# Non-orthogonal Spin-adaptation of Coupled Cluster Methods with Quadruple Excitations

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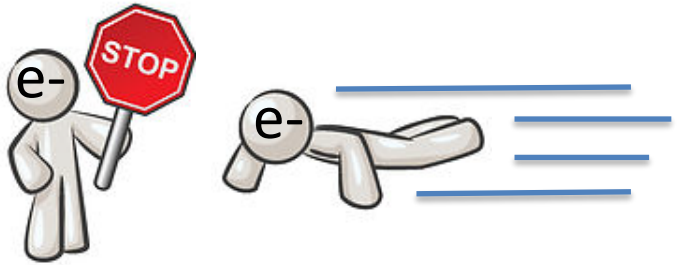
# Why Coupled Cluster?

- CC treats “electron correlation”: the instantaneous interaction of electrons.



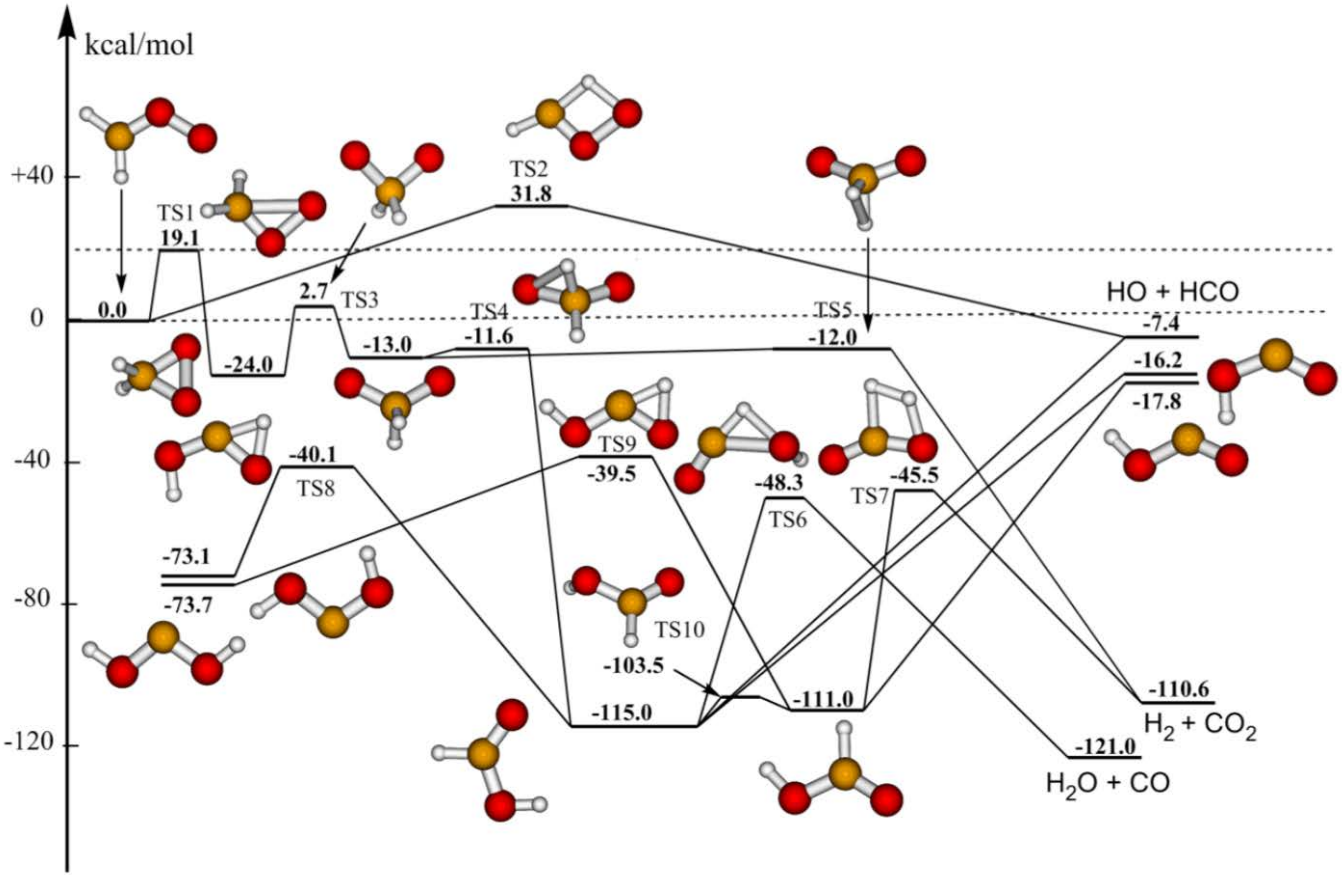

- CC is hierarchical, and converges to the exact answer.

CCSD → CCSDT → CCSDTQ → … → **FCI**

- CC is mathematically appealing: size extensivity, orbital invariance, naturally truncated (but not variational).

