Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 119 (2014) 100–106

Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Towards black-box calculations of tunneling splittings obtained from vibrational structure methods based on normal coordinates

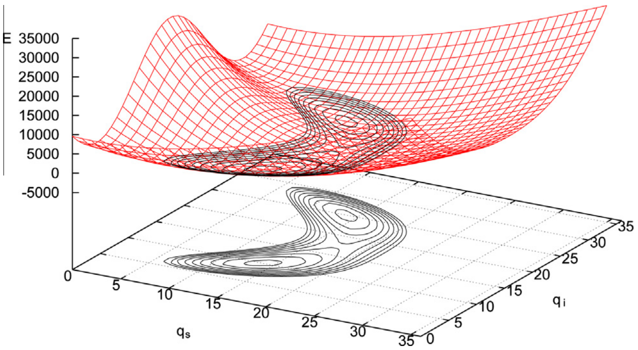
Michael Neff, Guntram Rauhut *

Institute of Theoretical Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany

HIGHLIGHTS

- Tunneling splittings of NH_3 and OH_3^+ can be computed by standard VCI approaches.
- Double-well potential energy surfaces can reliably be expanded in normal coordinates.
- Double-well PES expansions can be truncated after the 4-mode coupling terms.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Available online 14 March 2013

Keywords:
Tunneling splittings
Normal coordinates
VCI calculations
Hydronium ion
Ammonia

ABSTRACT

Multidimensional potential energy surfaces obtained from explicitly correlated coupled-cluster calculations and further corrections for high-order correlation contributions, scalar relativistic effects and core-correlation energy contributions were generated in a fully automated fashion for the double-minimum benchmark systems OH_3^+ and NH_3. The black-box generation of the potentials is based on normal coordinates, which were used in the underlying multimode expansions of the potentials and the μ-tensor within the Watson operator. Normal coordinates are not the optimal choice for describing double-minimum potentials and the question remains if they can be used for accurate calculations at all. However, their unique definition is an appealing feature, which removes remaining errors in truncated potential expansions arising from different choices of curvilinear coordinate systems. Fully automated calculations are presented, which demonstrate, that the proposed scheme allows for the determination of energy levels and tunneling splittings as a routine application.

© 2013 Elsevier B.V. All rights reserved.

Introduction

The accurate *ab initio* calculation of vibrational spectra beyond the harmonic approximation remains a challenging task for several reasons: (1) the well-known *curse of dimensionality* requires the introduction of approximations in order to limit the number of *ab initio* single-point calculations for representing important fractions of the multidimensional potential energy surface (PES). (2) each individual *ab initio* single-point calculation needs to be converged with respect to the orbital basis set and the electron correlation space, which require computationally very demanding calculations. However, for many applications even this scheme is not accurate enough, but requires the account of relativistic effects, corrections arising from spin-orbit couplings and other terms [1]. This renders the calculation of multidimensional potential energy surfaces a non-trivial and computationally demanding task. On the other hand, many modern quantum chemistry program packages offer the possibility to perform such complex single point calculations in a single run controlled by a simple input file. Besides these aspects related to electronic structure theory, the accurate calculation of the vibrational wave function is likewise demanding.

---

* Tel.: +49 711 685 64405; fax: +49 711 686 64442.
E-mail address: rauhut@theochem.uni-stuttgart.de (G. Rauhut).

1386-1425/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.saa.2013.02.033

(3) Once based on the Watson Hamiltonian [2] vibrational structure calculations need to be converged with respect to the expansion of the vibrational angular momentum terms and with respect to vibration correlation contributions. The Watson Hamiltonian is based on normal coordinates. These are given as

$$q_k = \sum_i^N \sum_\alpha \sqrt{m_i}\, l_{i\alpha k}\left(r_{i\alpha} - r^0_{i\alpha}\right) \tag{1}$$

where q_k denotes the kth normal coordinate, m_i is the mass associated with the ith atom at the instantaneous position $r_{i\alpha}(\alpha \in \{x, y, z\})$ in the Eckart frame. $r^0_{i\alpha}$ are the nuclear coordinates of the stationary reference structure and $l_{i\alpha k}$ specify the elements of the eigenvectors of the mass-weighted Hessian, which essentially weight the individual displacements of the atoms. Likewise, isolation of $r_{i\alpha}$ leads to [2]

$$r_{i\alpha} = r^0_{i\alpha} + \sqrt{1/m_i}\sum_k l_{i\alpha k} q_k \tag{2}$$

and thus the elements of the displacement vectors associated with each individual normal coordinate are given by $l_{i\alpha k}/\sqrt{m_i}$.

