Chapter 9
Describing Molecules in Motion by Quantum Many-Body Methods

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Abstract For a complete quantum description of molecular systems, it is necessary to solve Schrödinger equations for both electrons and nuclei. In this chapter, focus is given to approximate methods for solving the nuclear Schrödinger equation. Similarities and dissimilarities compared to the practice employed for the electronic case will be noted. A many-body view on potential energy surfaces will be used to motivate a many-body view on the general problem of solving the nuclear Schrödinger equation. A second quantization multimode formalism will be outlined and used to formulate many-body wave functions for nuclear motion. The vibrational self-consistent field (VSCF) method is introduced. Full vibrational configuration interaction (FVCI) is introduced as the reference, before primary attention is given to vibrational coupled cluster (VCC) theory. VCC theory is furthermore analysed from a tensor decomposition perspective and with a perspective to scaling with system size.

Keywords Molecules in motion · Anharmonic molecular vibrations · Vibrational coupled cluster · Many-body methods · Potential energy surfaces · Second quantization · Tensors

9.1 Introducing

Predicting the behaviour of molecules on the basis of quantum mechanics requires a quantum treatment of both the electrons and the atomic nuclei. In the Born-Oppenheimer approximation, we can can consider the electronic and the nuclear problem as two separate, but coupled problems. Through the years a number of computational tools have been developed for solving the electronic Schrödinger equation. Among the most successful of these methods are many-body methods such as perturbation theory and coupled cluster theory, and they are now text book methods [1, 2]. Today coupled cluster calculations are in many contexts the golden standard.

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In this chapter, we consider many-body methods for the nuclear Schrödinger equation. For solving the nuclear Schrödinger equation the application of many-body methods has been considerable less common, and for nuclear motion variational treatments using a linear expansion in a basis is prevailing. Nevertheless, there is still key advantages of a many-body approach. In the next chapter, I will highlight some general differences between electronic structure theory and vibrational structure theory. Thereafter, I will introduce hierarchies of approximations for the Hamiltonian that can be denoted many-body like and subsequently discuss construction of wave functions in second quantization, including, in particular, vibrational self-consistent field (VSCF), vibrational configuration interaction (VCI) and vibrational coupled cluster (VCC) methods. I will also present a chapter with a tensor perspective on the VCC wave function.

9.2 Electronic and Nuclear Schrödinger Equations

Consider a molecular system described by quantum mechanics in the non-relativistic time-independent Schrödinger picture

$$(T_e + T_n + V_{ee} + V_{nn} + V_{en})\Psi_{tot}(\mathbf{r}, \mathbf{R}) = E\Psi_{tot}(\mathbf{r}, \mathbf{R}) \tag{9.1}$$

Here **r** and **R** symbolize, respectively, electronic and nuclear coordinates. We invoke from the outset the Born-Oppenheimer approximation. The electronic Schrödinger equation for a set of clamped nuclei determines the energy $E_{el}(\mathbf{R})$ as a function of nuclear coordinates

$$(T_e + V_{ee} + V_{nn} + V_{en})\Psi_{el}(\mathbf{r}; \mathbf{R}) = E_{el}(\mathbf{R})\Psi_{el}(\mathbf{r}; \mathbf{R}) \tag{9.2}$$

This electronic energy appears as the potential in the nuclear Schrödinger equation, i.e. with $V = E_{el}(\mathbf{R})$, we write

$$(T_n + V)\Psi_n(\mathbf{R}) = E_n\Psi_n(\mathbf{R}) \tag{9.3}$$

where E_n is the total energy. In general, nuclear motion covers both translation, rotation and vibration.

Consider the vibrational motion of a nonlinear molecule with N atoms, leading to $M = 3N - 6$ vibrational degrees of freedom denoted *modes*, separating out translational and rotational motion. The internal relative nuclear motion is thereby described by a set of M coordinates denoted $q_1, q_2, \dots, q_M$. While electronic structure theory deals with indistinguishable electrons where each is described by a set of cartesian coordinates as well as a spin coordinate, the internal motion of molecules is described by a set of distinguishable degrees of freedom. The particular set of coordinates may be a set of normal coordinates (a rectilinear coordinate set) or general curvilinear coordinates, such as bond lengths, angles and dihedrals.

The immediate consequence of this is that in the electronic case the kinetic energy operator is simple (using atomic units throughout),

$$T_e = \sum_i \frac{1}{2} \nabla_i^2 \tag{9.4}$$

In contrast, already in normal coordinates the exact kinetic operator is more involved in the exact Watson [3] form for rovibrational motion (separating out translation)

$$T = -\frac{1}{2} \sum_k \frac{\partial^2}{\partial Q_k^2} + \frac{1}{2} \sum_{\alpha\beta} (J_\alpha - \pi_\alpha) \mu_{\alpha\beta} (J_\beta - \pi_\beta) - \frac{1}{8} \sum_\alpha \mu_{\alpha\alpha} \tag{9.5}$$

Here J_α is the total and π_β the vibrational angular momenta, respectively, $\mu_{\alpha\beta}$ is the inverse of the effective moment of inertia. Considering a non-rotating molecule through putting $J = 0$, we observed there are still some terms with the μ tensor left. These terms are often neglected for larger molecules as the inverse of the moment of inertia will decrease their importance. With their neglect a simple kinetic operator is obtained for the vibrational motion (separating out rotation)

$$T = -\frac{1}{2} \sum_k \frac{\partial^2}{\partial Q_k^2} \tag{9.6}$$

Neglecting the additional Watsonian terms can be a significant approximation for small molecules and/or vibrations with light atoms. The remaining coupling in the Watson in Eq. (9.5) derives from the interaction between rotation and vibration and the fact that the rotational set of coordinates is not a rectilinear set of coordinates. In more general curvilinear coordinates the vibrational kinetic energy operator is even more complicated. Thus, unlike electronic structure theory the kinetic energy operator may generally bring coupling between the different degrees of freedom in the quantum treatment of nuclear motion.

The primary cause of couplings between the modes is the potential. In the case of the electronic Schrödinger equation, the electron–electron interaction is of Coulomb type and thus of two-body nature. In contrast, the vibrational structure potential is the Born-Oppenheimer potential which formally couples all degrees of freedom. The Coulomb potential is known exactly and before any calculation and is similar for all molecules. In other words, the potential is universally defined. The potential of the nuclear Schrödinger equation will not be known exactly, and it is unique for each different molecule.

The above points show clearly the different outsets for electronic and nuclear theories. Since the spaces and the Hamiltonians are fundamentally different our method of solution will also differ. Nevertheless, we shall discuss how one can recover in certain ways a many-body view on describing coupling in many mode systems that is somewhat similar to many-body theory for electrons.

In passing I note that though the relevance of time-dependent electronic theory is becoming more and more clear, the overwhelming majority of quantum chemical studies up to this day are based on time-independent quantum theory, and some of the extensions to time-dependent theory are furthermore restricted to special cases, such as periodic perturbations. For nuclear motion, time-dependent approaches are generally a much more equal part of the bigger field of describing nuclear motion. For example, a general method like the multi-configurational time-dependent Hartree (MCTDH) has shown great applicability for both time-dependent and time-independent phenomena. However, in this chapter we shall stay with a time-independent description.

