Nearer the nearsightedness principle:
Large-scale quantum chemical calculations

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Introduction

Density functional theory (DFT)

- Most widely used method for chemical and material calculations
- Simulations limited by size of system as computational effort is cubic-scaling

ONETEP [1]

- World-leading DFT software
- Density matrix is constructed from localised orbitals (NGWFs)

$$\rho(\boldsymbol{r},\boldsymbol{r}') = \sum_{\alpha,\beta} \varphi_\alpha(\mathbf{r}) \boldsymbol{K}^{\alpha\beta} \varphi^*_\beta(\mathbf{r}')$$

- Using the principle of nearsightedness [2], O(N) scaling achieved via truncating the density kernel $\boldsymbol{K}^{\alpha\beta}$

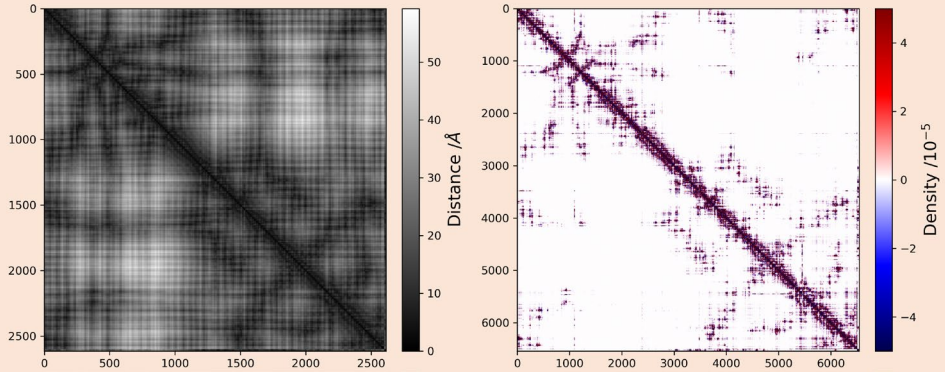
$$\rho(\boldsymbol{r},\boldsymbol{r}') = 0 \;\; when \;\; |\mathbf{r}-\mathbf{r}'| < r_{cut}$$

- One-for-all cut-off is insensitive, more fine-tuned truncation scheme was developed in this project:

$$\rho(\boldsymbol{r}_i,\boldsymbol{r}_j) = 0 \;\; when \;\; |\boldsymbol{r}_i - \boldsymbol{r}_j| < r_{ij}$$

where i and j are chemical elements

Methodology



Distance array between all atoms (left) and the sparsity pattern of the converged density kernel (right, ∞ cut-off) of T4 Lysozyme L99A/M102Q. Due to nearsightedness, the vast majority of kernel elements are zero and/or negligible.

- We performed single point energy calculations on T4 Lysozyme [3], varying the traditional cut-off distance parameter
- Compared total energies, sparsity patterns. We also studied convergence rates in ONETEP's inner and outer loop, which optimise $\boldsymbol{K}^{\alpha\beta}$ and $\{\varphi_\alpha(\mathbf{r})\}$, respectively
- Based on thresholds for entries of $\rho(\boldsymbol{r},\boldsymbol{r}')$ we proposed atom-pair kernel cut-offs. E.g., see part of Python script on the right:

```
Threshold: 1e-5
N-N     79.738 bohr
N-H     69.893 bohr
N-C     77.998 bohr
N-S     57.767 bohr
N-O     77.007 bohr
H-H     71.716 bohr
H-C     74.603 bohr
H-S     53.087 bohr
```

Results and Discussion

- New method outperformed calculations with similar density kernel filling w.r.t. total energy, but convergence rates were poorer
- The atom-pair truncation scheme is promising, future research should investigate effects of NGWF radii
- Atom-pair distances can serve as Machine Learning descriptors

References and Acknowledgement

[1] Skylaris, C. K. et al. The ONETEP Linear-Scaling Density Functional Theory Program. J. Chem. Phys. 2020, 152 (17).
[2] Kohn, W. Density Functional and Density Matrix Method Scaling Linearly with the Number of Atoms. Phys. Rev. Lett. 1996, 76 (17).
[3] Dziedzic, J. et al. Large-Scale DFT Calculations in Implicit Solvent - A Case Study on the T4 Lysozyme L99A/M102Q Protein. Int. J. Quantum Chem. 2013, 113 (6).

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