NWChem Overview

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NWChem 6.0 Overview

- **Open Source License:** ECL 2.0 — Apache 2.0 with patent modifications for academic users.
- **Wiki:** http://www.nwchem-sw.org
- **Capability:** The most diverse collection of quantum chemical methodology of any code. Notable missing features: TDDFT and CC analytic gradients.
- **Portability:** Runs on laptops/workstations (Linux, Mac and Cygwin), clusters (e.g. Fusion) and supercomputers (e.g. Intrepid and Jaguar).

Prerequisites

Required:

- **Software:**
  GNU/Linux environment or equivalent.
- **Hardware:**
  A real computer (not a cell phone).

If you want performance:

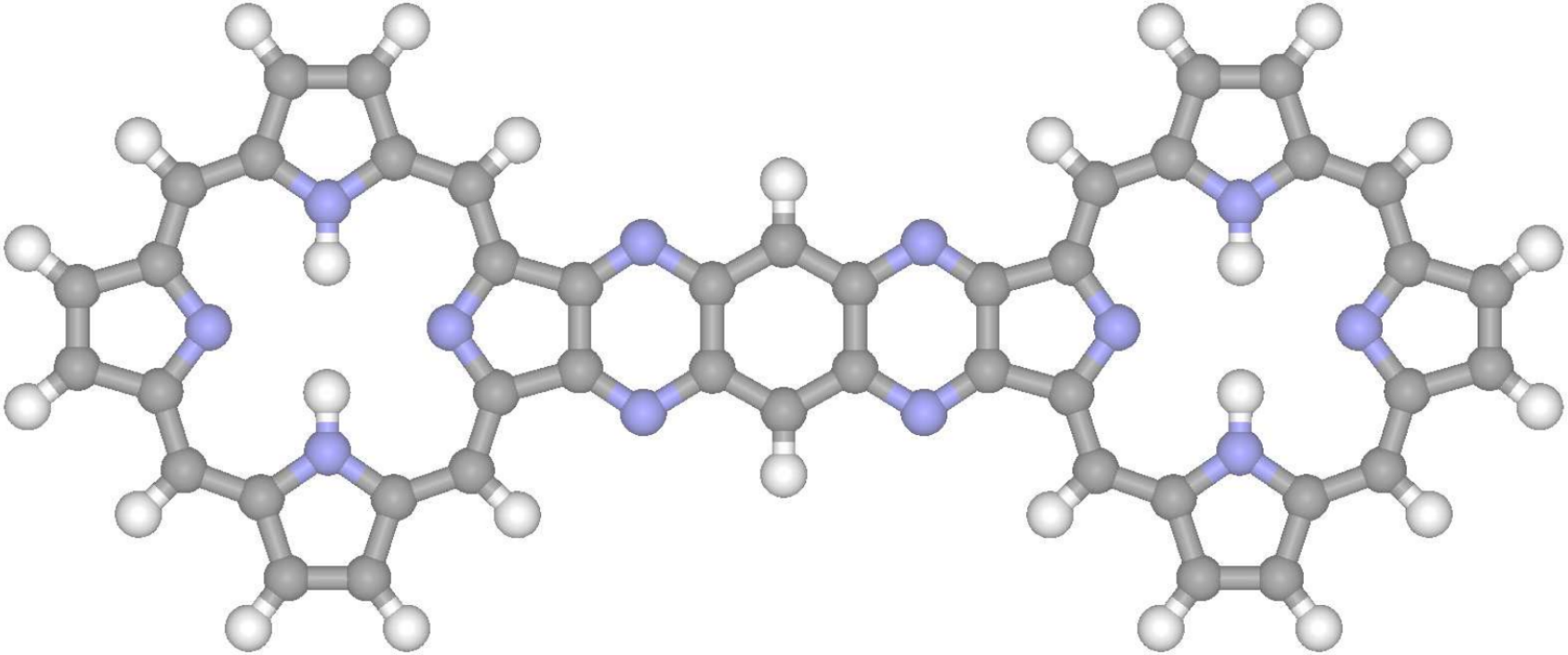
- **Software:**
  MPI, BLAS, LAPACK, ScaLAPACK.
- **Hardware:**
  Infiniband cluster or supercomputer.