9.3 Many-Body Expansion of the Hamiltonian

The potential is decisive for accuracy and efficiency. We have already established that the potential originates from solving the electronic Schrödinger equation. The electronic Schrödinger equation cannot be solved exactly for non-trivial systems, and the first primary cause for concern is thus the accuracy of the electronic structure methodology used in a concrete case. This is the subject of electronic structure theory and will not be pursued further here. However, we shall consider other decisive factors such as how to deal with the dimensionality of the potential. How can we represent the PES in many dimensions? And how can we obtain the effect of the PES from calculating only a restricted set of points on the PES?

One classical way of obtaining a PES is through Taylor expansion. Thus, following geometry optimization and subsequent harmonic analysis, higher (than second) order derivatives are calculated up to a maximum order. The third (cubic) and fourth (quartic) order potential terms describe the lowest order anharmonicity. Their calculation and use have perfect meaning in a perturbation theoretical sense, using the normal coordinate harmonic oscillator as the zeroth order description. However, in a broader perspective Taylor expanded potentials are problematic. First of all, the radius of convergence is likely small and for larger distortions from the reference structure, the PES can be quite unphysical. It is for example common that the Taylor expanded PES have "variational holes". That is, at some distortions from the reference, the PES becomes unphysically of lower energy than at the reference structure. Applying a Taylor expanded PES in a variational calculation is obviously risky.

There are, however, also some attractive features of the Taylor representation. One attractive feature is that the corresponding Hamiltonian becomes a sum over products (at least if either the simple kinetic energy operator is used or the inverse moment of inertia in the kinetic energy terms is treated in a similar Taylor expansion). Thus, the Hamiltonian contains a sum of $q_i^{n_i} q_j^{n_j} q_k^{n_k} \cdots$ terms with prefactors. A general sum over product Hamiltonian can be written as a sum over T product terms

$$\hat{H} = \sum_{t=1}^{T} c_t \prod_{m=1}^{M} \hat{h}^{m,t} \tag{9.7}$$

giving a similar simple product structure for integrals over direct product basis functions. This is in turn decisive for efficient wave function calculations, since this means that each term is separable into a product over the involved modes. This feature is in fact so important that even if we do not pursue it directly by Taylor expansion, it is often desirable to fit the potential to the sum-over-product-form of Eq. (9.7). In other words, for the PES we can make a fit of energies calculated on a grid to the particular set of fit functions we choose. Here, we may use polynomials for fitting, but it is important to distinguish the fitting case from the polynomial obtained as Taylor expansion.

The above considerations, however, does not solve the problem of dimensionality. We will now introduce a particular type of many-body expansion of the potential. The basic idea of restricted mode–mode coupling has been pursued under different names such as n-mode representation [4], many-body expansion [5], mode-coupling expansion, cut-HDMR (High Dimensional Model Representation) [6], cluster expansion [7] and others [8–11]. As such it has been an integrated part of much recent research. The outcome is that the full PES is obtained as a sum of many lower-dimensional functions. Let a vector of mode indices be called a mode combination (MC), and $\mathbf{m}_n$ is such a vector of n indices $m_1, m_2, \dots, m_n$. Consider an expansion point and a set of coordinates defined to be all zero for the expansion point. Assume that $V(0, 0, 0, 0 \dots 0) = 0$, noting that an additional constant term can easily be added after our treatment. We can now write the PES in terms of the particular MCs that are relevant for the representation of the potential:

$$V \approx \sum_{\mathbf{m} \in \mathbf{MCR}\{\mathbf{V}\}} \bar{V}^{\mathbf{m}}, \tag{9.8}$$

Here MCR is a mode combination range—the set of MCs included in the potential. Equation (9.8) is the basis for introducing approximations. IA sequence of approximate potentials providing a more and more accurate description of the full coupling by including more and more mode couplings. The potentials $\bar{V}^{\mathbf{m}_n}$ are incremental potentials, defined such that they give zero if any coordinates in the set given by $\mathbf{m}_n$ are zero

$$\bar{V}^{\mathbf{m}_n}(\dots, q_i = 0, \dots.) = 0. \tag{9.9}$$

For the two-mode example

$$\bar{V}^{m_1 m_2} = V^{m_1 m_2} - V^{m_1} - V^{m_2} \tag{9.10}$$

where

$$V^{m_1} = V(0, \dots, 0, q_{m_1}, 0, \dots, 0) \tag{9.11}$$

$$V^{m_1 m_2} = V(0, \dots, 0, q_{m_1}, 0, \dots, 0, q_{m_2}, 0, \dots, 0) \tag{9.12}$$

etc. A two-mode representation of the PES can be written as

$$V^{(2)} = \sum_{m_1} \bar{V}^{m_1} + \sum_{m_1 < m_2} \bar{V}^{m_1 m_2} = \sum_{m_1 < m_2} V^{m_1 m_2} - (M-2) \sum_{m_1} V^{m_1} \tag{9.13}$$

The mode number indices m_i run from mode 1 to mode M and $m_i \neq m_j$. In the two-mode case, the PES of a three atomic system consists of three two-mode sub-PES and three one-mode sub-PES. Thus, the expression in Eq. (9.8) is an approximation to the full PES. Instead of computing the full PES, it is represented in terms of a number of sub-PES where each of these is restricted to a limited set of modes. This provides a much more realistic path to accurately representing the PES. Consider for example a grid-based approach for PES construction, where potential energy values are calculated on an appropriate set of points each called a single point (SP). For simplicity we assume that the number of SPs per coordinate is N_p and the same for all coordinates. Including up to n-mode couplings for a molecule with M modes gives rise to $\sum_{i=0}^{n} \binom{M}{i} \left(N_p\right)^i$ SPs as opposed to the full PES having N_p^M. This is a reduction from exponential to polynomial computational scaling in M. The leading scaling, $\binom{M}{n} \left(N_p\right)^n$ is the dominating computational effort. In the sequence of potentials converging to the full potential

$$V^{(1)}, V^{(2)}, V^{(3)}, \dots, V^{(M)} \tag{9.14}$$

where $V^{(n)}$ include all mode couplings up to and including n-mode couplings, it is typically only realistic to consider low-order methods, say $n = 2, 3, 4$. Still, we have obtained a converging sequence of potentials. We also see clearly the additional complexity compared to the electronic case with its universally defined two-body Coulomb potential.

The n-mode PES approach defined above has been used and tuned by many researchers in different contexts with respect to obtaining accurate potentials with as few SPs as possible. By fitting to a basis of functions, the sub-PES can be brought into a sum-over-product form. Thus, the total Hamiltonian can be numerically represented in an n-mode expanded sum-over-product form. This is highly convenient for the subsequent calculation and use of the matrix element of the Hamiltonian for the vibrational wave function calculation. Finally, one should be aware of the fact that the PES construction and the wave function calculation are not quite independent. A given wave function spans over a particular region of configuration space, and it is important the potential is fairly accurate in this region. On the other hand, the more involved the PES really is, or its representation, the more involved the vibrational structure calculation will be. An adaptive density guided approach (ADGA) has been developed, where the PES is calculated in accordance with the convergence of the combined wave function and PES calculation [12].

The restricted mode-coupling representation of the potential discussed above is in a certain sense a many-body expansion. Such expansions can be generalized and applied to the PES in other ways [13]. In particular, the many-body view is in agreement with the so-called incremental method for calculating electronic energies. In the incremental method, the full system is considered as composed of fragments. In practice some kind of cutting and capping of the full system into subsystems is required which will not be further discussed here. The idea is now that the electronic energy of the system can be calculated in a many-body expansion similar as above. Let A, B denote fragments. Then the energy of each SP can be written as

$$E_{el} = \sum_{A} E_A + \sum_{A>B} (E_{AB} - E_A - E_B) + \cdots \tag{9.15}$$

i.e. the energy is obtained as a sum over energies calculated for different fragments and different fragment combinations. This form of the energy evaluation can now be combined with potential expansion, such that each SP in the calculation of the many small sub-PES are expanded as in Eq. (9.15). This means that we have progressed from a full dimensional PES calculated from full dimensional SPs to a PES given in terms of sums of lower-dimensional sub-PESs calculated from energies obtained as sums of lower-dimensional SPs. We denote such approaches as double incremental, as it is in a certain sense simply the simultaneous application of the same idea in two different directions.

