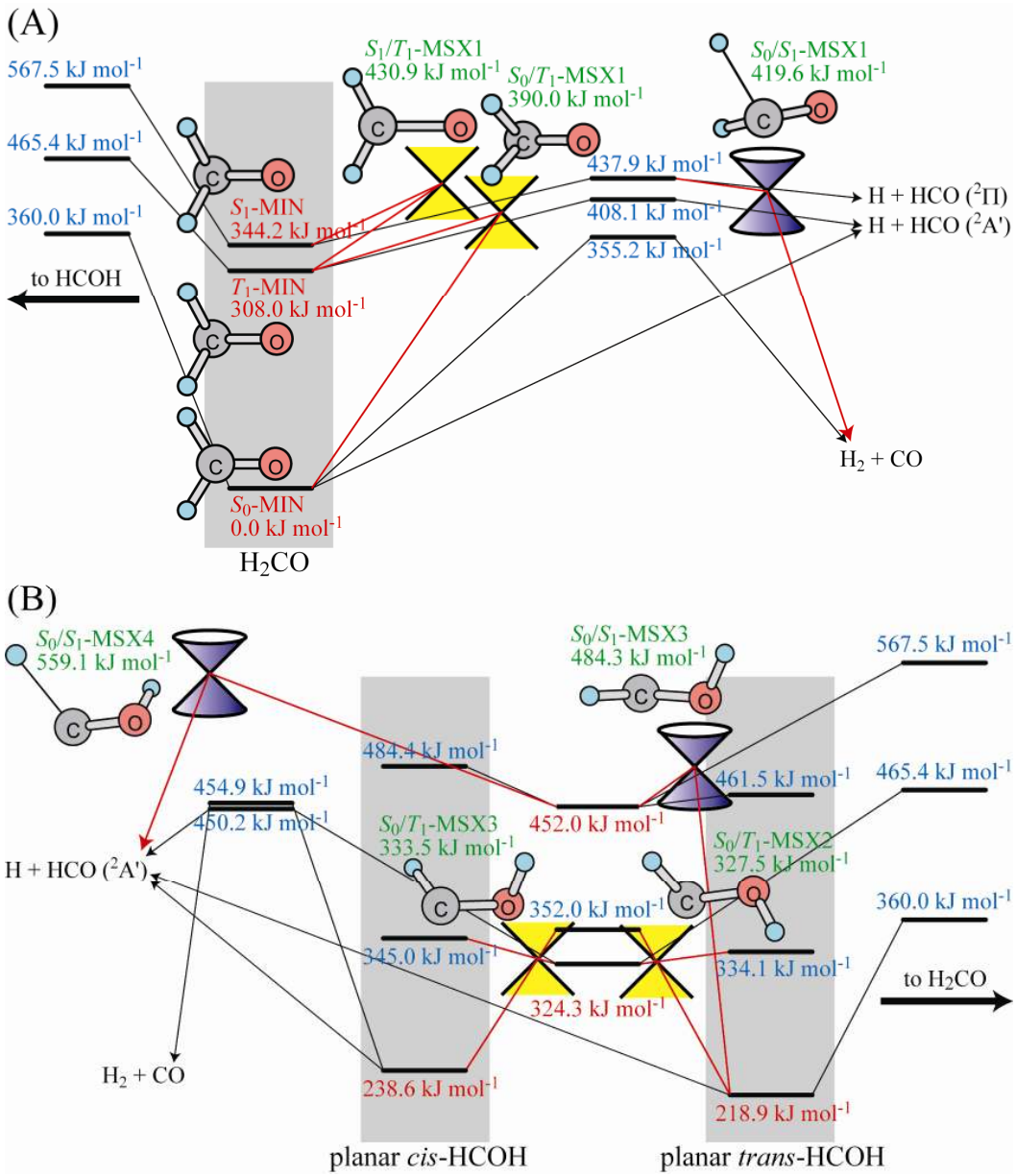
GRRM NEWS No. 003

GRRM NEWS reports recent developments of the ADD/SHS algorithm and its applications. Since the second version of the GRRM program (***GRRM***1.20) was released on 1 Feb. 2008, performance of the GRRM program has been considerably improved.