Why Use NWChem?

- **Open Source:** Modify the code as needed.
- **Free:** Use anywhere.
- **Scalable:** No need to switch codes from laptop to supercomputer.
- **Functionality:** No need to use N codes for 1 project.
- **Support:** Responsive developers and user community via nwchem-users@emsl.pnl.gov.
- **Potential:** Actively developed by multiple DOE labs and user community.

NWChem Highlight Reel

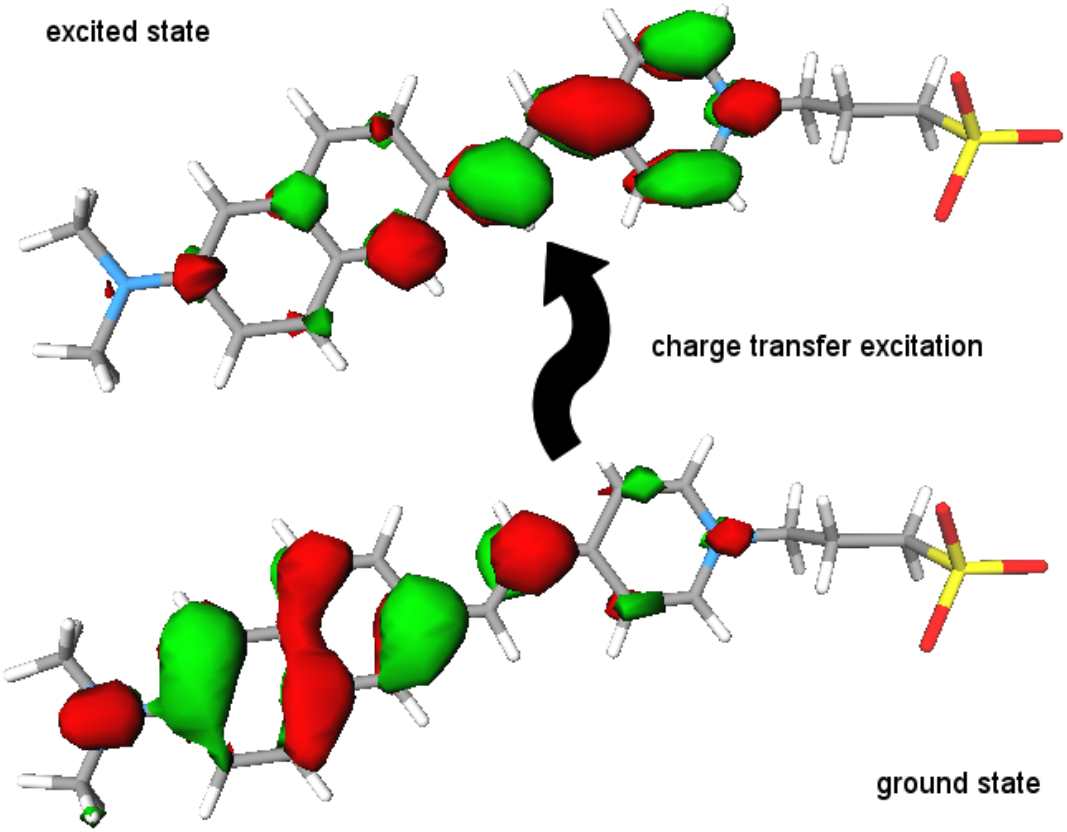
Largest Coupled-cluster Excited-state Calculation



