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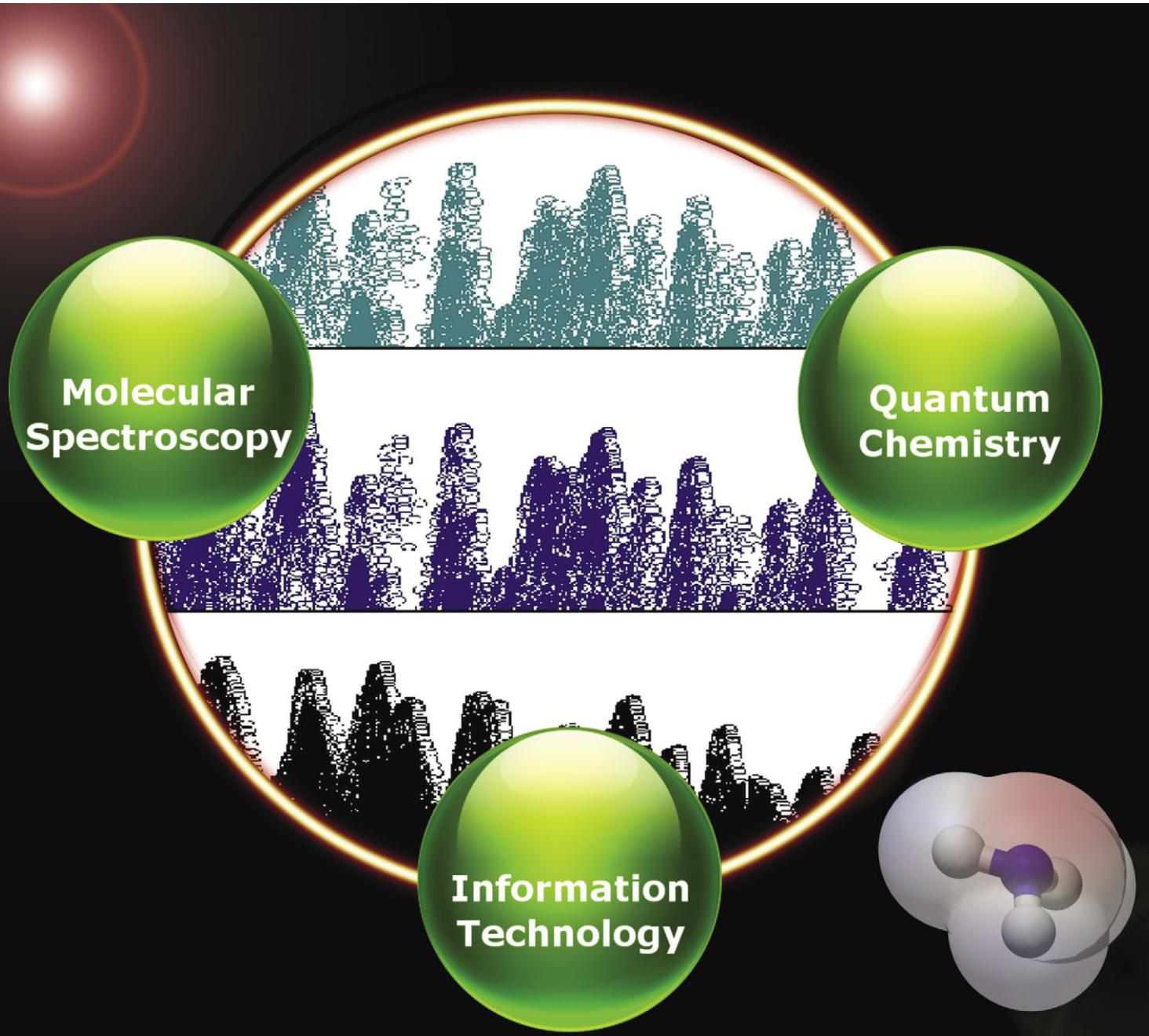
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PERSPECTIVE

The fourth age of quantum chemistry: molecules in motion

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Developments during the last two decades in nuclear motion theory made it possible to obtain variational solutions to the time-independent, nuclear-motion Schrödinger equation of polyatomic systems as "exact" as the potential energy surface (PES) is. Nuclear motion theory thus reached a level whereby this branch of quantum chemistry started to catch up with the well developed and widely applied other branch, electronic structure theory. It seems to be fair to declare that we are now in the fourth age of quantum chemistry, where the first three ages are principally defined by developments in electronic structure techniques (G. Richards, *Nature*, 1979, **278**, 507). In the fourth age we are able to incorporate into our quantum chemical treatment the motion of nuclei in an exact fashion and, for example, go beyond equilibrium molecular properties and compute accurate, temperature-dependent, effective properties, thus closing the gap between measurements and electronic structure computations. In this Perspective three fundamental algorithms for the variational solution of the time-independent nuclear-motion Schrödinger equation employing exact kinetic energy operators are presented: one based on tailor-made Hamiltonians, one on the Eckart–Watson Hamiltonian, and one on a general internal-coordinate Hamiltonian. It is argued that the most useful and most widely applicable procedure is the third one, based on a Hamiltonian containing a kinetic energy operator written in terms of internal coordinates and an arbitrary embedding of the body-fixed frame of the molecule. This Hamiltonian makes it feasible to treat the nuclear motions of arbitrary quantum systems, irrespective of whether they exhibit a single well-defined minimum or not, and of arbitrary reduced-dimensional models. As a result, molecular spectroscopy, an important field for the application of nuclear motion theory, has almost black-box-type tools at its disposal. Variational nuclear motion computations, based on an exact kinetic energy operator and an arbitrary PES, can now be performed for about 9 active vibrational degrees of freedom relatively straightforwardly. Simulations of high-resolution spectra allow the understanding of complete rotational–vibrational spectra up to and beyond the first dissociation limits. Variational results obtained for H_2O, H_3^+, NH_3, CH_4, and H_2CCO are used to demonstrate the power of the variational techniques for the description of vibrational and rotational excitations. Some qualitative features of the results are also discussed.

1 Introduction

For about 200 years,[1–6] atomic and molecular spectroscopy has been a pioneering field for and a principal source of improving our understanding of chemical phenomena. About 80 years ago,[7–9] in order to provide a qualitative explanation of the available experimental results, quantum mechanics was adapted to chemical (molecular) systems and thus the development of quantum chemistry has begun. Molecular systems were treated using a quantum mechanical description of the electrons moving in the field of clamped nuclei, *i.e.*, employing the Born–Oppenheimer (BO) approximation.[10–15] This readily provided a successful qualitative description of many available experimental results. Besides the "numerical" achievements, the theoretical framework of molecular systems corresponding to the quantum mechanical description of electrons moving in the field of fixed, classical nuclei provided a formal ground to many important chemical constructs, like the concept of distinct potential energy surfaces (PES),[16–21] equilibrium structures,[22–26] transition states,[27–29] and atomic and molecular orbitals.[8,9] These concepts have remained central to our understanding of chemical phenomena. In influential publications and related lectures, Richards[30] and Schaefer[31,32] categorized the development of computational quantum chemistry

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into three ages and called this the first age of quantum chemistry. As the numerical methods for solving the electronic Schrödinger equation evolved and improved, electronic structure theory started to result in more accurate, already at least semi-quantitative description of experimentally measurable quantities. This period of extensive method development within electronic structure theory was coined the second age of quantum chemistry.[30–32] Later, perhaps as early as in 1970,[30] theoretical predictions with an accuracy comparable to contemporary measurements were provided by the numerically precise solution of the electronic Schrödinger equation, marking the beginning of the third age of quantum chemistry. In this era application of state-of-the-art quantum chemical methods produced results which could legitimately challenge existing experiments or provide significant challenges for the design and execution of new experiments.

As experimental spectroscopy developed and provided more and more detailed and accurate results for a number of more and more complex systems, it became evident that electronic structure theory with fixed nuclei is not sufficient for simulating experiments. The computation of equilibrium properties, *i.e.*, properties corresponding to nuclei fixed at a local minimum of the PES, restricted the picture of a molecule to a rigid or at least semirigid structure, or maybe to a handful of (semi-)rigid structures or conformations.[33] Electronic structure theory[34–36] has been quite successful in yielding equilibrium quantities which can be related to experimental observables but are distinct from them. Quantitative agreement with results of most experiments can only be expected if the motion of the nuclei are considered explicitly, as well. It is hoped in this respect that in the fourth age of quantum chemistry, which we are living in, efficient quantum chemical

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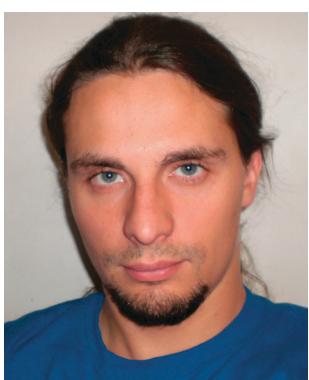
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(electronic structure *and* nuclear motion) computations can be performed which not only treat all particles of a molecule quantum mechanically but can bridge the gap between "effective", experimental observables and "equilibrium" computed quantities at even elevated temperatures of interest, thus providing treatment of molecules in constant and rapid motion.[37]

Molecules are non-rigid assemblies of electrons and nuclei.[22,38] "Effects" due to the rotations and vibrations of the nuclei are omnipresent whether one takes them into account explicitly or not. Nevertheless, the BO separation of the motion of electrons and nuclei is a remarkably good approximation for chemistry.[22,25,39–42] Thus, after solving the electronic problem, the motion of nuclei can be considered on a PES provided by electronic structure theory.[20] One of the simplest dynamical descriptions of molecules is introduced by considering the classical motion of the nuclei on a PES.[43,44] This classical description is useful in a semi-quantitative understanding of many dynamical processes,[45] but the zero-point energy of molecules[45–47] and the tunneling of nuclei,[48–52] most importantly that of protons, are not readily incorporated in this model and must be considered as special "effects", showing limitations of this approach.

A next significant step toward a sophisticated and detailed, quantitative description of molecular phenomena is the consideration of nuclei as quantum particles moving on a PES. As to the conceptual part, this framework naturally includes not only various conformational changes of the molecular structure but also the zero-point vibrational energy of molecules as well as the "tunneling" of protons or other nuclei. As to the numerical results, after decades of methodological developments of quantum nuclear motion theory, see, *e.g.*, ref. 19, 53–80, the joint technology provided by electronic structure and nuclear motion methods is now able to yield, among other quantities less relevant for this Perspective, remarkably accurate rovibrational energies and related transitions, state-to-state and overall reaction rates, as well as effective, temperature-dependent molecular structure parameters and a detailed understanding of "exotic" chemical phenomena such

as resonance states and tunneling. As in all fields of rapid development, there are various trends within nuclear motion theory, including time-dependent[81–83] and time-independent (treated in detail below) descriptions, perturbational[84,85] and variational (treated in detail below) algorithms, various forms of rovibrational Hamiltonians,[39,86–89] as well as different numerical representations of the Hamiltonians.[90–96] One may wonder which is the best combination of the numerous possible choices or whether a unified protocol would soon emerge. At this point we have to leave these questions open and say that the applications should determine the most appropriate choices. What can be said with confidence is that the extensive use of the different algorithms and protocols indicates that the current quantum chemical adaptation of quantum mechanics to molecular systems is a successful one. As a result, the outcome of quantum chemical simulations based on the technology developed can be used in applied fields of science and engineering, for instance for improving the outcome of atmospheric radiative models.[97,98]

The spectacular development of experimental spectroscopic techniques continues and as it can be seen at present there are two major directions. On one hand, not only smaller models but larger and larger molecular systems, including bio-mimetics, true biomolecules and biopolymers, are studied with the ultimate goal of a molecular-level understanding of life. On the other hand, more and more accurate experiments are designed in order to test physical theories, fundamental symmetries, and perhaps their violations in molecular systems.[6,99,100] The development of experimental spectroscopy in either direction will certainly continue challenging molecular-scale theoretical methods and serve as a driving force, as it did in the past, for their improvement.

We feel that at this point it is important to mention another direction of the development of theoretical chemistry, namely that dealing with the collection, critical evaluation, and validation of the increasing amount of data on molecular systems,[101–107] which goes toward the completion of information and aims at providing extensive and reliable knowledge on molecules.

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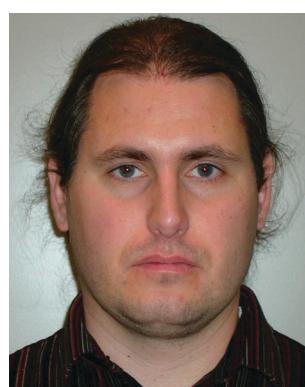
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In spectroscopy, this involves joint efforts of high-resolution but narrow-band as well as broad-band but maybe lower-resolution techniques together with computer-aided handling of spectroscopic networks[108] and related large-scale data-bases.[107,109–111] Ultimately it is the joint utilization of (spectro-scopic) experiments, quantum theory, and information technology which helps to secure and extend our firm chemical knowledge and makes it applicable in diverse scientific and engineering areas.

