

# Q-Chem 5: Facilitating Worldwide Scientific Breakthroughs



AffinityScience

Select features that make Q-Chem Stand Apart from the Competition:

## 1. DENSITY FUNCTIONALS

The most complete set of density functionals, from the latest innovative functionals to all classic functionals for exploring your complex chemistry.

- **Combinatorially designed functionals:**
  - Mardirossian and Head-Gordon
  - B97M-V,  $\omega$ B97X-V,  $\omega$ B97M-V
- **Constraint-based density functionals:**
  - Perdew and co-workers
  - SCAN family, MS1, MS2
- **Latest Minnesota functionals:**
  - MN15 and MN15-L
- **Full range of dispersion corrections:**
  - VdW functionals
  - D3 corrections with choice of damping
- **All other significant functionals:**
  - More than 200 to choose from

Functional	NCED	NCEC	NCD	IE	ID	TCE	TCD	BH
SPW92	2.14	37.77	7.60	2.22	6.76	42.23	65.35	19.55
PBE	1.96	4.08	3.26	1.15	6.53	9.22	15.58	9.17
TPSS	2.58	8.90	2.63	1.39	8.44	5.94	10.45	8.03
B3LYP	2.86	8.91	1.77	1.49	11.10	5.24	11.97	5.96
PBE-D3(BJ)	0.46	5.78	3.67	0.71	5.19	9.67	17.20	9.99
revPBE-D3(BJ)	0.49	6.60	2.54	0.77	5.21	6.60	9.91	8.30
BLYP-D3(BJ)	0.34	2.18	2.82	0.68	11.40	6.63	11.11	9.91
B97-D3(BJ)	0.47	4.82	2.52	0.78	9.15	4.66	7.92	8.32
TPSS-D3(BJ)	0.38	2.28	3.06	0.69	6.47	5.88	8.86	8.72
SCAN-D3(BJ)	0.54	9.18	3.41	0.55	4.46	5.25	6.39	7.83
M06-L	0.55	2.20	1.87	0.71	10.16	5.44	12.97	6.85
B97M-rV	0.22	0.67	2.04	0.28	6.45	3.57	4.78	4.36
PBE0-D3(BJ)	0.44	4.45	2.28	0.58	3.47	4.76	8.72	4.91
B3LYP-D3(BJ)	0.31	3.02	1.88	0.49	8.51	3.72	5.97	5.65
$\omega$ B97X-D	0.37	1.01	1.46	0.67	3.11	3.44	5.79	2.34
$\omega$ B97X-V	0.24	0.64	1.23	0.27	2.72	3.41	5.01	2.44
TPSSH-D3(BJ)	0.36	1.73	2.49	0.62	5.29	5.55	5.92	6.63
M06-2X	0.43	2.52	0.99	0.50	5.56	3.29	7.23	2.57
MN15	0.47	1.83	0.96	0.71	4.06	3.76	6.44	1.98
$\omega$ B97M-V	0.18	0.48	1.13	0.28	2.05	2.48	4.30	1.68

RMS errors for 8 datatypes for 20 classic and modern density functionals on nearly 5000 data points. NCED=easy non-covalent dimers, NCEC=easy NC clusters, NCD=difficult NC, IE/ID=easy/difficult isomerization, TC=thermochemistry, BH=barrier heights.

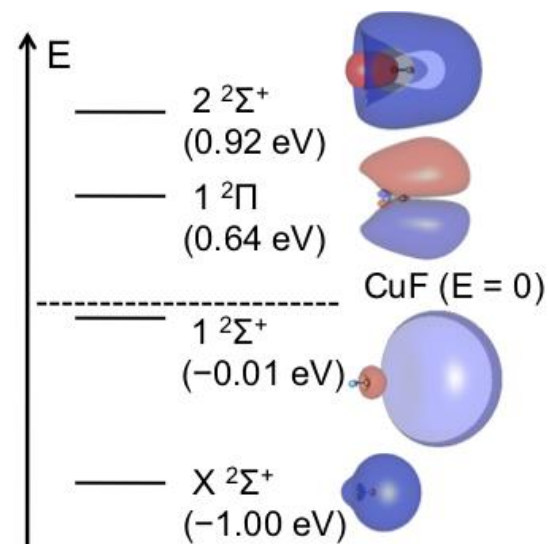
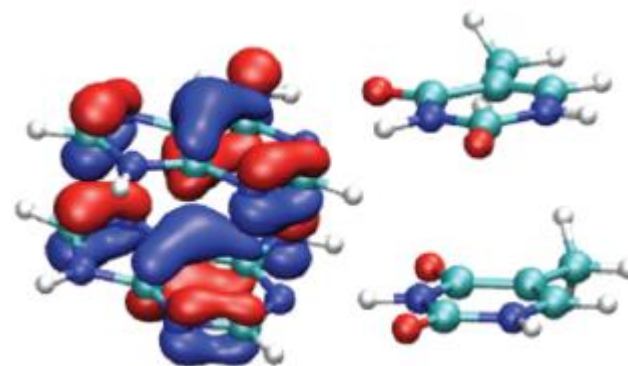
## 2. POST HARTREE-FOCK FEATURES