**Kinetics** and **thermodynamics** require very high accuracy.

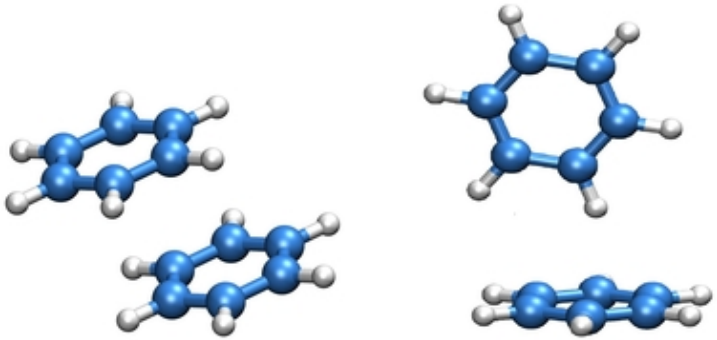
Combined methods including **CCSDTQ** generally give "sub-chemical" accuracy: < 1 kJ/mol.



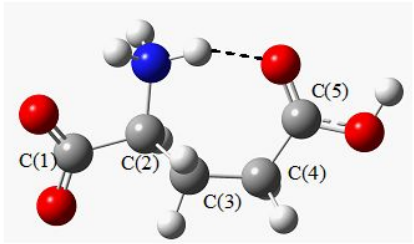

Nguyen, T. et al., unpublished

**Conformational structures** can be separated by very small energy differences.

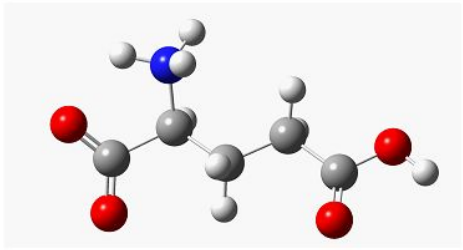
High accuracy needed to distinguish them.



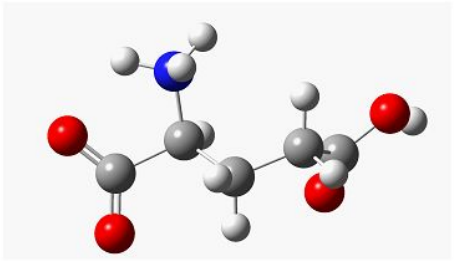
Schnell, M. et al. *Angew. Chem.*, **125**, *2013*, 5288–5292.