There have been many successes, some extensively reviewed,[56,74–79] in the nuclear motion theory branch of quantum chemistry. In the present work we focus on some of the recent developments of quantum nuclear motion theory which, together with electronic structure theory, provide a comprehensive description of molecules in motion. The litera-ture even of this restricted field is extensive and in this Perspective we admittedly present a more thorough overview of those areas where we have gained experience during the last ten years or so and describe recent developments in our group on BO quantum nuclear motion theory and focus on using (quasi-)variational procedures for the solution of the time-independent rovibrational Schrödinger equation.

2 Nuclear motion theory

In spite of various unification efforts, different variants of quantum chemical nuclear motion theory coexist and they often serve different purposes. Nevertheless, a unified descrip-tion of the basics is attempted here.

2.1 Time-independent Schrödinger equation of the nuclei

The fundamental equation for this study and for the computa-tion of stationary nuclear-motion states Ψ of molecular systems containing $\mathcal{M}$ nuclei considered as quantum particles is the time-independent nuclear Schrödinger equation corres-ponding to the Hamiltonian $\hat{H}'$,

$$\hat{H}'\Psi = \left(-\sum_{i=1}^{\mathcal{M}} \frac{1}{2m_i}\Delta_{\mathbf{X}_i} + \hat{V}\right)\Psi = E\Psi, \qquad (1)$$

written in atomic units. In eqn (1), m_i denote the masses associated with the nuclei, which in practice are either the atomic or the nuclear masses of the nuclei (or perhaps some-where in between to mimic non-BO behavior),[112] and $\mathbf{X}_i$ are the position vectors in the laboratory-fixed (LF) frame with the corresponding Laplace operator $\Delta_{\mathbf{X}_i}$. Out of the possible mathe-matical solutions of eqn (1), the physically relevant solutions are constrained by the spin statistics theorem,[33] i.e., by considering the spin associated with each nucleus. In what follows $\hat{V}$ is chosen as a geometric potential, depending only on the inter-nuclear distances and is identified with the PES corresponding to the ground electronic state of the molecular system (though any separated excited electronic state could also be chosen). The system is considered to be isolated, no external fields are acting, and no hyperfine couplings are considered; thus, the angular momentum corresponding to the overall rotation of the mole-cular system is a conserved quantity.

After separating the translational motion of the nuclear center of mass from $\hat{H}'$ in eqn (1), the translationally invariant Hamiltonian[38,113] is considered with the domain of square-integrable functions, L^2, for bound states, characterized by real eigenvalues, and a manifold with complex eigenvalues for non-bound, resonance states.[114]

2.2 (Quasi)-variational solutions

Stationary rovibrational states are computed by solving the time-independent Schrödinger equation (TISE) of the nuclei, eqn (1), by approximating the rotational–vibrational wave function as a linear combination of carefully chosen basis functions. The matrix representation of the translationally invariant, rovibrational Hamiltonian employing this basis set is constructed using various efficient numerical methods. The overall procedure is termed quasi-variational, as in the practical schemes the matrix elements may not be computed analytically, and thus the eigenvalues may not necessarily satisfy the variational principle. The essential parts of this approximation technique are discussed in this subsection.

2.2.1 The coordinate dilemma. The coordinate "dilemma"[115–119] in spectroscopy and kinetics originates from the traditional reasoning that it is useful to set up the rotational–vibrational problem of molecular systems using coordinates more or less adapted to the various types of nuclear motion[120–123] and thus provide the most separable zeroth-order basis functions for quantum dynamics. These motions are drastically different for the different systems and energy regimes; thus, there is little hope to find a unique set of coordinates which is widely applicable. Furthermore, the coordinate domains must allow for a one-to-one corres-pondence with the geometrical domain of the molecule. In some cases the use of coordinates which mimic the point-group or MS-group[33] symmetry of the system under study or help to reduce the complexity of the rovibrational kinetic energy operator is advantageous.

Coordinate systems and their transformations employed in the description of molecular systems have been presented in thorough and formal discussions by Sutcliffe.[38,113] The first step is the separation of the overall translational motion of the center of mass of the nuclei by defining translationally invar-iant Cartesian coordinates introduced via a simple linear transformation of the original Cartesians. Then, a frame is introduced attached to the non-rigid body (body-fixed frame (BF), embedding, or gauge) and three variables are introduced to describe the orientation of the BF with respect to the LF frame.[86,124–126] Furthermore, $3\mathcal{M} - 6$ internal coordinates are defined to describe the internal motion of the nuclei. Mathe-matical and technical complications are introduced as this transformation of the translationally invariant Cartesian coordinates is nonlinear and the resulting orientational and internal coordinates are curvilinear. This makes the formalism somewhat involved and it also results in a Hamiltonian which has to be defined over a slightly more restricted domain, due to the vanishing Jacobian, than the original one.[120]

2.2.2 Quantum chemical Hamiltonians. Starting from the TISE, the kinetic energy operator is expressed in terms of internal coordinates, q_k ($k = 1,2,\ldots,D \leq 3\mathcal{M} - 6$) with D active coordinates, and orientational coordinates,

α_a (a = 1(x), 2(y), 3(z)), in order to obtain a rotational–vibrational Hamiltonian. In what follows the most essential expressions are collected, for a more detailed discussion see, for example, ref. 66 and 71, as well as ref. 39, 74, 127–130.

The coordinate transformation is accomplished either by applying the chain rule for the kinetic energy operator[131] or by writing down the classical Lagrangian and Hamiltonian in the new, internal and rotational coordinates and employing the correspondence principle together with the properties of differential operators, as suggested by Podolsky.[132] The rotational–vibrational Hamiltonian obtained either way is

$$\hat{H}^{\text{rv}} = \frac{1}{2}\sum_{k=1}^{D+3}\sum_{l=1}^{D+3}\tilde{g}^{-1/4}\hat{p}_k^\dagger G_{kl}\tilde{g}^{1/2}\hat{p}_l\tilde{g}^{-1/4} + \hat{V} \qquad (2)$$

with

$$\hat{p}_k = -i\frac{\partial}{\partial q_k}, \quad k = 1, 2, \ldots, D \qquad (3)$$

and

$$\hat{p}_{D+a} = -i\frac{\partial}{\partial \alpha_a} = \hat{J}_a, \quad a = 1(x), 2(y), 3(z), \qquad (4)$$

where $\hat{J}_a$ refers to the body-fixed components of the rotational angular momentum if the three α_as are chosen to describe rotations around the three orthogonal axes of the BF frame. Furthermore, for non-vanishing $\tilde{g}$ = det **g**

$$G_{kl} = (\mathbf{g}^{-1})_{kl}, \quad k, l = 1, 2, \ldots, D+3 \qquad (5)$$

with

$$g_{kl} = \sum_{i=1}^{\mathscr{M}} m_i \frac{\partial \mathbf{X}_i}{\partial q_k} \cdot \frac{\partial \mathbf{X}_i}{\partial q_l}, \quad k, l = 1, 2, \ldots, D+3 \qquad (6)$$

where $\mathbf{X}_i$ gives the position vector of the ith nucleus in the space-fixed reference frame and q_k refers to either the q_k internal or the α_k rotational coordinates. The corresponding volume element is

$$dV = dq_1 dq_2 \ldots dq_D d\alpha_1 \, d\alpha_2 \, d\alpha_3. \qquad (7)$$

For some choices of the BF frame and internal coordinates the quantum chemical Hamiltonian can be written down explicitly and maybe after some formal rearrangements its matrix representation implemented in a computer code. There are various possible choices for the coordinates for the $\mathscr{M}$ nuclei and the corresponding quantum chemical Hamiltonians have different forms.[120,131,133–135] All the different mathematical forms can be used in a computer code resulting in many different implementations. A special and popular choice is the use of the Eckart embedding[86] and rectilinear coordinates,[136] resulting in a Hamiltonian whose most compact form was derived by Watson.[87,88] We prefer to call this the Eckart–Watson Hamiltonian, its detailed form and an implementation in a computer code is discussed in Section 3.2.

2.2.3 Potential energy hypersurfaces.

The concept of a PES is so fundamental to the understanding of most branches of chemistry that it is worth discussing it separately even in this Perspective on nuclear motions.

There are many possible ways to define PESs applicable for nuclear motion computations. *Ab initio* construction of PESs usually involves[20] (a) choice of a physically correct and robust electron correlation methodology, including choice of a non-relativistic[35,36] or relativistic[137,138] Hamiltonian; (b) application of a highly flexible and still compact basis set[139] describing both the correlation hole and the longer-range region of the electronic wave function; (c) inclusion of all "small corrections"[140,141] affecting the precision of composite PESs; (d) design of a suitable geometrical grid for the electronic structure computations defined;[142] and (e) an artful selection of a functional form resulting in a flexible and compact interpolating and extrapolating function.[16,54,143–146]

There are basically three distinct families of PESs used, hypersurfaces for (ro)vibrational spectra, chemical reactions, and intermolecular interactions. While these surfaces have a lot in common, there are many important and noteworthy differences in their construction.

For the computation of measured (ro)vibrational spectra and the related dynamics it is often sufficient to have the PES in the vicinity of a minimum (or of a stationary point). Thus, techniques based on power series expansions about a single stationary point can be highly useful.[147,148] These expansions define what is usually referred to as an anharmonic force field. Force fields are usually expanded up to quartic terms and they are independent of the nuclear masses only if are based on geometrically defined internal coordinates. There are several minor issues which should be considered when employing force field representation of the PES during the variational computation of rotational–vibrational spectra.[57] Generation of complex PESs, not employing any force field expansions, for (ro)vibrational spectrum simulations is abundant.[53,54,149]

During the course of chemical reactions bonds are broken and formed. The global requirements for these PESs[21,150,151] are considerably more stringent than those used for spectroscopy and regions have to be sampled where most electronic structure methods perform quite unevenly.

Intermolecular surfaces,[152,153] a prime target of non-covalent chemistry, are always multi-dimensional, which is often the greatest obstacle in obtaining quantitative accuracy for them.

2.2.4 Basis sets.

In multidimensional cases the basis functions are usually taken as products of one-dimensional (1D) functions. The frequently used 1D functions, called primitive basis functions, are eigenfunctions of analytically solvable (model) problems, such as the harmonic[136] or Morse[154] oscillators. One can also use more sophisticated, so-called potential optimized (PO) basis functions,[94,155,156] obtained by solving a 1D Schrödinger equation with a potential that is well adapted for the physical problem of interest. For the numerical solution of the 1D problem one usually uses primitive basis functions; thus, the PO basis functions are linear combinations of the primitive functions.

The simplest way for constructing a multidimensional basis set is to use the direct product of a set of 1D, primitive or PO, functions. The resulting basis set is called a direct-product basis. These direct-product basis sets are widely employed in nuclear motion computations since their use results in matrix representations with special structure, where the matrix elements

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can be computed straightforwardly by using standard numerical integration techniques.[157,158]

One can construct nondirect-product basis sets *via* different ways, such as (a) truncating a direct-product basis; (b) introducing couplings between the product functions; or (c) using non-product multidimensional basis functions. (c) is rarely employed, whereas (a) and (b) are widely used. (a) is the simplest way to reduce the size of the multidimensional basis set by getting rid of the basis functions that are expected to have the smallest coefficients in the wave function. In a discrete variable representation (DVR)[90–92] of the Hamiltonian (see Section 2.2.5), the truncation can be simply achieved by throwing out grid points based on, for example, an energy cutoff parameter by checking the function value of the potential at the given multidimensional grid point. In a finite basis representation (FBR), truncations are usually made using the idea of the n-mode representation,[159,160] *i.e.*, each basis function has a maximum dimensionality of n, where n is (much) less than the full dimension of the physical problem investigated.

As will be mentioned in Section 3, singularities in the Hamiltonian can come into play when a radial coordinate becomes zero. Furthermore, when the radial coordinate goes to zero, an angle usually becomes undefined; thus, the radial and angular singularity is coupled. Therefore, an efficient basis is always a nondirect-product of functions depending on the coupled coordinates. One can construct such a basis *via* introducing couplings between the product functions. A typical example is a basis having structure similar to that of spherical harmonics.[161,162] Even if a nondirect-product basis provides a more compact representation of the wave function, in many applications the direct-product basis can be computationally more efficient due to its simplicity.