### • Coupled-Cluster, Equation-of-Motion, and Adiabatic Diagrammatic Construction Methods:

- o Significantly enhanced coupled-cluster codes rewritten for better performance on multicore systems
- o RI and Cholesky decomposition within CC/EOM-CC for improved performance and access to larger molecules
- o Energy, gradient, and properties for CCSD, EOM-EE/SF/IP/EA-CCSD (canonical and RI/CD implementations)
- o More properties: two-photon cross-sections, ground- and excited-state polarizabilities, non-adiabatic and spin-orbit couplings, Dyson orbitals
- o Complex absorbing potentials within CC/EOM-CC framework for metastable electronic states: Energies, gradients and Dyson orbitals
- o Approximate EOM-CC methods for larger molecules
- o PCM and EFP for ADC and EOM-CC wave functions
- o New ADC and EOM methods for core-ionized and core-excited states

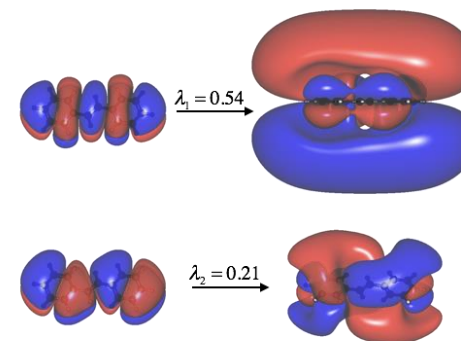
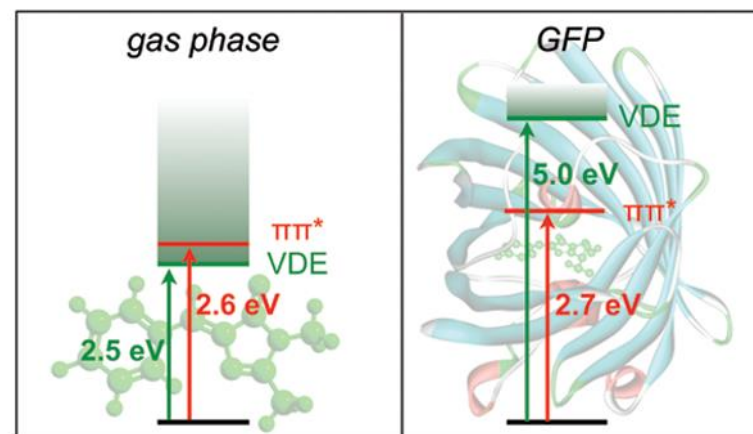
### • New Approaches for Strong Correlation:

- o Perfect quadruples and perfect hexuples methods for strong correlation problems
- o Coupled Cluster Valence Bond (CCVB) and related methods for multiple bond breaking
- o RAS-nSF methods



### 3. EXCITED STATES AND OPEN-SHELL SPECIES

- **EOM-CC Methods for Excited (EE), Ionized/Electron-Attached (IP/EA), and Diradical States (SF, DIP)**
  - Analytical gradients, properties, multicore parallelization, RI/Cholesky decomposition, interface with PCM and Effective Fragment Potential Method
- **ADC Family of Methods (EE/SF/IP/EA) Including ADC(2X) and ADC3**
- **RI-SOS-CIS(D): N<sup>4</sup> Excited-State Method**
- **Restricted Active Space Double SF Method for Polyradicals and Multiple Bond Breaking**
- **Collinear and Non-Collinear SF-DFT for Strongly Correlated Species**
  
