# Global Analytical Potential Energy Surfaces for High Resolution Molecular Spectroscopy and Reaction Dynamics

**R. Marquardt, M. Quack**

**ETH Zürich, Laboratory of Physical Chemistry, Wolfgang-Pauli-Str. 10,
CH-8093 Zürich, Switzerland, Email: Martin@Quack.ch**

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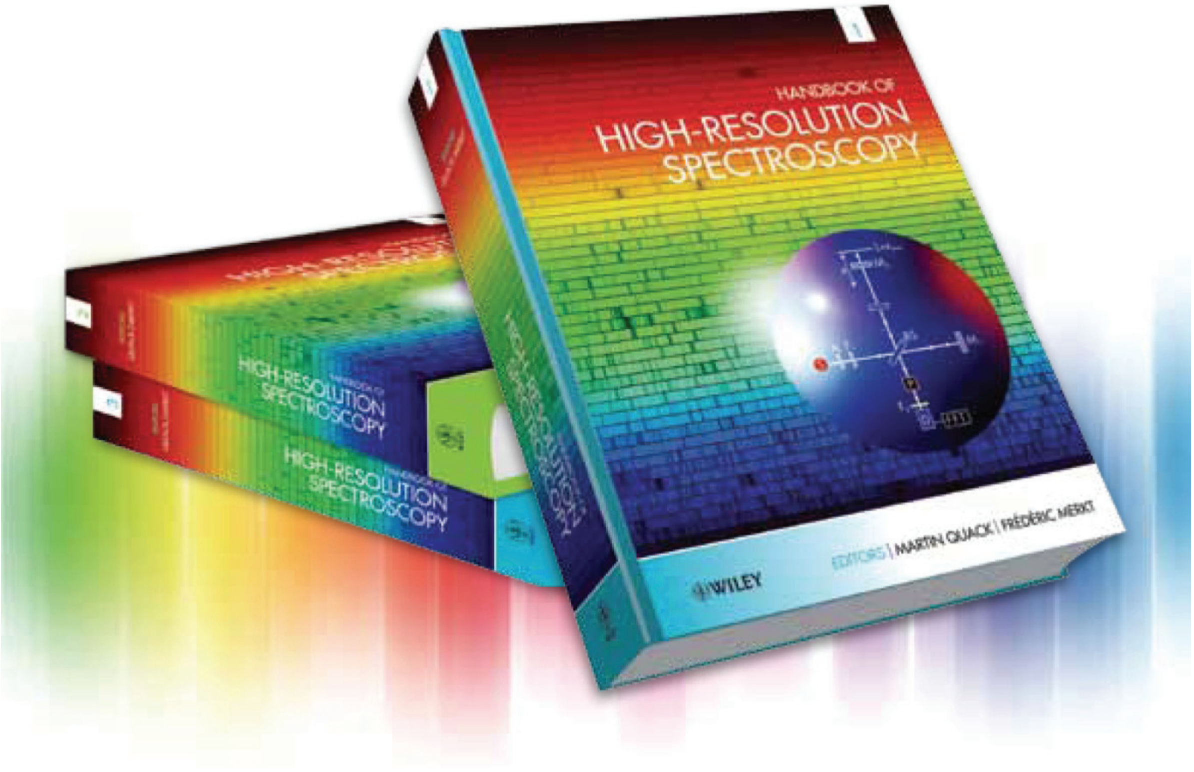

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## Abstract

Analytical representations of potential energy hypersurfaces for the nuclear motion in polyatomic molecules from ab initio theory and experiment are discussed in a general way. The qualification of potential hypersurface representations from ab initio theory regarding the description of experimental data from rovibrational high-resolution spectroscopy and chemical reaction kinetics is analyzed in more detail for a restricted group of molecules including methane, $CH_4$, ammonia, $NH_3$, $H_2O_2$, and $(HF)_2$. Current methods for the derivation of analytical representations of potential energy surfaces as well as some applications are reviewed.

Keywords: ab initio theory; potential energy hypersurfaces; overtone spectroscopy; quantum dynamics; wave packets; $CH_4$; methane; $NH_3$; ammonia; $H_2O_2$; hydrogen peroxide; $(HF)_2$; hydrogen fluoride dimer; isotopes; Born–Oppenheimer approximation

# Global Analytical Potential Energy Surfaces for High-resolution Molecular Spectroscopy and Reaction Dynamics

**Roberto Marquardt**[1] **and Martin Quack**[2]

[1] *Laboratoire de Chimie Quantique, Institut de Chimie, UMR 7177 CNRS, Université de Strasbourg, Strasbourg, France, roberto.marquardt@unistr.fr*
[2] *Laboratorium für Physikalische Chemie, ETH Zürich, Zürich, Switzerland, martin@quack.ch*

## 1 INTRODUCTION

### 1.1 A Brief History

The modern understanding of molecular dynamics is based on quantum mechanics and on the electromagnetic interaction between nuclei and electrons, at least with respect to the majority of observable effects, excluding here effects from the parity violating weak interaction, which is important in chiral molecules (Quack 2002, 2011). Nevertheless, finding answers to the questions regarding what are the effective forces driving the atoms in an isolated molecule to move around, to adapt themselves in a new geometrical arrangement, or to go apart one from the other and dissociate remains a continuous challenge to both theoreticians and experimentalists in the field of molecular physics. Quite amazingly, the hypothesis that the motion of electrons and nuclei may be treated separately was formulated in the days of the old quantum theory in an article by Bjerrum (1914a) on the interpretation of spectral bands of gas phase molecules.[a] Furthermore, following Bjerrum, the nuclei move due to “valence forces”, which should be determinable from recorded spectra.[b] With this idea in mind, and the additional working hypothesis that the motion of the nuclei correspond to (harmonic) vibrations, Bjerrum derived a quadratic force field from the term values of observed fundamental vibrational transitions in $CO_2$, thus proposing perhaps the first formulation of an analytical representation of an effective molecular potential energy hypersurface. Later on, anharmonic force fields were derived in a similar way from well-resolved infrared spectra of halogen hydrides (Kratzer 1920). These force fields were developed as truncated Taylor series expansions of nuclear displacements from equilibrium. The spectra also allowed one to clearly recognize the relationship between rotations and vibrations (Bjerrum 1914b). Analogous work on the harmonic force field of ammonia (Dennison 1926) and methane (Dennison 1925) followed soon thereafter.

The origin of the effective potentials for the nuclear motion is explained in the theoretical framework set up by Born and Heisenberg (in the old formulation of quantum theory, Born and Heisenberg 1924), Condon (1927a,b),[c] Slater (1927),[d] Heitler and London (1927)[e] as well as by Born and Oppenheimer (1927).[f] In these theories, the assumption made is that the motion of electrons and nuclei is adiabatically separable: the nuclei move relatively slowly with respect to the electrons, which adapt themselves rapidly to any displacement of the nuclei. While being an approximation to real molecular dynamics, it remains in many respects an excellent approximation until today. This assumption has been a pillar to understanding the chemical bond (Pauling 1940, Mulliken *et al.* 1949) and the spatial structure of molecules as atomic arrangements at the bottom of effective potential wells obtained from the solution of the Schrödinger equation (Herzberg 1945a,b, 1966).

The formulation by Born and Oppenheimer for the solution of the molecular Schrödinger equation for nuclei and electrons, based on the adiabatic separation, allows one in

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the first step to obtain the electronic states at fixed nuclear coordinates. The electronic energies thus become functions of the position of the nuclei. Then nuclear coordinates are varied and the electronic energies calculated before are interpreted as effective attractive and repulsive potentials for the motion of the nuclei, mediated by the rapid motion of the electrons around the nuclei, in addition to the repulsive Coulomb repulsive potential between the nuclei. This effective potential is then used in the second step to obtain rovibrational states for the nuclei alone from a reduced Schrödinger equation. In the so-called Born–Oppenheimer approximation, molecular eigenstates are given as a product of the adiabatically separated electronic and rovibrational states. This ansatz is the starting point for many modern techniques for obtaining solutions of the Schrödinger equation in molecular many-particle systems from ab initio calculations (see, e.g., Bader and Gaugi (1975), Schaefer III (1977a,b), Truhlar (1981), Hehre *et al.* (1986), Dunning (1990), Harding (1990), Bauschlicher and Langhoff (1991), Szabo and Ostlund (1996), Jensen (1999), Helgaker *et al.* (2000), and also several articles in this handbook). *See also* Merkt and Quack 2011: **Molecular Quantum Mechanics and Molecular Spectra, Molecular Symmetry, and Interaction of Matter with Radiation** and references cited therein.

In their original work, Born and Oppenheimer considered only "small" amplitude vibrations of the nuclei around their equilibrium positions.[g] In Condon's work (Condon 1927b) one finds representations of one-dimensional potential energy functions, which, however, do not reach dissociation. Shortly later, a hypothesis was formulated that the adiabatic separation of electronic and nuclear motion following Born and Oppenheimer may also be used to describe predissociation and unimolecular decay (Rice 1929, and references therein[h]). Large amplitude motion of atoms in bound molecular systems may lead to bond dissociation, formation of new bonds, or new molecular conformations (e.g., structural isomerizations). Later reformulations of the original Born–Oppenheimer theory by Born and Huang (1954) allow for nonperturbative treatment of large amplitude molecular dynamics even in cases where the adiabatic separation turns out to be a poor approximation, such as at conical intersections (Domcke *et al.* 2004).

Effective potentials that allow us to describe the dynamics in the entire configuration space of the nuclei are called *global* representations of potential energy (hyper-)surfaces. The use of global representations of potential energy surfaces (PESs) has gained importance as a conceptual tool and working hypothesis in the theoretical understanding of chemical reaction dynamics. Because of its complexity, chemical reaction dynamics is commonly described approximately on the basis of statistical theories such as the "RRKM" theory (Rice and Ramsperger 1927, Kassel 1928, Marcus and Rice 1951), the "transition state theory" (Evans and Polanyi 1935, Eyring 1935), or the "statistical adiabatic channel model (SACM", Quack and Troe 1974, 1998). While these theories (and related theories, see Hofacker (1963), Robinson and Holbrook (1972), Quack and Troe (1981), Gilbert and Smith (1990), Truhlar *et al.* (1996), Baer and Hase (1996), Holbrook *et al.* (1996)) are still of much use today, PESs have been used mainly to provide characteristic parameters employed therein. With increasing computer resources, results from statistical theories have been tested using the calculation of classical trajectories on the multidimensional PESs (Gilbert and Smith 1990, Baer and Hase 1996). In many such test calculations, the representations of PESs were not global because they were represented only along certain reaction channels (*reaction paths*). Since the last decade, "exact" quantum mechanical calculations of scattering processes became feasible, mainly between atoms and diatomic molecules (Schatz 1996), as well as photodissociation processes (Schinke 1993) and stereomutation (Fehrensen *et al.* 1999, 2007).

From this historical perspective, we conclude first that PESs have been introduced in molecular physics as force fields derived from experimental vibrational spectra; secondly, PES were then interpreted within the Born–Oppenheimer approximation, which allowed their calculation from first principles; and thirdly, PES have both the property of characterizing vibrational spectroscopy and chemical reaction dynamics. Representations of PES that allow for the description of all reaction channels within a given energy range have the property of being global. The focus of this work is global representations of PESs that have adequate spectroscopic accuracy.

## 1.2 Ab initio Calculations of Potential Energy Surfaces

In the Born–Oppenheimer approximation, the first step is to solve the molecular Schrödinger equation for the electronic states at fixed nuclear geometries. This procedure is based on first principles and is carried out in many modern computer codes for ab initio calculations (*see also* Yamaguchi and Schaefer 2011: **Analytic Derivative Methods in Molecular Electronic Structure Theory: A New Dimension to Quantum Chemistry and its Applications to Spectroscopy**; Tew *et al.* 2011: **Ab Initio Theory for Accurate Spectroscopic Constants and Molecular Properties**; Breidung and Thiel 2011: **Prediction of Vibrational Spectra from Ab Initio Theory**; Mastalerz and Reiher 2011: **Relativistic Electronic Structure Theory for Molecular Spectroscopy**; Wörner and Merkt 2011: **Fundamentals of Electronic Spectroscopy**, this handbook). Despite the great advances made in computer technology since the early days of quantum mechanics, traditional ab initio calculations can yield only approximate values of electronic energies because many-electron molecular systems are highly correlated (Löwdin 1959). The computational effort of ab initio methods increases exponentially with the number of electrons, while the accuracy of computed data decreases because a higher degree of approximation is needed. In many applications involving large molecular systems, density functional theory (DFT, Hohenberg and Kohn 1964, Kohn and Sham 1965) has become a valuable alternative to ab initio calculations, which focus on the calculation of the electronic wavefunction. In DFT, the electronic density is calculated, which is a function of three degrees of freedom only. The most severe drawback of DFT is that the functionals used to calculate the exchange and correlation terms are not known. Therefore, many authors refer to DFT as not being an ab initio method.

Benchmark ab initio calculations of molecular spectroscopic states exist for $H_2$, for instance. Highly accurate calculations of the electronic ground-state (Wolniewicz 1993) and excited state potential energy functions (Yu and Dressler 1994) allowed these authors to obtain wavenumbers of rovibronic transitions, which agree with experimental values to within $0.1\,\mathrm{cm}^{-1}$ for all stable isotopomers of $H_2$ up to the corresponding dissociation limit. Rovibronic states are obtained from the diagonalization of the full hamiltonian matrix set up in the basis of the adiabatically separated product states and include not only corrections to the Born–Oppenheimer approximation but also corrections due to relativistic effects and quantum electrodynamics. Calculated ionization and dissociation energies agree with experimental values to within $0.001\,hc\,\mathrm{cm}^{-1}$: (Piszczatowski *et al.* 2009, Liu *et al.* 2009, 2010). When nonadiabatic effects are neglected, the error is $0.05\,hc\,\mathrm{cm}^{-1}$ (Kolos and Rychlewski 1993). The remaining discrepancies are related to the neglect of the additional nonadiabatic effects, but the overall agreement between theory and experiment in this simplest molecular system is an excellent illustration of the validity of the Born–Oppenheimer approximation. In this context, we also mention the recent work of Bytautas and Ruedenberg (2009), Bytautas *et al.* (2007, and references cited therein) on $F_2$, which uses a correlation energy extrapolation by an intrinsic scaling method and gives a high-quality description of long-range interactions.

For polyatomic molecules, it is much more difficult to obtain similarly accurate results from ab initio calculations. Adiabatic PESs are usually calculated on a grid of points in molecular configuration space (the term *configuration* may be used in different ways; see endnote (i)), i.e., for a finite set of nuclear coordinates. This set can become quite large, even for smaller polyatomic molecules. For a nonlinear five-atomic molecule, for instance, on the order of $10^9$ points are needed, if each of the nine independent internal degrees of freedom has to be sampled by a grid of 10 points, which in a rather small interval of 300 pm would correspond to a coverage of points separated by 30 pm.

In addition to this large number of points, difficulties also arise from the fact that high-quality calculations require the use of expensive computational methods that take appropriate account of electronic correlation. Traditional calculations of the electronic wave function account for correlation via *configuration interaction* (*CI*) methods[i] (Löwdin 1959, Buenker and Peyerimhoff 1975, Shavitt 1998). Because of finite, limited computer memory, expansions of the wave function need to be truncated, which induces approximation errors. The accuracy of electronic energy values obtained from ab initio calculations can be assessed by benchmark calculations at the *full-CI* limit (see Knowles and Handy (1984), Bauschlicher *et al.* (1990), and also Shavitt (1998), Ansaloni *et al.* (2000), Kállay *et al.* (2003), Dutta and Sherrill (2003), for more recent reviews). Quite often, however, potential energy surfaces can be calculated with sufficient accuracy at lower levels of theory.

The current best methods for obtaining ab initio PESs of moderate sized molecules to up to 100 electrons that approach (vibrational) spectroscopic accuracy criteria are based on the *coupled cluster* expansion of the electronic wave function (see Bartlett and Musial (2007), and references cited therein, for a modern review on coupled-cluster theory). The calculation of vibrational spectra requires solving of the vibrational Schrödinger equation and is discussed later together with a review of benchmark results (see also Section 3.2).

The coupled-cluster method is essentially based on a single determinant description of the electronic wave function. In vibrationally excited regions of configuration space, however, where substantial changes of molecular structure become important, the electronic wavefunction might change the character of its underlying determinant or its description might need to be based on multiple determinants. This is often the case when, for instance, different reaction channels are to be described in the same energy region. Currently, the method of choice for the calculation of PESs describing bond ruptures or other important stereomutation reactions is *multireference configuration interaction* methods (MR-CI, Siegbahn 1984, and MRD-CI, Buenker and Peyerimhoff 1975).

Modern techniques pertaining to specific ab initio calculations of dynamically important regions of PESs such as local minima or transition structures for reaction dynamics are discussed by Yamaguchi *et al.* (1994), Yamaguchi and Schaefer (2011): **Analytic Derivative Methods in Molecular Electronic Structure Theory: A New Dimension to Quantum Chemistry and its Applications to**

**Spectroscopy**, this handbook and reviewed by Dunning (1990). Applications of such techniques to derive accurate PESs for systems larger than five-atomic molecules involving not more than 50 electrons are hardly found, however. Some examples are discussed below.

There is a clear need to extend the applicability of ab initio calculations to larger systems. With the development of quantitatively improved functionals, DFT has received attention not only in the calculation of molecular structure but also in the vibrational spectroscopy of large molecules (Sousa *et al.* 2007). Recent benchmark calculations on organic (Bento *et al.* 2008) and organometallic reactions (Rayón *et al.* 2008), as well as molecular properties of smaller polyatomic compounds (Mohn *et al.* 2005), vibrational spectroscopy of biomolecules (Herrmann and Reiher 2007), and adiabatic ionization energies (Feller *et al.* 2008), show undeniably that the accuracy of PESs is not better than 10 kJ mol$^{-1}$, typically, at critical points, which is far below the standard needed for a quantitative understanding of high- resolution vibrational spectroscopy.

Alternatively, the electronic ground-state energy can be calculated from stochastic algorithms (see, for example, the diffusion quantum Monte Carlo (DQMC) calculations of the electronic ground state of methane by Anderson (1975)). There has also been a discussion on the possibility of obtaining PESs from the study of topological aspects, rather than from *ab initio* calculations (Mezey 1987).

