Self-consistent geometry in the computation of the vibrational spectra of molecules

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An exact and general approach to study molecular vibrations is provided by the Watson Hamiltonian. Within this framework, it is customary to omit the contribution of the terms with the vibrational angular momentum and the Watson term, especially for the study of large systems. We discover that this omission leads to results which depend on the choice of the reference structure. The self-consistent solution proposed here yields a geometry that coincides with the quantum averaged geometry of the Watson Hamiltonian and appears to be a promising way for the computation of the vibrational spectra of strongly anharmonic systems.

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I. INTRODUCTION

The computation of vibrational spectra of polyatomic molecules has been a challenging problem since the advent of quantum mechanics [1–4]. During the last decades, the availability of new methodologies and the continuing development of computational capabilities have led to the possibility of conducting calculations previously beyond reach [5].

In the study of molecular vibrations, the adiabatic separation of electronic and nuclear degrees of freedom is normally employed [6,7]. In this approximation, the electronic energy defines a multidimensional potential-energy surface (PES), which is a function of the nuclear positions. Then, in the absence of external fields, the rovibrational problem is usually described in a frame of reference that rotates with the molecule. In this body-fixed rotating frame, nuclei are described in terms of vibrational internal coordinates. We distinguish in the literature two major trends to represent internal coordinates: curvilinear vibrational coordinates—usually bond lengths and angles—and rectilinear vibrational coordinates. (Two recent well-written reviews can be found in Refs. [5,8].) For curvilinear vibrational coordinates, the transformation of the kinetic-energy operator for the nuclei leads to complicated expressions [5,8]. Nowadays, curvilinear coordinate methods are routinely used to study up to tetratomic [9] and pentatomic molecules [10]. A useful approach is the multiconfiguration time-dependent Hartree method [11], which has been used to study molecules containing up to nine and ten atoms [12].

In this work, we focus on rectilinear vibrational coordinates whose significant advantage is their generality. These coordinates are defined after choosing a reference molecular structure (or reference configuration). In terms of these coordinates, the Watson Hamiltonian provides a general framework for the description of the rovibrational problem of any molecule [3]. The numerical solution of the Watson Hamiltonian is mainly limited by the number of degrees of freedom. Several methods have been developed over the years [13,14]. Among them, MULTIMODE and its extensions [15,16] are state-of-the-art in this field.

Because of their generality, the use of rectilinear vibrational coordinates and the Watson Hamiltonian is preferable when extending the study to large molecules. However, since the complexity of the problem increases with the number of atoms, it has been common practice to resort to approximations. For example, the computation of low-lying vibrational states is often based on the vibrational-self-consistent-field (VSCF) method and its extensions [17]. The VSCF is a powerful methodology [18], where one employs an approximate form of the Watson Hamiltonian that ignores the complicated contribution of the terms containing the vibrational angular momentum and the Watson term. (In the following, we shall refer to these two terms as the "Watson correction terms" or simply "Watson corrections.") The effect of the Watson correction terms is probably less significant for larger molecules, but they may become important for very anharmonic systems or when computing highly excited states. In general, these terms present an extra computational challenge and their omission is often desirable.

In this work, we investigate the consequences of neglecting the Watson corrections in the computation of molecular vibrational spectra. It will turn out that the choice of molecular reference structure plays an important role in the quality of the results. In order to avoid introducing any further approximation, besides the omission of the Watson correction terms, we restrict our study to triatomic molecules for which the vibrational problem can be solved numerically exactly. We first analyze the case of water molecule as an example of a semirigid system. We observe that the omission of the Watson correction terms leads to results that depend on the choice of the reference structure. However, we are more interested in the description of highly excited states and in floppy molecules, both characterized by a large delocalization of the vibrational wave function. To this end, we study a model triatomic molecule, which is constrained to move only in two dimensions (2Ds). This model exhibits a symmetric double-well potential. We observe that here the choice of the reference structure becomes crucial. So far, in order to deal with the symmetric double well appearing in floppy molecules, such as NH_3 and $H_5O_2^+$, the reference structure has been chosen *ad hoc* at the inversion saddle point [16]. However, the choice of an optimal reference structure is not obvious *a priori* for more general anharmonic potentials.

