

Chapter 5

Introduction to Quantum Vibrational Spectroscopy



Krzysztof B. Beć, Justyna Grabska, and Thomas S. Hofer

Abstract In this chapter, the quantum mechanical basis for computational studies of near-infrared spectra (NIR) is discussed. Since this topic is rarely covered in detail in the literature, the necessary prerequisites are provided as well, which include (i) the coordinate frame for the description of molecular vibrations, (ii) methods for the determination of the vibrational potential, (iii) the principles of the harmonic approximation, and (iv) its role as the foundation for methods taking anharmonic effects into account. The details of various anharmonic approaches in quantum vibrational spectroscopy are discussed, including methods based on the vibrational self-consistent field (VSCF) approach, vibrational perturbation theory (VPT) as well as one- and multidimensional grid-based methods. The merits and pitfalls of these approaches are critically assessed from the perspective of applications in NIR spectroscopy. Selected examples from recent literature are included to demonstrate how these methods can be applied to solve practical problems in spectroscopy. The aim of this chapter is to provide a comprehensive presentation of the topic aimed at a spectroscopic audience, while remaining accessible and focused on the key details. Although primarily intended for readers interested in NIR spectroscopy, the essential information provided in this chapter represents a fundamental perspective on quantum vibrational absorption spectroscopy and is useful for a more general readership as well.

Keywords Quantum vibrational spectroscopy · Harmonic approximation · Overtone and combination transitions · Anharmonic methods

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5.1 Introduction

The aim of this chapter is to present the essential information required to obtain a fundamental understanding of quantum vibrational absorption spectroscopy, in particular near-infrared (NIR) spectroscopy. The discussion highlights the critical aspects to provide an in-depth and accessible overview aimed at a spectroscopic audience. The necessary basics include the commonly used coordinate frame for the description of molecular vibrations, an overview of the role of the vibrational potential and methods for its determination, as well as the critical factor in all applications of quantum chemistry being the computational complexity of a given approach. Considerable attention is focused toward the harmonic approximation, the fundamental framework underlying most applications of theoretical vibrational spectroscopy. The harmonic approximation is in general not sufficiently accurate for the needs of NIR spectroscopy. However, it is an essential foundation for advanced anharmonic treatments. The majority of these methods are either built on the basis of a harmonic Hamiltonian (VPT2), adopt a harmonic Hessian as the reference state (VSCF) or use the harmonic analysis (i.e., harmonic normal modes) in the process of probing the true vibrational potential (grid-based methods). The details of various anharmonic approaches are discussed, and their specific merits and shortcomings examined from the point of view of applications in NIR spectroscopy. This outline is based on several examples selected from recent literature.

5.2 Normal Modes of Vibration

Commonly, literature introducing the principles of vibrational spectroscopy mainly employs the example of a simple diatomic molecule. However, this kind of two-body system is limited to a single mode of vibration resulting from a one-dimensional potential and is not suitable for a complete presentation of the main concepts in vibrational analysis [1–4]. The total number of degrees of freedom (DOF) in a chemical system is $3N$, where N is the number of atoms. Translational and rotational motion can only be defined in an external coordinate system; thus, the translational and rotational DOF are invariant in the molecule's frame of reference. This sets them apart from the internal DOF (vibrational DOF; vibrational modes). The number of vibrational DOF equals to $3N - N_{\text{inv}} \cdot N_{\text{inv}}$ is generally partitioned into three translational and three rotational DOF (along the x , y , z directions); however, no change in the potential energy is associated to the rotation over the main rotational axis of linear molecules (including diatomic ones). Additionally, N_{inv} of periodic systems only considers uniform translational DOF (x , y , z) of the entire lattice. This effectively leaves $3N - 6$ modes for nonlinear molecules, $3N - 5$ modes for linear molecules, and $3N - 3$ modes for periodic systems. Note that these different DOFs need to be separated, e.g., no translation of the molecule's center of mass may occur along the vibrational mode. The concept of normal modes in computational chemistry has its

origin in the formalism of the harmonic approximation and will be outlined in detail in Sect. 5.4 of this chapter.

In polyatomic systems, symmetric and antisymmetric modes occur due to symmetry factors [1, 2]. In addition, deformation modes appear as well; they involve change of valence and dihedral angles between the atoms in the system. As a rule, force constants associated with stretching modes are typically higher, and thus, the wave numbers of these vibrations are higher compared to associated deformation modes. For instance, CO_2 is a linear molecule and thus has $3N - 5 = 4$ modes of vibration (Fig. 5.1). Among them are the two stretching modes, being symmetric and antisymmetric. The CO_2 symmetric stretch (ν_1) is IR inactive because there is no change in the dipole moment of the molecule along the associated vibrational coordinate. In contrast, the antisymmetric stretching vibration (ν_3) generates a significant net change of the dipole moment giving rise to a strong IR band observed at ca. 2345 cm^{-1} in gas phase. The two deformation modes of CO_2 involve the bending of the OCO angle in the molecule. These two modes differ only from the point of view of an external coordinate system; the vibrations occur along perpendicular planes. However, from the molecule's point of view, they are indistinguishable, and their energies (and thus wavenumbers) are degenerate giving rise only to a single IR absorption band ν_2 located at 667 cm^{-1} in gas phase. Therefore, despite possessing four vibrational degrees of freedom, only two fundamental bands of CO_2 are observed in the respective IR spectrum. However, IR spectra of gaseous molecules are further complicated because of rotational–vibrational coupling. Water serves as an archetypical nonlinear molecule; it has $3N - 6 = 3$ vibrational degrees of freedom, with only a single deformation mode ν_2 (Fig. 5.1).

Since the center of mass of the vibrating molecule may not change its position in space, the atomic displacements associated to these normal modes often involve displacements of all atoms in the molecule. These are not necessarily large amplitude motions, however. Water serves a good example, as large amplitude motions of the light-weighted hydrogen atoms are accompanied by a low-amplitude motion of the heavy oxygen atom; this is reflected in an exaggerated way in Fig. 5.1. These complex

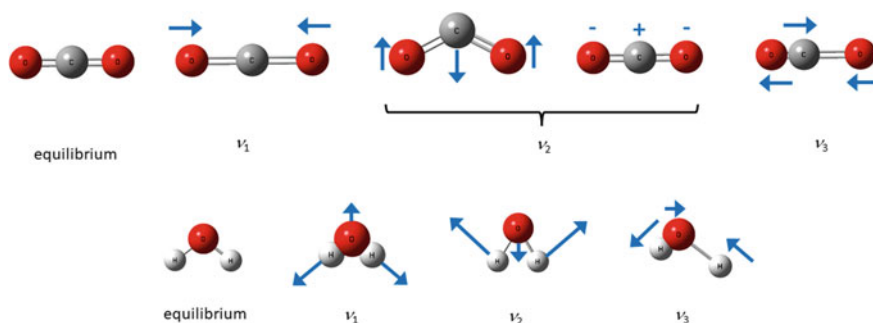


Fig. 5.1 Equilibrium geometries and normal modes of a carbon dioxide (top) and a water (bottom) molecule, respectively

atom displacements defined in normal coordinate system are difficult to interpret in larger systems; normal coordinates are also specific to a given molecular symmetry and not transferrable to other ones. Nevertheless, similarities exist between vibrations of molecules constituting similar functional groups and having comparable structures. A more useful description of vibrational motion is achieved by defining an alternative coordinate system based on the structural parameters of the systems such as bond lengths, valence, and dihedral angles. The commonly accepted standard is the internal coordinate system proposed by Pulay et al. [5]; often referred to as natural coordinate system. The deformation vibrations of functional groups most commonly found in organic molecules (methyl, $-\text{CH}_3$; and methylene sp^3 ; $>\text{CH}_2$) defined in natural coordinates are presented as an example in Table 5.1 and Fig. 5.2. The definitions of the other vibrations can be found in Ref. [5]. The transformation of

Table 5.1 Recommended internal coordinate system at the example of methyl and methylene (sp^3) groups. The complete definition for other types of functional groups can be found in Ref. [5]

Bond stretchings	Individual coordinates rather than combinations; possible exceptions: methyl and methylene groups where symmetrized combinations of the CH stretchings may be used
Methyl deformation	Sym. def. = $\alpha_1 + \alpha_2 + \alpha_3 - \beta_1 - \beta_2 - \beta_3$
	Asym. def. = $2\alpha_1 - \alpha_2 - \alpha_3$
	Asym. def.' = $\alpha_2 - \alpha_3$
	Rocking = $2\beta_1 - \beta_2 - \beta_3$
Methylene (sp^3) deformation	CH_2 scissoring = $5\alpha + \gamma$
	CXY scissoring = $\alpha + 5\gamma$
	CH_2 rocking = $\beta_1 - \beta_2 + \beta_3 - \beta_4$
	CH_2 wagging = $\beta_1 + \beta_2 - \beta_3 - \beta_4$
	CH_2 twisting = $\beta_1 - \beta_2 - \beta_3 + \beta_4$

Sym.—symmetric; asym.—antisymmetric; def.—deformation

Adopted with permission from Pulay et al. [5]. Copyright (1979) American Chemical Society

