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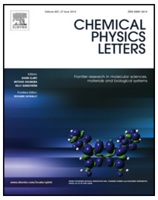

A simple state-average procedure determining optimal coordinates for anharmonic vibrational calculations

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ABSTRACT

A simple methodology for calculating state average energies in the context of vibrational self-consistent field (VSCF) is suggested. The suggested state average energy is employed in the optimization of coordinates for anharmonic vibrational wave function calculations where an orthogonal matrix of transformation between normal and optimized coordinates is variationally optimized. The convergence to the exact limit for approximate vibrational configuration interaction and vibrational coupled cluster wave functions is studied, comparing the performance of state average optimized coordinates, ground state optimized coordinates and standard normal coordinates. Exploratory calculations are presented for water, formaldehyde, the water dimer and trimer, and ethylene.

1. Introduction

The choice of coordinates is an important factor in the description of the internal dynamics of molecules. For accurate computation of anharmonic vibrational frequencies the standard choices includes rectilinear normal coordinates and curvilinear internal coordinates. Although well tested and successful for many purposes these two general choices are not entirely perfect in all circumstances. The normal coordinates are calculated based on a second order approximation to the potential, and as such they become less relevant when the amplitude of the motion is large. The couplings between some vibrational motions will in accurate anharmonic calculations be found to be larger in the rectilinear normal coordinates than in curvilinear internal coordinates. On the other hand, the use of internal coordinates is not straightforward requiring generally more effort for selecting the set of coordinates for each particular system under study as well as for determining the rather complex kinetic energy operator. Early works [1–5] have suggested to instead define the coordinates as being optimal for the vibrational energy calculated with the real anharmonic potential. Although this direction did not receive much immediate follow up work, there has recently been a revival of interest in this general idea. One of the authors [6] has implemented and performed efficient numerical optimization of a set of coordinates using the vibrational self consistent field (VSCF) method for providing the ground state energy in an anharmonic potential and determining the optimized coordinates as an orthogonal transformation of the normal coordinates of the system. We denote this approach optimized coordinate VSCF, oc-VSCF. There are significant advantages of the use of these rectilinear optimized coordinates. In particular, it has been illustrated that the convergence of approximate anharmonic wave function to the exact limit is improved using the optimized coordinates relative to normal coordinates. The ground state optimized coordinates have been used in subsequent calculation of many states using different methods, including vibrational configuration interaction (VCI) [6], vibrational coupled cluster (VCC) [7] and vibrational quasi-degenerate perturbation theory (VQDPT) [8], with very encouraging results.

In the mentioned recent studies the coordinates were made optimal for the VSCF ground state energy only. In the majority of applications of anharmonic vibrational theory, not only one vibrational state is of interest, but rather several states and transitions between them are in focus. It is an obvious question, whether optimization of the coordinates for other states than the ground state would give substantially different results.

The second order Taylor expansion of the potential employed to determine normal coordinates, gives a realistic description for infinitesimal distortions from the equilibrium structure. Optimizing the coordinates relative to vibrational motion in the vibrational ground state includes the effects of a significant part of the potential energy surface. However, excited vibrational wave functions clearly

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involves larger distortions, and the optimal set of coordinates will depend on the state under study. If all states are independently optimized the whole procedure becomes quite elaborate. Furthermore it raises some theoretical concerns. E.g. the ground state and the excited state will have different sets of coordinates complicating calculation of vibrational transition probabilities. In this work we follow a chain of arguments leading to a very simple method for optimizing coordinates including more states based on a state-averaging procedure. In this method, a set of virtual states of a standard VSCF calculation is used to define a state-average energy obtainable with a computational cost that is essentially the same as an ordinary VSCF calculation. Employing this method in coordinate optimization we obtain an approach denoted optimized coordinate state-average virtual VSCF (oc-sa-vVSCF) that is applicable in practice to any system in which oc-VSCF is applicable. The performance of the new set of coordinates is explored in calculations on water, formaldehyde, the water dimer and the water trimer, as well as ethylene.

The letter is organized as follows. In the next section we describe the theory and the chain of arguments leading to our new method. In Section 3 we describe the computational details, before we in Section 4 present the results. Section 5 presents a summary.

2. Theory

2.1. Coordinate optimization

In coordinate optimization of orthogonal coordinates we relate two sets of orthogonal coordinates to each other by an orthogonal transformation of the coordinates

$$\tilde{\boldsymbol{Q}} = \boldsymbol{U}^T \boldsymbol{Q} \tag{1}$$

As input we use a set of $M = 3N_{atom} - 6$ ($M = 3N_{atom} - 5$ for a linear molecule) normal coordinates as $\boldsymbol{Q} = (Q_1, Q_2, \ldots, Q_M)^T$, which in turn is given in terms of the orthogonal transformation of mass-weighted cartesian displacement coordinates corresponding to diagonalizing the mass-scaled molecular Hessian. We then seek to identify the rotation matrix $\boldsymbol{U}$ such that a given success quantity denoted E is minimized (or maximized).