## 1.3 Calculation of Rovibrational States

The essential test of the quality of a PES $V(\boldsymbol{x}^{(\mathrm{n})})$ is the comparison with observable quantities, which in relation to high-resolution spectroscopy involves the calculation of rovibrational states and transition frequencies $\nu$ with $\Delta E = h\nu$ between them from the solution of the (time independent) Schrödinger equation in the reduced space of nuclear coordinates $\boldsymbol{x}^{(\mathrm{n})}$:

$$H^{(\mathrm{n})}\,\psi_k^{(\mathrm{n})}(\boldsymbol{x}^{(\mathrm{n})}) = E_k\psi_k^{(\mathrm{n})}(\boldsymbol{x}^{(\mathrm{n})}) \qquad (1)$$

where

$$H^{(\mathrm{n})} = T(\boldsymbol{x}^{(\mathrm{n})}, (\partial)_{\boldsymbol{x}^{(\mathrm{n})}}) + V(\boldsymbol{x}^{(\mathrm{n})}) \qquad (2)$$

The superscript "n" indicates that the Schrödinger equation (1) involves only nuclear degrees of freedom within the Born–Oppenheimer approximation. The index $k$ numbers rovibrational levels. In principle, wavefunctions and eigenvalues carry a second index, which also numerates the potential hypersurface $V$, but this index may be omitted, for simplicity, whenever restriction to a single electronic state is a sufficiently good approximation (*see* Albert *et al.* 2011: **Fundamentals of Rotation–Vibration Spectra**, this handbook). For other cases, we refer to the review by Wörner and Merkt (2011): **Analytic Derivative Methods in Molecular Electronic Structure Theory: A New Dimension to Quantum Chemistry and its Applications to Spectroscopy**, this handbook. General, exact solutions of this problem are difficult to obtain and intense research is being carried out currently in this field (see also Domcke *et al.* 2004).

For bound states, which fall into the domain of classical spectroscopic studies, this problem may be tackled analytically with the harmonic approximation as a starting point, where vibrations are treated in terms of harmonic oscillators of the nuclei around their equilibrium positions. In this case, the kinetic energy operator $T(\boldsymbol{x}^{(\mathrm{n})}, (\partial)_{\boldsymbol{x}^{(\mathrm{n})}})$ becomes almost separable: this is the so-called Watson hamiltonian (Watson 1968). Anharmonicity and other neglected expressions such as Coriolis coupling terms may then be included by means of perturbation theory to derive spectroscopic term formulae for rovibrational states and transitions (Papoušek and Aliev 1982). It is generally assumed that perturbation theory gives reasonable results in the low-energy domain, typically to up to the region of CH or NH stretching fundamentals, and in the absence of resonances. In the higher energy domain involving overtones and combination bands, this method is less adequate, and substantially more complex numerical algorithms are needed to solve equation (1).

Most current algorithms are based on the variational principle. Numerical results suffer essentially from two different types of error, apart from standard numerical round-off errors: these are errors arising from truncation of the variational basis and errors from the numerical quadrature used to calculate matrix elements of the hamiltonian.

A review on conventional variational methods used up to 1985 and based on one-dimensional wave functions of harmonic and anharmonic oscillators as variational basis functions is given by Carter and Handy (1986). Such methods use analytical expressions for wave functions and, when PESs are represented analytically by Taylor expansions around an equilibrium position, also for matrix elements. The restriction to polynomial forms of the PES is a rather serious limitation, as is discussed below. The advantage of using analytical expressions for wave functions and matrix elements is that numerical quadrature errors become essentially zero with these methods.

With the increase in computer power in the last decades, grid methods (Meyer 1970, Bačić and Light 1986, Luckhaus and Quack 1992, Ha *et al.* 1992) have become quite popular again. They represent, today, a valuable alternative to solve equation (1) based a quasivariational principle (Light and Carrington 2000). Within the *discrete variable representation* (DVR), the matrix of the potential energy operator becomes diagonal. However, the matrix of the kinetic energy operator is nondiagonal. Semiseparable analytical expressions of kinetic energy operators have been derived when particle positions are described by the so-called polyspherical coordinates (Gatti *et al.* 1998a,b, 2001, Mladenović 2000a,b,c, 2003, Gatti and Iung 2009). Other possibilities include numerical $Z$-matrix-type representations of the kinetic energy (Luckhaus 2000, 2003, Lauvergnat and Nauts 2002). Such expressions have been implemented using DVR or *finite basis representations* (FBRs, Light and Carrington 2000). Vibrational eigenstates may be obtained by diagonalization of the resulting Hamilton matrix. While almost complete, direct diagonalization of the rovibrational hamiltonian has been carried out for a triatomic molecule such as the water molecule to up to two-thirds of the dissociation energy (Shirin *et al.* 2003), the treatment of tetra-atomic or larger molecules requires using contraction schemes (such as shown by Luckhaus and Quack (1992), Luckhaus (2000)) or iterative schemes, such as developed by Wang and Carrington (2003a,b). A recent article reviews variational quantum approaches for computing vibrational energies of polyatomic molecules (Bowman *et al.* 2008), albeit somewhat incompletely. In this handbook, the articles by Carrington (2011): **Using Iterative Methods to Compute Vibrational Spectra** and Tennyson (2011): **High Accuracy Rotation–Vibration Calculations on Small Molecules**, this handbook deal with this topic. Additional, older reviews were given by Handy (1989), Bačić and Light (1989), and Tennyson *et al.* (1992), including a time-dependent perspective by Quack (1992). There has also been recent progress in terms of "black box" programs for calculations along those lines in the group of Attila Császár (Mátyus *et al.* 2009).

For very large systems, there are approximating algorithms based on variational methods, which effectively reduce the linear space of basis functions to "active spaces" (Wyatt 1989), or that make use of a multimode character of the wave functions (Carter *et al.* 1998), as well as algorithms based on adiabatic solutions of the time-dependent Schrödinger equation (with typically more than 100 degrees of freedom, Jungwirth and Gerber 1995). Recently, an improved relaxation method has been applied to calculate vibrational eigenstates within the multiconfigurational time-dependent Hartree method (Richter *et al.* 2007, Vendrell *et al.* 2007, Doriol *et al.* 2008).

An alternative, nonvariational method for obtaining vibrational energies is based on Monte Carlo algorithms, which, in principle, allow for energy level calculations including upper and lower error bounds (Quack and Suhm 1991, Lewerenz and Watts 1994, and references therein).

States above the dissociation threshold can be calculated using several variants of quantum scattering theory (Bowman 1994, Schatz 1996, Bradley Moore and Smith 1996, Truhlar *et al.* 1996). Observables from reaction dynamics such as state- or energy-specific reaction rates or product state distributions may as well be derived from statistical theories (Quack and Troe 1981, 1998) or from classical or quasiclassical trajectories on PESs (Truhlar *et al.* 1996, Baer and Hase 1996, Bradley Moore and Smith 1996), which allow to conclude on the quality of specific topographical features of the employed PESs.

In general, a quantitative agreement between theoretical and experimental scattering observables to within 5–20% is considered satisfactory. Bound state observables can be obtained more accurately. Higher accuracy can be achieved in energy level calculations. For instance, in the above-mentioned work on water molecule, experimental rovibrational term values with $J \leq 10$ can be predicted to up to $25\,000\,\mathrm{cm}^{-1}$ with a standard deviation of $0.1\,\mathrm{cm}^{-1}$ Shirin *et al.* (2003). State-of-the-art calculations of vibrational eigenstates of tetra-atomic and larger molecules yield deviations on the order of typically $1-5\,\mathrm{cm}^{-1}$ in the midinfrared, and $5-50\,\mathrm{cm}^{-1}$ in the near-infrared to visible range of overtone transitions and combination bands. The quality of bound vibrational eigenfunctions may be assessed by comparison of integrated absorption cross sections or transition dipole moments, which also critically depends on the quality of the dipole moment surface; given that experimental values are accurate to within 20–30%, comparison of transition dipole moments evolutions from fundamental to overtones are often considered to be satisfactory, if orders of magnitude match (Ha *et al.* 1990, Hollenstein *et al.* 1994, 1995, Signorell *et al.* 1996, Marquardt *et al.* 2003a, Yurchenko *et al.* 2005b). The agreement may be much better, though, for fundamental transitions (Rosmus *et al.* 2008).

More specific examples of the use of PESs are given in Section 3.

## 1.4 Organization of the Article

This article is roughly organized as follows. Section 2 provides an overview of approaches toward analytical representations of potential energy hypersurfaces including a discussion of some general aspects. Section 3 discusses, in some detail, several examples of such analytical representations from diatomic to five-atomic systems. Section 4 presents special global analytical representations for $XY_n$ molecules including, in particular, also the examples of methane $CH_4$ and ammonia $NH_3$. Section 5 discusses a general approach of semiglobal representations for hydrogen-bonded clusters with the particular example of $(HF)_n$, hydrogen fluoride clusters, and the relation to spectroscopy and dynamics. Section 6 presents results for the chiral hydrogen peroxide potential hypersurface, which is prototypical for stereomutation reactions between enantiomers and of importance also for the problem of molecular parity violation and for atmospheric chemistry and combustion.

## 2 ANALYTICAL REPRESENTATIONS

### 2.1 General Aspects

Analytical representations of ab initio calculated potential energy hypersurfaces are practical and, as is discussed in detail in this section, they are also quite helpful tools for the determination of effective potential surfaces determined directly from spectroscopy (sometimes called *model potentials*). Figure 1 schematically illustrates the role played by analytical representations. Clearly, PESs may be obtained directly from ab initio calculations of the electronic structure in the Born–Oppenheimer approximation as a collection of discrete points in the multidimensional configuration space (solid arrow on the left-hand side of the scheme). However, they may also be obtained, on the one hand, from ab initio data by the intermediate of analytical representations. On the other hand, PESs may be obtained from experiments via intermediate analytical (model) potentials (solid arrows on the right-hand side of the scheme), an idea used already by Bjerrum (1914a). The loop formed by the solid and the interrupted arrows on the right-hand side of the scheme illustrates that model potentials can be improved iteratively by intermediate quantum dynamical calculations and comparison with experimental data from spectroscopy and kinetics. Sometimes, it can be of interest to compare experiment and theory at the level of intermediate, effective experimental parameters such as effective hamiltonian parameters with the "spectroscopic constants" from spectroscopy (Quack 1995, 2001, Albert *et al*. 2011: **Fundamentals of Rotation–Vibration Spectra**; Albert *et al*. 2011: **High-resolution Fourier Transform Infrared Spectroscopy**; Hippler *et al*. 2011: **Mass and Isotope-selective Infrared Spectroscopy**, this handbook).

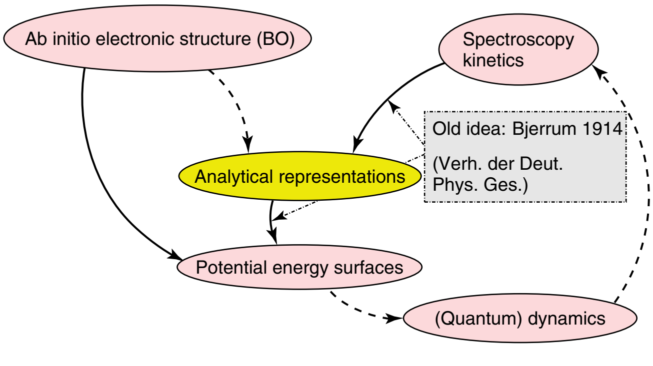

**Figure 1** Schematic view showing the role played by analytical representations of potential energy surfaces.

Analytical representations condense the large amount of information needed to characterize a complicated potential energy hypersurface in a set of a few mathematical expressions with a limited number of numerical parameters; under certain circumstances, they may also lead to conceptually new solutions of the rovibrational problem. Among the most frequently used analytical functions are multidimensional polynomial forms ("*force fields*"), which yield model potentials that are adequate approximations of the potential energy hypersurface in the vicinity of stationary points. The coefficients of the polynomial expansion may be determined from an adjustment of the model potential to ab initio calculated energy points or to experimental data after a quantum dynamical calculation.

Particularly important are functional forms that furthermore allow to obtain, with a very limited set of adjustable parameters, a *global* representation of the PES, specially in those regions of configuration space that become important for reaction dynamics. Early examples of global functional forms are the Morse potential (Morse 1929), which gives a qualitatively correct description of the general behavior of the one-dimensional potential pertaining to a covalent chemical bond, and the Pöschl–Teller oscillator (Pöschl and Teller 1933). The Schrödinger equation can be solved for such model potentials analytically, which also holds for a series of other, one- dimensional potentials (Senn 1986, and work cited therein). Such solutions may facilitate the analysis of general features of vibrational eigenstates, but not the calculation of real eigenstates.

A wide range of methods used to analytically represent PESs is reviewed in the book by Murrell *et al*. (1984), which covers the literature up to 1984. Another article covers the literature on analytical representations relevant for chemical reactions until 1990 (Schatz 1990). A review of the approaches to describe analytical potentials for hydrogen-bonded clusters such as $(HF)_n$ including the many-body expansion starting out from very accurate pair potentials has been presented by Quack and Suhm (1997). In this context, we can also mention the book by Stone (2002). Additional methods and the more recent literature are discussed below.

In polyatomic molecules, both the ab initio calculation of energy points and the analytical representation of adequate model potentials are difficult. This is particularly true for those model potentials that would simultaneously allow to describe the nuclear dynamics both in the vicinity of stable equilibrium molecular structures and in regions of highly excited states, from where a chemical reaction might take place. In this sense, adequate model potentials have to fulfill a number of criteria, which we summarize here as follows:

1. accuracy
2. flexibility and robustness
3. global character.

## 2.2 Accuracy

Regarding the first criterion, standard quantum chemical methods allow us even today to describe the energy in certain regions of the potential hypersurface "only" with *chemical accuracy* ($\sim$1 k cal mol$^{-1}$ = 4.184 kJ mol$^{-1}$ = 0.0069 aJ) (Bauschlicher *et al.* 1990, Yamaguchi *et al.* 1994, Röhse *et al.* 1994, Noga *et al.* 1997). State-of-the-art calculations enable one, however, to describe specific molecular structures and atomization energies to within 0.4 kJ mol$^{-1}$(Feller and Peterson 2007, Feller *et al.* 2008). However, it is practically impossible to extend such calculations to the entire configuration space. The currently best ab initio predictions of rovibrational term values for fundamental transitions are accurate to within 5 cm$^{-1}$ in smaller polyatomic molecules and to up to 50 cm$^{-1}$ in the region of overtones (the accuracy is sensibly higher for triatomic molecules). This accuracy might be sufficient, in some cases, for the assignment of complicated, poorly resolved, and therefore apparently structureless experimental spectral bands, thus allowing for a rudimentary interpretation of the data. However, it is insufficient for a reliable calculation of the time-dependent dynamics, as is explained in more detail in Section 3.2. Higher accuracy has been achieved for diatomic molecules and the exceptional case of $H_3{}^+$ (Jaquet *et al.* 1998, Röhse *et al.* 1994).

Analytical representations offer the possibility of adjusting them directly to experimental data via intermediate dynamical calculations (Figure 1, the "historical" access to PESs and nuclear motion). Several examples exist today for such "empirically" determined PESs, spectroscopically in many cases, which also reproduce other experimental data with sufficient accuracy (in Murrell *et al.* (1984) some examples are given for empirically determined potential energy surfaces to up to tetra-atomic molecules). We have already mentioned the $H_2O$ surface determined by Shirin *et al.* (2003); another empirically determined $H_2O$ surface is that of Polyansky *et al.* (1994). In this context, it is also worth mentioning the HCN/HNC-surface derived by Carter *et al.* (1993), which was obtained empirically and includes the region of the isomerization reaction, and the HOOH surface of Kuhn *et al.* (1999). A highly accurate semiglobal potential hypersurface for the hydrogen bond dimer $(HF)_2$ has been derived in a series of papers (Quack and Suhm 1991, Klopper *et al.* 1996, 1998). The global potential energy hypersurfaces for the five-atomic methane molecule $CH_4$ (Marquardt and Quack 1998, 2004) are discussed in more detail below.

## 2.3 Flexibility and Robustness

Bjerrum had remarked that some of the forms he tried out in the spirit of an ansatz failed to describe the observed spectroscopic lines. Today, it is well known that polynomial forms in terms of displacements of valence bond coordinates (bond lengths and angles) from a given equilibrium molecular structure allow for a greater flexibility and that linear combinations thereof that are adapted to the particular molecular symmetry of the equilibrium structure may be used to reduce the number of effectively adjustable coefficients without loss of flexibility (Duncan and Mills 1964). Such *force fields*, which are typically of fourth order in the expansion power, are sometimes adequate to describe the potential hypersurfaces in the neighborhood of the equilibrium structures, and allow to compute low-lying rovibrational term values in the harmonic approximation with corrections from perturbation theory that agree well with experimental data, as discussed above. However, the precise calculation of high-energy states requires that many expansion coefficients be considered (Lewerenz *et al.* 1988, Carter *et al.* 1993). It is also known that not all force field parameters may be obtained without ambiguity from experimental data (Ha *et al.* 1978, Ozkabak *et al.* 1990). This may have particularly bad consequences when the force field is used to describe regions of configuration space which contain sparse experimental information. The model potential hypersurface may become unrealistic, for instance, because it may lead to an infinite dissociation energy, deep negative potential minima, or otherwise unphysical, local minima. An example of such problems is discussed in a paper by Lewerenz and Watts (1994, p. 1083 therein) on several potential hypersurfaces for the $H_2CO$ molecule (some among them are from the book by Murrell *et al.* (1984)). Such undesirable effects can be avoided by using *robust* functional forms for the model potentials. A characteristic of robust model potentials is that they are formally invariant, while potential parameters vary during an overall adjustment process. Furthermore, parameters of robust model potentials show little or nil correlation among themselves. The form of robust model potentials may often be guessed from the behavior of the true potential itself. Therefore, inexpensive, low-level ab initio calculations may be quite helpful for the determination of robust model potentials.

