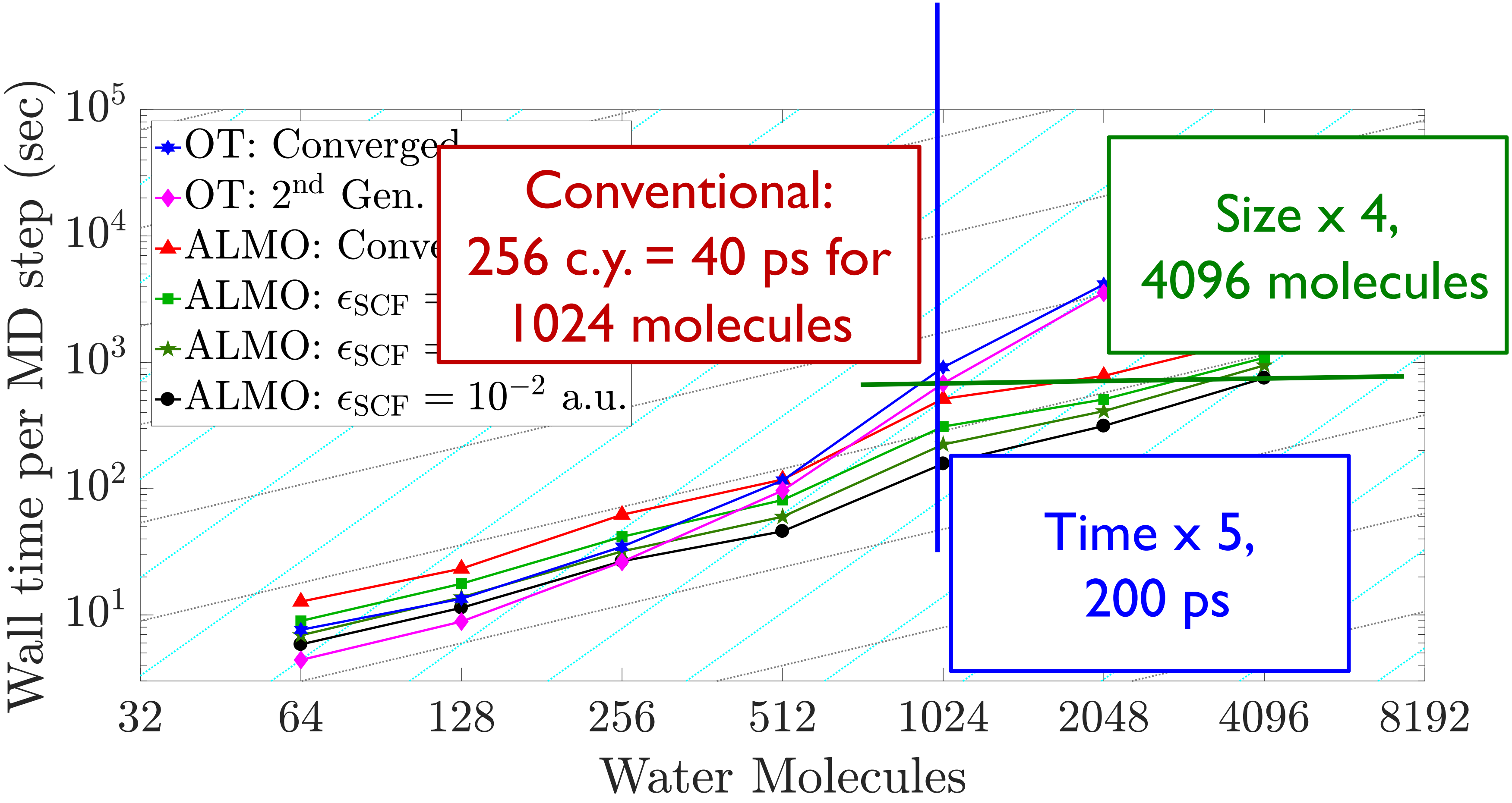
Timing benchmark

- 256 compute cores, liquid water, BLYP/TZV2P, ⟨Neig⟩≈13



Timing benchmark

- 256 compute cores, liquid water, BLYP/TZV2P, ⟨Neig⟩≈13

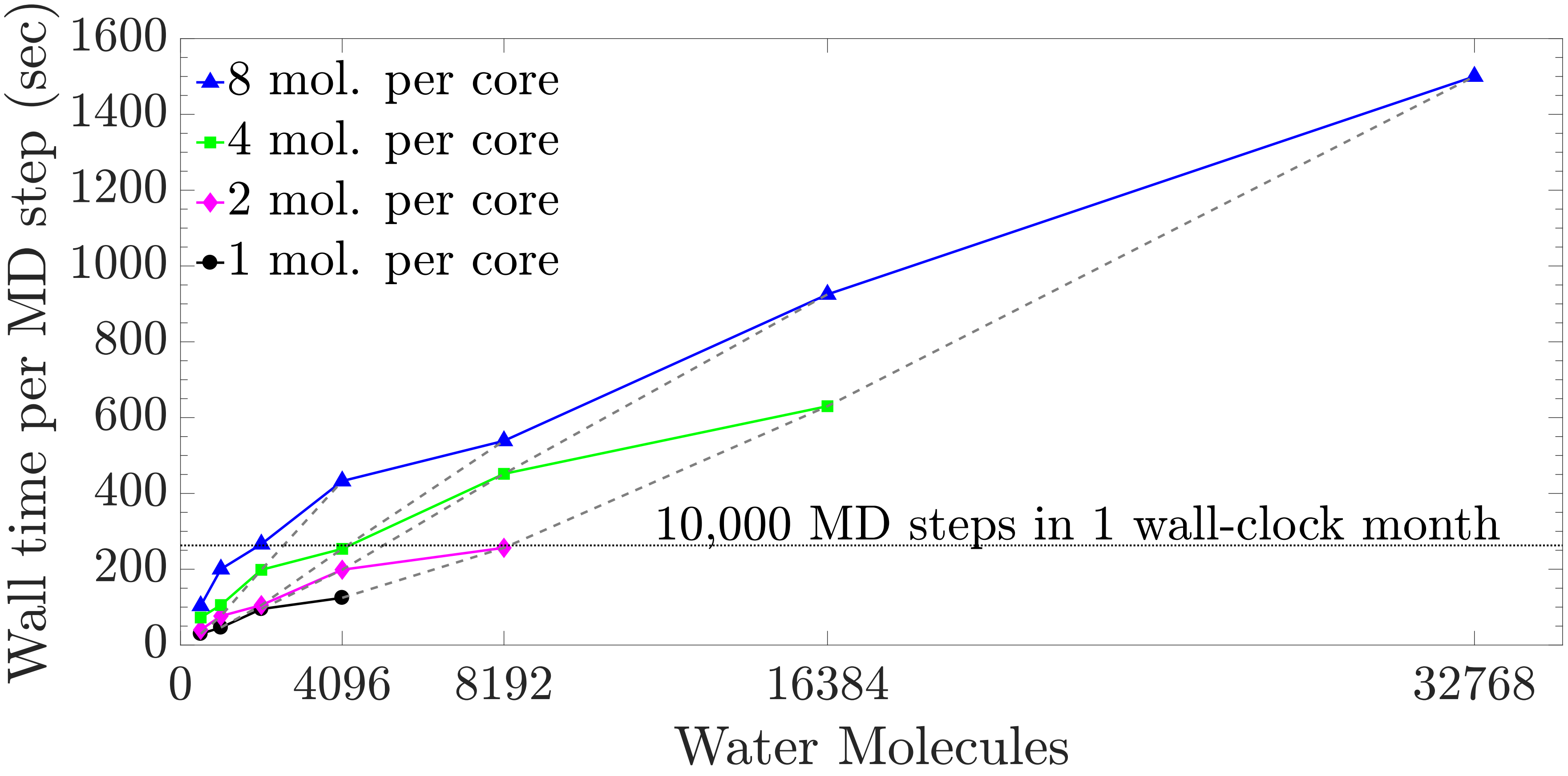


Conventional:
256 c.y. = 40 ps for
1024 molecules

Size x 4,
4096 molecules

Time x 5,
200 ps

Weak-scaling benchmark

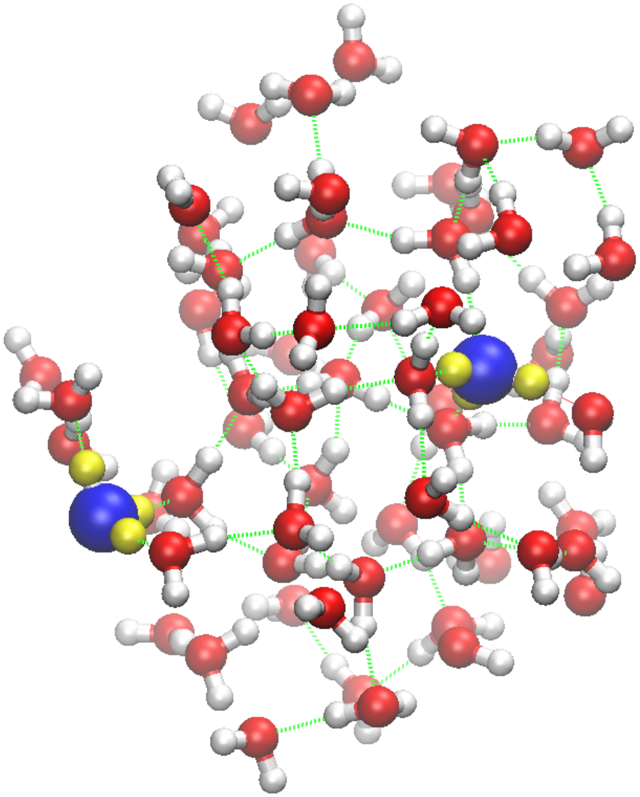


AIMD based on the 2018 method

- WARNING: we have performed only a limited number of tests AIMD runs using the 2018 ALMO method. While the first results are promising further tests are required.