The concrete procedure used in previous works has been an iterative Jacobi-sweep algorithm. Here, inside each iteration pairs of coordinates are rotated in a series of Givens rotations. Thus, the total rotation matrix becomes

$$\mathbf{U} = \mathbf{U}^{(1)}\mathbf{U}^{(2)}\ldots\mathbf{U}^{(n_{iter})} = \prod_{n=1}^{M(M-1)/2} \mathbf{U}_n^{(1)} \prod_{n=1}^{M(M-1)/2} \mathbf{U}_n^{(1)} \cdots \prod_{n=1}^{M(M-1)/2} \mathbf{U}_n^{(n_{iter})} \tag{2}$$

where the products over n are over all $M(M-1)/2$ pair rotations. Further details of the optimization procedure will not be described here. We refer to Ref. [6] for general aspects and the first implementation, and to Ref. [7] for the embarrassingly parallel implementation used here. The essential feature is that fast evaluation of a success quantity E is needed for efficiently performing the $n_{iter}M(M-1)/2$ one-dimensional optimizations of the rotation angles in the Jacobi-sweep procedure. That is, the rotation angles are chosen to minimize E.

The outcome of the procedure obviously depends on the quantity E to be optimized. So far the VSCF ground state energy has been used, making the procedure comply to the quantum mechanical variational principle. It should be noted, that the exact energy is invariant under the choice of coordinates. However, the quality of approximate energies and wave functions will depend on the choice of coordinates. Thus, the optimization is a way to improve approximate treatments by providing better convergence to the exact results, and to obtain wave functions that in more concise manners represent the important physical effects. In the coming section we shall describe briefly the VSCF ground state energy as choice of E, before describing generalizations aiming at including more than one state in the optimization.

It is important that the Hamiltonian is in a form that is invariant under the transformation. Obviously the exact Hamiltonian is invariant, but approximate potentials are not necessarily invariant. One example that is invariant is a Taylor expanded force field such as a quartic force field, motivating this choice in the particular examples. An example that is not invariant is a many-mode expansion of the potential truncated to an order less than total number of modes.

2.2. Vibrational Self-consistent field and beyond

A cornerstone in this work is the use of VSCF. The VSCF energy

$$E_{\mathbf{i}} = \langle \Phi_{\mathbf{i}} | \hat{H} | \Phi_{\mathbf{i}} \rangle \tag{3}$$

for a given set of coordinates and a given vibrational Hamiltonian, $\hat{H}$, is optimized under variation of the orthonormal one-mode functions $\phi^m_{i_m}(Q_m)$ entering into the VSCF direct product wave function ansatz

$$\Phi_{\mathbf{i}}(\mathbf{Q}) = \prod_{m=1}^{M} \phi^m_{s_m}(Q_m) = \phi^1_{i_1}(Q_1)\phi^2_{i_2}(Q_2)\ldots\phi^M_{i_M}(Q_M). \tag{4}$$

The $\mathbf{i}$ vector is an M-dimensional index vector defining which one-mode function for each mode is 'occupied' in the VSCF state.

In the process of going from having the potential available at a restricted set of grid points, to a representation in a vibrational structure program, it is computationally convenient to work with a Hamiltonian in the sum over products (SOP) form,

$$H = \sum_{t=1}^{N_t} c_t \prod_{m \in \mathbf{m}^t} h^{m,o^t} \tag{5}$$

Here N_t is the number of terms in the operator, $\mathbf{m}^t$ is a mode combination(MC) denoting the set of active modes for the term t. The active modes for a term are the set of modes with one-mode operators h^{m,o^t} different from the unit operator in that particular term. The superscripts m, o^t defines which particular one-mode operator is present for a given mode m and term t. An example of a Hamiltonian operator in the form of Eq. (5) is

$$H = -\frac{1}{2}\sum_m \frac{\partial^2}{\partial Q_m^2} + V^{Taylor} \tag{6}$$

where V^{Taylor} is a Taylor expanded potential, for example a quartic force field. This is the concrete Hamiltonian used in the calculations presented in this work.

The variational procedure leads to the non-linear VSCF equations

$$F^{m,\mathbf{i}} \phi^m_{i_m}(Q_m) = \epsilon^m_{i_m} \phi^m_{i_m}(Q_m) \tag{7}$$

for the one-mode functions $\phi^m_{i_m}(Q_m)$ from here on denoted modals. The effective mean-field operator for mode m, $\hat{F}^{m,\mathbf{i}}$, is essentially obtained by averaging the Hamiltonian over all other modes. In the formulation of Ref. [9] the mean field operator can be written as

$$F^{m,\mathbf{i}} = \sum_{t \in \{t_{\mathrm{act}}\}} (c_t \prod_{m' \in \mathbf{m}^t \setminus m} h^{m',t}_{i_{m'} i_{m'}}) h^{m,t}, \tag{8}$$

here only the terms that are active for the particular mode m is included in the mean field operator, thus $\{t_{\mathrm{act}} | t : \mathbf{m}^t \cap \{m\} = \{m\}\}$.