The efficiency of the double incremental idea can be strongly boosted by using coordinates with a well-defined locality, meaning that a given coordinate is known to move only a limited set of atoms relative to each other. To understand this, note that standard normal coordinates will be formally delocalized over the full systems. This means, that in the calculation of every sub-PES the displacement of the coordinates will mean that there are slight variations in all fragment combinations. This means that all fragments must be recalculated. On the other hand, if we consider a sub-PES for coordinates that a completely localized to atoms within a few fragments, then the calculation of this sub-PES requires only calculations for the fragment combinations that actually change.

It has been shown how an algorithm for flexible adaptation of local coordinates of nuclei (FALCON) [14] can be used to provide a set of coordinates with a well-defined locality. Following the above considerations, the double incremental approach with FALCON coordinates (denoted DIF) is computationally much more efficient than the double incremental approach in normal coordinates (denoted DIN). Using the particular structure of FALCON coordinates, the efficiency can be even further improved by applying DIF with auxiliary coordinate transformations (DIFACT). With the DIFACT approach one can achieve linear scaling of the total accumulated cost of the SP calculations [13]. This should be contrasted to the original mode-coupling expansion case where the accumulated cost of the SP calculations would scale as $M^{n_{max}} \times N^s$ where N is the number of orbitals of the systems and s is the characteristic scaling of the applied quantum chemical method, i.e. $s = 7$ for CCSD(T).

The ideas in the double incremental expansion approach are likely extendable to other local coordinates than FALCON coordinates, such as various sets of internal coordinates. It does require a molecule of some size for the fragmentation procedure to make chemical sense. However, the potentially huge reductions in computational effort in the construction of the PES is highly encouraging for future applications to larger systems.

9.4 Second Quantization

Second quantization formulations have proven very productive in many contexts of many-body theory, for example for the electronic structure of molecules. The commutation or anti-commutation relations of the fundamental creation and annihilation operators brings to live the symmetry or antisymmetry requirements of the wave function with respect to particle permutation. The interest in developing many-body methods for nuclear motion lead to the development of SQ formulations for systems with distinguishable degrees of freedom [15, 16] and will be briefly summarized.

Assume that for mode m we have a complete basis $\{\phi^m_{p^m}(q_m)\}$ indexed by $p^m = 0, 1, \dots, N^m - 1$. Here N^m is the number of one-mode basis functions for mode m. We may generate basis functions in the M-mode space as products of the one-mode basis functions

$$\boldsymbol{\Phi}_{\mathbf{s}}(q_1, q_2, \dots, q_M) = \prod_{m=1}^{M} \phi^m_{s^m}(q_m) \tag{9.16}$$

The one-mode functions shall be denoted *modals* while their M-mode product states are denoted Hartree products. We consider the system as composed of M distinguishable degrees of freedom, and accordingly we do not consider any symmetrization

In setting up second quantization we describe the system in terms of occupation-number vectors (ONVs) where there per construction is a one-to-one correspondence between second quantization ONVs and first quantization Hartree products. The ONVs are of the form

$$|\mathbf{k}\rangle = \left| \{k^1_0, k^1_1, \dots, k^1_{N^1-1}\}, \dots, \{k^m_0, k^m_1, \dots, k^m_{N^m-1}\}, \dots, \{k^M_0, k^M_1, \dots, k^M_{N^M-1}\} \right\rangle \tag{9.17}$$

The integer $k^m_{p^m}$ is the occupation number for modal p^m of mode m.

The vacuum state is the state with only zero occupation $|\text{vac}\rangle = |0, 0, \dots, 0\rangle$ and is normalized as well, i.e. $\langle \text{vac}|\text{vac}\rangle = 1$. Similar to the overlap between two Hartree products for an orthonormal basis, the ONV inner product for an orthonormal basis is

$$\langle \mathbf{k}|\mathbf{l}\rangle = \prod_{m=1}^{M} \prod_{p^m=1}^{N^m} \delta_{k^m_{p^m} l^m_{p^m}} = \delta_{\mathbf{kl}} \tag{9.18}$$

while for a general vector $|\mathbf{c}\rangle = \sum_{\mathbf{k}} c_{\mathbf{k}}|\mathbf{k}\rangle$ the inner product is defined as,

$$\langle \mathbf{c}|\mathbf{d}\rangle = \sum_{\mathbf{kl}} \langle \mathbf{k}|c^*_{\mathbf{k}} d_{\mathbf{l}}|\mathbf{l}\rangle = \sum_{\mathbf{kl}} c^*_{\mathbf{k}} d_{\mathbf{l}} \delta_{\mathbf{kl}} = \sum_{\mathbf{k}} c^*_{\mathbf{k}} d_{\mathbf{k}} \tag{9.19}$$

In the ONV space creation and annihilation operators can be introduced with commutator relations,

$$[a^{m\dagger}_{p^m}, a^{m'\dagger}_{q^{m'}}] = [a^{m}_{p^m}, a^{m'}_{q^{m'}}] = 0, \tag{9.20}$$

$$[a^{m}_{p^m}, a^{m'\dagger}_{q^{m'}}] = \delta_{mm'}\delta_{p^m q^{m'}}. \tag{9.21}$$

The action of $a^{m\dagger}_{p^m}$ is to create a vibration in mode m, level p^m while $a^{m}_{q^m}$ annihilates a vibration in level q^m of mode m. In particular, an annihilation operator acting on the vacuum state gives zero

$$a^{m}_{p^m}|\mathrm{vac}\rangle = 0 \tag{9.22}$$

The physically relevant subspace of all $|\mathbf{k}\rangle$ that correspond to the set of M-mode Hartree products are those where only one $k^m_{i^m}$ is equal to 1 for each mode m and all the others are 0.

Defining some further terminology is useful: **m** denotes a set of modes combined in a mode combination (MC). A MC may include from 1 to M modes, and we shall occasionally use a subscript to indicated the dimensionality.