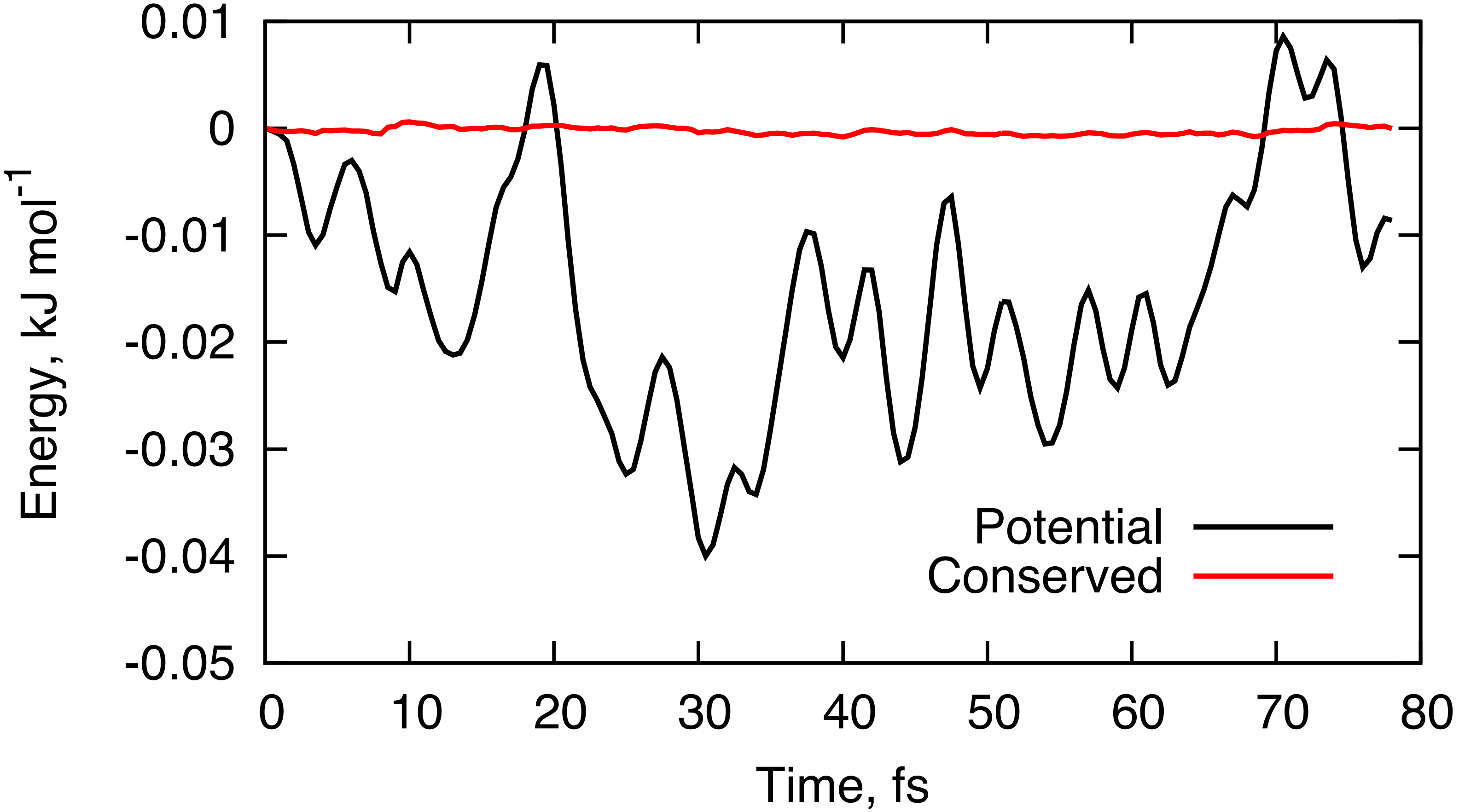
Solvated protons

- Solvated H^+ cluster form in ESI in mass spectroscopy.
- ALMO AIMD is stable with atomic partitioning and bond breaking processes.



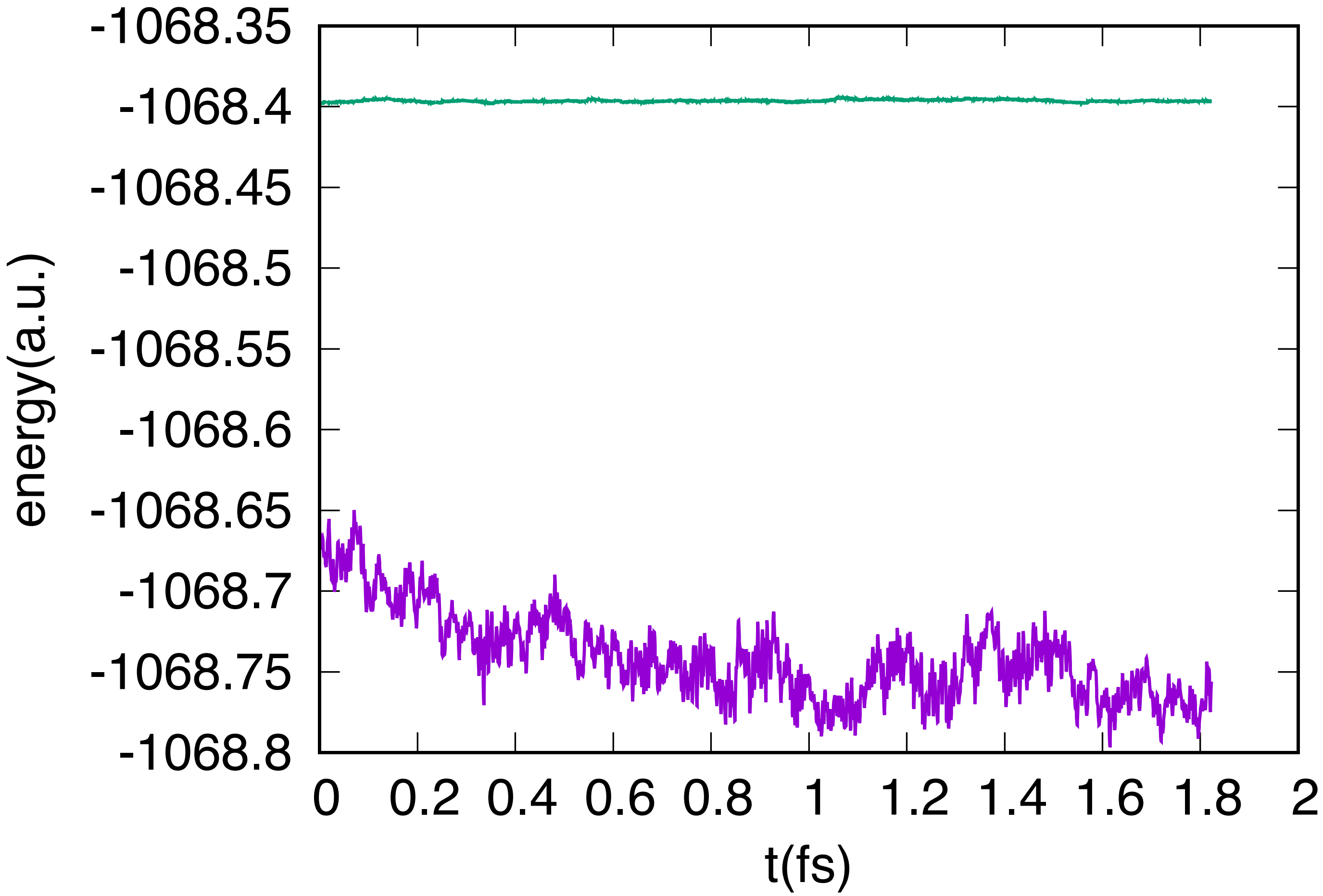
Solvated protons

- NVT at 298K, $(H^+)_2(H_2O)_{62}$ cluster, BLYP/TZV2P, ⟨Neig⟩≈9.2



Solvated protons

- NVT at 298K, $(H^+)_2(H_2O)_{62}$ cluster, BLYP/TZV2P, ⟨Neig⟩≈9.2



ALMO AIMD job in CP2K

- The idea is the same as for static calculations

1. Set up a DFT-based MD simulation.
2. Assign atoms, basis set functions, and electrons to localization centers.
3. Specify electron localization radius (radii) to create electron localization domains.
4. Control how the ALMO forces are computed using the same ALMO keywords, but
5. Make sure that the error in the ALMO forces is properly compensated in the MD integrator.

