



CASPT2 Method: Current Limitations and Benchmarks

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Multiconfigurational second-order perturbation method CASPT2 [1] is known as a reliable computational tool for the electronic structure calculations [2]. However, quite often this method is associated with calculations of very small molecules.

Recent development of CASSCF and CASPT2 codes in Molcas 7 package [3,4] allows to extend the limits for the calculations which can be produced with these methods. The purpose of this study is to demonstrate the possibility to use CASSCF/CASPT2 approach for relatively large molecules, and molecular systems.

Methods

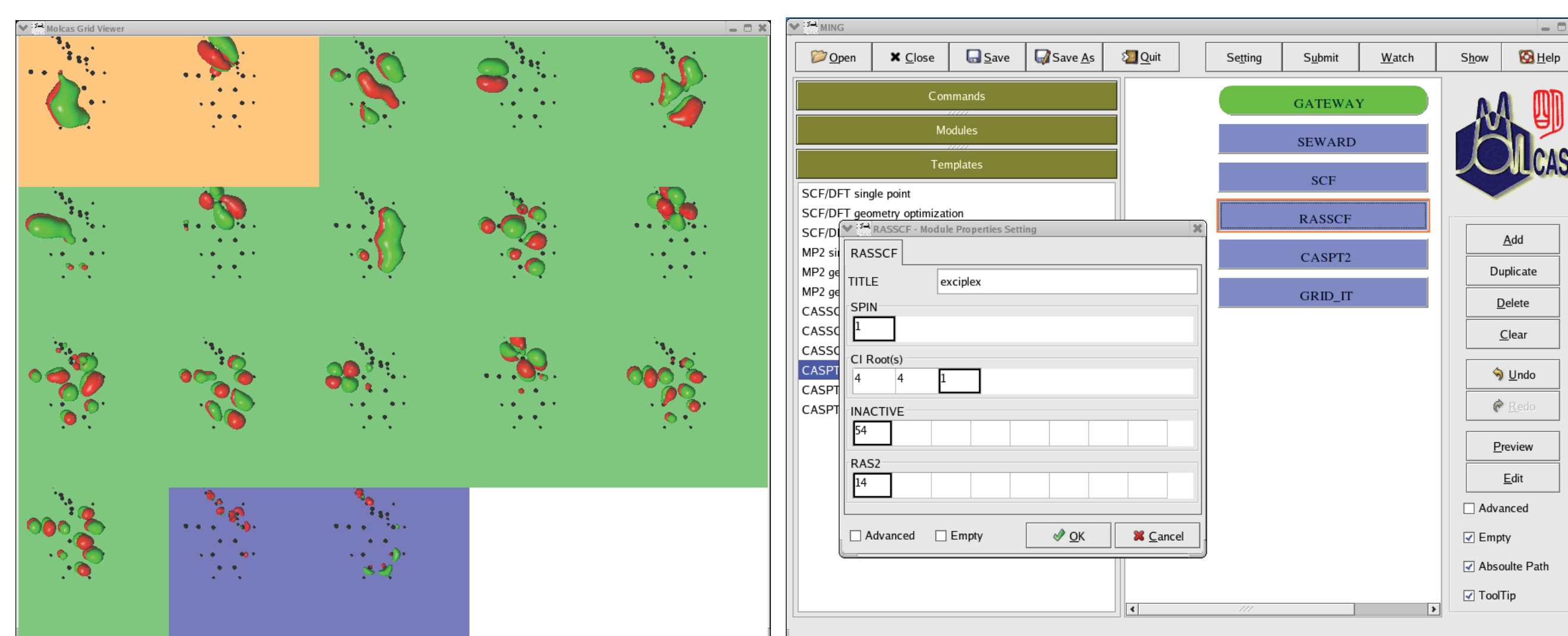
The program system MOLCAS is a package for calculations of electronic and structural properties of molecular systems in gas, liquid, or solid phase. MOLCAS contains a number of modern quantum chemical methods for studies of the electronic structure in ground and excited electronic states, including Hartree-Fock, Density Functional Theory, Coupled-Cluster, multiconfigurational SCF (CASSCF) with dynamical electron correlation treated with multi-reference CI or second order perturbation theory (MS-CASPT2). Automatic geometry optimization using analytical gradient techniques are available for HF/DFT and CASSCF wave functions. CASPT2 structures may be obtained using a numerical gradient procedure. These procedure can be used to obtain equilibrium geometries, transition states, etc. both for ground and excited electronic states.

