Adaptive Expansions of the Vibrational Hamiltonian in Curvilinear Coordinates

(Adaptive Entwicklungen des Schwingungshamiltonoperators in krummlinigen Koordinaten)

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unendlicher Raum
Komplexität zermürbend
dennoch Konvergenz

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Abstract

Linear and non-linear spectroscopic experiments in the infrared spectral range provide insight into dynamical properties of molecules, however, in an indirect way. The computation of spectra complements experiments and yields a thorough understanding of the underlying processes. For a rigorous simulation of molecular vibrations a quantum mechanical description of the molecular system is inevitable. To this end, the system Hamiltonian and the dipole operator must be formulated such that they can be represented efficiently by numerical methods. Otherwise, the *curse of dimensionality* prevents the simulation of even moderately sized systems by standard numerical approaches.

A nuclear motion Hamiltonian in arbitrary curvilinear coordinates was derived, from which a vibrational Hamiltonian can be deduced. It is general w. r. t. vibrational coordinates and, hence, is not restricted to certain molecular systems or coordinates.

The potential energy surface, serving as potential for the vibrational Hamiltonian, is a high dimensional scalar field. Decomposed into a many-body expansion, approximate potential energy surfaces can be constructed from low dimensional terms. The convergence of the expansion depends strongly on the coordinates, which is why curvilinear coordinates are favourable. On the contrary, curvilinear coordinates cause the Jacobian to be non-linear. By employing the hierarchical expansion of the kinetic energy operator, the coordinate dependent terms of the kinetic energy operator, such as the metric tensor or the pseudopotential, can be expanded to arbitrary precision in principle. Adaptively truncated expansions allow for approximations with controlled precision and enable applications to larger molecular systems.

To handle the many-body expansions for the potential energy surface and the hierarchical expansion of the kinetic energy operator in a numerically efficient way, adaptive sparse grids were introduced. Sparse grid basis-splines were modified so that they cooperate well with many-body expansions. Based on the vibrational self-consistent field and vibrational configuration interaction methods, adaption criteria were developed that allow for approximate error control. Hence, the complete system Hamiltonian can be tailored to specific molecules. Application to a test set of molecules demonstrated the efficiency and accuracy of the approach.

In conclusion, the combination of curvilinear coordinates with modern numerical techniques like adaptive sparse grids enable the quantum mechanical simulation of molecular vibrations in a black box way for moderately sized molecules.

Zusammenfassung (Abstract in German)

Lineare und nichtlineare spektroskopische Experimente im infraroten Spektralbereich gewähren Einsicht in die dynamischen Eigenschaften von Molekülen, allerdings indirekt. Die Berechnung von Spektren ergänzt die Experimente und ermöglicht ein tiefgreifendes Verständnis der zugrundeliegenden Prozesse. Für eine präzise Simulation molekularer Schwingungen ist eine quantenmechanische Beschreibung des molekularen Systems unverzichtbar. Zu diesem Zweck muss der Systemhamiltonoperator und der Dipoloperator so formuliert werden, dass sie mit Hilfe numerischer Methoden effizient dargestellt werden können. Andernfalls verhindert der *Fluch der Dimensionalität* bereits die Simulation von Systemen moderater Größe mittels numerischer Standardmethoden.

Ein Kernbewegungshamiltonoperator in beliebigen krummlinigen Koordinaten wurde hergeleitet aus dem ein Schwingungshamiltonoperator abgeleitet werden kann. Er ist generell bezüglich Schwingungskoordinaten und daher nicht auf bestimmte molekulare Systeme oder Koordinaten beschränkt.

Die Potentialenergiefläche, die als Potential im Schwingungshamiltonoperator dient, ist ein hochdimensionales Skalarfeld. Zerlegt in eine Mehrteilchenentwicklung können genäherte Potentialenergieflächen aus niedrig dimensionalen Termen konstruiert werden. Die Konvergenz der Entwicklung hängt stark von den Koordinaten ab, daher sind krummlinige Koordinaten vorzuziehen. Auf der anderen Seite wird die Jacobimatrix durch krummlinige Koordinaten nichtlinear. Durch die hierarchische Entwicklung des kinetischen Energieoperators können die koordinatenabhängingen Terme des kinetischen Energieoperators, wie der metrische Tensor oder das Pseudopotential, im Prinzip bis zu beliebiger Genauigkeit entwickelt werden. Adaptiv abgeschnittene Entwicklungen erlauben Näherungen mit kontrollierter Genauigkeit und die Anwendung auf größere molekulare Systeme.

Um Mehrteilchenentwicklungen für die Potentialenergiefläche und die hierarchische Entwicklung des kinetischen Energieoperators auf numerisch effiziente Art und Weise zu handhaben, wurden adaptive dünne Gitter eingeführt. Basispolynomzüge für dünne Gitter wurden so modifiziert, dass sie die Anforderungen der Mehrteilchenentwicklungen erfüllen. Basierend auf der Methode des selbstkonsistenten Feldes und der Methode der Konfigurationswechselwirkung wurden Adaptionskriterien entwickelt die eine approximative Fehlerkontrolle liefern. Daher kann der vollständige Systemhamiltonoperator an ein spezifisches molekulares System angepasst werden. Anwendung auf einen Testsatz an Molekülen zeigte die Effizienz und Genauigkeit des Ansatzes.

Abschließend kann festgestellt werden, dass die Kombination von krummlinigen Koordinaten mit modernen numerischen Techniken, wie dünnen Gittern, die quantenmechanische Simulation von molekularen Schwingungen für Moleküle moderater Größe erlaubt, ohne dass der Anwender nähere Kenntnis der Methode benötigt.

1. Introduction

This thesis is a publication based dissertation implying that original research was published in international scientific journals. Summaries of the published articles are provided, although the focus of this thesis is to discuss theoretical methods on which results are based and to relate these results to relevant literature. In line with publication practice in international journals, citations are omitted if references are made to general knowledge in the current field of study. It should be emphasized that the purpose of chapters 1 and 2 is only to give an overview on existing methods and theories and not to present any new developments.

Quantum mechanics is fundamental to theoretical chemistry and is employed to study molecular properties that depend on wave functions (WFs) describing electrons and nuclei. Although these electronic and nuclear properties cannot be studied independently in general, the famous Born-Oppenheimer approximation[1,2] yields a separation into two independent subproblems and remains valid as long as the coupling of different electronic states is not too large. It is assumed that the Born-Oppenheimer approximation can be safely applied in the context of this thesis. Non-Born-Oppenheimer effects, e. g. being present at conical intersections,[3] are not considered. Consequently, two subproblems, one Schrödigner equation (SE) for the electrons and one for the nuclei, arise.

The electronic SE depends parametrically on the positions of the nuclei and yields one point on the potential energy surface (PES) when solved for an eigenvalue.[*] Theoretical methods that allow for the pointwise evaluation of the PES are referred to as electronic-structure methods. They may be categorized into density functional theory (DFT)[4] and WF based methods.[2,5] Both, DFT and WF based methods, are subjects of ongoing research which aims at improved accuracy of energy eigenvalues[6–9] and efficiency w. r. t. molecular size.[10,11]

When studying the dynamical properties of nuclei, the existence of an accurate electronic-structure method, that can evaluate the PES efficiently, is a prerequisite. The PES serves either as potential energy operator in the nuclear SE or, if nuclei are approximated by classical particles, as potential to be explored via classical trajectories. Depending on the observables of interest, classical mechanics can give reasonable results in a computationally efficient way.[12] However, if high accuracy is required, tunneling, of e. g. protons, is relevant, or observables that depend on phase relations of WFs are of interest, a quantum mechanical description of the nuclei is inevitable. This motivates the need for efficient quantum mechanical methods to solve the nuclear SE. Their development is furthermore justified by the accuracy and efficiency of state of the art electronic-structure methods, which enable the exploration of PESs for molecules of moderate size,[13–15] yet remain a bottleneck for larger systems.

[*]For bound systems there are, in general, many eigenvalues, each one corresponding to a certain PES. In the current context though, it is sufficient to consider the electronic ground state as PES.

Hence, quantum mechanical methods to solve the nuclear SE must be designed in such a way that the required amount of PES evaluations is kept as small as possible. This may be achieved by focusing on two major aspects. One is the mathematical formulation of the nuclear SE. Specifically, the Hamiltonian must be derived in such a way that numerical methods can be employed to yield reliable approximate solutions. The selection and development of the numerical approaches itself are the second aspect. That means finding efficient decompositions, grids, and bases to expand terms of the Hamiltonian and the WF. These two aspects are, however, not independent.

Coordinates, or variables equivalently, for the nuclear motions are important in several ways. They are not only fundamental to the formulation of the Hamiltonian but also influence the convergence of numerical approaches, e. g. of PES decompositions. Hence, it is important to find a *good* set of coordinates which Jacobi concisely formulated in 1866 already, while employing curvilinear coordinates to study dynamics of many-particle systems.

"Die Hauptschwierigkeit bei der Integration gegebener Differentialgleichungen scheint in der Einführung der richtigen Variablen zu bestehen, zu deren Auffindung es keine allgemeine Regel giebt."[*16]

This quote of Jacobi's Lectures on Dynamics highlights not only the importance of coordinates but also the difficulty to find them.

Coordinates for the nuclear motion Hamiltonian should separate rigid body transformations, i. e. translation and rotation, from internal motions. This is helpful for several reasons. The PES is invariant under these transformations, translational motions of the whole molecule can be separated exactly, and rotations can be partially decoupled (exactly for the rotational ground state). The specific definition of vibrational coordinates for internal motions[**] is more subtle. Ideally, the coordinates should yield a Hamiltonian that can be decomposed into a small number of low dimensional terms. If a certain coordinate set has the requested effect is, however, hard to forecast.

While coordinates may improve the convergence of the PES expansion, they can simultaneously complicate the expression for the kinetic energy operator (KEO). As soon as any of the coordinates are curved, which rotational coordinates always are and vibrational coordinates may be, the KEO involves a coordinate dependent metric tensor, its derivatives, and the Jacobian determinant.[17] In general, there is always a trade-off between couplings in the PES and kinematic couplings in the KEO.[18]

A specific form of decomposition, which is well-established for the PES, is the many-body expansion (MBE),[19,20] sometimes also called high dimensional model representation.[21] Thereby, the high dimensional PES is expanded in terms of sums of lower dimensional functions. It does, however, not imply any specific representation of the expansion terms. Thus, further numerical techniques, like grid based methods, are required to obtain an explicit expansion.

The MBE approach can be also applied to terms of the KEO. If rectilinear vibrational coordinates are employed, it is sufficient to expand the non-linear ro-vibrational coupling terms.[22]

[*] the quote may be translated as: "The main difficulty when integrating given differential equations seems to lie in the introduction of proper variables, for whose finding there is no general rule."

[**] In quantum mechanics, there is no clear separation between internal motions and vibrations, which is why these terms are used interchangeably.