For semi-rigid systems with an isolated local minimum the use of rectilinear normal coordinates within the automatic generation of meaningful parts of the potential energy surface is without any problems and usually leads to reliable results once the expansion of the PES has not been truncated too early. Many examples in the literature support this statement [3,4]. However, for rotational degrees of freedom or double-minimum potentials curvilinear coordinates are much more appropriate. The problems associated with normal coordinates are on hand: low order terms of the multimode expansion, which represent n-dimensional cuts of the PES, – spanned by the normal coordinates – are able to describe the important fractions of the PES in the region close to the equilibrium structure, but not so for the outer regions. Simply, the displacement vectors may point into the wrong direction and thus the low-order terms may describe unimportant regions of the potential, typically being very high in energy. This is most obvious for curved valleys on the PES. Hence, the question is not, if we can expand potential energy surfaces in terms of normal coordinates at all, but if we can restrict the multimode or Taylor expansion of the PES solely to low order terms for such systems. The most likely answer to this will be, that we need additional high-order terms, e.g. $(n + 1)$ or $(n + 2)$ rather than n-dimensional cuts only, in order to obtain meaningful results. However, for practical reasons another aspect enters into the discussion: once the displacement vectors point into directions which lead to a steep increase of the energy, the fitting of the PES may run into trouble. Of course, in principle there is no need for fitting at all, but computationally efficient implementations, which try to minimize the number of *ab initio* single point calculations, typically rely on any type of fitting procedure. As the range of energies rises the absolute fitting error rises as well and thus many data points and many fit functions need to be provided in order to keep the final error small. In the worst case even the electronic structure calculations may cause trouble due to low-lying electronically excited states. As a result the underlying Hartree–Fock calculations may not converge and the user has to switch to multi-reference calculations with all the associated problems. For a recent discussion of this issue see for example Ref. [5]. The question remains, why we should use normal coordinates at all? Historically it was the complicated expression of the kinetic energy operator in curvilinear coordinates [6], which made normal coordinates rather popular and an attractive alternative. However, this argument is obsolete as very nice implementations for the kinetic operator in arbitrary coordinates have been presented in the (recent) past [7,8]. In our opinion, the most important argument in favor of normal coordinates is their unique definition. For larger systems, i.e. more than 6 or 7 atoms, the expansion of the potential has to be truncated prior to full convergence of the vibrational state energies. This at least will be true in standard applications and is common practice in electronic structure calculations with respect to the correlation space. Using internal coordinates will thus lead to truncation errors in the final results, which depend on the definition of the coordinate system. Moreover, for larger systems the definition of a good coordinate system in terms of internal coordinates is not trivial and requires certain experience. In some cases, e.g. molecular or atomic clusters, the definition may not be clear at all or even allows for several solutions. As a result, the setup of the coordinate system is error prone, far from being of black box nature and thus remains the realm of experts. However, it is the ease of use which makes a method attractive to the broad community – for sure this is at least one reason why many users prefer single-reference coupled-cluster approaches so much over multi-reference methods, which require to fiddle around with the active space. In that respect normal coordinates must be considered superior to internal coordinates. *We explicitly like to point out here that we do not intend to advocate normal coordinates for all kinds of calculations, but simply want to explore their useful range of applicability in the context of accurate vibrational structure calculations*. Most likely, the best solution with respect to the dilemma of the choice of a good coordinate system would be a linear combination of internal coordinates, which needs to fulfill some mathematical condition in order to allow for a unique definition. Attempts in that direction have been undertaken by several authors but experience with those in the field of accurate vibrational structure calculations is still very limited [9].

We have chosen NH_3 and OH_3^+ as benchmark systems for several reasons: (a) the vibrational spectra of both molecules have been carefully investigated in the past and thus for both systems extremely accurate experimental [10–13] and theoretical data [14–17] are available. (b) Both molecules are small enough in order to allow for highly accurate electronic structure calculations, which minimize the errors in this part of the calculations. (c) The vibrational spectra, which are strongly affected by tunneling splitting, are very sensitive with respect to the shape of the surface. Concerning the tunneling splittings, OH_3^+ is the more interesting system as the splittings are significantly larger than for NH_3. In contrast to that, the generation of the PES is more challenging as the inversion barrier of NH_3 is almost three times as high as for OH_3^+. As the literature about the vibrational spectra of these two systems is vast, we cannot summarize the entire history of these systems here, but rather want to focus on a limited number of articles being relevant for our work. Between 1999 and 2003 Handy, Carter and co-workers published a series of papers about NH_3 and OH_3^+ and the associated isotopologues [18–23]. In this series they focussed primarily on the development of an accurate kinetic energy operator in internal coordinates. The potential energy surfaces used by these authors has been determined at the density functional theory (DFT) level or the coupled-cluster level with a perturbational treatment of the triple-excitations. Since the authors realized that the uncorrected potential energy surfaces are not accurate enough in order to get excellent agreement with experimental data, they refined their surfaces with respect to experimental data. Using this scheme they obtained excellent results for both, the vibrational transitions and the inversion barrier. About the same time Bowman, Carter and co-workers studied the PES and vibrational spectrum of the OH_3^+ cation [24,25]. Besides studies in internal coordinates these authors also used normal coordinates, but the accuracy of their potential energy surface did not allow for final conclusions, if the remaining errors are due to the use of normal coordinates or deficiencies in the electronic structure calculations. The most accurate studies in this

Download English Version:

https://daneshyari.com/en/article/1233091

Download Persian Version:

https://daneshyari.com/article/1233091

Daneshyari.com