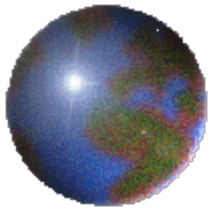

# *Augmented orbital minimization method for O(N) electronic structure calculations*

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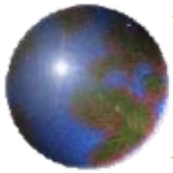


# *Density-Functional Theory (DFT)*

- DFT provides very accurate description of many systems within the same framework.
- DFT plays an important role in materials science, life science, mineral science, …
- I will introduce an efficient algorithm for linear scaling  electronic-structure calculations.

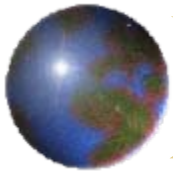
# *Kohn-Sham Equation (I)*

$$\mathcal{H}\,\psi_i = \epsilon_i \psi_i, \quad i = 1, ..., M$$

**Hamiltonian**

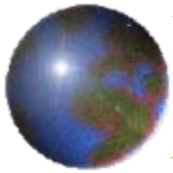
$$\mathcal{H} = -\frac{1}{2}\nabla^2 + V(\boldsymbol{r}) + \int \frac{n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} d\boldsymbol{r}' + \mu_{xc}(n(\boldsymbol{r}))$$

**Electron density** $$n(\boldsymbol{r}) = \sum_{i=1}^{M} |\psi_i(\boldsymbol{r})|^2$$



# *Kohn-Sham Equation (II)*

- Nonlinear eigenvalue problem
  - Computational cost grows as O(N^3)
  - Systems of > 1000 atoms intractable
- Linear scaling algorithms
  - Reduce computational cost based on approximation
  - S.Goedecker, Rev.Mod.Phys.**71** (1999) 1085.



# *Linear scaling methods*

- Divide and Conquer
  - Y.Wang
- Density Matrix
  - Li, Nunes, and Vanderbilt
- Fermi Operator Expansion
  - S.Goedecker
- Orbital Minimization Method (**OMM**)
  - Galli and Parrinello

We focus on OMM in this talk.

# *O(N^3) algorithm*

- Total energy

$$\widetilde{E}_{\mathrm{total}}[\widetilde{\psi}] = \sum_{i=1}^{N} \widetilde{H}_{ii},$$

is minimized under orthonormality constraints

$$<\widetilde{\psi}_i \mid \widetilde{\psi}_j> = \delta_{ij},$$

# *Maximally Localized Wannier Functions (MLWFs)*

- Total energy is invariant under any unitary transformation
- MLWFs minimize the spread S

$$S = \sum_{n=1}^{N} \left( \langle w_n | r^2 | w_n \rangle - \langle w_n | \mathbf{r} | w_n \rangle^2 \right)$$

among the unitary transformation of the ground state

# *Orbital Minimization Method (I)*

- Total energy functional:

$$E_{\text{total}}[\psi] = \sum_{i,j=1}^{N} (S^{-1})_{ij} \cdot H_{ij},$$

- Total energy is minimized wrt $\psi$ without any constraint
  - Implicit orthonormalization

# *Orbital Minimization Method (II)*

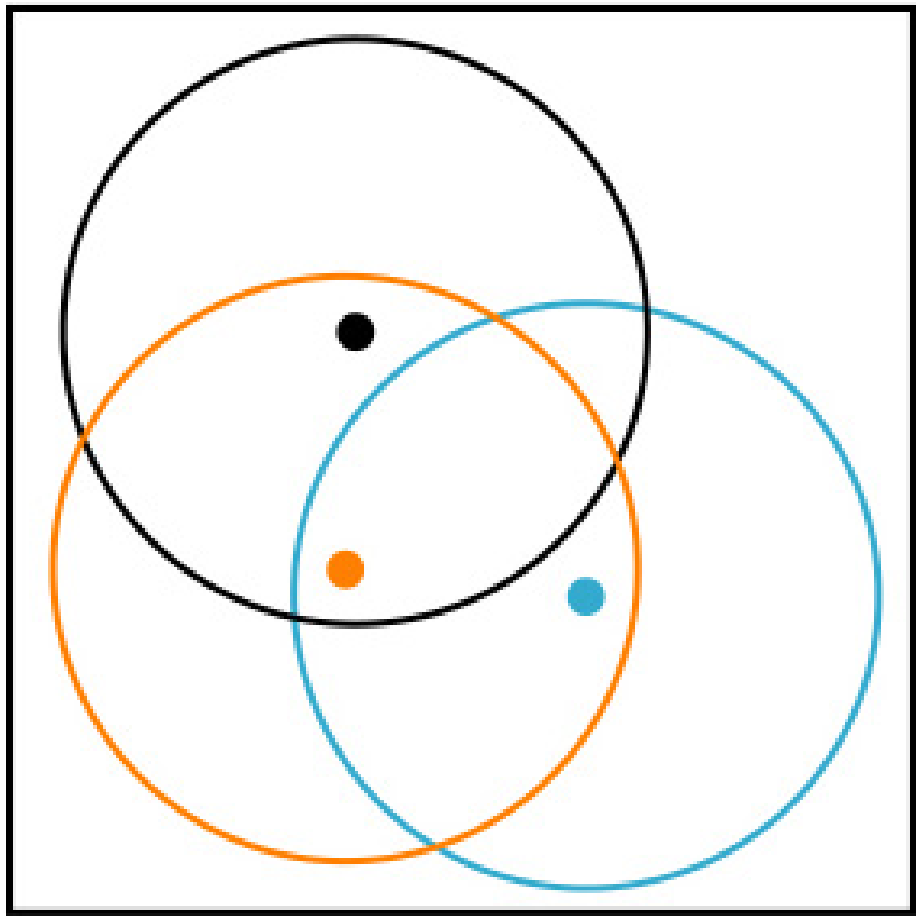
- Total energy is invariant under any transformation:

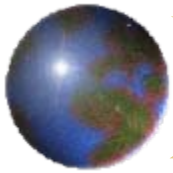
$$|\psi_i> = \sum_j X_{ij} |\psi'_j>$$

where Xij is nonsingular

# *Localization regions (LR)*

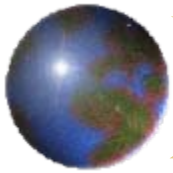
- Achieving O(N)
  - Localization constraints on the orbitals
    - Centers of LRs ≒ centers of MLWFs
  - good approximation for insulators & semiconductors





# *Properties of OMM (I)*

- Energy gap is required
  - Also assumed in most O(N) methods
- Nonorthogonal basis functions can be treated easily
- Variational principle
  - Total energies always converge from above