The creation and annihilation operators can in turn be used to construct all SQ states and operators such that there is a one-to-one correspondence between all matrix elements and thereby all measurable quantities between calculations done in first and second quantization. The one-mode shift operators $E^m_{p^m q^m}$ that moves occupation in mode m from modal q^m to p^m is highly useful in this regard. They are defined as

$$E^m_{p^m q^m} = a^{m\dagger}_{p^m} a^{m}_{q^m}. \tag{9.23}$$

The general Hartree Product above can now be expressed as

$$|\Phi_{\mathbf{s}}\rangle = \prod_{m=1}^{M} a^{m\dagger}_{s^m}|\mathrm{vac}\rangle. \tag{9.24}$$

We may pick out a reference state described by an M-dimensional vector $\mathbf{i} = \left(i^1, i^2, \ldots, i^M\right)$

$$|\Phi_{\mathbf{i}}\rangle = \prod_{m=1}^{M} a^{m\dagger}_{i^m}|\mathrm{vac}\rangle. \tag{9.25}$$

We can now generate other Hartree products in the M-mode space by applying excitation operators,

$$\tau^{\mathbf{m}}_{\mu^{\mathbf{m}}} = \prod_{m\in\mathbf{m}} a^{m\dagger}_{a^m} a^{m}_{i^m} \tag{9.26}$$

to this reference state. In doing so we "excite" all modes in the MC **m** from the occupied modals i^m to the virtual modals a^m. The nomenclature of using indices i, j to denote occupied modals and a, b, to denote modals unoccupied (virtual) in the reference product function is standard. The index μ is a compound index including the necessary information on the specific modals involved. Examples of one and two-mode excitation operators are,

$$\tau^{m_1}_{a^{m_1}} = a^{m_1\dagger}_{a^{m_1}} a^{m_1}_{i^{m_1}} = E^{m_1}_{a^{m_1} i^{m_1}} \tag{9.27}$$

$$\tau^{\mathbf{m}_2}_{\mu^{\mathbf{m}_2}} = \tau^{m_1 m_2}_{a^{m_1} a^{m_2}} = a^{m_1\dagger}_{a^{m_1}} a^{m_2\dagger}_{a^{m_2}} a^{m_1}_{i^{m_1}} a^{m_2}_{i^{m_2}} = E^{m_1}_{a^{m_1} i^{m_1}} E^{m_2}_{a^{m_2} i^{m_2}} \tag{9.28}$$

Note here that the **i** vector is often implied, meaning that it is only relevant to keep track of the unoccupied indices.

The commutator relations can be used to show that all excitation operators commute,

$$[\tau^{\mathbf{m}}_{\mu^{\mathbf{m}}}, \tau^{\mathbf{m}'}_{\nu^{\mathbf{m}'}}] = 0 \tag{9.29}$$

which is of great practical importance. The Hermitian adjoint of the excitation operator $\tau^{m_1}_{a^{m_1}}$ is a de-excitation operator

$$\tau^{m_1\dagger}_{a^{m_1}} = a^{m_1\dagger}_{i^{m_1}} a^{m_1}_{a^{m_1}} \tag{9.30}$$

From the killer condition for the annihilation operator working on the vacuum state, we have corresponding killer conditions for the excitation operators

$$(\tau^{\mathbf{m}}_{\nu^{\mathbf{m}}})^{\dagger} |\Phi_{\mathbf{i}}\rangle = 0 = \langle \Phi_{\mathbf{i}} | \tau^{\mathbf{m}}_{\nu^{\mathbf{m}}} \tag{9.31}$$

Note that $\tau^{\mathbf{m}}_{\mu^{\mathbf{m}}}$ and $(\tau^{\mathbf{m}'}_{\nu^{\mathbf{m}'}})^{\dagger}$ do not generally commute. The excited states are orthogonal to the reference ket $|\Phi_{\mathbf{i}}\rangle$ and the set of states $\{|\Phi_{\mathbf{i}}\rangle, \tau_{\mu}|\Phi_{\mathbf{i}}\rangle\}$ thus forms a basis for the full M-mode space when all possible μ are included.

9.5 Vibrational Self-consistent-field Theory and the Mode–Mode Correlation Problem

The vibrational self-consistent field (VSCF) approach [17, 18] is a mean-field theory applied to the anharmonic vibrational problem. We seek to variationally optimize the energy

$$E_{\mathbf{i}} = \langle \Phi_{\mathbf{i}} | \hat{H} | \Phi_{\mathbf{i}} \rangle \tag{9.32}$$

under variation of orthonormal one-mode functions $\phi^m_{i^m}(q_m)$ for a given Hartree Product state. The reference index vector **i** specifies which reference occupation is used for each mode as in the previously introduced notation.

The variational conditions with orthonormality constraints leads to the self-consistent-field equations

$$\hat{F}^{m,\mathbf{i}}\phi^m_{i^m}(q_m) = \varepsilon^m_{i^m}\phi^m_{i^m}(q_m) \tag{9.33}$$

where the mean-field operator $\hat{F}^{m,\mathbf{i}}\phi^m_{i^m}(q_m)$ for mode m is obtained as the average of the Hamiltonian over all the other degrees of freedom (here given in first quantization)

$$\hat{F}^{m,\mathbf{i}} = \langle \prod_{m'=1,\neq m}^{M} \phi^{m'}_{i^{m'}}(q_{m'})|\hat{H}| \prod_{m''=1,\neq m}^{M} \phi^{m''}_{i^{m''}}(q_{m''})\rangle \tag{9.34}$$

After solving the coupled VSCF equations (Eq. (9.33)) self-consistently resulting in VSCF optimized modals (in analogy to Hartree-Fock orbitals for electrons). The total energy is obtained from Eq. (9.32) using the converged VSCF modals. In analogy to the electronic case, we thus have a well-defined mean-field state with a well-defined energy. This energy is based on an averaged interaction between modes as clearly seen from the averaging in Eq. (9.34). The VSCF approach thus immediately defines a correlation problem. VSCF can be implemented to give a fast and efficient evaluation of anharmonic wave functions, see Ref. [19], but will not be further discussed here. Instead we will focus on methods that goes beyond VSCF, and thereby explicitly includemany-body effects.

The basic ansatz for proceeding beyond the single Hartree Product wave function is vibrational configuration interaction (VCI). The VCI wave function can be written as

$$|\mathrm{VCI}\rangle = (1 + \mathrm{C})|\Phi_{\mathbf{i}}\rangle = |\Phi_{\mathbf{i}}\rangle + \sum_{\mu} \mathrm{C}_{\mu}\tau_{\mu}|\Phi_{\mathbf{i}}\rangle \tag{9.35}$$

using intermediate normalization $1 = \langle \Phi_{\mathbf{i}}|\mathrm{VCI}\rangle$. The intermediate normalization is convenient for later comparisons, but is not essential for the theory, and normally standard unit norm normalization is used. The **i** index vector is, as mention earlier, implied for all V excitation operators (τ_μ) and the related VCI parameters (C_μ) and is not explicitly included in the notation here and in the following. The VSCF state is used for reference here, but it is trivial to use any other Hartree Product state.

We may write the operator generating the VCI wave function in more detail as

$$C = C_1 + C_2 + C_3 + \cdots C_M = \sum_{j=1}^{M} \sum_{\mu_j} c_{\mu_j}\tau_{\mu_j} \tag{9.36}$$

where the extra j index denotes the excitation level.

In the case where we use all configurations possible we have a N^M dimensional space, and a similar number of free parameters to determine, assuming there are N modals for each of the M degrees of freedom. Approximate VCI wave functions are introduced by limiting the space considered. This can be done in many ways. Here, we shall limit ourself to discuss the hierarchy in which we limit the summation over excitation levels in Eq. (9.36) to a maximum level n. The VCI wave function corresponding to this truncation is denoted VCI[n]. In the limit of no truncation we obtain the Full VCI solution, FVCI = VCI[M]. The linear variational approach implicit to VCI (using VSCF modals or another set of one-mode functions) has been the traditional approach to addressing the solution of the M-mode system [20–22]. When convergence close enough to FVCI can be obtained this is obviously fully satisfactory. The problem comes only from the increased size of the space needed for increasing systems size, which requires special treatments to be required. While treating large spaces in such linear expansions are becoming possible [23], we will here switch to the another parameterization and later show this has interesting properties for increasing system size.