J. Chem. Phys. **132**, 154103 (2010).

Charge-transfer Excited-states of Biomolecules

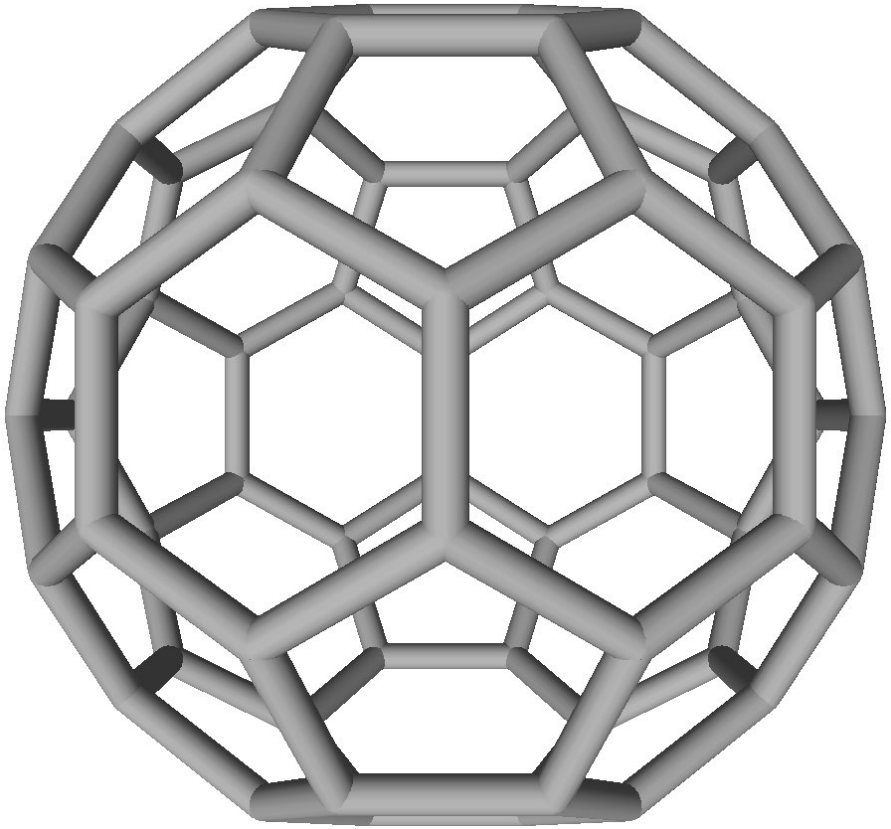
CR-EOMCCSD(T)/6-31G* — 1 hour on 256 cores



Joint work with Karol Kowalski (PNNL) and Benoît Roux (UC/Argonne).