In the general case of curvilinear vibrational coordinates, all terms can be expanded as MBEs yielding the hierarchical expansion of the kinetic energy (HEKE).[23–26] For small molecules the non-linear terms of the HEKE may be evaluated numerically directly[27] or the KEO can even be derived analytically.[28–34] For a certain kind of coordinates, polyspherical coordinates, analytic KEOs can also be derived for larger systems via an automated procedure.[35]

After having expanded all parts of the Hamiltonian, the computation of observables is the next step. Most commonly, fundamental excitation energies, determined from eigenvalues, are compared to experimental values from linear absorption infrared (IR) spectra. Alternatively, the spectrum can be computed via the dipole auto-correlation function from quantum dynamics[36] or approximated from classical dynamics.[37] However, for a rigorous simulation of linear absorption spectra as well as non-linear multidimensional spectra, a quantum description of the system is inevitable. Especially 2D or 3D spectra can comprise complicated peak patterns.[38–40] While they contain detailed information about coupling of vibrational modes in principle, understanding them without help of calculated spectra can be tough. To obtain IR spectra from first principles, the Hamiltonian and dipole operator for the system must be computed accurately for all relevant states. These states either influence the spectrum directly through an absorption band or indirectly through coupling to optically active states. Once adequate representations of the Hamiltonian and dipole operator are constructed they can be employed for the computation of response functions or spectra.[40]

This thesis presents approaches focusing on the efficient expansions of the vibrational Hamiltonian and dipole operator. The vibrational Hamiltonian restricts the nuclear motion Hamiltonian to the rotational ground state and omits the exactly separated (trivial) translational part. Note that the vibrational Hamiltonian does not exclude large amplitude motions. Thus, it is sometimes also called internal motion Hamiltonian.[41]

To this end, a KEO in general curvilinear coordinates was derived, which allows for a unified treatment of KEOs in arbitrary rectilinear and curvilinear coordinates.[42] Thereby it was shown how well-known KEOs for rectilinear or internal curvilinear coordinates are related and how more general non-internal curvilinear coordinates can be employed. This formulation of the KEO enables a general implementation of the HEKE operator. A discretized representation of the Hamiltonian is obtained from the combination of the vibrational self-consistent field (VSCF)[23,43,44] method with the vibrational configuration interaction (VCI) method.[45] Both cooperate well with the HEKE and PES-MBE.[46]

As stated above, a MBE does not specify how individual terms are represented. Instead of employing simple polynomials or regular grids, a powerful numerical method, sparse grids (SGs), was introduced to this problem.[46] Being well-established for interpolation and integration,[47,48] SGs have not been employed in the context of quantum mechanics before. General SGs were modified to cooperate with MBEs. Hence, the Hamiltonian can be tailored to specific systems via adaptively expanding the PES and KEO in terms of MBEs and SGs. To this end, refinement criteria, based on VSCF and VCI states, were developed. This gives distinct control over the accuracy of the fully adaptive Hamiltonian and yields a unified description of the KEO and the PES.[46]

The combination of coordinates, leading to rapidly converging HEKE and PES-MBEs with adaptive SGs yields an efficient technique to tailor the vibrational Hamiltonian to a specific system and observable. With mild assumptions about the physical properties, such as moderate coupling strength and single reference character of the WF, the VSCF/VCI method can be straightforwardly applied to molecules of moderate size.[46]

Concepts, fundamental to understand the route to a vibrational spectrum from first principles, are discussed in the subsequent chapter 2. It includes a brief derivation of the vibrational Hamiltonian in section 2.1 building the basis for the theory. Furthermore, the famous harmonic approximation (section 2.2), as well as the VSCF (section 2.4) and VCI (section 2.5) methods are discussed, which opens the way to a theoretical method yielding vibrational states of arbitrary precision in principle. Apart from these considerations of numerical aspects, curvilinear coordinates, applicable to vibrational problems, are introduced in section 2.6. The route towards spectra, focusing on the aspects relevant for the adaption of the Hamiltonian and dipole operator, is outlined in section 2.7. The following chapter 3 contains summaries of the articles this thesis is based on and finally, conclusions are drawn in the last chapter 4.

2. From the Vibrational Hamiltonian to Spectra

The vibrational Hamiltonian can be divided into the KEO and the PES. To obtain a vibrational Hamiltonian the nuclear motion Hamiltonian must be derived in such a way that translational motions are separated exactly and that the rotational ground state can be integrated out. This is, however, only possible if coordinates are chosen appropriately and if angular momenta for the rotational motions are employed. A sketch of such a derivation is given in section 2.1 and can be found in detail in Ref. 42.

Approximate solutions, i. e. eigenstates, of the SE that employs the vibrational Hamiltonian can be computed via various methods. The harmonic approximation is the crudest, but also most prominent one, and yields an analytically solvable eigenproblem in the normal mode basis. Although the limited accuracy of the harmonic frequencies is not sufficient in many cases, the coordinates that result from the harmonic approximation are often employed by more accurate methods. That is why the harmonic approximation is subject of section 2.2.

More accurate vibrational states can be obtained from a vibrational self-consistent field (VSCF) calculation. In this mean-field approach the high dimensional Hamiltonian is decoupled to a set of one dimensional effective Hamiltonians. Approximate states can be generated from these in an iterative way until self-consistency is reached. The VSCF theory is outlined in section 2.4. Since the accuracy is still limited by the mean-field, the resulting states often just serve as basis for a subsequent vibrational configuration interaction (VCI) calculation, which can give results of arbitrary accuracy in principle. This allows for a formal definition of the exact solution in section 2.5. In practice though, results are limited by computational resources.

Perturbative approaches,[49,50] as alternative to the VCI method, are excluded from the following sections for three reasons: first, the assumption that the perturbation is small is often not valid for at least some vibrational states, second, convergence is not guaranteed and leads to unpredictable error behaviour for finite orders of perturbation theory and, third, numerical instabilities can arise from the high densities of states.

The Hamiltonian and the formulation of the VSCF and VCI methods is completely general w. r. t. the definition of vibrational (curvilinear) coordinates. It is the coordinate system, which decides if the VSCF and VCI approach leads to reliable results in an efficient way. Hence, construction schemes for vibrational coordinates, like the prominent internal valence coordinates are discussed in section 2.6.

All these sections summarize the basic theory on vibrational states, which was employed and further developed during the work of this thesis. There exist of course various alternative approaches and variations to the presented methods and theories. Where necessary, references to alternative approaches are made, reviewing all approaches exhaustively is, however, beyond the scope of this thesis.

2.1. Vibrational Hamiltonian

The starting point for the derivation of the vibrational Hamiltonian is the classical kinetic energy for a free system of N particles,

$$T = \frac{1}{2} m_a \mathbf{v}_a^2, \tag{2.1}$$

confined to non-linear geometries. The constant particle masses m_a and velocities $\mathbf{v}_a$ ($\mathbf{v}_a^2 = \|\mathbf{v}_a\|_2^2$) are given in a frame rotating with angular velocity $\boldsymbol{\omega}$ and moving with the center of mass $\mathbf{R}$ by

$$\mathbf{v}_a = \dot{\mathbf{R}} + \boldsymbol{\omega} \times \mathbf{r}_a + \dot{\mathbf{r}}_a. \tag{2.2}$$

In these equations, and the following, particles are indexed by a and Einsteins sum convention is used. The positions of the particles w. r. t. the rotating frame $\mathbf{r}_a$ are parametrized by $n = 3N - 6$ variables s_i,

$$\mathbf{r}_a = \mathbf{r}_a(s_1, s_2, \ldots). \tag{2.3}$$

This yields velocities

$$\dot{\mathbf{r}}_a = \frac{\partial \mathbf{r}_a}{\partial s_j} \dot{s}_j = \mathbf{A}_{aj} \dot{s}_j. \tag{2.4}$$

With the matrices

$$Z_{ij} = m_a \left(\mathbf{r}_a \times \mathbf{A}_{aj}\right)_i, \tag{2.5}$$

$$G_{ij}^{-1} = \mathbf{A}_{ai}^\top m_a \mathbf{A}_{aj}, \tag{2.6}$$

and

$$\boldsymbol{\mu} = \left(\mathbf{I} - \mathbf{Z}\mathbf{G}\mathbf{Z}^\top\right)^{-1}, \tag{2.7}$$

where $\mathbf{I}$ is the moment of inertia tensor, the classical Hamiltonian is derived via differentiation of the Lagrangian $L = T - V$. The function V is the PES, which is invariant under translation and rotation for a free system of particles.

Definition of vibrational angular momenta,

$$\boldsymbol{\pi} = \mathbf{Z}\mathbf{G}\mathbf{p}, \tag{2.8}$$

with momenta $\mathbf{p}$ conjugate to coordinates $\mathbf{s}$, yields the Hamiltonian

$$H = \frac{1}{2} \left(\frac{1}{m} \mathbf{P}^2 + (\mathbf{J} - \boldsymbol{\pi})^\top \boldsymbol{\mu} (\mathbf{J} - \boldsymbol{\pi}) + \mathbf{p}^\top \mathbf{G} \mathbf{p} \right) + V, \tag{2.9}$$

in which $\mathbf{J}$ are angular momenta and $\mathbf{P}$ are linear momenta conjugate to $\mathbf{R}$. The total mass of the system is denoted by m. Since H can be written as a quadratic form in the momenta, the quantum mechanical Hamiltonian is, following Podolsky,[17] given by

$$H = \frac{1}{2} g^{-1/4} \left(\frac{g^{1/2}}{m} \mathbf{P}^2 + (\mathbf{J} - \boldsymbol{\pi})^\top g^{1/2} \boldsymbol{\mu} (\mathbf{J} - \boldsymbol{\pi}) + \mathbf{p}^\top g^{1/2} \mathbf{G} \mathbf{p} \right) g^{-1/4} + V. \tag{2.10}$$

The determinant g factors into

$$g = \det(\boldsymbol{\mu}^{-1}) \det(\mathbf{G}^{-1}), \tag{2.11}$$

the operators $\mathbf{J}$ are body fixed angular momentum operators, and the momenta $\mathbf{P}$ and $\mathbf{p}$ are the well known quantum mechanical momentum operators. The dependence on the determinant g may be separated into a pseudopotential[51] by application of differentiation rules. The formulation of the Hamiltonian of Eq. (2.10) is valid under the scalar product employing the volume element

$$dv = dR_1 \, dR_2 \, dR_3 \, d\boldsymbol{\Omega} \, ds_1 \, ds_2 \, \dots \, ds_n, \tag{2.12}$$

where $d\boldsymbol{\Omega}$ is the volume element for any specific choice of rotational coordinates.