II. THEORY

The Watson Hamiltonian provides a general framework for the description of the rovibrational problem of any molecule [3]. This Hamiltonian is expressed in terms of rectilinear (locally defined) vibrational coordinates together with the Euler angles. For the sake of simplicity, we study states with zero total angular momentum ($J=0$), where the nuclear wave function does not depend on the Euler angles. For a nonlinear molecule with N atoms, the Watson Hamiltonian reads as

$$\hat{H}_W^{J=0} = \frac{1}{2}\sum_{\alpha,\beta} \mu_{\alpha\beta}\hat{\pi}_\alpha\hat{\pi}_\beta + \frac{1}{2M}\sum_{k=1}^{3N-6} \hat{P}_{\zeta_k}^2 + U + \mathcal{E}_\zeta, \quad (1)$$

where $3N-6$ is the number of (mass-scaled) vibrational coordinates, α,β are the Cartesian coordinates x, y, z, in the rotating frame of reference, and M is the common mass of the mass-scaled coordinates as defined in Ref. [19]. Matrix elements $\mu_{\alpha\beta}$ are the components of the effective reciprocal inertia tensor,

$$\mu_{\alpha\beta} = (I')_{\alpha\beta}^{-1}, \quad (2)$$

with

$$I'_{\alpha\beta} = I_{\alpha\beta} - M \sum_{k,l,m=1}^{3N-6} \xi_{ml}^\beta \xi_{kl}^\alpha \zeta_m \zeta_k, \quad (3)$$

where $I_{\alpha\beta}$ is the instantaneous moment of inertia tensor and

$$\xi_{kl}^\gamma = \sum_{\mu=1}^{N-1} \sum_{\alpha,\beta} \epsilon_{\alpha\beta\gamma} A_{k,\mu\alpha} A_{l,\mu\beta} \quad (4)$$

gives the coupling of the vibrational coordinates. Matrix A defines the vibrational coordinates from a set of coordinates relative to the center of mass [19]. The function $\mathcal{E}_\zeta$ is the PES expressed in terms of the vibrational coordinates and U is the so-called Watson term, which is proportional to the trace of the effective reciprocal inertia tensor (2)

$$U = -\frac{1}{8}\hbar^2\sum_\alpha \mu_{\alpha\alpha}. \quad (5)$$

Finally, $\hat{\pi}$ is the vibrational angular momentum, whose components are given by

$$\hat{\pi}_\alpha = \sum_{l,k=1}^{3N-6} \xi_{lk}^\alpha \zeta_l \hat{P}_{\zeta_k}, \quad (6)$$

where $\hat{P}_{\zeta_k} = -i\hbar\,\partial/\partial\zeta_k$. The volume element for integration is

$$dV = (\sin\chi d\chi d\phi d\theta)(d\zeta_1 d\zeta_2 \cdots d\zeta_{3N-6}), \quad (7)$$

and $\sin\chi$ is the weight factor of the volume element [5]. It is important to note that the Watson Hamiltonian (1) is exact; no approximations have been introduced in its derivation and no limit is placed on the amplitude of the vibrations. In Ref. [19], it was demonstrated numerically that the full solution of the Watson Hamiltonian does not depend on the choice of the reference structure. In fact, we had found that within numerical accuracy, not only the energy but also the quantum averaged geometry, [20] for each vibrational state, were independent of the reference configuration.

In the past, the applicability of the Watson Hamiltonian for nonlinear triatomic molecules has been questioned [21] because the Hamiltonian becomes singular at the linear configuration. If the Watson Hamiltonian is nevertheless used, vibrational excursions that sample the linear configuration must be avoided [14,22]. In a forthcoming publication, we explain in detail how we have dealt with this issue [23].