CCSD-LR Dynamic Polarizability

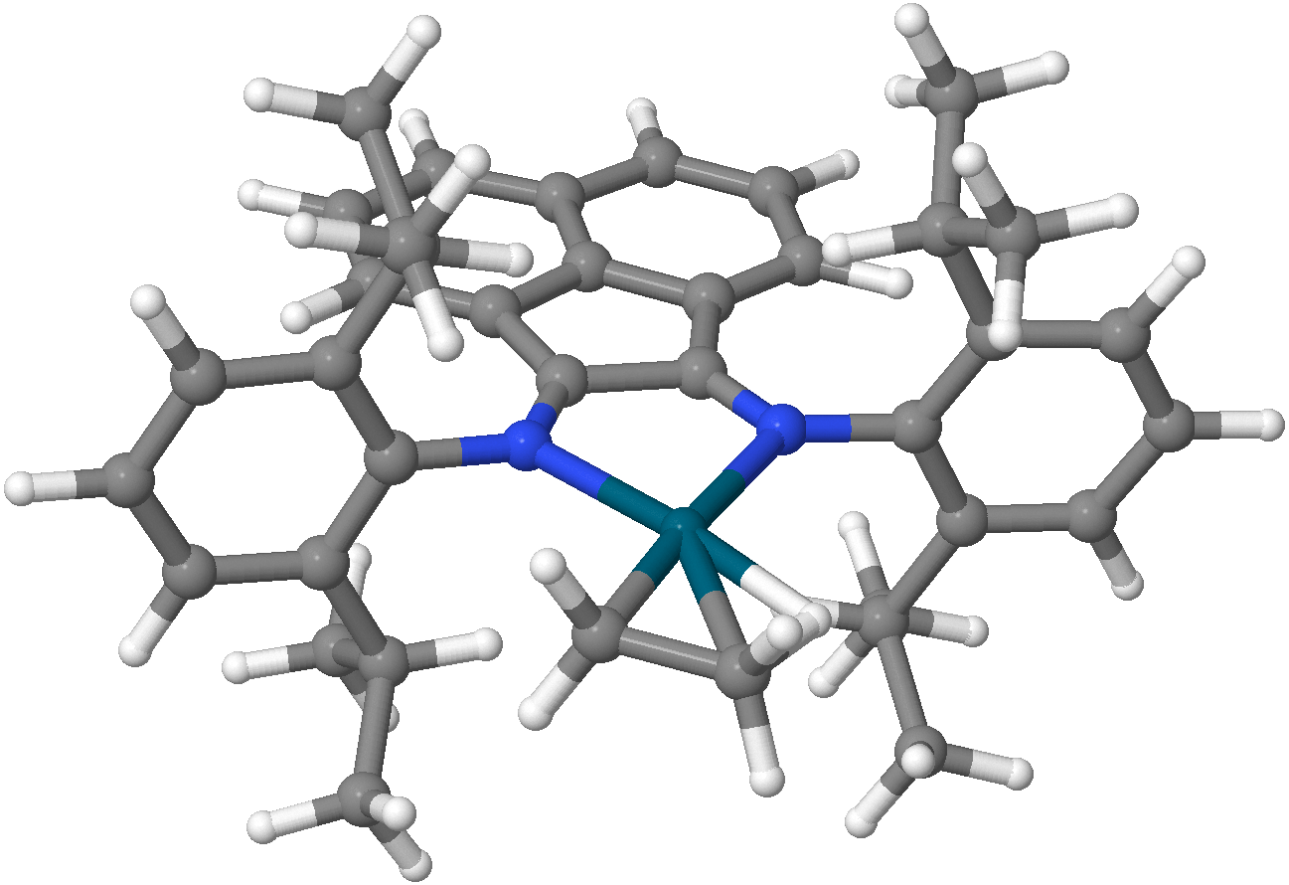
1080 b.f. — 40 hours on 1024 processors



J. Chem. Phys. **129**, 226101 (2008).

Large Fifth-rung DFT (B2PLYP)