Package

MOLCAS runs on almost all UNIX-like platforms and also on MS Windows and Mac OS X. It has a straightforward installation from a source code and a set of configuration files for different platforms and compilers. For Linux operating system MOLCAS could be compiled by g77, gfortran, Intel, PGI, NAG, PathScale compilers. The code can benefit from various BLAS/LAPACK libraries - Atlas, MKL, ACML. MOLCAS 7.2 can use Cholesky decomposition for two-electron integrals [5] in HF/DFT, MP2, CASSCF and CASPT2 codes.

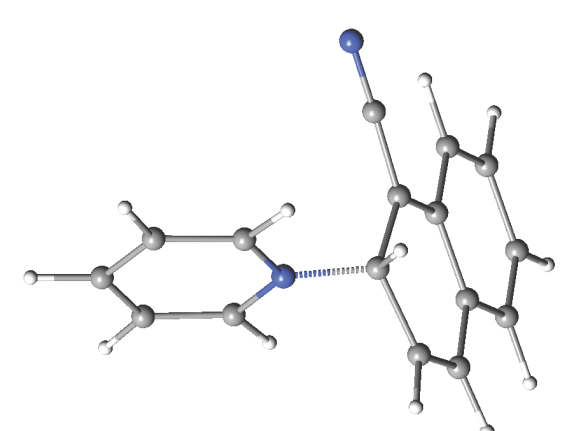
MOLCAS interfaced to various external programs: Tinker (QM/MM), EPCISO (spin-orbit CI), COLUMBUS (multi-reference CI), MOLSIM (MC/MD)

MOLCAS 7.2 contains Graphical User Interface to create input files (MING) and visually select active space for RASSCF/CASSCF calculations (GV).



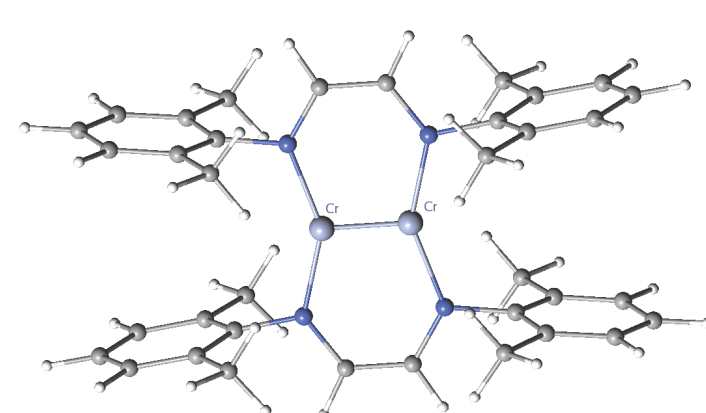
On going applications within CASSCF/CASPT2 approach:

Applications

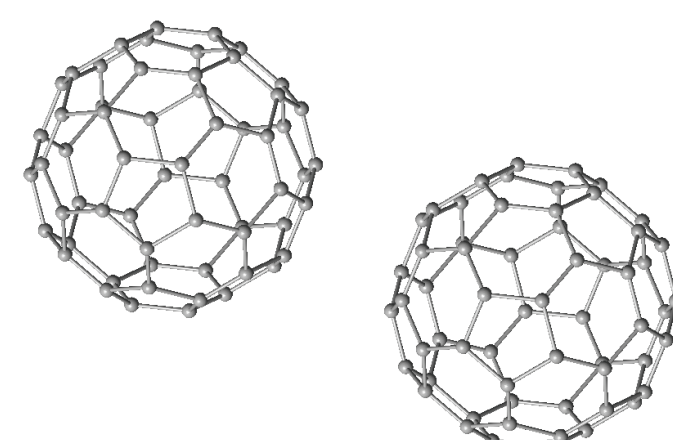


Geometry and electronic structure of exciplex, formed by 1-cyanonaphthalene and pyridine
 $C_{16}N_2H_{12}$, Basis set ANO-S-VDZP

