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Density matrices and iterative natural modals in vibrational-structure theory

Giovanni Battocchio^{a *}, Niels Kristian Madsen^{b **}, and Ove Christiansen^{b †}

^aDepartment of Chemistry, University of Padova, via Marzolo 1, 35131 Padova, Italy

^bDepartment of Chemistry, Aarhus University, 8000 Aarhus C, Denmark

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Abstract

It is demonstrated how the second-quantization formulation of multi-mode dynamics leads to expressions for vibrational density matrices. The properties and different representations of these matrices are discussed. Diagonalizing the one-mode density matrices defines a set of natural modals for each vibrational mode. The theory and first implementation of the iterative natural modals (ItNaMo) method for correlated vibrational-structure models is presented. In the ItNaMo method, natural modals are used as basis functions for a subsequent correlated calculation. This optimization of the one-mode basis is repeated until the changes in the basis functions become sufficiently small. Ground-state and excited-state energy calculations are presented for water, formaldehyde, and ethylene. It is shown that using optimized coordinates for the water calculation makes the occupation numbers converge to zero much faster and thereby allows for large reductions in the required number of basis functions. For the higher-order wave-function models the ItNaMo method results in smaller energy errors compared to full vibrational configuration interaction (FVCI) and thereby facilitates a more accurate description of the wave function.

KEYWORDS

Density matrix; Natural orbitals; Vibrational-structure theory

1. Introduction

The concept of density matrices originates from statistical thermodynamics expressing the phase-space probability distribution for a given system. The quantum-mechanical analog developed in 1927 by von Neumann is the matrix representation of the density operator describing the quantum state of both pure and mixed ensembles [1]. Later Husimi introduced reduced density matrices that determine the internal particle distribution functions in many-body quantum theory [2]. In the context of molecular quantum mechanics, density matrices describe the mixing or correlation between the set of one-particle basis functions. In a sense the off-diagonal elements determine to which degree the occupation of a given basis function depends on the other occupations.

Density matrices have been used extensively in electronic-structure theory. For any N -electron wave function a first-order density matrix can be constructed and diagonalized which defines the *natural orbitals* and *natural orbital occupation numbers* first introduced by Per-Olof Löwdin in 1955 [3]. Thereby the concept of molecular orbitals and their occupation is not restricted to mean-field theory such as Hartree-Fock (HF). Löwdin showed that the natural orbitals ensure

*Email: giovanni.battocchio@studenti.unipd.it, Telephone: +39 3473501443

**Email: nielskm@chem.au.dk, Telephone: +45 51250790

†Corresponding author: Email: ove@chem.au.dk, Telephone: +45 51526145

the fastest possible basis-set convergence for full configuration interaction (FCI) calculations. Therefore natural orbitals are in a sense the best possible one-particle functions to describe the exact state of the system.

Because electrons are indistinguishable with only pairwise interactions, the energy of any atom or molecule can be expressed as a linear functional of the second-order reduced density matrix [4, 5]. This formulation suggested the tantalizing possibility of employing this second-order reduced density matrix rather than the N -electron wave function to compute the ground-state energy of an atom or molecule. In 1955 Mayer [6] and Löwdin published similar second-order reduced-density-matrix-based expressions with Mayer performing a variational calculation. Later density matrices became textbook material for quantum chemistry [7, 8]. Density matrices are used internally in many advanced electronic-structure methods. Also natural orbitals are used for analysis purposes, e.g. natural occupations calculated by Møller-Plesset 2nd-order perturbation theory (MP2) have been used to make the appropriate selection of active orbital spaces in multiconfiguration self-consistent field (MCSCF) calculations [9, 10].

While the concept of density matrices is well-established within electronic-structure theory, it has scarcely been used in the context of molecular vibrations, see however their role in vibrational MCSCF and multiconfiguration time-dependent Hartree (MCTDH) theory [11, 12]. The vibrational problem is quite different from the electronic one in the sense that the system is composed of distinguishable vibrational modes. The total wave function is parameterized in terms of one-mode functions known as *modals* analogous to molecular orbitals in the electronic-structure case. Because the modes are distinguishable, it is possible to separate the degrees of freedom and introduce a one-mode density matrix with corresponding *natural modals* and *natural modal occupation numbers* for each mode. These modals are then assumed to recover the largest amount of correlation energy for at given vibrational calculation. Furthermore, the vibrational problem is not limited to two-body interactions since all modes can be coupled by the vibrational Hamiltonian. It is therefore relevant to introduce n -mode density matrices. Accounting for mode correlation is accomplished by introducing a hierarchy of correlated vibrational wave-function methods. A mean-field description of the interacting modes is obtained by *vibrational self-consistent field* (VSCF) [13–17] that serves as a reference state for correlated models such as *vibrational configuration interaction* (VCI) [14, 18, 19] and *vibrational coupled cluster* (VCC) [20, 21].