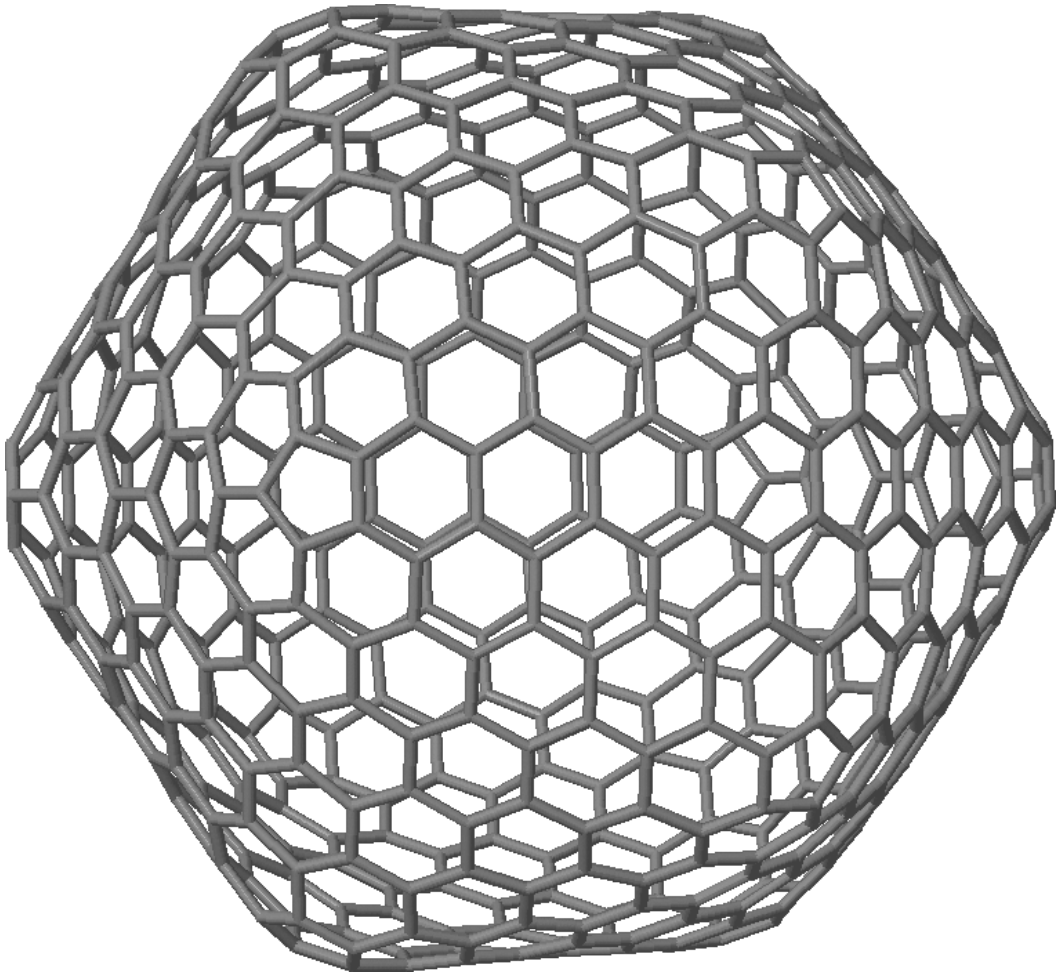
2154 b.f. — 7 hours on 256 cores



Organometallics **29**, 1750-1760 2010.

Large Hybrid DFT (PBE0)

no symmetry, 7560 b.f. — 6 hours on 1024 cores



Coupled-cluster theory

Coupled-cluster theory

The coupled–cluster (CC) wavefunction ansatz is

$$|CC\rangle = e^T |HF\rangle$$

where $T = T_1 + T_2 + \cdots + T_n$.

T is an excitation operator which promotes n electrons from occupied orbitals to virtual orbitals in the Hartree-Fock Slater determinant.

Inserting $|CC\rangle$ into the Schödinger equation:

$$\hat{H} e^T |HF\rangle = E_{CC} e^T |HF\rangle \qquad \hat{H}|CC\rangle = E_{CC}|CC\rangle$$

Coupled-cluster theory

$$
\begin{aligned}
|CC\rangle &= \exp(T)|0\rangle \\
T &= T_1 + T_2 + \cdots + T_n \quad (n \ll N) \\
T_1 &= \sum_{ia} t_i^a \hat{a}_a^\dagger \hat{a}_i \\
T_2 &= \sum_{ijab} t_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i \\
|\Psi_{CCD}\rangle &= \exp(T_2)|\Psi_{HF}\rangle \\
&= (1 + T_2 + T_2^2)|\Psi_{HF}\rangle \\
|\Psi_{CCSD}\rangle &= \exp(T_1 + T_2)|\Psi_{HF}\rangle \\
&= (1 + T_1 + \cdots + T_1^4 + T_2 + T_2^2 + T_1 T_2 + T_1^2 T_2)|\Psi_{HF}\rangle
\end{aligned}
$$

Coupled-cluster theory

Projective solution of CC:

$$\begin{aligned} E_{CC} &= \langle HF|e^{-T}He^{T}|HF\rangle \\ 0 &= \langle X|e^{-T}He^{T}|HF\rangle \quad (X = S, D, \ldots) \end{aligned}$$