What we have termed the Watson corrections are defined as follows:

$$\hat{W} = \frac{1}{2}\sum_{\alpha,\beta} \mu_{\alpha\beta}\hat{\pi}_\alpha\hat{\pi}_\beta + U. \quad (8)$$

With this, the Watson Hamiltonian (1) reads as

$$\hat{H}_W^{J=0} = \hat{H}_0 + \hat{W}, \quad (9)$$

where

$$\hat{H}_0 = \frac{1}{2M}\sum_{k=1}^{3N-6} \hat{P}_{\zeta_k}^2 + \mathcal{E}_\zeta. \quad (10)$$

In the rest of the paper, we employ $\hat{H}_0$ above to solve approximately the vibrational problem.

III. DEPENDENCE OF RESULTS ON THE REFERENCE STRUCTURE

When one neglects the contribution of the Watson corrections, the exact solution of the approximate Hamiltonian $\hat{H}_0$ exhibits a strong dependence on the reference geometry (RG). To illustrate this effect, we first study the water molecule. The reader is referred to Ref. [19], where a general method was presented explaining how to construct a local set of rectilinear vibrational coordinates for a given a reference structure of a nonlinear molecule. For the water molecule, we use the PES by Partridge and Schwenke [24] for which the equilibrium structure corresponds to an oxygen-hydrogen distance of $d_{OH}=1.81$ bohr and an internal angle of $\Omega = 104.44°$. We solve the approximate problem at equilibrium and take the resulting spectrum as our target. We then consider two arbitrary nonstationary reference configurations: (a) $d_{OH}=2$ bohr, $\Omega=120°$ and, (b) $d_{OH}=1.8$ bohr, $\Omega=90°$. For each one of these configurations, we define the local set of vibrational coordinates and compute the approximate vibrational spectra using $\hat{H}_0$. Figure 1 shows the differences of the resulting spectra (black triangles and red circles) from the target spectrum (green triangles). The magnitude of the energy differences clearly highlights the dependence of results on the reference structure. The root-mean-square (rms) deviation from the target spectrum is about 40 cm^{-1} from both reference geometries, whereas this value reduces to 0.01 cm^{-1} if the full Watson Hamiltonian is used (see Fig. 3 in Ref. [19]). Based on this observation, we conclude that the Watson corrections in the Watson Hamiltonian compensate for the effect of different reference structures. A few questions now arise: as the results for the approximate Hamiltonian appear to depend on the choice of the reference structure, is it meaningful to search for a structure from which the
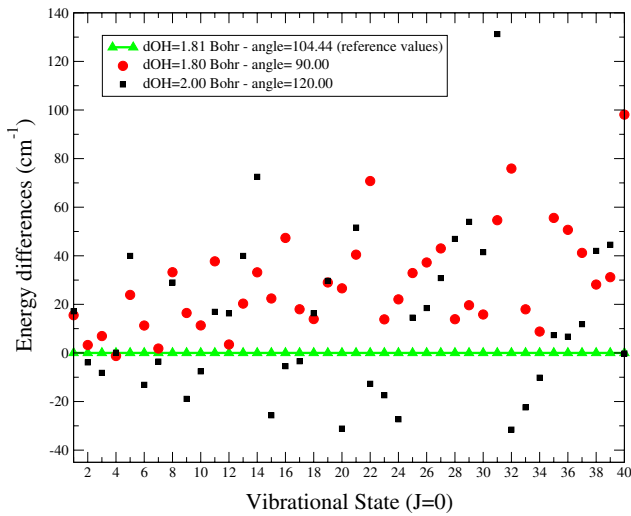
FIG. 1. (Color online) Effect of the choice of the reference structure in water molecule $J=0$ for the approximate Hamiltonian without Watson corrections.

FIG. 2. (Color online) Self-consistent procedure.

results will be more accurate than from other structures? If so, what would this optimal reference structure be? Could it be determined without using the Watson corrections?

In relation to the search for an optimal geometry, we discovered that for all our calculations from different structures, the input reference structure and the output quantum average structure differed. Therefore, none of the calculations in Fig. 1 were a self-consistent solution of the approximate Hamiltonian $\hat{H}_0$.