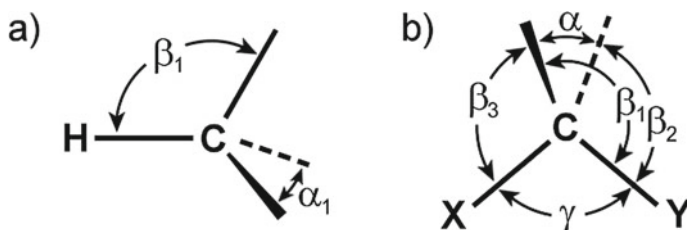


Fig. 5.2 Definition of internal coordinates in: **a** a methyl ($-\text{CH}_3$) group; **b** a methylene sp^3 ($>\text{CH}_2$) group

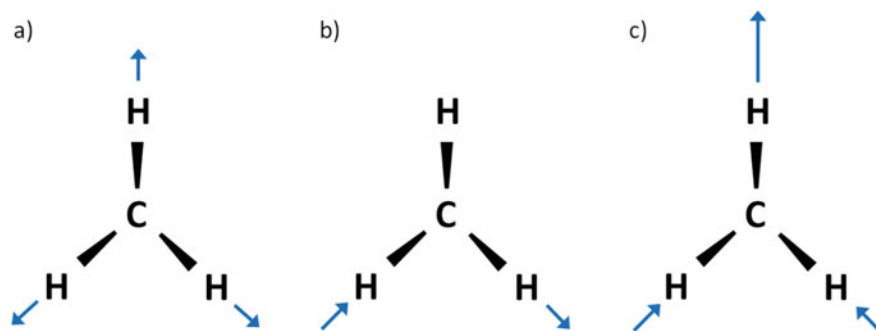


Fig. 5.3 Methyl stretching vibrations; **a** symmetric mode; **b, c** two kinds of antisymmetric modes

molecule-specific normal coordinates into natural coordinates enables a straightforward comparison between the vibrational properties of different molecules, providing considerable benefits when analyzing IR spectra.

The concept of Pulay's natural coordinate system suggest not to group stretching vibrations, but rather treat them as individual bonds. The allowed exceptions include methyl and methylene group, for which symmetrized combinations of C–H stretching vibrations may be used. The number of stretching vibrations specific to these functional groups is ruled by the number of involved DOF. Considering an archetypical system with a methyl group, $X-CH_3$ ($N = 5$), the number of vibrations is $3N - 6 = 9$. This is partitioned into five deformation vibrations (symmetric, two kinds of antisymmetric, and two kinds of rocking vibrations; Table 5.1) and four stretching vibrations. One stretching mode involves the $X-C(H_3)$ bond, leaving three possible stretching vibrations of the CH_3 moiety itself; one symmetric and two kinds of antisymmetric stretching modes (Fig. 5.3). A methylene group features just two degrees of freedom due to stretching vibrations, being symmetric and antisymmetric.

5.3 The Underlying Phenomena

5.3.1 The Potential Energy of a Molecular Oscillator

From the point of view of quantum vibrational spectroscopy, the primary problem focuses on the determination of the potential energy function along the spatial coordinate describing the molecular oscillator, or in other words, the motion of the nuclei (Fig. 5.4) [6]. The potential is the key property that dictates the quantum states (i.e., the vibrational wavefunctions) of a molecular oscillator. Following the fundamental approximation of quantum chemistry, the Born–Oppenheimer approximation, the motion of nuclei can be treated separate from the motion of the electrons in the majority of cases. Consequently, in vibrational problems, the electronic structure is reduced to the source of an external potential energy. Therefore, prior to any step

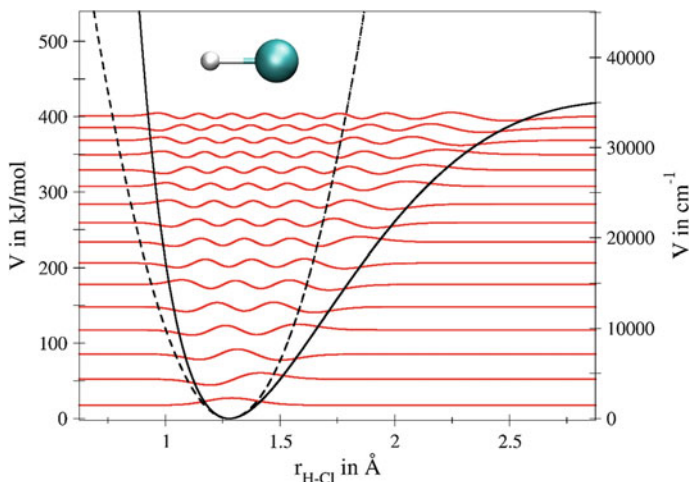


Fig. 5.4 Interatomic potential (solid black) and the associated harmonic approximation (dashed black) of the HCl molecule in the gas phase at CCSD(T)/aug-cc-pVQZ level and the respective vibrational wavefunctions (red) obtained via the Numerov approach. The associated energy differences between the individual states correspond to the wavenumbers measured via vibrational spectroscopy

made into quantum vibrational spectroscopy, the electronic structure of the system under consideration needs to be determined [6]. This can be accomplished with a large array of different approaches, aimed at providing various approximations to balance the accuracy of results and the computational demand.

5.3.2 *Quantum Chemical Methods for the Determination of the Electronic Structure of Molecular Systems*

An approach for the determination of the electronic structure of a quantum system (Fig. 5.5) may follow two principal ways of categorization; conceptual and practical. From the conceptual point of view, these methods differ by how the energy of the system is described. The major approaches will be presented in Sects. 5.3.2.1, 5.3.2.2, 5.3.2.3, 5.3.2.4, 5.3.2.5, and 5.3.2.6. More exhaustive information can be found in topic-oriented textbooks [6]. The practical categorization mostly concerns their computational complexity, with the cost versus accuracy factor of the available methods being a key consideration, which translates into their respective applicability to certain problems.

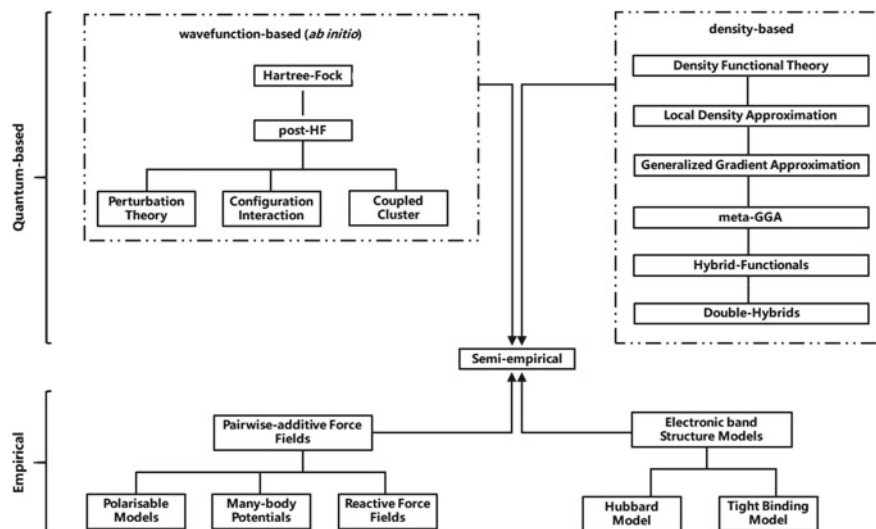


Fig. 5.5 Overview of computational chemistry methods commonly used for the determination of electronic structure in molecular systems and crystals

5.3.2.1 Hartree–Fock Theory

Any quantum-based treatment assumes that a wavefunction is the primary entity describing the state and therefore all observables such as the energy of a quantum many-body system. Hartree–Fock (HF) theory provides the fundamental and most straightforward approach in this category. This method is based on solving an approximate time-dependent Schrödinger equation (HF equation), which describes the state of a quantum mechanical system and the associated energy. All methods that are in practical use are based on the Born–Oppenheimer approximation, which limits the role of the nuclei to the source of an external potential. The interaction between the electrons involves the exchange and the correlation potential. Within the HF formalism, only the former is treated appropriately. The exchange energy results from the indistinguishability of electrons and is reflected in the HF procedure by antisymmetric properties of the wavefunction. This step is accomplished by deriving a single Slater determinant, an antisymmetrized product of one-electron wavefunctions (i.e., orbitals), to approximate the wavefunction of an N -body quantum system. In other words, the HF formalism assumes that the problem of interactions between the many electrons in the molecule is separable into a set of electron–electron problems, coupled through an averaged effective potential that describes the interaction with all other electrons in the system.

