Implementation of Coupled-Cluster molecular properties based on the Cholesky decomposition of two-electron integrals

Many-Body Theory: Nuclear Physics Meets Quantum Chemistry

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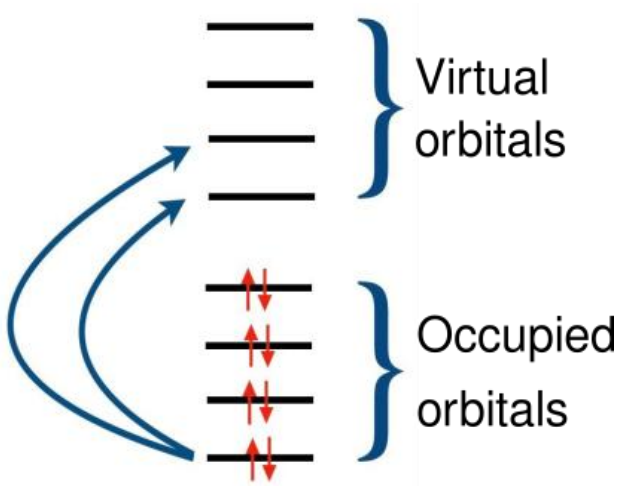
Where do we start?

$$|\Psi\rangle = e^{\hat{T}}|0\rangle$$

Coupled-Cluster (CC) theory:

+ Accurate and systematic

− High computational cost and memory requirements



Numerical strategies to mitigate the cost

$$(\mu\nu|\rho\sigma) = \sum_{P=1}^{N_{ch}} L_{\mu\nu}^{P} L_{\rho\sigma}^{P}$$

Cholesky decomposition (CD):

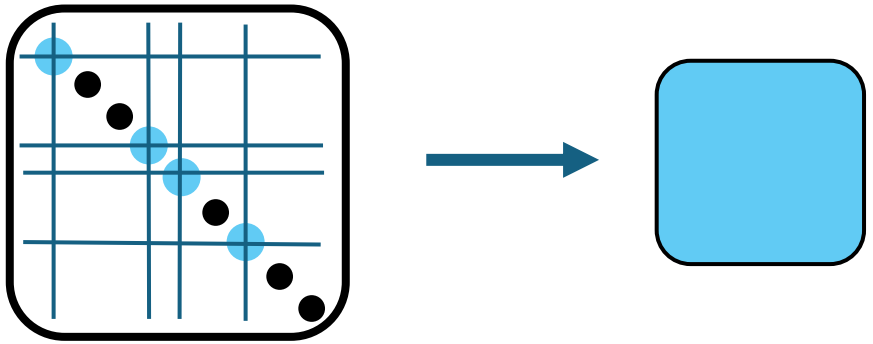
- Efficient compression of the information stored in the ERI matrix ✓
- Rigorous control of the approximation error ✓
- More expensive than other rank-reducing techniques… ✘

U. Bozkaya, C. D. Sherrill, *J. Chem. Phys.*, 144, 174103 (2016)
X. Feng, E. Epifanovsky, J. Gauss, A. I. Krylov, *J. Chem. Phys.*, 151, 014110 (2019)
H. Koch, A. Sánchez de Merás, T. B. Pedersen, *J. Chem. Phys.*, 118, 9481 – 9484 (2003)

Two-step CD algorithm

- **First step**: determine the Cholesky basis

$$L^P_{\sigma\rho} = \widetilde{(\mu\nu|\nu\mu)}^{-\frac{1}{2}} \left[(\sigma\rho|\nu\mu) - \sum_Q^{P-1} L^Q_{\sigma\rho} L^Q_{\mu\nu} \right]$$



- **Second step**: effectively compute the Cholesky vectors

$$L^P_{\mu\nu} = \sum_Q (\mu\nu|Q) K^{-T}_{QP}$$

Full exploitation of Abelian **point-group symmetry**

$$\Gamma_P = \Gamma_\mu \otimes \Gamma_\nu$$

Speed up of the decomposition procedure

F. Aquilante *et al.*, Chap. 13, *Linear Scaling Techniques in Computational Chemistry and Physics*, Springer (2011)
S. D. Folkestad, E. F. Kjønstad, H. Koch, *J. Chem. Phys.*, 150, 194112 (2019)
T. Zhang, X. Liu, E. F. Valeev, X. Li, *J. Phys. Chem. A*, 125, 4258-4265 (2021)