A reasonable strategy to obtain accurate, robust model potentials is to combine experimental data and ab initio energy points in the adjustment process. There are some examples of successful applications of this semiempirical ansatz in the literature. Historically, the work of Eyring and Polanyi (1931) on the PES for the $H_2 + H$ exchange reaction, a milestone in chemical reaction dynamics, is worth mentioning. The starting point of this work is the Heitler–London theory (Heitler and London 1927) for the calculation of activation energies, from which an analytical representation is derived that is finally refined experimentally after "employing optical data" (to quote Eyring 1930). More recently, Botschwina has used this strategy to derive analytical representations for a series of smaller polyatomic molecules and molecular ions, where he started from energy points obtained from rather high-level ab initio calculations and then considered experimental term values in a final, refining adjustment step (Botschwina 1982, 1988, and references therein). Špirko and Kraemer (1989) have determined an analytical potential hypersurface for ammonia in a two step procedure: first they adjusted parameters to spectroscopic data and then they refined the general behavior of the potential under consideration of ab initio calculated energy points. At ETH-Zurich, this strategy has been used to derive analytical representations of PESs in the three-dimensional space of the alkyl CH chromophore in substituted methanes (Lewerenz and Quack 1988, Dübal *et al.* 1989, Marquardt and Quack 1991, Luckhaus and Quack 1992, Beil *et al.* 1994, 1996), multidimensional hypersurfaces for hydrogen-bonded complexes of hydrogen fluoride (Quack and Suhm 1991, 1997, Quack *et al.* 1993, 2001), and hydrogen peroxide (Kuhn *et al.* 1999, Fehrensen *et al.* 1999, 2007).

The $H_2O$ surface discussed above is another example of a successful application of the mixed ab initio/experimental stategy to obtain not too flexible analytical representations: Shirin *et al.* 2003 have adjusted "morphing" functions to a pure ab initio set of energy points, very similar to the approach used by Quack and Suhm (1991) and Beil *et al.* (1994). In the past decade, a series of papers on empirically refined PESs have appeared, which were reviewed by Hutson (1990), Suhm (1993), and Suhm and Nesbitt (1995). More examples are discussed explicitly in Section 3.

## 2.4 Global Character

Despite the use of reasonable strategies, the search for model potentials that are simultaneously flexible and robust is a difficult enterprise.[j] While too inflexible model potentials may easily lead to artificial representations, too little robust potentials may lead to unphysical representations. To circumvent this problem, the use of parameter-free representations has been advocated (Suhm 1993, Ho and Rabitz 1995), which are essentially based on information from ab initio calculations. The drawback of such representations is that an a posteriori experimental refinement of the representation is difficult to achieve. In this context, one may mention approaches in which observables are calculated directly using classical trajectories in combination with electronic potentials calculated "on the fly" point by point using DFT (Car and Parrinello 1985). These and similar approaches usually have insufficient accuracy for high-resolution spectroscopy.

In addition to being accurate, flexible, and robust, analytical representations of PESs should be *global*, in the sense that a single mathematical function should connect all regions of configuration space in the description of the connected potential energy hypersurface.

While the general, global form of model potentials for van der Waals bonded complexes can be guessed rather easily from the multipole expansion of static or induced charge distributions (Maitland *et al.* 1981, Stone 2002), the global analytical representation of covalently bound polyatomic molecules is much more complicated to tackle because there is almost no formal ansatz for it, apart perhaps from the Heitler–London theory and the general form of the Morse potential related to it. The description of large amplitude vibrations along angular deformation modes is particularly unsatisfactory. Very often, to guarantee a greater flexibility to reproduce the spectral structure, popular potential forms for the angular degrees of freedom are of the polynomial form, having the disadvantage that the resulting model potentials are not global.

Global model potentials must provide at least a qualitatively correct description of certain topographical properties that play a central role in the chemical reaction dynamics, such as saddle points for isomerization reactions and bifurcation points of different reaction channels. Such properties may become particularly interesting when different electronic states become dynamically relevant, for instance, when potential surfaces obtained by the connection of energy points pertaining to different adiabatic electronic states cross, such as at a conical intersection; hypersurfaces obtained in this way are called *adiabatic*.[k] At such a point, adiabatic surfaces cannot be described analytically by a single hypersurface because of the occurrence of cusp singularities. In some cases, a theory related to multivalued potential functions can be applied (Murrell *et al.* 1984, Chapter 9 therein). However, in the vicinity of conical intersections, the overall dynamics of all molecular particles—nuclei and electrons—is very often dominated by terms neglected in the Born–Oppenheimer approximation, and the inclusion of such coupling terms of adiabatic states is normally taken into account by transforming from the adiabatic to the *diabatic* representation of electronic states.[l]

Alternatively, the choice can be made to effectively describe the region of a conical intersection by a smooth, analytical function. The justification of this ansatz is that adiabatic or diabatic representations of molecular *states* including both nuclear and electronic degrees of freedom are anyway inappropriate representations of molecular eigenstates in regions close to conical intersection seams, and that the nuclei will move on the lowest adiabatic PES, while approaching and departing from the regions defining a conical intersection, whenever their kinetic energy is sufficiently small compared to the coupling energy given by the nonadiabatic terms neglected in the Born–Oppenheimer approximation, or other coupling terms neglected additionally, such as spin–orbit coupling terms.

# 3 EXAMPLES OF ANALYTICAL REPRESENTATIONS: SPECTROSCOPY AND DYNAMICS

## 3.1 General Aspects

In this section, we discuss in more detail recent examples of analytical representations of small and medium-sized molecules which are relevant in the context of high-resolution spectroscopy and dynamics. The discussion also focuses on the comparison between theoretical and experimental data.

A large amount of very accurate experimental data exists today that are relevant to the definition of PESs and that enable to interpret and understand molecular motion. We mention at first place line positions and line strengths from high-resolution spectroscopy (Quack 1981, 1990, 2003, and references cited therein). These spectroscopic data form the basis for the high-resolution spectroscopic approach to short time intramolecular quantum dynamics. The first "experimental" quantum wavepackets in the femtosecond domain derived from this were obtained using effective hamiltonians and three-dimensional subspaces of the potential hypersurfaces (Marquardt *et al.* 1986, Marquardt and Quack 1991), but the approach is, in principle, general (Quack 1995, 2001, Marquardt and Quack 2001). Other types of data stem from measurements of reaction enthalpies and activation energies using thermochemical (Chase *et al.* 1985, Lias *et al.* 1988, Nefedov *et al.* 1992, Berkowitz *et al.* 1994) or photochemical methods in molecular beams, for which a multitude of special techniques exist (see, for instance, the reviews by Polanyi and Zewail (1995), Baer and Hase (1996), Bradley Moore and Smith (1996), Neumark (1996) as well as many contributions in the conference proceedings by Manz and Wöste (1995)). Additional relevant data from reaction dynamics are state-specific rate constants from time-resolved kinetic experiments (Lupo and Quack 1987, Manz and Wöste 1995), in particular, data from femtosecond time-resolved laser experiments related to coherent wave packet evolutions (Khundkar and Zewail 1990, Baumert *et al.* 1992, Zewail 1993). Some experiments, such as "Coulomb explosion imaging" (Zajfman *et al.* 1991, Kella and Vager 1995), allow to extract specific information on the form of the wave packet evolution. Other experiments, such as "photodetachment transition state spectroscopy" (Neumark 1993, 2005) and "femtosecond transition state spectroscopy" (Dantus *et al.* 1989, Zewail 1993), may yield information on the local topography of saddle points that describe transition structures of elementary reactions. Important data include transition frequencies in the region of overtones, which can be accessed today very accurately with sensitive techniques from Fourier transform infrared spectroscopy (FTIR) or laser experiments such as multiphoton ionization (Quack 1990, Hippler and Quack 1994, 2005, and references cited therein). They yield the experimental information needed to describe PESs in the intermediate energy domain between fundamental vibrations and large amplitude vibrations leading to isomerization or dissociation of a molecule.

## 3.2 Spectroscopy and Intramolecular Dynamics, Diatomic, and Triatomic Systems

Theoretical and experimental spectroscopic data have been mentioned for $H_2$ and $F_2$ in Section 1.2, for $H_2O$ in Section 1.3, and in general for polyatomic molecules in Sections 2.1 and 2.2. Here we give some more exemplary comparisons of the typical performance of the theoretical description of experimental data. For small electronic systems, the R12 CISD or CCSD ab initio method relying on exact geminal wave functions for the electronic structure (Röhse *et al.* 1994) yields highly accurate vibrational term values. For the $H_3{}^+$ molecule, for instance, theoretical predictions for individual line transitions to up to $7000\,\mathrm{cm}^{-1}$ deviate less than $0.5\,\mathrm{cm}^{-1}$ from experimental values (Dinelli *et al.* 1995). For the HF molecule, Table 1 summarizes accurately calculated vibrational transitions from the work by Müller *et al.* (1998). This table shows that ab initio predictions of vibrational transitions become accurate only at higher level of calculations, which are consequently more costly and still prohibitive for larger systems with more electrons. High accuracy needs inclusion of correction terms such as relativistic corrections and terms neglected in the Born–Oppenheimer approximation. Such corrections have also been included in the derivation of the $H_2O$ potential energy hypersurface by Shirin *et al.* (2003) where, however, the excellent agreement between theory and experiment was achieved only after experimental refinement of the analytical representation. Müller *et al.* (1998) represent the one-dimensional potential function analytically, at each level of ab initio theory, by modified

**Table 1** Vibrational levels of the HF molecule[a,b].

| $n$ | $\tilde{\nu}_n^{\mathrm{exp}}/(\mathrm{cm}^{-1})$ | $(\tilde{\nu}_n^{\mathrm{th}} - \tilde{\nu}_n^{\mathrm{exp}})/(\mathrm{cm}^{-1})$ | | | | |
|---|---|---|---|---|---|---|
| | | CCSD[T] | CCSD[T]-R12 | CCSDT | CCSDT-R12 | CCSDT-R12+rel |
| 10 | 32311.79$^{(a)}$ | −53.68 | 4.55 | −18.05 | 29.53 | 5.83 |
| 9 | 29781.33$^{(a)}$ | −21.66 | 17.05 | −1.02 | 29.86 | 8.42 |
| 8 | 27097.87$^{(a)}$ | −0.41 | 23.63 | 10.51 | 28.74 | 9.48 |
| 7 | 24262.18$^{(a)}$ | 12.26 | 25.72 | 17.16 | 26.26 | 9.18 |
| 6 | 21273.69$^{(a)}$ | 18.43 | 24.66 | 19.81 | 22.75 | 7.90 |
| 5 | 18130.97$^{(a)}$ | 19.05 | 21.58 | 19.44 | 18.61 | 6.04 |
| 4 | 14831.63$^{(b)}$ | 18.39 | 17.49 | 17.04 | 14.33 | 4.10 |
| 3 | 11372.78$^{(b)}$ | 14.85 | 12.89 | 13.29 | 9.50 | 2.25 |
| 2 | 7750.79$^{(c)}$ | 10.22 | 8.22 | 8.84 | 6.05 | 0.76 |
| 1 | 3961.42$^{(c)}$ | 5.15 | 3.84 | 4.29 | 2.62 | −0.07 |

[a] Adapted from Müller *et al.* 1998.

[b] The left-most column gives experimental vibrational energy levels $\tilde{\nu}_n^{\mathrm{exp}} = E_n/hc$ by von Puttkamer and Quack (1989), He *et al.* (2007), and Web and Rao (1968). The subsequent columns give the differences between theoretical and experimental values at several levels of theory. The right-most column includes scalar relativistic corrections. Data were taken from (a) Web and Rao (1968), (b) von Puttkamer and Quack (1989), and (c) He *et al.* (2007). References to further literature can be found in these sources. He *et al.* 2007 give a careful discussion of the accuracy of the line frequency measurements for calibration purposes and a guide to previous literature. In that work the HF lines in the frequency range 7500–7 900 cm$^{-1}$ are accurate to better than $10^{-4}$ cm$^{-1}$ and $v = 2$ level is given as 7750.79339(9) cm$^{-1}$, which may serve as an example of the experimental accuracy.

Morse potentials. Even when all corrections are included, one finds from Table 1 an error in theory of almost 1 cm$^{-1}$ for the $n = 2$ level. The experimental accuracy has been carefully discussed in He *et al.* (2007) and the uncertainty in the experiment is estimated as $10^{-4}$ cm$^{-1}$. Thus, even at the highest theoretical level in Table 1, true “spectroscopic” accuracy is by no means achieved. For higher vibrational levels, the theoretical error increases to about 10 cm$^{-1}$, but the experimental uncertainties are less well known.

The drawback of the original R12-method by Kutzelnigg and Klopper (1991) is the computational cost. More recently, a nonlinear variant of this method, the F12-method (CCSD(T)-F12 (Adler *et al.* 2007), MP2-F12 (Werner *et al.* 2007)), has been used to derive accurate potential energy functions for a series of diatomic molecules including elements of the third row (Yousaf and Peterson 2008) at a cost that is lower by a factor of 2, when compared to the original method (*see also* Tew *et al.* 2011: **Ab Initio Theory for Accurate Spectroscopic Constants and Molecular Properties**, this handbook).

It is widely accepted that coupled-cluster methods give the current best theoretical results for vibrational term values in the regions of fundamental transitions. As shown in Table 1, the CCSD (“coupled-cluster including single and double excitations”) method allows for a reasonable description of vibrational band centers, when triplet excitations are included perturbatively (CCSD[T] or CCSD(T)$^{\mathrm{m}}$). Full iterative triplet excitation (CCSDT) leads to a relatively minor improvement at the price of much more expensive calculations. Computation times scale as $K^7$, for CCSD(T), and as $K^8$, for CCSDT calculations, where $K$ is the number of atomic basis functions for orbital representations. The quality of the CCSD(T) method for the calculation of potential energy surfaces in the neighborhood of equilibrium nuclear configurations has been investigated systematically by Thomas *et al.* (1993), independently of the use of intermediate analytical representations, with the aid of analytical gradients. Different types of basis functions and different variants of the coupled cluster calculations have been analyzed and found to be superior to the previously much used SCF-MP2 (Handy *et al.* 1987, Amos *et al.* 1988, Maslen *et al.* 1991) or CISD-methods (Clabo *et al.* 1988, Allen *et al.* 1990), while the CCSD(T)-method yielded the best benefit/cost ratio, although even this method becomes prohibitively costly for electronic systems larger than typically 10–30 electrons. Table 1 is extremely instructive in that one cannot expect any of these methods to provide an accuracy of much better than 10 cm$^{-1}$, unless non-Born–Oppenheimer and relativistic effects are included in the calculations. The highest accuracy has been achieved for $H_2$, where experimental and theoretical values of the dissociation energy agree now to within $10^{-3}$ cm$^{-1}$ after inclusion of nonadiabatic and relativistic corrections, as well as corrections from quantum electrodynamics (Piszczatowski *et al.* 2009, Liu *et al.* 2009, 2010). On the other hand, for the very difficult case of $F_2$ even with the highest accuracy in theory larger discrepancies between theory and experiment remain (Bytautas *et al.* 2007, Bytautas and Ruedenberg 2009), rather similar to HF.

Current calculations of spectroscopically relevant PESs use normally cc-VTZP or cc-VQZP bases (“correlation consistent valence triple- (or quadruple-) zeta bases plus polarization functions”$^{\mathrm{n}}$). Such methods and bases have been used to generate PESs, mostly in the form of quartic force fields, for a series of molecules involving first- and second-row elements: $H_2O$ (Bartlett *et al.* 1987), $O_3$ (Lee and Scuseria 1990), $NH_3$ (Martin *et al.* 1992), $BH_3$ (Martin and Lee 1992), $N_2O$ and $CO_2$ (Martin *et al.* 1993b), and $CH_4$ (Lee *et al.* 1995). With such force fields, it is possible to derive theoretical term values that agree to within $1-20\,\mathrm{cm}^{-1}$ with fundamental transitions from experiment. When resonances occur, and for the inversion motion in ammonia, perturbation theory fails, and discrepancies are larger.

More recently, for ammonia, Thiel and collaborators have calculated a large number of energy points at the CCSD(T) level using aug-cc-VTZ,[o] VQZ and V5Z basis sizes, and applied an interpolation and extrapolation procedure to complete basis set limit (CBS) (Lin *et al.* 2002, Yurchenko *et al.* 2005a,b,c). These data were used to set up representations of the ground-state PES for ammonia, which are locally defined around the two pyramidal minimum structures by means of polynomial expansions. Those representations were used to calculate vibrational term values and transition dipole moments that agree very well with experimental data from high-resolution spectroscopy (deviations are a few $\mathrm{cm}^{-1}$ to up to the near-infrared). Drawbacks of these representations are, first, that they are not global, because the CCSD(T) data have a local definition range: it was shown (Marquardt *et al.* 2005) that indeed the data correlate asymptotically with a reaction channel that corresponds to a higher electronic state. Secondly, these representations are not sufficiently compact, because of the rather long polynomial expansion used. We return to the discussion of these and further representations of the PES of ammonia in Section 4.

## 3.3 $H_2CO$ and HCN/HNC

Ab initio PESs at the CCSD(T) level have been calculated for a variety of molecules. Here, we mention formaldehyde $H_2CO$ (Martin *et al.* 1993a, Romanowski *et al.* 1984), for which quartic force fields have been formulated in terms of Simons–Parr–Finlan coordinates (Simons *et al.* 1973) and used within a FBR variational method to yield vibrational transitions that differ less than $20\,\mathrm{cm}^{-1}$ from experimental term values in the region to up to $5000\,\mathrm{cm}^{-1}$. The PES of the formaldehyde molecule has been revisited more recently by Zhang *et al.* (2004) with the aim of deriving realistic global analytical representations thereof to be used in the context of the still very intriguing photodissociation reaction dynamics of this molecule. The derivation is based on energy point sets calculated ab initio at the CCSD(T) level of theory, for geometries in the vicinity of the equilibrium structure, including the saddle point for hydrogen and carbon monoxide formation (Section 3.5), and using the MR-CI method for geometries far from the equilibrium molecular structure. The strategy chosen to represent the data points analytically is discussed below. To our knowledge, the accuracy of the resulting global PES with respect to high-resolution spectroscopy has not yet been verified.

While MR-CI points are essential for the determination of a global PES for the formaldehyde molecule, it has been shown previously that CCSD(T) data can be used to generate a PES for the hydrogen cyanide molecule that includes the HCN/HNC isomerization (Bowman *et al.* 1993). Vibrational transitions to up to $23\,000\,\mathrm{cm}^{-1}$ have been calculated with this surface, which deviate from experimental values on an average by $20-50\,\mathrm{cm}^{-1}$, maximal deviations being as large as $80\,\mathrm{cm}^{-1}$. Term values obtained from the spectroscopically determined PES by Carter *et al.* (1993) are much closer to experimental data, deviations are one to two orders of magnitude smaller, but the latter analytical representation describes the region of the isomerization barrier less well.