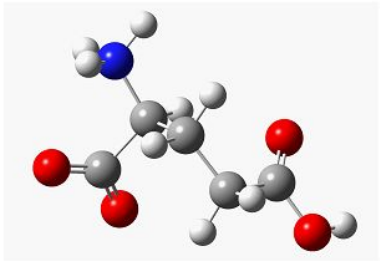

*tg*



*tt*



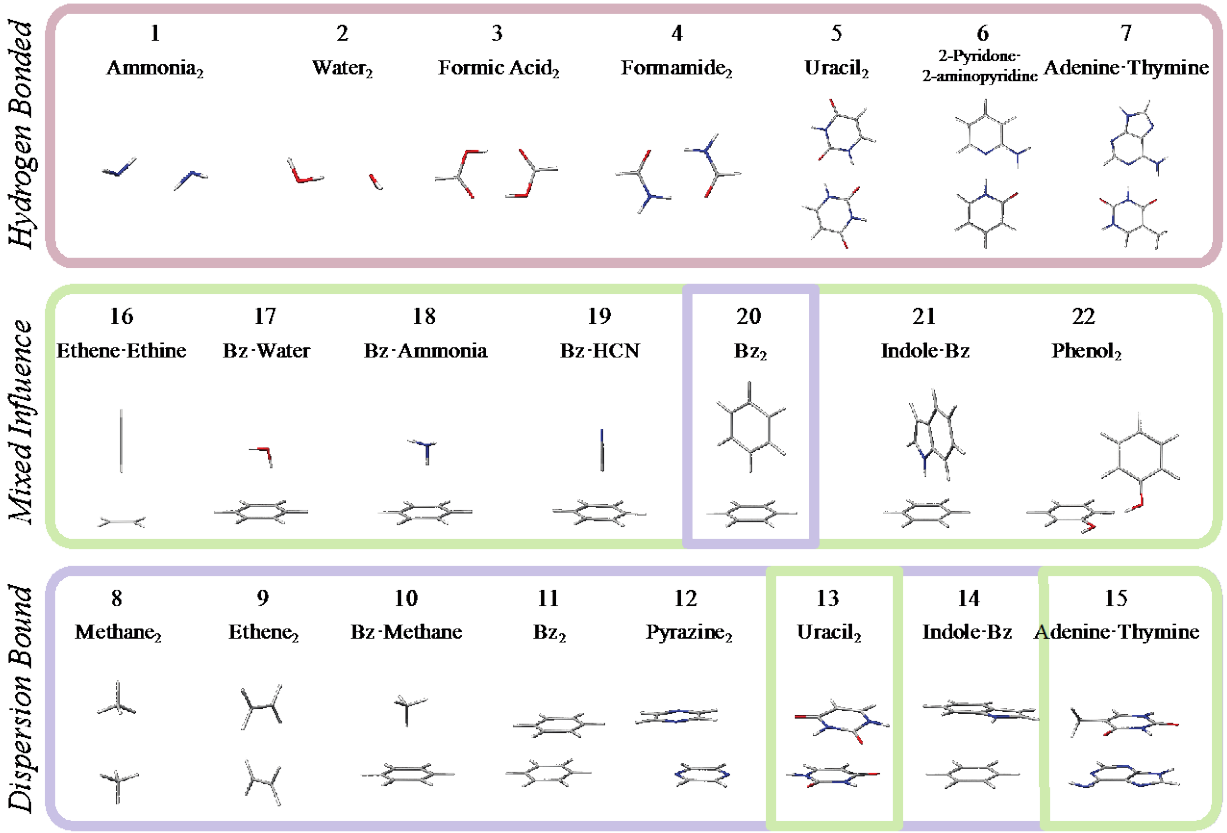
*tg'* (β)



*gg* (α)

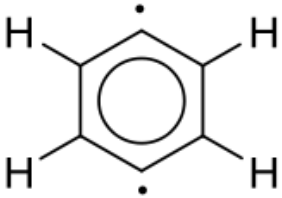
Redinha, J.S. et al., "Crystallization: From the Conformer to the Crystal" in Advanced topics on Crystal Growth