1. CCSD first-order properties

(Electric dipoles, geometrical gradients)

CCSD first-order properties

$$\hat{T} = \hat{T}_1 + \hat{T}_2$$
$$\hat{\Lambda} = \hat{\Lambda}_1 + \hat{\Lambda}_2$$

$$\mathcal{L} = \langle 0|(1+\hat{\Lambda})e^{-\hat{T}}\hat{H}e^{\hat{T}}|0\rangle + 2\sum_{ai} D_{ai}F_{ai} + \sum_{pq} I_{pq}(\boldsymbol{C}^T\boldsymbol{S}\boldsymbol{C} - \boldsymbol{I})_{pq}$$

1. Solve the **t-equations**
2. Solve the **Λ-equations**
3. Solve the **Z-vector equations** (for orbital relaxation effects)
4. Compute the CCSD one-body and two-body **density matrices**
5. Compute the **first-order property**

$$D_{pq} = \langle 0|(1+\hat{\Lambda})e^{-\hat{T}}\{\hat{p}^\dagger\hat{q}\}e^{\hat{T}}|0\rangle$$
$$\Gamma_{pqrs} = \langle 0|(1+\hat{\Lambda})e^{-\hat{T}}\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\}e^{\hat{T}}|0\rangle$$

J. Gauss, J. F. Stanton, R. J. Bartlett, *J. Chem. Phys.*, 95 (4), 2623-2638 (1991)
A. K. Schnack-Petersen *et al., J. Chem. Phys.*, 156 (24), 244111 (2022)

The particle-particle ladder

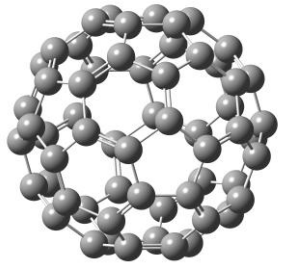
The rate-determining step is the computation of the particle-particle ladder (PPL) term:

$$Z_{Ab}^{lj} = \sum_{Ef} \mathcal{W}_{EfAb} \lambda_{Ef}^{lj}$$

$$\mathcal{W}_{EfAb} = \langle Ef|Ab\rangle - \sum_{m} t_m^f \langle Em|Ab\rangle - \sum_{M} t_M^E \langle Mf|Ab\rangle + \frac{1}{2} \sum_{Mn} \tau_{Mn}^{Ab} \langle Mn|Ef\rangle$$

1. O^2V^4 scaling for FLOPs
2. V^4 memory requirements

V: virtual orbitals
O: occupied orbitals



$\langle Ef|Ab\rangle$

3400 GB

vs.

$\sum_{P} L_{AE}^{P} L_{bf}^{P}$

29 GB

Our implementation strategy

$$\mathcal{W}_{EfAb} = \langle Ef|Ab\rangle - \sum_m t_m^f \langle Em|Ab\rangle - \sum_M t_M^E \langle Mf|Ab\rangle + \frac{1}{2}\sum_{Mn} \tau_{Mn}^{Ab} \langle Mn|Ef\rangle$$

1. Of course, perform the **Cholesky decomposition** of the integrals:

$$\mathcal{W}_{Ef\,Ab} = \sum_P \left[(L_{EA}^P - t_{EA}^P) L_{fb}^P - \sum_m t_m^f L_{EA}^P L_{mb}^P \right] \qquad t_{EA}^P = \sum_M t_M^E L_{AM}^P$$

2. Now, perform the contraction within a loop over virtual MOs (and parallelize it)

OpenMP

3. Exploit Abelian point-group symmetry

$$\Gamma_a \otimes \Gamma_b = \Gamma_e \otimes \Gamma_f = \Gamma_i \otimes \Gamma_j$$

Reduction up to a factor h^2

L. Melega, T. Nottoli, J. Gauss, F. Lipparini, *J. Phys. Chem. A,* 130 (10), 2097-2111 (2026)

Our implementation strategy

$$Z_{Ab}^{Ij} = \sum_{Ef} \mathcal{W}_{EfAb} \lambda_{Ef}^{Ij}$$

4. Apply the **symmetric-antisymmetric** algorithm:

Gain a pre-factor of 1/4

$$Z_{Ab}^{Ij} = S_{A\geq b}^{I\geq j} + A_{A\geq b}^{I\geq j}$$

$$S_{A\geq b}^{I\geq j} = \sum_{E\geq f}{}^{+}\lambda_{E\geq f}^{I\geq j}\,{}^{+}\mathcal{W}_{E\geq f,A\geq b} \qquad A_{A\geq b}^{I\geq j} = \sum_{E\geq f}{}^{-}\lambda_{E\geq f}^{I\geq j}\,{}^{-}\mathcal{W}_{E\geq f,A\geq b}$$