Within this framework, we can identify two well-defined geometries that play a role in this study. The first is the quantum averaged geometry that results from the solution of the full Watson-Eckart Hamiltonian and is independent of the choice of the input RG [19]. We refer to it as the Watson geometry (WG). When we use the WG as the reference structure, the vibrational excursions will be minimized and the Watson corrections will be small. For these reasons, we expect that a calculation involving the approximate Hamiltonian $\hat{H}_0$ from that structure would yield more accurate results than from other structures. The second well-defined geometry arises when employing the approximate Hamiltonian: it is the one for which the input RG and the output quantum averaged geometry coincide [we call it the self-consistent geometry (SCG)]. This geometry corresponds to the self-consistent solution of the approximate Hamiltonian $\hat{H}_0$. The surprising result of our work is that for all cases we studied, even in the extreme case of tunneling, the WG and the SCG coincide to an excellent extent.

IV. SELF-CONSISTENT METHODOLOGY

To determine the self-consistent geometry of a given vibrational state, we propose the algorithm shown in Fig. 2: starting from an initial input reference configuration (which is not necessarily stationary), we calculate the vibrational coordinates ζ [19] and compute the vibrational wave func-
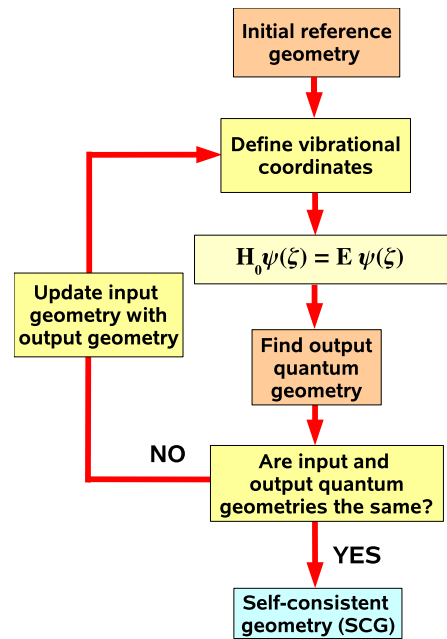
tion $\psi(\zeta)$ for that particular state and the corresponding quantum geometry (QG). Then, the input reference configuration is replaced by this new QG and the procedure is repeated until convergence is reached, i.e., until the (input) RG coincides with the (output) QG yielding the SCG of that particular vibrational state.

For the vibrational states of the water molecule, we found that the SCG and the WG for each state were almost the same: the bond lengths were the same to numerical accuracy and the internal angles were the same within a hundredth or at most a tenth of a degree. Only for the few pathological states reported in Ref. [19] where convergence was difficult, we found that the SCG and the WG differed by a couple of degrees. However, convergence of the full Watson results was also in doubt for these states.

Approximately, to first order, the effect of the Watson corrections in the energy spectrum can be included by calculating their expectation value in terms of the wave function $\psi(\zeta)$ computed from the approximate Hamiltonian $\hat{H}_0$. In this way, considering the Watson correction terms $\hat{W}$ as a perturbation of $\hat{H}_0$, we can evaluate the first-order energy correction (FOC) of the vibrational spectrum by

$$E^{FOC} = \langle \psi(\zeta)|\hat{H}_0|\psi(\zeta)\rangle + \langle \psi(\zeta)|\hat{W}|\psi(\zeta)\rangle. \quad (11)$$

This first-order correction also depends on the RG and we found that it is small at the SCG (where it was often but not always exactly minimized). This is consistent with the theoretical expectation since the SCG almost coincides with the WG and, for the latter, the Watson corrections are small [2].