2.2.5 Matrix representation of the Hamiltonians. There are several representations developed for the Hamiltonians of Section 2.2.2 which can be employed in variational-type nuclear motion theory: the variational basis representation (VBR),[56] the finite basis representation (FBR),[56] and several grid-based representations. During the last decades the use of grid-based techniques,[76,90–92,163–181] almost revolutionized the variational-type quantum chemical treatment of nuclear motions by allowing the development of much improved algorithms. Application of these algorithms contributed to an improved understanding of highly excited states of molecules, studied experimentally *via* high-resolution molecular spectroscopy,[53–55,62–66,69–72,103,104,182–187] as well as quantum reaction dynamics.[170,188–195]

It is generally appreciated that grid-based techniques are not strictly variational. This is due to the fact that the variational principle for the eigenenergies holds if the Hamiltonian matrix elements are evaluated "exactly". This can be achieved either by their analytic computation, corresponding to what is called the VBR, or by highly accurate numerical procedures, whereby arbitrarily accurate quadrature schemes are employed, as in a general FBR. In more approximate and apparently more useful schemes, like in a discrete variable representation (DVR),[90–92] quadratures and basis functions are entangled and one looses the monotonic convergence of the eigenvalues offered by the variational principle. Nevertheless, the improved numerical behavior of the DVR more than offsets this inconvenience. For the present Perspective, DVR techniques hold a special place and only these techniques are discussed in some detail below.

Based on earlier work,[90,91] the DVR technique was introduced to quantum chemistry by Light and co-workers[76,92,167,172] for the efficient variational quantum chemical treatment of nuclear motions. It has been used in a number of variational computational spectroscopic studies, even to determine full rotational–vibrational spectra of triatomic molecules, involving a large number of converged eigenvalues and eigenvectors.[183–187] Some useful properties of the DVR: (a) it is built upon a compact underlying quadrature scheme; (b) the potential matrix is diagonal and these matrix values are simply local values of $\hat{V}$; (c) all multiplicative operators also have a diagonal form due to the "local-diagonal" or "quadrature" approximation; and (d) it provides a highly efficient framework for the computation of expectation values and integrals involving rovibrational wave functions.

It is important to stress that in DVR computations the matrix elements of operators dependent only upon coordinates are inexact. Using a given basis set and quadrature scheme for numerical integration, the FBR and the DVR are equivalent representations in the sense that they lead to the same eigenvalues. Since an N-point Gaussian quadrature gives exact result for any integrand which is a polynomial of degree less than or equal to $2N - 1$,[157,158] many elements in the FBR of the Hamiltonian are exact. This and the equivalence of the FBR and DVR representations explain why the DVR based on Gaussian quadrature gives highly accurate eigenvalues and eigenfunctions in spite of the inaccuracy of the DVR matrix elements.[186,196]

Singular terms always arise in the nuclear motion Hamiltonian when it is expressed in internal coordinates.[113] A common singular term in practical applications, often present in rovibrational Hamiltonians, is the term r^{-2} with $r \in [0, \infty)$. Several useful strategies have been devised for treating singularities in grid-based applications.[161,185,197,198] These approaches include the use of different coordinate systems devoid of essential singularities and nondirect-product basis sets. When applying the diagonal DVR approximation for the calculation of matrix elements of r^{-2}, numerical computations employing basis functions with suitable boundary conditions result in accurate eigenvalues showing fast convergence.[186] This becomes especially important, for example, for the computation of complete spectra.

2.2.6 Determination of required eigenvalues and eigenvectors. Most applications of nuclear motion theory involve very large Hamiltonian matrices from which a large number of eigenvalues and eigenvectors need to be computed. One general, *a priori* strategy is to aim at lower-dimensional Hamiltonian matrices *via* sequential contraction of the basis. This results in non-direct-product bases and a dense Hamiltonian matrix. Other strategies, based on direct-product bases, produce sparse but much larger matrices with a special structure. In order to compute the required many (thousands of) eigenvalues for medium-sized molecules, an iterative eigensolver (the usual choice is the Lanczos[199–202] technique) must be implemented, adapted specifically to the features and requirements of the nuclear motion protocol. The following criteria should be

considered when the effectiveness of a particular "diagonalization" method is investigated: (a) maximum amount of main memory required; (b) disk storage requirements (minimize input/output operations); (c) efficiency of matrix-vector multiplication and the sheer number of such operations; (d) independence of the solution strategy to the characteristics of the problem at hand; and (e) parallelizability of the resulting code. One of the prime features making iterative eigensolvers particularly attractive in this context is the fact that the Hamiltonian matrix does not need to be constructed explicitly, only its product with a vector is required. This can be done very efficiently, as demonstrated several times.[64,121,203]

In order to compute the lowest or interior eigenvalues instead of the largest ones the original Hamiltonian matrix must be transformed so that the required eigenvalues become the largest eigenvalues of the transformed matrix. There are several possibilities to set up such a spectral transformation.[204–207] The cost of the transformation and the spectral properties of the resultant matrix can be very different. Polynomial, exponential, and shift-invert transformation techniques were studied in detail in ref. 64.

In the case of the Lanczos method, there are three main factors that contribute to the total timing of the iterative diagonalization approach: (a) the number of matrix-vector multiplications in a single Lanczos step, which is generally the most CPU-intensive part of the computation; (b) reorthogonalization of the Lanczos vectors to maintain (semi-) orthogonality among them, which is an I/O-intensive step and CPU usage becomes significant only if the size of the Krylov subspace is very large; and (c) the convergence rate of the total Lanczos iteration influenced by the relative separation of the eigenvalues of the matrix introduced in the Lanczos iteration. After having studied the interplay of these three factors in considerable detail, we found[64,72] that for larger applications, specifically for the computation of the lowest few hundred eigenpairs of five-atomic molecules, a simple and clever choice is the usage of the shift-fold filter, periodic reorthogonalization, and the thick-restart Lanczos method. When not the lowest eigenvalues but an interior part of the spectrum is to be computed, the shift-invert technique seems to be an appealing choice, but to find an efficient black-box method to carry out the spectral transformation is challenging. A safe and practical technique might be the usage of a carefully optimized shifted version of the exponential transformation, the shift-Gaussian filter.

The computation of interior eigenvalues opens a promising route toward the computation of a very large number of eigenvalues and eigenvectors, i.e., toward the determination of the complete spectrum. This task could be distributed to practically independent computing nodes by distributing smaller ranges of the spectrum to different machines. This would make the computation of a very large number of eigenpairs an embarrassingly parallel problem. Eigenpairs from different ranges of the spectrum can be converged independently, i.e., the lower end of the spectrum could be computed using a smaller grid. If only very few interior eigenvalues, e.g., 10 eigenvalues, are required in each run, the total storage requirement, Lanczos and a few auxiliary vectors, of the computation fits into the main memory of nowadays standard machines, which eliminates the time-consuming I/O operations on the hard disk.

2.3 Post-processing

Three topics relevant after executing a variational nuclear motion computation and the required eigenvalues and eigenfunctions become available are discussed next.

The complete internal wave function, a product of the rovibronic and nuclear spin wave functions, has important symmetry restrictions dictated by quantum statistics.[33] Thus, the allowed nuclear spin states, different for the different isotopologues of a molecule, determine which computed rovibronic states are allowed. This practically means that out of the legitimate eigenstates computed for a given rovibronic Hamiltonian some could be forbidden due to symmetry restrictions. Thus, statistical weights need to be determined for the different symmetry classes of the molecular symmetry (MS) group. If the statistical weight is zero for a given isotopologue (e.g., for $^{14}NH_3$ this is the case for the A_1' and A_1'' irreducible representations of the $D_{3h}(M)$ group) and a given class, those energy levels are forbidden and cannot "participate" in rovibronic transitions. The symmetry restrictions and spin statistical weights should also be taken into account when (temperature-dependent) rovibronic averaging of molecular properties is performed (see Section 4.4).

An ideal labeling scheme applicable for eigenstates computed through the variational solution of the nuclear Schrödinger equation would be physically incisive and independent of the coordinates and basis functions used to represent the Hamiltonian and the wave function. However, assignment schemes can be very useful even if these requirements are not fully met. Among the techniques that have been employed in the analyses of variationally computed nuclear-motion wave functions are "node counting" along specified cuts of coordinate space,[54,187] the determination of "optimally separable" coordinates,[115,116,208–216] the use of natural modal representations,[54,217] and the evaluation of coordinate expectation values.[187] An alternative approach to assigning molecular eigenstates is provided by effective Hamiltonian methods, particularly in relatively low-energy regions. The canonical models of the vibrations and rotations of a molecule are the quantum mechanical harmonic oscillator (HO)[136] and rigid rotor (RR)[218] approximations, respectively. The low-lying states of semirigid molecules have traditionally been described by labels based on multidimensional normal-mode vibrational wave functions conjoined with rigid-rotor rotational wave functions represented in a symmetric-top basis. A widespread preference for RRHO labels persists, both for the appealing simplicity of the underlying models and for historical reasons. Of course, the RRHO labeling scheme is inherently model-dependent, unlike methods based on natural modals, for example. Variational (ro)vibrational computations have often[63,64,74,85,89,159,219–228] employed the Eckart–Watson Hamiltonian expressed in normal coordinates,[86–88] which leads straightforwardly to an RRHO labeling of the lower-lying eigenstates. For more details on an RRHO labeling scheme see Section 4.3.

To connect nuclear motion computations to spectroscopic experiments, it is often particularly important to compute not only transition (line) energies but also line intensities and even line shapes (the latter is not discussed here). For one-photon

absorption and emission spectra this requires the availability of a dipole moment surface (DMS).[229,230] This DMS, together with the rovibrational wave functions, can result in, *via* expectation-value-type computations, line intensities. Line intensities have an extremely large dynamical range. Computation of a DMS has similar challenges as that of a PES detailed in Section 2.2.3, composite schemes are again highly useful, but the fitting process is even more elaborate and even more prone to significant errors.[229]

3 Practical implementations

In this section different choices for the nuclear motion Hamiltonian are presented and discussed. The computations built upon these Hamiltonians give some insight into the current status of nuclear motion theory. As to the technical details, in actual implementations the various steps are not necessarily distinct parts of the computer code, as an overall consideration of the algorithm might result in a more efficient implementation. In Table 1 characteristics of those codes are summarized which our group developed for spectroscopic applications.

3.1 Tailor-made Hamiltonians, DOPI

One of the traditional ways to treat nuclear motions variationally is based on Hamiltonians expressed in a given choice of curvilinear coordinates,[120,121] *e.g.*, orthogonal[122,123] or valence[136] internal coordinates. This approach is feasible for a small number of nuclei.[57,58,121,182,203,231–236] The required explicit knowledge of the Hamiltonian, in fact of the kinetic energy operator,[131,133–135] offers the advantage that appropriate basis sets can be chosen, and with proper and efficient representations, matrix element computations, and diagonalization techniques one could compute the complete bound-state eigenspectrum of molecules. The most important drawback of this so-called tailor-made Hamiltonian approach is that the explicit construction of the kinetic energy operator is needed for the different internal coordinate choices, which can be demanding in many cases. However, for small molecules this is still one of the simplest possible strategies for variational nuclear motion computations, and a possible algorithm can be set up as follows: the Hamiltonian is expressed in orthogonal (O) coordinates, its matrix is represented by the discrete variable representation (D, see Section 2.2.5) coupled with a direct product (P) basis (see Section 2.2.4), and advantage can

be taken of the sparsity and special structure of the resulting Hamiltonian matrix whose required eigenvalues can be determined extremely efficiently by variants of iterative (I) "diagonalization" techniques (see Section 2.2.6). In our own work, a three-atomic variant of the tailor-made approach is termed D³OPI,[57,58,186] standing for discrete variable representation for all three internal coordinates, while the rest of the abbreviations are explained above.

Focusing only on triatomic cases, program suites can be developed which use a generalized Hamiltonian[120] containing parameters which can be fixed to different values giving different Hamiltonians corresponding to different (orthogonal and non-orthogonal) internal coordinate choices. Assuming that an orthogonal coordinate system is chosen, the Sutcliffe–Tennyson rovibrational Hamiltonian[120] of a triatomic molecule, incorporating the radial part of the Jacobian, can be written in the R_1 embedding as

$$
\begin{aligned}
\hat{H}^{\mathrm{rv}} = & -\frac{1}{2\mu_1}\frac{\partial^2}{\partial R_1^2} - \frac{1}{2\mu_2}\frac{\partial^2}{\partial R_2^2} - \left(\frac{1}{2\mu_1 R_1^2} + \frac{1}{2\mu_2 R_2^2}\right) \\
& \times \left(\frac{\partial^2}{\partial \theta^2} + \cot\theta\frac{\partial}{\partial\theta} - \frac{\hat{j}_z^2}{\sin^2\theta}\right) + \frac{1}{2\mu_1 R_1^2} \\
& \times (\hat{J}^2 - 2\hat{J}_z\hat{j}_z - \hat{J}_+\hat{j}_- - \hat{J}_-\hat{j}_+) + \hat{V}(R_1, R_2, \theta),
\end{aligned}
\tag{8}
$$

where μ_1 and μ_2 are effective masses related to the actual masses in a way that depends on how precisely the orthogonal coordinate system is chosen, R_1 and R_2 are two radial internal coordinates whose form may be chosen at will within the limits imposed by the coordinate orthogonality constraint, θ is the angle between the two radial coordinates, while $\hat{J}$ and $\hat{j}$ refer to the appropriate[120] rotational angular momenta.