A solution to the HF equation is found by invoking the variational principle, in which a set of N -coupled equations for the N spin orbitals is derived, yielding the Hartree–Fock wavefunction and energy of the system. The HF framework belongs to the family of self-consistent field (SCF) methods, as self-consistency is a criterion

that needs to be fulfilled within the iterative procedure of solving the Hartree equations. The most far-reaching approximation assumed in the HF approach is neglecting the Coulomb correlation, which is often described as the mean-field charge distribution approximation of the electron correlation, since the HF method effectively averages the electron–electron interactions. This causes an inherent inability of the method to properly describe London dispersion. In order to step beyond a mean-field approximation of independent particles, so-called post-HF methods have been developed. The HF theory has a critical historical importance, being the first developed quantum theory with practical implementation. Nowadays, pure HF calculations are rarely used. However, the method is still widely adopted for calculations of the initial wavefunction of a quantum system, thus representing the preliminary step for calculations at higher levels of theory. On the other hand, a hierarchy of increasingly accurate methods based on the HF results exist, in which more than one Slater determinant is employed.

5.3.2.2 Post-HF Approaches

Different populations of atomic orbitals by electrons or electron configurations in a quantum system are possible. When any given electron changes its configuration, which can be described as an excitation into another orbital, the distribution of the other electrons in the molecule adjusts to minimize the total energy of the system. Thus, the motion of electrons is not independent but correlated, which lowers the total energy of the system. However, in the HF approach, any given electron only interacts with the average potential of all the other electrons in the system. To amend this shortcoming, post-HF methods aiming at a more accurate treatment of electron correlation effects were introduced. This may be accomplished in different ways, but unequivocally increases the computational complexity of the method by orders of magnitude.

In the simplest case, the electron correlation energy can be treated as a perturbation of the electronic state described in the HF formalism. As long as electron correlation has a relatively small contribution to the total energy, it can be expressed via a perturbing Hamiltonian corresponding to a correction added to the HF Hamiltonian. Since the unperturbed HF state is known, the perturbative correction is solvable using approximate methods, e.g., via an asymptotic series. The practical formulation of this approach is based on Møller–Plesset theory (MP) of a given order k . Zeroth-order wavefunction corresponds to an unperturbed HF state, and the first-order perturbation correction (MP1) to the HF energy can be shown to be equal to zero, which implies that only second- (MP2) and higher-order MP expressions are practically meaningful. Among those, MP2 bears the highest practical usefulness and finds broad applications. In most cases, higher-order perturbations (such as MP3, MP4, and MP5) do not improve the accuracy by an acceptable margin and display a huge computational demand. The MP2 method has become particularly widely applied since it is the most efficient approach to take electron correlation

effects into account. However, there are limitations in the applicability of MP theory, which led to the development of more advanced approaches.

Unlike the HF formalism, configuration interaction (CI) theory utilizes multiple Slater determinants to construct configuration state functions (CSF), which are then linearly combined to describe the wavefunction of the quantum system. The first term in the expansion of the CI wavefunction is equivalent to the HF ground-state wavefunction, while the higher terms capture the effects of the correlated motion of the electrons. In the CI formalism, the wavefunction is a combination of the HF reference states plus all possible excited states. This is reflected by mixing the ground CSFs and the excited CSFs. If all possibilities of orbital occupations are included (full-CI, FCI), an exact solution to the electron correlation problem can be achieved. Unfortunately, the number of excited configurations is enormously large, and in practice, the number of CI terms representing the electronic excitations needs to be truncated. The abbreviations for truncated CI variants reflect the excitation levels treated; ‘S’ for single excitations, ‘D’ for double, ‘T’ for triple, ‘Q’ for quadruple. This leads to CI single and double excitations (CISD), CI single, double, and triple excitations (CISDT), etc. From the point of view of quantum theory, CI is the most complete approach to describe the electronic structure of molecular systems. However, this corresponds only to FCI, that is, the case in which all orbital occupations possible for the quantum system are treated. The FCI method is useful for validation and benchmarking purposes of lower-level quantum methods, where its extensive computational cost remains manageable. In practical terms, unless FCI conditions are achieved, the application of truncated variants is often linked to considerable inaccuracies. Truncated CI methods capture a rapidly decreasing amount of the ‘exact’ correlation energy with an increase of the system size, which limits their usefulness in treating larger molecules and heavy atoms. Multiconfigurational self-consistent field (MCSCF) is an analogous approach that additionally applies a similar CI-like concept also to derive the one-electron functions that are subsequently used to construct CSFs.

Coupled-cluster theory (CC) expands the molecular orbitals obtained at HF level using an exponential cluster operator (acting as the excitation operator) and constructs a multi-electron wavefunction that includes electron correlation. The CC formalism may be considered as an alternative to CI, which produces an equivalent combination of one-electron functions to yield the multi-electron wavefunction. However, unlike linear combination assumed in the latter, the exponential expansion used in the former grants its size-extensivity resulting in an improved limiting behavior of the CC correlation energy upon truncation to a given excitation level (e.g., CCSD). Similar practical limitations as those found in CI apply here as well. The number of treated electronic excitations needs to be limited in order to make the method applicable in terms of the associated computational demand. This leads to variants, abbreviated analogous to CI variants, e.g., CCSD, CCSDT, etc. Unfortunately, in practical use, the CCSD level yields moderately correct results considering its cost, while the more accurate CCSDT proves to be too expensive for most applications. For this reason, CCSD(T) was introduced as a variant approximating the triple excitations via perturbation theory. Note, however, that when truncated at the same level,

CC approaches still capture a higher fraction of the correlation energy than their CI counterparts do, albeit at a higher computational cost. The CCSD(T) variant is highly valued for its high accuracy achieved at a relatively acceptable computational cost, and is often considered as the “golden standard of quantum chemistry.”

5.3.2.3 Density-Functional Theory

Inclusion of electron correlation in wavefunction-based methods leads to a steep increase in their computational complexity. This gave an impulse for the development of a fundamentally different concept known as density-functional theory (DFT) [7, 8]. It is based on the Hohenberg–Kohn theorems postulating that the state of a many-electron system can be described based on a unique functional (i.e., a function acting on another function), which in this case is the spatially dependent electron density function. The benefit of this formalism is a reduction of the dimensionality of the problem from that of a multidimensional ($3N$) N -electron wavefunction to a three-dimensional electron density function. The practical implementation of DFT became possible due to the formulation of the Kohn–Sham equations, which enabled the reduction of an intractable problem of interacting electrons in a static external potential to a tractable problem of non-interacting electrons in a local effective potential, i.e., the Kohn–Sham potential. The latter is constituted by the external potential plus electron exchange and correlation effects expressed via the associated exchange–correlation functional E_{xc} . Unfortunately, the exact E_{xc} is unknown except for the limiting case of a free electron gas, which became known as the local-density approximation (LDA; E_{xc}^{LDA}). While this formalism is applicable in case of metals and simple ionic solids, the LDA approximation fails to deliver satisfactory results for more complex systems. The meaningful development of DFT within the regime of chemistry started with the introduction of the generalized-gradient approximation (GGA) level, which was followed by more advanced approximations, such as meta-GGA functionals. A significant progress in the underlying theory was marked with the introduction of hybrid Kohn–Sham theory and the resulting hybrid formulation for E_{xc} . A hybrid E_{xc} is constructed as a linear combination of GGA and/or LDA (explicit) functionals and a HF ‘exact’ exchange functional (implicit functional). This inclusion of an ab initio electron exchange term in hybrid functionals greatly improved the accuracy and applicability of DFT. Popular hybrid functionals include the B3LYP, PBE0, HSE, and M06 functionals. Further advancement was achieved with the development of double-hybrid functionals. These approaches represent a natural progression from hybrid functionals, as in addition to the exchange term, ab initio correlation is included as well. The correlation is calculated similar to post-HF methods, e.g., MP2 correlation is employed in B2PLYP, mPW2PLYP, PBE0DH, or PBEQIDH double-hybrids. In addition to a much improved treatment of electron correlation, double-hybrid functionals also enable a better implementation of HF exchange; however, they are significantly more expensive than single-hybrid functionals.

The DFT concept is a rigorous re-interpretation of the quantum many-body problem. It offers a significant improvement in the affordability of calculations. Unfortunately, its practical implementation needs to include approximated electron exchange and correlation. The formulation of DFT limits the ability to improve its quality systematically. Instead, different functionals have been parametrized (i.e., calibrated) toward better accuracy when applied to certain systems. Inherent limitations of DFT, e.g., poor description of long-range (dispersive or non-covalent) interactions were recently mitigated by introduction of empirical corrections of dispersion, e.g., the series of Grimme's dispersion models (GD). Despite some shortcomings, DFT offers highly favorable cost versus accuracy level that made it particularly widely used in spectroscopic studies.