The two examples mentioned above are also useful to discuss the accuracy of calculated vibrational transitions, which depends not only on the quality of the underlying PES but also on the methods used to solve equation (1). Bramley and Carrington (1993) used, for instance, a DVR method coupled to a Lanczos eigensolver and applied this method to the formaldehyde PES developed by Romanowski *et al.* (1984) to obtain vibrational transitions that deviate in the average similarly from experimental data, but for different transitions. In a more recent work, the theoretical results using the same potential energy surface have been improved (Poulin *et al.* 1996). In a previous paper (Bentley *et al.* 1992), a DVR method was used on a potential energy surface for the HCN/HNC system of similar quality as that developed by Bowman *et al.* (1993), and deviations from experimental vibrational term values were as large as $150\,\mathrm{cm}^{-1}$. With improved computer power and the development of refined algorithms to solve equation (1), the numerical precision of calculations of vibrational eigenvalues given a PES has increased, in the last years, to better than $1\,\mathrm{cm}^{-1}$ for to up to penta-atomic molecules, typically (Wang and Carrington 2003a,b, Luckhaus 2003, Shirin *et al.* 2003, Richter *et al.* 2007, Iung and Pasin 2007, Bowman *et al.* 2008). The largest uncertainties as compared to experiment thus arise from the underlying potential hypersurface.

## 3.4 Substituted Methane Derivatives

Systematic comparison between experimental and theoretical values for overtone transitions in larger polyatomic molecules is rare. Here we mention the well-studied system of overtone transitions pertaining to the alkyl CH infrared chromophore in symmetrical $CHX_3$ (Peyerimhoff *et al.* 1984, Dübal and Quack 1984a, Baggott *et al.* 1985, Segall *et al.* 1987, Carrington *et al.* 1987, Lewerenz and Quack 1988, Dübal *et al.* 1989, Davidsson *et al.* 1991, Luckhaus and Quack 1993, Marquardt *et al.* 1995, Hippler and Quack 1996) and asymmetrical CHXYZ (Dübal and Quack 1984b, Luckhaus and Quack 1992, Luckhaus *et al.* 1993, Beil *et al.* 1994, Hippler and Quack 1996, Beil *et al.* 1997) compounds (and references cited therein). For methane ($CH_4$), several PESs have been proposed in the past,[p] among which we mention here the spectroscopically determined quartic force field of Gray and Robiette (1979) and other ab initio potentials (Duchovic *et al.* 1982, Peyerimhoff *et al.* 1984, Duchovic *et al.* 1984, Brown and Truhlar 1985, Hirst 1985, Schlegel 1986, Brodersen and Lolck 1987, Sosa *et al.* 1988, Dübal *et al.* 1989, Wu and McWeeny 1994, Lee *et al.* 1995, Schwenke and Partridge 2001), refined empirically (Lewerenz and Quack 1988), or semiempirically (Aboumajd 1984, Brodersen and Lolck 1987, Iung and Leforestier 1989, 1992, 1994, Halonen 1997, Marquardt and Quack 1998, 2004). We give a more detailed discussion of some of these PESs in Section 4.

At this point, we discuss some general findings regarding overtone spectroscopy that still hold today. The potential surface of Lewerenz and Quack (1988) for the CH chromophore in $CHD_3$ has been obtained from the adjustment of an effective, three-dimensional analytical model to a set of experimental vibrational transitions to up to $18\,000\,\mathrm{cm}^{-1}$ via an iterative variational calculation, the largest deviation between experimental and theoretical vibrational terms being $4\,\mathrm{cm}^{-1}$ (Marquardt *et al.* 2000, Marquardt and Quack 2004). The alkyl CH chromophore system is characterized spectroscopically by the presence of a strong 1 : 2 Fermi resonance between stretching and bending vibrations. The corresponding Fermi resonance coupling constant from the PES of Lewerenz and Quack (1988) is $k'_{\mathrm{sbb}} = (30 \pm 15)\,\mathrm{cm}^{-1}$, which agrees well with the value determined from the analysis of an effective, spectroscopic hamiltonian (Peyerimhoff *et al.* 1984). The same model was also adjusted to data from ab initio calculations at the MRD-CI level (Peyerimhoff *et al.* 1984, Lewerenz and Quack 1988), which leads, however, to a stronger mismatch between experiment and theory on the order of $50-100\,\mathrm{cm}^{-1}$ for transitions in the mid- and near-infrared, and $300\,\mathrm{cm}^{-1}$ for high-overtone transitions (Dübal *et al.* 1989, Lewerenz *et al.* 1988). Even though the pure ab initio predictions are systematically too high, when compared to experiment, they allow us to unambiguously confirm magnitude (and sign) of the experimental value of the Fermi coupling constant. As has been discussed by Lewerenz and Quack (1988), the cubic force constant $C_{\mathrm{sbb}}$ cannot be set equal to the Fermi resonance coupling constant $k_{\mathrm{sbb}}$. Rather, the latter contains contributions from many higher terms ($C_{\mathrm{ssbb}}$ etc). Marquardt and Quack (1991) give simple analytical approximations to the relationship, but in general an accurate numerical transformation is necessary. There has been some progress also in perturbative and variational approaches on the spectrum of $CHD_3$ (Wang and Sibert 1999) and more recently in highly accurate experiments (Ulenikov *et al.* 2010, *see also* Albert *et al.* 2011: **Fundamentals of Rotation–Vibration Spectra**, this handbook).

An SD-CI method has been used to calculate ab initio the overtone spectrum of $CHF_3$ (Dübal *et al.* 1989). Results are qualitatively equivalent to those obtained for $CHD_3$: theoretical term values are systematically too high compared to the experimental ones—deviations are larger than in the case of $CHD_3$. Nonetheless they allow us to quantitatively rationalize the value for the effective Fermi resonance coupling constant for this molecule ($k'_{\mathrm{sbb}} = 100\,\mathrm{cm}^{-1}$). This value also followed from another ab initio determination of the PES and nine-dimensional calculations of vibrational eigenstates (Maynard *et al.* 1995; see also Doriol *et al.* 2008). In these calculations, the description of electron correlation was considered at the level of MP2 perturbation theory and at the CEPA-1 (Botschwina 1982) level for points related to large distortions in the CH chromophore space. Quite importantly, a basis set was used that was at least of triple zeta quality and included polarization functions (f-functions on the carbon atom were found to be needed to correctly describe the bending potential).

Quite generally, the structure of the alkyl CH overtone spectrum to up to the visible domain can be reproduced in a semiquantitative correct way by a PES calculated ab initio at an MR-CI or a CEPA level. Hartree–Fock calculations are insufficient to describe this structure even qualitatively (Gelessus and Thiel 1995, Marquardt *et al.* 1995). Similar results also apply to the overtone spectrum related to term values of the symmetric stretching vibration in $NH_3$ to up to $18\,000\,\mathrm{cm}^{-1}$ (Lehmann and Coy 1988). The following conclusions may be drawn, corroborating previously established results (Lewerenz *et al.* 1988): first, to obtain a qualitatively reliable set of calculated vibrational overtone transitions, the potential energy surface must be well described by a substantially large coverage of configuration space, even within the reduced three-dimensional model of CH chromophore vibrations; secondly, ab initio methods must include electron correlation adequately also at high excitation energies to guarantee a quantitatively correct reproduction of spectroscopic constants such as the Fermi resonance coupling constant. The second point is elucidated in Section 4.

Before concluding this section, we briefly discuss the currently available accuracy of purely ab initio derived PESs with respect to overtone spectroscopy in the near-infrared to visible range. A wave number difference related to an inaccuracy on the order of $100\,\mathrm{cm}^{-1}$ of a vibrational term value corresponds to one of the fastest experimentally known timescales for the redistribution of vibrational energy (300 fs, Marquardt *et al.* 1986, Quack 1995), which has been confirmed by the explicit calculation of the wave packet motion in configuration space on realistic model potentials (Marquardt 1989, Marquardt and Quack 1991). Inaccuracies in this order of magnitude may show up in the quantum dynamical calculation of atomic motion on timescales between 0.3 and 1 ps and make them unreliable for longer times. In the intermediate energy range of spectral overtones, where fundamental primary processes of nuclear rearrangement take place, which influence the following chemical reaction kinetics, the precise theoretical prediction of experimental data is essential. Quite generally, the accuracy of current PESs derived purely ab initio is insufficient to account for a simulation of the time-dependent molecular (quantum) dynamics that would be reliable on timescales longer than 1 ps. A special situation arises, however, for quasiadiabatic channel above barrier tunneling which is frequently well predicted even on long time scales (Fehrensen *et al.* 2007, Hippler *et al.* 2011: **Mass and Isotope-selective Infrared Spectroscopy**, this handbook).

## 3.5 Spectroscopy and Reaction Dynamics in the $CH_4$ System

As mentioned above, in general, current quantum chemical methods allow us to describe the energy to within *chemical accuracy* ($\sim\pm1$ kcal mol$^{-1}$) (Bauschlicher *et al.* 1990, Yamaguchi *et al.* 1994, Röhse *et al.* 1994, Noga *et al.* 1997), or better (Feller and Peterson 2007, Feller *et al.* 2008), if coupled cluster, MR-CI, or equivalent methods are used for the calculation of the correlation energy. We discuss this feature here using the example of the dissociation reaction:

$$(^1\mathrm{A}_1)\ \mathrm{CH}_4 = \left(^2\mathrm{A}_2''\right)\ \mathrm{CH}_3 + \left(^2\mathrm{S}_{\frac{1}{2}}\right)\ \mathrm{H} \qquad (3)$$

It was noted earlier by Peyerimhoff *et al.* (1984) that a multireference method (MRD-CI) is necessary in order to describe the shape of the potential along the dissociation path properly. A calculation using the CCSD(T) method with large, correlation consistent basis sets (to up to quintuple zeta) for all electrons yields $D_\mathrm{e} = 469.085$ kJ mol$^{-1}$ (Partridge and Bauschlicher 1995; 112.114 kcal mol$^{-1}$, 0.779 aJ) at optimized reactant and product equilibrium geometries that are in good agreement with data obtained from the analysis of experimental rotational constants (Gray and Robiette 1979, Hollenstein *et al.* 1994). The quality of this calculation is verified from a comparison with a multireference method (Pepper *et al.* 1995). From this value, and estimated anharmonic zero point energies (Grev *et al.* 1991), one obtains the zero kelvin reaction enthalpy $D_0 = \Delta_\mathrm{r} H_0^{\ominus} = 432.63$ kJ mol$^{-1}$, which agrees fairly well with the thermo- and photochemically determined value $432.9 \pm 0.1$ kJ mol$^{-1}$(Weitzel *et al.* 1999). Marquardt and Quack (2004) show that zero point energy estimations based on anharmonic force fields may carry uncertainties on the order of 0.5–2 kJ mol$^{-1}$. The geometry optimized, absolute electronic energy of methane was calculated by Grev and Schaefer (1992) at the CCSD(T) level in an all electron calculation to be $-40.501\ E_\mathrm{h}$,[q] which is roughly 0.06 aJ above a "realistic" value of $(-40.514 \pm 0.002)\ E_\mathrm{h}$ (Pople and Binkley 1975). Garmer and Anderson (1987) obtained the value of $(-40.506 \pm 0.002)\ E_\mathrm{h}$ on the basis of a quantum Monte Carlo method, and Pepper *et al.* 1995 give the value $-40.516\ E_\mathrm{h}$. Since then, there has not been any fundamental improvement and we conclude from these values that in general current ab intio prediction of absolute electronic energies are at least 1 order of magnitude more uncertain than relative energies.

While relative energies such as bond dissociation energies can thus be relatively well described by the coupled-cluster method, the continuous description by this method of the potential energy function along a bond length is not always reliable, when the electronic wave function has multireference character, such as in methane dissociation (Peyerimhoff *et al.* 1984, Sosa *et al.* 1988, Dutta and Sherrill 2003). The shape of the PES at large displacements from the equilibrium structure influences not only the outcome of the theoretically determined overtone spectrum but also that of rate constants and reaction cross sections. More generally, for the description of elementary reactions via statistical theories, PESs often need to be evaluated along a reaction path (Quack and Troe 1974, 1998, Kraka and Dunning 1990). In a pioneering paper Merkel and Zülicke (1987) provided an ab initio estimate of relevant potential parameters for the statistical adiabatic channel model in the bond fission reaction of $CH_3$.

The comparison between experiment and theory is considered as satisfactory if orders of magnitude of rate constants or product distributions coincide. For methane, for instance, several classical, semiclassical, and quantum methods of statistical theories have been applied to investigate the thermal rate constant for the bimolecular recombination reaction (Quack 1979, Cobos and Troe 1985, Duchovic and Hase 1985, Hase and Duchovic 1985, Hase *et al.* 1987, Hu and Hase 1991, LeBlanc and Pacey 1985) as the reverse process to unimolecular bond fission:

$$\left(^2\mathrm{A}_2''\right)\mathrm{CH}_3 + \left(^2\mathrm{S}_{\frac{1}{2}}\right)\mathrm{H} \xrightarrow{k} \left(^1\mathrm{A}_1\right)\mathrm{CH}_4 \qquad (4)$$

resulting in slightly temperature-dependent theoretical values ranging from $k \approx 5.0 \times 10^{-10}\,\mathrm{cm}^3\,\mathrm{s}^{-1}$ to $k \approx 4.3 \times 10^{-10}\,\mathrm{cm}^3\,\mathrm{s}^{-1}$ (Quack 1979, Cobos and Troe 1985), which are slightly larger than the experimental estimate $(3.5 \pm 0.7) \times 10^{-10}\,\mathrm{cm}^3\,\mathrm{s}^{-1}$ (Brouard *et al.* 1985). Values obtained within the statistical adiabatic channel model (Quack 1979, Cobos and Troe 1985) agree with a value of the parameter $\alpha \approx 1\ \text{Å}^{-1}$ that enters an empirical model with exponential decay of the lowest adiabatic reaction channel (from the work of Quack and Troe (1974, equation 13), see also (Quack 1979, Quack and Troe 1998)). More recently, this parameter was reevaluated on two newly developed, global analytical PESs (Marquardt and Quack 1998, 2004), the analytical form of which is discussed in Section 4. One surface (METPOT3) was determined using ab initio data obtained at the MR-CI level, and the other (METPOT4) was refined semiempirically to match overtone spectra in $\mathrm{CHD_3}$. Both surfaces have been used to perform quasiadiabatic channel quantum Monte Carlo calculations, which are ‘basically DQMC calculations at fixed values of the CH bond length $r$ (“clamped DQMC”, Suhm 1990, Quack and Suhm 1991, Quack *et al.* 2001). The result obtained corresponds to the lowest quasiadiabatic channel $V_{\mathrm{adi}}(r)$ for the dissociation reaction equation (3). The functions $V_{\mathrm{adi}}(r)$ obtained herewith were then used to estimate values for the interpolation parameter $\alpha$: $\alpha = (0.80 \pm 0.03)\ \text{Å}^{-1}$ for METPOT3 and $(0.66 \pm 0.03)\ \text{Å}^{-1}$ for METPOT4 (Marquardt *et al.* 2003a).

### 3.6 Reactions of Formaldehyde

Another system that has recently received attention is formaldehyde, the lowest dissociation channel of which yields the exothermic reaction ($\Delta_r H_0^{\ominus} \approx -9\ \mathrm{kJ\ mol^{-1}}$, Feller *et al.* 2000):

$$\left({}^1\mathrm{A}_1\right)\ \mathrm{H_2CO} = \left({}^1\Sigma_g^+\right)\ \mathrm{H_2} + \left({}^1\Sigma^+\right)\ \mathrm{CO} \tag{5}$$

The reaction path for this reaction goes over a high-energy saddle point. A CI-SD calculation yields the value 374 kJ mol$^{-1}$, a CCSDT calculation with a VTZP basis set the value 341 kJ mol$^{-1}$ for the barrier energy (variation of the zero point energy included harmonically), while experimental estimates range from 326 to 339 kJ mol$^{-1}$ (Yamaguchi *et al.* 1994; 344 kJ mol$^{-1}$, Feller *et al.* 2000). Zhang *et al.* (2004) obtain the value 339 kJ mol$^{-1}$from a CCSD(T) calculation and an aug-cc-PVTZ basis (zero point energy corrections included harmonically).

The analytical representation of the formaldehyde PES by Zhang *et al.* (2004) is global and properly describes several reaction and isomerization channels into the high-lying metastable structural isomers *cis*- and *trans*-hydroxycarbene, including different saddle points. The strategy used to derive this representation is based on large polynomial expansions of the potential in terms of multinomial, Morse-type functional forms, the arguments of which are the six internuclear distances (Zhang *et al.* 2004; see also equation 7). Several analytical forms are used to describe different regions of configuration space, which is sampled, in addition, by two types of electronic structure data, CCSD(T) and MR-CI, where the latter is used essentially to sample the H + HCO and H + H + CO region, where electronic structure is of multireference character. All forms are first adjusted independently to a given data set and then finally connected by appropriate switching functions. The resulting overall representation is quite smooth, indeed, although the adjustment procedure itself is complicated. More than 25 000 symmetry unique energy points have been used at the CCSD(T) level, and on the order of 46 000 points at the MR-CI level, to which were adjusted a total of roughly 2700 terms. This analytical representation was used in connection with quasiclassical trajectory calculations of the formaldehyde photodissociation

$$\mathrm{H_2CO} \xrightarrow{h\nu} \mathrm{H} + \mathrm{HCO} \tag{6}$$

($E^{\text{threshold}} \approx 30\,278\ hc\ \mathrm{cm}^{-1} \sim \Delta_0 H^{\ominus} \approx 362\ \mathrm{kJ\,mol^{-1}}$ Dulligan *et al.* 1997, Zhang *et al.* 2004), revealing a “roaming” atom mechanism (Lahankar *et al.* 2006).

Similar strategies were applied by Bowman and collaborators to obtain analytical potential energy surfaces for other molecules. Here we mention the more recent examples including the highly floppy $\mathrm{CH_5}^+$ cation (Jin *et al.* 2006), malonaldehyde (Wang *et al.* 2008a), recent global analytical representations for the water dimer and trimer (Huang *et al.* 2008a, Wang *et al.* 2008b), and a global acetaldehyde PES (Shepler *et al.* 2008), revealing “roaming” atom dynamics. While these surfaces represent valuable tools for studying reaction dynamics, they should be also of good accuracy in the neighborhood of equilibrium structures. Wang *et al.* (2008a) report tunneling splittings for water dimers that agree with experimental values to within 2–3 cm$^{-1}$; vibrational frequencies agree to within 4% (Huang *et al.* 2008a). This can be compared with earlier results on $\mathrm{(HF)_2}$ summarized by Quack and Suhm (1998) and Manca *et al.* (2008). Spectroscopic data have not yet been calculated for formaldehyde at low energy, to our knowledge, using the global PES developed by Zhang *et al.* (2004). Rather than using the global PES, Koziol *et al.* (2008) adjust a new analytical representation locally to calculate spectroscopic data for the high-lying hydroxycarbene isomers, which agree with the sparse, experimentally available fundamental vibrational term values to within 10 cm$^{-1}$, roughly.