- **Analytical Gradient and Hessian for TDDFT/TDA and Full TDDFT**
- **Non-Adiabatic Couplings within CIS, TD-DFT, and EOM-CC Frameworks**
- **Spin-Orbit Couplings within EOM-CC and ADC**
- **Non-Linear Optical Properties for EOM-CC and ADC (Two-Photon Absorption and Polarizabilities)**
- **Wave-function analysis for EOM-CC, ADC, TDDFT, and CIS: Natural Orbitals, Natural Transition Orbitals, Exciton Size, Attachment-Detachment Densities and More**



## 4. PROPERTY ANALYSIS

- **New second generation Absolutely Localized MO Energy Decomposition Analysis (ALMO-EDA).**

- Interaction energy between fragments is divided into frozen (FRZ), polarization (POL), and charge-transfer (CT) terms.
- New fragment electric response function (FERF) model gives valid basis set limit for POL and CT.
- New frozen decomposition separates FRZ into dispersion, electrostatics and Pauli repulsion terms.
- New adiabatic EDA connects FRZ, POL, CT to observables such as structure, and vibrational frequencies (see figure at right)

- **Electron Transfer and Excitation Energy Transfer**

- CDFT leads to charge-constrained states. CDFT-CI describes configuration interaction among these constrained states.
- Direct coupling method, in its '1+1' version, uses the product of fragment wavefunctions to compute the coupling.
- Fragment charge (or excitation or spin) difference methods compute ET and EET couplings between eigenstates or in multi-states
- Diabatization with Boys or Edmiston-Ruedenberg localization

- **Nonadiabatic Couplings**

- Analytic derivative couplings between electronic/excited states computed within the (SF)CIS, (SF)TDDFT and the ab initio Frenkel-Davydov exciton frameworks

- **Fast NMR Shifts Calculations (made possible with advanced solvers of response equations) and Much More.**