5.3.2.4 Semi-empirical Concept

Semi-empirical quantum chemistry methods are derived by insertion of pre-determined parameters into quantum mechanical calculation schemes. The most straightforward semi-empirical treatment replaces the relatively most time-consuming calculation procedures in the HF ansatz, i.e., two-electron integrals are omitted and their values are provided as empirical parameters to produce the expected results. These parameters are most often obtained from higher-level quantum mechanical calculations performed for small-scale models, and then used universally. Semi-empirical methods are significantly more affordable than their corresponding quantum mechanical frameworks, and thus suitable for the treatment of large molecules. Conceptually, in some cases semi-empirical schemes are relatively more complete, as empirical parameters may better describe some phenomena (e.g., electron correlation effects) than the *ab initio* approach with necessary approximations. Accordingly, as long as the considered system fits the conditions of the parametrization, semi-empirical calculations may yield more accurate results than when treated with a pure HF formalism. However, semi-empirical calculations are prone to produce erroneous results if they are applied outside of their area of parametrization. Therefore, they need to be used with care. Semi-empirical schemes based on a wavefunction ansatz include the Austin Model 1 (AM1), the parametric model family of methods (e.g., PM3, PM5) that implement the neglect of differential diatomic overlap (NDDO) principle (all two-electron integrals involving two-center charge distributions are neglected) as well as a number of additional approximations and corrections, depending on the particular method. A similar concept may also be applied to density-based methods. For example, density-functional-based tight-binding (DFTB) inserts pre-calculated parameters into the DFT calculation scheme, in which a minimal basis and only nearest-neighbor interactions are employed. The resulting deficiency in the description of long-range interactions is corrected with empirical dispersion (analogous to those developed for DFT functionals). The resulting approach yields reasonably accurate results at a fraction of the cost of DFT calculations. Although primarily popular decades ago, when the technology barrier prevented wider use of higher-level quantum methods,

semi-empirical methods remain continuously evolving with newer variants developed, e.g., PM6, PM7, or new concepts introduced such as self-consistent charge density-functional tight binding (SCC DFTB).

5.3.2.5 Molecular Mechanics

An alternative to QM-based approaches is the description of interatomic potentials in an entirely empirical way. These methods are typically referred to as molecular mechanics (MM) or force fields (FF) [9–11]. In this approach, the potential energy is calculated as a function of the nuclear coordinates using empirical (i.e., pre-parametrized) interaction potentials. Accordingly, MM uses classical mechanics to describe the forces acting between the atoms in a molecule. In the most fundamental approach, the interatomic potential energy is described as a sum of non-covalent pair-wise interactions resulting from electrostatic (Coulomb) and van-der-Waals (e.g., Lennard-Jones) contributions, while covalent contributions such as bond and valence angle interactions are often represented via harmonic potentials centered on preoptimized equilibria. These pair-wise additive approaches comprise the simplest possible description of the systems and are typically applied in the regime of (bio)organic chemistry (e.g., peptide/protein systems, nucleic acids, organic polymer materials) as well as for the treatment of simple solid-state systems such as oxide materials. In order to improve the accuracy of these approaches over the pair-wise additive character, a variety of improved MM methods have been developed. One of the simplest approaches to improve the pair-wise additive character is the inclusion of explicit coupling terms for bonded interactions with the Urey–Bradley angular term and the Axilrod–Teller three-body potential being typical examples. More advanced frameworks comprise the inclusion of polarization effects, which can for example be achieved using charge-on-spring/shell models, explicit polarization approaches as well as charge equilibration schemes. While these approaches are essentially linked to the Coulombic character of the interaction, many-body potentials such as the Finnis–Sinclair and embedded-atom models (EAMs) attempt to improve the description of the non-Coulombic contributions with typical applications being in the area of metals, alloys, and semiconductors. A comparably challenging yet highly intriguing development enjoying increased success in recent years is the formulation of dissociative/reactive force field approaches, capable of adequately describing the formation and cleavage of chemical bonds along the calculation.

The approximate nature of the interatomic forces described this way implies that force fields need to be heavily parametrized to yield an accurate description of the potential energy surface of a molecular system. The practical concept of MM is based on the assumption that a force field parametrized on the basis of a small-scale model, for which more accurate QM methods may be used, is reasonably well transferable to larger systems. The parametrization may be also based on experimental data, if available. This fundamentally different approach has a significant consequence in the terms of accuracy versus complexity factor. Consequently, MM is applicable to extensively complex molecular systems counting up to millions of atoms.

Therefore, MM is the only method of computational chemistry presently capable of treating multiscale chemical systems. Examples include large biological systems, solvated systems involving a large solvent volume, as well as composite materials. The unmatched affordability of MM makes it useful for molecular dynamics simulations. It is possible, e.g. to obtain vibrational spectra of the molecular models treated by molecular dynamics by calculating the dipole moment autocorrelation function. From the point of view of NIR spectroscopy, however, the MM potentials are too approximate to yield useful results. Briefly mentioned here should be hybrid quantum mechanics/molecular mechanics (QM/MM) approaches, in which only the chemically most relevant part of the molecular system is treated quantum mechanically while MM potentials are considered as sufficiently accurate to model all remaining interactions. These QM/MM schemes enable a more accurate treatment of the potential in key molecular fragments important from the point of view of a particular study.

5.3.2.6 The Fundamental Dilemma in Computational Chemistry; Cost Versus Accuracy Factor

With few exceptions, in computational chemistry, a higher accuracy can only be achieved with a significant increase in the demand for resources, understood mostly as calculation time or/and memory requirements. The nominal complexity of a method is limited to the number of electrons/atoms in the systems and scales distinctly different among the methods presented here. From the point of view of practical applications in spectroscopy, this should be a fundamental consideration as the application of higher levels of theory to the molecular system of interest may become prohibitively expensive. In the most straightforward case, the computational complexity of MM simulations is proportional to the square of the number of treated atomic centers N , $O(N^2)$, whereas advanced implementations are capable of reducing the scaling to $O(N \log N)$. The simplest ab initio HF method formally scales as $O(N^4)$. However, those schemes are widely regarded as not being sufficiently accurate for spectroscopic applications. The significant improvement in accuracy of post-HF approaches comes at a steep increase in their complexity, e.g., starting from $O(N^5)$ for MP2, $O(N^7)$ for CCSD(T), and $O(N^8)$ scaling for CCSDT. The CI formalism elevates this trend further, with CISD $O(N^6)$, CISDTQ $O(N^{10})$, while FCI is known to scale factorial with respect to the system size. In addition, post-HF methods require a larger number of functions describing the distribution of each electron (i.e., basis sets of one-electron functions) to provide accurate results. This gives an answer to the question that may arise at some point, about the root cause for numerous approximations that have been introduced to quantum theory in practical implementations. Such consideration explains the impact that DFT has in the field of practical applications, as it scales as $O(N^3)$, proportionally to the spatial dimensionality of the electron density function. Calculations performed with popular hybrid functionals such as B3LYP nominally scale as $O(N^4)$ but their practical effectiveness is enhanced by a decisively more rapid basis set convergence typical for DFT in comparison with

wavefunction-based approaches. In combination with further computational techniques such as efficient pre-screening approaches, the use of sparse matrix algebra routines, as well as convergence accelerators aimed at keeping the number of iterations small, DFT offers a remarkably favorable level of efficiency, an advantage which is well-reflected by the popularity of its use in spectroscopic studies.

5.4 Harmonic Frequency Evaluation

5.4.1 *Molecular Geometry Optimization Toward the Energy Minimum*

Geometry optimization, or energy minimization, is the procedure of determination of the atomic (nuclear) coordinates of a molecule, which result in the lowest total potential energy of the system. A molecule's potential energy $V(Q)$ is a many-parameter function of its atomic coordinates, represented as the vector $Q = \{q_1, q_2, \dots, q_{3N-N_{\text{inv}}}\}$. In principle, geometry optimization is a purely mathematical optimization problem of finding Q that minimizes $V(Q)$. In other words, it is a search for atomic coordinates of the molecule that minimize its potential energy. For a stationary point on the potential energy surface (PES), the energy gradient (the derivative of the energy with respect to all atomic coordinates, $\partial V/\partial q_i$) is zero. A generic implementation of the geometry optimization procedure is an iterative process of adjusting Q by following the gradient toward zero. Note, the definition of the atomic coordinates is not implicitly imposed. These may be, e.g., Cartesian coordinates, or internal coordinates describing bond lengths, bond angles, and dihedral angles. The quantum theory model that provides $V(Q)$ is also not imposed from the point of view of the optimization problem. As it will be demonstrated in the next section, geometry optimization performed in order to bring the system to its local minimum on the potential energy surface is a mandatory step prior to the execution of a harmonic frequency analysis.

5.4.2 *Harmonic Approximation*

Quantum chemical approaches to vibrational motion are in many points analogous to the problem of electronic structure. Accordingly, the theory of the vibrational structure is based on the time-independent vibrational (nuclear) Schrödinger equation [2]. The Born–Oppenheimer approximation still applies, but in this case, the electronic structure is reduced to the role of the source of an external potential upon which the motion of nuclei depends. The vibrational Hamiltonian of a polyatomic oscillator can be expressed as (Eq. 5.1)

$$H = -\frac{1}{2} \sum_i \frac{1}{m_i} \frac{\partial^2}{\partial q_i^2} + \frac{1}{2} \sum_i m_i \omega_{0i}^2 q_i^2 + \sum_{i \leq j \leq k} k_{ijk} q_i q_j q_k + \sum_{i \leq j \leq k \leq l} k_{ijkl} q_i q_j q_k q_l + \dots \quad (5.1)$$

where m_i is the reduced mass of the i -th normal mode and ω_{0i} the corresponding harmonic frequency given as

$$\omega_{0i} = \sqrt{\frac{k_i}{m_i}} \quad (5.2)$$

with k_i being the harmonic force constant. The third and higher terms in the expansion describe anharmonic contributions to the vibrational Hamiltonian via the associated cubic and quartic force constants, k_{ijk} and k_{ijkl} , respectively. Commonly, anharmonic contributions diminish consecutively toward higher terms, with the third (cubic) and fourth (quartic) terms capturing the majority of the total anharmonicity.