Note that it is not always computationally most efficient to make an orthogonal coordinate choice. Furthermore, even when making this choice, one particular scheme can prove to be better than another, as can a particular choice of attaching a body frame to the molecule.

Although tailor-made Hamiltonians of tetratomic molecules and beyond most often lead to codes suitable for a unique type of physical system and are not appropriate for a general, black-box-type approach for nuclear motion computations, this uniqueness leads to high efficiency. Choosing internal coordinates which reflect the physical nature of the system under investigation can have many advantages. Properly chosen coordinates and coordinate frame embeddings make

Table 1 Characteristics of nuclear motion codes developed in our group for spectroscopic computations and their applications

Characteristics	DOPI[57,58,186]	DEWE[63,64,72]	GENIUSH[66,71]
Coordinate system	Orthogonal (O) internal, *e.g.*, Jacobi[122] or Radau[123]	Rectilinear normal[136]	Arbitrary internal (I),[136] *e.g.*, Z-matrix
Embedding	R_1, R_2, bisector[120]	Eckart[86]	Arbitrary
Hamiltonian	tailor-made, Sutcliffe–Tennyson[120]	Eckart–Watson (EW)	General (GE), numerical (N), user-specified (US)
Basis	Direct product (P) + Wang symmetric-top eigenfunctions	Direct-product Hermite + Wang symmetric-top eigenfunctions	Direct-product Hermite, Legendre + Wang symmetric–top eigenfunctions
Matrix representation	DVR (D), DVR–FBR	DVR (D)	DVR
Eigensolver	Iterative (I), Lanczos	Iterative, Lanczos	Iterative, Lanczos
Applications	H_2O,[53,187] H_3^+,[186] CH_2[58]	CH_4,[64] H_2CCO[72]	NH_3[71]

it easier to exploit the symmetry of the system,[237,238] or grant the possibility of using basis functions well adopted to the internal coordinates, leading to a compact expansion of the wave function. Well-defined internal coordinates and embeddings can also help by leading to singular terms, necessarily present in Hamiltonians expressed in internal coordinates, for which singular nuclear configurations are at a physically hardly reachable region of the PES. It is also worth mentioning that inspecting different Hamiltonians given in different coordinate embeddings and internal coordinates, one might even decide between various possible matrix representations, some leading to special matrix structures which can be exploited for the sake of efficiency.

Referring to even just the most important applications of tailor-made Hamiltonians is beyond the scope of this Perspective; thus, we only mention a few works which we consider to be representative examples of the method. To make use of the possible high efficiency of a well-chosen Hamiltonian and matrix representation, many studies were carried out to optimize the computational protocols, for example treating numerical issues arising from singularities[162,186,239] or optimizing basis sets[155,186,198] and numerical integral evaluation.[161] The latest applications include various computations of eigenenergies and spectra of molecules up to dissociation, which requires PESs adequate near dissociation. Having such PESs available, high accuracy computations on the water isotopologues have been carried out, producing a nearly complete set of vibrational labels for $H_2^{16}O$[187] and, with the help of a dipole moment surface, a huge amount of data on the line list of the water isotopologues.[240,241] Highly accurate computations were also carried out on the H_3^+ molecular ion resulting in vibrational eigenenergies of cm^{-1} accuracy up to nearly all vibrational states below dissociation and line lists for the H_3^+ isotopologues.[242,243]

3.2 The Eckart–Watson Hamiltonian, DEWE

The Eckart–Watson Hamiltonian has numerous implementations,[59,63,64,72,85,188,220,221,224–226] though seemingly only one of them[63,64,72] has at present the capability to perform an "exact" computation of rovibrational eigenpairs corresponding to a given PES for molecules with more than four nuclei. In this section this implementation is reviewed. A special feature of this implementation is that symmetry labels of the corresponding largest Abelian molecular symmetry group with ± 1 characters only are automatically distributed to the computed rotational–vibrational levels (see Section 3.5).[72]

The coordinates are defined by specifying a non-linear Eckart reference structure, $\mathbf{c}$, which fixes through the Eckart conditions[86] the Cartesian coordinates in the BF, $\mathbf{x}_i$,

$$\sum_{i=1}^{\mathcal{M}} m_i \mathbf{x}_i = \mathbf{0} \text{ and } \sum_{i=1}^{\mathcal{M}} m_i \mathbf{c}_i \times \mathbf{x}_i = \mathbf{0}. \quad (9)$$

Furthermore, orthogonal, rectilinear internal coordinates are introduced[87]

$$Q_k = \sum_{i=1}^{\mathcal{M}} \sqrt{m_i} \mathbf{l}_{ik} (\mathbf{x}_i - \mathbf{c}_i), \ k = 1, 2, \ldots, 3\mathcal{M} - 6, \quad (10)$$

with specifying the constants $\mathbf{l}_{ik} \in \mathbb{R}^3$ which satisfy the orthogonality and the Eckart conditions. As a special case,

$\mathbf{c}$ is the equilibrium structure and Q_ks are the normal coordinates corresponding to a given PES.

The compact and popular form of the rovibrational Hamiltonian corresponding to this coordinate choice was first given by Watson[87] for nonlinear molecules. For convenience, the corresponding vibrational, rotational, and rotational–vibrational coupling terms of the kinetic energy operator can be denoted separately by $\hat{T}^v$, $\hat{T}^r$, and $\hat{T}^{rv}$, respectively. Then, the Eckart–Watson Hamiltonian is

$$\hat{H}^{rv} = \hat{T}^v + \hat{T}^r + \hat{T}^{rv} + \hat{V}, \quad (11)$$

where

$$\hat{T}^v = \frac{1}{2} \sum_{k=1}^{3\mathcal{M}-6} \hat{P}_k^2 + \frac{1}{2} \sum_{\alpha\beta} \hat{\pi}_\alpha \mu_{\alpha\beta} \hat{\pi}_\beta - \frac{\hbar^2}{8} \sum_\alpha \mu_{\alpha\alpha}, \quad (12)$$

$$\hat{T}^r = \frac{1}{2} \sum_\alpha \mu_{\alpha\alpha} \hat{J}_\alpha^2 + \frac{1}{2} \sum_{\alpha<\beta} \mu_{\alpha\beta} [\hat{J}_\alpha, \hat{J}_\beta]_+, \quad (13)$$

and

$$\hat{T}^{rv} = -\sum_{\alpha\beta} \mu_{\alpha\beta} \hat{\pi}_\beta \hat{J}_\alpha \quad (14)$$

with $\hat{P}_k = -i\frac{\partial}{\partial Q_k}$ and the components of the rotational angular momentum $\hat{J}_x$, $\hat{J}_y$, and $\hat{J}_z$ in the BF. The Coriolis operator and the generalized inertia tensor have here the usual definition

$$\hat{\pi}_\alpha = \sum_{kl=1}^{3\mathcal{M}-6} \zeta_{kl}^\alpha Q_k \hat{P}_l \text{ and } \zeta_{kl}^\alpha = \sum_{\beta\gamma} e_{\alpha\beta\gamma} \sum_{i=1}^{\mathcal{M}} l_{\beta ik} l_{\gamma il} \quad (15)$$

$$\mu_{\alpha\beta} = (\mathbf{I}'^{-1})_{\alpha\beta} \text{ and } I'_{\alpha\beta} = I_{\alpha\beta} - \sum_{klm=1}^{3\mathcal{M}-6} \zeta_{km}^\alpha \zeta_{lm}^\beta Q_k Q_l, \quad (16)$$

where $e_{\alpha\beta\gamma}$ denotes the Levi–Civita symbol, $I_{\alpha\beta}$ is the instantaneous inertia tensor, and $[\hat{J}_\alpha, \hat{J}_\beta]_+$ is the anticommutator of $\hat{J}_\alpha$ and $\hat{J}_\beta$. The volume element of the integration is

$$dV = d\phi \ \sin\theta d\theta d\chi dQ_1 \ dQ_2 \ldots dQ_{3\mathcal{M}-6}$$

where ϕ, θ, and χ are Euler angles with $\phi, \chi \in [0,2\pi]$, $\theta \in [0,\pi]$, and $Q_k \in (-\infty, \infty)$. Whenever $\det\mathbf{I}'$ equals zero the Hamiltonian is singular.[244]

In our own work, the protocol based on the Eckart–Watson Hamiltonian is termed DEWE,[63,64,72] standing for discrete variable representation (D) of the Eckart–Watson Hamiltonian (EW) with an exact (E) inclusion of an arbitrary PES.

In DEWE, after specifying the reference structure, $\mathbf{c}$, and the coefficients, $\mathbf{l}$, a matrix representation of the vibrational terms of the Hamiltonian are considered on a direct-product Hermite-DVR basis (grid). In order to represent the rovibrational Hamiltonian for a given J value, the direct product of the vibrational basis and the Wang combination of symmetric-top eigenfunctions is formed. Analytic matrix elements are computed for Q_k, $\hat{P}_k$, $\hat{P}_k^2$, and the various angular momentum operators containing $\hat{J}_\alpha$ in the BF. At the same time, any coordinate-dependent operator terms which do not contain differential operator are expressed in terms of the actual internal coordinates, Q_k, and are approximated by a diagonal

matrix in the direct-product Hermite DVR. A Hamiltonian matrix thus constructed is real. The matrix element evaluation is facilitated by the insertion of the truncated resolution of identity in the vibrational basis between every $\mu_{\alpha\beta}$ and $\hat{\pi}_\alpha$ and $\hat{\pi}_\beta$ terms occurring in the Hamiltonian. As a result the matrix representation of the Hamiltonian can be written as a sum of products of simple operators. In the actual implementation the matrix representation of the Hamiltonian is not constructed explicitly, as the Lanczos eigensolver (see Section 2.2.6) requires only the multiplication of the Hamiltonian matrix with a trial vector. This allows a substantial reduction in storage requirements, which nevertheless scales linearly with the overall dimension of the direct product vibrational grid (storage of the diagonal $\mathbf{V}$ and $\boldsymbol{\mu}_{\alpha\beta}$ terms) and also linearly with J due to the required storage of Lanczos vectors. The Hamiltonian matrix-vector multiplication step is one of the most time-consuming parts of the program, with an almost linear scaling with the size of the direct product space and J, and is parallelized with OpenMP. If a large number of eigenvalues *and* eigenvectors are required for a five atomic molecule the overall storage requirement can exceed, say, 10 GB, and the Lanczos vectors are stored on hard disk.[64,72] An optimized storage and input/output operation sequence allowed the computation of a few hundred of (ro)vibrational eigenvalues and eigenvectors of five-atomic molecules and six-atomic semi-rigid species deem to be tractable in the near future.

A rationalized vibrational subspace (VS) procedure[72] (see Section 3.4) developed for the computation of rotational–vibrational energy levels *and* wave functions corresponding to large J values is interfaced with the presented rovibrational DEWE program, thus extending the possibilities of handling semi-rigid molecules.

Approaches based on the Eckart–Watson Hamiltonian have well-defined limitations. The rectilinear nature of the coordinates Q_k is not well suited for the treatment of some vibrations, *e.g.*, highly excited bends. Furthermore, as the Eckart conditions are based on the existence of a single and well-defined energy minimum on the PES, it is difficult to apply this method for the description of molecules which exhibit multiple accessible minima.

3.3 General internal-coordinate Hamiltonians, GENIUSH

The third choice for a rovibrational Hamiltonian incorporates the advantages of the above two Hamiltonians. It is general for all molecular systems, employs curvilinear, arbitrarily chosen internal coordinates, allows the selection of the most suitable embedding, and ready for reduced-dimensional treatments. In contrast to the first method, the rotational–vibrational Hamiltonian is represented numerically; thus, the explicit, analytical construction of the kinetic energy operator is circumvented. In our own work, this approach is called GENIUSH,[66,71] in reference to its main characteristics: general (GE) code with numerical (N), internal-coordinate (I), user-specified (US) Hamiltonians (H). This numerical approach to the use of kinetic energy operators has also been pursued by others, for example by Luckhaus and co-workers,[61,70,245,246] Lauvergnat *et al.*,[62,247] Yurchenko *et al.*,[69] and Makarewicz.[129]

The coordinate choice (and dilemma, see Section 2.2.1) is left to the user as much as possible. A Z-matrix-type reader is implemented to help the coordinate definition but in principle any specification of the BF Cartesian coordinates, $\mathbf{x}_i$ corresponding to the chosen body-fixed frame, in terms of the chosen q_k internal coordinates can be provided, *e.g.*, Jacobi coordinates.