# S22

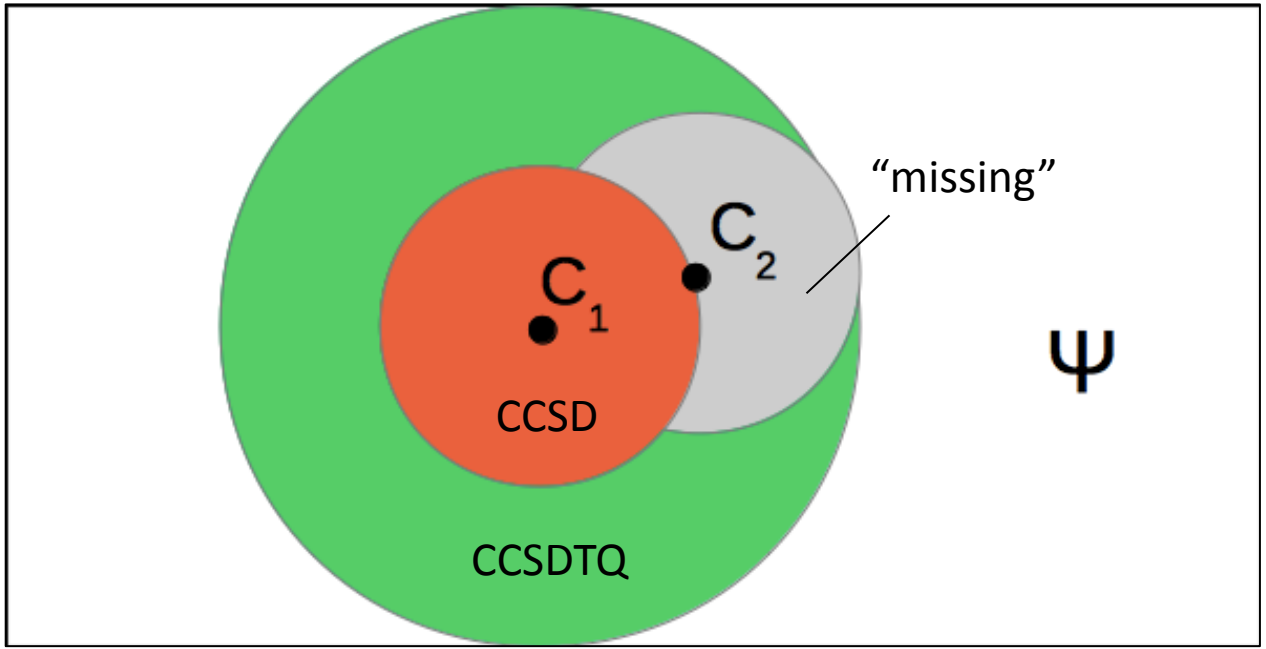



Quadruple excitations (CCSDTQ) can account for a significant fraction of the binding energy for some **complexes**.

High accuracy is needed for even **qualitative** description of the binding.




$$\Psi \sim |C_1\rangle \pm |C_2\rangle$$




**Multireference** (radical) systems don’t fit well with a single-reference method.

Adding excitations helps to fill in “missing” portions of the configuration space.

Real multireference CC methods are still in development.

# What is Coupled Cluster?

**SCF**:
Ignores electron correlation,
but still ~90% of total energy.

**Exact (CC ansatz)**:
Cluster operator **T** excites
electrons into “virtual” orbitals.

$$|\Phi_0\rangle \longrightarrow e^{\hat{T}}|\Phi_0\rangle$$

Truncating **T** is not exact, but improves rapidly the more you add.

$$\hat{T} = \overbrace{\hat{T}_1 + \hat{T}_2 + \hat{T}_3} + \hat{T}_4 + \ldots + \hat{T}_n$$