For the water molecule, the improvement of the results using the SCG is not significant. The water molecule is a semirigid molecule and the vibrational wave functions are quite localized around the minimum, even for some highly excited states. Consequently, the calculated SCGs are close
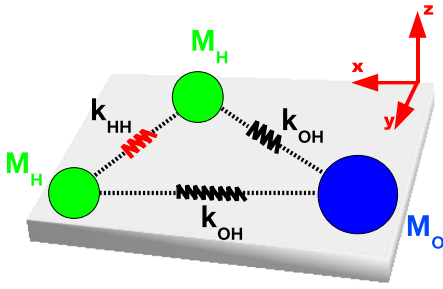
FIG. 3. (Color online) A triatomic C_{2v} model molecule confined in the xy plane.

to the reference geometry at the minimum of the PES. The energy differences for the low-lying vibrational states with respect to the Watson spectrum are less than 2% and, with the FOC, most of the effect is recovered (within 0.2%). To our mind, these results justify the omission of the Watson corrections for the calculation of semirigid molecules and the use of the minimum of the PES as the choice of the reference geometry [17].

V. TRIATOMIC C_{2v} MOLECULE IN A PLANE

To investigate the effects of the Watson corrections in highly anharmonic systems, we employed a simplified C_{2v} triatomic model molecule constrained to move in the fixed x-y plane of the laboratory frame of reference. The main difference with the three-dimensional (3D) case is that while a bent triatomic in 3D does not tunnel [25], tunneling becomes possible when the same molecule is confined in 2D. Tunneling is not possible in 3D because the two minimum-energy configurations that would be explored by the "tunneling" vibrational coordinate—if tunneling were possible—are actually connected by an out-of-plane rotation and in the rotating frame of reference the two configurations coincide. In our model (Fig. 3), the interaction between atoms is simulated by harmonic springs and the nuclear masses have been chosen like those in the water molecule.

In the rotating frame of reference (i.e., rotating in the xy plane), there are two nonequivalent equilibrium structures (these configurations are denoted by **A** and **C** in Fig. 4). To go from one to the other, the molecule has to overcome the inversion barrier at the linear configuration. If the atoms are displaced from the equilibrium configuration **A** along the direction of the arrows, they reach the linear configuration **B**.
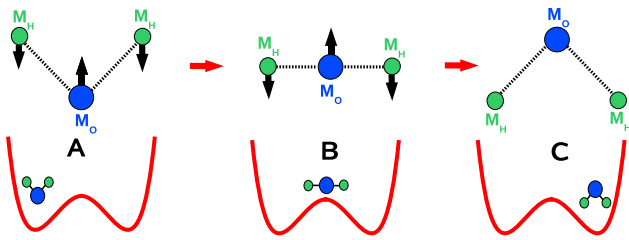

FIG. 4. (Color online) Qualitative picture of the process to overcome a potential barrier in a triatomic C_{2v} model molecule that is constrained to move in a plane.

Analogously, from the linear configuration **B** they reach configuration **C**. Clearly, it is necessary to overcome a potential barrier to go from configuration **A** to **C** following the minimum-energy path [26]. In this path, the linear configuration **B** corresponds to the stationary saddle point.

The rovibrations of the 2D model are characterized by one Euler angle θ and three vibrational degrees of freedom. Based on Watson's work [3], the form of the Watson Hamiltonian for this planar triatomic model can be readily obtained. The difference from the Watson Hamiltonian in 3D is that the latter exhibits a singularity when the molecule becomes linear [14], while the Hamiltonian is not singular when the molecule is restricted in a plane. As before, we restrict to states with zero total angular momentum ($J=0$). The expression of the Watson Hamiltonian reads as

$$\hat{H}_{W,2D}^{J=0} = \frac{1}{2}\mu_{zz}\hat{\pi}_z\hat{\pi}_z + \frac{1}{2M}\sum_{k=1}^3 \hat{P}_{\zeta_k}^2 + U_{2D} + \mathcal{E}_\zeta, \quad (12)$$

where μ_{zz} is now given by

$$\mu_{zz} = \frac{1}{I'_{zz}} \quad (13)$$

and

$$I'_{zz} = I_{zz} - M\sum_{k,l,m=1}^3 \xi_{ml}^z\xi_{kl}^z\zeta_m\zeta_k. \quad (14)$$