9.6 Vibrational Coupled Cluster

The vibrational coupled cluster ansatz is given in terms of an exponential operator working on the reference wave function $|\boldsymbol{\Phi}_{\mathbf{i}}\rangle$

$$|\mathrm{VCC}\rangle = \exp(T)|\boldsymbol{\Phi}_{\mathbf{i}}\rangle, \tag{9.37}$$

Here T is the so-called cluster operator which we in general write as

$$T = \sum_{\mu} t_{\mu}\tau_{\mu}. \tag{9.38}$$

The t_μ parameters are the cluster amplitudes and the free parameters of the methods, while τ_μ are the corresponding excitation operators. All are indexed by μ—a compound index giving all necessary information to specify the excitation. As for the VCI case the cluster operator can be written as

$$T = T_1 + T_2 + T_3 + \cdots T_M = \sum_{j=1}^{M}\sum_{\mu_j} t_{\mu_j}\tau_{\mu_j} \tag{9.39}$$

The one- and two-mode excitations can be written out as

$$T_1 = \sum_{\mu_1} t_{\mu_1}\tau_{\mu_1} = \sum_{m_1}^{M}\sum_{a^{m_1}} t_{a^{m_1}}^{m_1}\tau_{a^{m_1}}^{m_1}, \tag{9.40}$$

$$T_2 = \sum_{\mu_2} t_{\mu_2} \tau_{\mu_2} = \sum_{m_1 < m_2}^{M} \sum_{a^{m_1}} \sum_{a^{m_2}} t^{m_1 m_2}_{a^{m_1} a^{m_2}} \tau^{m_1 m_2}_{a^{m_1} a^{m_2}}. \tag{9.41}$$

We may also write the cluster operator in terms of MC notation as

$$T = \sum_{\mathbf{m} \in MCR[T]} \sum_{\mu^{\mathbf{m}}} t^{\mathbf{m}}_{\mu^{\mathbf{m}}} \tau^{\mathbf{m}}_{\mu^{\mathbf{m}}} \tag{9.42}$$

where $\mathbf{m}$ is simply one of the allowed MCs. The definition of a VCC cluster operator requires thus in general a definition of the set of different MCs allowed in the cluster operator. This set (a mode combination range, MCR) is denoted $MCR[T]$ in Eq. (9.42).

Introducing now the VCC ansatz into the Schrödinger equation and premultiplying with $\exp(-T)$, we obtain

$$\exp(-T)\hat{H}\exp(T)|\Phi_{\mathbf{i}}\rangle = E|\Phi_{\mathbf{i}}\rangle \tag{9.43}$$

Projecting onto the reference state and the excited Hartree Products, we obtain respectively the VCC energy

$$E_{VCC} = \langle \Phi_{\mathbf{i}} | \exp(-T)\hat{H}\exp(T)|\Phi_{\mathbf{i}}\rangle = \langle \Phi_{\mathbf{i}}|\hat{H}\exp(T)|\Phi_{\mathbf{i}}\rangle. \tag{9.44}$$

and the VCC amplitude equations

$$e^{\mathbf{m}}_{\mu^{\mathbf{m}}} = \langle \mu^{\mathbf{m}} | \exp(-T)\hat{H}\exp(T)|\Phi_{\mathbf{i}}\rangle = 0. \tag{9.45}$$

Solving first the VCC amplitude equations in Eq. (9.45) we can calculate the energy as in Eq. (9.44).

Truncating the cluster operator at the excitation level n, we obtain a hierarchy of VCC methods, VCC[1], VCC[2], VCC[3], VCC[4], etc. In the limit of no truncation, we obtain the Full VCI solution, FVCC = FVCI.

The requirements for a VCC calculation is that a Hamiltonian is available in some suitable set of coordinates together with an appropriate choice of basis set such that the necessary integrals of the Hamiltonian are available. In the sum-over-product form this means that when the Hamiltonian expansion coefficients c_t and the one-mode integrals of the $h^{m,t}$ operators are available (see Eq. (9.7)), we can first do a VSCF calculation defining the VCC reference state. Then we have to select the set of states to excite to. This is typically done by selecting the MCR, e.g. in the hierarchical sense of one-, two- and higher mode couplings up to a given maximum coupling level. This then defines the VCC calculation for the given reference state.

The nonlinear equations are determined by some iterative methods. From a particular guess for the solution vector $\mathbf{t}$ containing all the amplitudes, one evaluates the similarly sized error vector defined by Eq. (9.45). If this error vector is not below a given threshold in size an improved guess for the $\mathbf{t}$ is made and the process continued. Different methods of quasi-Newton nature. Sufficient here is to state that this procedure usually works relatively smoothly as long as the reference is a reasonable description of the final state. The computational most challenging part is the evaluation of the error vector. The error vector can be very complicated for high-level couplings in the Hamiltonian and high-level excitations included. For example VCC[3] with a three-mode Hamiltonian already contains thousands of terms [24]. In the current preferred approach, all these terms are automatically derived in details, analysed for computational efficiency and finally evaluated by the programme.

In principle, the above procedure is applicable to both ground and excited states. Excited states are, however, often immersed in a dense manifold of states. Solving the nonlinear VCC equations for each state in a state by state fashion can be technically difficult with respect to convergence and raises a number of theoretical concerns such as the potential lack of orthogonality between states. For that purpose, it is in most cases preferable to use response theory to access excited states or alternatively use the attractive option of directly calculating the spectrum. We shall here avoid at all entering into the long details of response theory. All our considerations, however, also apply to response theory calculations of excited states and spectra.

The above VCC theory is the one we have developed and the one we shall further investigate here. Our approach is based on the described SQ and applies to any basis and thereby any reference state, including the VSCF reference state. We note that there exist other exponential CC-like parameterizations of the vibrational wave function. The other approaches have been denoted bosonic CC and are by construction based on a harmonic oscillator like ground state [25, 26].

Let us now investigate further the wave function itself. The wave function for the case of an untruncated cluster expansion can be expanded as

$$\begin{aligned} |\mathrm{VCC}\rangle = |\Phi_{\mathbf{i}}\rangle + T_1|\Phi_{\mathbf{i}}\rangle + (T_2 + \frac{1}{2}T_1^2)|\Phi_{\mathbf{i}}\rangle + (T_3 + T_1T_2 + \frac{1}{6}T_1^3)|\Phi_{\mathbf{i}}\rangle \\ + (T_4 + T_1T_3 + \frac{1}{2}T_2^2 + \frac{1}{2}T_1^2T_2 + \frac{1}{24}T_1^4)|\Phi_{\mathbf{i}}\rangle \ldots . \end{aligned} \tag{9.46}$$

The linear VCI and nonlinear VCC parameterization are two alternative ways of parameterizing the exact wave functions in the untruncated limit. For an exact wave functions they are therefore related through

$$\begin{aligned} C_1 &= T_1 \\ C_2 &= (T_2 + \frac{1}{2}T_1^2) \\ C_3 &= (T_3 + T_1T_2 + \frac{1}{6}T_1^3) \\ C_4 &= (T_4 + T_1T_3 + \frac{1}{2}T_2^2 + \frac{1}{2}T_1^2T_2 + \frac{1}{24}T_1^4) \end{aligned} \tag{9.47}$$

and so on. It is easy to turn this around and obtain

$$
\begin{aligned}
T_1 &= C_1 \\
T_2 &= C_2 - (\frac{1}{2}T_1^2) \\
T_3 &= C_3 - (T_1T_2 + \frac{1}{6}T_1^3) \\
T_4 &= C_4 - (T_1T_3 + \frac{1}{2}T_2^2 + \frac{1}{2}T_1^2T_2 + \frac{1}{24}T_1^4)
\end{aligned}
\tag{9.48}
$$

and so on. We may thus transform between the linear VCI and the exponential VCC formats. This means that if we have a set of excitations in the straight linear picture, we can decompose them into a cluster representation. If such expansions has meaning it is expected that the amplitudes in the cluster representation decay faster with increasing excitation level, as compared to the linear parameterization. Thus higher-mode excitations are expected to be dominated by products of lower excitations.