CC ansatz

$$e^{\hat{T}}|\Phi_0\rangle$$

+

Schrödinger equation

$$\hat{H}|\Psi\rangle = E|\Psi\rangle$$

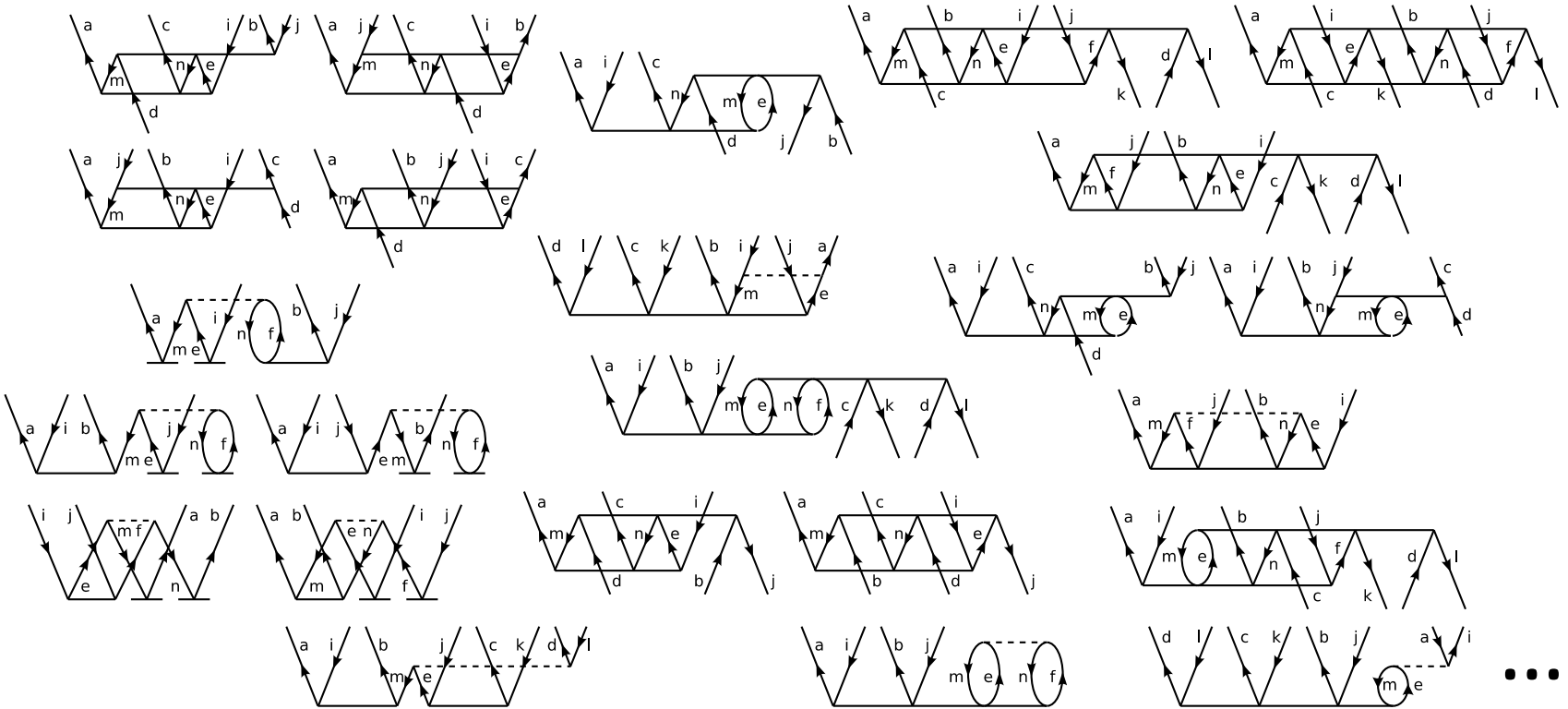
$$\langle\Phi_0|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = E_{CC}$$

- Similarity transform preserves spectrum for exact **T**.
- BCH expansion terminates naturally at $\mathbf{T}^4$.

$$\langle\Phi_{ij\ldots}^{ab\ldots}|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = 0$$

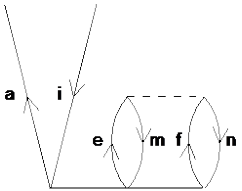
- Determines weights (amplitudes) of **T**.
- Non-linear coupled equations, requires iterative solution.

$$\langle \Phi_0 | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = E_{CC} \qquad \langle \Phi_{ij\ldots}^{ab\ldots} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0$$