The Hamiltonian H reduces directly to the Wilson Howard Hamiltonian,[52] if rectilinear normal modes are employed. In this case $\mathbf{G}$ reduces to the identity matrix and the elements of $\mathbf{Z}$ become linear functions of the coordinates involving the Coriolis coupling constants. Vibrational coordinates are internal if they are invariant under translation and rotation, or equivalently if

$$\mathbf{r}_a \times \mathbf{A}_{ai} = \mathbf{0} \tag{2.13}$$

is fulfilled globally for all values of $\mathbf{s}$. In this case, it can be shown[42] that H can be transformed into

$$\tilde{H} = \frac{1}{2} g^{-1/4} \left(\frac{g^{1/2}}{m} \mathbf{P}^2 + \left(\mathbf{J}^\top \mathbf{C}_a - \mathbf{p}^\top \mathbf{B}_a \right) g^{1/2} m_a^{-1} \left(\mathbf{C}_a^\top \mathbf{J} - \mathbf{B}_a^\top \mathbf{p} \right) \right) g^{-1/4} + V. \tag{2.14}$$

The matrices $\mathbf{B}_a$ and $\mathbf{C}_a$ are defined by

$$\mathbf{B}_a = \begin{pmatrix} \frac{\partial s_1}{\partial \mathbf{r}_a} & \frac{\partial s_2}{\partial \mathbf{r}_a} & \dots & \frac{\partial s_n}{\partial \mathbf{r}_a} \end{pmatrix}^\top \tag{2.15}$$

and

$$\mathbf{C}_a = \begin{pmatrix} \frac{\partial \theta_x}{\partial \mathbf{r}_a} & \frac{\partial \theta_y}{\partial \mathbf{r}_a} & \frac{\partial \theta_z}{\partial \mathbf{r}_a} \end{pmatrix}^\top, \tag{2.16}$$

respectively. Differentiation w. r. t. $\mathbf{r}_a$ is to be interpreted elementwise, which yields the second dimension of the matrices $\mathbf{B}_a$ and $\mathbf{C}_a$. The symbols θ_x, θ_y and θ_z denote rotations around the three axes of the rotating frame. Both, $\mathbf{B}_a$ and $\mathbf{C}_a$, are functions of the vibrational coordinates only. However, the explicit form of $\mathbf{C}_a$ depends on the definition of the rotating frame. The Hamiltonian $\tilde{H}$ (Eq. (2.14)) is a compact and general formulation of the Hamiltonian for internal vibrational coordinates.[41,53–55]

In many cases one is interested in vibrational motions only and therefore considers non-rotating ($J = 0$) vibrational states. As long as the rotational ground state is explicitly included in the calculations, any total Hamiltonian can be chosen. It is preferable though, to derive a purely vibrational $J = 0$ Hamiltonian which yields exactly these vibrational states without explicit treatment of the rotational wave function.[41] All quantities in Eq. (2.10) and Eq. (2.14), except $\mathbf{J}$, are functions of the vibrational coordinates $\mathbf{s}$ only. Hence, the $J = 0$ vibrational Hamiltonian $\mathcal{H}$ for arbitrary coordinates reduces to

$$\begin{aligned}\mathcal{H} &= \frac{1}{2} g^{-1/4} \mathbf{p}^\top g^{1/2} \left(\mathbf{G}\mathbf{Z}^\top \boldsymbol{\mu} \mathbf{Z}\mathbf{G} + \mathbf{G} \right) \mathbf{p} g^{-1/4} + V \\ &= \frac{1}{2} g^{-1/4} \mathbf{p}^\top g^{1/2} \boldsymbol{\mathcal{G}} \mathbf{p} g^{-1/4} + V, \end{aligned} \tag{2.17}$$

where $\boldsymbol{\mathcal{G}}$ was defined implicitly. The Hamiltonian may be rearranged to a different form

$$\mathcal{H} = \frac{1}{2} \mathbf{p}^\top \boldsymbol{\mathcal{G}} \mathbf{p} + V_g + V, \tag{2.18}$$

where all terms of the KEO that do not involve a derivative of the wave function are moved into the pseudopotential V_g.[42,51] For internal coordinates a simpler expression may be employed to compute $\boldsymbol{\mathcal{G}}$,

$$\boldsymbol{\mathcal{G}} = \mathbf{B}_a m_a^{-1} \mathbf{B}_a^\top, \tag{2.19}$$

and is, in the case of internal valence coordinates, commonly called Wilson G Matrix.[56] It is noteworthy, that the $J = 0$ Hamiltonian is independent of the definition of the rotating frame[41] in the case of internal coordinates, while this is not the case for general coordinates.

An explicit expression for the PES cannot be given. To handle V in an efficient way it is common to decompose it in a MBE around a reference geometry $\mathbf{s}^{\text{ref}}$. Formally the MBE is given by

$$V(\mathbf{s}) = V^{(0)} + \sum_{i}^{n} V_i^{(1)}(s_i) + \sum_{i>j}^{n} V_{ij}^{(2)}(s_i, s_j) \ldots + V_{12\ldots n}^{(n)}(s_1, s_2, \ldots, s_n). \tag{2.20}$$

This decomposition is exact if all terms up to order n are included. Truncating this expansion results in an approximate PES, whose accuracy depends on the truncation scheme, on the underlying coordinates $\mathbf{s}$, and on the reference geometry $\mathbf{s}^{\text{ref}}$. Each k dimensional expansion term is defined in the subspace spanned by k coordinates. It can be evaluated by setting all other coordinates to the value given by $\mathbf{s}^{\text{ref}}$ and by subtracting all lower dimensional expansion terms included in the subspace. Hence, the zeroth order term $V^{(0)}$ is a scalar, first order terms are one dimensional functions and so forth.

The explicit mathematical form of each expansion term, i. e. a form which can be integrated in the end, remains unspecified at this point. A special case of MBE is the Taylor series, in which V may be expanded. If truncated to second order, this yields the harmonic approximation (see section 2.2).

In general, $\mathcal{G}_{ij}$ and V_g are functions of $\mathbf{s}$ as well and the same MBE approach can be applied. This leads to the hierarchical expansion of the kinetic energy (HEKE) operator.[23–26]

2.2. Harmonic Approximation

It was shown in section 2.1, that both, KEO and PES, are high dimensional operators that cannot be expressed by simple analytical expressions in general. However, under the assumption that vibrational amplitudes are small, KEO and PES can be approximated by analytic model operators yielding a Hamiltonian, for which eigenvalues and eigenfunctions are known.

To obtain the harmonic model Hamiltonian, all coordinate dependent terms of the exact vibrational Hamiltonian $\mathcal{H}$ from Eq. (2.17), specifically $\boldsymbol{\mathcal{G}}$, g, and V, can be expanded as Taylor series at a certain geometry $\mathbf{r}^0 = \mathbf{r}(\mathbf{s}^{\mathrm{ref}})$. Truncating the KEO terms g and $\boldsymbol{\mathcal{G}}$ after zeroth order and the PES after second order yields

$$h = \frac{1}{2} g|_0^{-1/4}\, \mathbf{p}^\top g|_0^{1/2}\, \boldsymbol{\mathcal{G}}|_0\, \mathbf{p}\, g|_0^{-1/4} + \left(V|_0 + \left.\frac{\partial V}{\partial \mathbf{r}_a}\right|_0 \mathbf{r}_a + \frac{1}{2}\mathbf{r}_a^\top \left.\frac{\partial^2 V}{\partial \mathbf{r}_a \partial \mathbf{r}_b}\right|_0 \mathbf{r}_b \right). \tag{2.21}$$

Since $g|_0$ is constant it commutes with $\mathbf{p}$ and cancels out. The term $V|_0$ is a global offset to all energies and may be taken as reference. Furthermore, $\mathbf{r}^0$ can be restricted to minima of the PES, thereby also fixing $\mathbf{s}^{\mathrm{ref}}$, which is reasonable since bound states corresponding to small amplitude vibrations are considered. In this case, the gradient of V vanishes and with the definition of the Hessian $\mathbf{F}_{ab}$ of V

$$h = \frac{1}{2}\mathbf{p}^\top \boldsymbol{\mathcal{G}}|_0\, \mathbf{p} + \frac{1}{2}\mathbf{r}_a^\top\, \mathbf{F}_{ab}|_0\, \mathbf{r}_b \tag{2.22}$$

is obtained. As of yet, the Hamiltonian of Eq. (2.22) depends on some unspecified vibrational coordinates $\mathbf{s}$, through the definition of $\mathbf{p}$, and the rotating frame coordinates $\mathbf{r}_a$. A certain set of specific vibrational coordinates $\mathbf{s}$ is given by the rectilinear normal modes $\mathbf{q}$, formally defined by

$$q_i = \mathbf{Q}_{ai}^\top m_a^{1/2} \mathbf{r}_a. \tag{2.23}$$

The linear transformation $\mathbf{Q}_{ai}$ has the properties

$$\mathbf{Q}_{ai}^\top m_a^{-1/2} \mathbf{F}_{ab}|_0 m_b^{-1/2} \mathbf{Q}_{bj} = f_i \delta_{ij} \tag{2.24}$$

and

$$\mathbf{Q}_{ai}^\top \mathbf{Q}_{aj} = \delta_{ij}. \tag{2.25}$$

If the normal modes are furthermore restricted to be locally orthogonal to the rotational subspace,*

$$\mathbf{Z}|_0 = \mathbf{0}, \tag{2.26}$$

a very simple form of the Hamiltonian h is obtained,

$$h = \sum_{i=1}^{n} h_i = \sum_{i=1}^{n} -\frac{1}{2}\frac{\partial^2}{\partial q_i^2} + \frac{1}{2} f_i q_i^2. \tag{2.27}$$

*Vibrational coordinates that are locally orthogonal to translations and rotations are simply determined by forming $\mathbf{Q}$ from all eigenvectors of $m_a^{-1/2}\mathbf{F}_{ab}|_0 m_b^{-1/2}$ that correspond to non-zero eigenvalues. This is valid because the null space of $m_a^{-1/2}\mathbf{F}_{ab}|_0 m_b^{-1/2}$ is the tangent space of translations and rotations at $\mathbf{r}^0$.

Since there is no coupling between the one dimensional Hamiltonians h_i, the n dimensional SE separates into n one dimensional harmonic oscillator SEs

$$h_i\,\psi_i^{(k)} = \varepsilon_i^{(k)}\,\psi_i^{(k)}, \tag{2.28}$$

whose eigenfunctions are well-known

$$\psi_i^{(k)} = \left(\frac{\omega_i}{\pi}\right)^{1/4} \frac{1}{\sqrt{2^k k!}}\,\mathscr{H}_k(q_i\sqrt{\omega_i})\;e^{-\frac{q_i^2\omega_i}{2}} \qquad k \in \{0,1,2,\ldots\}\,. \tag{2.29}$$

The wave function $\psi_i^{(k)}$ is expressed in terms of the Hermite polynomial $\mathscr{H}_k$ of degree k and the harmonic frequency $\omega_i = \sqrt{f_i}$. The spectrum of each one dimensional Hamiltonian is given by the equidistantly spaced eigenvalues

$$\varepsilon_i^{(k)} = \omega_i\left(k + \frac{1}{2}\right) \qquad k \in \{0,1,2,\ldots\}\,. \tag{2.30}$$

The total spectrum results from all combinations of k values for each mode.

In summary, the harmonic model Hamiltonian is obtained from the first non-vanishing Taylor series terms of $\boldsymbol{\mathcal{G}}$, $\boldsymbol{g}$, and V. This simplifies $\boldsymbol{\mathcal{G}}$ and $\boldsymbol{g}$ to constants and V to a quadratic form. Hence, from a computational perspective the major costs arise from the calculation of the Hessian and its diagonalization. In the end, the spectrum is completely determined by the eigenvalues of the mass-weighted Hessian f_i, which implicitly depend on the geometry $\mathbf{r}^0$ and the masses m_a.