9.7 A Tensor Perspective on VCC

A quantity with d indices can be denoted a tensor, of *order* d. Hence, a vector is a first order tensor, a matrix is a second order tensor, a 3-way array is an third order tensor, etc. It is natural to represent tensors in terms of their d-way arrays. However, if there are N possible values for each index for each dimension there in total N^d numbers are required to specify the full tensor. This exponential increase in the data with increasing number of dimensions is often referred to as the curse of dimensionality. To address this, we seek in tensor decomposition to numerically represent the same tensor in terms of simple quantities. That is generally, in stead of one full d-way arrays we seek to represent the tensor in terms of a set of arrays of lower dimensions and/or smaller set of index values. For a general overview and descriptions of tensors and tensor decomposition we refer to the literature, see for example Ref. [27]. We will proceed by focusing specifically on the simplest variant of tensor decomposition (CP, see below) as well as on relating the idea to VCC theory.

The most obvious tensor decomposition is CANDECOMP/PARAFAC or canonical polyadic decomposition, abbreviated as CP decomposition. Here a tensor is represented as a sum of vector outer products with $\otimes$ denoting a tensor outer product

$$
\mathscr{X} \approx \sum_r^R \mathbf{a}_r^{(1)} \otimes \mathbf{a}_r^{(2)} \otimes \cdots \otimes \mathbf{a}_r^{(d)} \tag{9.49}
$$

where R of Eq. (9.49) is the *rank*. The rank together with the $\mathbf{a}_r^{(n)}$ vectors which can be collected as column vectors in d $\mathbf{A}^{(n)}$ factor matrices specifies decomposition. Note that the CP format is often represented with a weight factor λ_r for each term but this prefactor is here (as in many other places) absorbed into the columns of one (or more) of the factor matrices. The smallest number of vector outer products that are needed to reproduce the tensor exactly is the tensor rank in a similar fashion to the rank of a matrix. The CP decomposition shares in this sense some similarity to the singular value decomposition of matrices. Unfortunately there is no general simple way to determine the rank of a tensor, and it becomes a numerical exercise to seek CP "fits" that reproduce the tensor to high enough accuracy.

9.7.1 Vibrational Coupled Cluster as a Tensor Decomposition

As is perhaps clear from the two preceding sections, a CC formatted wave function is in a certain sense a decomposition format for the FVCI wave function. We can view the equations representing the VCI excitation in terms of the VCC excitations as a kind of tensor decomposition. In other words, we can consider

$$T_n = f^1(C_n, T_1, \ldots, T_{n-1}) = f^2(C_1, C_2, \ldots ., C_n) \tag{9.50}$$

Similar equations holds at the mode excitation level, where only the excitations for a given MC, **m**, is considered. The cluster excitation operator is written in the form

$$T^{\mathbf{m}} = \sum_{\mu^{\mathbf{m}}} t^{\mathbf{m}}_{\mu^{\mathbf{m}}} \tau^{\mathbf{m}}_{\mu^{\mathbf{m}}} \tag{9.51}$$

and similarly for the VCI excitations. Based upon the MC, **m** we construct the set of MCRs, SMCR[**m**], where the union of all MCs in each MCR is identical to the original MC, **m**. Summing over these MCR[s] we have

$$C^{\mathbf{m}} = \sum_{MCR[s] \in SMCR[\mathbf{m}]} \prod_{\mathbf{m}_k \in MCR[s]} T^{\mathbf{m}_k} \tag{9.52}$$

Here the sum is over all partitions of the set **m** meaning a sum over all ways the set **m** can be obtained as union of disjoint subsets. Thus a set of MCR where the union of all the non-overlapping sets in each gives the original **m**.

We may interpret Eq. (9.52) for the operators to be a tensor decomposition of the VCI correlation amplitudes

$$c^{\mathbf{m}} = \sum_{MCR[s] \in SMCR[\mathbf{m}]} \otimes_{\mathbf{m}_k \in MCR[s]} T^{\mathbf{m}_k} \tag{9.53}$$

In terms of the amplitudes, we have the following set of equations in low order

$$\begin{aligned}
c^{m_1}_{a_1} &= t^{m_1}_{a_1} \\
c^{m_1 m_2}_{a_1 a_2} &= t^{m_1 m_2}_{a_1 a_2} + t^{m_1}_{a_1} t^{m_2}_{a_2} \\
c^{m_1 m_2 m_3}_{a_1 a_2 a_3} &= t^{m_1 m_2 m_3}_{a_1 a_2 a_3} + t^{m_1}_{a_1} t^{m_2 m_3}_{a_2 a_3} + t^{m_2}_{a_2} t^{m_1 m_3}_{a_1 a_3} + t^{m_3}_{a_3} t^{m_1 m_2}_{a_1 a_2} + t^{m_1}_{a_1} t^{m_2}_{a_2} t^{m_3}_{a_3} \\
&= t^{m_1 m_2 m_3}_{a_1 a_2 a_3} + (1 + P_{12} + P_{13}) t^{m_1}_{a_1} t^{m_2 m_3}_{a_2 a_3} + t^{m_1}_{a_1} t^{m_2}_{a_2} t^{m_3}_{a_3}
\end{aligned} \tag{9.54}$$

etc., where $P_{ij}f_{ij} = f_{ji}$. Thus, recasting the FVCI wave function as a FVCC wave function corresponds implicitly to a decomposition of the correlation amplitudes. Either set of correlation amplitudes provide adequate descriptions and are permissible as departure of approximations.

An approximate VCC is not actually obtained as a decomposition of VCI parameters. Rather, approximations are introduced by restricting the excitation level/rank of the decomposition quantities as described in the above VCC sections. Thus, we formally still have a set of FVCI correlation amplitudes. But we proceed from expressing

$$c_n = F_n(t_1, \dots, t_n) \tag{9.55}$$

to

$$c_n = F_n^{\text{app}}(t_1, \dots t_{n_{max}}) \tag{9.56}$$

The cluster amplitudes are not found by "fitting of tensors" but from equations for the immersed approximation of the VCC ansatz into a projected Schrödinger equation. Still, the general decomposition perspective is enlightening and a potential source for new approximations.

9.7.2 Decomposed Correlation Amplitudes with CP

For the VCC wave function we may consider the full set of amplitudes as one vector, but we can also consider it as a number of sub-vectors, one vector for each MC. Each of these vectors are in turn a vectorization of a n-th order tensor, where n is the number of elements of the particular MC. Thus the whole set of VCC or VCI correlation amplitudes can be considered as a stack of tensors.