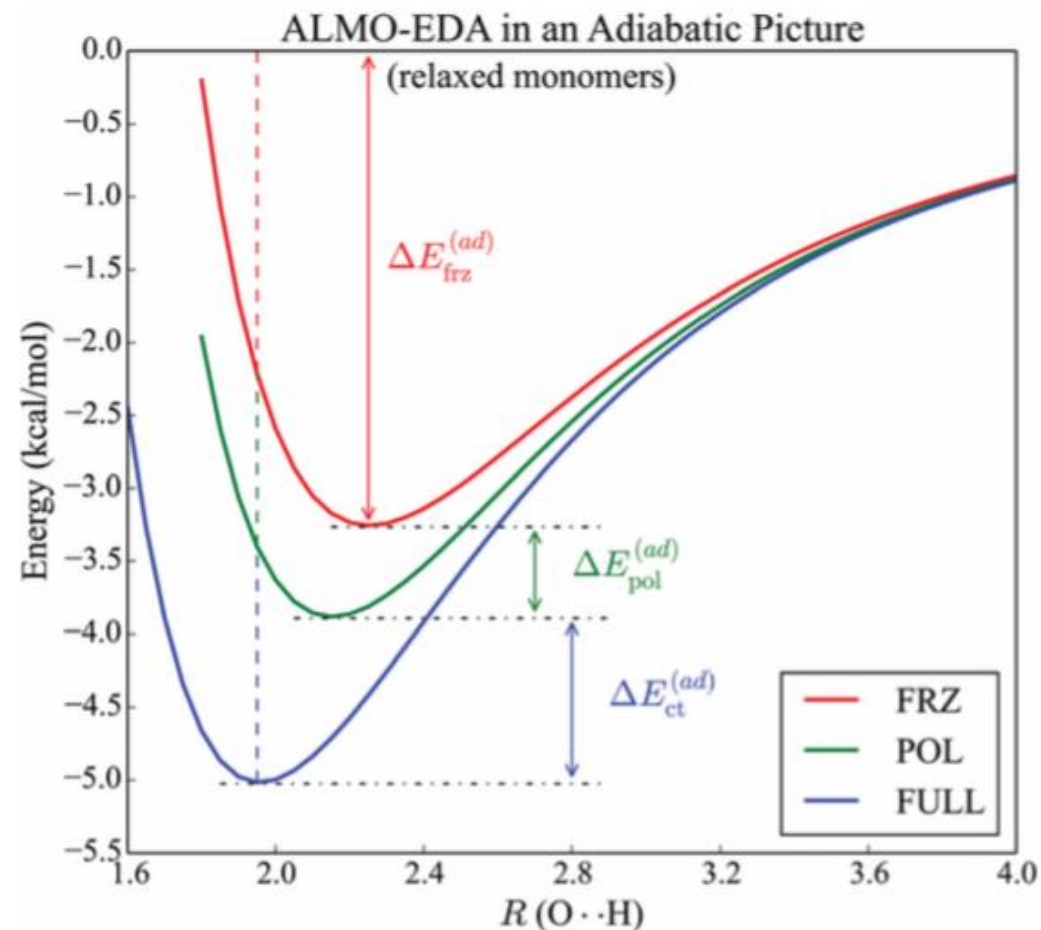


Illustration of the adiabatic EDA applied to the water dimer, as a function of the intermolecular OH separation. The development of the characteristic hydrogen bond distance from FRZ to POL to FULL can be clearly seen. Interestingly, the linear hydrogen bond is recovered at the FRZ level, showing that it arises from the interplay of permanent electrostatics and Pauli repulsion, a balance which is not disturbed by adding POL and CT.

## 5. REACTION PATHS, VIBRATIONAL ANALYSIS, & MOLECULAR DYNAMICS

### • Automated Reaction Path Finding

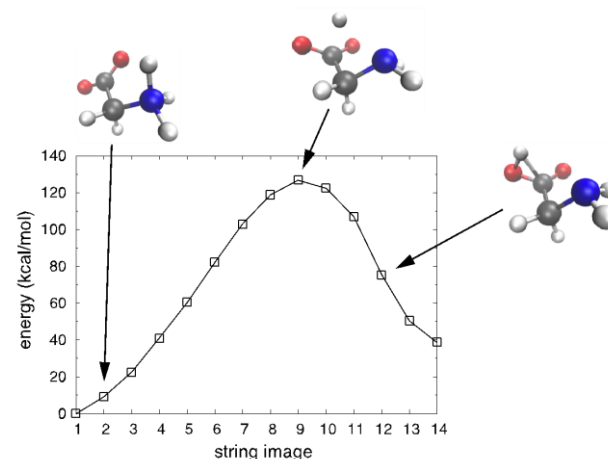
- Freezing and Growing String methods
- Generate a transition state guess given only reactant and product structures
- Hessian-free transition-state search does not require an initial frequency calculation

### • Harmonic & Anharmonic Vibrational Frequencies

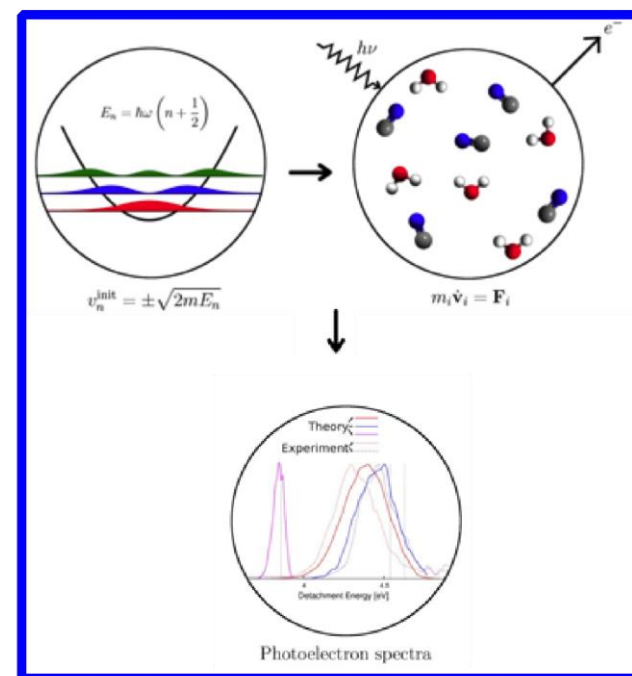
- Partial Hessian calculations reduce the cost of harmonic frequencies by perturbing only a subset of the atoms
- Anharmonic frequencies via vibrational configuration interaction, vibrational perturbation theory, or Transition-Optimized Shifted Hermite (TOSH) theory