Step 4. ALMO SCF in AIMD

```
&FORCE_EVAL
 &DFT

   &ALMO_SCF
      ALMO_EXTRAPOLATION_ORDER     4
      XALMO_EXTRAPOLATION_ORDER    5

      &ALMO_OPTIMIZER_DIIS
        MAX_ITER                  50
        !MAX_ITER_EARLY            5
        EPS_ERROR                 1.0E-6
        EPS_ERROR_EARLY           1.0E-4
      &END ALMO_OPTIMIZER_DIIS

      &XALMO_OPTIMIZER_PCG
        MAX_ITER                  50
        !MAX_ITER_EARLY            3
        EPS_ERROR                 1.0E-6
        EPS_ERROR_EARLY           1.0E-2
      &END XALMO_OPTIMIZER_PCG
    &END ALMO_SCF

  &END DFT
&END FORCE_EVAL
```

- SCF can be stopped without reaching convergence in both first and second stages.
- Positive MAX_ITER_EARLY or EPS_ERROR_EARLY are used as criteria to stop SCF prematurely.
- Even with premature stopping, several initial MD steps require full SCF convergence and are still governed by MAX_ITER and EPS_ERROR.
- It is recommended to use WF extrapolation (order 3 to 5), with our without early stopping.

Step 5. &MOTION for ALMO AIMD

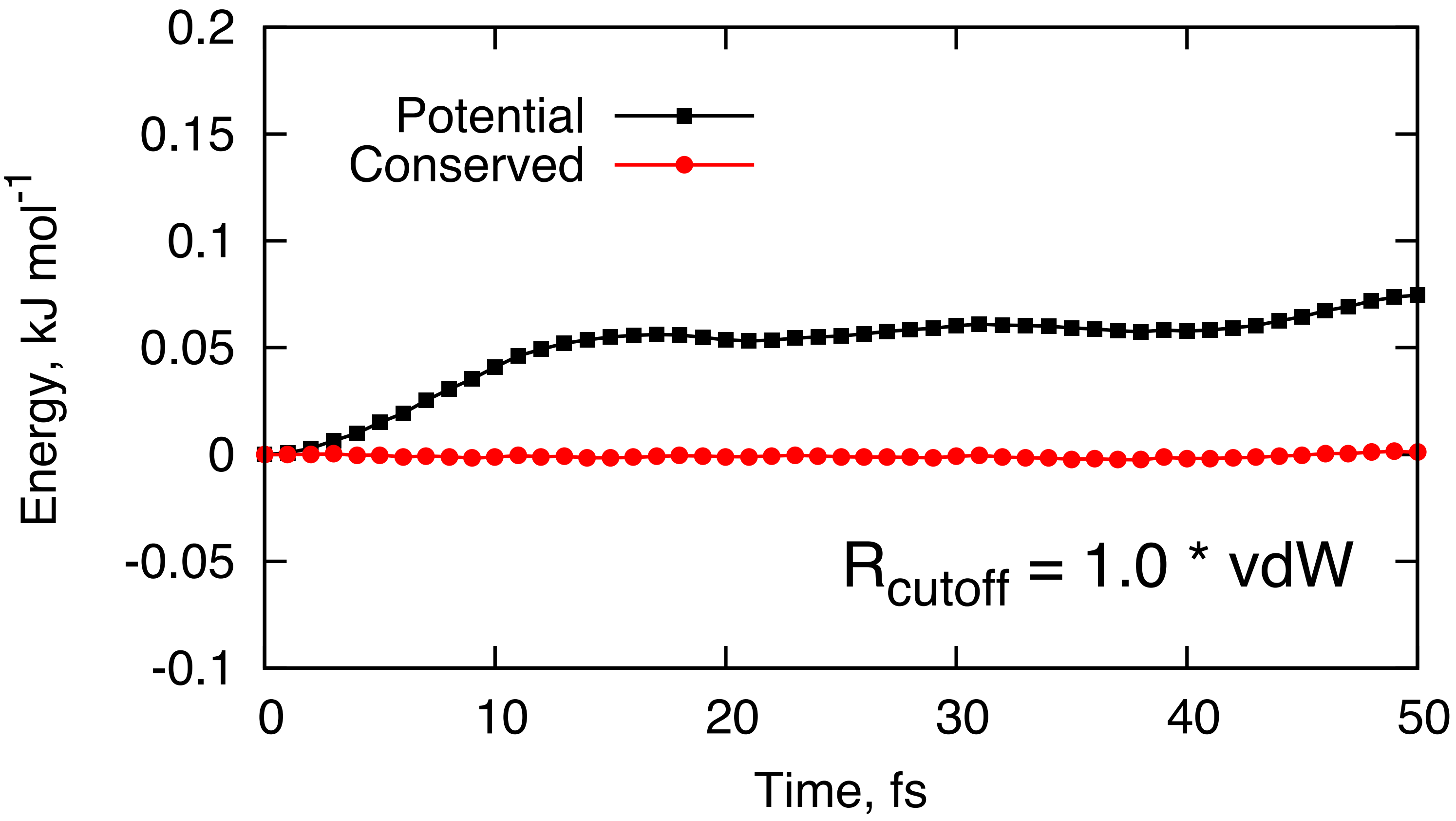
```
&MOTION
  &MD
    ENSEMBLE LANGEVIN
    TEMPERATURE 300
    &LANGEVIN
      GAMMA         0.001
      NOISY_GAMMA   0.00006
    &END LANGEVIN
  &END MD
&END MOTION
```

- Compensate for the errors in ALMO forces by adjusting the NOISY_GAMMA in the Langevin integrator:
  - Positive – stronger noise
  - Negative – weaker noise
- ALMO errors are insignificant and any integrator can be used if:
  - early stopping is not used, and
  - R_c is sufficiently large, and
  - only tiny "bad modes" are filtered.