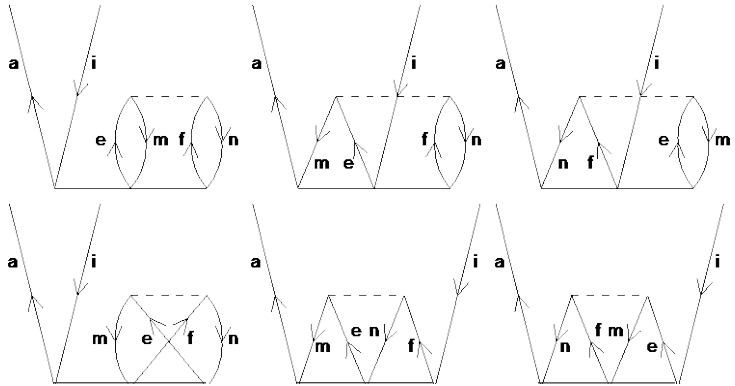
# Non-orthogonal Spin-adaptation

Spin-orbital (Brandow)




$$\frac{1}{4}\sum_{efmn} v_{ef}^{mn} t_{imn}^{aef}$$

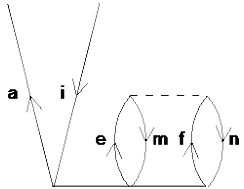
Orbital (Goldstone)




$$2\sum_{efmn} v_{ef}^{mn} t_{imn}^{aef} - \sum_{efmn} v_{ef}^{mn} t_{min}^{aef} - \sum_{efmn} v_{ef}^{mn} t_{nmi}^{aef}$$
$$- \sum_{efmn} v_{fe}^{mn} t_{imn}^{aef} + \frac{1}{2}\sum_{efmn} v_{fe}^{mn} t_{min}^{aef} + \frac{1}{2}\sum_{efmn} v_{fe}^{mn} t_{nmi}^{aef}$$

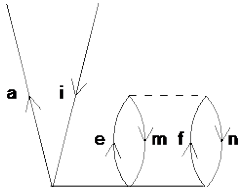
**Yuck!**

Spin-orbital (Brandow)




$$\frac{1}{4}\sum_{efmn} v_{ef}^{mn} t_{imn}^{aef}$$

Orbital (NOSA)




$$\frac{1}{2}\sum_{efmn} v_{ef}^{mn} t_{i\check{e}\check{f}}^{a\check{m}\check{n}}$$

Same equations as Goldstone approach, but:

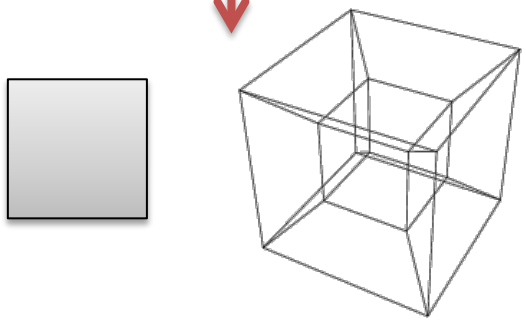
- Many fewer diagrams,
- Simple, factorized equations from the get-go,
- Easily applicable to any CC or CC-like method (including EOM, gradients, etc.).