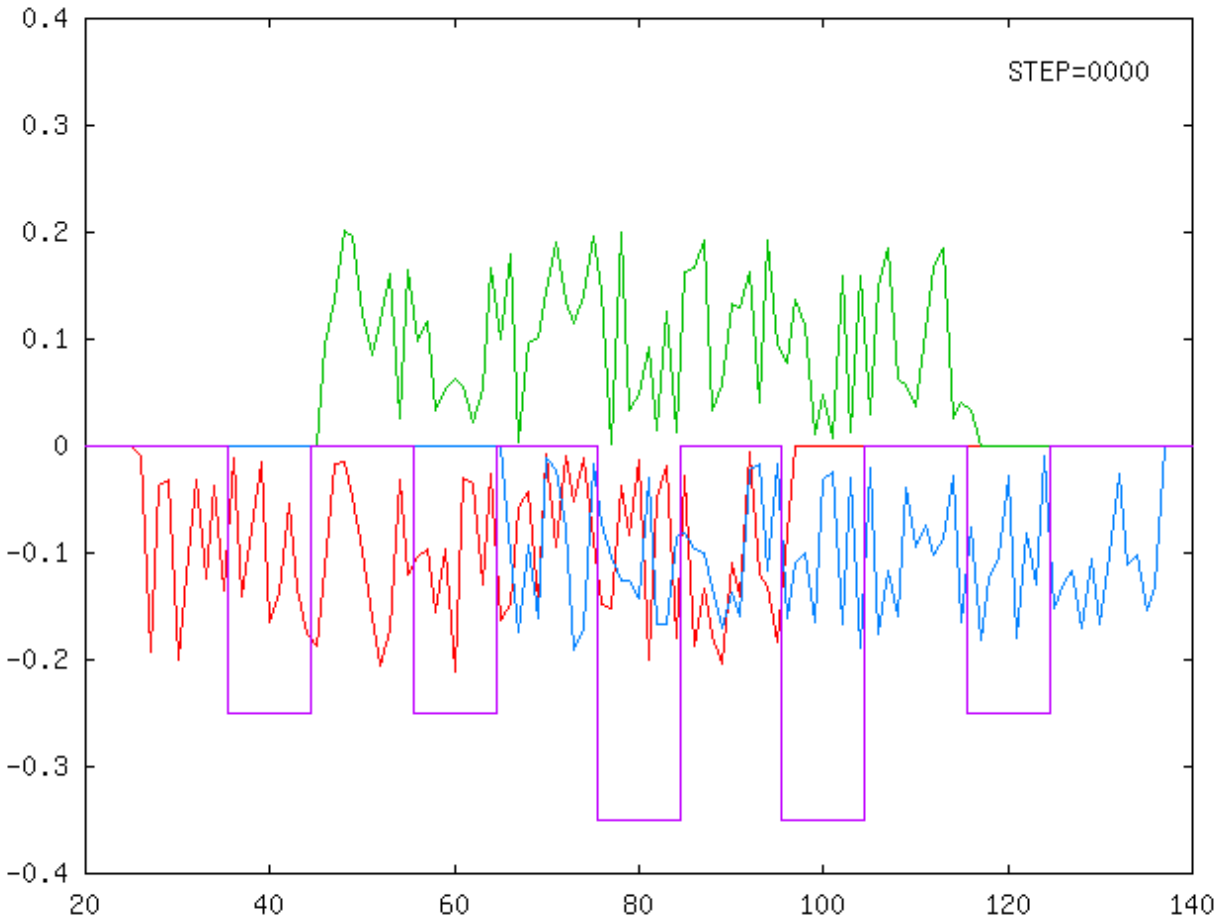
# *Properties of OMM (II)*

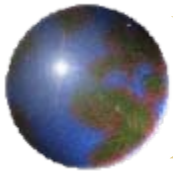
- Small overhead
  - No unoccupied states taken into account
  - Crossover at small system
- Easy to implement
  - analogous to conventional algorithm

# *Problems with OMM (I)*

- Extremely slow convergence
  - Often > 1000 iterations
- Presence of local minima
  - Ionic forces are also inaccurate
- These problems must be overcome for routine use of OMM !

# *Orbitals in OMM (3/5)*





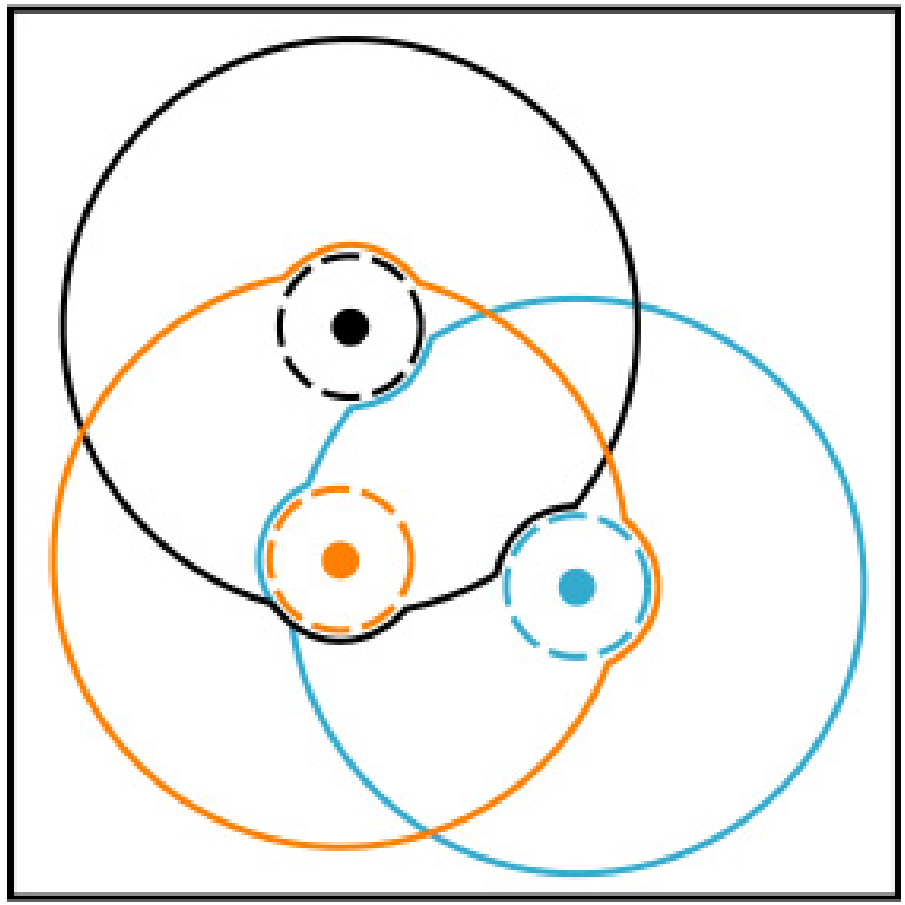
# *Problems with OMM (II)*

- Ideally, the orbitals should automatically converge to MLWF-like states at the minimum
  - case small LRs: OK
  - case large LRs: MLWF-like states have only minor (or no) advantage in total energy

    → total energy alone is insufficient to ...