Adjusting R_c for stable AIMD

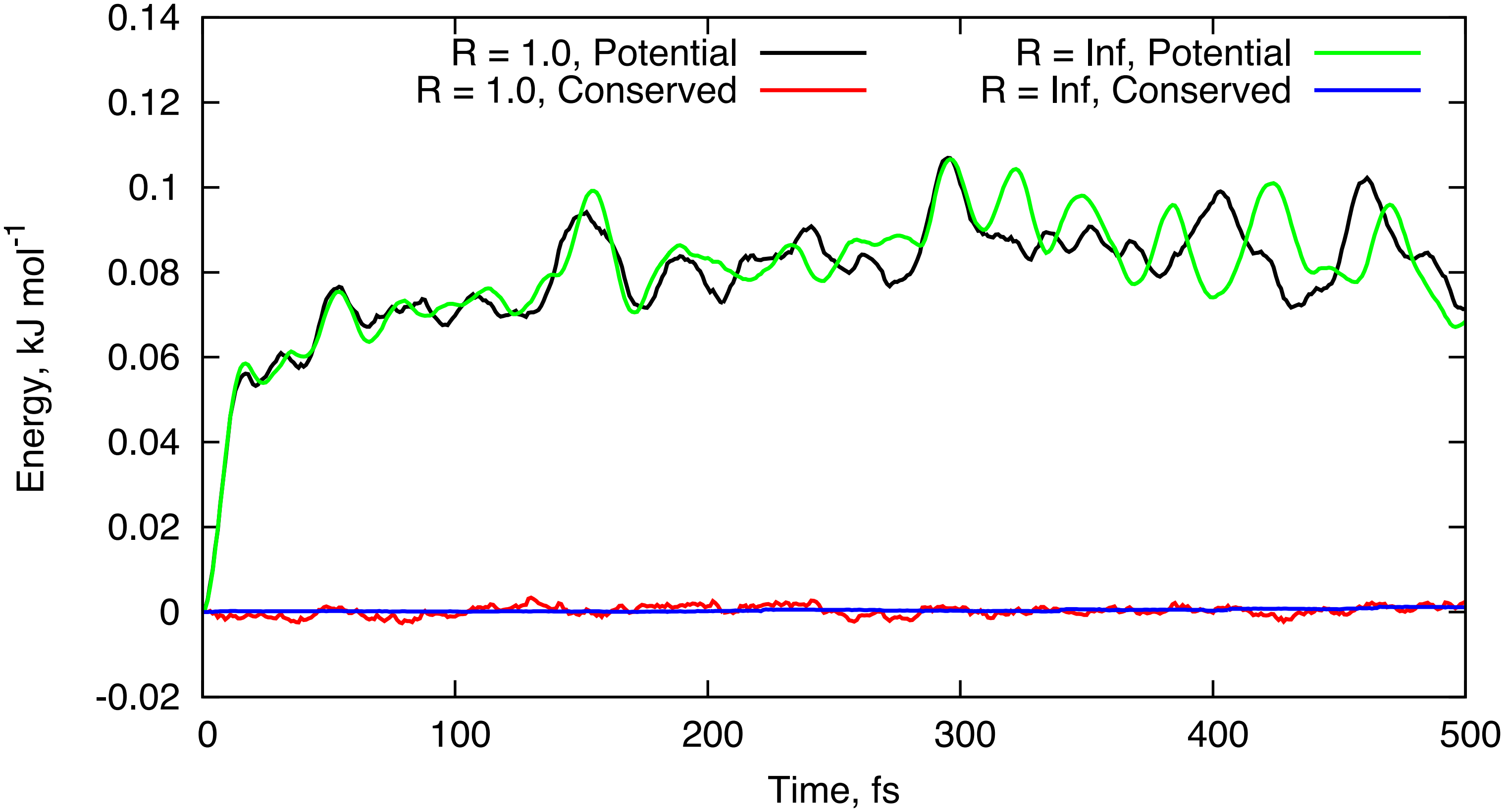
- 2013 method, NVT at 298 K, rutile TiO_2, BLYP/DZVP

⟨Neighbors⟩≈17



Adjusting R_c for stable AIMD

- 2013 method, NVT at 298 K, rutile TiO_2, BLYP/DZVP
  ⟨Neighbors⟩≈17 vs ⟨Neighbors⟩≈ALL

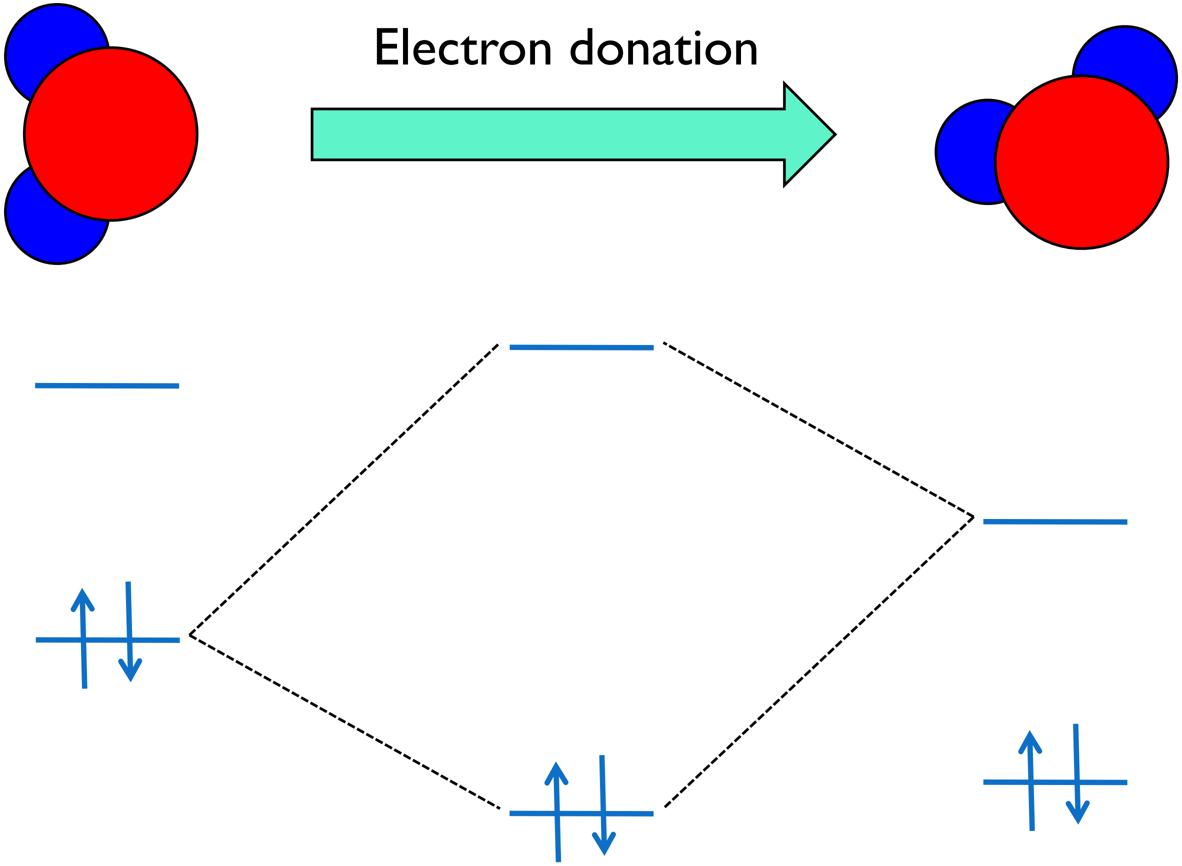


Next:
ALMOs for physical insight

Physics of intermolecular interactions

- Atoms in molecules, clusters, liquids, and solids interact via:
  - fixed charges, dipoles, quadrupoles, etc. (FRZ)
  - induced dipoles, quadrupoles, etc. (POL)
  - intermolecular donor-acceptor charge-transfer, aka covalent component (COV)

Donor-acceptor interactions

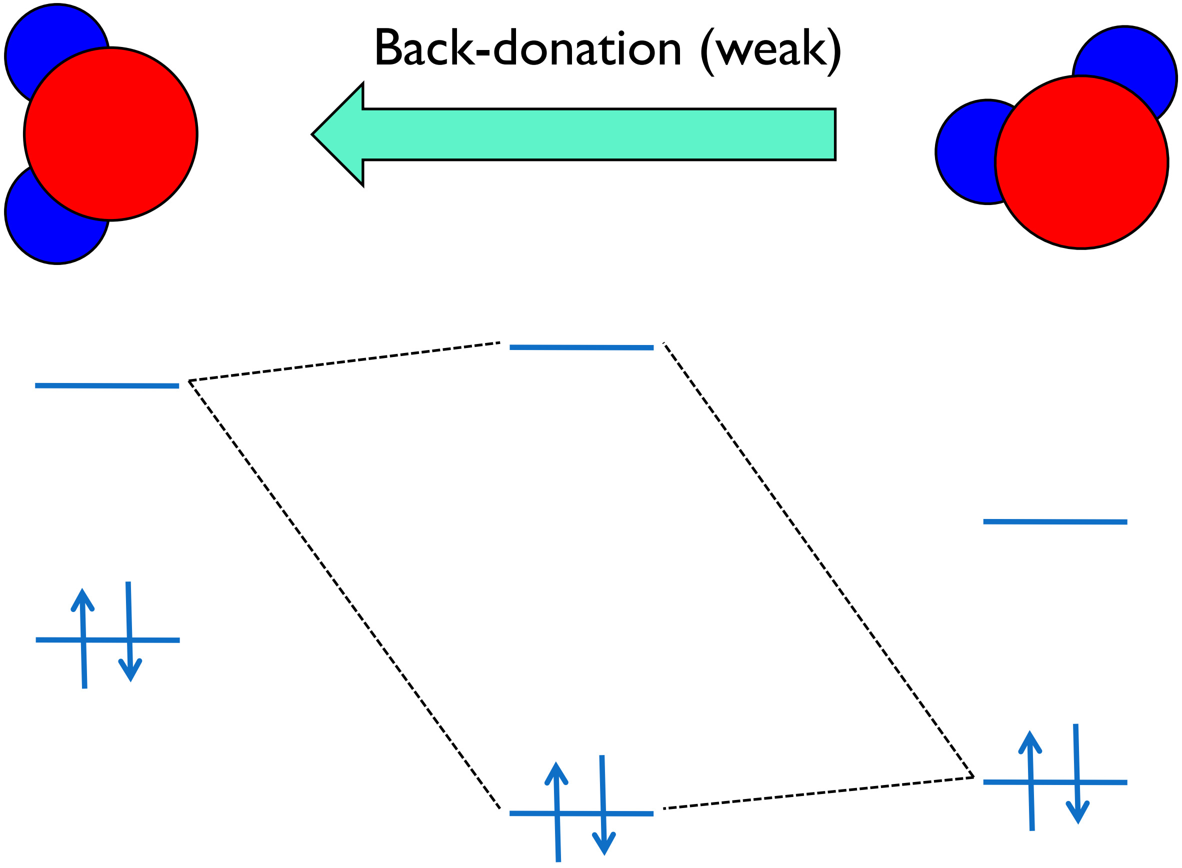


Electron donation

Molecule A

Molecule B

Donor-acceptor interactions



Back-donation (weak)