Quite a different adjustment strategy leading to considerably more compact analytical representations has been developed elsewhere (Marquardt and Quack 1998, Cuvelier *et al.* 2004, Marquardt *et al.* 2005, 2010), and is discussed in the next section.

# 4 SPECIAL GLOBAL ANALYTICAL REPRESENTATIONS FOR XY$_n$ MOLECULES

## 4.1 General Aspects

As discussed in Section 2, analytical forms chosen to represent PESs should be flexible and robust in order to allow for accurate and global representations. The criteria "flexibility" and "robustness" may be merged into a single one: *compactness*. Compact analytical forms should cover a large portion of configuration space while needing a very limited set of adjustable parameters. An example of a compact form is the Morse (1929) type functional form, here in terms of the "Morse coordinate $y$":

$$y = \frac{1 - \exp(-a(r - r^{(\mathrm{eq})}))}{a} \tag{7}$$

where $a$ and $r^{(\mathrm{eq})}$ are adjustable parameters, and $r$ is a molecular coordinate. When applied to a diatomic molecule, $r$ may be interpreted as the bond length, $r^{(\mathrm{eq})}$ as the equilibrium bond length, and $a$ as the anharmonicity parameter. Quite generally, when Morse-type functional forms are used, the coordinate $r$ represents an interatomic distance, but, with exception of diatomic molecules, $r^{(\mathrm{eq})}$ cannot be interpreted as the equilibrium value of this coordinate.

Before addressing the question of more general compact analytical forms in polyatomic molecules, it is necessary to discuss the definition of appropriate coordinates. Quite frequently, mainly in the context of high-resolution spectroscopy, normal coordinates, or the dimensionless variants thereof (Wilson *et al.* 1955, Herzberg 1945b), are used as Taylor expansion coordinates of the PES around a stationary point. This approach is justified, to some extent, when limited expansions are sufficient to describe spectral features pertaining to vibrations limited to regions around the equilibrium position, i.e., small-amplitude vibrations of fundamental transitions in the absence of resonances. In that case, the expansion coefficients to quadratic order are proportional to the square of the normal, harmonic frequencies, but note that, even if equation (1) may be solved analytically in the quadratic approximation using normal modes, at least a quartic order approximation is needed to quantitatively describe experimental vibrational transitions, even in the region of fundamentals, because of anharmonicity. Normal mode expansions need to include many orders, if high overtones are to be described (more than 30, in the case of the alkyl CH chromophore, Lewerenz and Quack 1988).

Interatomic distances are certainly more adequate coordinates to describe PESs analytically. In valence bond theory, intramolecular forces are expressed naturally in terms of bond lengths and bond angles. While the Morse-type functional form from equation (7) has been widely used in the past as a function of bond lengths to describe bond stretching potentials, there seems to be no well-established compact form for bending potentials. However, it has been found that often the simple Morse potential is not sufficiently flexible to achieve spectroscopic accuracy and that modified versions thereof need to be used, which include polynomial expansions in the argument of the exponential function in equation (7) (Müller *et al.* 1998). Furthermore, for large values of the bond length, the Morse potential does not have the correct asymptotic behavior related to weak intermolecular forces.

In this section, we review some theoretical developments on new, compact analytical forms that were devised to fill this gap (Marquardt and Quack 1998, Cuvelier *et al.* 2004, Marquardt *et al.* 2005, Marquardt and Sagui 2007, Marquardt *et al.* 2010) and discuss applications regarding global analytical representations of molecules of the type XY$_n$, with emphasis on methane (Marquardt and Quack 1998, 2004) and ammonia (Marquardt *et al.* 2003a,b, 2005).

## 4.2 Stretching Potentials in XY$_n$ Type of Molecules

The stretching potential is given by the expression

$$V_{\mathrm{stretch}} = \sum_{i=1}^{n} \frac{f_{\mathrm{s}}\, {y_{\mathrm{s}}}^2(r_i)}{2} \tag{8}$$

where $r_i$ is the $i$th bond length. Here, we have introduced the new functional form

$$y_{\mathrm{s}}(r) = \frac{\exp(-a_{\mathrm{s}}[r - r^{(\mathrm{eq})}])}{a_{\mathrm{s}}} \left(1 + \sum_k \epsilon_k \exp\left(-\left(\frac{r_k^{(\epsilon)}}{r}\right)^k\right)\right) \tag{9}$$

which is a further generalization of the original Morse functional form that allows for a more flexible description of both the anharmonicity of the stretching potential (by the parameter $a_{\mathrm{s}}$) and the energy related to a single bond rupture,

$$D_e = \frac{f_s}{2{a_s}^2}\left(1 + \sum_k \epsilon_k\right)^2 \tag{10}$$

The parameters $r_k^{(\epsilon)}$ in equation (9) should satisfy the condition $r_k^{(\epsilon)} \gg r^{(\mathrm{eq})}$, in order to ensure the interpretation of $r^{(\mathrm{eq})}$ as the equilibrium length of bond $k$. Asymptotically, say for $r_1 \to \infty$, the stretching potential becomes

$$V_{\mathrm{stretch}} \approx \underbrace{\sum_{i=2}^{n} \frac{f_s\ y_s(r_i)^2}{2}}_{V'_{\mathrm{stretch}}} + D_e - \sum_k C_k \left(\frac{r_k^{(\epsilon)}}{r_1}\right)^k \tag{11}$$

where $V'_{\mathrm{stretch}}$ is the stretching potential of the product molecule $XY_{n-1}$ and $D_e$ is the dissociation energy given in equation (10). The potential energy, thus, obtains asymptotically radial contributions that are of the type of a multipole expansion. The lowest power in the expansion could, for instance, be $k = 3$, if the dissociation products have permanent dipole moments. In the case of neutral products, and one nonpolar product molecule, the lowest power is $k = 6$, and the corresponding expansion parameter $\epsilon_6$, which can be interpreted as being proportional to the induction or dispersion constant $C_6$, should be positive. For practical reasons, one may limit the description to use one or two expansion coefficients only, e.g., $\epsilon_6$ and $\epsilon_8$. However, in principle, no additional limitation is imposed (Hobza and Zahradnik 1980, Stone 2002). Figure 2 visualizes the effect of nonvanishing parameters $\epsilon$ in equation (9) on model stretching functions.

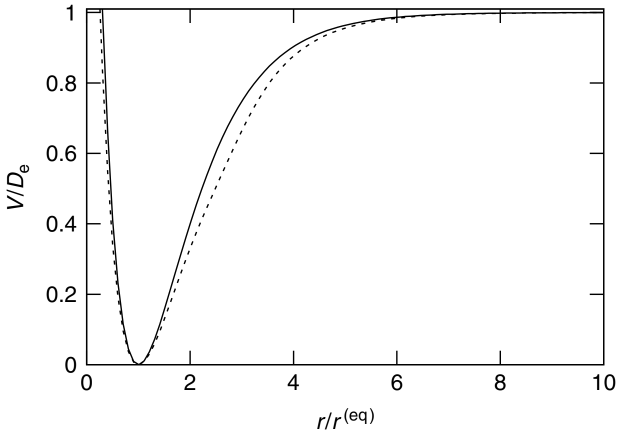

**Figure 2** One-dimensional functions of the type $V(r) = 1/2\, f_s {y_s}^2(r)$, where $y_s(r)$ is defined in equation (9), showing the effect of different values of parameter $\epsilon_k$ on the potential function ($k = 6$, here), and $D_e$ is given by equation (10); ——— : $\epsilon_6 = 0.0$; - - - : $\epsilon_6 = 0.1$; $r_6 = 3\, r^{(\mathrm{eq})}$.

A subtlety is hidden in this rather general formulation of the analytical stretching potential for $XY_n$ type of molecules. More details are discussed in the original papers (Marquardt and Quack 1998, Marquardt *et al.* 2005); here, we give only a brief survey. Clearly, the sum over all bonds in equation (8) is one possible way to account for symmetry. Indeed, the form of equation (8) is of $A_1$ symmetry species in the $S_n$ symmetric group. However, a molecule such as methane also possesses quadratic order terms composed of $F_2$ irreducible representations of the tetrahedral group $T_d$. Can those terms be described by equation (8)?

They can, indeed. The subtlety is that all parameters introduced in equation (8) are in fact *slowly* varying functions of the bond lengths. This is so because, in the case of a bond rupture, the analytical forms used to describe the bond stretching potentials of the parent molecule $XY_n$ can be formally used to describe the product $XY_{n-1}$. The description becomes quantitative if parameters are switched accordingly:

$$V_{\mathrm{stretch}}(XY_n) = \sum_{i=1}^{n} \overbrace{v_s(r_i)}^{f_s, a_s, r^{(\mathrm{eq})}, \ldots} \tag{12}$$

$$V'_{\mathrm{stretch}}(XY_{n-1}) \overset{r_n \to \infty}{=} \sum_{i=1}^{n-1} \underbrace{v_s(r_i)}_{{f_s}', {a_s}', r^{(\mathrm{eq})\prime}, \ldots} + D_e \tag{13}$$

Appropriate multidimensional switching functions have been developed by Marquardt and Quack (1998), which fully account for all permutation symmetries and so naturally induce all allowed compositions of irreducible representations in equation (8).

## 4.3 Bending Potentials

To our knowledge, there is no previous analytical form that would describe bond bending potentials in a compact way similar to that of the Morse-type form in the case of a bond stretching potential. The following ideas have served as a guide to derive simultaneously robust and flexible forms of bending potentials (Marquardt and Quack 1998).

Let $\alpha$ be a bond angle formed between atoms A, B, and C, with atom B being located at the vortex (atoms YXY, in the case of a $XY_n$ molecule). The simplest robust form is the positive definite quadratic form in the displacement coordinate $\Delta\alpha = \alpha - \alpha^{(\mathrm{eq})}$, where $\alpha^{(\mathrm{eq})}$ is the equilibrium bond angle:

$$V_{\mathrm{bending}}(\alpha) = \frac{1}{2} f_b(\alpha - \alpha^{(\mathrm{eq})})^2 \tag{14}$$

Špirko and Bunker (1982), Jensen (1989), Furue *et al.* (1991), and later Marquardt and Quack (1998) found that a more appropriate form to adjust to the ab initio data is by using the cosine of the valence angle. In addition to that, two reasons might motivate the use of the cosine function: first, the cosine of the bond angle is directly proportional to the dipole–dipole contact term of the two local bond dipoles; secondly, at a linear ABC configuration, the cosine naturally yields a stationary point. We, therefore, rewrite the foregoing equation as

$$V_{\text{bending}}(\alpha) = \frac{1}{2} f_{\text{b}}(\cos(\alpha) - \cos(\alpha^{(\text{eq})}))^2 \tag{15}$$

However, this form is yet not sufficient to account for the anharmonicity of the bending potential. One normally assumes, to remedy this deficiency, a polynomial expansion in the displacement coordinate $\Delta_{\text{c}}(\alpha) = \cos(\alpha) - \cos(\alpha^{(\text{eq})})$:

$$V_{\text{bending}}(\alpha) = \frac{1}{2} f_{\text{b}} \left( \Delta_{\text{c}}(\alpha)^2 + \sum_{k\geq 3} a_k^{(\text{b})}\, \Delta_{\text{c}}(\alpha)^k \right) \tag{16}$$

where $a_k^{(\text{b})}$ are "bending" anharmonicity parameters. This form lacks, however, robustness, since it is not positive definite. To correct this, a form of the type

$$V_{\text{bending}}(\alpha) = \frac{1}{2} f_{\text{b}} \left( \Delta_{\text{c}}(\alpha) + \sum_{k\geq 3} a_k^{(\text{b})}\, \Delta_{\text{c}}(\alpha)^k \right)^2 \tag{17}$$

might be used, which is at least positive definite. Yet, this form does not exclude the formation of high-lying local minima, if higher expansion orders are included in the sum without appropriate information from ab initio data and, in this sense, it is less robust that the modified Morse-type functional form of equation (9).

In polyatomic molecules, forms as given in the equations above might be used for all angles between atoms A, B, and C, where the covalent interactions between atoms AB, on one hand, and CB, on the other hand, are clearly bonding. As a consequence, one might expect that the dependence of the overall potential on the variation of such a bond angle would vanish as soon as a bond becomes sufficiently long. It is therefore reasonable to include *damping* factors on the angular coordinates, e.g., of the type

$$\Delta_{\text{c}}(r_i, r_j, \alpha_{ij}) = \left(\cos(\alpha_{ij}) - \cos(\alpha_{ij}^{(\text{eq})})\right)\; y_{\text{d}}(r_i, r_j, \alpha_{ij}) \tag{18}$$

where $\alpha_{ij}$ is a bond angle between bonds $i$ and $j$, $r_i$ and $r_j$ are the corresponding bond lengths, and the damping function $y_{\text{d}}$ has the properties $y_{\text{d}} \approx 1$, if both $r_i$ and $r_j$ are close to their equilibrium values, $y_{\text{d}} \to 0$, if either $r_i \to \infty$ or $r_j \to \infty$, and $y_{\text{d}}$ is symmetrical with respect to bond permutation. Ideally, an exponential form might be used. Marquardt and Quack (1998) use damping functions that do not depend on the angular coordinate. In other cases, more complex damping functions were needed to account for more flexible functional forms (Marquardt and Quack 2004, Marquardt *et al.* 2005). The form defined in equation (18) is a rather compact one that leads inherently to the description of interaction terms between stretching and bending vibrations. A similar ansatz has been used earlier (Wolf *et al.* 1986, Isaacson 1992). Also that idea is somewhat related to the "BEBO" analysis (bond-energy–bond-order, Johnston 1966).

In a polyatomic molecule, the overall bending potential could thus be set as a sum over all bond pairs $ij$ having a common bond angle $\alpha_{ij}$:

$$V_{\text{bending}}(\alpha_{12}, \alpha_{13}, \ldots) = \frac{1}{2} \sum_{ij} f_{\text{b}}{}^{(ij)} \left( \Delta_{\text{c}}(r_i, r_j, \alpha_{ij}) + \sum_{k\geq 3} a_k^{(ij;\text{b})}\, \Delta_{\text{c}}(r_i, r_j, \alpha_{ij})^k \right)^2 \tag{19}$$

where $f_{\text{b}}^{(ij)}$ and $a_k^{(ij;\text{b})}$ are bond-specific parameters. In molecules of higher symmetry, such as XY$_n$ molecules, this sum contains parameters that become rapidly redundant when the power order of the included terms is increased. To avoid redundancy, and also with the aim of obtaining more compact representations, symmetry-adapted expressions of high power orders may be used (Marquardt and Quack 1998, 2004). Marquardt and Sagui (2007) present a systematic derivation of symmetry-adapted expressions of bending coordinates which have been derived to up to fourth order systematically for the major point groups, and symmetric groups $\mathbf{S}_n$ with $n \leq 4$, where a computer algebra program specially devised for this purpose has been published.

## 4.4 Methane

Analytical forms of the type presented in the two previous sections were used to derive a global analytical representation for methane. The representation was adjusted to an MRD-CI ab initio data set for methane, which partly originated from Peyerimhoff *et al.* (1984). During the adjustment, different kinds of additional conditions have been considered in the spirit of giving to the resulting representation an "experimental refinement".

One measure was to scale bond lengths used in the ab initio calculations so as to recover the best experimental estimation for $r^{(\mathrm{eq})} \approx 108.58$ pm (Gray and Robiette 1979). Secondly, the harmonic force field has been adapted to obtain the same values as derived by Gray and Robiette (1979). For this purpose, the global PES was developed analytically to second order in the displacement coordinates and the resulting coefficients were calculated as functions of the parameters of the analytical representation. Setting these coefficients to the harmonic force field from Gray and Robiette (1979) yields analytical conditions $C_i$, where the index $i$ runs over all harmonic force field components. By the introduction of Lagrange multipliers $\mu_i$ in a modified version of the Levenberg–Marquardt optimization algorithm (Marquardt 1963, 1997), in which

$$\chi'^2 = \chi^2 + \sum_i \mu_i C_i \tag{20}$$

is minimized, where $\chi^2$ is the sum over the square of deviations between analytically and ab initio calculated data, one is able to optimize the parameter set with respect to the ab initio data while respecting the additional conditions imposed by the experimentally determined harmonic force field. An additional nonlinear condition on the adjustable parameters is the dissociation energy (equation 10), which should equal the value estimated from the experimentally reaction enthalpy extrapolated to zero kelvin, and zero point energies as discussed by Grev *et al.* (1991).

Thirdly, after an adequate parameter adjustment was found, a subset of parameters were readjusted to a new data set of energy points, which included, in addition to the original *ab initio* energies, a sample of energies pertaining to the experimentally derived, three-dimensional PES of the CH chromophore (Lewerenz and Quack 1988), ranging to up to half the dissociation energy.