(1) An extension of the GRRM method based on the ADD/SHS algorithm has been made for the excited electronic states. Automated global mapping of minimal energy points on seams of crossing (MSX) among excited-state surfaces has first been performed for H_2CO as a benchmark. This extension makes it possible to open new area of computational studies in photochemistry and photophysics.

Important MSX, which had been unexpected, were newly discovered (J. Phys. Chem. A 2009, 113, 170401710).

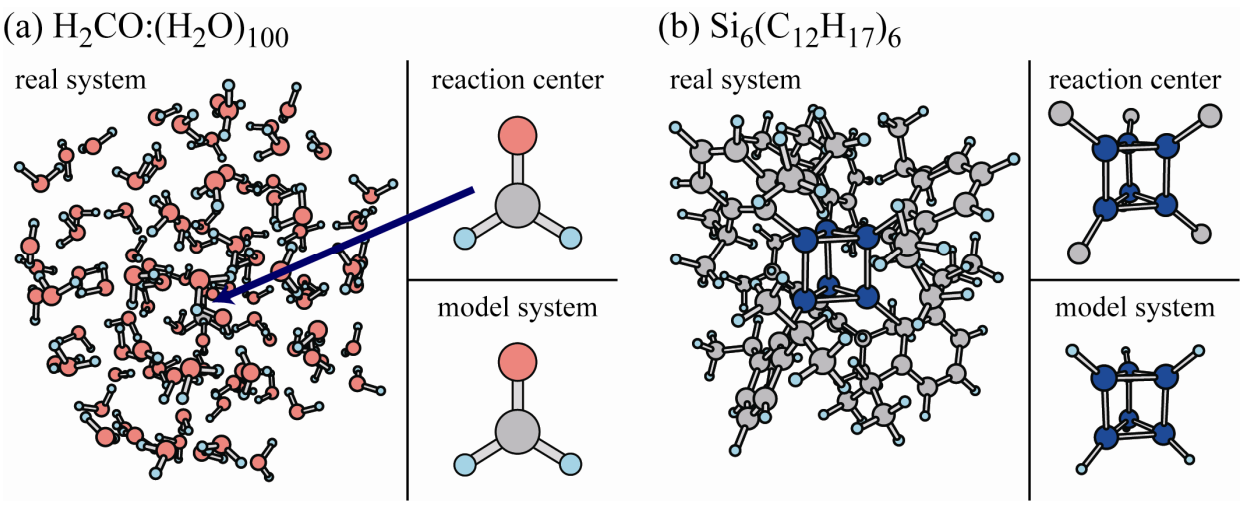


(2) An application to vibrational spectroscopy has been made for efficient construction of high-quality potential surfaces with small numbers of ab initio sampling points. The efficient SHS algorithm for searching anharmonicity on the potential energy surfaces is used to create analytical potential energy functions expanded to the sixth order (SHS-PF6). This SHS-PF6 technique enables us to obtain vibrational frequencies and intensities not only for the fundamentals but also for overtones and combinations or even for Fermi multiplets.

Vibrational frequencies of water clusters could be calculated very accurately and efficiently by this new technique SHS-PF6 (J. Chem. Phys. 2008, 128, 144111-(1,11), ibid, 2008, 129, 074315-(1,9)), as can be seen in the next Table.

Water Dimer Vibrations	MULTIMODE CCSD(T)	GAMESS CCSD(T)	SHS-PF6 MR(G3:MP2)	Obsd. (Gas)
Acceptor Bend	1589.5	1567	1589.4	1600.6
Donor Bend	1616.1	1603	1612.7	~1620
Donor Bond OH	3590.0	3499	3585.0	3601
Acceptor Symm OH	3625.4	3560	3660.4	3660
Donor Free OH	3697.6	3665	3725.3	3735
Acceptor Asymm OH	3717.6	3608	3741.8	3745.48
Average Error / cm^{-1}	21.0	76.7	8.0	
ab initio Sampling	30000	1000	750	

(3) Huge systems of larger than several hundreds of atoms can now be treated by the GRRM program. By combining the GRRM method with the microiteration technique, a microiteration-ADDF (μ-ADDF) method for automated and systematic TS exploration has been developed for large flexible molecular systems, such as shown in the next figure (J. Comp. Theoret. Chem. 2009, in press).