Unfortunately, the harmonic approximation has very limited accuracy. It may suffice for the ground state energy and fundamental excitations for rigid molecules. Many molecules, however, exhibit strong anharmonicities, which especially impact excited states, and hence more accurate methods are required to obtain reliable results. Nevertheless, normal modes may still be employed as coordinates in more elaborate approaches, since they do decouple the vibrational Hamiltonian at least approximately. This is detailed in section 2.6.

2.3. Basis Set Expansions

Instead of approximating the Hamiltonian to obtain a form which can be solved analytically, the Hamiltonian as well as the eigenfunctions may be expanded in bases. In practice, the solutions are still approximate due to truncation in finite bases but, in principle, can be refined to arbitrary precision by increasing the size of these bases. Computational resources and system size finally limit the accuracy of basis set expansions of Hamiltonian and wave function.

The SE in arbitrary vibrational coordinates

$$\mathcal{H}(\mathbf{s})\Psi^{(k)}(\mathbf{s}) = E^{(k)}\Psi^{(k)}(\mathbf{s}) \tag{2.31}$$

can be transformed to a discrete problem by expanding the wave function in a basis formed by basis functions $\Phi_i(\mathbf{s})$.

$$\Psi^{(k)}(\mathbf{s}) = C_i^{(k)}\Phi_i(\mathbf{s}). \tag{2.32}$$

Projecting on all basis functions yields the generalized eigenvalue problem

$$\langle \Phi_i | \mathcal{H} | \Phi_j \rangle C_j^{(k)} = E^{(k)} \langle \Phi_i | \Phi_j \rangle C_j^{(k)}. \tag{2.33}$$

Finding eigenstates is thus transferred to the problem of finding eigenvectors of finite matrices. For big matrices, this can be challenging, even on modern supercomputers. However, for the moment it shall be assumed that the required eigenstates can be found via standard numerical techniques. The accuracy of the energies depends only on the size of the basis, if all quantities in Eq. (2.33) are evaluated exactly. This, is of course impossible in general. Hence there remain two open questions: how can the basis $\Phi_i(\mathbf{s})$ be constructed and how can Hamiltonian matrix elements be evaluated? The tensor product basis is the simplest approach to form n dimensional basis functions,

$$\Phi_i(\mathbf{s}) = \mathrm{vec}\left(\bigotimes_{j=1}^{n} \boldsymbol{\phi}_j(s_j) \right)_i , \tag{2.34}$$

where $\bigotimes$ denotes the Kronecker product. Thereby all possible products from sets of one dimensional basis functions,

$$\boldsymbol{\phi}_i(s_i) = \begin{pmatrix} \phi_{i1}(s_i) & \phi_{i2}(s_i) & \dots \end{pmatrix}^\top , \tag{2.35}$$

which span one dimensional subspaces, are formed. In the context of vibrational wave functions, the products $\Phi_i(\mathbf{s})$ are also called Hartree products and the space, spanned by the tensor product basis is denoted configuration space.

After a basis for the wave functions is defined, Hamiltonian matrix elements, $\langle \Phi_i | \mathcal{H} | \Phi_j \rangle$, must be computed in that basis to obtain the matrix eigenvalue problem of Eq. (2.33). Computing the overlap matrix $\langle \Phi_i | \Phi_j \rangle$ is also necessary, but is trivial, especially if an orthogonal basis is employed. The Hamiltonian involves n dimensional scalar fields and derivative operators, which makes integration a challenging task. Exemplarily, the matrix element of the PES will be discussed, since the generalization to matrix elements involving derivatives is straightforward but requires some lengthy notations.[46] The matrix element

$$\mathcal{V}_{ij} = \langle \Phi_i | V | \Phi_j \rangle , \tag{2.36}$$

being part of the Hamiltonian matrix element cannot be evaluated as long as $V(\mathbf{s})$ is not in a form that allows for integration. In general, $V(\mathbf{s})$ may be expanded in a suitable basis, leading to

$$V(\mathbf{s}) = a_i \Gamma_i(\mathbf{s}). \tag{2.37}$$

The n dimensional basis functions $\Gamma_i(\mathbf{s})$ can again be formed as tensor product basis from one dimensional basis functions

$$\Gamma_i(\mathbf{s}) = \mathrm{vec}\left(\bigotimes_{j=1}^{n} \boldsymbol{\gamma}_j(s_j) \right)_i . \tag{2.38}$$

Hence, the evaluation of the matrix element $\mathcal{V}_{ij}$ reduces to

$$\mathcal{V}_{ij} = a_k \langle \Phi_i | \Gamma_k | \Phi_j \rangle . \tag{2.39}$$

This can be expressed in terms of products and contractions of integral tensors,

$$I_{ijkl} = \int\limits_{D_i} ds_i\, \phi_{ij}(s_i)\gamma_{ik}(s_i)\phi_{il}(s_i), \tag{2.40}$$

straightforwardly, although the explicit expression is rather lengthy due to the index transformations.* The integration domain D_i is the domain of the Hilbert space spanned by the basis functions $\phi_{ij}(s_i)$. Generalizing this integral tensor to

$$I^{(s,t)}_{ijkl} = \int\limits_{D_i} ds_i\, \phi_{ij}(s_i) \left(\frac{\partial^s}{\partial s_i^s} \gamma_{ik}(s_i) \right) \frac{\partial^t}{\partial s_i^t} \phi_{il}(s_i) \tag{2.41}$$

is sufficient to compute the integrals arising in the kinetic energy operator as well. For details see Ref. 46.

All these formal definitions reduce the mathematical problem of solving the SE for a specific system to definitions of appropriate bases for wave functions and operators plus solving the integrals $I^{(s,t)}_{ijkl}$. If the primitive basis functions are analytic expressions, usually involving polynomials and Gaussians, the integrals can be solved analytically as well. However, the more challenging aspect is to find bases and coordinates that allow for an efficient implementation of all the basis expansions.

Only for very small values of n, i. e. $n \lessapprox 3$, tensor product bases on regular grids, being the simplest approach, can be directly employed. In all other cases the PES, scalar fields involved in the KEO, as well as the expansion of $\Psi^{(k)}(\mathbf{s})$ must be restricted to subspaces of the complete product bases. Imposing these restrictions in a clever way, from a mathematical and from a implementation viewpoint, is the subject of the development of methods that yield vibrational eigenstates in the end. Thereby, physical properties of vibrating molecules should be taken into account. Truncated MBEs, that reduce the MBE to a sum of low dimensional subspaces, have already been mentioned in section 2.1. Additionally, sparse grids, being one example of a modern, adaptive, numerical approach, can be employed for the representation of individual MBE terms. This is detailed in Ref. 46 and section 3.2.

Multilevel schemes can reduce the computational costs for the PES evaluation further. Thereby, higher orders of MBE terms are computed from electronic-structure methods of lower accuracy, since the impact of these terms is usually less pronounced.[57,58] Instead of computing the high order couplings explicitly, they may also be modeled or extrapolated.[15,59,60] The drawback of this approach is that the error, caused by multilevel or model approaches, is hard to control.

2.4. Vibrational Self-Consistent Field

Before discussing the route towards states of arbitrary precision, another approximate scheme, vibrational self-consistent field (VSCF),[23,43,44] shall be discussed. Thereby, the wave function is limited to a product of one dimensional functions. These, in contrast to the harmonic approximation (see section 2.2), can be eigenfunctions of arbitrary one dimensional Hamiltonians.

*Since implementations do not follow these index rules anyway, because explicit tables for index transformations are usually employed, there is no benefit of an explicit index transformation at this point.

The mean-field approach to transform a coupled Hamiltonian into a set of uncoupled effective one dimensional Hamiltonians is well-known from electronic-structure theory, where it leads to the Hartree Fock method.[2] A similar method for vibrations is obtained from a Hartree product ansatz for the wave function

$$\bar{\Psi}(\mathbf{s}) = \phi_1(s_1)\phi_2(s_2)\ldots\phi_n(s_n). \tag{2.42}$$

The state index k on $\bar{\Psi}^{(k)}(\mathbf{s})$ and the second indices on $\phi_{ij}(s_i)$ are omitted as long as only one Hartree product is considered. An effective Hamiltonian for a certain coordinate can be obtained by integrating out all but one coordinate. This leads to the set of one dimensional effective Hamiltonians $\bar{h}_i(s_i)$,

$$\phi_i(s_i)\bar{h}_i(s_i)\phi_i(s_i) = \int\limits_{D_1} ds_1 \ldots \int\limits_{D_{i-1}} ds_{i-1} \int\limits_{D_{i+1}} ds_{i+1} \ldots \int\limits_{D_n} ds_n\, \bar{\Psi}(\mathbf{s})\, \mathcal{H}(\mathbf{s})\, \bar{\Psi}(\mathbf{s}). \tag{2.43}$$

Eigenfunctions of each $\bar{h}_i$ can be computed by standard numerical techniques like Gaussian collocation,[61] discrete variable representation,[62] or expansion in a harmonic oscillator basis.[50] All these have in common, that $\phi_i(s_i)$ is expanded in some kind of basis,

$$\phi_i(s_i) = c_{ij}\varphi_j(s_i). \tag{2.44}$$

The representation of $\bar{h}_i(s_i)$ in that basis can be diagonalized straightforwardly, since the matrices are small for the one dimensional effective Hamiltonians. It should be noted, however, that the formal definition of $\bar{h}_i(s_i)$ (Eq. (2.43)) requires all factors $\phi_j(s_j)$, for $j \neq i$, to be known already. To circumvent this problem, effective Hamiltonians are generated iteratively. Starting from a guess wave function* a set of effective Hamiltonians can be generated and diagonalized. From the set of states $\phi_i(s_i)$ a new set of effective Hamiltonians can be constructed, which is iterated until convergence, denoted as self-consistency.**

It is noteworthy that there exists a whole spectrum for each one dimensional Hamiltonian, as in the harmonic approximation, which yields a set of states $\boldsymbol{\phi}_i(s_i)$ (Eq. (2.35)). Combining the one dimensional states to Hartree products, denoted as configurations, yields a basis for the set of total wave functions (see section 2.3). The Hartree products themselves are not eigenfunctions of the total Hamiltonian, which is why the expansion of the Hamiltonian in the configuration space is not diagonal. Nevertheless, since this Hamiltonian matrix is usually diagonally dominant, the energy expectation values on the diagonal can be viewed as approximate eigenvalues. For the case, where there are no couplings between modes, this approximation becomes exact. In general, the accuracy of a VSCF energy depends on the coupling strength to other states or equivalently on off-diagonal elements of the Hamiltonian matrix. Usually, the most accurate energy is obtained for the state which was employed to build the mean-field. That is why VSCF calculations can also be performed specifically for each state of interest to obtain a good approximation within the VSCF scheme. The drawback is that the set of states generated by state specific VSCF calculations is neither orthogonal nor is it guaranteed that it spans the same space as each configuration space from

*The simplest guess is setting $\bar{\Psi}(\mathbf{s}) = 0$.