In this case, the Watson term reads as

$$U_{2D} = -\frac{1}{8}\hbar^2\mu_{zz} \quad (15)$$

and the volume element for integration is

$$dV_{2D} = (d\theta)(d\zeta_1 d\zeta_2 d\zeta_3). \quad (16)$$

The inversion barrier has to be low to allow for appreciable tunneling between the two equilibrium configurations. We have chosen the minimum geometry to correspond to an O-H bond length of 1.8 bohr and a bending angle of 122°. Setting the spring constants to be 0.4 and 0.16 hartree/bohr^2 for k_{OH} and k_{HH}, respectively, the inversion barrier is 1987.6 cm^{-1}.

We note by symmetry that for the planar model triatomic molecule, a good choice for the reference geometry must correspond to the linear configuration. Still, the optimal reference bond length cannot be guessed by symmetry and the question remains on how to obtain an optimal geometry in the general case, when it will not be possible to predict it using symmetry arguments.

When we solve the approximate Hamiltonian, starting from one of the two minima (minimum I), we find for the ground state that the output geometry is at the other well (minimum II). This is because when the local vibrational coordinates at minimum I are extrapolated to minimum II, they acquire a partly rotational character there. As the PES is constant along a rotational coordinate, the PES around minimum II (in terms of the vibrational coordinates of minimum I) appears less stiff and the ground state tends to localize around it.
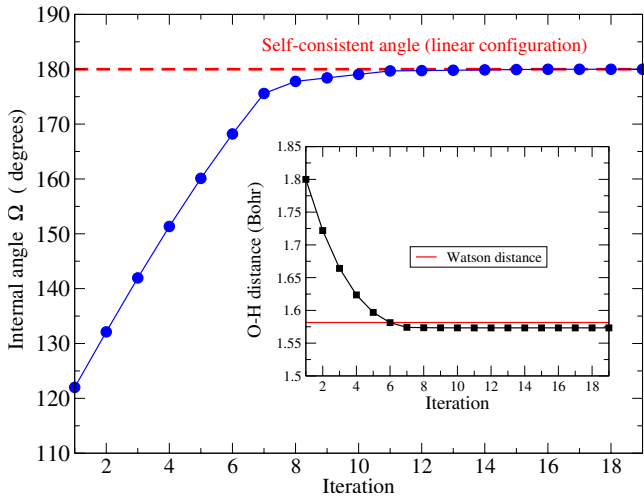
FIG. 5. (Color online) Convergence of the geometrical parameters toward self-consistency (ground state).

To aid convergence during the iterative procedure (Fig. 2), we mix input and output geometries and observe that the probability of finding the particle in the other well builds up until the two potential wells become symmetric at the linear configuration. A similar trend is observed for the excited states although the corresponding self-consistent O-H distances are different.

Figure 5 demonstrates the convergence to self-consistency using the algorithm (Fig. 2) for the planar model. Both the internal angle and the O-H distance converge toward their self-consistent values. It is worth mentioning that the SCG can be determined in fewer number of steps (from three to five steps depending on the vibrational state) by optimizing the mixing between output and input geometries.

The SC parameters (angles as well as bond lengths) coincide with the WGs obtained from the solution of the exact Watson Hamiltonian. In this case, the double-well nature of the problem forces all the quantum averaged geometries to be at the linear configuration but the bond lengths vary. For the low-lying vibrational states (those reported in Table I), the rms deviation of the SC bond lengths from the WG values is 0.01 bohr.

Table I shows the low vibrational excitation spectrum calculated at the minimum of the PES and at the SCG (fourth and fifth columns) in comparison with the full Watson Hamiltonian results (eighth column). Vibrational coordinates ζ_1, ζ_2, and ζ_3 are similar to symmetric stretching, breathing, and asymmetric stretching motion, respectively [19]. There is a noticeable improvement when using the corresponding SC geometry.

