**GRRM NEWS** reports recent developments of the ADD/SHS algorithm and its applications. Since the second version of the GRRM program (GRRM1.20) 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 $\text{H}_2\text{CO}$ 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.

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

(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.

- **GRRM 1.20** automatically explores unknown isomers.
- **GRRM 1.20** automatically explores unknown synthetic routes.
- **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 be 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: olhnok@mail.tains.tohoku.ac.jp


15) A Computational Study of Titanocene-Catalyzed Dehydrocoupling of Me₂NH-BH₃ Adduct: An Intramolecular, Stepwise Mechanism, Y. Luo and K. Ohno, *Organometallics* 26,