While the average root mean square deviations obtained are in the expected range of 100–500 $hc\,\mathrm{cm}^{-1}$(see Marquardt and Quack 1998, for further details), which is quite acceptable for a global PES, the finally obtained METPOT4 potential energy surface for methane yields an overtone spectrum of the CH chromophore in $\mathrm{CHD_3}$, which differs from the experimental spectrum by $17\,\mathrm{cm}^{-1}$, in average (Marquardt and Quack 2004, Table 7, column III). This is the best currently available overtone spectrum ranging to up the visible region which can be obtained from a global PES. The very same surface describes the stereomutation of methane in very good agreement with high-level ab initio calculations of local properties of potential saddle point structures (Pepper *et al.* 1995). Figure 3 describes

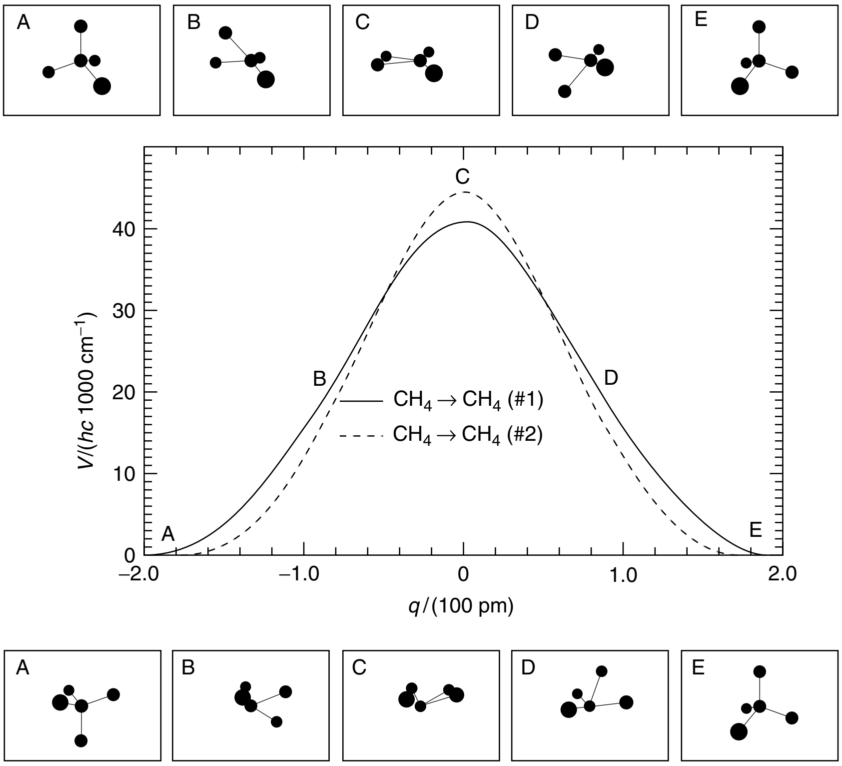

**Figure 3** Potential and stereomutation motion of the nuclei over the $C_{2v}$ saddle point (saddle point ♯2, broken curve, upper snapshot series) and the $C_s$ saddle point (saddle point ♯1, continuous curve, lower series). The coordinate $q$ follows the path of steepest descent. [Reproduced with permission from Marquardt and Quack 2004.]

cuts along the corresponding paths of steepest descent (mass unweighted), which may start from a $C_{2v}$-saddle (broken curve) or a $C_s$-saddle point (continuous curve). The corresponding change of nuclear configurations is shown by snapshots for the $C_{2v}$ (upper series) and $C_s$ inversion motion structures (lower series).

Further possible reactions occurring in the energy range of the simple CH bond rupture are the elimination of molecular hydrogen:

$$({}^1\mathrm{A}_1)\mathrm{CH}_4 \longrightarrow ({}^3\mathrm{B}_1)\mathrm{CH}_2 + ({}^1\Sigma_g^+)\mathrm{H}_2 \qquad (21)$$

with triplet methylene as product ($\Delta_R H_0^0 = 456$ kJ mol$^{-1}$, Berkowitz *et al.* 1994) or

$$({}^1\mathrm{A}_1)\mathrm{CH}_4 \longrightarrow ({}^1\mathrm{A}_1)\mathrm{CH}_2 + ({}^1\Sigma_g^+)\mathrm{H}_2 \qquad (22)$$

with singlet methylene roughly 38 kJ mol$^{-1}$ higher than for reaction in equation (21), as shown by Bunker *et al.* (1986). The reaction in equation (21) is properly described by METPOT4.

## 4.5 Ammonia

Ammonia belongs, as methane does, to the family of XY$_n$ molecules. Two major differences exist, however, which make the global analytical representation of the adiabatic lowest potential energy surface considerably more difficult than in the case of methane, despite the lower, total dimensionality: these are the very shallow barrier for inversion, and a conical intersection involving the reaction channel into ground-state azanyl ($^2$B$_1$) NH$_2$:

$$({}^1\mathrm{A}_1)\,\mathrm{NH}_3 \longrightarrow ({}^2\mathrm{B}_1)\,\mathrm{NH}_2 + ({}^2\mathrm{S}_{(1/2)})\,\mathrm{H} \qquad (23)$$

Figure 4 shows the lowest ammonia dissociation channels, as obtained from a CASPT2 calculation (Marquardt *et al.* 2005) for planar ammonia and 120° valence angles; only one NH bond is elongated (abscissa $r_{\mathrm{NH}} = r$), while the remaining NH bonds are kept fixed at roughly 100 pm. One sees that at around $r_{\mathrm{NH}} \approx 200$ pm, the two singlet states intersect. This point belongs to a well-known conical intersection seam in ammonia. The lowest adiabatic state leading to the formation of ($^2$B$_1$) NH$_2$ has thus a cusp hypersurface (of dimension 4, the dimension of the conical intersection seam) and, strictly, its analytical representation is therefore impossible. However, on a conical intersection seam, the notion of a PES loses sense anyway, because of the inherent coupling between electronic and vibrational motion, which leads unavoidably to a strong mixing of adiabatic states at resonances of the electronic structure, or when else relativistic couplings dominate. Following a more generalized, kinetic point of view, a global, smooth representation of the global analytical representation of a PES might be conceivable in cases when the nuclei will move on the lowest adiabatic PES, while approaching and departing from the regions defining a conical intersection,

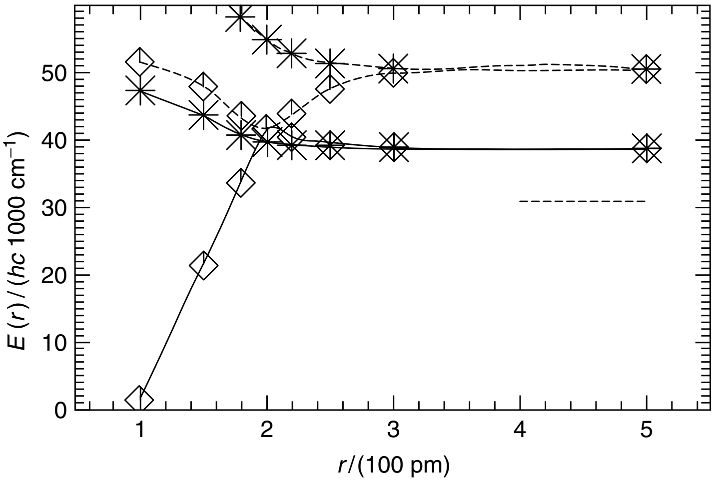

**Figure 4** Lowest adiabatic singlet (◇) and triplet (∗) states of ammonia at different values of the NH bond length; HNH angles and the two remaining NH bond lengths are kept fixed at 120° (planar ammonia) and 100 pm, roughly. Points are energies calculated at the CASPT2 level of theory on an (8,7) complete active space of a triple zeta-type basis set (Marquardt *et al.* 2005), the connecting lines are guide-of-the-eye cubic spline interpolations of the data.

— — $({}^1\mathrm{A}_1)\,\mathrm{NH}_3 \longrightarrow ({}^3\Sigma^-)\,\mathrm{NH} + ({}^1\Sigma_g^+)\,\mathrm{H}_2$, $\Delta_r\mathrm{H}_0^{\ominus} \approx 414$ kJ mol$^{-1}$ (Chase *et al.* 1985)
——— $({}^1\mathrm{A}_1)\,\mathrm{NH}_3 \longrightarrow ({}^2\mathrm{B}_1)\,\mathrm{NH}_2 + ({}^2S_{(1/2)})\,\mathrm{H}$, $\Delta_r\mathrm{H}_0^{\ominus} \approx 448$ kJ mol$^{-1}$ (Chase *et al.* 1985, Berkowitz *et al.* 1994)
– – – $({}^1\mathrm{A}_1)\,\mathrm{NH}_3 \longrightarrow ({}^2\mathrm{A}_1)\,\mathrm{NH}_2 + ({}^2\mathrm{S}_{(1/2)})\,\mathrm{H}$, $\Delta_r\mathrm{H}_0^{\ominus} \approx 590$ kJ mol$^{-1}$ (Chase *et al.* 1985).

whenever their kinetic energy is sufficiently small compared to the coupling energy given by the nonadiabatic terms neglected in the Born–Oppenheimer approximation, or other neglected coupling terms. For instance, while the nonadiabatic terms vanish by symmetry at planar geometries of ammonia (Nangia and Truhlar 2006), additional couplings arising from spin–orbit interaction might be important, due to the vicinity of the "spin-forbidden" reaction channel

$$(^1\mathrm{A}_1)\,\mathrm{NH}_3 \longrightarrow (^3\Sigma^-)\,\mathrm{NH} + (^1\Sigma_g^+)\,\mathrm{H}_2 \qquad (24)$$

which is actually the lowest dissociation channel of ammonia, as indicated schematically in Figure 4. In this sense, the lowest adiabatic PES of ammonia has been described with a single-valued analytical representation (Marquardt *et al.* 2005), which includes interconversion crossings and describes both reaction channels (equations 23 and 24). Within such a representation, the region pertaining to a conical intersection is modeled with smooth functions, rather than cusps. Those functions might give rise to local maxima in low-dimensional sections of the potential energy hypersurface. Studies on the four-dimensional conical intersection seam of ammonia and the nonadiabatic couplings have been reported (Yarkony 2004, Nangia and Truhlar 2006). Nangia and Truhlar (2006) and Li *et al.* (2007) derive a two-sheet analytical representation of the lowest adiabatic electronic states of ammonia from a direct calculation of diabatic states. Viel *et al.* (2006) present a three-sheet analytical representation for the ammonia cation from a different diabatization ansatz. Very little is known, however, about the spectroscopic accuracy of these representations.

In contrast to this, the representation AMMPOT2 was developed by Marquardt *et al.* (2005), with the aim of describing both reaction channels and bound vibrational motion. A variational calculation yields a vibrational spectrum that differs 50 cm$^{-1}$, on the average, from experimental term values to up to 6000 cm$^{-1}$, where deviations for individual transitions may be as large as 30 cm$^{-1}$, which is not very good for a fitted surface. Tunneling splittings are described better. The ground-state tunneling splitting is 0.6 cm$^{-1}$, on AMMPOT2, which is 25% off the experimental value of 0.79 cm$^{-1}$ (Urban *et al.* 1981). Marquardt *et al.* (2005) also reviewed other PESs for ammonia that are important from the prospective of high-resolution spectroscopy (Lin *et al.* 2002, Yurchenko *et al.* 2005a,b,c, Rajamäki *et al.* 2003, Leonard *et al.* 2003). In a more recent work, Huang *et al.* (2008b) have developed another representation of the same type. All these representations are built from truncated Taylor expansions using different types of coordinates. The spectroscopic accuracy of these analytical representations is rather high; Rajamäki *et al.* (2003) report deviations inferior to 5 cm$^{-1}$ for transitions to up to 15 000 cm$^{-1}$. Despite this high accuracy, it remains questionable whether such representations might be used in the context of quantum dynamical calculations of chemical reactions. As already mentioned above, the representations derived by Lin *et al.* (2002), Yurchenko *et al.* (2005c) do neither correspond asymptotically to the lowest adiabatic reaction channel nor are they diabatic. And the representation derived by Rajamäki *et al.* (2003) is not global; it leads even to an artificial, unphysical behavior of the potential surface in regions of configuration space that are energetically close to the location of vibrational term values that it so well reproduces. Figure 5 shows sections of different PESs discussed by Marquardt *et al.* (2005). The one-dimensional section of each surface is along the angle $\alpha$, for planar ammonia, while one NH bond is elongated at 150 pm and the other two bonds are kept fixed at 100 pm, roughly. One sees that only the representation AMMPOT2 is capable of reproducing the ab initio data in the intermediate region, leading to the reaction products of equation (23). By this way, asymptotically, the latter reproduces correctly, for $\mathrm{NH}_2$, the double-well potential in $\alpha$, with a barrier to linearity of approximately 12 000 $hc\,\mathrm{cm}^{-1}$. It is also worth mentioning that AMMPOT2 requires the adjustment of 31 parameters (with 10 additional, nonlinear conditions imposed via equation (20)), while the representations by Lin *et al.* (2002) need 84, those by Leonard *et al.* (2003) need 91, and those by Rajamäki *et al.* (2003) need 812 parameters to be adjusted.

The representation AMMPOT2 (Marquardt *et al.* 2005) is an example of a compact representation which can be improved systematically. Indeed, in current work

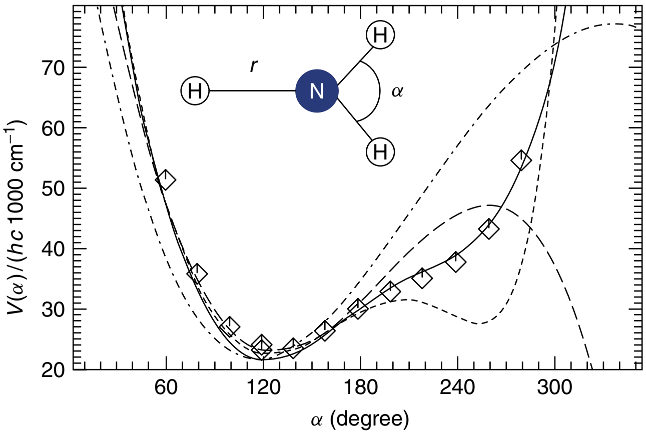

**Figure 5** One-dimensional sections of the potential energy surface of planar ammonia as a function of the bond angle $\alpha$ (see detail). Bond lengths are 100 pm but for one, which is $r = 150$ pm. The other bond angles are $(180^\circ - \alpha)/2$ each. ◇ CASPT2 data from (Marquardt *et al.* 2005); ———— AMMPOT2 (Marquardt *et al.* 2005); — — — — (Rajamäki *et al.* 2003); – – – – – – (Leonard *et al.* 2003); —·—·—·— (Lin *et al.* 2002).

(Marquardt *et al.* 2011) it is shown that this global analytical representation yields a vibrational spectrum, which is considerably improved with respect to experimental term values (average root mean square deviations of 32 bands to up to $5000\,\mathrm{cm}^{-1}$ is $11\,\mathrm{cm}^{-1}$, deviations of individual transitions do not exceed $4\,\mathrm{cm}^{-1}$, the ground-state tunneling splitting is $0.75\,\mathrm{cm}^{-1}$).

# 5 POTENTIAL SURFACES FOR HYDROGEN-BONDED CLUSTERS: THE HYDROGEN FLUORIDE SYSTEM, SPECTROSCOPY, AND FULL-DIMENSIONAL QUANTUM DYNAMICS

## 5.1 General Aspects

Potential surfaces for hydrogen-bonded clusters $(HF)_n$ with variables $n = 2, 3, 4, \ldots$ are of interest as prototypes for the description of evaporation and condensation phenomena in hydrogen-bonded liquids and crystals. Indeed, $(HF)_n$ may serve as the simpler relative of the practically important $(H_2O)_n$. Many of the concepts developed originally for $(HF)_n$ can be (and in part have been) translated to the $(H_2O)_n$, water system. The goal of such studies is nothing less than that of obtaining a fully microscopical, quantum dynamical description of homogeneous condensation and evaporation dynamics in hydrogen-bonded liquids (and crystals), ultimately based on high-resolution spectroscopy of individual clusters $(HF)_n$. Here we follow the systematic approach of Quack and Suhm (1997) and also refer to this paper for further references on these developments. We should state at the outset that the surfaces to be discussed are semiglobal in the sense that the objective here is to describe only the "low-energy" hydrogen bond dynamics of the type

$$(HF)_n \rightleftharpoons (HF)_{n-1} + HF \qquad (25)$$

also including hydrogen bond switching processes such as that shown in the scheme of Figure 6, and related more complex processes in the larger cluster. However, "high-energy " reactive processes such as

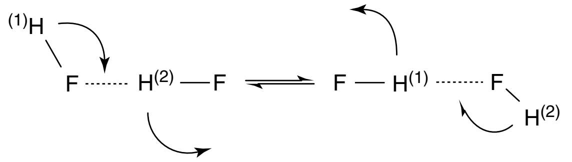

**Figure 6** Schematic view of a hydrogen bond switching process in $(HF)_2$.

$$HF \longrightarrow H + F \qquad (26)$$

are not described by the "semiglobal" surfaces, which thereby are not truly "global". However, the processes of the type in equation (26) are at least a factor of 2 higher in energy than any of the processes of relevance for the hydrogen bond dynamics, most of which actually occur at energies less than 10% of the energy for the reaction of equation (26). It, therefore, makes good sense to separate the description of such processes.

## 5.2 The Many-body Decomposition of the Potential

As discussed by Quack and Suhm (1997, 1998) and Quack *et al.* (1993, 2001), the many-body expansion is a natural starting point for the formulation of semiglobal potential hypersurfaces. To a first approximation, the interaction potential for a cluster $(HF)_n$ can be written as the sum over all monomer potentials $V^{(1)}$ and all the $(n-1)n/2$ ordered pair interactions $V^{(2)}$

$$V_{i_1,i_2,i_3\ldots i_n} \simeq \sum_{k=1}^{n} V_{i_k}^{(1)} + \sum_{k=1}^{n}\sum_{l=k+1}^{n} V_{i_k i_l}^{(2)} \qquad (27)$$

We note that many descriptions of model potentials for liquids use this "pair potential" approximation often with the further assumption that the monomer bond length $r_{\mathrm{HF}}$ is fixed. For our present purpose, we use an accurate monomer potential from spectroscopy to energies corresponding to excitation with several HF-stretching quanta (Table 1) and an accurate pair potential derived from ab initio theory and spectroscopy of the dimer $(HF)_2$ (Klopper *et al.* 1998). These contributions are then held fixed in the following steps. The pair potential approximation equation (27) for the cluster $(HF)_n$ already contains many of the physical features, but is not a sufficient approximation for $(HF)_n$ dynamics. The conventional "two-body" (pair) potential $V_{12}^{(2)}$ could be written as

$$V_{12}^{(2)} = V_{12} - V_1 - V_2 \qquad (28)$$

To obtain better approximations, one can now add a three-body term in describing the potential of the $(HF)_n$ approximately by equation (29):

$$V_{i_1,i_2,i_3\ldots i_n} \simeq \sum_{k=1}^{n} V_{i_k}^{(1)} + \sum_{k=1}^{n}\sum_{l=k+1}^{n} V_{i_k i_l}^{(2)} + \sum_{k=1}^{n}\sum_{l=k+1}^{n}\sum_{m=l+1}^{n} V_{i_k i_l i_m}^{(3)} \qquad (29)$$

The three-body term can be written accordingly as

$$V_{1,2,3}^{(3)} = V_{123} - V_{23} - V_{13} - V_{12} + V_1 + V_2 + V_3 \qquad (30)$$

An analytical three-body interaction potential for (HF)$_n$ clusters has been presented by Quack *et al.* (1993, 2001) including a FORTRAN77 subroutine in the appendix of the latter reference. It was concluded that the three-body potential makes a very significant contribution to the structures, potentials, and dynamics of (HF)$_n$ clusters.