The advantage of choosing the SCG becomes evident when the effect of the Watson correction terms is introduced as a FOC (results in sixth and seventh columns in Table I). At the minimum of the PES, the resulting spectrum is still a poor estimate of the full Watson results. In fact, the order of some vibrational states is reversed leading to an unphysical negative tunneling frequency. On the other hand, results at the SCG are considerably improved. The tunneling frequency is very well predicted (within a 10% error) considering that this value is a very sensitive quantity.

VI. CONCLUSIONS AND DISCUSSION

We observed that the omission of Watson correction terms in the solution of the Watson Hamiltonian leads to results that depend on the choice of the reference geometry. This is in contrast with the results of the full Watson Hamiltonian.

Wondering how to determine an appropriate geometry to improve the accuracy of the approximate results, we argued that probably the best geometry should be the quantum averaged geometry from the solution of the Watson Hamiltonian. We realized, however, that the plethora of different choices for the RG is only apparent because different input RG geometries lead to different output quantum averaged geometries and the solution of the approximate Hamiltonian H_0 is not self-consistent in general. Nevertheless, a SC solution can be obtained and the SCG turns out to coincide with the WG to an excellent extent.

For a semirigid molecule, the SCG is close to the equilibrium geometry (minimum of the PES) and this justifies the routine omission of Watson corrections and the use of the classical equilibrium reference geometry in the literature. However, for highly anharmonic systems, the improvement of using the SCG can be significant.

TABLE I. Comparison of low vibrational excitation spectrum of exact Watson results with approximate results, from the minimum and at the SCG, when Watson corrections are neglected or included within FOC.

v_{ζ_1}	v_{ζ_2}	v_{ζ_3}	H_0		H_0+FOC		Watson
			Min	SCG	Min	SCG	
0	0	0	3648.47	4177.16	4672.85	4375.34	4357.68
0	1	0	705.45	0.42	−316.90	0.71	0.78
0	2	0	1088.55	1028.61	991.30	985.82	983.88
0	3	0	1677.74	1055.13	706.14	1026.67	1026.45
0	4	0	1980.93	1749.64	1638.51	1652.08	1660.12
0	5	0	2431.88	2025.13	1741.17	1989.65	1990.42
0	6	0	2897.31	2555.46	2375.10	2521.72	2523.98
0	7	0	3456.27	3098.58	2950.94	3091.68	3088.16
	Error (MSD)		463.59	43.33	209.48	3.52	

In this context, it is worth recalling that for highly anharmonic systems, such as tunneling molecules, it is believed that the use of normal modes at the minimum reference geometry is not suitable to describe tunneling within the framework of the VSCF method (with its omission of the Watson corrections). It is further argued that a multireference wave function composed of the wave functions at different minima would be appropriate to describe tunneling [17].

Our observation (Fig. 1) that the accuracy of the approximate description depends strongly on the reference geometry suggests that an inappropriate choice of reference structure is probably behind the failure to describe tunneling. It is also worth remembering that the wave functions at different minima (corresponding to different structures) are defined in different vibrational spaces and building a linear combination of them is not straightforward. Our results on the tunneling triatomic model suggest, instead that the use of rectilinear vibrational coordinates together with the employment of the SCG as the reference geometry is a promising way to describe approximately a general molecule exhibiting strong anharmonicity.

For large molecules, obtaining the self-consistent solution for each vibrational state can be expensive computationally and, therefore, the methodology to determine the SCG for each vibrational state will not be practical as a routine method. In addition, different vibrational states will generally have different SCGs and the resulting vibrational states will belong to different vibrational spaces. Therefore, calculating matrix elements between the different vibrational states will not be an easy task. As a practical routine scheme, we propose instead to use an "average" SCG that would correspond to a set of vibrational states. For example, one could compute the average SCG by performing a thermal average over a set of vibrational states. This would allow the approximate computation of vibrational spectra and thermochemical quantities as a function of temperature.

However, when the full Watson Hamiltonian cannot be used and the best possible accuracy of the results is required, especially when the target is a small number of vibrational states with particularly large amplitude of motion, then, employing the SCG as the reference is the best strategy.

ACKNOWLEDGMENTS

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