# Nuts and Bolts - CCSDTQ

$$\hat{H} = \hat{F} + \hat{V}$$

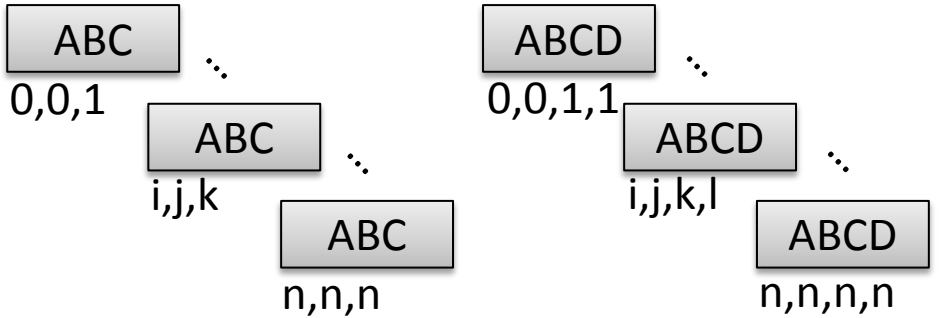
$$\hat{T}_1 \quad \hat{T}_2$$

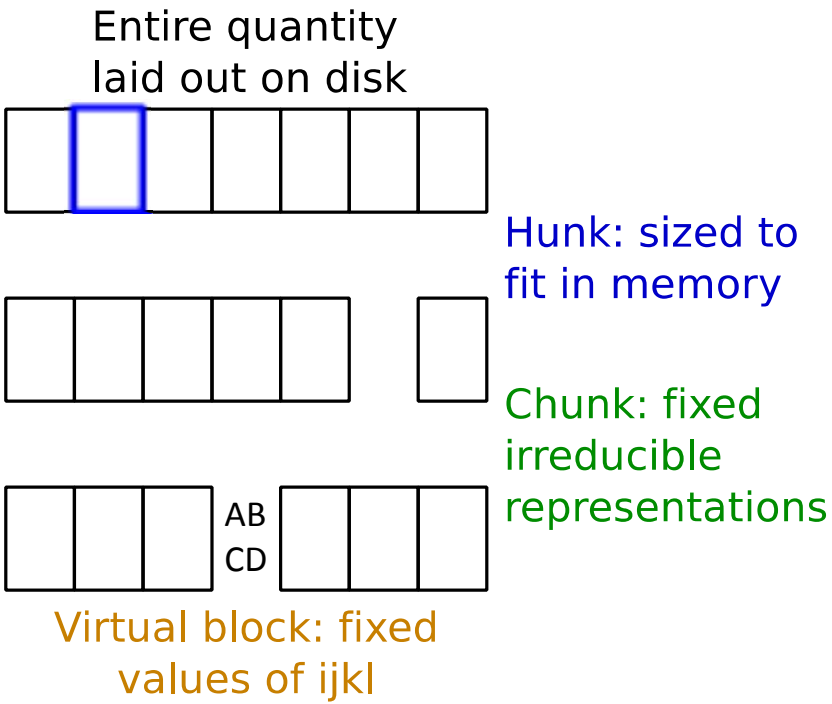
$$f_q^p \quad v_{rs}^{pq} \quad t_i^a \quad t_{ij}^{ab}$$



$$\hat{T}_3 \qquad \hat{T}_4$$

$$t_{i \le j \le k}^{abc} \qquad t_{i \le j \le k \le l}^{abcd}$$

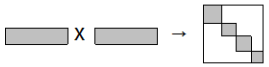




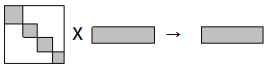

- Minimize disk I/O and other operations (permutation, spin-summation) by fitting as many ABC or ABCD blocks in memory as possible.
- Sort blocks by spatial symmetry so that non-matching blocks can be skipped.
- Use indices specified in each contraction to determine which blocks can match up.
- Use GEMM on the dense tensor ABC, ABCD, F, V, etc. parts.

18 types of tensor contractions can use GEMM "efficiently" (considering spatial symmetry):