# *Kernel Regions (KR)*

- KR and LR have same centers
- Each KR includes a MLWF center
- KRs do not overlap
- No partial overlap between KR and LR



# *Kernel Functions*

- Each kernel function ($\chi$) approximates the MLWF
  - Localized within each KR
  - Normalized
  - Orthogonal (by construction)
  - Not unique

# *Augmented Orbital Minimization Method (AOMM)*

- For any i,j (i ≠ j),

$$< \chi_j \mid \psi_i > = 0$$

  is required

- Orhogonalize each orbital approximately to MLWFs on other LRs, in the hope that $\psi \rightarrow$ MLWF on this LR

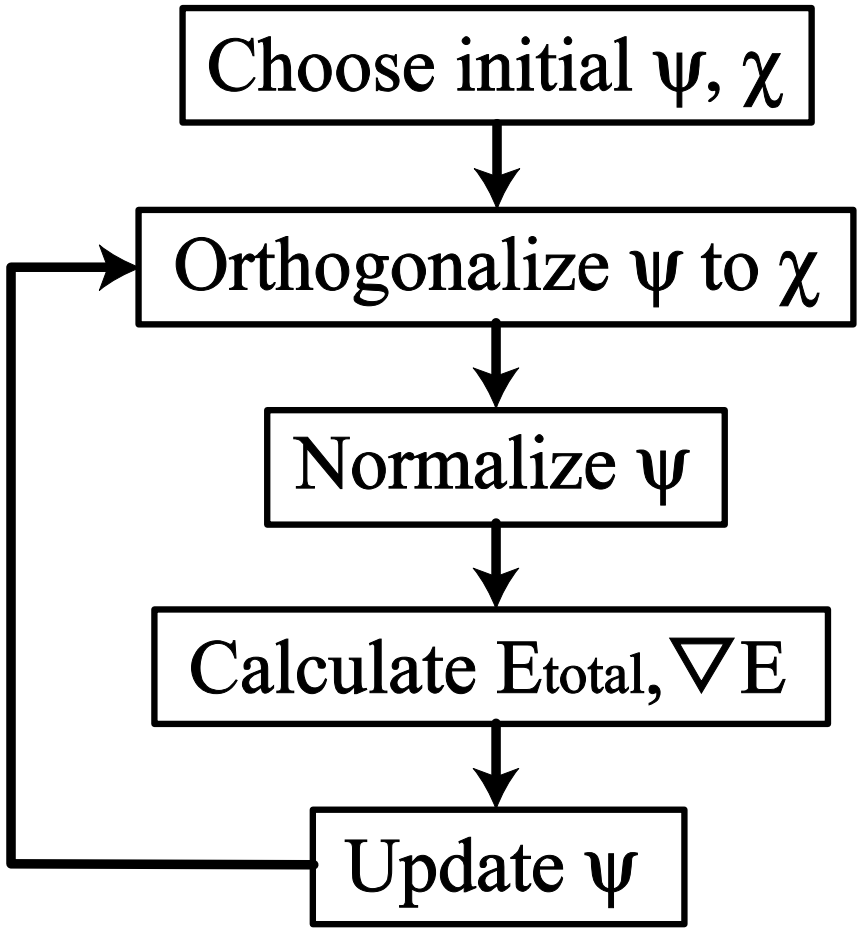
# *Explicit orthogonalization*

$$|\psi_i'> = \hat{P}_i |\psi_i>$$

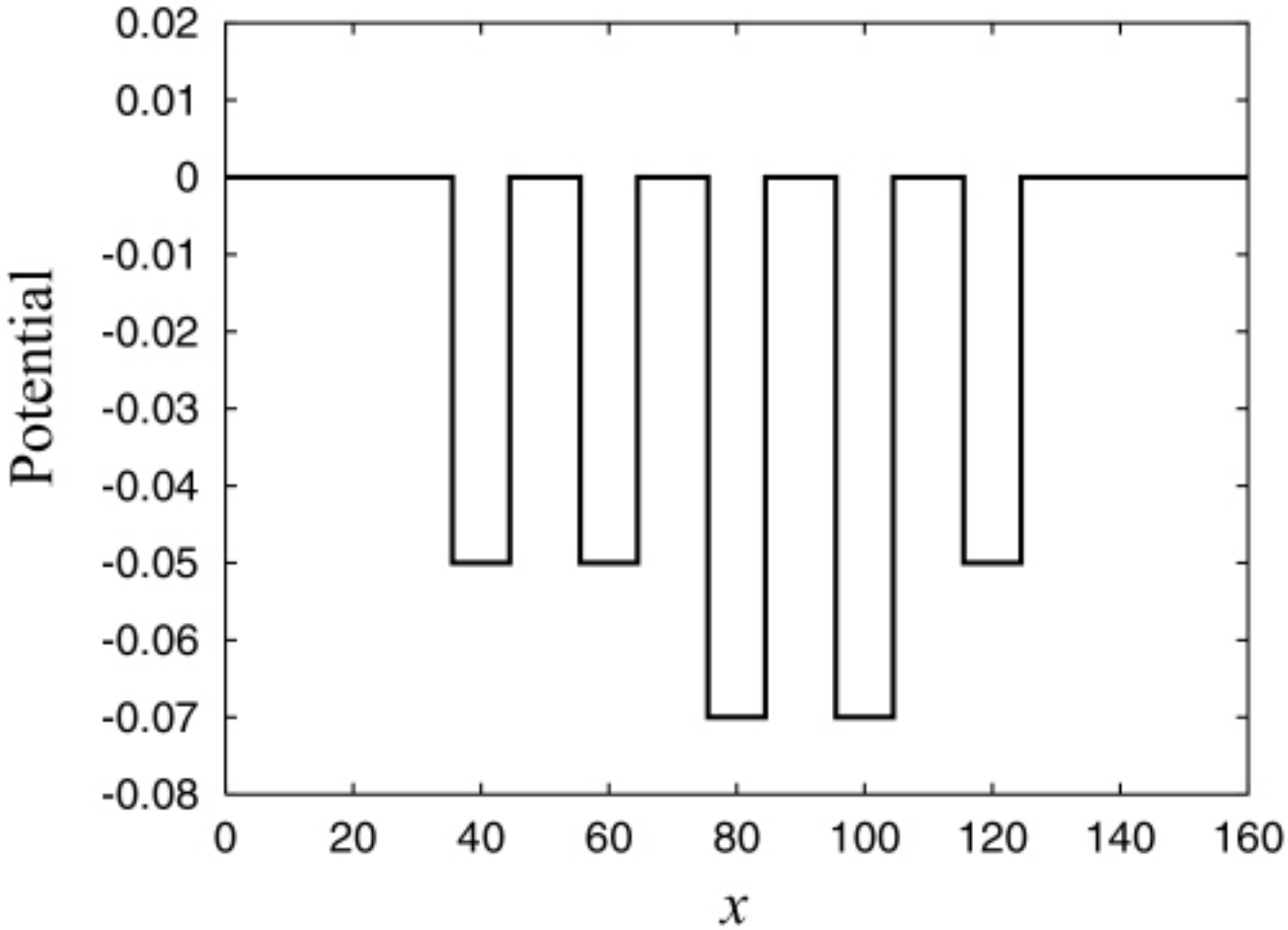
$$\hat{P}_i = I - \sum_{j \neq i} |\chi_j><\chi_j|$$