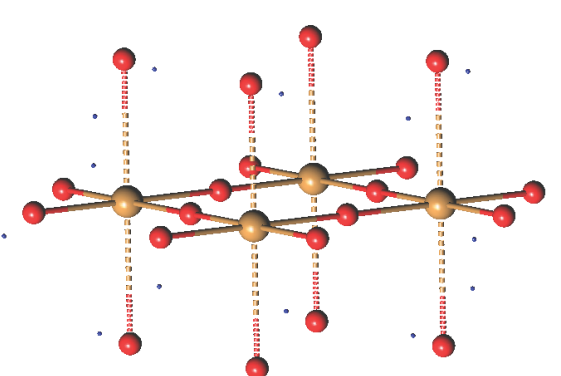
Scan of geometries from 1.4Å to 2.8Å between molecules
CASSCF: 14-on-14, multistate calculation (4 roots)



A study of the chemical bond in a compound with unusual short Cr-Cr distance
 $Cr_2C_{36}N_4H_{40}$, Basis set Cr:ANO-RCC-VTZP, ANO-RCC-VDZP
CASSCF: 12-on-13



Interaction between two negatively charged C_{60} molecules. Study of localization of atomic charges on fullerenes.
 C_{120}^{-n} , (n=6) Basis set ANO-S-VDZ
CASSCF: 18-on-12 (for n=6)



Oxygen displacement in Cu-O plane in HTSC
 Cu_4O_{20} (with a set of external charges), Basis Set ANO-RCC-VTZP
CASSCF: 8-on-14

Calculations has been performed on two different machines Intel Core2 (2.4GHz, Cache 4Mb, 2Gb RAM), and Intel Xeon (2.83GHz, Cache 6Mb, 64Gb RAM). In test calculations the performance difference between these two machines is about 1.2. Xeon machine has been used for C120 calculations, which require 16Gb of memory. The Molcas code has been compiled by Intel compiler 10, with MKL libraries. The total time of a calculation is approximate, since it depends on an initial guess for CASSCF calculation.

Benchmarks

Molecule	Symmetry	Basis functions	Number of determinants	Active Orbitals	Frozen in CASPT2	CASPT2 wall time	Total time
$C_{16}N_2H_{12}$	C_1	312	5,891,028	14/14	18	77h (20h for 1-root)	105h
$Cr_2C_{36}N_4H_{40}$	C_{2v}	878	369,090	12/13	130	1h	6h
C_{120}	C_i	1080	12,210	18/12	177	3.5h	11h
Cu_4O_{20}	D_{2h}	836	125,768	8/14	76	5h	8h

Conclusions

There are two components which made possible to extend the limits of CASPT2 calculations in MOLCAS. One is the Cholesky decomposition of integrals, which reduces the amount of data transferred from the disk. Usage of MKL library allows to process BLAS computations (about 80% of the total time spent in CASSCF and CASPT2) on another core(s) of a multicore CPU.

The size of the active space is a hard limit for CASSCF/CASPT2 approach. However, it is now possible to make precise calculations of relatively large molecules even on a "normal" personal computer.

References

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- [2] M. Schreiber, M. Silva-Junior, S. Sauer, and W. Thiel. Benchmarks for electronically excited states: CASPT2, CC2, CCSD and CC3. *J. Chem. Phys.* 128:134110, 2008
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- [5] F. Aquilante, P.-Å. Malmqvist, T. B. Pedersen, A. Ghosh, and B. O. Roos. Cholesky Decomposition-Based Multiconfiguration Second-Order Perturbation Theory (CD-CASPT2): Application to the Spin-State Energetics of $CoIII(diiminato)(NPh)$, *J. Chem. Theory and Comput.*, 4:694 2008