As it will be demonstrated further, taking into account anharmonic contributions staggeringly increases the complexity of the vibrational problem. However, a universal rule in physics states that the harmonic motion is a generic feature for sufficiently low-amplitude vibrations. This applies reasonably well for a number of molecular vibrations as reflected by relatively low contributions from the anharmonic terms in Eq. 5.1. Based on this premise, an approach called harmonic approximation is constructed. Within this approximation, no coupling between modes is permitted, which implies that all k_{ijk} , k_{ijkl} , and higher-order constants are set to zero. In other words, the normal vibrations of harmonic oscillator are entirely independent. Therefore, in Eq. 5.1, all terms beyond the second one are ignored, in many cases with an acceptable loss of accuracy. Next, the potential in the vicinity of the equilibrium is approximated as a Taylor series (Eq. 5.3)

$$V(Q) = V_0(Q) + \Delta Q^T \cdot g(Q) + \frac{1}{2} \Delta Q^T \mathbf{H} \Delta Q + \dots \quad (5.3)$$

with the higher terms in the expansion being neglected. At a stationary point on the PES, i.e. minima and transition states, the gradient $g(Q)$, and hence the second term in Eq. 5.3, is equal to zero as well. This results in a quadratic function as the approximation of the potential, corresponding to a harmonic potential. In practical applications, the mass-weighted second-derivative matrix of the potential, or mass-weighted Hessian \mathbf{H} is introduced, which elements are given as:

$$H_{i,j}^{mw} = \frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 V(Q)}{\partial q_i \partial q_j} \quad (5.4)$$

Diagonalization of the mass-weighted Hessian yields a matrix with $3N - N_{\text{inv}}$ columns consisting of orthonormal eigenvectors that describe the vibrational motion of the system within the harmonic approximation, the so-called mass-weighted normal modes. The $3N - N_{\text{inv}}$ diagonal elements of the eigenvalue matrix \mathbf{h} are proportional to the square frequency of the associated normal mode.

$$\mathbf{h} = \mathbf{U}^T \mathbf{H} \mathbf{U} \quad (5.5)$$

The example of how the harmonic approximation simplifies the true behavior of a vibrating molecule is demonstrated for the case of a water molecule, H₂O (Fig. 5.6), considering a two-dimensional example limited to the two OH stretching vibrations. The corresponding two-dimensional potential energy surface $V(r_{\text{OH1}}, r_{\text{OH2}})$ is described by the interatomic distances r_{OH1} and r_{OH2} (the corresponding coordinates are depicted in Fig. 5.6a as black lines). In this example, the true potential was determined with high accuracy using the CCSD(T)/aug-cc-pVTZ level of theory employing a tight grid spacing.

As outlined above, the problem of the harmonic oscillator is only solvable at a stationary point of the molecule's PES. In the present example, this means that prior to the evaluation of the Hessian, r_{OH1} and r_{OH2} need to be optimized to identify the

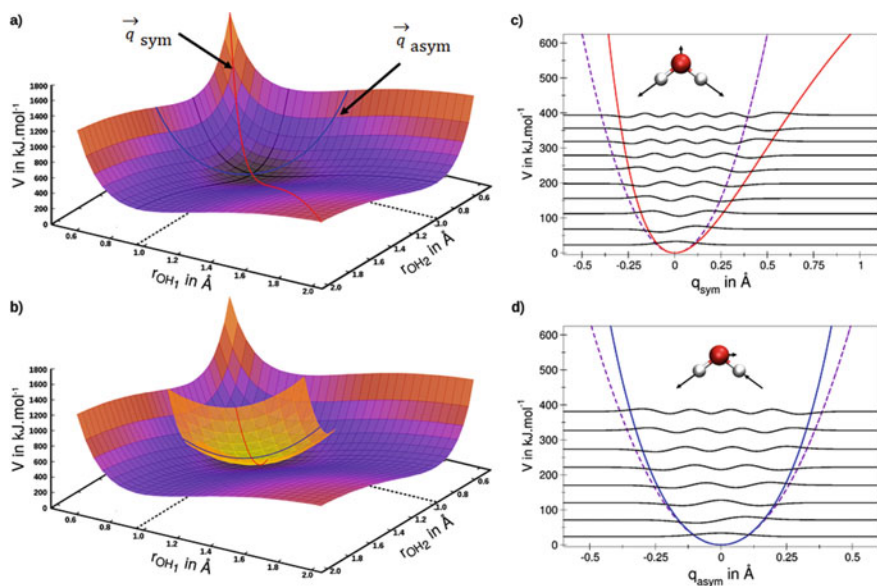


Fig. 5.6 Harmonic analysis at the example of the stretching vibrations of water ν_1 (symmetric; \mathbf{q}_{sym}) and ν_3 (antisymmetric, \mathbf{q}_{asym}); **a** the true nature of normal modes on the potential energy surface (red line: \mathbf{q}_{sym} ; blue line: \mathbf{q}_{asym}); **b** the nature of the harmonic approximation applied to these modes; **c** harmonic and anharmonic Morse-like potential curve of \mathbf{q}_{sym} ; the spacing between subsequent energy levels is increasing; **d** harmonic and quartic anharmonic potential curve of \mathbf{q}_{asym} ; in contrast to \mathbf{q}_{sym} , the spacing between the levels demonstrates a increase upon higher excitation

minimum on the $V(r_{\text{OH1}}, r_{\text{OH2}})$ surface. To obtain harmonic modes, $V(r_{\text{OH1}}, r_{\text{OH2}})$ needs to be approximated via the potential of a 2D harmonic oscillator V^{harm} . The key approximation in this case is that the harmonic potential is additive.

$$V^{\text{harm}} = V(r_{\text{OH1}}) + V(r_{\text{OH2}}) \quad (5.6)$$

Equation 5.6 requires that the potential does not depend simultaneously on r_{OH1} and r_{OH2} , i.e., there is no coupling potential. This implies that the vibrational wavefunction is a product of 1D wavefunctions, and the respective energy eigenvalues are additive (same as the potential case shown above), as described by Eqs. 5.7 and 5.8.

$$|\Psi(r_{\text{OH1}}, r_{\text{OH2}})\rangle = |\Psi(r_{\text{OH1}})\rangle \cdot |\Psi(r_{\text{OH2}})\rangle \quad (5.7)$$

$$E(r_{\text{OH1}}, r_{\text{OH2}}) = E(r_{\text{OH1}}) + E(r_{\text{OH2}}) \quad (5.8)$$

In this case, the Hessian would be diagonal. To match the latter criterion, a reorientation of the coordinate frame is required, which corresponds mathematically to the diagonalization of the mass-weighted Hessian described in Eq. 5.5. The frequency of the harmonic vibration are obtained from the square root of the diagonal entries in \mathbf{h} , while the columns in the matrix \mathbf{U} (i.e., the eigenvectors) provide the new coordinates highlighted in red and blue in Fig. 5.6. The data in the matrix \mathbf{U} lead to Eqs. 5.9 and 5.10 describing how to recombine r_{OH1} and r_{OH2} to obtain the harmonic normal modes, \mathbf{q}_1 and \mathbf{q}_3 .

$$q_1 = q_{\text{sym}} = \frac{1}{\sqrt{2}}r_{\text{OH1}} + \frac{1}{\sqrt{2}}r_{\text{OH2}} \quad (5.9)$$

$$q_3 = q_{\text{asym}} = \frac{1}{\sqrt{2}}r_{\text{OH1}} - \frac{1}{\sqrt{2}}r_{\text{OH2}} \quad (5.10)$$

This means for \mathbf{q}_1 that if r_{OH1} increases, so does r_{OH2} . In contrast, for \mathbf{q}_3 , if r_{OH1} is elongated, r_{OH2} is shortened (and vice versa). Therefore, \mathbf{q}_1 and \mathbf{q}_3 refer to symmetric and antisymmetric stretching normal modes, respectively. The representation of the potential in the harmonic approximation now corresponds to the paraboloid depicted in yellow in Fig. 5.6b. Every position on this paraboloid (any point on the harmonic potential surface) is given as the addition of the points lying on the main axes of the re-oriented coordinate frame, i.e., the red and blue line shown at the surface of the paraboloid. This surface dictates the stretching vibrations of the water molecule; symmetric (v_1) and antisymmetric (v_3). Note that the additive character of the harmonic potential directly implies its paraboloid shape in a geometrical sense.