**Convergence is met if e. g. the VSCF energy, i. e. the expectation value $\langle \bar{\Psi} | \mathcal{H} | \bar{\Psi} \rangle$, does not change for consecutive iterations within a given tolerance.

a single VSCF calculation would. Hence, in the following it is always assumed that the VSCF calculation is performed for the ground state. The configuration space, generated from this single VSCF calculation, can then be employed for a subsequent vibrational configuration interaction calculation (see section 2.5).

In comparison to the previously discussed harmonic approximation (section 2.2) the VSCF method can give more accurate results. However, it is computationally significantly more expensive, since a sufficiently accurate representation of the PES is required to get meaningful results. The evaluation of the PES is the most expensive part of a VSCF calculation, while the iterative procedure is comparatively cheap.

Although being more accurate than the harmonic approximation, the mean-field approximation can still cause significant errors since correlation of vibrational modes is missing from the mean-field approach by definition. The correlation energy is defined by the difference between the exact energy and the VSCF energy $\langle \bar{\Psi} | \mathcal{H} | \bar{\Psi} \rangle$. In the VSCF approach it is assumed that correlation is small, or equivalently that coupling between modes is weak. There are molecules, where this is not the case. Especially those that exhibit multiple PES minima that are not well separated, can lead to a breakdown of the VSCF approach. It is possible in some cases to find coordinates that transform such a multi reference problem to a single reference system in some cases.[23,24] In general, however, it is not clear if such coordinates exist or how to find them.

Apart from interpreting VSCF states as approximate physical quantities, the VSCF approach can be employed to obtain an improved basis for the vibrational configuration interaction method, which will be discussed in the subsequent section 2.5.

2.5. Vibrational Configuration Interaction

The limited accuracy of the VSCF approach can be overcome by expanding the wave function in a configuration space (Eq. (2.32)), leading to the vibrational configuration interaction (VCI) method.[45] It requires two computationally expensive tasks, first, build-up of the VCI matrix, i. e. the Hamiltonian matrix in configuration space, and second, search for eigenpairs or diagonalization of the VCI matrix. The costs for both tasks depend on the size of the VCI space, which is why it is important to choose the VCI space as small as possible. Employing a complete tensor product basis is not feasible for systems with more than a few vibrational modes ($n \gtrapprox 3$). Instead, VCI spaces may be restricted to the space spanned by a set of low dimensional tensor product bases of overlapping subspaces. For example, all M dimensional subspaces may be combined leading to a significantly smaller VCI space, if $M \ll n$. This implies, of course, that high dimensional ($> M$) correlations are negligibly small. Furthermore, the one dimensional bases, forming the tensor products, may be truncated to decrease the size of the tensor products further. Thereby the truncation order can be chosen differently for different values of M. How these truncations and M have to be chosen to obtain a certain accuracy of an eigenvalue cannot be said *a priori* since it depends on the specific basis and on the Hamiltonian. Adaptive schemes can yield configuration spaces tailored to a specific system. To that end, the impact of subspaces and single configurations must be estimated to decide which configuration should be kept in the VCI space.[63,64] Alternatively, the VCI expansion of the wave function may be parametrized by an exponential ansatz, leading to the vibrational coupled cluster theory.[65] Although the full expansion of the exponential ansatz is identical to the full VCI wave function, truncated expansions lead to different approximate configuration spaces than VCI schemes.[65]

Building the basis for the VCI space from VSCF states is the most common approach, since the basis functions, i. e. the VSCF states, are already approximately decoupled. Even if some strong couplings remain, they are often restricted to small subspaces and can be resolved by truncated VCI spaces.

It is noteworthy that the correct choice of the configuration space does not only depend on the Hamiltonian and the VSCF basis, it also requires to predefine which states should be resolved to which accuracy. While for thermodynamic properties it is sufficient to include the thermally populated low lying states it is much more difficult to single out states that are spectroscopically relevant for a certain kind of spectrum, e. g. for a linear absorption spectrum.

If more than a single state is of interest, there exist two routes to obtain the corresponding eigenstates.[13,43,45,57,66] First, a state selective VCI may be performed. To this end, a VSCF basis is built for each state of interest. Then, a VCI matrix is built and a single eigenpair is extracted. This state specific VCI has the advantage that VCI spaces can be chosen small due to the fast convergence in the state specific VSCF basis. A disadvantage is, however, that VSCF calculations for excited states can be difficult to converge and that the VCI states are all expanded in different bases, which is unfavorable if some subsequent calculations shall be performed that require a common basis. The second approach to compute a set of eigenstates via a VCI matrix is the virtual VCI approach. Thereby a single VSCF calculation is performed, usually for the ground state, and a single VCI matrix is built, from which all eigenstates are extracted. The convergence of excited states in the ground state VSCF basis can be slower than in a state specific VCI. Therefore, the virtual VCI matrix must be chosen larger than VCI matrices in the state specific approach. However, all eigenstates can then be computed by a single diagonalization and all VCI states are expanded in the same orthogonal basis.

As said, the build-up of the VCI matrix is the first computationally expensive step in a VCI calculation. If the KEO and PES are sums of low dimensional terms, like it is the case in MBEs, Slater-Condon[2] like rules can be applied for the evaluation of a matrix element. Consider exemplarily a PES-MBE term $V^{(3)}_{ijk}(s_i, s_j, s_k)$ depending on three coordinates, then a matrix element can be computed from

$$\langle \phi_1\phi_2\phi_3\ldots|\, V^{(3)}_{ijk}\, |\phi'_1\phi'_2\phi'_3\ldots\rangle = \langle \phi_i\phi_j\phi_k|\, V^{(3)}_{ijk}\, |\phi'_i\phi'_j\phi'_k\rangle \prod_{l\notin\{i,j,k\}} \langle \phi_l|\phi'_l\rangle \,. \tag{2.45}$$

The overlaps $\langle \phi_i|\phi'_i\rangle$ reduce to zero or one for orthonormal one dimensional bases that come out of a VSCF calculation. If one of these overlap factors is zero, the complete matrix element vanishes. This property must be exploited in efficient implementations. Furthermore, the relatively low dimensional terms of the form $\langle \phi_i\phi_j\phi_k|\, V^{(3)}_{ijk}\, |\phi'_i\phi'_j\phi'_k\rangle$ can be (partially) precontracted for all basis functions in that subspace to avoid recomputation of the integral.

The second bottleneck of the VCI method is the computation of eigenstates or observables from the VCI matrix. As stated, it depends on the observables of interest how they can be extracted efficiently from the VCI matrix. In general, the VCI matrix has typically a very high density of states, especially in higher energy regions. Thus, only the ground state or a few low lying states, can be computed straightforwardly by iterative solvers like the Lanczos algorithm. For high lying states, the convergence of iterative solvers is usually rather slow due to the high density of states. Direct solvers, give reliable results for all states, but are memory consuming and scale with $\mathcal{O}(k^3)$, where k is the matrix dimension. Hence, their application is limited to matrices of moderate size and it is required to keep the configuration space as small as possible. Alternatively, spectra may be computed directly from the VCI matrix via propagation techniques.[40,67,68] This has, however, the drawback that no eigenvectors are obtained which could be employed to estimate the error of the finite configuration space. It is therefore preferable to start with a small VCI space, compute eigenvectors, select the most significant configurations and increase the VCI space iteratively until the desired accuracy of the eigenvalues is reached. These configuration selective VCI variants[63,64] can yield small VCI spaces with approximate error control.

Although the VCI matrix can give eigenstates of arbitrary accuracy in principle, it is limited by the accuracy of the Hamiltonian and the size of the VCI space. These two errors from finite basis expansions and the error inherent in the PES itself must be balanced to get a consistent model of the system where the remaining error in the eigenstates can be estimated.

2.6. Curvilinear Coordinates

The accuracy of the VSCF approach and the convergence within the VCI space depends on the system, but also strongly on the coordinates $\mathbf{s}$. Finding coordinates that decorrelate the Hamiltonian to some extent is therefore fundamental. It is experience and the adaption to physical properties that allow for the construction of proper coordinates. Currently, two classes of coordinates are well-established, internal curvilinear coordinates and rectilinear coordinates. Coordinates are internal if they are invariant under rotation and translation (Eq. (2.13)).[41] Hence, only curvilinear coordinates can be internal, since rectilinear coordinates cannot be orthogonal to rotations globally.

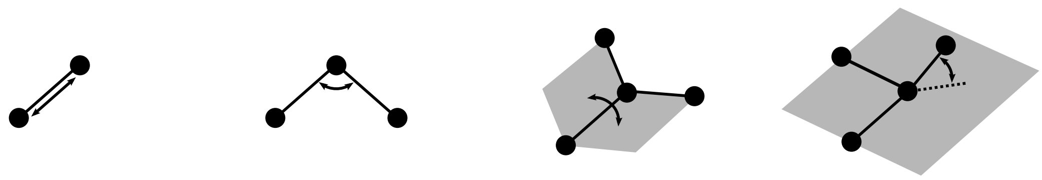
Normal modes (NM), known from the harmonic approximation (section 2.2), are the simplest vibrational coordinate system. They decouple the quadratic approximation of the PES completely and can be quasi uniquely defined for a certain molecular geometry.[*] As long as the amplitudes of the vibrational motions are small, these coordinates may be sufficient. For less rigid molecules, that involve larger amplitude motions, a Hamiltonian expanded in rectilinear coordinates often requires relatively high order couplings in the PES.[46,57]

Alternatively to the NM curvilinear coordinates can be constructed.[56,69,70] Combining internal valence coordinates is one of the most prominent approaches for the parametrization of moleculer vibrations.[56] These coordinates reflect the nature of chemical bonds at the equilibrium geometry.[71] That implies that bond stretching motions are separated from angle variations between bonds since the forces for these two types of motions are usually locally orthogonal. Hence, also the convergence of the PES-MBE can be faster than with rectilinear coordinates.[46,72]

Internal valence coordinate systems comprise stretch, bend, torsion, and out-of-plane coordinates shown in Figure 2.1. A stretch, Figure 2.1(a), is defined via the distance between two

[*]In case of degenerate modes, the definition is not entirely unique, since the subspace spanned by the degenerate modes may be spanned by an arbitrary basis.

atoms. The bending coordinate, Figure 2.1(b), is given by the included angle of three nuclei. Notice that an angle variation becomes arbitrary in the vicinity of π. Hence, geometries leading to a linear geometry of the three atoms must be excluded. Four nuclei can be employed to define a torsional coordinate, Figure 2.1(c). The included angle of two planes serves as coordinate. Each plane is defined via three of the four nuclei. This coordinate remains well-defined as long as no linear dependencies arise in the definition of the planes. The fourth coordinate, rarely employed, is the out-of-plane coordinate, Figure 2.1(d). To this end, three nuclei define a plane. The included angle of the line connecting one nucleus in the plane and the one not in the plane and the projection of this line onto the plane serves as coordinate. To keep this coordinate definition well-defined, no linear dependency must arise in the definition of the plane and the out-of-plane angle must be different from $\pi/2$.