CCD is:

$$\begin{aligned} E_{CC} &= \langle HF|e^{-T_2}He^{T_2}|HF\rangle \\ 0 &= \langle D|e^{-T_2}He^{T_2}|HF\rangle \end{aligned}$$

CCSD is:

$$\begin{aligned} E_{CC} &= \langle HF|e^{-T_1-T_2}He^{T_1+T_2}|HF\rangle \\ 0 &= \langle S|e^{-T_1-T_2}He^{T_1+T_2}|HF\rangle \\ 0 &= \langle D|e^{-T_1-T_2}He^{T_1+T_2}|HF\rangle \end{aligned}$$

Notation

$$
\begin{aligned}
H &= H_1 + H_2 \\
&= F + V
\end{aligned}
$$

F is the Fock matrix. CC only uses the diagonal in the canonical formulation.

V is the fluctuation operator and is composed of two-electron integrals as a 4D array.

V has 8-fold permutation symmetry in V_{pq}^{rs} and is divided into six blocks: V_{ij}^{kl}, V_{ij}^{ka}, V_{ia}^{jb}, V_{ij}^{ab}, V_{ia}^{bc}, V_{ab}^{cd}.

Indices $i, j, k, \ldots$ $(a, b, c, \ldots)$ run over the occupied (virtual) orbitals.

CCD Equations

$$R_{ij}^{ab} = V_{ij}^{ab} + P(ia,jb)\Big[T_{ij}^{ae} I_e^b - T_{im}^{ab} I_j^m + \frac{1}{2} V_{ef}^{ab} T_{ij}^{ef} + \frac{1}{2} T_{mn}^{ab} I_{ij}^{mn} - T_{mj}^{ae} I_{ie}^{mb} - I_{ie}^{ma} T_{mj}^{eb} + (2T_{mi}^{ea} - T_{im}^{ea}) I_{ej}^{mb}\Big]$$

$$\begin{aligned}
I_b^a &= (-2V_{eb}^{mn} + V_{be}^{mn}) T_{mn}^{ea} \\
I_j^i &= (2V_{ef}^{mi} - V_{ef}^{im}) T_{mj}^{ef} \\
I_{kl}^{ij} &= V_{kl}^{ij} + V_{ef}^{ij} T_{kl}^{ef} \\
I_{jb}^{ia} &= V_{jb}^{ia} - \frac{1}{2} V_{eb}^{im} T_{jm}^{ea} \\
I_{bj}^{ia} &= V_{bj}^{ia} + V_{be}^{im} (T_{mj}^{ea} - \frac{1}{2} T_{mj}^{ae}) - \frac{1}{2} V_{be}^{mi} T_{mj}^{ae}
\end{aligned}$$

Turning CC into MMM

Some tensor contractions are trivially mapped to GEMM:

$$
\begin{aligned}
I^{ij}_{kl} &+= V^{ij}_{ef} T^{ef}_{kl} \\
I^{(ij)}_{(kl)} &+= V^{(ij)}_{(ef)} T^{(ef)}_{(kl)} \\
I^{b}_{a} &+= V^{b}_{c} T^{c}_{a}
\end{aligned}
$$

Other contractions require reordering to use BLAS:

$$
\begin{aligned}
I^{ia}_{bj} &+= V^{im}_{be} T^{ea}_{mj} \\
I_{bj,ia} &+= V_{be,im} T_{mj,ea} \\
J_{bi,ja} &+= W_{bi,me} U_{me,ja} \\
J^{ja}_{bi} &+= W^{me}_{bi} U^{ja}_{me} \\
J^{(ja)}_{(bi)} &+= W^{(me)}_{(bi)} U^{(ja)}_{(me)} \\
J^{z}_{x} &+= W^{y}_{x} U^{z}_{y}
\end{aligned}
$$