GRRM*1.20** is an ***updated version of the first program based on the **SHS** algorithm for an automated exploration of reaction pathways by using energies from solutions of $H\Psi = E\Psi$.

***GRRM* 1.20** copes with various problems in chemistry by automated exploration of reaction pathways.

O ***GRRM* 1.20 automatically explores unknown isomers.**

O ***GRRM* 1.20 automatically explores unknown synthetic routes.**

O ***GRRM* 1.20 automatically explores unknown dissociation channels.**

***GRRM* 1.20** develops an unexplored world of chemistry by elucidating unknown reaction networks.

○ ***GRRM* 1.20 is useful for production of the Atlas for the chemical world.**

○ ***GRRM* 1.20 is useful for design of new chemical compounds and reactions.**

○ ***GRRM* 1.20 is useful for designing new tactics for energy/environment problems.**

○ ***GRRM* 1.20 is useful for elucidation of catalysis and design of new catalysts.**

***GRRM* 1.20** is an epoch-making program of potential analyses for the following problems.

- **Normal coordinate analysis** Normal coordinate calculations can be made at arbitrary structures. Optionally, enthalpy and Gibbs energies can also be obtained.
- **Optimization of equilibrium structures** Equilibrium structures can be optimized by **SIRFO** and **BFGS** methods**.**
- **Optimization of transition structures** Transition structures can be optimized by **SIRFO** and **Bofill's** methods**.**
- **IRC search** **IRC** can be traced by **Page** and **McIver** methods**.**
- **GRRM search** Global reaction route mapping (**GRRM**) can be made for the potential surface of a given chemical formula. Starting from an equilibrium structure, automated search of dissociation and isomerization can be performed to explore **GRRM** corresponding to the Atlas of chemical reaction routes. Optionally, exploration of reaction routes can be made for the limited region around a particular structure.
- **One step TS search** An efficient search of the reaction pathway via a transition structure (**TS**) between a reactant and a product can be made automatically without initial guess, and this technique is much more rapid and applicable than any other methods.
- **Intermediate search** Intermediates between a pair of isomers can be found, even if they are far apart. The **SHS** method in the hypersphere-contraction-mode enables us to explore multi-step reaction pathways, even if they amount to several tens of steps.
- **Large ADD following (LADD)** A very efficient search of lower lying structures can be made by the LADD algorithm, which is especially suitable for systems with huge numbers of isomers.
- **ONIOM and various QM&MM methods** ONIOM as well as various methods available in the Gaussian program can been used as options in combination with the above techniques.

***Program Package & Requirement for GRRM* 1.20**

***GRRM* 1.20** utilizes energies obtained by **Gaussian03**.

Conventional packages other than Gaussian03 can also be used with additional data handling.

***GRRM* 1.20** can be used under a Linux/Unix environment.

***GRRM* 1.20** can be used for research and education, after application to the following address by E-mail. ohnok@mail.tains. tohoku.ac.jp