(a) (b) (c) (d)

Figure 2.1.: Sketch of the four internal valence coordinates: stretch (a), bend (b), torsion (c), and out-of-plane (d). See text for details.

In general there are many options to choose a set of primitive coordinates forming a locally valid coordinate system. The explicit choice strongly influences the convergence of the PES-MBE and the strength of couplings in the PES and the KEO. Instead of employing the primitive coordinates directly, defining linear combinations of primitive coordinates may result in improved coordinate systems.

To that end, the NM can be mapped on to the tangent space of the internal coordinate system at the reference geometry $\mathbf{s}^{\text{ref}}$. This yields linear combinations v_i of primitive internal coordinates u_i,

$$v_i = \mathbf{B}_{ia}|_0 \, m_a^{-1/2} \, \mathbf{Q}_{aj} \, u_j. \tag{2.46}$$

These linear combinations can be considered as internal curvilinear NM since they resemble the NM at equilibrium geometry and hence also decouple the quadratic Hamiltonian. For finite displacements, however, the coordinates are different and separate angle variations from bond stretching to some extent.

The valence coordinates are a special case of polyspherical coordinates.[73] Another class of polyspherical coordinate systems are Jacobi coordinates,[69] where centers of masses of molecular subunits are connected and lengths and angles of these vectors serve as coordinates. These coordinates are favourable for the description of reactions and scattering.[74]

Different attempts have been made to define curvilinear coordinates in an adaptive way. The motivation was to exploit some information about the PES, e. g. from a few PES points, and construct coordinates in such a way, that the PES-MBE convergence is improved. The two approaches, that can be applied on top of any other coordinate system, such as internal valence coordinates or normal modes, are documented in appendix A. However, since these approaches did not yield the expected results, i. e. improved PES representations, it is not advisable to employ the proposed construction schemes.

2.6.1. Dealing with the Kinetic Energy Operator in Curvilinear Coordinates

Up to this point it was emphasized that curvilinear coordinates can yield better PES expansions than rectilinear coordinates. On the contrary, they complicate the expression for the KEO. This does not imply that the KEO of the Watson Hamiltonian,[75] valid for rectilinear NM, is trivial. It is not, because it contains terms being non-linear in the vibrational coordinates, which arise from the curvilinear rotational coordinates. However, for molecules with large moments of inertia these non-linear functions may be approximated by low order expansions[22] or completely neglected. This is valid because rotation vibration couplings become smaller with system size. In the resulting approximation, the metric tensor $\boldsymbol{\mathcal{G}}$ becomes the identity matrix, and hence, the KEO is identical to the KEO of the harmonic approximation. Although the harmonic approximation is crude for the PES, it can be very accurate for rectilinear NM and large molecules for the KEO. This highlights, that the KEO can become simple in the limit of large molecules.

The situation is different for curvilinear coordinates. In this case, the coordinate dependencies of $\boldsymbol{\mathcal{G}}$ and $\boldsymbol{g}$ do not vanish for big molecules. Hence, they must be included in the Hamiltonian. Various approaches have been developed. For small molecules up to about six atoms, analytical KEOs, employing different curvilinear coordinate systems, were derived explicitly (see e. g. Refs. 28, 29, 31–33). Employing these in a general method is unfavourable, since it would require individual implementations for each KEO, and explicit derivations for molecules with more atoms can become very cumbersome. Recently, the derivation procedure for polyspherical coordinates was automated.[35] Although this kind of procedure yields exact KEOs for larger molecules efficiently, it is cumbersome to implement and does still limit KEOs to the class of polyspherical coordinates. To explore new coordinate systems, that are curvilinear, but may not be internal, numerical approaches are favourable.[27,76,77] One implementation aiming in this direction is the TNUM approach.[27] This approach allows for the evaluation of the metric tensor on a grid, enabling arbitrary coordinates in principle. As with the PES, evaluating a n dimensional function on a grid faces the *curse of dimensionality* for more than a few atoms. Since $\boldsymbol{\mathcal{G}}$ contains $\mathcal{O}(n^2)$ terms that depend on n coordinates, the limits of modern computers are reached very quickly with a direct grid approach.

Expanding each individual term of $\boldsymbol{\mathcal{G}}$ as a MBE yields the hierarchical expansion of the kinetic energy (HEKE) operator,[23,24] which can be adapted to specific systems[26,46] and limits coordinate dependencies to sums of low dimensional subspaces. To explore new coordinate systems, e. g. the knotted coordinates or rotated coordinates discussed in appendix A, an efficient implementation that can deal with arbitrary coordinates is fundamental.

The HEKE approach can be applied to internal and non-internal curvilinear coordinates, including NM, and arbitrary rotating frames if Jacobians for the rotational and vibrational coordinates are provided.[42] The approach is very efficient if these Jacobians can be computed analytically, as it is the case for the Eckart frame[78] as rotating frame and NMs or internal valence coordinates, including curvilinear NM, as vibrational coordinates.

2.7. Vibrational Spectra

The previous sections focused entirely on the Hamiltonian and corresponding eigenfunctions. Computing these, is, however, not sufficient to obtain spectroscopic observables, which, in general, depend on light matter interactions and on the time evolution of the wave function. Reviewing all the approaches and approximations that lead to vibrational spectra is beyond the scope of this thesis. Here, the focus lies on the development of methods, that provide operator representations, suitable for the simulation of vibrational spectra. For basic considerations about light matter interactions and time evolution of wave functions see Refs. 39, 79, and 80. Recent developments of methods to compute accurate (non-linear) IR spectra can be found in Ref. 40 and references therein. Within the long wavelength approximation,[79] the dipole operator is the key quantity to compute interactions of LASER pulses and the molecular system. In general, the dipole operator,

$$\boldsymbol{\mu}(\mathbf{s}) = \begin{pmatrix} \mu_x(\mathbf{s}) & \mu_y(\mathbf{s}) & \mu_z(\mathbf{s}) \end{pmatrix}^\top, \tag{2.47}$$

is a non-linear vector field depending on the vibrational coordinates $\mathbf{s}$. Notice, that the dipole is not rotationally invariant, so the definition of the rotating frame matters. This is especially relevant, if internal coordinates are employed.

Like the PES, the dipole operator can be evaluated pointwise from electronic structure calculations. A representation in a basis is obtained straightforwardly, if the components are expanded in MBEs as well. The SG approach, that can be applied to the KEO and the PES may also be employed. Since the dipole components are usually less structured than the PES it is sufficient to add all grid points where the PES is evaluated also to dipole MBEs. Hence, adaptive refinement criteria are not required for the dipole operator and no additional electronic structure calculations are required if the dipole can be extracted from PES evaluations.

Once the Hamiltonian and dipole operator is expanded in a basis, the simplest spectroscopic experiment, the linear absorption spectrum, can be computed from the Einstein $\mathscr{B}$ coefficient of absorption.[56] The intensity of a spectral line, corresponding to the transition from state i to j, is given by

$$\mathscr{B}_{ij} = \frac{2\pi}{3} \left\| \langle \Psi_i | \boldsymbol{\mu} | \Psi_j \rangle \right\|^2 . \tag{2.48}$$

Assuming that the system is initially in the ground state, this kind of coefficient is sufficient to compute the complete linear absorption spectrum. If other low lying states are significantly populated, e. g. due to a thermal population, also stimulated and spontaneous emission must be taken into account via $\mathscr{B}_{ij}$ and $\mathscr{A}_{ij}$, respectively.

Non-linear spectroscopy experiments, (see Refs. 38 and 39 for an overview) such as the three pulse photon echo experiment can give more detailed information about the system. In general, the non-linear polarization density

$$\mathbf{P}(t) = \langle \psi(t) | \boldsymbol{\mu} | \psi(t) \rangle \tag{2.49}$$

can be computed from the time evolution of a wave function and the dipole operator $\boldsymbol{\mu}$. The non-trivial time-dependency of the wave function arises from a time-dependent Hamiltonian. Within the dipole approximation, this Hamiltonian for a spectroscopic experiment

$$H(t) = H_0 + \varepsilon_i(t)\, \mu_i \tag{2.50}$$

is given by the system Hamiltonian H_0 plus the scalar product of the electric field $\boldsymbol{\varepsilon}(t)$ and the dipole $\boldsymbol{\mu}$. The time evolution of the wave function is determined by the time-dependent SE from which a formal solution for the polarization density may be derived[80]

$$\mathbf{P}(t) = \sum_{k=1}^{\infty} \int_0^{\infty} dt_k \int_0^{\infty} dt_{k-1} \dots \int_0^{\infty} dt_1 \varepsilon_i(t - t_k)\varepsilon_j(t - t_k - t_{k-1}) \dots \varepsilon_l(t - t_k - \dots - t_1) \times \mathbf{S}^{(k)}_{ij\dots l}(t_k, t_{k-1} \dots, t_1). \quad (2.51)$$

The sum over all integrals, involving the non-linear response functions $\mathbf{S}^{(k)}_{ij\dots l}(t_k, t_{k-1} \dots, t_1)$ determines the response of the system to an electric field. Except for the first order term, which is the linear response function, the response function is non-linear w. r. t. the electric field $\boldsymbol{\varepsilon}(t)$. In contrast to the polarization density $\mathbf{P}(t)$, which depends on the electric field and the system, the response function is completely determined by the system alone via H_0 and $\boldsymbol{\mu}$.*

Qualitatively, $\mathbf{S}^{(k)}_{ij\dots l}(t_k, t_{k-1} \dots, t_1)$ arises from terms comprising $k+1$ combinations of a time evolution under the field free Hamiltonian H_0 and the action of the dipole operator on an initial state $|\psi(0)\rangle$.

In contrast to the linear response function, that carries information about states absorbing energy, the non-linear response function does also contain information about the dynamical redistribution of absorbed energy. Since energy flux depends on coupling of building blocks of the complete system, there is indirect information about molecular structure or spatial relations of subsystems. Even interaction with the environment can be determined from the non-linear response function.[38]

The experimental measurement of non-linear system responses as well as their computation from a given Hamiltonian and dipole operator is challenging already.[38,40] However, to gain a reliable understanding from the interplay of measured and simulated spectra, it is fundamental, that the description of the system via H_0 and $\boldsymbol{\mu}$ is accurate enough to undoubtedly establish an understanding of non-linear spectroscopic effects.

*It is common to derive the response function within the density matrix formalism. This is convenient, though not necessary, to compute the response of a statistical ensemble or to introduce other effects like dephasing or relaxation.[40] Regardless of the formalism employed, the response of non-interacting systems leads to a superposition of the individual responses of each system, but not to a superposition of wave functions.

3. Publications

The two following sections provide summaries of Refs. 42 and 46 on which this thesis is based on.

