

GRRM NEWS No. 001

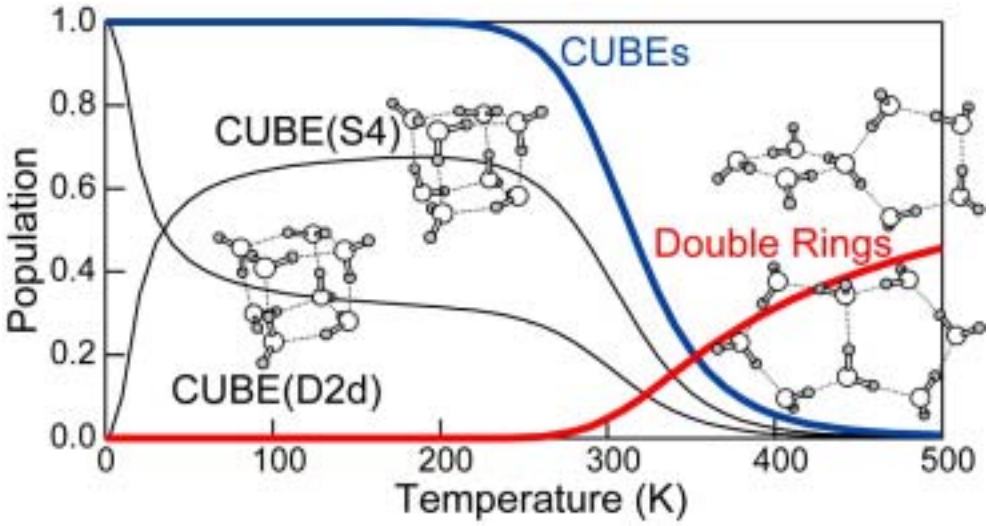
GRRM NEWS reports recent developments of the SHS algorithm and its applications. Since the first release of ***GRRM***1.00, considerable progresses have been made in addition to the standard usage of the GRRM program listed at the end of this news. Brief guides to novel extensions and applications are summarized below. Details should be referred to the references. If the readers are interested in the recent developments of the GRRM program in more detail, they are required to contact with the following e-mail address.

Inquiry to: ohnok@qpcrkk.chem.tohoku.ac.jp

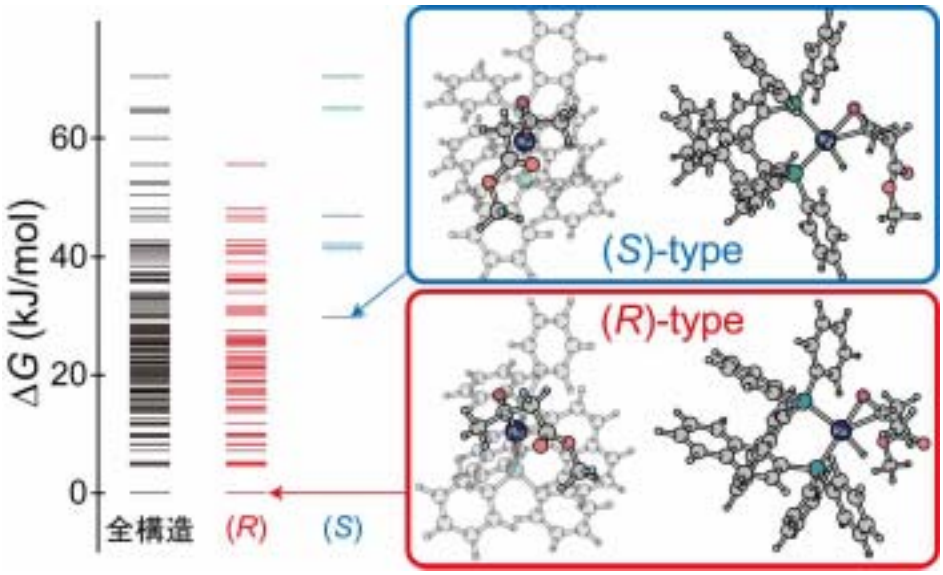
○ **Lower parts of potential energy surfaces can be explored very efficiently**, by limiting SHS pathways following ADD (anharmonic downward distortion) to large ADDs (LADD). In addition, initial geometries of the search can be extended to include several ones by stochastic generation of the structures. This ADD treatment together with random generation of initial geometries dramatically decreases the numbers of pathways to be searched, without losing the ability of the SHS method discovering reaction pathways, transition structures, and stable structures one after another. Low lying structures can be discovered with drastically decreased computational demands. Although such an improvement does not guarantee the global reaction route mapping (GRRM), realistic problems finding a global minimum together with low lying minima can be performed very economically.

○ **Multi-processor execution becomes possible** to make the entire efficiency increased by the factor of the number of cores (processors) available at the same time in the computing system. For example, when the computing system has two pairs of quad core Xeon, then the efficiency will become 8 times faster than the single core computation. This is especially effective for large systems of more than ten atoms. If the computing system has 1024 cores, the cpu time for GRRM will become decreased by the factor of 1024, which means 10^3 times faster than the use of a single core computer. This characteristic of the SHS algorithm is quite different from the usual parallel processing of quantum chemical calculations. In the parallel computing, it is not easy to linearly increase the efficiency larger than ten times in quantum chemical calculations by conventional program packages. However, the SHS algorithm has no such limitation, as long as the system has many equilibrium geometries.