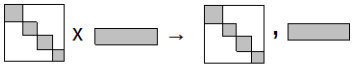
$a \cdot b \rightarrow ab$



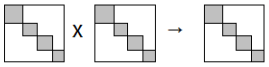
$[ab,ba] \cdot b \rightarrow a$



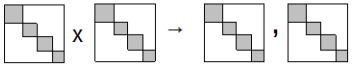
$ab \cdot c \rightarrow abc$



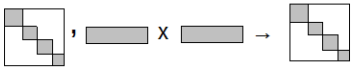
$[ab,ba] \cdot [bc,cb] \rightarrow ac$



$ab \cdot cd \rightarrow abcd$

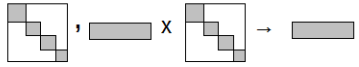


$abc \cdot c \rightarrow ab$

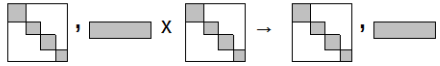


$abc \cdot d \rightarrow abcd$

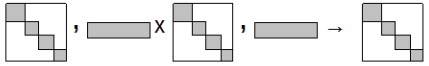
$abc \cdot ab \rightarrow c$



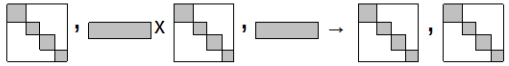
$abc \cdot [cd,dc] \rightarrow abd$



$abc \cdot abd \rightarrow cd$

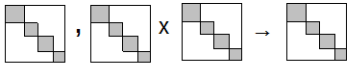


$abc \cdot dec \rightarrow abde$

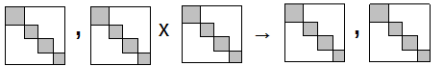


$abcd \cdot d \rightarrow abc$

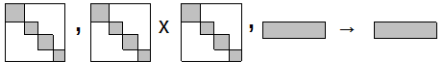
$[abcd,cdab] \cdot cd \rightarrow ab$



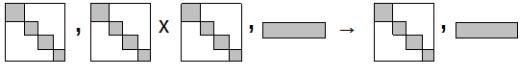
$abcd \cdot [de,ed] \rightarrow abce$



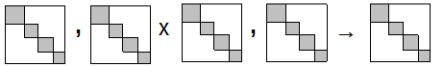
$abcd \cdot abc \rightarrow d$



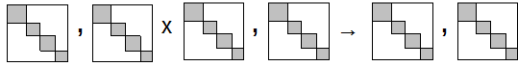
$[abcd,cdab] \cdot cde \rightarrow abe$



$abcd \cdot abce \rightarrow de$



$[abcd,cdab] \cdot [cdef,efcd] \rightarrow abef$



# Was It Worth It?

# Was It Worth It? Yes!

## CCSDTQ Timings (CPU sec.)

| | | | | CCSDT Iteration | | | CCSDTQ Iteration | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $n_o$ | $n_v$ | CFOUR | MRCC | Speedup | CFOUR | MRCC | Speedup |
| HSOH | cc-pVDZ | 7 | 29 | 3.73 | 28.5 | 7.6 | 559[a] | 3467[a] | **6.2** |
| $H_2O$ | aug-cc-pVTZ | 4 | 87 | 7.3 | 48.2 | 6.6 | 1179[a] | 5144[a] | **4.4** |
| $H_2C_4H_2$ | DZ | 10 | 34 | 8.65 | 68.1 | 7.9 | 2105[a] | 11028[a] | **5.2** |
| $O_3$ | aug-cc-pVDZ | 9 | 57 | 14.5 | 132 | 9.1 | 5973[b] | 36994[b] | **6.2** |
| $FO_3^-$ | cc-pVDZ | 13 | 39 | 32.2 | 170 | 5.3 | 14476[b] | 71030[b] | **4.9** |

## CCSDT(Q) Timings (CPU sec.)

| | | | | CCSDT Iteration | | | (Q) Contribution | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $n_o$ | $n_v$ | CFOUR | MRCC | Speedup | CFOUR | MRCC | Speedup |
| HSOH | cc-pVTZ | 7 | 79 | 222 | 1791 | 8.1 | 5131 | 169889 | **33.1** |
| $H_2O$ | cc-pVQZ | 4 | 110 | 18.1 | 123 | 6.8 | 351 | 36002 | **102.6** |
| $H_2C_4H_2$ | cc-pVDZ | 10 | 62 | 75.2 | 694 | 9.2 | 2632 | 47912 | **18.2** |
| $O_3$ | aug-cc-pVDZ | 9 | 57 | 14.5 | 132 | 9.1 | 447 | 12840 | **28.7** |
| $FO_3^-$ | cc-pVDZ | 13 | 39 | 32.2 | 170 | 5.3 | 739 | 12720 | **17.2** |

# Thanks!

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