- Each orbital remains as localized as the original one

# *Flow chart of AOMM*



# *Model Potential*



# *Computational details (I)*

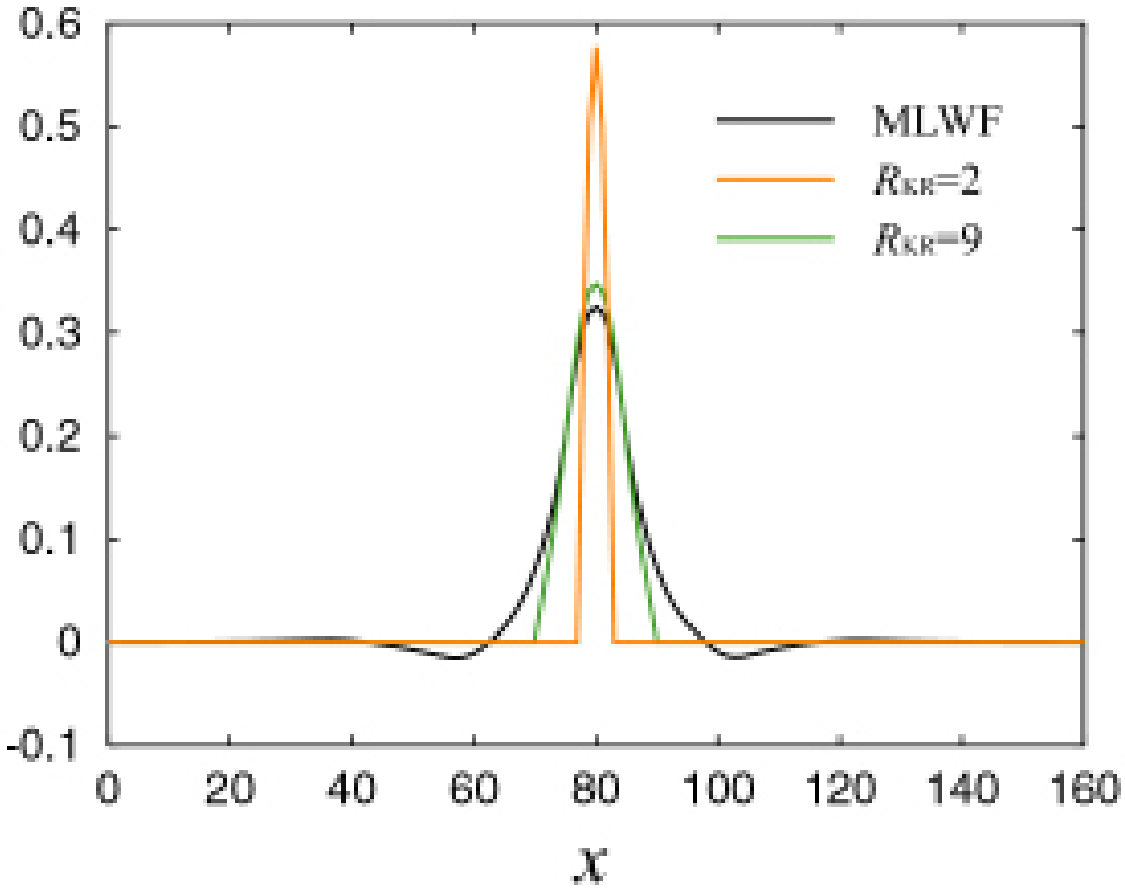
- 5 lowest occupied states
- LRs/KRs centered at x=40,60,80,100,120
  - consistent with potential wells
- Tridiagonal Hamiltonian:

$$\mathcal{H} = \begin{pmatrix} 2+v_0 & -1 & & & \\ -1 & 2+v_1 & -1 & & \\ & \cdots & \cdots & \cdots & \\ & & -1 & 2+v_{159} & -1 \\ & & & -1 & 2+v_{160} \end{pmatrix}$$

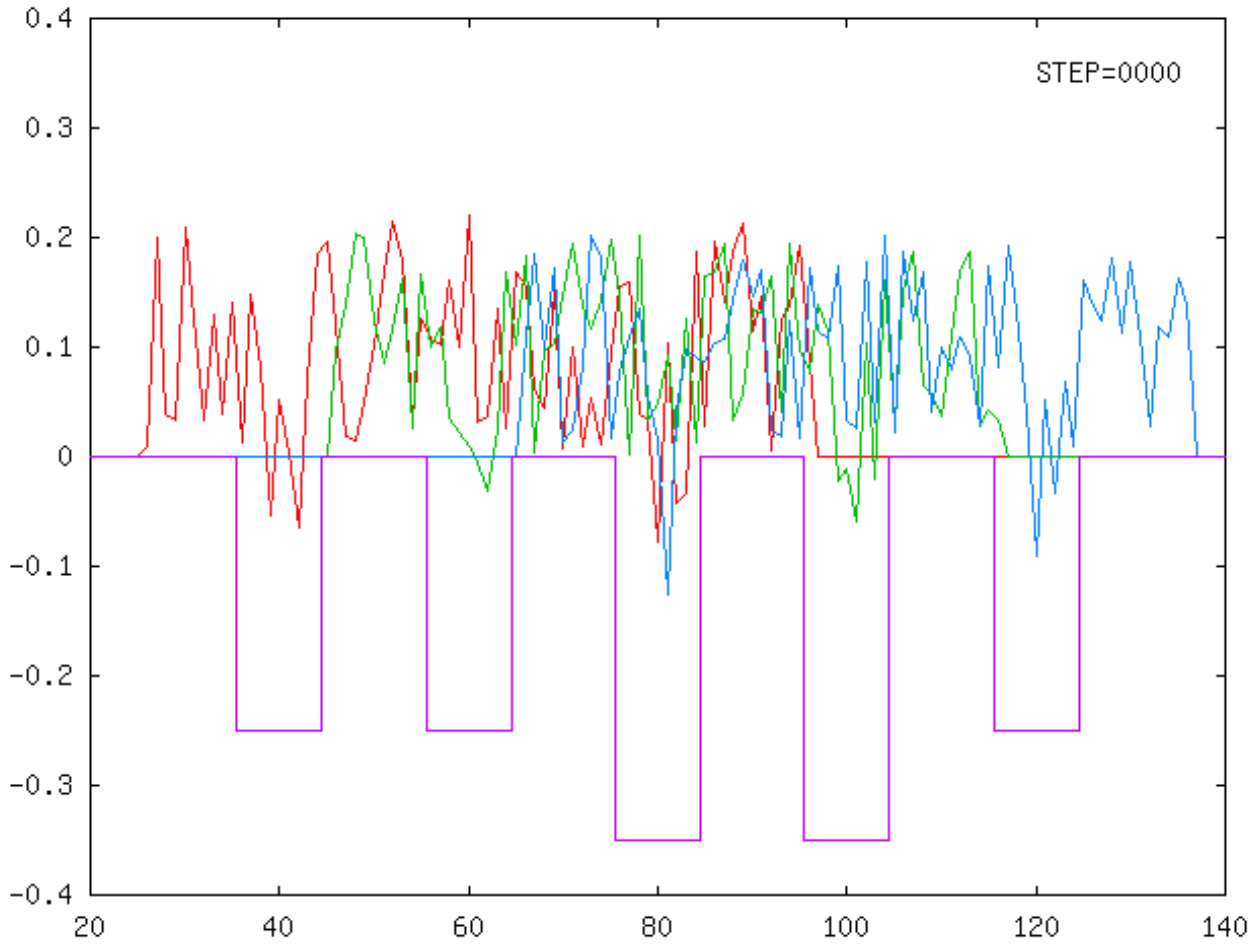
# *Computational details (II)*

- 100 ground state calculations
  - Random initial states
  - Iterative minimization with conjugate gradient method
  - “Failure” if exceeds 1000 iterations
    - excluded from statistics