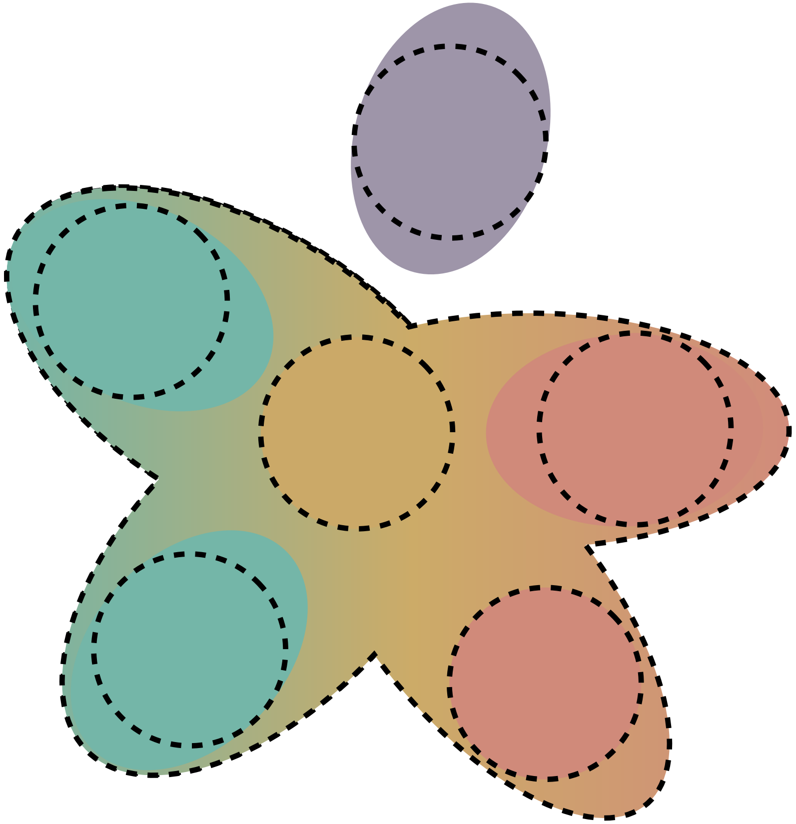
Molecule A

Molecule B

Energy decomposition analysis

- Normal electronic structure methods give us only the total intermolecular energy (**FRZ**+**POL**+**COV**).
- Energy decomposition analysis (EDA) computes the strength of individual components **FRZ**, **POL**, and **COV**:
  - Absolutely localized molecular orbitals (ALMOs) are constructed to confine electrons to their own molecules play the key role in EDA.

4 key electronic states



1. MOs on isolated molecules

ΔE(FRZ)

2. Bring molecules together, do NOT relax ALMOs

ΔE(POL)

3. Turn polarization ON: relax ALMOs

ΔE(COV)

4. COV interactions ON: no locality, normal MOs

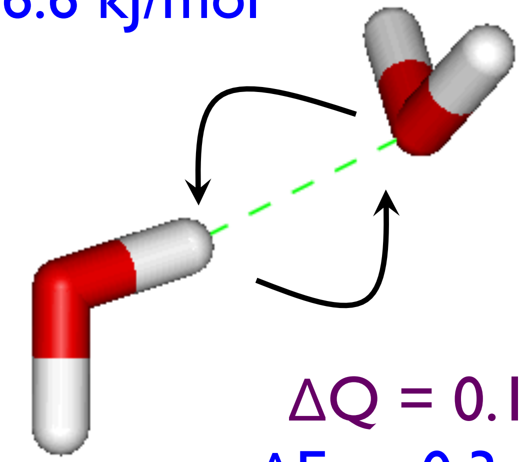
R.Z. Khaliullin, E.A. Cobar, R. Lochan, A.T. Bell, M. Head-Gordon, *JPC A*, **111**, 8753 (2007)

Important ALMO EDA features

- Covalent components of **individual bonds:** forward and backdonation **COV** terms are obtained for each pair of atoms/molecules in the many body system.
- The strength of COV interactions can be measured using
  - **Charge scale ΔQ(COV)**: fraction of electron density transferred from one molecule to another
  - **Energy scale ΔE(COV):** stabilization due to the transfer
  - Charge scale measures electron reorganization and is defined in full agreement with the energy scale.
- Unlike other codes, ALMO EDA in CP2K is generalized to periodic systems. Example: applicable to liquid water

(Review) R.Z. Khaliullin, T.D. Kuehne, *PCCP*, **15**, 15746 (2013)

Water Dimer



ΔQ = 3 mē
ΔE = -6.6 kJ/mol

ΔQ = 0.1 mē
ΔE = -0.3 kJ/mol

Term	kJ/mol
ΔE(FRZ)	-5.2
ΔE(POL)	-6.5
ΔE(COV)	-6.9
ΔE(TOT)	**-18.6**

* B3LYP/aug-cc-pVQZ

R.Z. Khaliullin, A.T. Bell, M. Head-Gordon, *Chem. Eur. J.*, **15**, 851 (2009)

Physical insight

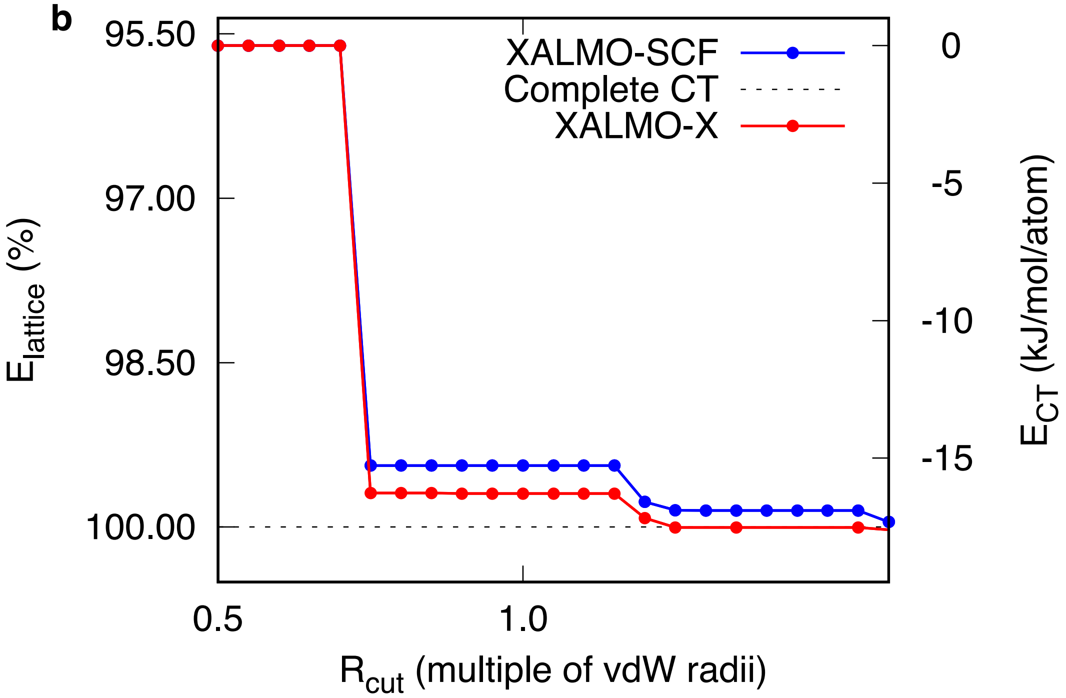
- The ability to control electron localization enables us to gain deeper insight into electronic effects responsible for intermolecular/chemical bonding.
- Donor-acceptor interactions give rise to many interesting spectroscopic features of liquid water:
  - **XAS:** T Kühne, RZK, *Nature Commun.* 4, 1450 (2013)
  - **XAS:** RZK, T Kühne, *PCCP* 15, 15746 (2013)
  - **IR:** C Zhang, RZK, D Bovi, L Guidoni, TD Kühne, *JPCL* 4, 3245 (2013)
  - **NMR:** H Elgabarty, RZK, T Kühne, *Nature Commun.* 6, 8318 (2015)
  - **X-ray scattering:** T Kühne, RZK, *JACS* 136, 3395 (2014)