In the following the principles of the harmonic approximation, a fundamental simplification that has found extensive use in spectroscopy, are summarized. A complex shape of the true vibrational potential is replaced by the corresponding

harmonic potential; as described in Eq. 5.3, this step is determined by the diagonalization of the Hessian evaluated at the respective energy minimum. In the process, a paraboloid approximating the shape of the true potential is derived. This process may be interpreted as the rotation of the coordinate system until Eq. 5.3 is fulfilled.

A positive-definite Hessian (all-positive eigenvalues) corresponds to a positive curvature of the potential along all directions from the reference point. On the other hand, in case a negative curvature is present along a specific direction, an imaginary frequency is obtained in the solution of the harmonic approximation, which is for instance employed to evaluate the properties of a transition state or/and reaction coordinates. Hence, the analysis of the Hessian at the stationary point (at which $g(Q)$ is equal to zero, i.e., no slope of the potential) enables the identification of the local minima (positive curvatures), local maxima (negative curvatures), and transition states (mixed occurrence of positive and negative curvature).

Since the harmonic potential depends on the Hessian, the efficiency of its determination by means of electronic structure theory is critical. The methods for which an analytical solution to the Hessian is available (e.g., HF, DFT, MP2, CIS) are far more efficient as the basis for a harmonic analysis than those for which the Hessian can only be calculated numerically (e.g., CC). Regardless, the harmonic approximation leads to a dramatic simplification of the vibrational problem in terms of complexity. The diagonalization of the Hessian yields the full vibrational solution: harmonic frequencies and the associated normal modes. For small to intermediate-sized molecules, this is a computationally inexpensive step (although it may become a bottleneck in studies of large systems using FF approaches), which made the harmonic approximation particularly important for early advances in vibrational spectroscopy. However, it is an extensive approximation of the real molecular oscillator. Firstly, the shape of the potential is fixed as a quadratic function. This is well-reflected in Fig. 5.6, as seen in three-dimensional space (Fig. 5.6a, b) as well as in one-dimensional projections respective to each of the modes (Fig. 5.6c, d). In this example, the true potential along the symmetric stretching mode of H₂O is asymmetric with respect to the equilibrium position (i.e., anharmonic) and resembles a Morse-like curve (Fig. 5.6c). This type of anharmonic potential is well-known, as it is often discussed in case of diatomic molecular oscillators (Fig. 5.4). Unlike the harmonic solution, the true vibrational levels are not equidistant. Morse-like anharmonicity (high contribution from the cubic terms in Eq. 5.1) leads to a subsequent reduction of the energy gaps between consecutive levels. However, the potential of the antisymmetric stretching mode of H₂O, although symmetric in shape, also deviates from the harmonic potential (Fig. 5.6d). This is due to significant contribution in the quartic terms in Eq. 5.1. The quartic anharmonicity leads to widened distances between consecutive vibrational levels.

Nevertheless, with some exceptions, e.g., of X–H stretching modes, in many cases the deviation between the harmonic approximation and the true molecular oscillator is relatively moderate. Consequently, in case of fundamental transitions, harmonic frequencies corresponding to those vibrations remain overestimated but not dramatically. This effect can be mitigated by an empirical correction, applied a posteriori in the form of a scaling of harmonic frequencies. Hence, the calculation of harmonic

normal modes provides an effective route to enable approximate computational IR and Raman spectroscopy. However, in the majority of cases, this approach is too error prone to provide a reasonable prediction of overtones. In addition, the fundamental point of the harmonic approximation, the additive nature of the harmonic potential, does not take the coupling between individual modes into account, as reflected by the assumed zero cross-derivatives, or anharmonic force constants in Eq. 5.1. This fact leads to a critical limitation of the harmonic approximation, being its inability to describe combination transitions, rendering it inapplicable to NIR spectroscopy.

5.5 Beyond the Harmonic Approximation

5.5.1 Anharmonic Approaches Formulated on the Basis of the Harmonic Approximation

For the reasons explained above, the harmonic approximation is unsuitable for the calculation of NIR transitions. The inclusion of anharmonic effects to vibrational structure theory may be treated in an analogous way as electron correlation is included into the theory of the electronic structure. Accordingly, vibrational self-consistent field (VSCF) is the most straightforward anharmonic approach and an analogy to HF theory. The VSCF method is based on the concept that for each vibrational state k of the oscillator, the wavefunction Ψ is separable into a product of single-mode (harmonic) wavefunctions ϕ_i^k (Eq. 5.11), or a Hartree product.

$$\Psi_k(q_1, \dots, q_n) = \prod_i^n \phi_i^k(q_i) \quad (5.11)$$

Through this, the multidimensional vibrational Schrodinger equation for the molecular oscillator in mass-weighted coordinates q_1, \dots, q_n (Eq. 5.11) is given as:

$$\left[-\frac{1}{2} \sum_{i=1}^n \frac{\partial^2}{\partial q_i^2} + V(q_1, \dots, q_n) \right] \Psi_n(q_1, \dots, q_n) = E_n \Psi_n(q_1, \dots, q_n) \quad (5.12)$$

which leads to a set of one-dimensional (single-mode) equations (Eq. 5.13)

$$\left[-\frac{1}{2} \frac{\partial^2}{\partial q_i^2} + \bar{V}_i^{(n)}(q_i) \right] \Psi_i^{(n)}(q_i) = \varepsilon_i^{(n)} \Psi_i^{(n)}(q_i) \quad (5.13)$$

To fulfill the condition of separability, an effective potential $\bar{V}_i^{(n)}$ has to be introduced, through which the modes are coupled in form of a mean-field. It implies that there is no explicit mode–mode correlation, which is the major simplification in

the VSCF concept. In other words, the potential for each normal mode is averaged over all other normal modes. Interestingly, the accuracy of the basic VSCF method increases relatively with the system size, as the average treatment of mode couplings applies better to extensively multidimensional (i.e., multimodal) systems.

To reduce the complexity of the problem further, a truncated pair-wise representation of the potential may be applied (Eq. 5.14)

$$V(q_1, \dots, q_n) = \sum_{i=1}^n V_i^{\text{diag}}(q_i) + \sum_i \sum_{j>1} W_{ij}^{\text{coup}}(q_i, q_j) \quad (5.14)$$

This way, the potential is approximated by a sum of single-mode potentials and interactions W_{ij}^{coup} between pairs of normal modes. Pair-wise potentials neglect contributions from any higher-order couplings (triplets, quartets, etc.).

Since the treatment of mode coupling in the basic VSCF scheme is approximated, no explicit correlations between modes is considered. As long as the coupling is relatively small, its impact may be evaluated more accurately through the addition of a correction by means of second-order perturbation theory. This leads to the VSCF-PT2 approach sometimes also called correlation-corrected VSCF, CC-VSCF. In this variant, the correction to the energy E_k^{corr} results from a potential V_k^{pert} defined as a small perturbation to the effective potential. Accordingly, the VSCF-PT2 ansatz leads to a perturbed VSCF Hamiltonian (Eq. 5.15)

$$H = H^{\text{SCF},(n)} + \Delta V(q_1, \dots, q_n) \quad (5.15)$$

and the associated correlation-corrected energy (Eq. 5.16)

$$E_n^{\text{VSCF-PT2}} = E_n^{\text{VSCF}} + \sum_{m \neq n} \frac{\left| \prod_{i=1}^n \Psi_i^{(n)}(q_i) | \Delta V | \prod_{i=1}^n \Psi_i^{(m)}(q_i) \right|^2}{E_n^{(0)} - E_m^{(0)}} \quad (5.16)$$

denotes for n -th state coupling with all other m -states of the oscillator.

Energy corrections obtained through higher-order levels of perturbation theory return no meaningful improvements. The VSCF-PT2 method yields more accurate vibrational energies, however, at a sizeable increase in its computational complexity. Moreover, it is prone to behave erroneously in the case of nearly degenerated states (i.e., with similar energies; $E_n^{(0)} - E_m^{(0)} \approx 0$); thus, it is not applicable to strongly coupled modes.

A more advanced concept of including explicit mode correlations into the VSCF wavefunction has been formulated in the form of vibrational configuration interaction (VCI) theory. Per analogiam to the HF scheme, the VSCF solution yields a number of unoccupied virtual ‘excited’ modals. In a CI-like approach, the VSCF modals can be linearly combined to yield a correlated vibrational wavefunction. In an alternative approach, instead of a linear one, an exponential expansion using a cluster operator

is proposed, leading to the vibrational coupled-cluster (VCC) scheme. VCI/VCC wavefunctions provide very good approximations to the exact vibrational wavefunction, and at the level of theory are not limited to any particular systems (such as those with weakly coupled modes). These approaches are capable of yielding very accurate results; however, they are extremely costly in their application to multimodal systems, and thus not suitable for spectroscopic studies of even moderate sized chemical systems.