○ Thermo-dynamic simulations of relative abundance of various conformers can be made by using partition functions estimated from the output data of the *GRRM* 1.00. It is possible to anticipate most probable conformers for clusters and flexible molecules, which are important in many fields of molecular sciences including molecular physics and molecular biology. (See Ref.13 and Ref.16)



○ Stereo-selective catalysis for syntheses of chiral systems can be studied based on the output data of *GRRM*1.00. In combination with the ONIOM method, limitation of the disposable sizes became relaxed to a considerable extent. For example, BINAP systems with more than one hundred atoms can be treated for estimation of an enantiomer selectivity of the reaction. (See Ref.18)



Technical Notes of the GRRM program

1. Recognition of Dissociation Channel

Recognition of dissociation channels in the GRRM program is performed by the following criterion as described in the User-Manual. ***When the nearest interatomic distance between fragments becomes sufficiently larger than a suitable limit, the path can be considered to be a dissociation channel (DC).*** Default treatments are based on typical bond radii R_b listed in Table 1. If users would like to change the standard treatment, parameters may be varied by themselves according to the User-Manual, though they should be careful about too much computation time or unreliable results due to the employed level of calculations.

Table1. List of atoms available and their bond radii R_b (Å).

Atom	R_b	Atom	R_b	Atom	R_b	Atom	R_b	Atom	R_b
H	1.138	Mg	1.907	V	1.988	Se	1.808	Rh	2.217
He	1.232	Al	3.022	Cr	2.904	Br	1.843	Pd	1.916
Li	2.926	Si	2.205	Mn	1.673	Kr	1.866	Ag	2.123
Be	1.568	P	1.816	Fe	1.666	Rb	4.414	Cd	1.582
B	1.946	S	1.685	Co	1.600	Sr	2.877	In	3.274
C	1.468	Cl	1.776	Ni	1.642	Y	2.794	Sn	2.524
N	1.235	Ar	1.754	Cu	2.016	Zr	2.460	Sb	2.153
O	1.236	K	4.145	Zn	1.266	Nb	2.595	Te	1.983
F	1.433	Ca	2.703	Ga	3.039	Mo	2.415	I	1.956
Ne	1.175	Sc	2.409	Ge	2.287	Tc	2.263	Xe	2.075
Na	3.127	Ti	2.130	As	1.939	Ru	2.253		

The above treatments of DC in GRRM do not yield dissociation energies (DE) directly. Energies described in DCn.log, which just shows energies of the structures when they are recognized as DC, cannot be used for estimating DE. In order to obtain the energy of the dissociation limit, users are recommended to calculate energies of fragments separately. Since fragment species appear many times in full GRRM, the present treatment avoids unnecessary duplication of calculations.

2. New Developments

New GRRM program, *GRRM* 1.00/08, is now under construction for release. Limited search of large ADD (LADD) will be incorporated in *GRRM* 1.00/08. Parallel processing using multi core cpu (degree of parallel processing is limited) will also be incorporated in *GRRM* 1.00/08. A request for reservation of the special use of the new version should be sent to the following address.

Request to: ohnok@qpcrkk.chem.tohoku.ac.jp

References of the SHS method and the GRRM program.

1) A Scaled Hypersphere Search Method for the Topography of Reaction Pathways on the Potential Energy Surface.
Chem. Phys. Lett. 384(4-6), 277-282 (2004).
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2) Ab initio Studies on Synthetic Routes of Glycine from Simple Molecules via Ammonolysis of Acetolactone: Applications of the Scaled Hypersphere Search Method.
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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.
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7) A Scaled Hypersphere Interpolation Technique for Efficient Construction of Multidimensional Potential Energy Surfaces.
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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.
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13) Structures of Water Octamers $(H_2O)_8$: Exploration on Ab Initio Potential Energy Surfaces by the Scaled Hypersphere Search Method.
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14) Insight into Global Reaction Mechanism of [C_2, H_4, O] System from ab initio Calculations by the Scaled Hypersphere Search Method.
J. Phys. Chem. A 111(23), 5099-5110 (2007).
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15) A Computational Study of Titanocene-Catalyzed Dehydrocoupling of Me_2NH-BH_3 Adduct: An Intramolecular, Stepwise Mechanism.
Organometallics 26, 3597-3600 (2007).
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18) Automated Exploration of Absorption Structures of an Organic Molecule on RuH_2-BINAP by the ONIOM Method and the Scaled Hypersphere Search Method
J.Phys.Chem.A (accepted: in press)
S. Maeda and K. Ohno

GRRM 1.00 is the first computer program based on the **SHS** algorithm for an automated exploration of reaction pathways by using energies obtained from solutions of $H\Psi=E\Psi$.

***GRRM* 1.00** copes with long standing fundamental problems in chemistry by automated exploration of chemical reaction pathways.

O ***GRRM* 1.00 automatically explores unknown isomers.**

O ***GRRM* 1.00 automatically explores unknown synthetic routes.**

O ***GRRM* 1.00 automatically explores unknown dissociation channels.**

***GRRM* 1.00** develops an unexplored world of chemistry by elucidating unknown chemical reaction networks.

○ ***GRRM* 1.00 is useful for production of the Atlas for the chemical world.**

○ ***GRRM* 1.00 is useful for design of new chemical compounds and reactions.**

○ ***GRRM* 1.00 is useful for designing new tactics for energy/environment problems.**

○ ***GRRM* 1.00 is useful for elucidation of catalysis and design of new catalysts.**

***GRRM* 1.00** 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 connecting a reactant and a product can be made to determine the transition structure (**TS**). This procedure can be done automatically without initial guess, and this technique is much more rapid and applicable than any other methods, such as the **NEB** method.
- **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.

***Program Package & Requirement for GRRM* 1.00**

***GRRM* 1.00** utilizes energies obtained by **Gaussian03**.

***GRRM* 1.00**, a 64-bit or a 32-bit version, can be used under a Linux/Unix environment.

***GRRM* 1.00** can be used for research and education, after application to the following address by E-mail. ohnok@qpcrkk.chem.tohoku.ac.jp