Our implementation favors the "t-vector" formalism, *i.e.*, evaluation of $\frac{\partial \mathbf{x}_i}{\partial q_k}$-type quantities is required in terms of internal coordinates, q_k. Thus, for convenience, the symmetric matrix $\mathbf{g}$ in eqn (6) is rearranged to

$$g_{kl} = \sum_{i=1}^{\mathcal{M}} m_i \frac{\partial \mathbf{x}_i}{\partial q_k} \cdot \frac{\partial \mathbf{x}_i}{\partial q_l} \qquad (17)$$

$$g_{a+D,l} = \sum_{i=1}^{\mathcal{M}} m_i (\mathbf{e}_a \times \mathbf{x}_i) \cdot \frac{\partial \mathbf{x}_i}{\partial q_l} \qquad (18)$$

$$g_{a+D,b+D} = \sum_{i=1}^{\mathcal{M}} m_i (\mathbf{e}_a \times \mathbf{x}_i) \cdot (\mathbf{e}_b \times \mathbf{x}_i), \qquad (19)$$

where $\mathbf{e}_a$ is the unit vector along the ath axis BF frame and $\mathbf{x}_i$ denotes the Cartesian coordinates of the ith nucleus in the BF frame. The elements of $\mathbf{G}$ and $\tilde{g}$ are expressed in terms of the internal coordinates and they are not functions of the orientational coordinates; thus, eqn (2) can be rearranged to

$$\hat{H}^{rv} = \hat{T}^v + \hat{T}^r + \hat{T}^{rv} + \hat{V} \qquad (20)$$

where

$$\hat{T}^v = \frac{1}{2} \sum_{k=1}^{D} \sum_{l=1}^{D} \tilde{g}^{-1/4} \hat{p}_k^\dagger G_{kl} \tilde{g}^{1/2} \hat{p}_l \tilde{g}^{-1/4}, \qquad (21)$$

$$\hat{T}^r = \frac{1}{2} \sum_{a=1}^{3} G_{a+D,a+D} \hat{J}_a^2 + \frac{1}{2} \sum_{a=1}^{3} \sum_{b>a}^{3} G_{a+D,b+D} [\hat{J}_a, \hat{J}_b]_+, \quad (22)$$

and

$$\hat{T}^{rv} = \frac{1}{2} \sum_{k=1}^{D} \sum_{a=1}^{3} (\tilde{g}^{-1/4} \hat{p}_k^\dagger G_{k,l+D} \tilde{g}^{1/4} + \tilde{g}^{1/4} G_{k,l+D} \hat{p}_k \tilde{g}^{-1/4}) \hat{J}_a, \qquad (23)$$

where $\hat{T}^v$ is the vibrational and $\hat{T}^r$ is the rotational kinetic energy and $\hat{T}^{rv}$ gives the coupling between vibration and rotation. In eqn (22) $[\hat{J}_a, \hat{J}_b]_+$ refers to the anticommutator of $\hat{J}_a$ and $\hat{J}_b$.

The "effective" vibrational Hamiltonian corresponding to rotational angular momentum $J = 0$ is ("Podolsky form")

$$\hat{H}^v = \hat{T}^v + \hat{V} = \frac{1}{2} \sum_{k=1}^{D} \sum_{l=1}^{D} \tilde{g}^{-1/4} \hat{p}_k^\dagger G_{kl} \tilde{g}^{1/2} \hat{p}_l \tilde{g}^{-1/4} + \hat{V}. \quad (24)$$

In applications the $\hat{T}^v$ term is often further rearranged ("rearranged form"),

$$\hat{T}^v = \frac{1}{2} \sum_{k=1}^{D} \sum_{l=1}^{D} \tilde{g}^{-1/4} \hat{p}_k^\dagger G_{kl} \tilde{g}^{1/2} \hat{p}_l \tilde{g}^{-1/4} = \frac{1}{2} \sum_{k=1}^{D} \sum_{l=1}^{D} \hat{p}_k^\dagger G_{kl} \hat{p}_l + U, \qquad (25)$$

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with the extrapotential term

$$U = \frac{1}{32} \sum_{k=1}^{D} \sum_{l=1}^{D} \left[\frac{G_{kl}}{\tilde{g}^2} \frac{\partial \tilde{g}}{\partial q_k} \frac{\partial \tilde{g}}{\partial q_l} + 4 \frac{\partial}{\partial q_k} \left(\frac{G_{kl}}{\tilde{g}} \frac{\partial \tilde{g}}{\partial q_l} \right) \right]. \quad (26)$$

Of course, by making use of the special properties of a chosen set of internal coordinates and the BF this form can be further rearranged, maybe simplified in order to obtain one of the various tailor-made Hamiltonians. Instead of this route, the early forms of the Hamiltonian, eqn (20)–(26), are considered and implemented in a computer program. The requirement of numerical stability and reproducibility of the computed results, certainly better than <0.01 cm^{-1}, requires a careful validation and often leads to a painful debugging of a pilot implementation. In GENIUSH both the Podolsky and the rearranged forms of the vibration-only kinetic energy operator were implemented. The Podolsky form has been used in rovibrational computations.

A matrix representation of the vibrational terms of the Hamiltonian were considered using a direct product DVR grid, which can be constructed using Hermite, Legendre, and other DVRs. The differential operators were constructed analytically, while the coordinate-dependent (non-differential) operators were approximated as diagonal matrices in DVR. Between the differential and coordinate-dependent operators the truncated resolution of identity (RI) was inserted. As the truncated RI had satisfactory numerical properties in this representation, in practice we preferred the use of the "Podolsky" form of the Hamiltonian as its matrix representation can be built by calculating only the first derivatives of the BF Cartesian coordinates with respect to internal coordinates, eqn (17)–(19), which can be evaluated either analytically or numerically in 8-byte real ("double precision" in Fortran) arithmetics. If the "rearranged form" of the kinetic energy operator is used, the extrapotential term, U, requires the evaluation of not only first, but also second and third derivatives, which assumes the knowledge of analytic derivatives or 16-byte real ("quadruple precision" in Fortran) arithmetics in order to provide a numerically stable and reliable implementation meeting the rigorous spectroscopic precision. These technical considerations explain our preference for the Podolsky-form.

Matrix representation of the rovibrational Hamiltonian, eqn (20), was constructed using the direct product of the vibrational terms in DVR and the rotational matrices constructed with the Wang functions.[71] The resulting Hamiltonian matrix is real.

Instead of an explicit construction of the Hamiltonian matrix the consecutive multiplication of its terms with a trial vector (parallelized with OpenMP) is implemented and used in a Lanczos eigensolver (see Section 2.2.6). The overall storage requirements scale linearly with the size of the DVR grid and the J rotational quantum number.

3.4 Rovibrational computations for high J values, vibrational subspace (VS) method

In this section a highly efficient method, inspired by the rigid rotor decomposition (RRD) algorithm detailed in Section 4.3.2, is described which is suitable for the computation of

rovibrational energy levels for high values of the J rotational quantum number and was first presented in ref. 72. This idea is related to a two-step procedure[120] advocated by Sutcliffe and Tennyson.

To start, the rovibrational Hamiltonian is split into a vibrational and a rovibrational part. After solving the

$$\hat{H}^v \phi_i = E_i \phi_i \quad (27)$$

Schrödinger-equation of the vibrations-only $\hat{H}^v$ Hamiltonian, it is worth employing the orthonormal ϕ_i, $i = 1,\ldots,n$ vibrational wave functions as vibrational basis functions for the expansion of the Ψ_i rovibrational wave function:

$$\Psi_i = \sum_{j=1}^{n} \sum_{k=1}^{2J+1} c_{jk}^i \phi_j R_k, \quad (28)$$

where R_ks are elements of an orthonormal rotational basis of dimension $2J+1$. If the R_k rotational basis functions are chosen to be the rigid rotor eigenfunctions of the molecule under examination, the absolute squares of the c_{jk}^i coefficients are equivalent to the RRD coefficients defined in Section 4.3.2. It is straightforward to derive generally the matrix elements of $\hat{H}^v$ in this basis as the ϕ_i functions are eigenfunctions of $\hat{H}^v$:

$$\mathbf{H}_{ij,kl}^v = \langle \phi_i R_j | \hat{H}^v | \phi_k R_l \rangle = E_i \cdot \delta_{ik} \cdot \delta_{jl}, \quad (29)$$

while matrix elements of the $\hat{T}^r$ and $\hat{T}^{rv}$ operators of eqn (11) cannot be given universally as they depend on the particular choice of the rovibrational Hamiltonian.

This vibrational subspace (VS) method exhibits the following advantages: (a) the vibrational basis is very compact (it consists of typically the first few hundred vibrational band origins), which results in a Hamiltonian of modest size even for high J values; (b) the RRD analysis, which facilitates the assignment of the variational rovibrational levels, becomes straightforward and its coefficients are easy to compute; (c) the vibrational basis functions are automatically symmetry adapted (as they are basis functions of the irreducible representations of the molecular symmetry group) which supports the easy exploitation of molecular symmetry during the computation; (d) once the necessary vibrational matrix elements for the construction of the representation of $\hat{T}^r$ and $\hat{T}^{rv}$ have been computed, they can be saved in a file of modest size for later use, which greatly reduces the cost of further computations; and (e) due to the modest size of the Hamiltonian one can use direct eigensolvers instead of the Lanczos algorithm, thus the density of the rovibrational energy levels does not affect the convergence rate of the eigenstates.

3.5 Symmetry in rovibrational computations

The starting point of symmetry considerations in nuclear motion theory is the concept of molecular symmetry (MS) groups.[33] In this section two approaches are outlined briefly, which proved to be successful in our recent spectroscopic applications. A technical and detailed description can be found in ref. 72. For other uses of symmetry in nuclear motion computations see, e.g., ref. 121 and 248.

The first application of symmetry in nuclear motion computations employs the symmetry-adapted Lanczos (SAL) method.[249–251] In our case, it was implemented within the

DEWE code. The current implementation is applicable to either vibrational or rovibrational variational computations but it is limited to the use of molecular symmetry groups having characters of ± 1. The basic idea behind SAL is the projection of the Lanczos vectors onto the irreducible representations of the MS group during the Lanczos iteration process. This is done by an efficient matrix-vector multiplication procedure as the matrix representation of the necessary projectors is sparse and has a special structure. Although this method obviously does not reduce the size of the Hamiltonian matrix, it has two main advantages over the simple Lanczos procedure: (a) the rovibrational energy levels and wave functions are computed with symmetry labels of the corresponding MS group; and (b) the spectral density of the eigenvalues reduces, resulting in an improved convergence of the Lanczos procedure.

In a second application of symmetry, a method based on the VS procedure can be constructed, which applies to degenerate groups, as well. The first step is to examine the product-type $\phi_j R_k$ rovibrational basis functions in the expansion of the Ψ_i rovibrational wave function (see eqn (28)). If the symmetry properties of the ϕ_j pure vibrational states and R_k rigid rotor states are known, one can deduce the irreducible representations spanned by the $\phi_j R_k$ basis functions. The only remaining step is to assign Ψ_i with the irreducible representation spanned by the $\phi_j R_k$s which are present in the expansion of Ψ_i. A detailed derivation, for Abelian groups, can be found in ref. 72, where this method has been succesfully employed to the five-atomic ketene molecule (C_2H_2O, $C_{2v}(M)$ symmetry group).

It would be preferable to employ symmetry to its full extent in a general nuclear motion protocol, *i.e.*, forming blocks of the original Hamiltonian. However, the details how to do this in the general case, to the best of our knowledge, have not been worked out. It seems[69] that exploitation of symmetry in a universal code employing DVR is not as straightforward as it is in an FBR.

4 Selected spectroscopic applications

At present the main field of application of the quantum theory of nuclear motion described in the previous sections is the computation and interpretation of high-resolution (rotational–vibrational) spectra. Other principal applications include the study of molecular dynamics and the quantum mechanical evaluation of reaction rates. While the latter two are challenging and especially important topics for chemistry which have received considerable attention,[51,188,252] they are not even touched upon in this section.

4.1 Spectroscopic networks

Complete characterization of high-resolution spectra of a considerable number of molecules, starting from the microwave and extending to the ultraviolet, is a pre-requisite for modeling and understanding many processes and phenomena in physics, chemistry, and engineering. Modelers often need detailed line-by-line information which only the joint consideration of elaborate spectroscopic measurements or sophisticated quantum chemical computations can provide.

