New developments in multiconfigurational Quantum Chemistry

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Multiconfigurational methods in Quantum Chemistry are precise and reliable tools to study the electronic structure of ground and excited states of molecular systems. The recent developments of multiconfigurational methods implemented in the MOLCAS package [1] opens up new horizons for research in the field.

Challenges in parallelization of CASPT2 [2]
Active Density Matrices ($N^2_{\text{act}}$)
scales well (independent tasks)
tasks bound by memory bandwidth
diagonalization handled by ScaLAPACK

Right Hand Side ($N^2_{\text{virt}}$)
scales reasonable

Speed-up in 3-body density matrix
diagonalization, PCG limits scalability

RASPT2: state-of-the-art calculations of chromium dimer

The ground state potential curve of the chromium dimer ($\text{Cr}_2$) has long been a challenging test case for computational quantum chemistry.

For two state functions $\Psi_1$ and $\Psi_2$, the bra and the ket binatural orbitals [3] express concisely the transition density matrix:

$$ \gamma(r_1, r_2) = \sum_{K} \lambda_K \Phi_{\text{Bra}}^{(r_1)}(r_1) \Phi_{\text{Ket}}^{(r_2)}(r_2) $$

where the sum over $K$ is short (typically 1-3).

The binatural orbitals represent the propagator,

$$ \langle \Psi(t) | \Phi^{(r_1)}(r_1) \Phi^{(r_2)}(r_2) | \Psi(0) \rangle $$

Bra and ket orbitals at times 0ps, 105ps and 210ps. Starting at time 0, the electron is on the left Au atom. After 210ps, it has moved to the right Au atom. At intermediate times, the orbitals are complex; the ket orbital is similar to that of the original transition density, the real part of the bra orbital has a growing amplitude on the right Au and a shrinking one on the left Au.

The interplay of real and imaginary part reflects the current density. Current flows, although slowly, and there is never much radical density on the PDDT chain.

Dissociation of water molecule on MgO and CaO surface.

Surface model: cluster $\text{M}_2\text{O}_3\text{(OH)}$ embedded into electrostatic field and AMP pseudo-atoms; partially frozen fragments [4].

Initial geometry scan of water position on the surface: DFT/B3LYP, followed by CASSCF/CASPT2 calculation (12/12)

Parallelization of CASPT2 code

RASPT2 calculations of water dissociation on oxide surfaces

CASPT2 calculations of water dissociation on oxide surfaces

References:


http://www.molcas.org