But what about this case?

$$M_{Bi}^{Dc} = \sum_{mn} \lambda_{Bi}^{Mn} \left(2\tau_{Mn}^{Dc} - \tau_{Nm}^{Dc}\right)$$

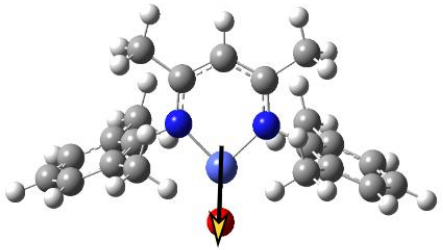
S. Saebø, P. Pulay, *J. Chem. Phys.*, 86, 914-922 (1987)

CCSD first-order properties

$$\Delta E^x = 2\sum_{\mu\nu} D_{\mu\nu} f^{(x)}_{\mu\nu} + \sum_{\mu\nu\rho\sigma} \widetilde{\Gamma}_{\mu\rho\nu\sigma} (\mu\nu|\rho\sigma)^x + 2\sum_{\mu\nu} I_{\mu\nu} S^x_{\mu\nu}$$

Electric dipole ← Electric field

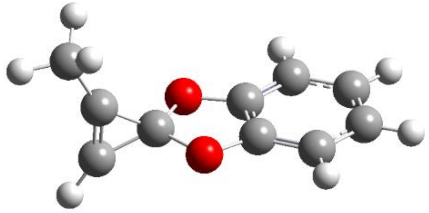
Nuclear displacements → **Geometrical gradients**



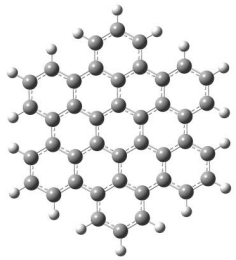
μ = 1.68 Debye

C_{2v} (nacnac)Co(III)O @ CD-CCSD/aug-*cc*-pVDZ

Without CD:
(<15 heavy atoms)



With CD:
(42 heavy atoms)



CD-CCSD geometrical gradients

$$(\mu\nu|\rho\sigma) = \sum_{PQ}^{N_{ch}} (\mu\nu|P)(KK^T)^{-1}_{PQ}(Q|\rho\sigma)$$

CD can reduce the computational cost, as we avoid transforming the two-body density matrix from the MO to the AO basis!

$$\frac{\partial(\mu\nu|\rho\sigma)}{\partial x} \approx \sum_{P} \left[\tilde{L}^{P}_{\mu\nu} \frac{\partial(P|\rho\sigma)}{\partial x} - \sum_{Q} \tilde{L}^{P}_{\mu\nu} \frac{\partial(P|Q)}{\partial x} \tilde{L}^{Q}_{\rho\sigma} + \frac{\partial(\mu\nu|P)}{\partial x} \tilde{L}^{P}_{\rho\sigma} \right]$$

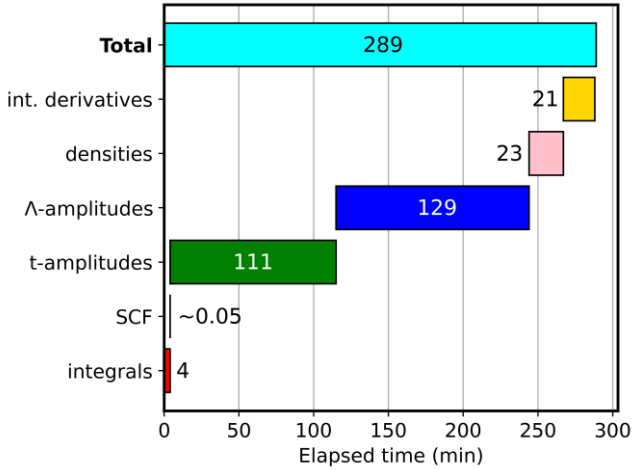
symmetry-adapted displacement

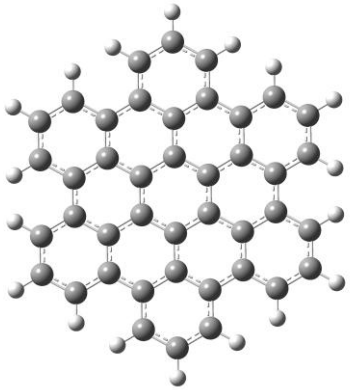
The symmetry-adapted gradient is then transformed into Cartesian coordinates!