For instance, for the trimer (HF)$_3$, it contributes about 10% to the hydrogen bond length, 20% to the binding energy, and 50% to the HF-stretching fundamental frequency shift. While one can thus hope for a rapid convergence of the many-body expansion, clearly an exact expansion will use all further contribution up to the $n$-body term in (HF)$_n$

$$\begin{aligned} V_{i_1,i_2,i_3\ldots i_n} \simeq{}& \sum_{k=1}^{n} V_{i_k}^{(1)} + \sum_{k=1}^{n}\sum_{l=k+1}^{n} V_{i_k i_l}^{(2)} \\ &+ \sum_{k=1}^{n}\sum_{l=k+1}^{n}\sum_{m=l+1}^{n} V_{i_k i_l i_m}^{(3)} + \cdots \\ &+ \sum_{k=1}^{n}\sum_{l=k+1}^{n} V_{i_1,i_2,i_3\ldots i_{k-1} i_{k+1}\ldots i_{l-1} i_{l+1}\ldots i_n}^{(n-2)} \\ &+ \sum_{k=1}^{n} V_{i_1,i_2,i_3\ldots i_{k-1} i_{k+1}\ldots i_n}^{(n-1)} + V_{i_1 i_2 i_3\ldots i_n}^{(n)} \qquad (31) \end{aligned}$$

The general systematic expression for an $m$-body term in this partitioning scheme is

$$\begin{aligned} V_{j_1 j_2 j_3\ldots j_n} ={}& V_{j_1 j_2 j_3\ldots j_m} + (-1)^1 \sum_{k=1}^{m} V_{j_1 j_2 j_3\ldots j_{k-1} j_{k+1}\ldots j_m} \\ &+(-1)^2 \sum_{k=1}^{n}\sum_{l=k+1}^{m} V_{j_1 j_2 j_3 \cdots j_{k-1} j_{k+1}\ldots j_{l-1} j_{l+1}\ldots j_m} \\ &+\cdots+\cdots(-1)^{m-2} \sum_{k=1}^{n}\sum_{l=k+1}^{m} V_{j_k j_l} \\ &+ (-1)^{m-1} \sum_{k=1}^{m} V_{j_k} \qquad (32) \end{aligned}$$

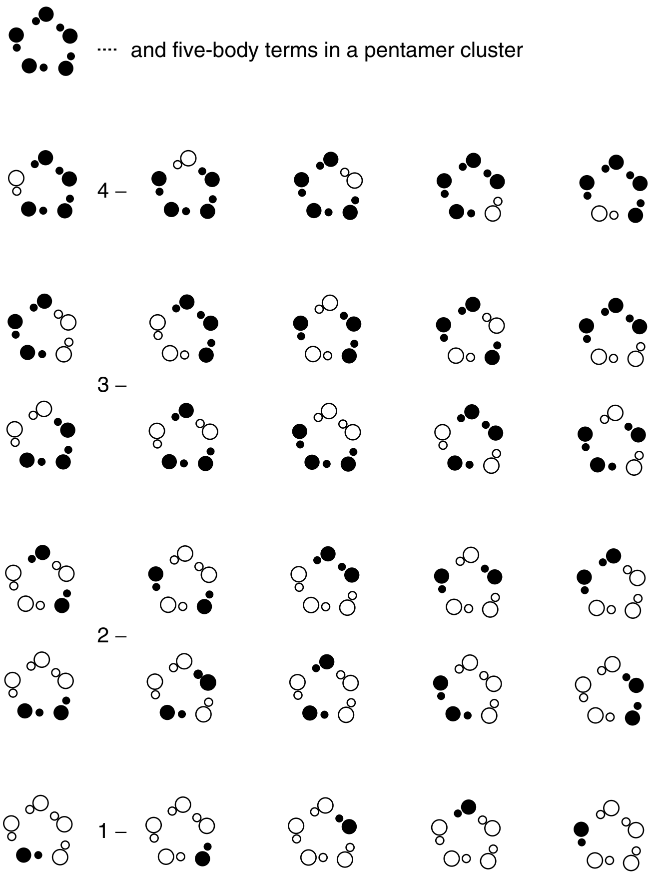

**Figure 7** Illustration of the one- to five-body contributions in the many-body expansion of the pentamer (HF)$_5$. Filled circles represent the molecules in a given $n$-body contribution. [By permission from Quack and Suhm (1997).]

We note that while equations (27) and (29) are written as *approximations* for the general cluster (HF)$_n$, equation (31) is by definition exact for (HF)$_n$ as the last ($n$-body) term can be chosen so as to describe the complete interaction potential. Figure 7 gives a schematic graphical representation of the contributions to the many-body expansion for the pentamer (HF)$_5$.

The purpose of using such a many-body expansion is obviously the hope that even for very large clusters (HF)$_n$ and ultimately the condensed phase the many-body expansion converges for some $m \ll n$. While $m = 2$ is obviously inadequate as is presumably $m = 3$ for (HF)$_n$ clusters, there is some evidence for rapid convergence thereafter, such that perhaps a truncation at $m = 5$ or 6 might be sufficient to describe the potentials of large clusters and the condensed phases adequately. The strategy for deriving the general potential of any cluster (HF)$_n$ from high-resolution spectroscopy (or ab initio theory) would then be to study first the dimer (for (HF)$_2$ this largely has been completed to good accuracy by Klopper *et al.* (1996, 1998)). The next step would be the study of the trimer $(HF)_3$. A first approach toward an accurate potential exists (Quack *et al.* 1993, 2001).

By continuing with spectroscopic and ab initio studies of $(HF)_4$, $(HF)_5$, and perhaps $(HF)_6$, one would then obtain finally perhaps sufficiently accurate description of the potential hypersurface for an arbitrary cluster $(HF)_n$ without the need to study this particular cluster itself. For a more detailed description of the approach and a summary of results from spectroscopy and ab initio theory for the hydrogen fluoride clusters, we refer to Quack and Suhm (1997, 1998) and to Quack *et al.* (1993, 2001). It is clear that the high-resolution spectroscopic approach to this very important general problem is still in its infancy and this is even more true for the water clusters $(H_2O)_n$, where many of the original developments for $(HF)_n$ are now being implemented in a similar manner (Goldman *et al.* 2005).

Before turning to dynamical applications of such potentials, we may quote here an important result from a theoretical investigation of $(HF)_n$ cluster potentials by Maerker *et al.* (1997). These authors find by comparison of DFT, using various functionals, with higher level ab initio approaches that DFT is quite inadequate to describe spectroscopy and dynamics of these clusters. This makes “exact” approaches such as the many-body expansion based on very high-level ab initio calculations combined with spectroscopic results even more necessary. We might also note in closing this description that we use the many-body expansion here with the *diatomic molecule* (HF) as unit, whereas commonly the many-body expansion has been used with *atoms* as the basic units Murrell *et al.* (1984), which would lead to quite a different physical description, although the formal mathematical aspects are the same.

## 5.3 Spectroscopy, Potential, and Classical and Quantum Dynamics of $(HF)_n$ on an Accurate Potential Hypersurface

The dimer $(HF)_2$ has been a prototype for a hydrogen bond dimer for a long time and some of the spectroscopic work can be found reviewed in the article by Snels *et al.* (2011): **High-resolution FTIR and Diode Laser Spectroscopy of Supersonic Jets**, this handbook. With the availability of highly accurate potential hypersurfaces Quack and Suhm (1991), Klopper *et al.* (1996, 1998), it lends itself to detailed theoretical studies by classical and quantum dynamics in comparison with spectroscopic results. We quote here from a recent study aimed at testing the validity of classical trajectory calculation in describing the dynamics of hydrogen-bonded clusters (Manca *et al.* 2008). Figure 8 shows an adiabatic channel diagram for this process. Table 2 summarizes the results for the predissociation lifetimes after excitation of the (HF) stretching modes with various combinations of quanta (of the free and the bonded HF units).

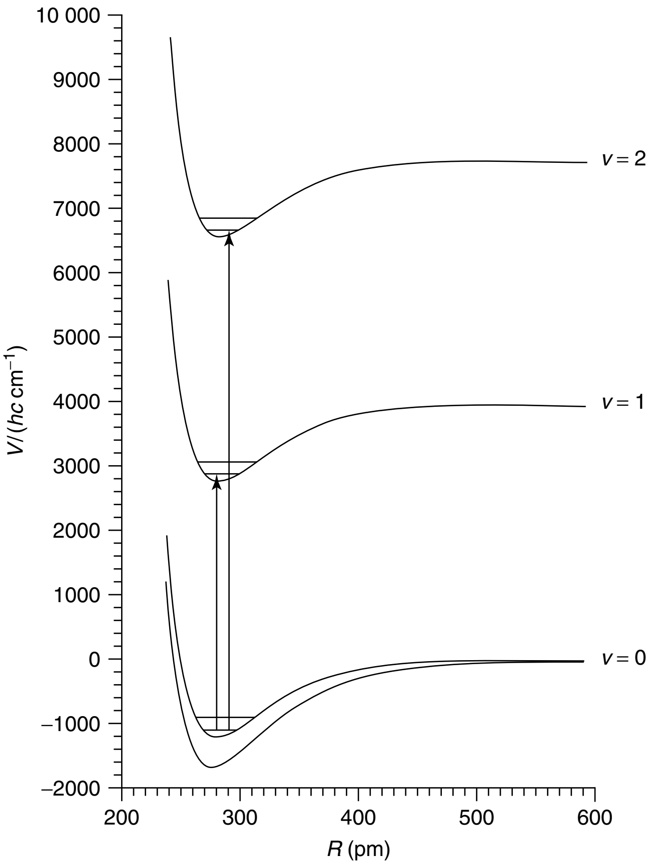

**Figure 8** Electronic potential (the lowest function) and several adiabatic channels (upper functions) as a function of the center of mass distance $R$ of the monomer units in $(HF)_2$ (see detailed discussion in the text). [Adapted from von Puttkamer and Quack (1989).]

The energy of excitation corresponds to a multiple of the bond dissociation energy $D_0/hc \simeq 1060\ \mathrm{cm}^{-1}$. In addition, the process considered refers to the heavy atom frame of the F atoms in the monomer units, which define in essence the separation of the monomer units. One might thus be tempted to think that classical dynamics of an accurate potential hypersurface should be a decent approximation. It is found, however, that classical trajectories at best give a fair description of qualitative trends. For a quantitative description, full quantum dynamics is required. This conclusion is particularly clear when classical and quantum dynamics on the *same* potential hypersurface are compared, e.g. for the predissociation from the $1_1$ polyad level at 3870 $\mathrm{cm}^{-1}$ with the SQSBDE surface. While this surface is not the best potential for the dynamics, comparison with experiment, classical and quantum

**Table 2** Experimental ($\tau_{\mathrm{PD}}^{\mathrm{exp}}$) and calculated ($\tau_{\mathrm{PD}}^{\mathrm{calc}}$) predissociation lifetimes of the HF dimer.

| Excitation | $\tau_{\mathrm{PD}}{}^{\mathrm{exp}}$ (ps) | $\tau_{\mathrm{PD}}{}^{\mathrm{calc}}$ (ps) | PES | #Simul. | Reference |
|---|---|---|---|---|---|
| $1_1 \simeq (v_b = 1,\ v_f = 0)$ | 480(40) | | | | (a) |
| $(HF)_2$ | | 3000 | SQSBDE$^{(b)}$ | | (c) |
| (3870 cm$^{-1}$) | | 3120/3300 | SQSBDE$^{(b)}$ | | (d) |
| | | **>9900** | **SQSBDE$^{(b)}$** | **23** | (e) |
| | | **2520(1050)** | **SO-3$^{(f)}$** | **23** | (e) |
| HF-DF | 1300(40) | | | | (g) |
| (2840 cm$^{-1}$) | | 7600 | SQSBDE$^{(b)}$ | | (h) |
| | | **>11700** | **SO-3$^{(f)}$** | **5** | (e) |
| DF-HF | 570(80) | | | | (g) |
| (3870 cm$^{-1}$) | | 4000 | SQSBDE$^{(b)}$ | | (h) |
| | | **>9300** | **SO-3$^{(f)}$** | **7** | (e) |
| $1_2 \simeq (v_b = 0,\ v_f = 1)$ | 16 800(900)/24 900(1900) | | | | (a) |
| (3930 cm$^{-1}$) | | 36 600/42 000 | SQSBDE$^{b)}$ | | (c) |
| | | 32 300/39 000 | SQSBDE$^{(b)}$ | | (l) |
| | | **>12 500** | **SO-3$^{(f)}$** | **23** | (e) |
| $2_1 \simeq (v_b = 2,\ v_f = 0)$ | 160(80) | | | | (i), (j) |
| (7550 cm$^{-1}$) | 50(10) | | | | (l), (j) |
| | | **410(96)** | **SO-3$^{(f)}$** | **64** | (e) |
| $2_2 \simeq (v_b = 0,\ v_f = 2)$ | 1730(80) | | | | (i), (j) |
| (7683 cm$^{-1}$) | 910(130)–2800(100) | | | | (i), (j) |
| | 1090(150)–1800(290) | | | | (k) |
| | | **880(820)** | **SO-3$^{(f)}$** | **64** | (e) |
| $2_3 \simeq (v_b = 1,\ v_f = 1)$ | >260 | | | | (i), (j), (l) |
| (7795 cm$^{-1}$) | 330(70) | | | | (i), (j), (l) |
| | | **480(374)** | **SO-3$^{(f)}$** | **60** | (e) |
| $3_1 \simeq (v_b = 3,\ v_f = 0)$ | 16 | | | | (m) |
| (11 043 cm$^{-1}$) | | **280(160)** | **SO-3$^{(f)}$** | **43** | (e) |
| $3_2 \simeq (v_b = 0,\ v_f = 3)$ | 1590 | | | | (m) |
| (11 274 cm$^{-1}$) | | **>1890** | **SO-3$^{(f)}$** | **38** | (e) |

All the excitations have been computed for $(HF)_2$ (except the $\nu_b$ excitation where few calculations for the mixed isotopomers are shown). The PES used for the calculations as well as number of simulations used for the averaged value are included. Symbols printed bold face refer to the work of Manca *et al.* (2008) from which this table is adapted. $v_b$ = quantum number for bonded HF stretching and $v_f$ = quantum number for free HF stretching.

(a) Pine and Fraser 1988 (experiment).
(b) Quack and Suhm 1991 (potential).
(c) Zhang and Zhang 1993 (quantum dynamics).
(d) Von Dirke *et al.* 1995.
(e) Manca *et al.* 2008 (classical dynamics).
(f) Klopper *et al.* 1998 (potential).
(g) Anderson *et al.* 1996 (experiment).
(h) Zhang *et al.* 1995 (quantum dynamics).
(i) Hippler *et al.* 2011 (experiment).
(j) He *et al.* 2007 (experiment).
(k) Suhm *et al.* 1992 (experiment).
(l) Hippler *et al.* 2011 (experiment).
(m) Chang and Klemperer 1994 (experiment).

dynamics on this surface disagree by a factor of 3 and more. Such a comparison is independent of the quality of the potential, provided the same potential is used. Of course, changing the potential (from SQSBDE to SO-3) also has a large effect.

## 6 POTENTIAL SURFACE FOR FULL-DIMENSIONAL REACTION DYNAMICS IN $H_2O_2$: SPECTROSCOPY AND WAVEPACKET DYNAMICS FOR STEREOMUTATION

The experience gained in the construction of global methane ($CH_4$) potential hypersurfaces (Marquardt and Quack 1998), and in particular the accurate semiglobal surface for the dimer $(HF)_2$, has been used to generate a global potential hypersurface for hydrogen peroxide $H_2O_2$ in a collaboration of the Lausanne und Zürich groups, where this molecule is also studied by spectroscopy (Kuhn *et al.* 1999). Hydrogen peroxide is an important prototype system to study one of the simplest chemical reactions, stereomutation between enantiomers of chiral molecules, given that the equilibrium structure for this molecule is nonplanar (Figure 9 shows the corresponding coordinate definition for a structure distorted away from equilibrium and Figure 10 the chiral equilibrium structure). $H_2O_2$ is furthermore of relevance as a prototypical chiral molecule in the study of molecular parity violation (Bakasov *et al.* 1998, Quack *et al.* 2008, Quack 2011). Finally, $H_2O_2$ is of great importance in atmospheric chemistry and combustion and it is also a major industrial product. Thus, the understanding of its reaction dynamics is of interest for a wide range of questions and a global potential hypersurface of great importance. Here we summarize some main features of the potential constructed by Kuhn *et al.* (1999) and discuss one particular application, the fully six-dimensional stereomutation quantum dynamics, which

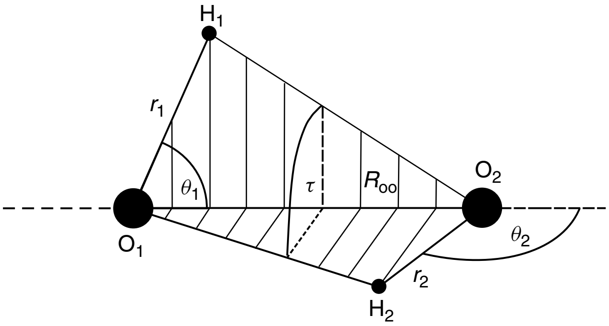

**Figure 9** Oxygen-centered internal coordinates for HOOH. $r_i$ $(i = 1, 2)$ denote the O–H bond lengths, $R_{OO}$ the O–O distance and $\theta_{1,2}, \tau$ the orientation and dihedral angles of the OH bond vectors with respect to the OO axis. [See Quack and Suhm (1996) and Kuhn *et al.* (1999) from where this figure is adapted. The atom numbering convention is $1 = H_1$, $2 = H_2$, $3 = O_1$, $4 = O_2$.]

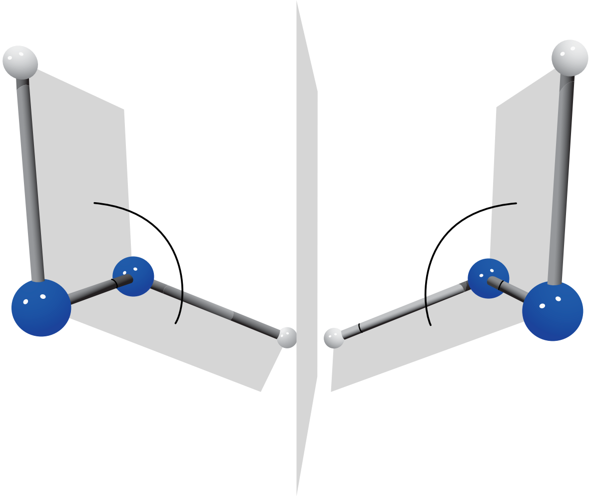

**Figure 10** $H_2O_2$ in its two enantiomeric equilibrium geometries: P-enantiomer on the left-hand side and M-enantiomer on the right-hand side. [Reproduced from Fehrensen *et al.* (2007) by permission.]