Going beyond liquid water

- The nature of interatomic bonding in materials
- Distance-dependent nature of covalent interactions

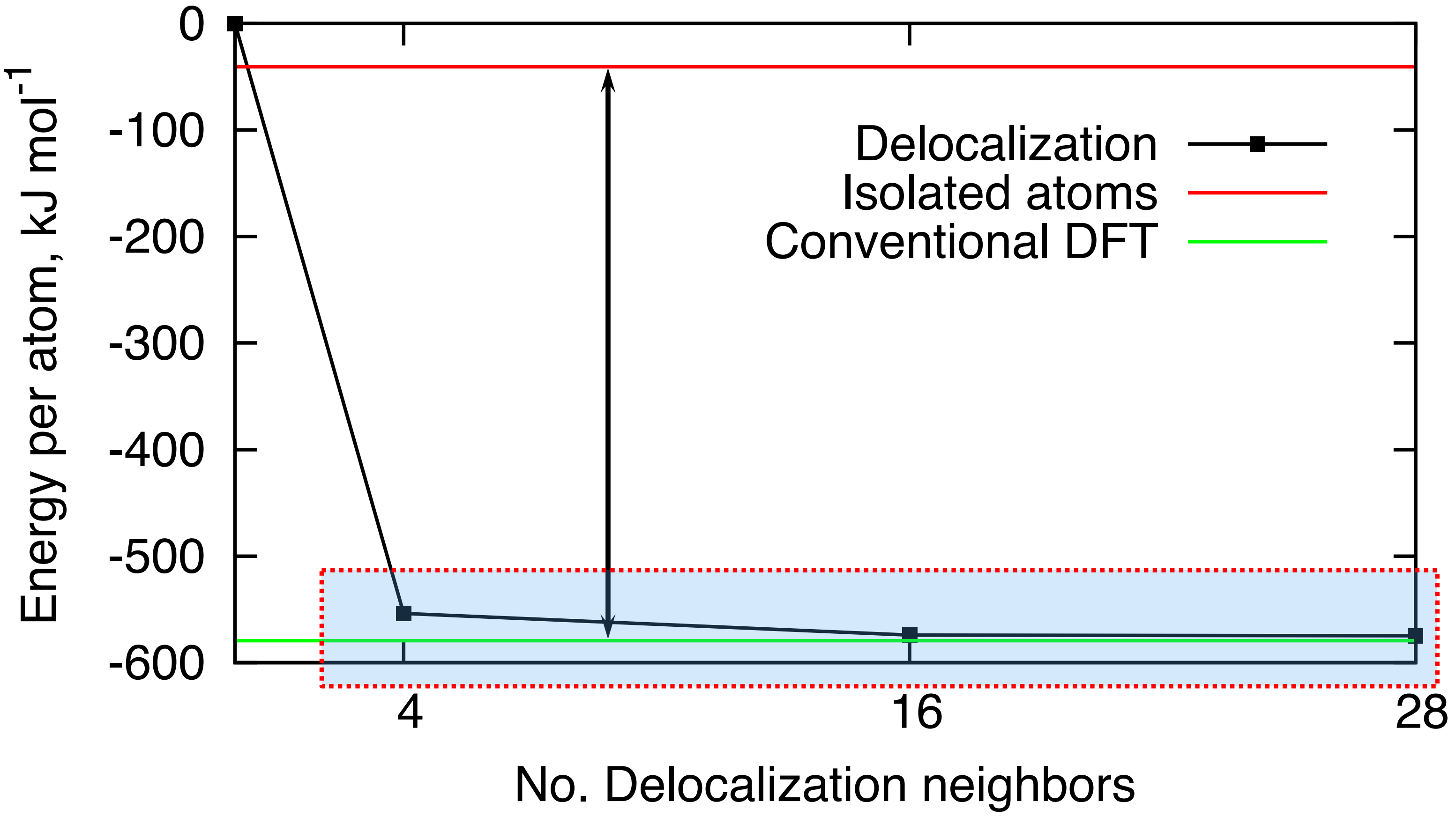
Ionic insulator

- NaCl, 2 interpenetrating fcc lattices, PBE/DZVP.
- No neighbors: 95.5% of lattice energy
- 6 neighbors: ~99% of lattice energy