CD-CCSD geometry optimizations

*D_{2h} is the point group enforced in the computation!

Geometry optimizations: convergence to 10^{-5} Hartree/Bohr (RMS gradient) by the BFGS method

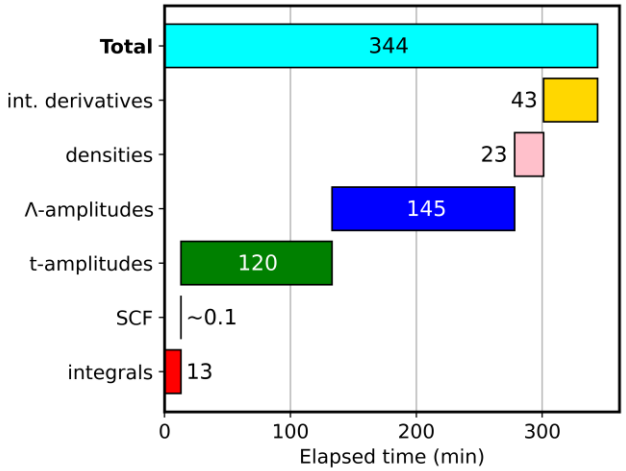


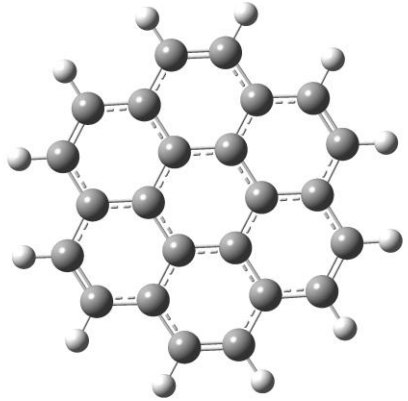


*D_{2h} hexabenzocoronene ($C_{42}H_{18}$)/*cc*-pVDZ (32 threads):

- 678 basis functions (135 occupied and 543 virtual MOs)
- ~3710 Cholesky vectors
- 24 optimization steps
- Total time: 4d 15h

@ AMD EPYC 7282 16 Core Processor (500 GB requested RAM)





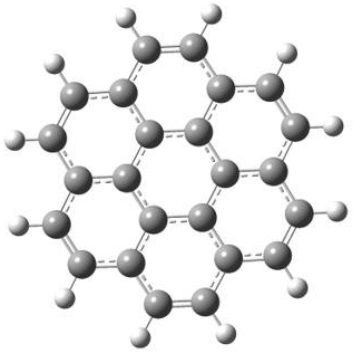
*D_{2h} coronene ($C_{24}H_{12}$)/*cc*-pVTZ (32 threads):

- 888 basis functions (78 occupied and 810 virtual MOs)
- ~4420 Cholesky vectors
- 8 optimization steps
- Total time: 2d

@ Intel Xeon Gold 6140 M (1TB requested RAM)

L. Melega, T. Nottoli, J. Gauss, F. Lipparini, *J. Phys. Chem. A,* 130 (10), 2097-2111 (2026)

Computational analysis



Factor of Reduction due to Symmetry (FRS) (for the O^2V^4 scaling term):

Theoretical FRS: 56
Achieved FRS: 19

$$\text{Theoretical FRS} = \frac{N_{C_1}}{N_{\text{sym}}}$$

$$N_{C_1} = O^2V^4 + V^4N_{ch}$$

Symmetry is worth it, even though the complex code structure leads to smaller, less efficient BLAS matrix-matrix products

$$N_{\text{sym}} = \sum_{\Gamma_1}\left[\left(\sum_{\Gamma_2} V_{\Gamma_2} V_{\Gamma_1\otimes\Gamma_2}\right)\left(\sum_{\Gamma_2} V_{\Gamma_2} V_{\Gamma_1\otimes\Gamma_2}\right)\left(\sum_{\Gamma_2} O_{\Gamma_2} O_{\Gamma_1\otimes\Gamma_2}\right)\right]$$
$$+\sum_{\Gamma_1}\left[\left(\sum_{\Gamma_2} V_{\Gamma_2} V_{\Gamma_1\otimes\Gamma_2}\right)\left(\sum_{\Gamma_2} V_{\Gamma_2} V_{\Gamma_1\otimes\Gamma_2}\right) N_{ch}(\Gamma_1)\right]$$