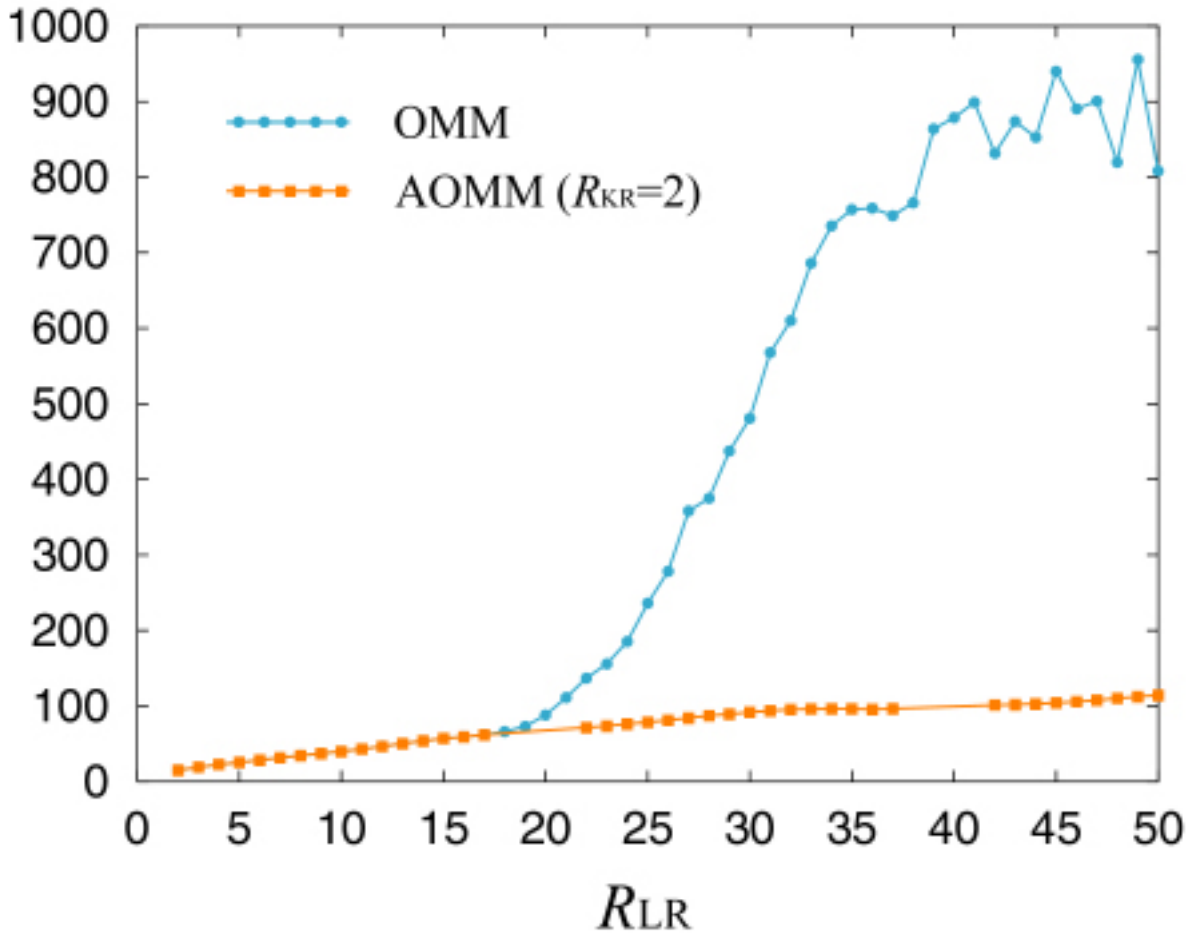
# *MLWF / Kernel functions*



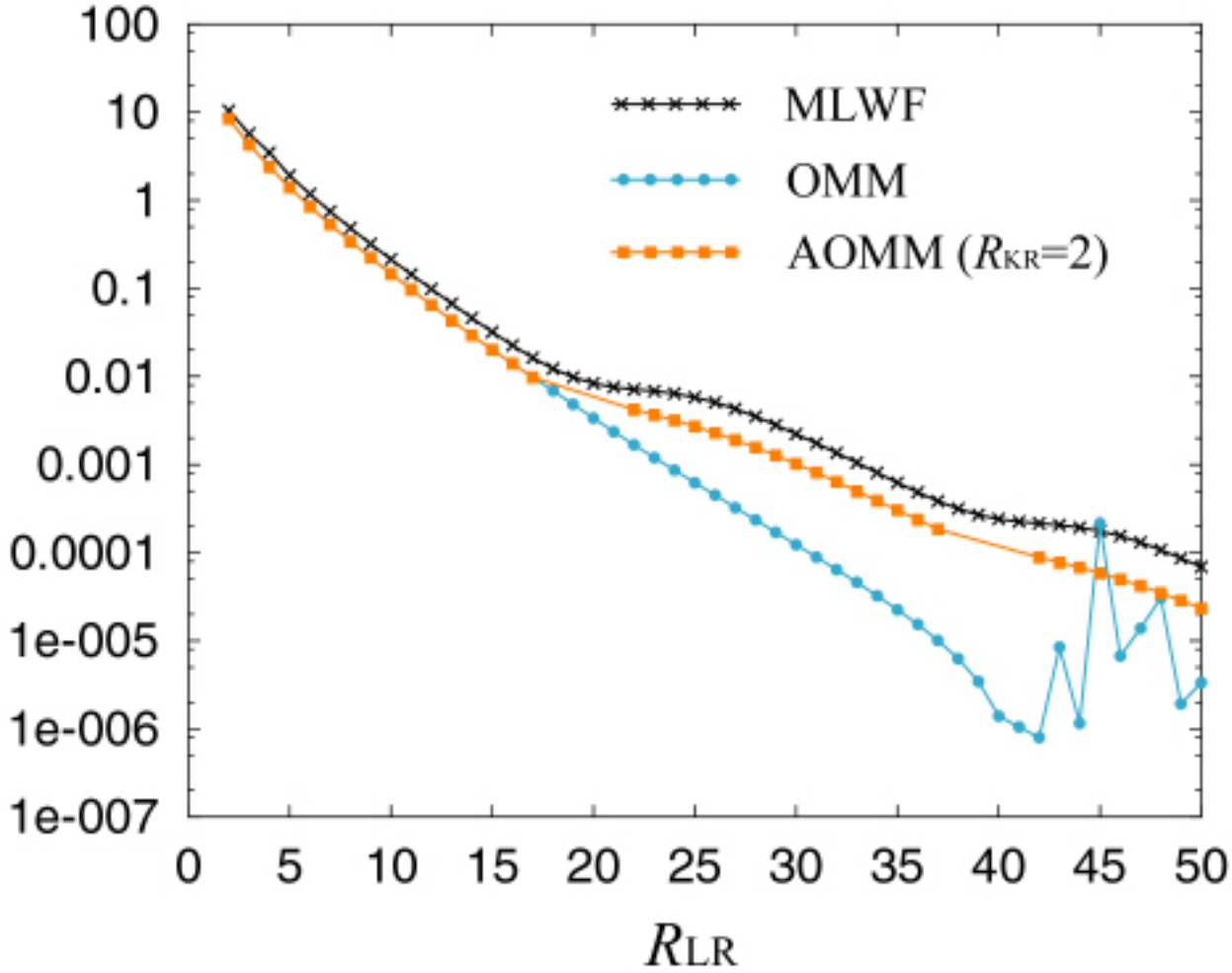
# *Orbitals in AOMM (3/5)*



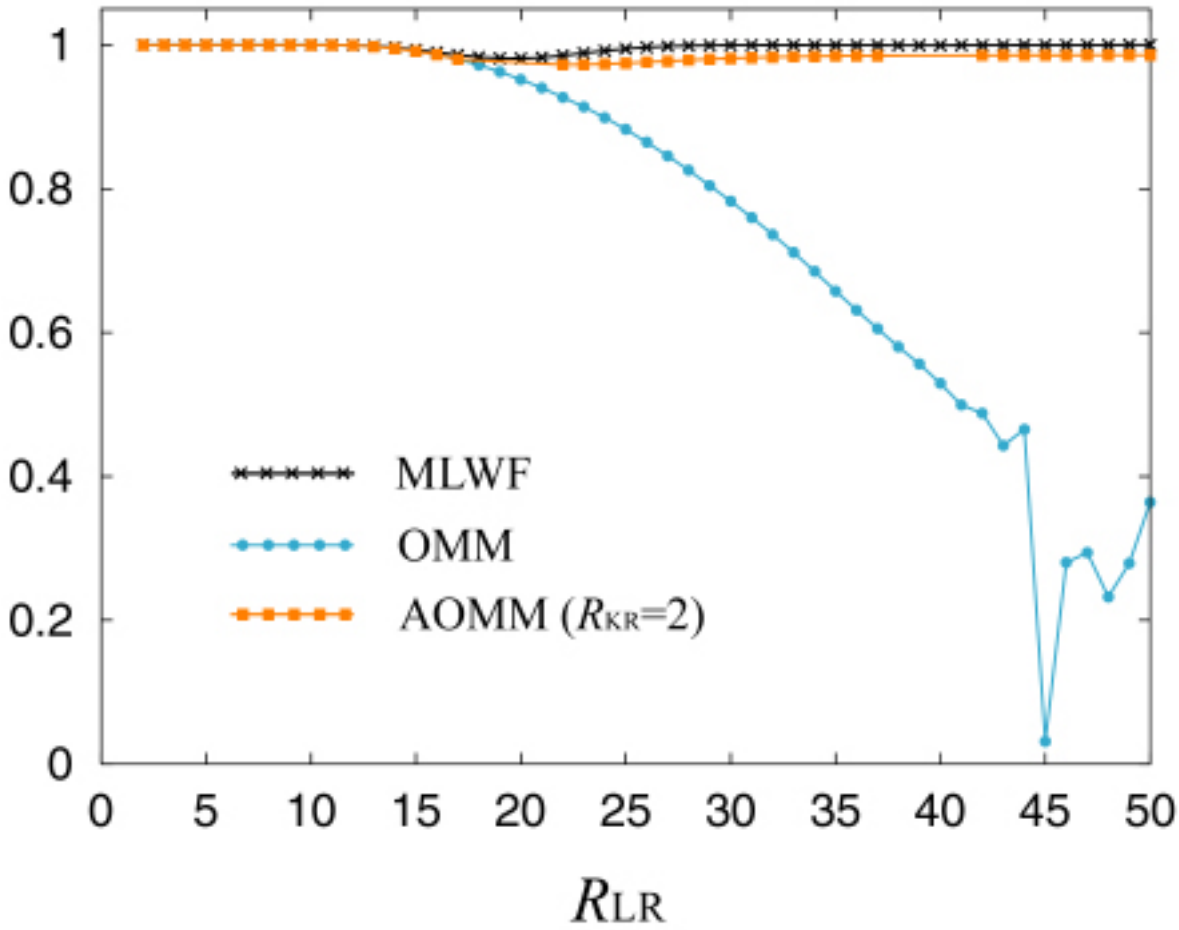
# *Average number of iterations*



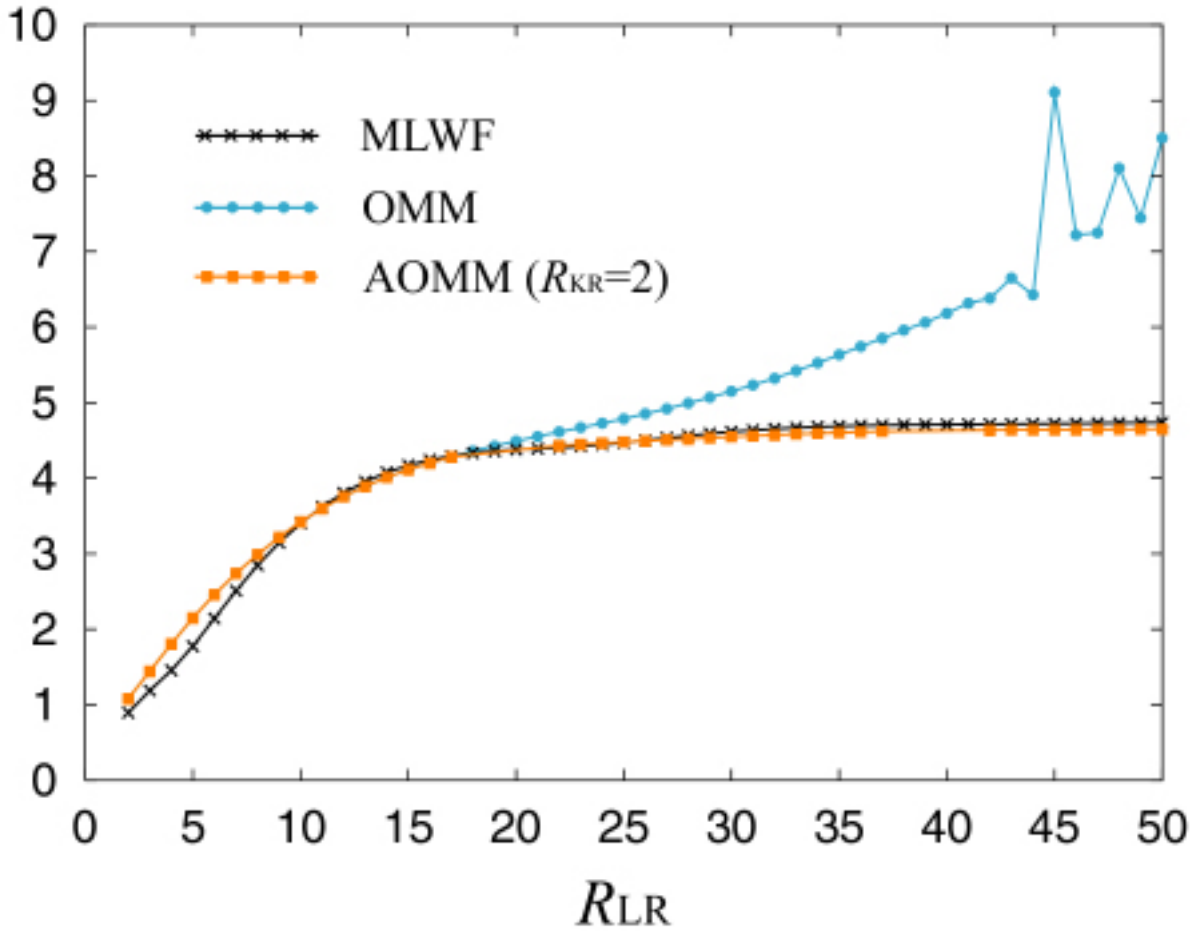