**Table 3** Summary of stationary points of various potential energy surfaces from the work of Kuhn *et al.* (1999).

| | PDB1 | PDBTB | PCP2 | PCPSDE |
|---|---|---|---|---|
| | Minimum ($C_2$) | | | |
| $r_1/a_0$ | 1.814 | 1.815 | 1.818 | 1.818 |
| $R_{OO}/a_0$ | 2.727 | 2.723 | 2.745 | 2.745 |
| $\theta_1/°$ | 100.4 | 100.6 | 99.8 | 99.8 |
| $\tau/°$ | 115.8 | 116.1 | 114.3 | 114.3 |
| | *Trans* saddle ($C_{2h}$) | | | |
| $r_1/a_0$ | 1.812 | 1.813 | 1.817 | 1.816 |
| $R_{OO}/a_0$ | 2.737 | 2.738 | 2.761 | 2.761 |
| $\theta_1/°$ | 99.4 | 99.2 | 98.3 | 98.3 |
| $\frac{E_{tr}}{hc\,cm^{-1}}$ | 256 | 319 | 345 | 361 |
| | *Cis* saddle ($C_{2v}$) | | | |
| $r_1/a_0$ | 1.815 | 1.815 | 1.819 | 1.818 |
| $R_{OO}/a_0$ | 2.734 | 2.729 | 2.753 | 2.754 |
| $\theta_1/°$ | 105.2 | 105.6 | 104.9 | 104.9 |
| $\frac{E_{cis}}{hc\,cm^{-1}}$ | 2551 | 2536 | 2530 | 2645 |
| | 2OH ($R_{OO} \rightarrow \infty$) | | | |
| $r_1/a_0$ | 1.832 | 1.832 | 1.833 | 1.833 |
| $\frac{D_e}{hc\,cm^{-1}}$ | 18 338 | 18 368 | 17 861$^{(a)}$ | 19 039$^{(a)}$ |
| | OOH + H ($r_2 \rightarrow \infty$) | | | |
| $r_1/a_0$ | 1.817 | 1.816 | 1.818 | 1.817 |
| $R_{OO}/a_0$ | 2.662 | 2.668 | 2.560 | 2.560 |
| $\theta_1/°$ | 101.1 | 100.9 | 107.0 | 107.0 |
| $\frac{D_e}{hc\,cm^{-1}}$ | 42 488 | 42 597 | 35 581 | 35 492 |

(a) Replacing the RKR with the Morse oscillator yields $D_e/hc = 17865\,cm^{-1}$ for PCP 2(M) and $D_e/hc = 19043\,cm^{-1}$ for PCPSDE(M).

is the first example of a full-dimensional treatment of this kind of process (Fehrensen *et al.* 1999, 2007).

Several analytical potentials were constructed by Kuhn *et al.* (1999) based on a combination of DFT (B3LYP) CASPT2 calculations and further adjustment to experimental (spectroscopic) properties of $H_2O_2$.

Table 3 summarizes results for the stationary point geometries for the various surfaces derived by Kuhn *et al.* (1999). The PCPSDE potential hypersurface turns out to be a good compromise for a potential hypersurface to study the quantum dynamics of this system.

Here, we address only the problem of the fully six-dimensional nuclear tunneling stereomutation dynamics, which has been the subject of some recent spectroscopic and theoretical investigations (Fehrensen *et al.* 1999, 2007). As can be seen from the data in Table 3, the stereomutation can be considered in a simplified picture as occurring along a one-dimensional torsional coordinate with two saddle points, a trans saddle point ($\tau = 180°$, and a barrier of $E_{\text{trans}} = 361\ hc\,\text{cm}^{-1}$) and a higher energy cis saddle point ($\tau = 0°$, $E_{\text{cis}} = 2645\ hc\,\text{cm}^{-1}$on PCPSDE). Conventional spectroscopic analyses use such one-dimensional quantum dynamics, which here might even be approximated by a double-well potential including tunneling through the lower trans barrier, as the cis barrier is much higher.

However, real quantum dynamics for this molecule happens in a space of the six internal degrees of freedom and a full-dimensional potential hypersurface allows for such a quantum dynamics study (Fehrensen *et al.* 1999, 2007), which then also allows us to study the dependence of tunneling dynamics upon the excitation of various nontorsional vibrational modes. This is shown in Figure 11. One sees an extremely mode-selective dependence of the tunneling splittings. These do not simply depend on energy, but depend exactly on which combination of modes is excited. There are both inhibiting and promoting modes for tunneling. Even more interesting is the fact that the stereomutation process on typical timescales between 100 fs and 20 ps essentially happens by a tunneling mechanism, even if the excitation in the nontorsional degrees of freedom is far above the lower trans barrier for stereomutation, as

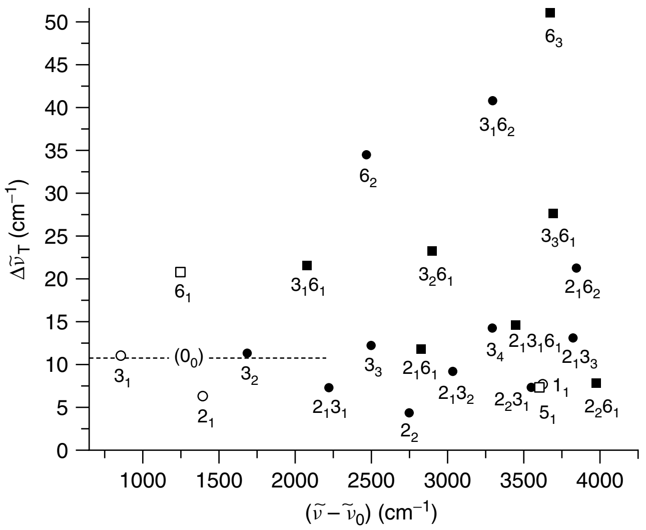

**Figure 11** Calculated torsional tunneling splittings $\Delta\tilde{\nu}_\tau$ as a function of vibrational excitation in the other modes ($\nu_1$, $\nu_2$, $\nu_3$, $\nu_5$, $\nu_6$) obtained from the exact six-dimensional DVR calculations. The abscissa gives the average excitation above the ground level $\tilde{\nu} = (\tilde{\nu}_+ + \tilde{\nu}_-)/2$ for each tunneling pair. Open symbols refer to fundamentals and full symbols refer to combinations and overtones. Circles are for levels with A-symmetry and squares for levels with B-symmetry. The assignment of the level is described by giving the mode $X$ with its vibrational quantum $v_x$ as right index. Modes in the ground level are not indicated. Thus, $2_13_16_1$ implies one quantum of vibration in each of the modes $\nu_2$, $\nu_3$ and $\nu_6$ and zero quantum in all other modes (see also Cohen *et al.* (2007) for this and other conventions on notation). The position of the ground-state tunneling splitting is given by a dashed line marked $0_0$ for the ground state. [Reproduced from Fehrensen *et al.* (2007) by permission.]

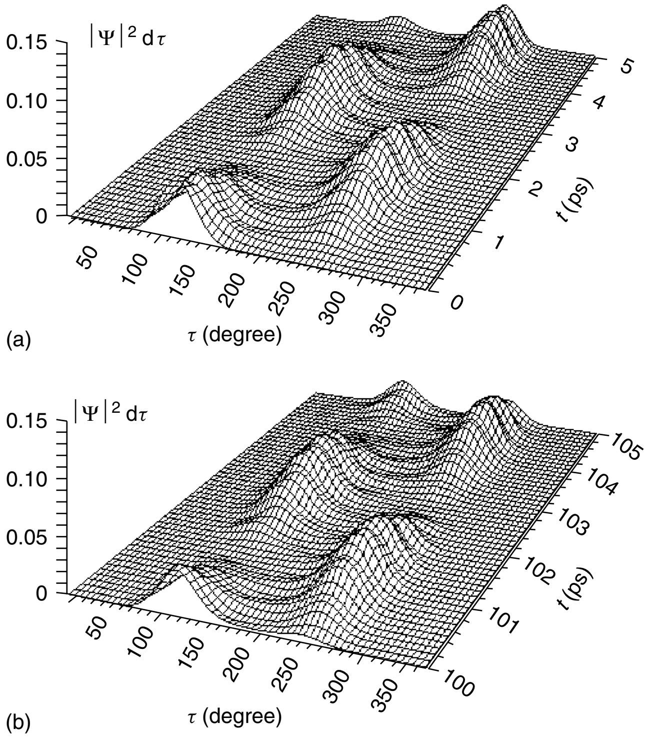

**Figure 12** Six-dimensional wavepacket evolution in $H_2O_2$. $|\Psi|^2\,d\tau$ shows the reduced time-dependent probability as a function of the torsional coordinate $\tau$, which is obtained by integrating the probability density over all other coordinates. (a) This shows the first 5 ps with an initial distribution localized on one side of the torsional barrier ($0 \leq \tau \leq 180°$) at the ground-state energy, roughly corresponding to a superposition of the lowest $A^+$ and $A^-$ tunneling levels. (b) The time range 100–105 ps with the initial condition at $t = 0$ as in (a). [Reproduced from Fehrensen *et al.* (2007) by permission.]

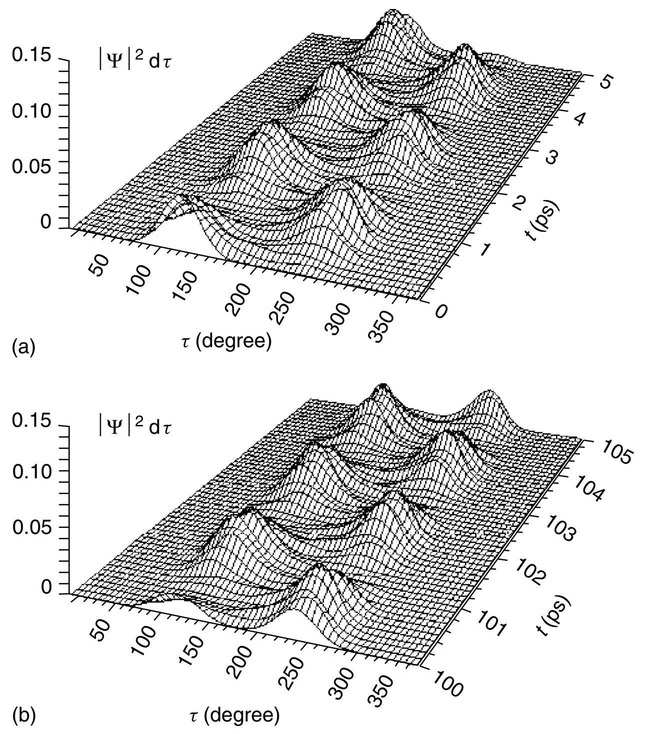

**Figure 13** Six-dimensional wavepacket evolution in $H_2O_2$ from exact six-dimensional DVR results with an initial condition including excitation with one quantum of the catalyzing antisymmetric OOH bending mode ($v_6 = 1$), otherwise as in Figure 12. [Reproduced from Fehrensen *et al.* (2007) by permission.]

can be seen from Figure 11. The conclusion by Fehrensen *et al.* (2007) is that one has essentially quasiadiabatic above barrier tunneling to very high vibrational energies.

A quasiadiabatic channel reaction path hamiltonian (RPH) approach provides a good approximation, indeed, for the full-dimensional quantum dynamics.

Figures 12–14 show the wavepacket dynamics in the ground state and with vibrational excitation of the OOH bending mode. Figures 12 and 13 show the exact six-dimensional quantum result, whereas Figure 14 gives the result from the RPH approximation, which is found to be quite good. Indeed, this presents the first example and foundation test for this approximation against a full-dimensional quantum calculation on a full-dimensional potential hypersurface.

## 7 CONCLUSIONS

PESs that describe the interaction between atoms in molecules have been essential theoretical tools for understanding molecular spectroscopy since the days of the old quantum theory and were used by spectroscopists even before the formulation of wave mechanics and the Born–Oppenheimer approximation. Analytical representations of potential energy surfaces are particularly interesting for spectroscopists.

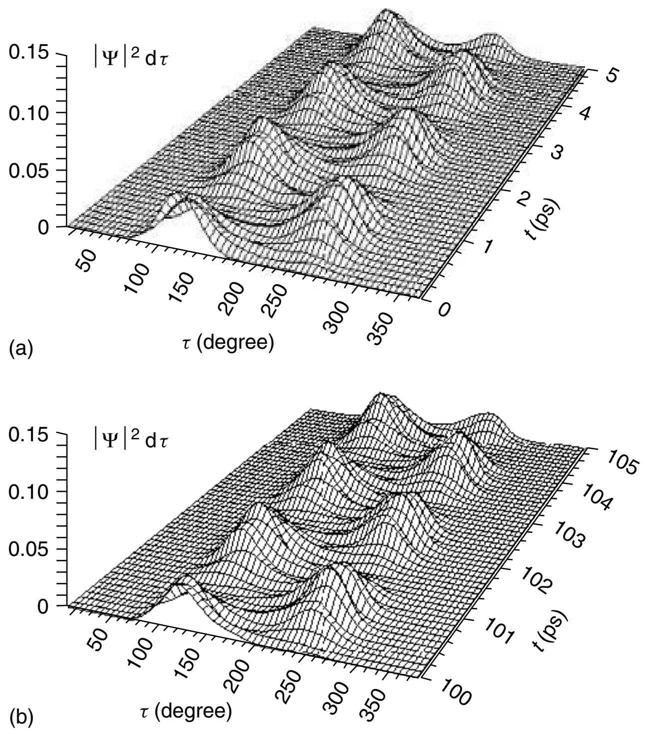

**Figure 14** Six-dimensional wavepacket dynamics in $H_2O_2$ calculated with the quasiadiabatic channel RPH approximation and one quantum of OOH bending ($v_6 = 1$), conditions, otherwise as in Figures 12 and 13. There is only a slight phase shift visible compared to Figure 13. [Reproduced from Fehrensen *et al.* (2007) by permission.]

In this article, we have given a brief historical review of analytical PESs within the context of high- resolution spectroscopy and molecular dynamics. We have summarized the current status of the construction of analytical, full-dimensional potential hypersurfaces of polyatomic molecules and clusters that satisfy three major criteria: global character, flexibility, and accuracy. The summary is illustrated with some pertinent examples.

It is clear that there is currently a bright outlook on future applications and extensions of such studies to successively larger polyatomic systems accessible to high-resolution spectroscopy and dynamics, both in the gas phase and at the gas–solid interface.

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## END NOTES

[a] The sentence “Nach neueren Untersuchungen entstehen die meisten ultraroten Spektralbanden durch Bewegungen von . . . Atomen oder Atomgruppen, während die Linien im sichtbaren und ultravioletten Spektrum auf Elektronenschwingungen beruhen” (Bjerrum 1914a) is likely referring to Drude (1904), Einstein (1907), and Nernst (1911).

[b] “Das Studium der ultraroten Spektren muss . . . für unsere Kenntnisse zu den Atombewegungen von grossem Nutzen sein können” (Bjerrum 1914a).

[c] Received 19 March 1927, submitted first in Göttingen, and then in Munich on 18 April 1927.

[d] Received on 26 April 1927.

[e] Received on 30 June 1927.

[f] Received on 25 August 1927.

[g] “Gibt es ein Wertsystem der relativen Kernkoordinaten $\xi_i$ von der Art, dass die Eigenfunktionen $\psi_n$ des Energieoperators (6), soweit sie von den $\xi_i$ abhängen, nur in einer kleinen Nachbarschaft dieses Wertsystems merklich von Null verschiedene Werte haben? Diese wellenmechanische Forderung entspricht offenbar der klassischen Bedingung, dass Kerne nur kleine Schwingungen um eine Gleichgewichtslage ausführen; denn $|\psi_n|^2$ ist die Wahrscheinlichkeit dafür, bei gegebener Energie eine bestimmte Konfiguration anzutreffen” (Born and Oppenheimer 1927, p. 465).

[h] “It will generally be conceded that the above unperturbed eigenvalues and eigenfunctions will give in a fairly correct manner the energy levels and dissociation limits of a diatomic molecule, and hence the corresponding perturbations will give correctly such things as the rate at which a molecule goes from a discrete state to a continuum” (Rice 1929, p. 1459).

[i] The term *configuration* used in the context of electronic correlation is equivalent to a Slater determinant; the term *configuration space* is used in the context of molecular dynamics and means all possible spatial arrangements of atoms in a molecule; and in stereochemistry, the term *configuration* has a special meaning (Moss 1996).

[j] “Analytical potential fitting in many coupled dimensions is a laborious, problem specific, artistic activity” (Suhm 1993).

[k] Adiabatic surfaces are the surfaces connecting the first, second, and third roots, etc of the secular equation of the electronic problem derived from the complete molecular Schrödinger equation in the Born–Oppenheimer approximation at fixed nuclear positions (Miller 1974).

[l] For a thorough discussion of this subject, see the book by Domcke *et al.* (2004).

[m] There are differing definitions of these acronyms. Following Bartlett and Musial (2007), pgs 313 and 314 therein, CCSD[T] includes triple excitations perturbatively to fourth order, and CCSD(T), which includes fifth order corrections, are slightly superior. Müller *et al.* (1998), however, give a different definition for CCSD[T] and it is claimed that CCSD(T) results lead fortuitously to a better agreement with experiment because of compensation of errors.

[n] Jensen (1999) presents a comprehensive discussion of basis sets for electronic structure calculations.

[o] Correlation consistent, valence zeta bases augmented by diffuse functions.

[p] The list should perhaps start with the pure spectroscopic work of Dennison (1925).

[q] $E_\mathrm{h}$ is a symbol adopted for the hartree (Cohen *et al.* 2007), $1E_\mathrm{h} \approx 4.360$ aJ.

## ABBREVIATIONS AND ACRONYMS

| | |
|---|---|
| BEBO | bond-energy–bond-order |
| CBS | complete basis set limit |
| CCSD | coupled-cluster including single and double |
| CI | configuration interaction |
| DFT | density functional theory |
| DQMC | diffusion quantum Monte Carlo |
| DVR | discrete variable representation |
| FBRs | finite basis representations |
| FTIR | Fourier transform infrared spectroscopy |
| MR-CI | multireference configuration interaction |
| PESs | potential energy surfaces |
| RPH | reaction path hamiltonian |
| SACM | statistical adiabatic channel model |

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