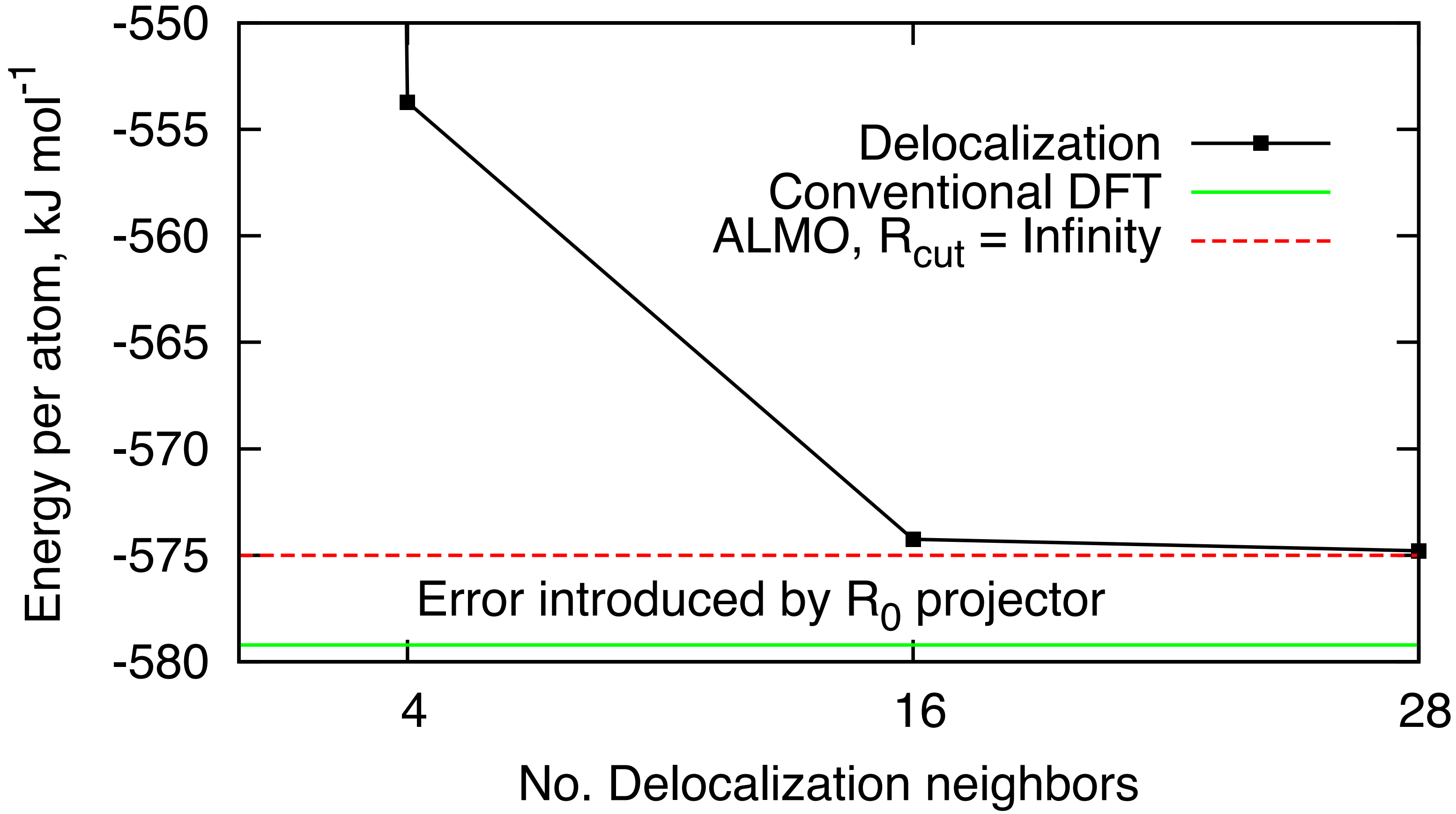
Covalent insulator

- Silicon, diamond lattice, PBE/DZVP



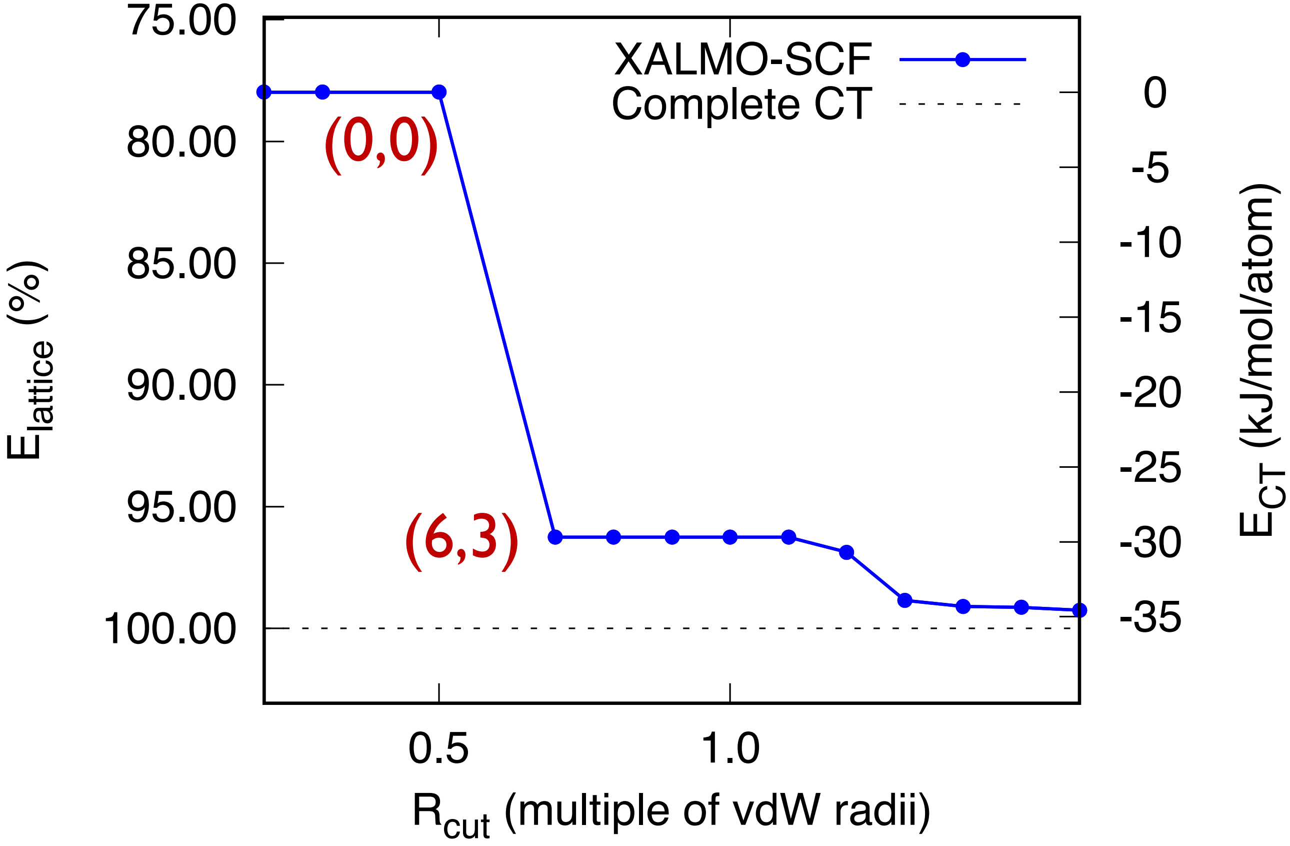
Covalent insulator

- Silicon, diamond lattice, PBE/DZVP



Is MgH_2 ionic or covalent?

- MgH_2, rutile lattice, PBE/DZVP



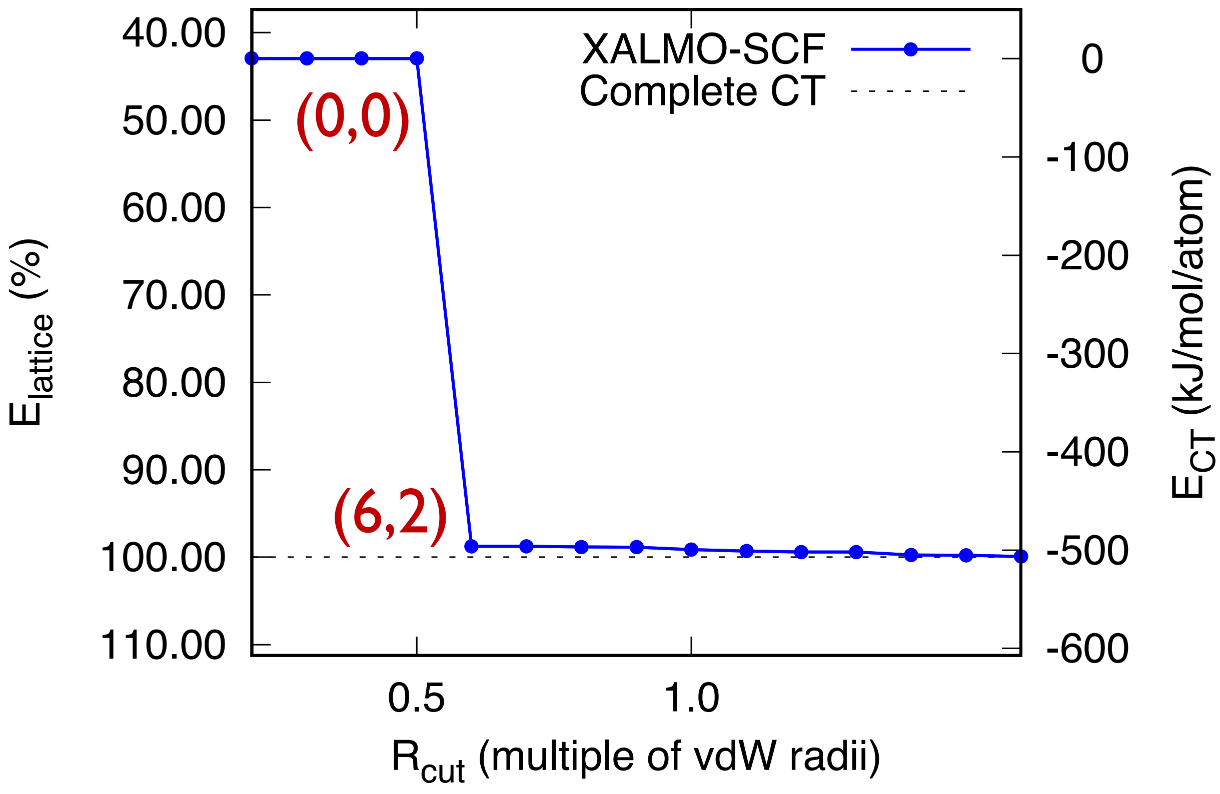
* Ionic component is 77% of lattice E

* Delocalization E is relatively small

IONIC!

ē delocalization in semiconductor

- TiO_2, rutile lattice, BLYP/DZVP



Keywords for ALMO EDA

```
&DFT

  &ALMO_SCF

    &ANALYSIS T
      FROZEN_MO_ENERGY_TERM    SUBLATTICE
      &PRINT
        &ALMO_EDA_CT
          FILENAME energy
        &END ALMO_EDA_CT
        &ALMO_CTA
          FILENAME charge
        &END ALMO_CTA
      &END PRINT
    &END ANALYSIS

    ALMO_SCF_GUESS             MOLECULAR
    DELOCALIZE_METHOD          FULL_X_THEN_SCF

  &END ALMO_SCF

  &SCF
    EPS_SCF 1.0E-6
  &END SCF

&END DFT
```

- Compute the energy of the 4 key electronic states:
  - Isolated
  - Frozen
  - Polarized
  - Delocalized

Keywords for ALMO EDA

```
&DFT

  &ALMO_SCF

    &ANALYSIS T
      FROZEN_MO_ENERGY_TERM    SUBLATTICE
      &PRINT
        &ALMO_EDA_CT
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        &END ALMO_EDA_CT
        &ALMO_CTA
          FILENAME charge
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      &END PRINT
    &END ANALYSIS

    ALMO_SCF_GUESS             MOLECULAR
    DELOCALIZE_METHOD          FULL_X_THEN_SCF

  &END ALMO_SCF

  &SCF
    EPS_SCF 1.0E-6
  &END SCF

&END DFT
```

- *Isolated and frozen states*
- Request by setting ALMO_SCF_GUESS to MOLECULAR and FROZEN_MO_ENERGY_TERM to SUBLATTICE
- Performs calculations on single centers (atoms or molecules) in the cell of the entire system. Expensive!
- Now, &SCF controls calculations on single molecules. Converge them tightly.