On the other hand, vibrational perturbation theory (VPT n) adopts the Møller–Plesset formalism of n -th order (e.g., second-order perturbation leading to VPT2) to re-introduce the anharmonic terms in Eq. 5.1 as a perturbation to the (harmonic) vibrational Hamiltonian. The VPT ansatz separates the anharmonic contributions in the vibrational Hamiltonian H (Eq. 5.17) into a set of individual terms (Eqs. 5.18–5.20).

$$H = H^{(0)} + H^{(1)} + H^{(2)} \quad (5.17)$$

$$H^{(0)} = \frac{1}{2} \sum \omega_i (p_i^2 + q_i^2) \quad (5.18)$$

$$H^{(1)} = \frac{1}{6} \sum \phi_{ijk} q_i q_j q_k \quad (5.19)$$

$$H^{(2)} = \frac{1}{24} \sum \phi_{ijkl} q_i q_j q_k q_l + \sum_{\tau=x,y,z} B_e^\tau \zeta_{ij}^\tau \zeta_{kl}^\tau \left(\frac{\omega_j \omega_l}{\omega_i \omega_k} \right) q_i p_j q_k p_l \quad (5.20)$$

with $H^{(0)}$ being the harmonic Hamiltonian. The first-order Hamiltonian $H^{(1)}$ includes the cubic anharmonic terms, while the second-order Hamiltonian $H^{(2)}$ the quartic terms.

Unlike in the VSCF-PT2 scheme, in which a perturbative correction is added to the VSCF Hamiltonian, the VPT2 ansatz operates on a harmonic Hamiltonian and a perturbative treatment is inserted at the lower level of the vibrational structure theory. Compared with the VSCF approach, VPT2 calculations typically require a lower number of potential evaluations to achieve a comparable accuracy. Hence, in practical implementations, the VPT2 approach may be more efficient. However, in its original formulation, this method is highly unreliable in treating nearly degenerated modes. The number of degeneracies rapidly increases for larger molecules, which makes VPT2 unsuitable for the description of such systems. With aim of providing a universal methodology, the ‘deperturbed’ VPT2 (DVPT2) ansatz was formulated, in which the terms describing nearly degenerated states are removed entirely from the calculation. Thus, the DVPT2 energies have a more approximate character, but are not likely to be affected by large errors. Further development of this concept led to its generalized variant GVPT2, in which the removed terms are re-evaluated using a variational approach. In principle, the GVPT2 method is applicable to any system regardless of its size, while maintaining a favorable cost versus accuracy ratio.

5.5.2 Grid-Based Approaches

Implementations of VSCF or VPT2 theory are constructed for an efficient treatment of moderately anharmonic modes. The relatively low number of energy evaluations, and the approximate probing of the vibrational potential yield high efficiency of these approaches. However, the amount of anharmonicity they effectively capture is limited. In order to predict the vibrational energy eigenstates with high accuracy, solving the time-independent Schrödinger as given in Eq. 5.21 for a one-dimensional problem yields a nearly exact solution of the vibrational problem for an accurately evaluated potential.

$$\frac{\partial^2 \Psi(q)}{\partial q^2} = \left\{ \frac{2m}{\hbar^2} \cdot (V(q) - E) \right\} \Psi(q) = f(q) \cdot \Psi(q) \quad (5.21)$$

Here, Ψ denotes the vibrational wavefunction along the respective normal coordinate q , while m and \hbar are the reduced mass of the vibrational mode and the reduced Planck constant, respectively. Typically, the potential $V(q)$ is provided on an equispaced grid with step length Δq , and E denotes the associated energy eigenvalue. The solution to Eq. 5.21 can be obtained by means of grid-based approaches such as discrete variable representation (DVR) and Numerov's method. The latter is based on a Taylor series of $\Psi(q)$ expanded around the point q of the normal coordinate with $\Psi^{(n)}$ representing the n -th derivative of the wavefunction with respect to Δq :

$$\Psi(q + \Delta q) = \Psi + \frac{1}{1!} \|\Delta q\| \Psi^{(1)} + \frac{1}{2!} \|\Delta q\|^2 \Psi^{(2)} + \frac{1}{3!} \|\Delta q\|^3 \Psi^{(3)} + \frac{1}{4!} \|\Delta q\|^4 \Psi^{(4)} + \dots \quad (5.22)$$

Summation of the Taylor expansion in forward and backward direction (i.e., $\pm \Delta q$) leads to the cancellation of all odd, and the doubling of all even entries. Next, higher-order derivatives (i.e., $\Psi^{(n)}$ with $n = 4, 6, 8, \dots$) are expressed via their associated finite differences employing the appropriate number of grid points $V(\pm m \cdot \Delta q)$ to achieve the desired accuracy. In the simplest case, the time-independent Schrödinger equation can be expressed via a three-point expression employing the two neighboring grid points $\pm 1 \cdot \Delta q$ of any given point on the equispaced grid (labeled as $\Psi_{-1}, \Psi_0, \Psi_{+1}$ for convenience)

$$\begin{aligned} & -\frac{\hbar^2}{2m} \cdot \frac{\Psi_{-1} - 2\Psi_0 + \Psi_{+1}}{\|\Delta q\|^2} + \frac{V_{-1}\Psi_{-1} + 10V_0\Psi_0 + V_{+1}\Psi_{+1}}{12} \\ & \approx E \cdot \frac{\Psi_{-1} + 10\Psi_0 + \Psi_{+1}}{12} \end{aligned} \quad (5.23)$$

Initial implementations of Numerov's approach employ an iterative process based on an initial guess in the energy eigenvalue E and are sometimes referred to as *shooting methods*. However, modern approaches assure Dirichlet boundary conditions (i.e., the wavefunction outside the considered interval is zero) which enables the

implementation of Numerov's approach in the form of a matrix eigenvalue problem. Accordingly, using the matrices \mathbf{A} and \mathbf{B} as well as the diagonal matrix \mathbf{V} , containing $V(q)$ as elements, the solution can be written as

$$\left(-\frac{\hbar^2}{2m}\mathbf{A} + \mathbf{B}\mathbf{V}\right)\Psi \approx \mathbf{B}\mathbf{E}\Psi \quad (5.24)$$

Rearrangement of Eq. 5.24 leads to the matrix representation of the time-independent Schrödinger equation $\mathbf{H}\Psi = E\Psi$, with

$$\mathbf{H} = -\frac{\hbar^2}{2m}\mathbf{B}^{-1}\mathbf{A} + \mathbf{V} \quad (5.25)$$

Eigen decomposition of \mathbf{H} simultaneously yields all energy eigenvalues along the diagonal of the energy matrix \mathbf{E} , and the associated eigenvectors are collected in Ψ . As the key advantage, these grid-based approaches do not require any assumption or pre-defined building blocks (e.g., basis sets) to formulate the wavefunction Ψ . These approaches are not limited to questions in vibrational spectroscopy and similar methods have also been employed in the description of quantum tunnelling and the electronic structure of atoms and small molecular systems.

The method can be extended to arbitrary orders in the numerical derivatives by truncating the Taylor series of higher degree (e.g., \mathbf{A} and \mathbf{B} matrices with seven diagonal entries would require a Taylor series of eight degree). To predict IR intensities, the transition moment integral μ_{mn} , consisting of the respective wavefunctions of the two involved states Ψ_m and Ψ_n , as well as the transition moment operator $\hat{\mu}(q)$, has to be calculated.

$$\mu_{mn} = \int_{-\infty}^{\infty} \Psi_m \hat{\mu} \Psi_n d\tau \quad (5.26)$$

In case of infrared spectroscopy, $\hat{\mu}(q)$ equals the dipole moment μ as a function of the molecule's normal coordinates q , making infrared measurements especially sensitive on polar function. The transition dipole moment is then employed to calculate the associated oscillator strength f_{mn}

$$f_{mn} = \frac{4\pi m_e}{3e^2 \hbar} \|\mu_{mn}\|^2 \nu_{mn} \quad (5.27)$$

where m_e denotes the electron mass, e the elementary charge, and ν_{mn} the transition energy between the two states m and n . Typically, the oscillator strength is normalized to that of the fundamental mode.

Within the 1D formalism, grid-based methods are capable of inherently taking arbitrary anharmonicities into account. However, the main benefit lies in the generalization of the grid-based methods to higher dimensions, which enables the inclusion

of intermode coupling contributions in addition to the adequate treatment of anharmonic effects. Especially when combined with sparse matrix algebra routines and advanced interpolation techniques to reduce the associated computational effort, grid-based methods are capable of delivering a highly accurate description of complex quantum mechanical systems.

5.6 Applications of Anharmonic Approaches in NIR Spectroscopy

Applications of VSCF theory in investigations of mid-infrared (MIR) spectra are reasonably popular in literature [12], yet relatively few examples aimed at the NIR region can be found. Although even the basic VSCF approach is capable of predicting up to third-order overtones and combination bands, it seems that an improved description of mode correlations (e.g., by means of PT2-VSCF, or VCI) is often necessary to yield a qualitatively correct prediction of NIR modes [13]. These approaches frequently prove to be prohibitively expensive for treating larger molecules, although examples exist of successful applications of the PT2-VSCF approach to molecules counting ca. 15 atoms (e.g., malic acid), when certain approximations are assumed (e.g., the application of a quartic force field, QFF) [13]. The anharmonic frameworks featuring a robust treatment of mode correlations (i.e., VSCF-VCI, VCC) are far more expensive. The applicability of these methods may improve in the future, however.