Recent advances in molecular spectroscopy led to a considerable increase in the extent of experimental high-resolution spectroscopic data, *i.e.*, assigned rovibrational transitions, energy levels, intensities, and line profiles. Some of these data have been deposited, sometimes in a critically evaluated and annotated form, in databases; see, for example, ref. 103, 104, 107, 253–256. Treatment of the rapidly increasing amount of information and the desire to turn information into knowledge requires sophisticated procedures for the generation, accumulation, validation, handling, visualization, and distribution of spectroscopic data. Some of these tasks can be helped by recognizing that for individual molecules spectra correspond to large-scale deterministic, undirected, (weighted) graphs (networks), made up of energy levels as vertices (nodes), allowed transitions between the levels as edges (links), and weights related to transition intensities. This way one defines spectroscopic networks (SNs).[105,108] The robust organizing principle of SNs is provided by quantum mechanical selection rules; different transitions and transition intensities characterize different spectroscopic techniques. It is important to emphasize that even in the experimentally most thoroughly studied cases the observable transitions form just a tiny part of all the transitions allowed.[103,104] The complete line list information about allowed transitions, corresponding to a very large SN, can only be determined *via* sophisticated variational rotational–vibrational computations.

The network-theoretical view of complex SNs detailed in ref. 108 offers certain advantages toward completing the characterization of high-resolution molecular spectra. The approximately scale-free property of the overall network structure[108] leads to the concept of hubs and thus straightforwardly to the design of new spectroscopic experiments. These experiments, with a minimum amount of effort, help to determine a more accurate and more robust SN by preferentially measuring, with improved accuracy, transitions in which less accurately known hubs are involved. Detailed comparison of measured and first-principle hubs helps to determine the "weakest nodes" among the energy levels in an existing experimental SN which, in turn, leads to the identification of transitions which should preferentially be investigated in new experiments designed specifically for their determination. The graph-theoretical view, through maximum weight spanning trees, should also help to connect components in the measured SN with a minimum amount of effort. Driven by the need of scientific and engineering applications, complex spectroscopic networks, perhaps as part of active databases,[103,104,109] are expected to become an intrinsic part of the description of the high-resolution spectra of molecules.

4.1.1 MARVEL: SNs from experiment. Experiments yield relatively small multiedge graphs, with a considerable number of parallel edges, while first-principles computations result in very large simple graphs. The existence of multiedge experimental SNs calls for a protocol which can invert the experimental transition information and yield experimental energy levels with well-defined uncertainties. Development of such inversion protocols has a long history in spectroscopy.[257–263] It must also be mentioned that similar inversion techniques have helped tremendously other areas of physical chemistry, including thermochemistry[110,111] and reaction kinetics.[264,265]

Our own inversion protocol is called MARVEL,[109] standing for Measured Active Rotational–Vibrational Energy Levels. The principal steps of applying MARVEL to an arbitrary molecule are as follows. (1) Collection, preliminary validation, and compilation of those measured transitions into a database which possess assignments and uncertainties. (2) Based on the database built this way, determination of those energy levels of the given species which belong to a component of a particular spectroscopic network. (3) Within a given SN, setting up of a vector containing all the experimentally measured transitions selected, another one comprising the requested MARVEL energy levels, and an extremely sparse matrix which describes the relation between the transitions and the energy levels, containing for each measured line only two non-zero entries, $+1$ and -1 for the upper and lower energy levels, respectively. (4) Solution of the set of linear equations corresponding to the chosen pair of vectors and the inversion (design) matrix. During solution of the set of linear equations uncertainties in the measured transitions can be incorporated which results in uncertainties of the energy levels determined.

The MARVEL technique has been used to handle and validate measured transitions of the following isotopologues of the water molecule: $H_2^{17}O$,[103,104] $H_2^{18}O$,[103,104] $HD^{16}O$,[104] $HD^{17}O$,[104] and $HD^{18}O$.[104] A summary of the characteristics of the MARVEL analyses for these five water isotopologues is presented in Table 2. It is clear that out of the millions of transitions which could technically be detected, only very few have been observed and assigned experimentally. The most extensive set of data is available for $HD^{16}O$ but even in this case only about 55 000 transitions and 9000 energy levels have been scrutinized by experimentalists. Note that MARVEL analysis of the parent isotopologue, $H_2^{16}O$, is in progress.

Fig. 1 demonstrates one of the principal virtues of a MARVEL-type analysis. It shows very vividly that even if only a very limited number of MARVEL energy levels can be deduced from the published experimental data, the transitions predicted by these MARVEL energy levels provide a much more substantial coverage of the spectrum. MARVEL has also been used to determine calibration standards based on the spectra of several water isotopologues.[266] The measured spectra of the parent isotopologue of ketene have also been subjected to a MARVEL analysis.[72]

The number of molecules subjected to MARVEL-type analyses is expected to grow substantially in the near future. These efforts have special relevance as even the most sophisticated quantum chemical techniques are not able to approach the accuracy of experiments for polyatomic and polyelectronic systems. The same can be said, though to a much lesser extent,

Fig. 1 Demonstration of the utility of accurate MARVEL energy levels of $HD^{18}O$ determined from the limited amount of experimentally observed and assigned transitions (first panel, "Measured") for predicting new transitions without any new measurements (second panel, "Measured + MARVEL"). All line intensities correspond to first-principles ("Variational") computed intensities. The first-principles variational results, yielding the complete spectrum, proved essential in other parts of the MARVEL analysis, as well.

about effective Hamiltonian approaches. Clearly, the most viable approach is to combine incomplete but highly accurate experimental information with complete but inaccurate first-principles results.

4.2 Determination of levels and lines

All the variational procedures discussed above are able to yield rovibrational energy levels of molecules. Table 3 contains selected rovibrational energy levels for the ground and ν_9 vibrational states of the parent isotopologue of the ketene molecule. Results obtained with the line inversion MARVEL process, by the first-principles DEWE-VS procedure, and by an effective Hamiltonian approach whose results can be found in ref. 268 are compared up to $J = 30$. Obtaining such extended coverage of rovibrational energy levels and thus lines can be done straightforwardly for a 5-atomic semirigid molecule, and possibly for systems up to 7 atoms.

Similarly extensive computations can be performed for molecules with more than one essential minima using the GENIUSH protocol and code. Such results are reported in ref. 71. A further advantage of GENIUSH, namely the ease with which reduced-dimensional nuclear motion computations can be performed for any molecule, including NH_3, are demonstrated by the 1D, 2D, 3D, and 6D results obtained in the same study and summarized in Table 4. The 1D model concentrates on the umbrella motion of ammonia, while all other coordinates are constrained. The 2D and 3D models add to the umbrella motion the symmetric stretching motion and the other two bending-type coordinates, respectively. In the

Table 2 Summary of the characteristics of the MARVEL analysis of five water isotopologues[103,104]

Characteristics	$H_2^{17}O$	$H_2^{18}O$	$HD^{16}O$	$HD^{17}O$	$HD^{18}O$
No. of expt. sources[a]	35	51	50	3	11
No. of expt. transitions	9036	31 748	54 740	485	8728
No. of validated transitions	9028	31 705	53 291	445	7186
No. of expt. energy levels	2723	5131	8819	162	1864

[a] No. of published articles with independent experimental line information.

Table 3 Selected J_{0J} rovibrational energy levels (in units of cm^{-1}) of the parent ketene molecule, H$_2$C=C=O, determined by the MARVEL line inversion process (with uncertainties given in parentheses in units of 10^{-6} cm^{-1}), by the DEWE-VS first-principles nuclear motion procedure, and by an effective Hamiltonian approach as reported in the CDMS[72] database[a]

J	K_a	K_c	GS			ν_9	
			MARVEL	DEWE-VS	CDMS	MARVEL	DEWE-VS
1	0	1	0.674106(0)	0.674	0.674107	440.061194(231)	440.062
2	0	2	2.022302(0)	2.022	2.022304	441.410911(216)	441.415
3	0	3	4.044557(0)	4.045	4.044562	443.438915(215)	443.444
4	0	4	6.740826(1)	6.741	6.740831	446.143029(137)	446.150
5	0	5	10.111046(1)	10.111	10.111050	449.522754(132)	449.531
10	0	10	37.067862(220)	37.069	37.068083	476.554409(364)	476.579
20	0	20	141.447550(576)	141.453	141.447591	581.196584(353)	581.290
30	0	30	312.900609(1398)	312.917	312.899634	752.995071(496)	753.227

[a] Variational results corresponding to a quartic force field expansion of the PES, see ref. 267 and 72. GS refers to the vibrational ground state. The DEWE-VS rovibrational energies reported for ν_9 were adjusted so that the DEWE-VS vibrational band origin matches the MARVEL value exactly.

Table 4 Full and reduced-dimensional zero-point vibrational energies and vibrational band origins of ^{14}NH$_3$ relative to the vibrational ground state energy, all in cm^{-1}, determined using the GENIUSH code and the "refined" PES of ref. 269

	1D	2D	3D	6D	Expt.[a]
$0^+(A_1', \text{GS})$	521.43	2256.74	2158.70	7436.82	—
$0^-(A_2'')$	1.13	1.28	1.70	0.79	0.79
$\nu_2^+(A_1')$	930.57	900.48	904.48	932.41	932.43
$\nu_2^-(A_2'')$	979.80	952.80	970.68	968.15	968.12
$2\nu_2^+(A_1')$	1586.97	1537.6	1550.06	1597.26	1597.47
$\nu_4^+(E')$	—	—	1659.43	1625.62	1626.28
$\nu_4^-(E'')$	—	—	1662.12	1626.73	1627.37
$2\nu_2^-(A_2'')$	1918.86	1868.39	1917.98	1882.18	1882.18

[a] The molecular symmetry group D_{3h}(M) is used to label the rotational–vibrational states. The D_{3h}(M) symmetry labels are given in parentheses. GS = ground state. The 1D and 2D models do not exhibit the ν_4^+ and ν_4^- vibrations as the two bending vibrational coordinates are fixed in these cases. Experimental results are taken from ref. 270 and have considerably higher accuracy than indicated here.

case of the 6D model all vibrational degrees of freedom are active. Clearly, the simplest 1D model is successful in reproducing the splitting of the first few pairs of vibrational band origins (VBOs), and those of the rotational levels they hold (not shown but given in ref. 71), and it is rather hard to substantially improve upon it.

Selected further applications of our codes to polyatomic molecular systems are discussed in the next subsections.

4.2.1 Complete bound-state spectra. One of the most important applications of variational nuclear-motion computations is the determination of all the states determining the complete rovibrational spectrum of a molecule. The goal of computing all bound vibrational states of triatomic molecules has been achieved for H$_2$^{16}O and H$_3^+$. The number of VBOs is 1150 and 1287 (counting the E symmetry states twice) for H$_2$^{16}O and H$_3^+$, respectively. Of course, depending on the PES these numbers can change by one or two, very close to the dissociation limit new states may arise or old ones disappear.

Due to the density of the rovibrational states and their complex character, the computation of energy levels close to the dissociation limit is problematic and requires the development

of specialized procedures and the use of large basis sets. These technical difficulties can be overcome up to rather large J values and thus extremely large line lists of molecules can be generated, as pioneered by Tennyson and co-workers.[241–243] The experimentally needed part of these line lists depends also on the temperature at which one is interested in the absorption or emission spectrum. These line lists store not only the computed (or to some extent experimental) energy levels and their assignments and transitions with pointers to the energy levels, but also the Einstein-A coefficients of the transitions so that the temperature-dependent intensities can be computed. It is expected that more or less complete line lists will appear in the near future not only for triatomic but also for important four- and five-atomic systems, such as NH$_3$ and CH$_4$.

The ability to compute highly excited rovibrational states means that a peculiar feature of rovibrational spectra, the clustering of highly-excited rovibrational states of molecules can be studied. Fig. 2 shows interesting clustering effects for the ground vibrational state of the parent isotopologue of methane, where data are shown up to $J = 50$. The computations employed the PES of ref. 271 and the DEWE-VS code.
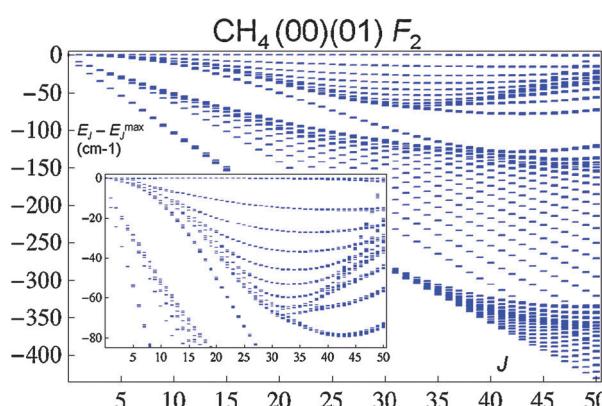
Fig. 2 Rotational clustering effects for the (00)(01) F_2 vibrational state of the parent isotopologue of methane molecule. $E_J - E_J^{\text{max}}$ differences, in cm^{-1}, plotted against the J rotational quantum number, where E_J and E_J^{max} denote an arbitrary and the maximum energy level for a given value of J, respectively. The computations are based on the PES of ref. 271 and obtained with the DEWE-VS code.

