Large-scale Normal Coordinate Analysis for Molecular Structures [1]

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Abstract

Normal Coordinate Analysis (NCA) plays an important role in understanding vibrational and thermal properties of molecular structures at the atomic level. To perform NCA, one must formulate an appropriate potential model and calculate the second derivatives of the potential with respect to the Cartesian coordinates. This process yields a so-called force constant matrix which is often sparse. The eigenvalues and eigenvectors of this matrix characterize the vibrational frequencies and displacement patterns of each atom. The probability distribution of the entire spectrum can be used to calculate thermodynamics quantities of the material such as the heat capacity.

Currently, the use of NCA has been limited to relatively small systems. This is partly due to the lack of efficient numerical algorithms for large-scale NCA calculation. In this talk, several techniques for improving computational efficiency of large-scale NCA will be presented. We will examine a special Hessian calculation technique that reduces the amount of work by utilizing a set of internal coordinates as intermediate variables. We will also discuss several strategies for accelerating large-scale eigenvalue calculations. In particular, we will present our experience in using the shift-invert technique on several types of high performance computers and point out its limitations. We will report our recent progress on developing factorization-free methods for calculating the desired eigenvalues and eigenvectors. Preconditioned iterative solvers are used in these methods to produce a subspace from which approximate spectral information are drawn. We have studied two types of preconditioners. The first type is purely algebraic and thus more general. It is constructed by combining incomplete Cholesky factorization with deflation. The second type of preconditioner takes advantage of known properties of the molecular structure. It is constructed by separating the bonded interaction from the non-bonded interaction and deflating the translational and rotational modes of the vibration. Numerical examples will be presented to demonstrate the performance of these preconditioners.

[1] Research sponsored by the Applied Mathematical Sciences Research Program, Office of Mathematical Information, and Computational Sciences, U.S. Department of Energy under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation.

Oak Ridge National Laboratory is managed by Lockheed Martin Energy Research Corporation for the United States Department of Energy under Contract No. DE-AC05-96OR22464.

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