

Acceleration of the vibrational structure calculation with optimized vibrational coordinates

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Theoretical vibrational analysis plays an important role to interpret the observed vibrational spectrum and to elucidate the dynamical behavior of molecules. One of the standard method to compute the spectrum is the vibrational self-consistent field (VSCF) and post-VSCF methods. These methods, combined with ab-initio electronic structure theory to generate the anharmonic potential, provide an accurate prediction of the spectrum for small to medium size of molecules. Nonetheless, the cost of these calculations grows steeply with respect to the size. For example, generation of a quartic force field (QFF) requires the Hessian calculation at $2f^2 + 1$ geometry points for f -mode systems. Therefore, theoretical development is still needed to make the application feasible to large molecular systems.

Recently, one of the author proposed a new algorithm to optimize the vibrational coordinates for anharmonic systems based on the VSCF (oc-VSCF) [1]. In this method, successive transformations of all pairs of coordinates are carried out iteratively to minimize the VSCF energy until convergence. However, the number of the pairs increases rapidly with system size.

In this work, in order to reduce the computational cost, we propose a rational index that selects pairs of coordinates to mix. We also investigate the performance of oc-VSCF with a cubic force field (CFF) requiring the Hessian matrices at $2f + 1$ points, which reduces the computational effort to obtain an anharmonic potential from quadratic to linear in f . We show that the proposed pair-selection scheme with CFF significantly reduce the computational cost without loss of accuracy [2]. Our method is applied to ethylene and *trans*-1,3-butadiene combined with vibrational quasi-degenerate perturbation theory [3]. Calculated fundamental frequencies have been found to be in good agreement with experimental results.

[1] Yagi, K., Keçeli, M., Hirata, S. *J. Chem. Phys.*, 137:204118, 2012.

[2] Yagi, K., Otaki, H., in preparation.

[3] Yagi, K., Hirata, S., Hirao, K. *Phys. Chem. Chem. Phys.*, 10:1781, 2008.