Similar clustering effects have been observed for higher vibrational states, as well.

4.2.2 Resonance states. Resonance states, also known as quasi-bound states, of a system are metastable states which have sufficient energy to break up the system into its subsystems. Though seldomly considered, they play an important role in atomic and molecular physics,[81,272–274] for example, in unimolecular reactions, in photodissociation and photoassociation studies, and in scattering phenomena.

Resonance wave functions can be associated with outgoing eigenfunctions of the Hamiltonian, diverging exponentially at infinity.[114] Due to the outgoing boundary condition, the eigenvalues corresponding to resonance states are complex, which are usually written as $E_n^{(\text{res})} = \varepsilon_n - \frac{i}{2}\Gamma_n$, where ε_n is the resonance position and Γ_n is the width (inverse lifetime) of the resonance state. Due to their diverging asymptotic behaviour resonance wave functions are not square integrable; thus, one would think at first that the L^2 methods discussed in this paper are not suitable for describing them. There are, however, several methods available which do make possible to compute resonance eigenstates using L^2 methods, usually based on employing modified non-Hermitian Hamiltonians whose eigenvalues with corresponding L^2 eigenfunctions can be used for evaluating or approximating resonance positions and widths. The two most popular methods are the complex coordinate method[114,275] and the complex absorbing potential (CAP) method,[276–278] from which the latter seems to be favored for calculating (ro)vibrational resonances of polyatomic molecules.[207,279–282]

In the CAP method, the Hermitian Hamiltonian is perturbed with a complex absorbing potential which damps the outgoing wave functions at the asymptotic region of the PES, making them square integrable and suitable for an L^2 basis expansion. Along with other alternatives,[277,279,281] resonance eigenvalues in the CAP method can be evaluated[277,279,282,283] by finding cusps in eigenvalue trajectories obtained by diagonalizing the complex symmetric Hamiltonian matrix with different CAP parameters. In recent works[279–282] it can be seen how being able to use L^2 methods for computing resonance eigenvalues can be exploited through efficiency and numerical techniques of the well developed L^2 methods.

While experimentally observed, near-threshold resonance structures of molecules have mostly defied detailed first-principles analysis,[284,285] it is clear that there are at least two well-defined mechanisms that lead to the formation of long-lived resonances. Rotational excitation of below-threshold vibrational states leads to a centrifugal barrier behind which high-energy rovibrational states can be trapped temporarily, giving rise to so-called shape resonances. The width of shape resonances is determined by the centrifugal barrier. Shape resonances can extend to hundreds of wavenumbers above the dissociation threshold and they result in narrow features in the spectrum due to their tunneling character. These resonances are responsible, for example, for part of the famous Carrington bands, the multitude of still unassigned lines observed in the near-dissociation spectrum of H_3^+.[284] Vibrational excitation into high-energy states which do not lead toward dissociation gives Feshbach (sometimes called Fano–Feshbach)

resonances. Both types of resonances have been identified in the near-threshold spectrum of the water vapor.[286,287] A combination of these two mechanisms has also been observed.[280] It is expected that as the method developments continue resonance state computations will become widespread for 3–5-atomic systems, extending considerably our knowledge[81,207,248,287–290] about them.

4.3 Assignment of rovibrational states

Assigning the large number of computed (and measured) rovibrational states of molecules below their first dissociation limits is an extremely demanding task, as shown, for example, for water in ref. 187. Without valid assignments, however, there is no hope of extending the information systems characterizing the spectroscopy of molecules beyond what is available at present.[103,104] The overall labeling of the rovibrational states, including proper molecular symmetry and the assignment of approximate quantum labels to the eigenstates are important aspects of nuclear motion computations.

4.3.1 Normal-mode decomposition (NMD) tables. Let us consider the n_Jth rovibrational wave function $\Psi_{n_J}^J(\mathbf{Q}, \phi, \theta, \chi)$ as a linear combination of rotational–vibrational basis functions:

$$\Psi_{n_J}^J(\mathbf{Q}, \phi, \theta, \chi) = \sum_{i=1}^{\mathcal{N}} \sum_{L=1}^{2J+1} c_{n_J,iL}^J \Phi_i(\mathbf{Q}) R_L^J(\phi, \theta, \chi), \quad (30)$$

where (ϕ, θ, χ) is the usual set of Euler angles, $\mathbf{Q} = (Q_1, Q_2,\ldots, Q_{3\mathcal{M}-6})$ denotes the normal coordinates of an $\mathcal{M}$-atomic molecule, J is the rotational quantum number, and $R_L^J(\phi, \theta, \chi)$ denotes the Wang-transformed symmetric-top rotational basis functions[218] indexed by L. The vibrational basis functions $\Phi_i(\mathbf{Q})$ are assumed to be products of one-dimensional functions in each vibrational degree of freedom, and $\mathcal{N} = N_1 N_2 \ldots N_{3\mathcal{M}-6}$ is the total size of the multidimensional vibrational basis.

In the case of a DEWE-like protocol, $\psi_m(\mathbf{Q})$ pure vibrational states ($J = 0$) are described as a linear combination of product functions of harmonic oscillators:

$$\psi_m(\mathbf{Q}) = \sum_{i=1}^{\mathcal{N}} C_{m,i} \Phi_i^{\text{HO}}(\mathbf{Q}). \quad (31)$$

Due to the normalization of the wave function and the orthonormality of the basis functions, $\sum_{i=1}^{\mathcal{N}}|C_{m,i}|^2 = 1$, and one can write

$$C_{m,i} = \langle \Phi_i^{\text{HO}}|\psi_m\rangle_{\mathbf{Q}}. \quad (32)$$

The $|C_{m,i}|^2$ coefficients are referred to as the elements of the normal-mode decomposition (NMD) table as they describe the variational wave function in terms of the harmonic oscillator basis functions. The labeling of "exact" vibrational wave functions, $\psi_m(\mathbf{Q})$, with harmonic oscillator quantum numbers can be accomplished by picking out the dominant contributors in eqn (31), which can be read directly from an NMD table. An NMD coefficient smaller than 0.5 does not mean that no good approximate quantum numbers can be found—it simply means that the HO approximation may not provide a good separation.

Obviously, it would be advantageous to be able to produce NMDs from arbitrary wave functions represented with arbitrary basis functions and coordinates. However, if the variational wave functions are computed by programs built upon the use of internal coordinates, the computation of NMDs is hindered considerably as the internal coordinate and the harmonic oscillator wave functions whose overlap must be computed are based on different ranges and volume elements.

The NMD analysis has been applied to $H_2^{16}O$, whereby the nuclear motion computations employed the PES of ref. 291 and 53, to NCCO,[292] *trans*-HCOH and *trans*-HCOD, and ketene. Here we present results only for the parent isotopologue of the 5-atomic ketene molecule, $H_2^{12}C^{12}C^{16}O$.

The vibrational states of ketene up to 1050 cm^{-1} exhibit little mixing and have dominant NMD coefficients $\geq 91\%$. However, most of the states in the 1050–1550 cm^{-1} window have much smaller leading NMD coefficients due to anharmonic resonances. The vibrational wave functions ($\psi_8, \psi_9, \psi_{10}, \psi_{11}$) lying at (1071, 1113, 1169, 1211) cm^{-1} involve a complicated ($2\omega_6$, $\omega_5 + \omega_6$, ω_4, $2\omega_5$) Fermi resonance tetrad that clouds the assignment of the C=C stretching fundamental (ν_4). A striking manifestation is that the $\omega_5 + \omega_6$ basis state contributes between 12% and 45% to all variational wave functions in the set (ψ_8–ψ_{11}). The NMD results differ substantially from the more approximate, non-variational coefficients extracted in ref. 293, attesting to the intricacies of the determination of the extent of vibrational mixing. Nevertheless, both studies concur in the assignment of the experimental band[294] at 1116.0 cm^{-1} to the ν_4 fundamental. The ν_3 (CH$_2$ scissoring) fundamental is also strongly mixed, in this case due to a resonance between (ω_4, $\omega_8 + \omega_9$) basis states, which contribute (43%, 50%) and (50%, 45%) to (ψ_{13}, ψ_{15}), respectively. In brief, the ketene molecule provides multiple examples in which the assignment of even the vibrational fundamentals is blurred. Such complications are expected to arise for other molecules, as well.

4.3.2 Rigid-rotor decomposition (RRD) tables. For the eigenstates of the field-free rovibrational Hamiltonian the J rotational quantum number is exact, while the widely used K_a and K_c labels are approximate and correspond to $|K|$ for the prolate and oblate symmetric-top limits of the asymmetric-top rigid rotor,[218] respectively. Recently we proposed[295] a two-step algorithm to match the computed rovibrational states with pure vibrational states and generate the K_a and K_c labels.

By rearranging eqn (30), one obtains

$$\Psi_{n_J}^J(\mathbf{Q}, \phi, \theta, \chi) = \sum_{L=1}^{2J+1} R_L^J(\phi, \theta, \chi) \left(\sum_{i=1}^{\mathcal{N}} c_{n_J,iL}^J \Phi_i(\mathbf{Q}) \right)$$

$$= \sum_{L=1}^{2J+1} R_L^J(\phi, \theta, \chi) \psi_{n_J L}^J(\mathbf{Q}). \tag{33}$$

From now on, $\psi_{n_J L}^J(\mathbf{Q})$ will be referred to as the Lth vibrational part of $\Psi_{n_J}^J(\mathbf{Q}, \phi, \theta, \chi)$. Let us introduce the overlap of the Lth vibrational part of $\Psi_{n_J}^J(\mathbf{Q}, \phi, \theta, \chi)$ and the

vibration-only $\psi_m(\mathbf{Q}) = \sum_{j=1}^{\mathcal{N}} c_{m,j} \Phi_j(\mathbf{Q})$ as $\mathscr{S}_{n_J L,m}^J$, and sum the absolute squares of the $\mathscr{S}_{n_J L,m}^J$ quantities with respect to L:

$$P_{n_J,m}^J = \sum_{L=1}^{2J+1} |\mathscr{S}_{n_J L,m}^J|^2 = \sum_{L=1}^{2J+1} \left| \sum_{i=1}^{\mathcal{N}} c_{n_J,iL}^J c_{m,i} \right|^2. \tag{34}$$

After converging M $J = 0$ and N_J $J \neq 0$ eigenstates by variational procedures, $N_J M$ square-overlap sums are computed over all of the $J = 0$ and $J \neq 0$ pairs. The quantities $P_{n_J,m}^J$ ($n_J = 1,2,\ldots,N_J$ and $m = 1,2,\ldots,M$) can be regarded as elements of a rectangular matrix with N_J rows and M columns. For a given J, those $(2J+1)$ $\Psi_{n_J}^J(\mathbf{Q}, \phi, \theta, \chi)$ rovibrational states belong to a selected $\psi_m(\mathbf{Q})$ pure vibrational state which give the $2J+1$ largest $P_{n_J,m}^J$ values. This means of identification is valuable because the rovibrational levels belonging to a given vibrational state appear neither consecutively nor in a predictable manner in the overall eigenspectrum.

The quantities $P_{n_J,m}^J$ depend on the embedding of the body-fixed frame and on the rotational constants chosen for the rigid-rotor basis functions. The use of the Eckart–Watson Hamiltonian involves the Eckart frame,[86] which is expected to be a trenchant choice for the overlap calculations due to a minimalized rovibrational coupling. This rotational labeling scheme can be employed in other variational rovibrational approaches employing arbitrary internal coordinates and embeddings.

After assigning $2J+1$ rovibrational levels to a pure vibrational state, the next step is to generate the K_a and K_c or the $\tau = K_a - K_c$ labels. To achieve this, one should set up what we call rigid-rotor decomposition (RRD) tables, by evaluating the overlap integral

$$S_{n_J,m,m_J}^J = \langle \Psi_{n_J}^J(\mathbf{Q}, \phi, \theta, \chi) | \psi_m(\mathbf{Q}) \cdot \varphi_{m_J}^J(\phi, \theta, \chi) \rangle_{\mathbf{Q}, \phi, \theta, \chi}. \tag{35}$$

We define the RRD coefficients as the absolute square of the overlaps, $|S_{n_J,m,m_J}^J|^2$, and arrange them in a rectangular table whose rows are the exact states under consideration, $\Psi_{n_J}^J(\mathbf{Q}, \phi, \theta, \chi)$, and whose columns are the "basis" states, $\psi_m(\mathbf{Q})\varphi_{m_J}^J(\phi, \theta, \chi)$, products of vibrational and rigid-rotor basis functions. The state with the largest RRD coefficient provides the label of the level.