3.1. A general nuclear motion Hamiltonian and non-internal curvilinear coordinates

The article, A general nuclear motion Hamiltonian and non-internal curvilinear coordinates[42] *appeared in The Journal of Chemical Physics and may be found at http://dx.doi.org/10.1063/1.4793627. All of the presented original work and the writing of the article was performed by the author of this thesis, Daniel Strobusch, under supervision of Dr. Christoph Scheurer. In the following section citations of Ref. 42 are omitted since it is a summary of this article.*

In Born-Oppenheimer approximation, typically two different classes of coordinates, rectilinear normal modes (NM) and internal coordinates (IC), are employed to describe the vibrational (or internal) motions of the nuclei. With translational and rotational motions plus the potential energy surface (PES), the complete nuclear motion Hamiltonian is obtained. Exact expressions for this Hamiltonian are well-known if coordinates are either restricted to NM[52,75,81] or IC.[41,54,55,82] Their relation is, however, not obvious due to their different forms and derivations. More general Hamiltonians have also been derived,[17,27,83] which, unfortunately, can also not be transformed to both expression for NM and IC in a straightforward way.

The article "A general nuclear motion Hamiltonian and non-internal curvilinear coordinates" focuses on the derivation of a Hamiltonian, which can be transformed into the well-established expressions for NM and IC. Therefore, general curvilinear coordinates, denoted non-internal coordinates, are employed. These include the other two coordinate classes, NM and IC as special cases. Employing the general Hamiltonian, it is demonstrated how it simplifies to the established expressions if coordinates are restricted to be either rectilinear or internal. Thereby, it is highlighted how Hamiltonians for NM and IC are related and how both can be derived from a more general Hamiltonian.

The kinetic energy part of the Hamiltonian is based on the Jacobian of vibrational coordinates in the rotating frame which renders the application to specific coordinates a simple task. This is not the case for the previously known general Hamiltonians, which were formulated in terms of derivatives in the static frame. Since there is no unique definition of a rotating frame it is not included in the general Hamiltonian explicitly. The principal axis system and the

Eckart frame, being the most prominent frames, are discussed explicitly and can be directly employed from the provided expressions.

The more general non-internal coordinates are not only an abstract concept to unify NM and IC, they can also be employed for direct application. To this end, simple non-internal curvilinear coordinates are derived from a generalization of NM. These coordinates serve as proof of concept for non-internal coordinates. They, NM and IC, were employed to compute the vibrational water spectrum from a simple model PES.[84] Thereby not only the applicability of the Hamiltonian is demonstrated but also its correctness is confirmed by the excellent numerical agreement of the spectra from all three types of coordinates.

3.2. Adaptive sparse grid expansions of the vibrational Hamiltonian

The article, Adaptive sparse grid expansions of the vibrational Hamiltonian[46] will appear in The Journal of Chemical Physics. All of the presented original work and the writing of the article was performed by the author of this thesis, Daniel Strobusch, under supervision of Dr. Christoph Scheurer. In the following section citations of Ref. 46 are omitted since it is a summary of this article.

The article, Adaptive sparse grid expansions of the vibrational Hamiltonian, presents an adaptive and efficient numerical approach to the nuclear motion Hamiltonian. It comprises two parts, the kinetic energy operator (KEO) and the potential energy surface (PES). Both are nonlinear functions of the coordinates, whether they are curvilinear or not,[42] which makes integration over the Hamiltonian a challenging task.

A new method is presented to allow for a grid point efficient and adaptive representation of all parts of the Hamiltonian, i. e. every term in the KEO and the PES. Assuming a smooth integrand, sparse grids (SGs) are more efficient than regular grids[85] and are well qualified for adaptivity due to the hierarchical structure of the grid points. Instead of applying SGs to the Hamiltonian directly, it is shown how they can be combined with well-established many-body expansions (MBEs). These formal decompositions were introduced to deal with high dimensional PESs[19,20] and were also successfully applied to the KEO.[23,24] Due to their hierarchical structure, MBEs can be refined adaptively as well.[26,57] To combine the SG technique with MBEs, modified B-spline functions that cooperate well with MBEs are derived. In the resulting MBE/SG hybrid approach, each MBE term is represented by an adaptive SG. Hence, adaptivity can be exploited on the MBE level for the hierarchical subspaces and on the SG level for each individual MBE term. Based on approximate wave functions from the vibrational self-consistent field (VSCF) and the vibrational configuration interaction (VCI) methods an adaption criterion is derived. This allows for local error estimations of MBE and SG terms, and, hence, yields approximate error control over the representation of the total Hamiltonian. Adapting a Hamiltonian to a global precision goal asserts a consistent accuracy, unlike truncated MBEs or regular grids. It can be high, for extremely precise calculations, or moderate, for computationally inexpensive Hamiltonians or larger molecules. In the end, a consistent description of a molecule is obtained by choosing the precision goal in the range of the error inherent in the PES and/or the experiment itself. Which level of accuracy is available depends on the molecule, the available electronic-structure methods, and the computational resources.

By applying the combination of the new MBE/SG hybrid approach and the VSCF/VCI methods to a set of test molecules, comprising water, formaldehyde, methanimine, and ethylene, the precision and efficiency of the adaptive technique is demonstrated. For a semi-empirical PM3 model PES high precision goals (up to $0.01\,\text{cm}^{-1}$) were employed to show convergence within the expected interval to exact results (relative to the PES). For the smallest molecule, water, the PES error was estimated from comparing a series of calculations at a one wave number precision goal and different levels of accuracy for the PES to experimental data. Fundamental excitation energies from the most accurate PES, based on CCSD(T)/aug-cc-pVQZ calculations, exhibit a maximal deviation of $4\,\text{cm}^{-1}$ from experimental values. Subsequently, calculations for all other molecules in the test set were performed at a five wave number precision goal at the CCSD(T)/aug-cc-pVTZ level of theory. Deviations from experimental values lie in the expected range and are maximally $17\,\text{cm}^{-1}$ in magnitude.

The application to the test set demonstrated that the adaption criterion works as expected and all assumptions about smoothness and hierarchy of the Hamiltonian are valid for this class of molecules. The successful application of the MBE/SG approach makes it very promising to be applied to a wider range of molecules as a black box like procedure, controlled by a single parameter, the precision goal. Only strongly correlated molecules or multireference systems must be excluded if the strong correlation is not restricted to a small subspace.

4. Conclusions

The computation of vibrational spectra requires the system Hamiltonian to be known in a form from which a discrete representation can be obtained efficiently via numerical techniques.

To that end, a general nuclear motion Hamiltonian was derived from which a vibrational Hamiltonian results straightforwardly. This Hamiltonian does not only simplify to the known Hamiltonians like the Watson Hamiltonian[75] or Meyer Günthard Hamiltonian[41] for rectilinear and internal coordinates, respectively, it also enables the class of non-internal curvilinear coordinates to be explored. Currently, though, no specific non-internal curvilinear coordinates were found that perform better than the established internal ones in general.

Nevertheless, the general Hamiltonian allows for the implementation of numerical techniques, like the hierarchical expansion of the kinetic energy operator, for all kinds of coordinates. Hence, normal modes as well as internal coordinates can be employed and new construction schemes for non-internal coordinates can be tested.

This lifts technical restrictions which could prevent the use of the best coordinates imaginable for a certain system. Curvilinear coordinates are important to approximately separate different kinds of nuclear motions. Nevertheless, vibrations remain coupled and numerical techniques are required to efficiently recover the couplings that remain in the Hamiltonian. Primarily, this involves couplings in the potential energy surface, but also kinematic couplings need to be taken into account.

To that end, the well-established many-body expansion can be employed to adaptively approximate all non-linear functions in the Hamiltonian. For the representation of individual expansion terms, sparse grids were introduced. This required some modifications of the sparse grid theory, well-known from other mathematical fields, to exploit the special structure of many-body expansion terms. Since sparse grids can be adaptively refined as well, a completely adaptive representation of the vibrational Hamiltonian is obtained and all parts of the Hamiltonian can be refined up to a predefined precision goal.

The adaption is based on criteria that take vibrational self-consistent field and vibrational configuration interaction wave functions into account. These two methods can, in the end, yield vibrational eigenstates that are comparable to experimental results.

Reconsidering that the potential energy surface is evaluated from electronic-structure calculations clarifies that the precision of vibrational states is bound by the error of the potential energy surface. Once this error is estimated, a precision goal of the same order of magnitude can be defined for the adaptive expansion of the vibrational Hamiltonian. In combination with a configuration selective configuration interaction method, a very efficient method is obtained that provides approximate error control for all steps from the Hamiltonian to vibrational states. Hence, reliable results within predefined precision can be obtained in a black box like way.

However, the definition of coordinates remains crucial and is hard to automate, but, with some knowledge about the system, good curvilinear coordinates can be defined in many cases yielding rapidly converging expansions.

Given a precision goal and a coordinate system, the remaining correlation determines the computational effort to be spent. It should be emphasized that for the computation of the vibrational states, the system size has significantly less impact than the strength of the correlation.*

The adaptive Hamiltonian was employed to compute vibrational spectra for a set of test molecules. Fundamental excitation energies were found to be in good agreement with experimental values within the expected error. Thereby the efficiency and accuracy was demonstrated.

In this thesis, the nuclear motion Hamiltonian and the sparse grid technique led to a vibrational configuration interaction Hamiltonian, which could then be diagonalized. As it turned out, for strongly correlated systems the build-up and diagonalization of the Hamiltonian becomes the most time consuming part. Hence, it could be more favourable in these cases to switch to propagation methods. This would require to develop adaption criteria that allow for a refinement of the Hamiltonian during the propagation of a wave packet. In principle, this should not be difficult and could yield an efficient way to study also strongly correlated systems as long as the adaptive expansion of the Hamiltonian converges.

*It should not be forgotten that the electronic-structure calculations, required for the evaluation of the potential energy surface, depend on system size as well and hence also the expansion of the vibrational Hamiltonian can get expensive, even if vibrational coordinates are barely coupled. In practice though, this is rarely the bottleneck, since the evaluation of coupling potentials usually requires most of the computational time spent in electronic-structure calculations.

A. Attempts to Improve Convergence of PES-MBEs via Adaptive Curvilinear Coordinates

This appendix documents two attempts to construct curvilinear coordinates that yield an improved convergence of the potential energy surface many-body expansion (PES-MBE). As these approaches did not lead to the expected results, they are documented for completeness and not for the purpose of application.