Keywords for ALMO EDA

```
&DFT

  &ALMO_SCF

    &ANALYSIS T
      FROZEN_MO_ENERGY_TERM     SUBLATTICE
      &PRINT
        &ALMO_EDA_CT
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          FILENAME charge
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    &END ANALYSIS

    ALMO_SCF_GUESS              MOLECULAR
    XALMO_TRIAL_WF              PROJECT_R0_OUT
    DELOCALIZE_METHOD           FULL_X_THEN_SCF

  &END ALMO_SCF

  &SCF
    EPS_SCF 1.0E-6
  &END SCF

&END DFT
```

- *Polarized state*
- Its energy is always computed in the two-stage ALMO SCF.
- Can be explicitly requested by setting XALMO_TRIAL_WF to PROJECT_R0_OUT

Keywords for ALMO EDA

```
&DFT

  &ALMO_SCF

    &ANALYSIS T
      FROZEN_MO_ENERGY_TERM     SUBLATTICE
      &PRINT
        &ALMO_EDA_CT
          FILENAME energy
        &END ALMO_EDA_CT
        &ALMO_CTA
          FILENAME charge
        &END ALMO_CTA
      &END PRINT
    &END ANALYSIS

    ALMO_SCF_GUESS              MOLECULAR
    XALMO_TRIAL_WF              PROJECT_R0_OUT
    DELOCALIZE_METHOD           FULL_X_THEN_SCF

  &END ALMO_SCF

  &SCF
    EPS_SCF 1.0E-6
  &END SCF

&END DFT
```

- *Final state with fully delocalized electrons (i.e. charge-transfer state)*
- DELOCALIZE_METHOD to FULL_SCF. The energy should reproduce the conventional SCF result exactly.
- Individual two-body COV can only be obtained with perturbation method: DELOCALIZE_METHOD to FULL_X. They are printed to the files specified in &PRINT.
- Recommendation use FULL_X_THEN_SCF to compute both perturbative and variational CT.

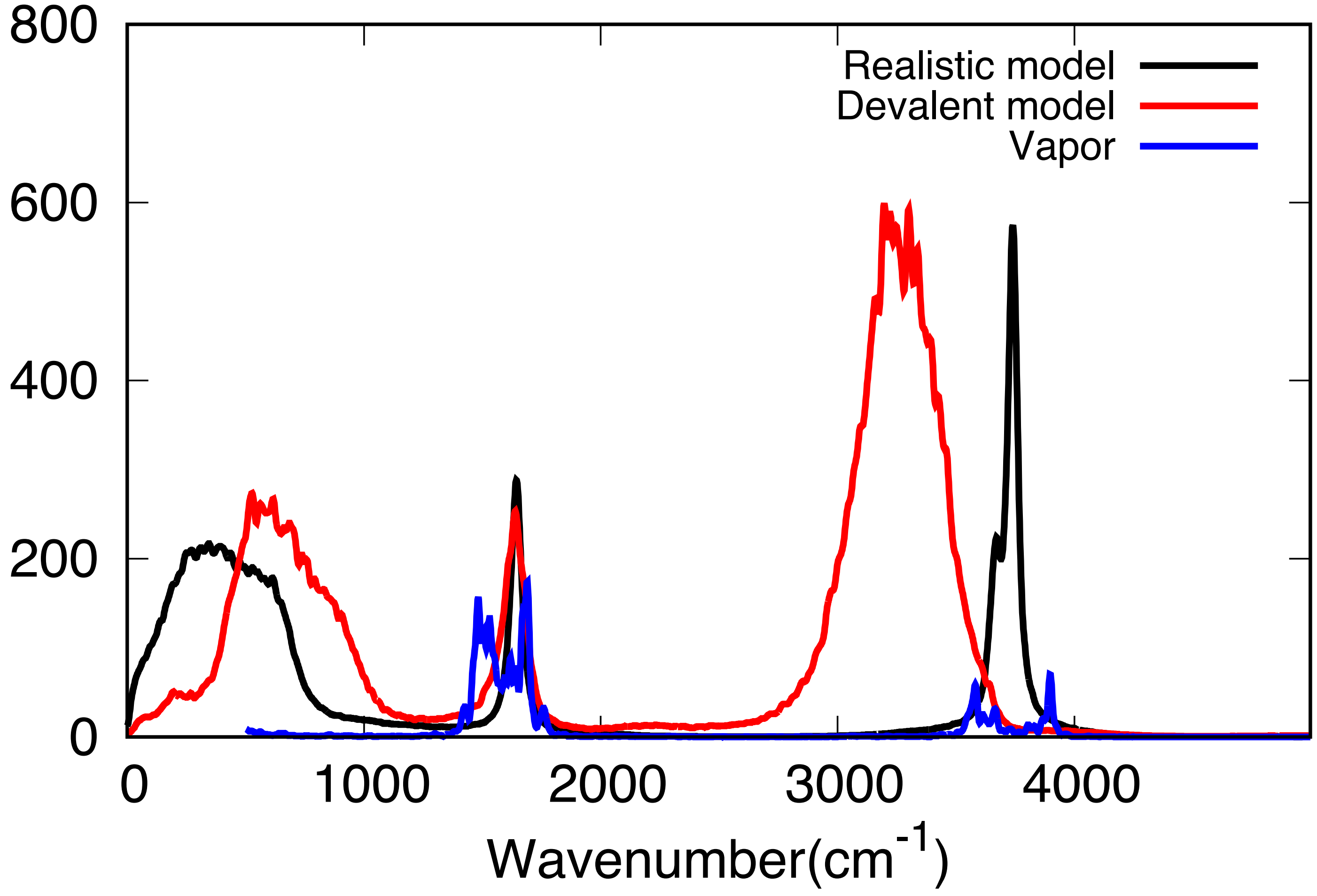
Contribution of COV to properties?

- ALMO DFT predicts, in agreement with other EDA, that:
  - Only 0.27% of an electron is transferred between molecules in a gas-phase water dimer
  - This transfer contributes 7 kJ/mol or ~35% of the overall stabilization.
  - In the cooperative H-bond network of liquid water, these are 1.1% of ē and 19 kJ/mol.

Fun facts on COV in liquid water

- ALMO AIMD shows that this seemingly small transfer has a profound effect on properties of liquid water. Without covalent interactions:
    - Self-diffusion coefficient is 7 times higher,
    - Viscosity coefficient is 1 order of magnitude smaller,
    - HB lifetime is 1 order of magnitude smaller,
    - Molecular dipole is half-way between gas-phase and liquid-phase value,
    - At the same time, dielectric constant is 2.5 times larger,
    - IR-spectrum is does not exhibit the characteristic shift and broadening in the O-H stretching region.

IR-spectra of liquid water



Devalent ALMO AIMD

```
&MOTION
  &MD
    ENSEMBLE NVT
    TEMPERATURE 300
  &END MD
&END MOTION

&FORCE_EVAL
 &DFT

    &QS
      ALMO_SCF T
    &END QS

    &ALMO_SCF
      DELOCALIZE_METHOD            NONE
    &END ALMO_SCF

  &END DFT
&END FORCE_EVAL
```

- &MD and &ALMO_SCF sections are standard. The Langevin error compensation trick is not required.
- DELOCALIZED_METHOD must be set to none to stop SCF at the block-diagonal ALMOs.

From quantity to quality

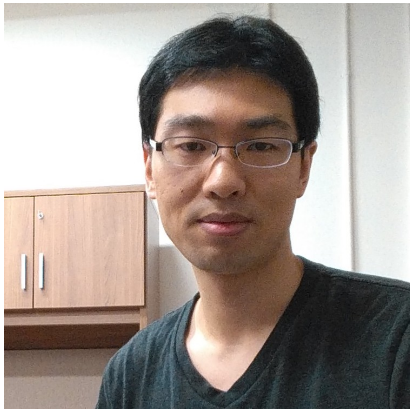
- The developed method can have a significant impact on modeling of complex systems making completely new phenomena accessible to AIMD:
  - Catalysis on interfaces.
  - Nucleation in liquid and solid phases.
  - Electronic structure and transport at heterojunctions.
  - Pressure-induced phase transition.
  - Modeling of complex phase diagrams.
  - Crystal structure search and prediction.
  - Free-energy simulations.
  - Calculation of accurate rate constants.

Summary

- **Approach:** confine electrons to a predefined localization radius by imposing constrains *directly on Kohn-Sham orbitals*.
- **Key:** robust SCF for localized orbitals with atomic(!) partitioning.
- **Key:** stable dynamics without sophisticated corrections.
- **Efficiency:** localization can be tuned to achieve substantial computational savings without compromising accuracy. Works extremely well with large basis set and shows early-offset linear-scaling behavior even for 3D systems.
- **Physics:** analysis of electronic effects responsible for chemical bonding and contribution of these effects to observable materials properties.
- **Limitations:** not efficient for metallic systems, further developments are underway.

Acknowledgements

Hayden Scheiber
Summer 2017



Dr. Yifei Shi

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