In the NMD + RRD scheme the complete rovibrational label includes the irreducible representation (irrep) Γ of the molecular symmetry (MS) group, the total rotational angular momentum quantum number (J), K_a and K_c values corresponding to the asymmetric rigid rotor, and perhaps the normal-mode vibrational quantum numbers (v_1, $v_2,\ldots$, $v_{3\mathcal{M}-6}$). It is worth emphasizing that the first two labels, Γ and J, are exact, as they are valid for the exact nonintegrable Hamiltonian, while the last labels, K_a, K_c, and (v_1, $v_2,\ldots$, $v_{3\mathcal{M}-6}$), are inexact designations arising from an approximate (RRHO) rovibrational Hamiltonian.

For lower-lying states, the $P_{n_J,m}^J$ diagnostics [eqn (34)] are frequently very close to their ideal, unmixed values of 1.00 and are almost always greater than 0.90, thus providing unambiguous quantum labels. Nevertheless, prominent exceptions sometimes occur due to resonances, which our

protocol identifies very successfully. For example, there is strong mixing between $J_{K_aK_c}$ states belonging to different combination levels of $H_2^{16}O$: the rovibrational eigenstate at $10\,177.6$ cm^{-1} is $79\%[3_{30} \,(\nu_1 \,+\, \nu_2)] \,+\, 20\%[3_{22}(\nu_2 \,+\, \nu_3)]$, while that for $10\,182.8$ cm^{-1} is $20\%[3_{30} \,(\nu_1 \,+\, \nu_2)] \,+\, 80\%[3_{22}(\nu_2 \,+\, \nu_3)]$. This pronounced resonance causes a switching in relative energy of the 3_{30} and 3_{31} levels of $\nu_1 + \nu_2$ relative to the expected rigid-rotor energy ordering $[E\,(3_{31}) < E\,(3_{30})]$, although the difference is less than 0.5 cm^{-1}. The ketene molecule is very nearly a symmetric top, with (A_0,B_0,C_0) close to $(9.410, 0.343, 0.331)$ cm^{-1}, in order.[293] Accordingly, a near double-degeneracy for all values of $K_a \geq 1$ is seen in the rovibrational levels of ketene.

As a test to see the range of applicability of the RRD labeling protocol, a massive amount of RRD coefficients were determined for the $H_2^{16}O$ molecule. $30(2J+1)$ number of rovibrational states were included in the labeling for each J rotational quantum number ranging from 1 to 20. For the RRD the vibrational labels were taken from ref. 187 by matching energies, while the $J_{K_aK_c}$ rotational labels were generated during the RRD analysis. Variational rovibrational computations were performed with the D^{2}FOPI[186] protocol using the PES of ref. 296. In terms of rovibrational states being the linear combination of the direct product functions obtained from vibrational and rigid-rotor eigenfunctions, rovibrational states become more "mixed" with increasing energy and J rotational quantum number. This naturally leads to less dominant overlaps (see eqn (35)). Fig. 3 shows the percentage of clearly assignable states as a function of the J rotational quantum number and the rovibrational energy. RRD labels were considered "well defined" if for the given rovibrational state the square of the largest $S^J_{n_J,m,m_J}$ coefficient (defined in eqn (35)) exceeded 0.5. As expected, less and less RRD labels are "well defined" with increasing energy and J quantum number. Nonetheless, for a wide range of both of these parameters a large amount of "well defined" labels can be assigned *via* the RRD protocol. Out of the total of $13\,200$
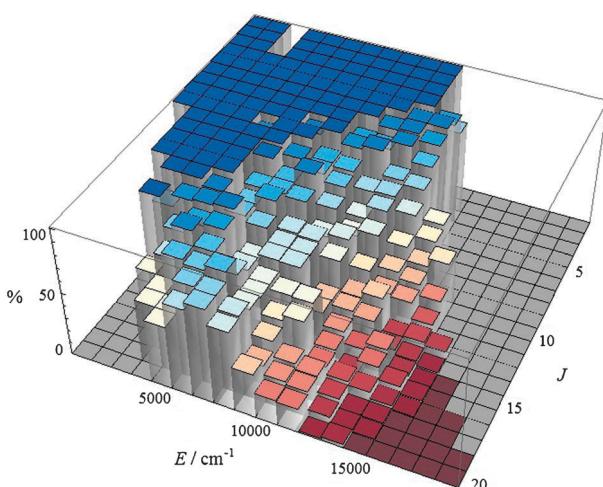
states included in Fig. 3, 5365 could be given a "well defined" status. It is noted that the choice of 0.5 as a lower limit for the square of the largest $S^J_{n_J,m,m_J}$ coefficients for considering an RRD label "well defined" is a rather strict one. With a lower threshold, one could extend the range of applicability of the RRD scheme considerably.

4.4 Temperature-dependent effective molecular structures

One of the problems of structural research is that it is impossible to measure the well-defined equilibrium molecular structures experimentally,[26,297,298] usually only (ro)vibrationally averaged temperature-dependent parameters can be determined. One can define either "distance" or "position" averages. These averages can be converted into each other using different assumptions. The simplest one, applicable to distances, is the use of diatomic paradigms (like the Morse oscillator).[154] For semirigid molecules perturbation theory yields approximate but rather accurate formulas for distance averages and distance conversions. The third, and by far the most elaborate and most accurate treatment involves variational computation of the nuclear wave functions and uses these wave functions to perform the rovibrational averaging. Only this approach is discussed here briefly.

A distance average of central importance is $r_{g,T}$, where "g" means "center of gravity of the probability distribution of the interatomic distance" and T stands for the temperature. The working definition to compute $r_{g,T}$ is

$$r_{g,T} = \sum_{\nu,J_\tau} W_{\nu,J_\tau}(T)\langle r\rangle_{\nu,J_\tau} \qquad (36)$$

$$\langle r\rangle_{\nu,J_\tau} = \langle \Psi_{\nu,J_\tau} \,|r|\, \Psi_{\nu,J_\tau}\rangle, \qquad (37)$$

where $\langle r\rangle_{\nu,J_\tau}$ is the expectation value of the distance corresponding to rovibrational states labeled by vibrational quantum numbers ν and rotational quantum numbers J_τ, the effect of temperature is taken into account by simple Boltzmann averaging, and W also contains degeneracy and nuclear spin factors. Computation of the multi-dimensional $\langle r\rangle$ integral is especially simple in the DVR representation. During rovibrational averaging one can take advantage of the fact that the internal coordinates do not depend on the Euler

Fig. 3 Percentage of clearly identifiable rotational–vibrational states of $H_2^{16}O$ based on RRD matrix elements larger than 0.5, given as a function of energy (ground state is at 0.0 cm^{-1}) and rotational quantum number J.

Table 5 Effective structural parameters of two symmetric isotopologues of the water molecule, taken from ref. 299

Distance type[a]	$H_2^{16}O$	$D_2^{16}O$
r_e^{ad}	0.95785	0.95783
r_g (0 K)	0.97565	0.97077
r_g (300 K)	0.97625	0.97136
r_g (GED, 302 K)	0.9763(30)	0.9700(30)
r_a (0 K)	0.97079	0.96724
r_a (300 K)	0.97138	0.96783
r_a (GED, 302 K)	0.9716(30)	0.9664(30)

[a] All results are given in Å. All computed results correspond to the adiabatic, so-called CVRQD PES of ref. 53 and 291. The isotope-dependent, adiabatic equilibrium structures, r_e^{ad}, of water are reported in ref. 24 and they are only very slightly different from the isotope-independent, Born–Oppenheimer equilibrium structure, r_e^{BO}, yielding 0.95782. For the nuclear masses employed in the nuclear-motion computations see ref. 299. GED = gas electron diffraction, data taken from ref. 300.

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angles describing the overall rotation of the molecule. Thus, the r_g-type distance basically means an $\langle r \rangle$ average, and could thus be called "mean" distance. Other distance averages of the type $\langle r^n \rangle^{1/n}$ can also be defined, most important among these is the $r_{a,T} = \langle r^{-1} \rangle^{-1}$, the so-called "inverse" distance. It is also important to note that the centrifugal distortion correction can be treated through a classical mechanical espression $\langle \delta r \rangle_{\text{rot}}^T = \sigma T$, where only the linear factor needs to be determined from a few simple rovibrational computations.

Temperature-dependent effective molecular structures have been computed for the $H_2^{16}O$ and $D_2^{16}O$ isotopologues of the water molecule.[299] Selected results are presented in Table 5, exemplifying the accuracy and extent of this procedure, especially when compared to experimental data.[300]

5   Conclusions

Powerful variational and variational-like methods are increasingly used for solving the nuclear-motion Schrödinger equation, extending the traditional rigid-rotor-harmonic oscillator (RRHO) and second-order vibrational perurbation theory (VPT2) treatments. Variational studies can help to advance our understanding and extend it in new directions in many areas of physical chemistry and chemical physics. For example, the nuclear-motion computations can be used to obtain improved potential energy and even property surfaces by adjusting *ab initio* computed surfaces to measurements. This approach is based on the fact that when the nuclear-motion Schrödinger equation with an exact kinetic energy operator is solved variationally the only significant approximation introduced is related to the surfaces. Variational nuclear-motion techniques can be used for computing accurate rovibronic states of polyatomic molecules. The more accurate the surfaces (*e.g.*, PES and DMS) employed, the better the simulations are. In these spectroscopic applications standard, automated procedures are needed for determining, assigning and interpreting the large collections of eigenstates resulting from variational computations, in order to solve chemical, physical and engineering problems and to compile self-consistent spectroscopic databases. Note in this respect that without detailed assignments of the experimentally measured lines the use of spectroscopic databases to model spectra obtained under different conditions (different pressures, foreign gases, and temperatures) is not possible. The seemingly best quantum chemical procedure offered is what we call GENIUSH, *i.e.*, a fully numerical use of a general internal-coordinate Hamiltonian. This holds not only for spectroscopic applications but also for quantum dynamics and reaction rate computations.

Variational nuclear motion computations complement and far extend techniques built upon effective Hamiltonians to build large-scale spectroscopic databases. The best use of approximate but complete variational quantities is to employ them as complementary information to accurate but incomplete measured results. The judicious use of all sets of results is a prerequisite to the development of spectroscopic information systems. The possible completeness of the computed rovibronic information can greatly help to determine, for example, molecular partition functions *via* direct summation, which

are the principal quantities of thermochemistry and most thermodynamic quantities of practical interest can be derived from them.

If the accuracy of the variational nuclear motion computations can be ensured *via* the use of accurate surfaces, they can lead not only to the discovery of or confirmation of "effects" for molecular systems which otherwise would have remained hidden but also to the design of new measurements to test the limits of quantum theory. Cases in mind include clustering of energy levels yielding higher apparent degeneracy than allowed by the symmetry of the systems, quantum monodromy, selection of almost strictly forbidden *ortho–para* transitions, and parity violating transitions in chiral molecules.

An interesting question of molecular vibrations concerns the range of validity of the harmonic oscillator approximation and of normal modes. One of the conclusions of the numerical results obtained from variational computations is that the normal-mode picture of the vibrational bands commonly breaks down even for some of the fundamentals of molecules. Considerable mixing among some of the low-energy states seems to be the rule rather than the exception for the cases studied so far. This finding may also be important for Eckart–Watson Hamiltonian-based vibrational self-consistent-field (VSCF) spectroscopy (and treatments based on such VSCF ansätze). Along with symmetry classification, the approximate vibrational and rotational labels attached to variationally computed rotational–vibrational eigenstates provide information much needed by experimental spectroscopists. NMD and RRD tables appear to be useful also for spectroscopic perturbation theory as they give a clear indication of extensive mixings among states which could be important when setting up the effective Hamiltonians used to interpret high-resolution spectroscopic experiments. Thus, NMD and RRD tables, resulting in complete rovibrational labels, should be routinely computed at least for semirigid molecules.

Without discounting the considerable achievements of nuclear motion theory, some of which were presented above, it must also be stressed that there are several outstanding challenges which should be met in the near future and require further developments of the existing methodologies. The so-called Carrington bands close to the first dissociation limit of the molecular ion H_3^+ still remain unassigned. In general, efficient computation of resonance states still requires further method developments. Treatment of highly excited states of molecules "with no structure", like the case of CH_5^+, and of weakly bound molecular systems, like those held together by H-bonds or dispersive interactions, is far from being solved. Computation of the hyperfine structure of measured spectra as well as the efficient joint treatment of several surfaces await further studies. Extending the applicability of nearly exact nuclear-motion treatments to much larger, flexible molecules requires further significant efforts. Computation of quantum rate constants and advancing quantum control are two areas where a lot of developments are expected in the near future. It is clear that in the fourth age of quantum chemistry method development and the application of the new techniques to outstanding problems of chemistry continue and continue with a hopefully increased speed.

Acknowledgements

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