We may now proceed by applying decomposition to the correlation amplitudes (on top of the inherent recasting of the VCC wave function). For example, the VCC three-mode excitations for the MC (m_0, m_1, m_2) can be represented in CP format as

$$t^{m_0,m_1,m_2}_{a_0,a_1,a_2} \approx \sum_{r=1}^{R^{m_0,m_1,m_2}} t^{(m_0,m_1,m_2),0}_{r,a_0} t^{(m_0,m_1,m_2),1}_{r,a_1} t^{(m_0,m_1,m_2),2}_{r,a_2} \tag{9.57}$$

Each different MC has a different set of one-mode factor matrices, or the other way around, each factor matrix is unique to each MC, and mode for this MC. It is decisive that the rank $R^{\mathbf{m}}$ is unique to the MC $\mathbf{m}$. This is a trivial but key aspect of the approach, therein that the rank can be adjusted to the importance of each MC. Thus, it has been confirmed in numerical studies that in adaptive iterative algorithms we can solve the equations in a manner such that each individual MC achieve each their own individual rank. The advantage of this is that specific couplings are very different and have different strength. This is advantageous because by allowing the rank to be flexible this opens for handling large systems with very many MCs, where the major fraction will have low rank including often zero rank, while only a smaller fraction of particularly important MCs will have a large rank.

We note in passing that our approach is one of following the mode-coupling expansion suggested from the potential, and the hierarchical approach to VCI and VCC we have taken. A different approach is to go back to the full wave function ansatz and directly decompose the FVCI wave function. Such approaches have been undertaken by other groups in various contexts. The drawback of this is that the FVCI tensor is huge. Our hierarchial approach involves much smaller tensors (for truncated VCC) but many of them. Furthermore, there are fundamental differences in performing the decompositions for VCC and VCI.

9.8 Seperability and VCC and VCI Compared

To put tensor decomposition for VCI and VCC in perspective, we will here consider the separability and scalability of energies and wave functions. This is directly related to concepts such as size-extensivity and size-consistency of electronic structure theory and to the property of extensivity of thermodynamics.

Consider the case where we combine the two non-interacting subsystems A and B into a super-system AB described by the Hamiltonian

$$H_{AB} = H_A + H_B \tag{9.58}$$

The two fragments each satisfies their own Schrödinger equation $H_A|A\rangle = E_A|A\rangle$, $H_B|B\rangle = E_B|B\rangle$. Using the SQ formalism the wave functions can be written in the form

$$|A\rangle = W_A|\text{vac}\rangle, \tag{9.59}$$

where W_A is a wave operator

$$W_A = \sum_{\mathbf{s}} C_{\mathbf{s}} \prod_{m=1}^{M} a^{\dagger}_{s_m} \tag{9.60}$$

The exact wave function for the compound system is required to satisfy the Schrödinger equation

$$H_{AB}|AB\rangle = E_{AB}|AB\rangle. \tag{9.61}$$

With the SQ formulation it is simple and rigorous to write up the exact wave function for the compound system in the multiplicatively separable form

$$|AB\rangle = W_{AB}|\text{vac}\rangle = W_A W_B|\text{vac}\rangle \tag{9.62}$$

Related to the product separable wave function, the exact energy is additively separable

$$E_{AB} = E_A + E_B. \tag{9.63}$$

For N non-interacting subsystems each with energy E_1 the total energy of the N-mer is NE_1, in complete analogy to the extensivity of properties in thermodynamics. The behaviour with increasing number of degrees of freedom is an important aspect of an approximate theory. Approximate wave functions can be classified according to whether the wave function is manifestly separable as a product and energy additively separable. This has for long been known to be an important aspect for electronic structure theory. It is also important for vibrational wave functions.

Above we considered that the Hamiltonian was additively separable, indicating that it can be separated into a part which only affects A and a part that only affects B. Actually, such a separability depends on the coordinates. Consider now the simple harmonic limit. If A and B were identical, they would have identical harmonic frequencies in separate harmonic analyses. We could use localized modes (i.e. modes either solely moving atoms in A or solely atoms in B) and have clearly a separable Hamiltonian, total energy and wave function. If we consider normal modes with the same frequencies in the case of two identical non-interacting subsystems combined into one system mixing the degenerate modes in an orthogonal transformation will produce new modes with the same frequencies but now delocalized over both A and B. Clearly, we still have an exact normal coordinate harmonic oscillator description, and as such the wave function and energy are in fact separable. It is, however, somewhat more obscured what goes on. One can then either choose to formulate the concepts to clarify the scalability in such general coordinate cases or else stick to the case of analysing for additively separable Hamiltonians above. We will follow the latter approach, as (i) it is simpler; (ii) it is the separability with distance we are interested in, and it is counterproductive to choose a coupled representation when an uncoupled one can be chosen; (iii), in continuation of the last point we prefer for real molecules also to have localized coordinates as far as possible (meaning unless their couplings become too large). We believe this is quite typical for the molecular case where we strive for low-coupling local coordinates. The case of solids may be different. Carrying out a similar analysis for solids using delocalized coordinates is possible [28], however, may to lead to considerations that are less relevant for isolated molecules where we would imagine vibrational coordinates to be somewhat localized. Our perspective here is that even with local coordinates the size-extensivity issue is non-trivial and important and there is in fact an important interplay between size-extensivity and tensor decomposition.

The VSCF wave function is trivially multiplicatively separable since the VSCF wave operator is a direct product of creation operators. Consider that we initiate the VSCF procedure with the direct product of the solution for VSCF calculations on A and B separately. In the averaging for obtaining the VSCF mean field for a mode localized to system A, we have that the averaging of H_B we simply obtain E_B^{VSCF}.

Accordingly, the VSCF mean-field operator for each subsystem is changed only by a constant factor, which leads to the same optimized VSCF modals. Thus, with

$$W_A^{VSCF} = \prod_{m \in A}^{M_A} a_{i^m}^{m\dagger} \tag{9.64}$$

and similarly for B, we find that the compound wave operator is multiplicatively separable as the exact wave operator,

$$W_{AB}^{VSCF} = W_A^{VSCF} W_B^{VSCF} \tag{9.65}$$

while the energy evaluated as an expectation value is additively separable

$$\begin{aligned} E_{AB}^{VSCF} &= \langle AB|H_{AB}|AB\rangle \\ &= \langle vac|/W_A^{VSCF})^\dagger H_A W_A^{VSCF} (W_B^{VSCF})^\dagger W_B^{VSCF} |vac\rangle \\ &\quad + \langle vac|/W_B^{VSCF})^\dagger H_B W_B^{VSCF} (W_A^{VSCF})^\dagger W_A^{VSCF} |vac\rangle \\ &= E_A^{VSCF} + E_B^{VSCF} \end{aligned} \tag{9.66}$$

Here commutativity of creation and annihilations operators have been used for modals and modes referring to different subsystems.

Consider now a VCC calculation using the VSCF reference state with its correct separability. For a similar super-system as discussed above it is easy to show that the cluster operator (for both exact and truncated VCC treatments)

$$T_{AB} = T_A + T_B \tag{9.67}$$

is a solution to the super-system VCC equations, where T_A and T_B are cluster operators for the subsystems. This means that $W_A^{VCC} = \exp(T_A) W_A^{VSCF}$ generates the VCC wave functions for subsystem A and correspondingly for B. Accordingly, the VCC wave function is multiplicatively separable

$$\begin{aligned} |\mathrm{VCC}_{AB}\rangle &= \exp(T_{AB})|\mathrm{VSCF}_{AB}\rangle \\ &= \exp(T_A)\exp(T_B) W_A^{\mathrm{VSCF}} W_B^{\mathrm{VSCF}} |\mathrm{vac}\rangle \\ &= W_A^{VCC} W_B^{VCC} |\mathrm{vac}\rangle \end{aligned} \tag{9.68}$$

where we have used that the cluster excitation operators commute. Similarly,

$$\begin{aligned} E_{AB} &= \langle \mathrm{VSCF}_{AB}|H_A + H_B|\mathrm{VCC}_{AB}\rangle \\ &= E_A^{VCC} + E_B^{VCC} \end{aligned} \tag{9.69}$$

As a direct consequence of the exponential parameterization and the commutativity of the excitation operators the VCC wave function is multiplicatively separable while the energy is additively separable in accord with the exact case for both exact and truncated wave functions. We see that the separability of VCC derives from including products of T_A and T_B that, as we have seen before, are necessary for correct separability. Such products will be missing in truncated VCI, where the product excitations will be partly or completely outside the space included in an approximate VCI.That is a two-mode times two-mode excitations will be outside the space of VCI[3]. This is an advantage of the exponential VCC parametrization over the linear VCI parametrization for the same excitation space and the same Hamiltonian. VCI will not give the correct separability of the energy and wave function. This means that as we increase the number of non-interacting systems the VCI solution for a given excitation level decays in completeness and accuracy. Or in other words, increasing the size of the system we can in VCC theory expect a fairly constant accuracy with a constant excitation level, while in VCI constant high accuracy would require increasing the excitation space.