To discuss the construction of coordinates it will suffice to limit the PES, $V(x_1, x_2)$, to two dimensions spanned by coordinates $\mathbf{x} = (x_1, x_2)$. Without loss of generality, it shall be assumed that the MBE is expanded at the coordinate origin and that $V(0,0) = 0$. Then, the complete MBE is given by

$$V(x_1, x_2) = V^{(1)}(x_1) + V^{(1)}(x_2) + V^{(2)}(x_1, x_2) \tag{A.1}$$

and each individual term is usually computed from

$$V_1^{(1)}(x_1) = V(x_1, 0), \tag{A.2}$$

$$V_2^{(1)}(x_2) = V(0, x_2), \tag{A.3}$$

$$V_{12}^{(2)}(x_1, x_2) = V(x_1, x_2) - V_1^{(1)}(x_1) - V_2^{(1)}(x_2). \tag{A.4}$$

$$\tag{A.5}$$

In a curvilinear coordinate space spanned by coordinates $\mathbf{s} = (s_1(x_1, x_2), s_2(x_1, x_2))$, with $\mathbf{0} = (s_1(0,0), s_2(0,0))$, the decomposition

$$V_1^{(1)}(s_1) = V(s_1, 0), \tag{A.6}$$

$$V_2^{(1)}(s_2) = V(0, s_2), \tag{A.7}$$

$$V_{12}^{(2)}(s_1, s_2) = V(s_1, s_2) - V_1^{(1)}(s_1) - V_2^{(1)}(s_2). \tag{A.8}$$

is different, especially w. r. t. the convergence behaviour. The nonlinear map from $\mathbf{x}$ to $\mathbf{s}$ must be locally bijective and continuously differentiable.[42] Introducing curvilinear coordinates is only advantageous if the PES-MBE converges faster than PES-MBE in rectilinear coordinates. Otherwise, spending additional effort on the more complicated kinetic energy operator would not be reasonable. The following sections list two approaches to construct such curvilinear coordinates adaptively. Basically, a map from $\mathbf{x}$ to $\mathbf{s}$ should be constructed such that the coupling term $V_{12}^{(2)}(s_1, s_2)$ is minimized. Both approaches could be applied on top of other curvilinear coordinates such as the internal valence coordinates. Unfortunately though, both approaches did not lead to a globally improved representation of vibrational Hamiltonians.

A.1. Knotted Coordinates

It is sufficient to restrict the following considerations to the domain $[0, a_1][0, a_2]$. Transformations to other quadrants may be performed by symmetry operations. A single parameter $c \in [2/3, 4/3]$ controls the shape of the grid and yields the regular grid for $c = 1$. The map from $\mathbf{x}$ to $\mathbf{s}$ is defined as follows. Given a point (x_1, x_2) compute the line integral l_1 along $p(z; 0, a_2, a_1c, a_2c)$ from $(0, a_2)$ to (a_1c, a_2c). The second order polynomial $p(z; 0, a_2, a_1c, a_2c)$ has properties $p(0; 0, a_2, a_1c, a_2c) = a_2$, $p(a_1c; 0, a_2, a_1c, a_2c) = a_2c$, and $p'(0; 0, a_2, a_1c, a_2c) = 0$. From the fourth order polynomial $q(z; l_1/a_1)$ defined by $q(0; l_1/a_1) = 0$, $q(1; l_1/a_1) = l_1/a_1$, $q'(0; l_1/a_1) = 1$, $q''(0; l_1/a_1) = 0$, and $q'(1; l_1/a_1) = l_1/a_1$ compute $u_1 = a_1q(x_1/a_1, l_1/a_1)$. The point $\mathbf{r}$ is given by r_1 which is determined such that the line integral along $p(z; 0, a_2, a_1c, a_2c)$ from $(0, a_2)$ to $(r_1, p(r_1; 0, a_2, a_1c, a_2c))$ equals u_1 and r_2 which follows from $r_2 = p(r_1; 0, a_2, a_1c, a_2c)$. Equivalently, the value l_2 is computed from the line integral along $p(z; 0, a_1, a_2c, a_1c)$ from $(0, a_1)$ to (a_2c, a_1c) which yields $u_2 = a_2q(x_2/a_2, l_2/a_2)$. The point $\mathbf{t}$ may be found analogously to $\mathbf{r}$. Finally, the intersection of $p(z; 0, x_1, r_2, r_1)$ and $p(z; 0, x_2, t_2, t_1)$ yields $\mathbf{s}$.

While this is a complex recipe to construct the identity map in case of $c = 1$ it is more general, since c is not restricted to this value. By varying c the point distribution can be adjusted. Furthermore, c can be chosen differently on each quadrant, which gives more flexibility to the grid (Figure A.1). This kind of coordinates does not affect the one dimensional subspaces, i. e. neither the displacements for single coordinates nor the Jacobi matrix for theses displacements are different from the original coordinates. Two dimensional subspace displacements can be constructed from the recipe presented. Higher dimensional displacements can be obtained from a generalization of the recipe. Then additional parameters, for each octant in three dimensions, result to control the shape of the grids.

To reduce the magnitude of a coupling term $V_{12}^{(2)}(s_1, s_2)$, the parameter c can be optimized w. r. t. some measure indicating the impact of $V_{12}^{(2)}(s_1, s_2)$. This optimization of c can be done for each quadrant and coordinate pair individually. As simple measure $|V_{12}^{(2)}(w_1, w_2)|$ at a certain point $\mathbf{w}$ lying on the respective quadrant can be chosen. Test applications did however not show a reasonable global reduction of the coupling strength, which is why this approach was discarded.

A.2. Rotated Coordinates

Rotations may be parametrized by

$$\mathbf{U}^{ij}(z; c) = \begin{pmatrix} 1 & & & & & & \\ & \ddots & & & & & \\ & & \cos(c\,z) & \dots & \sin(c\,z) & & \\ & & \vdots & 1 & \vdots & & \\ & & -\sin(c\,z) & \dots & \cos(c\,z) & & \\ & & & & & \ddots & \\ & & & & & & 1 \end{pmatrix}, \tag{A.9}$$

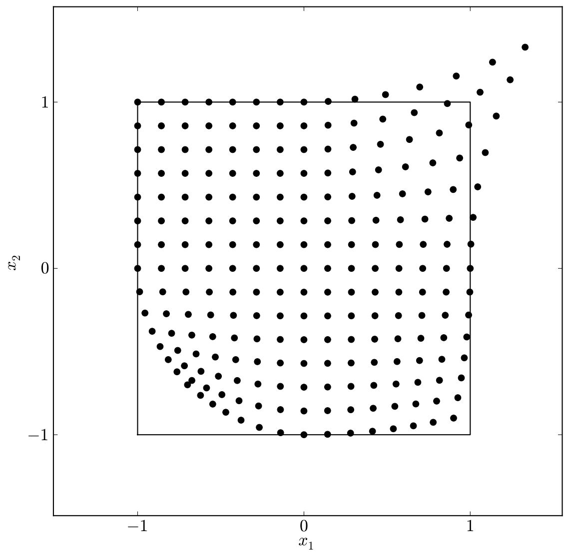


Figure A.1.: Grid produced by knotted coordinates for the domain $[-1, 1][-1, 1]$. The deformation parameter c is 1.33, 1.00, 0.70, and 0.90 for the first, second, third, and fourth quadrant, respectively.

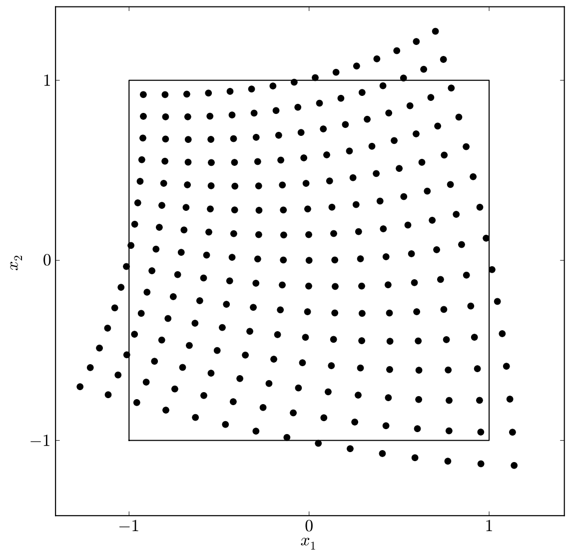


Figure A.2.: Grid produced by rotated coordinates for the domain $[-1, 1][-1, 1]$. The product of two rotation matrices, $\mathbf{U}^{12}(x_1; 0.2)\mathbf{U}^{12}(x_2; 0.2)$, defines the coordinates, see section A.2.

where indices i and j indicate the rotation plane. From a product of such rotations one can construct orthogonal transformations, often employed to transform from one rectilinear coordinate system to another. In this case, z, and c are constant values. By allowing z to be one of the coordinates, i. e. x_1 or x_2 in case of the two dimensional coordinate system, curvilinear coordinate systems can be constructed. For small values of c, the coordinate system is bijective and continuously differentiable in a local domain around the coordinate origin. The Jacobi matrix may even be computed analytically. Curvilinear coordinates $\mathbf{s}$ are, thus, formally given by

$$\mathbf{s} = \prod_k \mathbf{U}^{12}(x_k; c_n)\mathbf{x}. \tag{A.10}$$

The parameters c_n define the coordinates. In the two dimensional case, only one coordinate pair exists, which is why there is only $\mathbf{U}^{12}$. In higher dimensional space many pairs exists, from which several or all may be employed to modify the coordinates. Furthermore, there can be several rotation matrices for the same coordinate pair, since the coordinate dependency may be different. Rotations do not commute in general. Thus, the order of he rotation matrices matters and there can even be several rotation matrices acting on the same coordinates at different positions in the product. These properties make it difficult to define a curvilinear coordinate system uniquely from simple arguments. However, when adding new rotation matrices with small c_n to the coordinate definition in an iterative way, the non-commutativity of the rotation matrices has only little impact, since infinitesimal rotations do commute. An exemplary two dimensional grid, constructed from two rotation matrices is shown in Figure A.2.

To reduce the coupling in a PES-MBE one may choose a point stencil in a two dimensional i, j subspace, add rotation matrices $\mathbf{U}^{ij}(x_i, c_1)$, $\mathbf{U}^{ij}(x_j, c_2)$, and optimize the parameters c_1

and c_2 in such a way, that some measure of $V_{ij}^{(2)}(s_i, s_j)$ is minimized. Therefore, simply sums of the norms $|V_{12}^{(2)}(w_1^k, w_2^k)|$, where k indexes all points in the stencil, may be taken. While testing these coordinates it was found, that couplings in two dimensional subspaces may be decreased by these coordinates. However, the global convergence of the PES-MBE was sometimes worse than with rectilinear coordinates since the impact of higher order couplings did grow. This leads to the conclusion that these coordinates, constructed from non-constant rotation matrices, do not improve the PES-MBE since they transport correlation to higher dimensional subspaces. Different optimization techniques have been tested, however, none of them led to satisfying results, which is why this approach was discarded.

Abbreviations

aug-cc-pVXZ	augmented cc-pVXZ
B-spline	basis-spline
cc-pVXZ	correlation consistent polarized valence X-ζ basis set (X may be D, T, Q, 5, ... for double, triple, quadruple, quintuple, ..., respectively)
CCSD(T)	coupled cluster with single and double excitations and perturbative triple excitation corellations
DFT	density functional theory
HEKE	hierarchical expansion of the kinetic energy
HF	Hartree Fock
IC	internal coordinates
IR	infra red
KEO	kinetic energy operator
LASER	light amplification by stimulated emission of radiation
MBE	many-body expansion
NM	normal modes
PES	potential energy surface
PM3	parameterized model number 3 (semi-empirical electronic structure method)
SE	Schrödinger equation
SG	sparse grid
VCI	vibrational configuration interaction
VSCF	vibrational self-consistent field
WF	wave function

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