The primary advantage of the DVPT2-GVPT2 approach is efficiency and applicability to molecules that are in the center of attention of applied NIR spectroscopy. Additionally, the GVPT2 framework fully mitigates the typical shortcoming of perturbation theory being prone to produce meaningless description of tightly coupled modes that becomes increasingly probable upon an increase of the system size. Therefore, this framework finds a remarkably widening application area in solving spectroscopic problems. A good example is a recent investigation of the NIR spectroscopic properties of melamine [14]. This compound is of key interest to analytical NIR spectroscopy in the context of food quality control. However, as in many other cases, the NIR spectrum of melamine remained shallowly understood before. Spectra calculations by means of the DVPT2 and GVPT2 methods performed at B3LYP-GD3BJ/SNST level were able to accurately reconstruct all essential NIR absorption bands of melamine (Fig. 5.7). This yielded detailed and unambiguous band assignments for the compound, enhancing the ability to interpret the essential features of the multivariate models used for analyzing melamine content. It is noteworthy that at the same time, an interesting comparison was made. The present implementation of GVPT2 includes the ability to predict three quanta transitions (i.e., second overtones, ternary combination bands). The appearance of such bands in the experimental NIR spectrum of melamine could be directly assessed. As demonstrated in Fig. 5.7, this improves the interpretability of minor bands. However, the

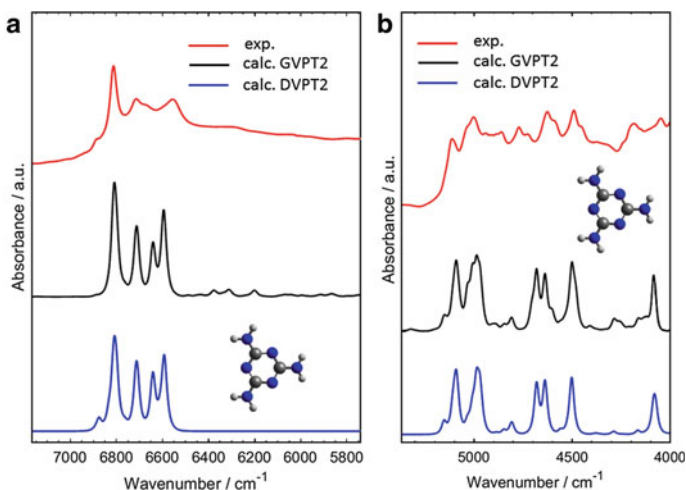


Fig. 5.7 Experimental diffuse reflectance NIR spectrum of polycrystalline melamine compared to the calculated spectra (DVPT2 and GVPT2 at B3LYP-GD3BJ/SNST level) in the regions **a** 7150–5750 cm^{-1} , and **b** 5400–4000 cm^{-1} . Reproduced from Ref. [14] under Creative Commons Attribution 4.0 International (CC BY 4.0)

spectrum of melamine in 7500–4000 cm^{-1} region is for the most part decided by two quanta transitions (i.e., first overtones and binary combinations).

Grid-based methods offer a nearly exact solution of the vibrational problem well exemplified in the case of the simplest molecular oscillator, a diatomic molecule such as HCl in gas phase. Figure 5.4 shows the associated interaction energy obtained using the accurate yet comparably expensive CCSD(T) method (i.e., coupled cluster with single, double, and perturbative triples) in conjunction with a large one-electron basis (augmented correlation consistent polarization valence quadruple zeta basis set, aug-cc-pVQZ). This bonding potential has been scanned in tight intervals of 0.005 Å in the region near the equilibrium distance $r_{\text{eq}} = 1.278$ Å. The Morse-like character of the bond showing a steep increase in the potential at low distances is clearly visible, which is lost when the harmonic approximation is applied to the region near r_{eq} (dashed line in Fig. 5.4). Solving the vibrational Schrödinger equation (in this case using Numerov’s approach) yields the vibrational wavefunctions and the associated energy eigenvalues. The respective differences between the eigenvalue of a particular excited state and the ground state correspond to the frequency measured in vibrational spectroscopy (see Table 5.2). It can be seen from the experimental values that the spacing between the energy levels is decreasing, which is adequately described when taking anharmonicity into account. The harmonic approximation on the other hand is known to perform poorly for the fundamental excitation in many cases and is effectively useless when aiming at the associated overtone vibrations. In case of a diatomic molecule, the inclusion of rotational coupling is comparably simple and can be realized by taking the changes in the moment of inertia of the molecule upon bond stretching into account. As can be seen from Table 5.2, this contribution referred to

Table 5.2 Vibrational wave numbers of the fundamental and four lowest overtones of HCl(g) in cm^{-1} obtained at CCSD(T)/aug-cc-pVQZ level via the harmonic approximation and the Numerov treatment (grid spacing 0.005 Å) with and without the rotational Watson potential, respectively. It can be seen that an explicit inclusion of anharmonic effects to the vibrational excitations is vital to obtain reliable estimates for higher excitations. Rotational coupling on the other hand only plays a minor role in this example

Transition	Harmonic	Numerov	Numerov–Watson	Experimental ^a
0 → 1	2990.2	2885.4	2885.5	2885.9
0 → 2	5980.3	5667.6	5667.7	5668.0
0 → 3	8970.5	8347.1	8347.3	8347.0
0 → 4	11960.6	10924.1	10924.4	10923.1
0 → 5	14950.8	13398.9	13399.2	13396.5

^aRef. [4], p. 193

as Watson potential has only a minor influence on the vibrational wave numbers in the case of HCl(g).

Grid-based approaches yield highly accurate solutions of the vibrational problem, but presently their applicability to larger molecules is limited because of their excessive cost. However, for studies of such systems, they remain effective in selective treatments of a particular mode of interest (one-dimensional grid). For example, in several cases, these methods have been used for an accurate prediction of the OH stretching overtone band [15, 16]. This strong band is highly sensitive to the chemical environment and is an important spectral feature frequently investigated by NIR spectroscopy (refer to the Chapter *NIR spectroscopy in physical chemistry*). Therefore, accurate calculations of the frequency and intensity is essential, e.g., for obtaining detailed insights into solvent effects [15]. On the other hand, grid-based methods may be used to improve theoretical NIR spectra obtained with different methods. Although in principle, the VPT2 approach is applicable to Morse-like potentials, in some cases, it provides unreliable results. For instance, the $2\nu(\text{OH})$ peak delivers a relatively easily accessible information on the conformational state of hydroxyl bearing molecules. In the case of cyclohexanol, it consists of two components due to the two major conformers. The wavenumber difference $\Delta\nu$ between these components was found to be 27 cm^{-1} in the experimental spectrum. A recent study reported a strongly underestimated VPT2 frequency for the major conformer, resulting in the splitting of the predicted peak ($\Delta\nu^{\text{VPT2}} = 260 \text{ cm}^{-1}$). However, the application of a grid-based approach yielded a much more reliable value of 30 cm^{-1} [16].

Further, grid-based methods are applicable universally, including low-lying torsional modes that are typically challenging for generalized methods (e.g., VSCF, VPT2). The highest potential for future advances is associated with multidimensional grid-based approaches covering full vibrational configuration of the system. Presently, state-of-the-art enables treatment of triatomic linear molecules (e.g., CO_2 , BeH_2 , HCN), which requires a four-dimensional grid [17]. In such case, the entirety of mode coupling is explicitly included and the predicted frequencies deviate by less than 1% from experimental data [17]. Feasible implementation of higher-dimensional

grid-based approaches should enable nearly exact prediction of NIR spectra of more complex molecules, which will form an essential progress in our understanding of NIR spectroscopy.

5.7 Summary and Future Prospects

Practical applications of the methods of quantum chemistry in NIR spectroscopy have mostly been limited by their computational cost. In the recent decade, a remarkable rise in practical applications of theoretical calculations in NIR spectroscopy was observed. This resulted from the development of quantum-based approaches and their implementation, as well as from the progress in technology resulting in a continuous increase in computational capacities. This allows for the anticipation of further advances in the forthcoming years, and a twofold development can presently be witnessed in this field. Firstly, studies of NIR spectra of increasingly complex systems are becoming feasible. This opens new opportunities, as the complexity of NIR spectra tends to scale steeply with the system size, and their interpretability by conventional spectroscopic methods is limited. Secondly, highly accurate grid-based methods are capable of yielding nearly exact results. At the moment, computational complexity of grid-based methods limits their applicability to few-atom systems. Nevertheless, they form an essential aid at the moment, as the established ‘universal’ anharmonic frameworks (e.g., VSCF, VPT2) have primarily been formulated with efficiency in mind. This could only be achieved through various approximations affecting their robustness and accuracy. Grid-based methods demonstrate their usefulness in directly correcting VPT2 results for a few selected modes of interest; this even applies for seemingly manageable modes such as OH stretching vibrations. As the primary factors limiting the applicability of computational chemistry in NIR spectroscopy are consistently challenged, a general conclusion may be drawn that in the next decade a markedly rapid expansion of NIR studies utilizing methods of quantum chemistry will be observed.

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