# *Errors in total energy*



# *Determinant of overlap matrix*



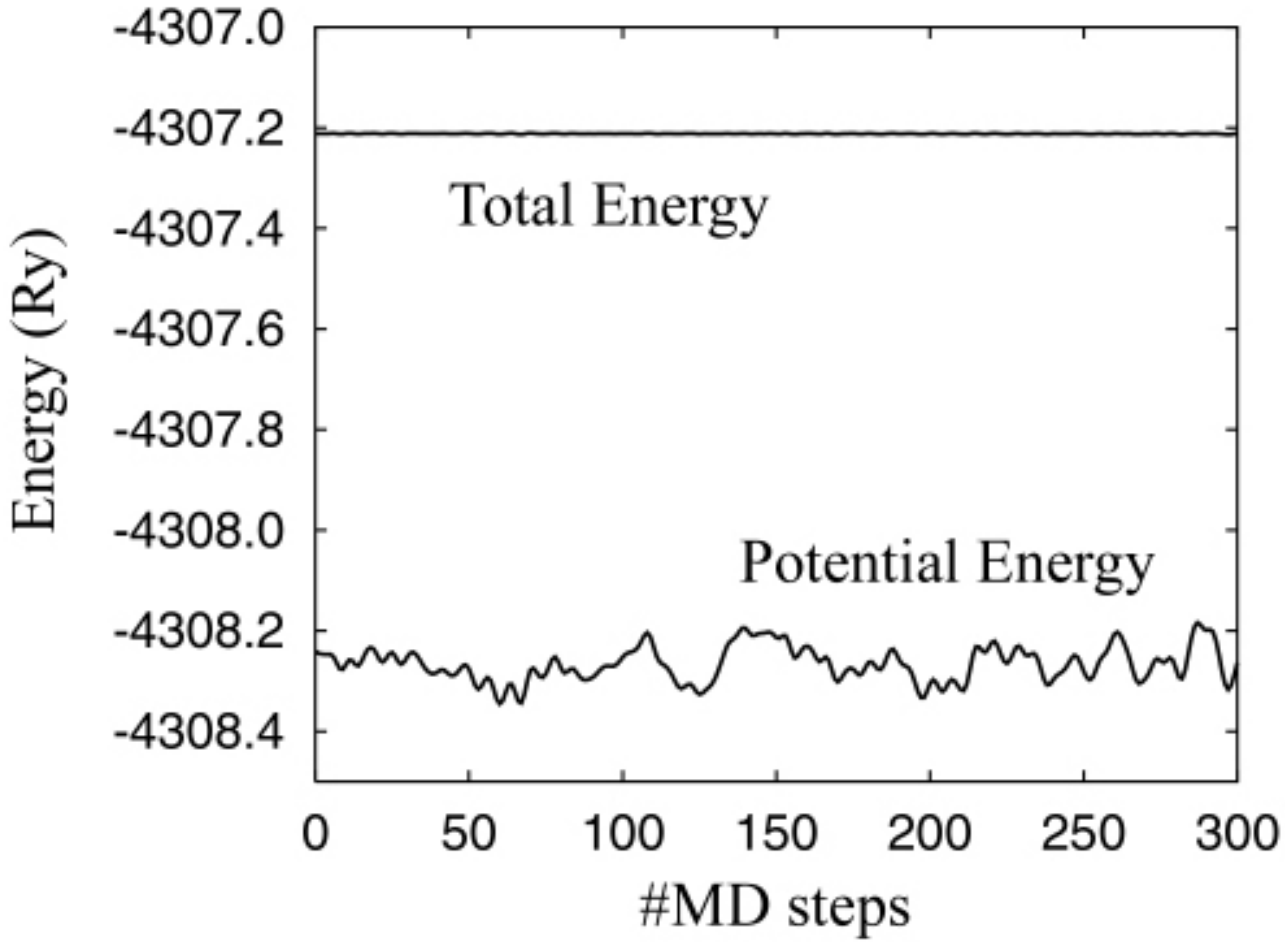
# *Average spread of orbitals*



# *Ab initio MD of liquid water*

- 125 water molecules in a supercell
  - L=29 Bohr
- GGA (PBE form)
- Normconserving pseudopotentials
- Born-Oppenheimer MD
  - timestep=40 a.u. (～0.97fs)
- Adaptive finite element basis
  - E. Tsuchida and M. Tsukada, J. Phys. Soc. Jpn. **67**, 3844 (1998).