SHS-GRRM Publication List

1) A Scaled Hypersphere Search Method for the Topography of Reaction Pathways on the Potential Energy Surface, K. Ohno and S. Maeda, *Chem. Phys. Lett.* 384(4-6), 277-282 (2004).
2) Ab initio Studies on Synthetic Routes of Glycine from Simple Molecules via Ammonolysis of Acetolactone: Applications of the Scaled Hypersphere Search Method, S. Maeda and K. Ohno, *Chemistry Letters* 33, 1372-1373 (2004).
3) No Activation Barrier Synthetic Route of Glycine from Simple Molecules (NH_3, CH_2, and CO_2) via Carboxylation of Ammonium Ylide: a Theoretical Study by the Scaled Hypersphere Search Method, S. Maeda and K. Ohno, *Chem. Phys. Lett*. 398 (1-3), 240-244 (2004).
4) A New Approach for Finding a Transition State Connecting a Reactant and a Product without Initial Guess: Applications of the Scaled Hypersphere Search method to Isomerization Reactions of HCN, $(H_2O)_2$, and Alanine Dipeptide, S. Maeda and K. Ohno, *Chem.Phys.Lett.* 404(1-3), 95-99 (2005).
5) Global Mapping of Equilibrium and Transition Structures on Potential Energy Surfaces by the Scaled Hypersphere Search Method: Application to ab initio Surfaces of Formaldehyde and Propyne Molecules, S. Maeda and K. Ohno, *J. Phys. Chem. A* 109(25), 5742-5753 (2005).
6) Global Investigation on Potential Energy Surface of CH_3CN: Application of the Scaled Hypersphere Search Method, Xia Yang, Satoshi Maeda, and Koichi Ohno, *J. Phys. Chem. A* 109(32), 7319-7328 (2005).
7) A Scaled Hypersphere Interpolation Technique for Efficient Construction of Multidimensional Potential Energy Surfaces, S. Maeda, Y. Watanabe, and K. Ohno, *Chem. Phys. Lett.* 414(4-6), 265-270 (2005).
8) Global Analysis of Reaction Pathways on the Potential Energy Surface of Cyanoacetylene by the Scaled Hypersphere Search Method, X. Yang, S. Maeda, and K.Ohno, *Chem. Phys. Lett*. 418(1-3), 208-216 (2006).
9) Generation Mechanisms of Amino Acids in the Interstellar Space via Reactions between Closed-Shell Molecules, S. Maeda and K. Ohno, *Astrophys. J.* 640, 823 (2006).
10) D-L Conversion Pathways between Optical Isomers of Alanine: Application of the Scaled Hypersphere Method to Explore Unknown Reaction Routes in a Chiral System, K. Ohno and S. Maeda, *Chemistry Letters* 35(5), 492-493 (2006).
11) Conversion Pathways between a Fullerene and a Ring among C_{20} Clusters: Remarkable Difference in Local Potential Energy Landscapes around the Fullerene and the Ring, S. Maeda and K. Ohno, *J. Chem. Phys*. 124, 174306-(1,7) (2006).
12) Global Reaction Route Mapping on Potential Energy Surfaces of Formaldehyde, Formic Acid, and their Metal Substituted Analogues, K. Ohno and S. Maeda, *J. Phys. Chem. A* 110(28), 8933-8941 (2006).
13) Structures of Water Octamers $(H_2O)_8$: Exploration on Ab Initio Potential Energy Surfaces by the Scaled Hypersphere Search Method, S. Maeda and K. Ohno, *J. Phys. Chem. A* 111(20), 4527-4534 (2007).
14) Insight into Global Reaction Mechanism of [C_2, H_4, O] System from ab initio Calculations by the Scaled Hypersphere Search Method, X. Yang, S. Maeda, and K. Ohno, *J. Phys. Chem. A* 111(23), 5099-5110 (2007).
15) A Computational Study of Titanocene-Catalyzed Dehydrocoupling of Me_2NH-BH_3 Adduct: An Intramolecular, Stepwise Mechanism, Y. Luo and K. Ohno, *Organometallics* 26,

3597-3600 (2007).

16) Quantum Chemistry Study of $H^+(H_2O)_8$: A Global Search for Its Isomers by the Scaled Hypersphere Search Method and Its Thermal Behavior, Y. Luo, S. Maeda, and K. Ohno, *J. Phys.Chem. A* 111(42), 10732-10737 (2007).

17) Global Reaction Route Mapping on Potential Energy Surfaces of $C_2H_7^+$ and $C_3H_9^+$, Y. Watanabe, S. Maeda, and K. Ohno, *Chem.Phys.Lett.* 447/1-3, 21-26 (2007).