All though the above considerations are simplified as they are derived for non-interacting systems, we believe they are good models for real molecular systems which will only be more complicated. For larger molecular system in fairly local coordinates we can envision significant mode-coupling terms between "close" modes in the Hamiltonian while couplings between distant modes are small. The above considerations give reasons to believe that VCC methods can handle this and obtain fairly constant accuracy with increasing size of the system.

Furthermore we may relate this discussion to the tensor decomposition analysis. Consider now the case where we perform a VCC[n] calculation and choose to dynamically decompose the amplitudes to lowest rank needed for each MC. With the VCC format, we thus obtain that the cluster amplitudes belonging to subsystem A and subsystem B are significant and have some non-zero rank. In the uncoupled limit, we should actually have $T_{AB} = 0$ thus it can be represented with rank zero. On the other hand, we cannot expect VCI amplitudes to give rank zero even for uncoupled systems, and this difference between VCC and VCI has been numerically confirmed [29, 30]. For example, four-mode excitations $C_{AB,4}$ will include contributions from for example $T_{A,2}T_{B,2}$ which will not be represented as rank zero, even if $T_{AB,4}$ has in fact zero rank. Thus, if two particular cluster operators with ranks R_A and R_B are multiplied, this will lead to rank $R_A \times R_B$ in the corresponding VCI representation. This means in other words, that the wave function separability of VCC is important from a tensor decomposition perspective. The expected decay of amplitudes for couplings between distant localized modes will be an important aspect of the ability to apply VCC to larger systems in the future. It can be exploited both by the tensor analysis above as well as by a careful selection of the excitation space. Rather than the standard inclusion of excitations solely according to the number of modes involved, we may with reference to Eq. (9.42) choose which MCs are included or excluded by an automatic numerical screening [31]. In such a screening, unimportant distant couplings will be screened away from the outset. Both the automatic screening and the use of tensor decomposition in VCC is still in its infancy. While the promise of tensor decomposition has been illustrated, the practical use of the CP format is difficult, both due to inherent mathematical limitations of the CP format, as well as the dynamical recompression to the CP format in the context of the very complex VCC equations.

9.9 Conclusions

The ability to solve the nuclear Schrödinger equation is important for high accuracy calculations of spectroscopy and dynamics. Many-body methods in general and coupled cluster methods in particular have proven highly successful in solving solving Shcrödinger equations. In this chapter, I have discussed many-body expansions in the context of calculating potential energy surfaces, as well as coupled cluster methods for solving the anharmonic vibrational Schrödinger equation. It has been emphasized that these methods have attractive features in relation to scalability with system size. Here scalability refers both to maintaining a realistic low computational effort as the size of the system increases, as well as maintaining a sufficiently high accuracy. Although further work is needed for unfolding their full potential, these many-body methods are expected to be decisive for pushing the boundaries for computational methods in spectroscopy and dynamics in the coming years.

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References

1. T. Helgaker, P. Jørgensen, J. Olsen, *Molecular Electronic Structure Theory* (Wiley, Chichester, 2000)
2. F. Jensen, *Introduction to Computational Chemstry*, 2nd edn. (Wiley, Chichester, 2006)
3. J.K.G. Watson, Mol. Phys. **15**, 479 (1968)
4. S. Carter, S.J. Culik, J.M. Bowman, J. Chem. Phys. **107**, 10458 (1997)
5. G.C. Schatz, Rev. Mod. Phys. **61**, 669 (1989)
6. H. Rabitz, O.F. Aliş, J. Math. Chem. **25**, 197 (1999)
7. H.-D. Meyer, WIREs: Comput. Mol. Sci. **2**, 351 (2012)
8. M. Griebel, Sparse grids and related approximation schemes for higher dimensional problems, in *Foundations of Computational Mathematics (FoCM05), Santander*, ed. by L. Pardo, A. Pinkus, E. Suli, M. Todd, (Cambridge University Press, 2006) pp. 106–161
9. J.O. Jung, R.B. Gerber, J. Chem. Phys. **105**, 10332 (1996)
10. K. Yagi, T. Taketsugu, K. Hirao, M.S. Gordon, J. Chem. Phys. **113**, 1005 (2000)
11. D. Toffoli, J. Kongsted, O. Christiansen, J. Chem. Phys. **127**, 204106 (2007)
12. M. Sparta, D. Toffoli, O. Christiansen, Theor. Chem. Acc. **123**, 413 (2009)
13. C. König, O. Christiansen, J. Chem. Phys. **145**, 064105 (2016)
14. C. König, M.B. Hansen, I.H. Godtliebsen, O. Christiansen, J. Chem. Phys. **144**, 074108 (2016)
15. O. Christiansen, J. Chem. Phys. **120**, 2140 (2004)
16. O. Christiansen, J. Chem. Phys. **120**, 2149 (2004)
17. J.M. Bowman, Acc. Chem. Res. **19**, 202 (1986)

18. R.B. Gerber, M.A. Ratner, Adv. Chem. Phys. **70**, 97 (1988)
19. M.B. Hansen, M. Sparta, P. Seidler, O. Christiansen, D. Toffoli, J. Chem. Theo. Comp. **6**, 235 (2010)
20. J.M. Bowman, T. Carrington, H. Meyer, Mol. Phys. **106**, 2145 (2008)
21. D. Oschetzki, M. Neff, P. Meier, F. Pfeiffer, G. Rauhut, Croat. Chem. Acta. **85**, 379 (2012)
22. O. Christiansen, Phys. Chem. Chem. Phys. **14**, 6672 (2012)
23. J. Brown, T. Carrington, J. Chem. Phys. **145**, 144104 (2016)
24. P. Seidler, O. Christiansen, J. Chem. Phys. **131**, 234109 (2009)
25. S. Banik, S. Pal, M.D. Prasad, J. Chem. Phys. **129**, 134111 (2008)
26. J.A. Faucheaux, S. Hirata, J. Chem. Phys. **143**, 134105 (2015)
27. T.G. Kolda, B.W. Bader, SIAM Rev. **51**(3), 455 (2009)
28. S. Hirata, M. Keçeli, K. Yagi, J. Chem. Phys. **133**, 034109 (2010)
29. I.H. Godtliebsen, B. Thomsen, O. Christiansen, J. Chem. Phys. A **117**, 7267–7279 (2013)
30. I.H. Godtliebsen, M.B. Hansen, O. Christiansen, J. Chem. Phys. **142**, 024105 (2015)
31. C. König, O. Christiansen, J. Chem. Phys. **142**, 144115 (2015)