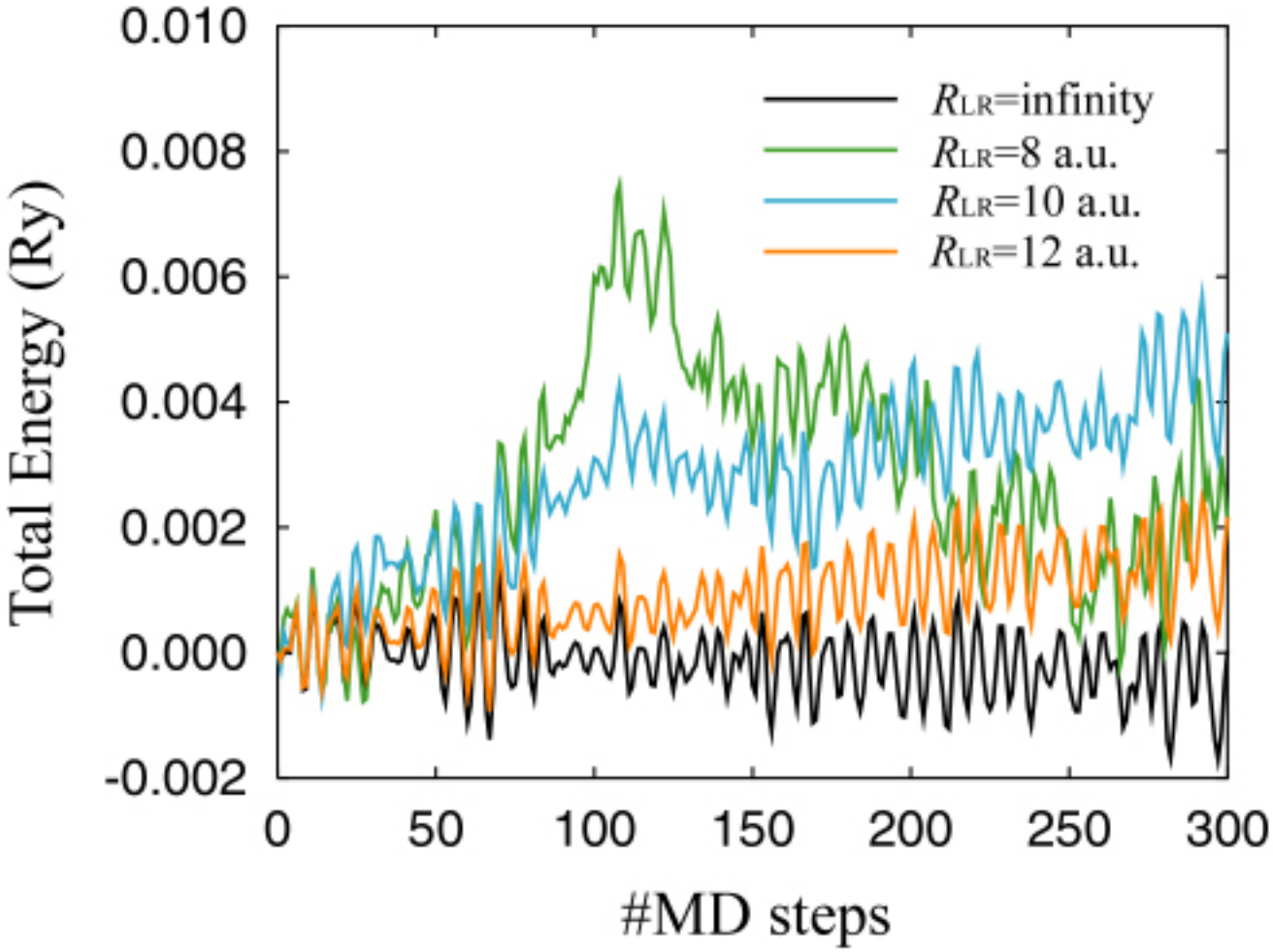
# *Case extended orbitals*



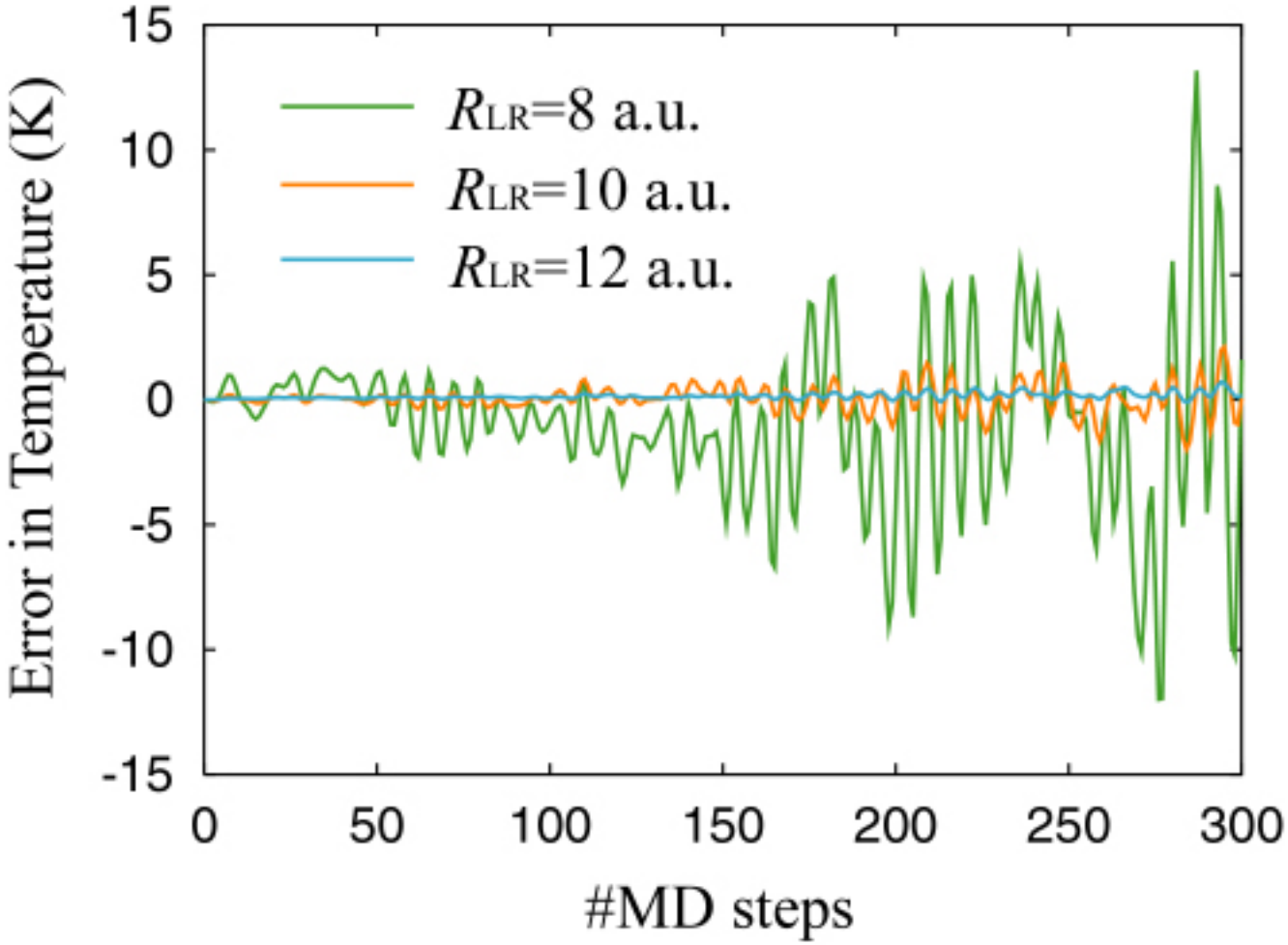
# *Case localized orbitals (O(N))*

- LRs and KRs centered at oxygen atoms
  - 4 orbitals /LR, KR
- Ionic forces evaluated assuming that LRs and KRs do not move
  - In practice, both move
  - Can have negative impact on total energy conservation

# *Total energy conservation*



# *Errors in ionic temperature*



# *Remaining problems*

- AOMM does not work when MLWF centers are unknown:
  - Use extended orbitals (only) for unpredictable ones
  - Adaptive localization centers (Fattebert et al.)

# *Conclusion*

- AOMM overcomes slow convergence and local minima problem
  - Computational overhead is minor
- Crossover with conventional method ~ 200-300 atoms
- Reference: **cond-mat/0608024**
  - pdf-file is available upon request