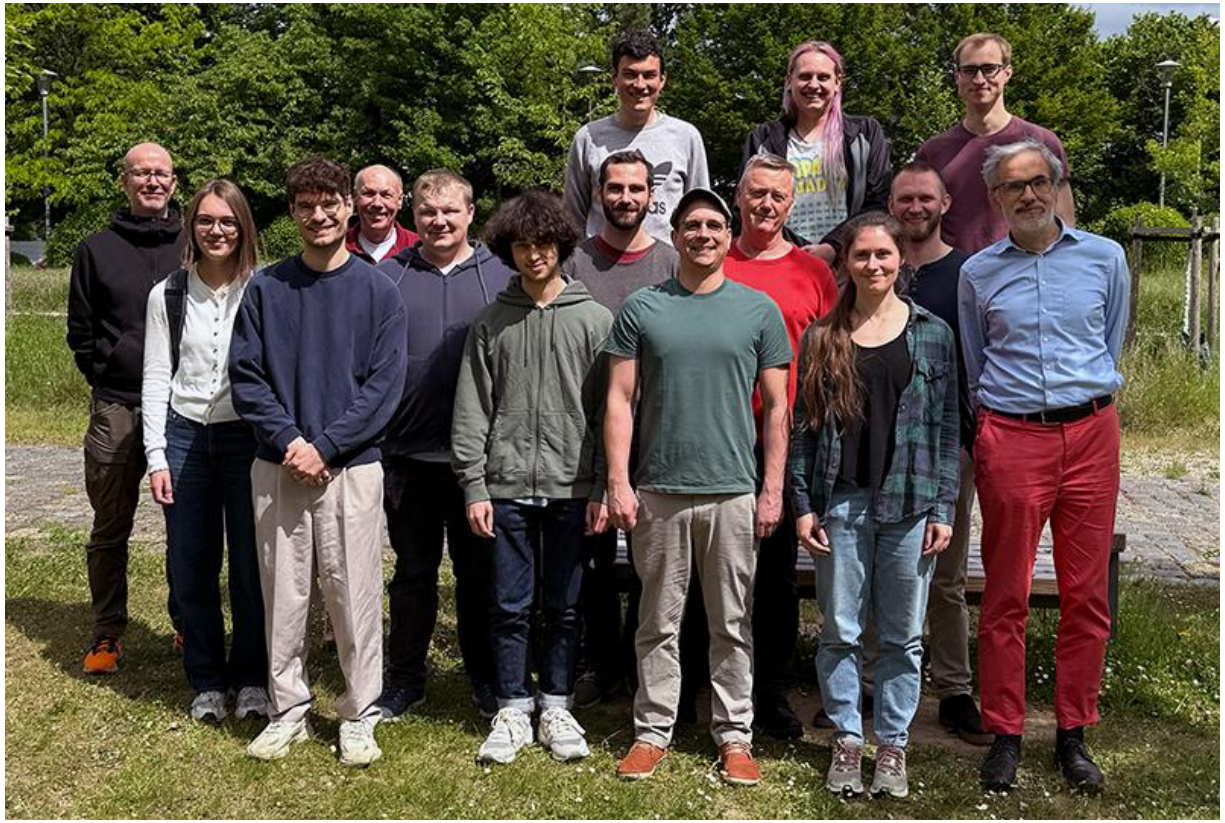
Conclusions and perspectives

- Symmetry-adapted **two-step CD** implementation ✓
- Parallelized symmetry-adapted implementation of **CCSD first-order properties** ✓

Future perspectives

- Finalization of implementation of CC **polarizabilities** and **magnetic properties**
- Inclusion of the effect of **perturbative triples (CCSD(T))** for chemical accuracy
- Implementation of **excited state** and **frequency-dependent** properties

Thank you for your attention!



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