### • Nuclear Quantum Effects and Spectra

- Path Integral Monte Carlo and Path Integral molecular dynamics describe both electronic and nuclear motions with quantum mechanics
- PIMC and PIMD naturally include H-atom tunneling and thermal averaging
- Quasi-classical trajectories for *ab initio* MD include vibrational zero-point energy into initial velocities, for simulating IR or photoelectron spectra



Auto-generated string for intramolecular proton transfer in glycine

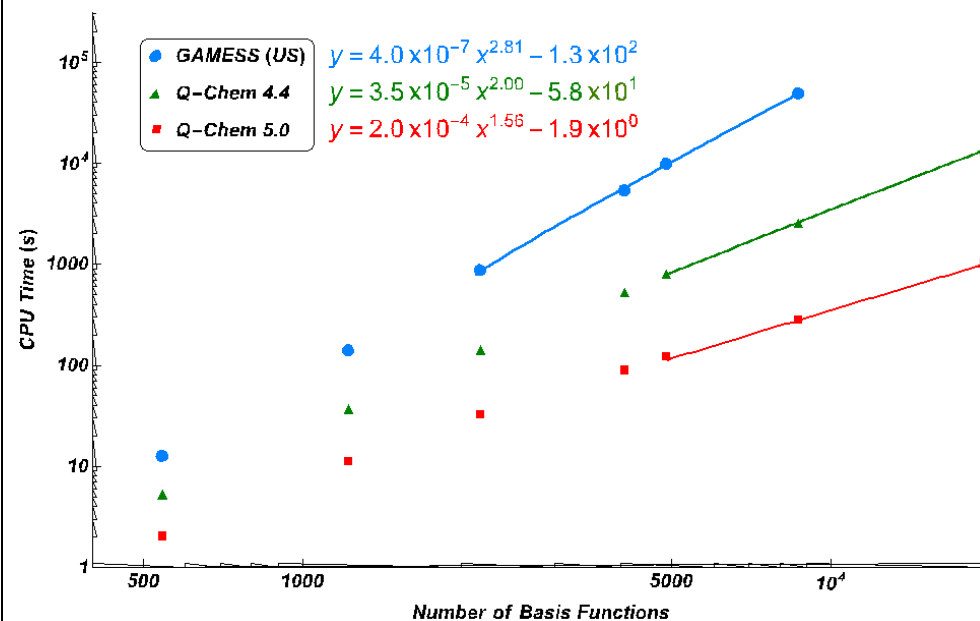


Quasi-classical simulation of  $\text{CN}^-$ (aq) photoelectron spectrum

## 6. EFFECTIVE CORE POTENTIALS FOR HEAVY ELEMENTS

New state-of-the-art algorithm for effective core potential calculations.

- **Arbitrary Basis Function and Effective Core Potential Angular Momentum**
  - Able to treat any basis set and effective core potential
  - Stuttgart-Bonn lanthanide and actinide effective core potentials are now accessible
- **Efficient Algorithm**
  - Uses novel screening and recurrence relations
  - Improves the formal cubic scaling to linear scaling
- **Analytical Gradients and Hessians**
  - Allows faster and more accurate geometry optimizations and frequency calculations



Effective core potential integral timings for a Pt slab using GAMESS-US (blue), Q-Chem 4.4 (green) and the new Q-Chem 5.0 algorithm (red). Each Pt atom has a SBKJC effective core potential.

## 7. ENVIRONMENTAL EFFECTS: SOLVATION MODELS, EFP, AND QM/MM

### • Popular Implicit Solvation Models

- SM8, SM12, SMD, COSMO, C-PCM, SS(V)PE, IEF-PCM, CMIRS, and more
- Intrinsically smooth discretization of the solute/continuum interface
- Poisson Equation solver for anisotropic dielectric boundary conditions

### • Effective Fragment Potential (EFP) for Modeling Explicit Solvent

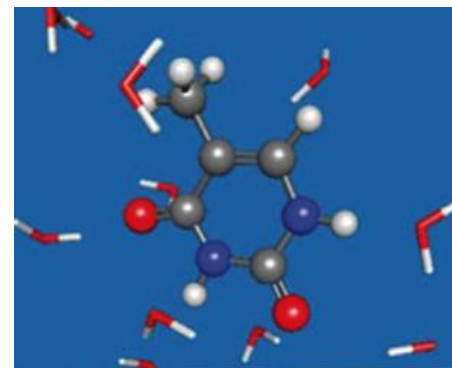
- Available for ground and excited states
- Interfaced with DFT and wave function based methods
- Built-in library of effective fragments