18) Automated Exploration of Absorption Structures of an Organic Molecule on RuH_2-BINAP by the ONIOM Method and the Scaled Hypersphere Search Method, S. Maeda, and K. Ohno, *J.Phys.Chem.A* 111, 13168-13171 (2007).

19) Microsolvation of Hydrogen Sulfide: Exploration of $H_2S \cdot (H_2O)_n$ and $SH^- \cdot H_3O^+ \cdot (H_2O)_{n-1}$ (n=5-7) Cluster Structures on Ab Initio Potential Energy Surfaces by the Scaled Hypersphere Search Method, S. Maeda and K. Ohno, *J.Phys.Chem. A* 112(13), 2962-2968 (2008).

20) Finding Important Anharmonic Terms in the Sixth-Order Potential Energy Function by the Scaled Hypersphere Search Method: An Application to Vibrational Analyses of Molecules and Clusters, S. Maeda, Y. Watanabe, and K. Ohno, *J.Chem.Phys.* 128, 144111-(1,11) (2008).

21) DFT Study on Isomerization and Decomposition of Cuprous Dialkyldithiophosphate and Its Reaction with Alkyl Radical, Y. Luo, S. Maeda, and K. Ohno, *J. Phys. Chem. A* 112(25), 5720-5726 (2008).

22) A New Global Reaction Route Map on the Potential Energy Surface of H_2CO with Unrestricted Level, S. Maeda and K. Ohno, *Chem. Phys. Lett.* 460, 55-58 (2008).

23) Intramolecular Vibrational Frequencies of Water Clusters $(H_2O)_n$ (n=2-5): Anharmonic Analyses Using Accurate Potential Functions based on the Scaled Hypersphere Search Method, Y. Watanabe, S. Maeda, and K. Ohno, *J. Chem. Phys.* 129, 074315-(1,9) (2008).

24) Automated Exploration of Reaction Channels, K. Ohno and S. Maeda, *Physica Scripta* 78, 058122 (8pp) (2008).

25) Decomposition of Alkyl Hydroperoxide by a Copper (I) Complex: Insights from Density Functional Theory, Y. Luo, S. Maeda, and K. Ohno, *Tetrahedron Lett.* 49, 6841-6845 (2008).

26) Lowest Transition State for the Chirality-Determining Step in Ru{(R)-BINAP}-Catalyzed Asymmetric Hydrogenation of Methyl-3-Oxobutanoate, S. Maeda and K. Ohno, *J. Am. Chem. Soc.* 130(51), 17228-17229 (2008).

27) Water-Catalyzed Gas-Phase Reaction of Formic Acid with Hydroxyl Radical: A Computational Investigation, Y. Luo, S. Maeda, and K. Ohno, *Chem.Phys.Lett*. 469(1-3), 57-61 (2009).

28) Automated Exploration of Stable Isomers of $H^+(H_2O)_n$ (n=5-7) via Ab Initio Calculations: An Application of the Anharmonic Downward Distortion Following Algorithm, Y. Luo, S. Maeda, and K. Ohno, *J. Comp. Chem.* 30(6), 952-961 (2009).

29) Automated Global Mapping of Minimum Energy Points on Seams of Crossing by the Anharmonic Downward Distortion Following Method: A Case Study on H_2CO, S. Maeda, K. Ohno and K. Morokuma, *J. Phys. Chem. A* 113(8), 1704-1710 (2009).

30) Systematic Search for Isomerization Pathways of Hexasilabenzene for Finding its Kinetic Stability, M. Moteki, S. Maeda, and K. Ohno, *Organometallics* 28(7), 2218-2224 (2009).

31) An Automated and Systematic Transition-Structure Explorer in Large Flexible Molecular Systems Based on Combined Global Reaction Route Mapping and Microiteration Methods, S. Maeda K. Ohno, and K. Morokuma, *J. Comp. Theoret. Chem.* (accepted: in press)