### • Stand-Alone QM/MM Capabilities

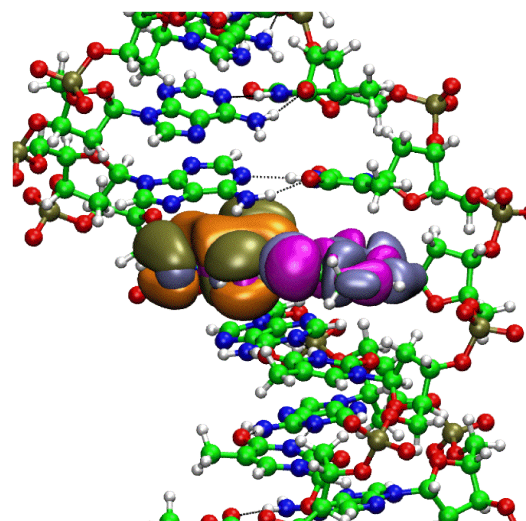
- Available for ground or excited states of the QM region
- Unique “Yin-Yang atom” approach to defining the QM/MM boundary
- Integration with PCM models (QC/MM/PCM)
- Many-body expansion can incorporate solvent molecules at a QM level

### • Interface to CHARMM

- QM/MM using CHARMM’s extensive set of sampling methods
- Full QM/MM Hessian, or its “mobile block-Hessian” approximation, facilitates study of vibrational entropic effects or large-scale conformational changes



EFP used to compute ionization energies and redox potentials of bulk-solvated species



HOMO and LUMO of a Watson-Crick base pair in a QM/MM description of double-stranded DNA

## 8. COMPUTATIONAL EFFICIENCY

### • Resolution of the Identity Algorithms for SCF and Post-SCF Calculations

- occ-RI-K algorithm for Hartree-Fock exchange
- RI-SCF gradient
- RI-MP2, SCS-MP2, SOS-MP2 methods
- RI-CCSD and RI-EOM energies and gradients

### • Fast Algorithms for DFT Calculations

- Algorithms for Coulomb (Continuous Fast Multipole Method, J engine, Fourier Transform Coulomb, Quantum Ewald Mesh)
- Algorithms for Hartree-Fock exchange (LinK, ARI-K) and numerical integration (mrXC)

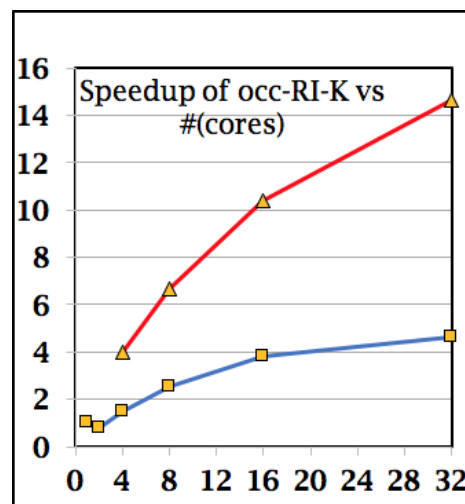
### • Perturbation Theory Calculations

- Fast integral transformations, Resolution-of-Identity approximation, scaling of different spin components, Laplace transform, dual-basis extrapolation, and the use of localized orbitals.

### • Coupled-Cluster Calculations

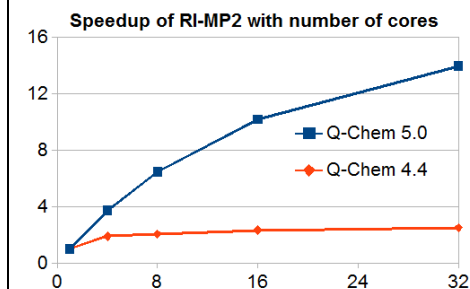
- Enhanced by a modern tensor library, Resolution-of-Identity approximation, and Cholesky decomposition.

### • Efficient Implementation on Shared-Memory Multicore Machines and Computer Clusters



Diamondoid\_octahedral (148 atoms: Red line)

Vitamin E (81 atoms: Blue line)



Vitamin E molecule  
(cc-pVDZ, 81 atoms, 684 basis functions)