In order to obtain the optimal set of modals for a given vibrational-structure model, the concept of iterative natural modals (ItNaMos) is introduced. This method diagonalizes the one-mode density matrices of all modes with an outer loop using the natural modals as basis set for the next iteration until all modes show only negligible changes of the modals. The idea of an iterative optimization of natural modals is completely similar to the idea of iterative natural orbitals which was proposed and investigated already decades ago in the context of electronic-structure theory [22–25].

The paper is structured as follows. The second-quantization formalism and the vibrational density matrices are introduced in Section 2. Expressions for density matrices for the approximate vibrational-structure models are derived in Section 2.6. Section 2.7 introduces the iterative natural modals while computational details of our pilot implementation and the corresponding results are presented in Sections 3 and 4, respectively. Finally Section 5 provides a summary and outlook.

2. Theory

2.1. Second quantization

Second quantization (SQ) was introduced by Dirac as an algorithm for the construction of quantum mechanics of assemblies of identical particles in 1927 [26]. One year later Jordan and Wigner noted that Dirac’s description is also useful for interacting many-particle systems and they extended the formalism to fermion systems [27].

The term *second quantization* originates from quantum field theory where the usual wave function is considered a *field operator* (this is the 'second' quantization). The fundamental creation and annihilation operators are then introduced by expanding these field operators in terms of one-particle functions. Thereby the clear distinction between operators and states present in first quantization (FQ) is replaced by a unified description employing the same fundamental operators. Second-quantization formulations have proven very productive in many different contexts. One of the strengths of the formalism is that it provides a convenient way of treating systems of indistinguishable particles. Here the symmetry or antisymmetry of the wave function with respect to particle permutation is transferred onto the algebraic properties of the fundamental operators, i.e. commutation or anti-commutation relations.

Much more recently, SQ formulations has also been suggested for systems with distinguishable degrees of freedom [17, 20]. To be more concrete, consider the vibrational motion of a molecule with N atoms. This results in $M = 3N - 6(5)$ vibrational modes described by the coordinates $q_1, q_2, \dots, q_M$. The calculation of the *potential energy surface* (PES) that governs the motion of the nuclei is a tremendous task requiring reliable approximate solutions to the electronic Schrödinger equation [7]. Many approximate electronic-structure models exist, but here the electronic problem will not be considered further. We simply assume that some approximate PES is available.

Assume now we have a (complete or truncated) one-mode basis set for each mode. That is, for mode m we have the basis $\{\phi_{p^m}^m(q_m)\}$ indexed by $p^m = 0, 1, \dots, N^m - 1$, where N^m is the number of modals for mode m . We may generate basis functions in the M -mode space as Hartree products of the modals which can be written as,

$$\Phi_s(q_1, q_2, \dots, q_M) = \prod_{m=1}^M \phi_{s^m}^m(q_m). \quad (1)$$

In most wave-function models, states are described relative to a reference state defined by an M -dimensional vector $\mathbf{i} = [i^1, i^2, \dots, i^M]$ that contains the index of the occupied modal for each mode. For example the ground-state Hartree product (assuming energetic ordering of the modals) is denoted $\mathbf{i} = [0, 0, \dots, 0]$. The usual nomenclature is that i denotes the occupied modals for a given mode in the reference product function, while a, b, c, d denote modals unoccupied in the reference product function.

Using Hartree products, we can expand any M -mode wave function that is expandable using the given modal basis. Note that we use simple Hartree products and have not been concerned with any symmetrization. While the individual nuclei (fermions or bosons) do have particular particle permutation symmetry, we are now considering a Schrödinger equation given in terms of some general coordinates and at the moment without reference to the original particles. We continue in this spirit without considering any deeper-lying particle symmetry, i.e. we do not enforce it, but neither do we break it at the outset. Similar considerations are implicit in many other methods in the field [11, 13–15, 28]. We thus consider the system as composed of M distinguishable degrees of freedom.

We now want to describe the system in terms of occupation-number vectors (ONVs) written in the form $|\mathbf{k}\rangle = |\{k_0^1, k_1^1, \dots, k_{N^1-1}^1\}, \dots, \{k_0^m, k_1^m, \dots, k_{N^m-1}^m\}, \dots, \{k_0^M, k_1^M, \dots, k_{N^M-1}^M\}\rangle$. Each ONV is filled with integers which are the occupation numbers $k_{p^m}^m$ for modal p of mode m . There is a one-to-one correspondence between second-quantization ONVs and first-quantization Hartree products, with the occupation numbers specifying how many times the modal enters the Hartree product. We are interested in the physically relevant subspace of all $|\mathbf{k}\rangle$ where only one $k_{i^m}^m$ is equal to 1 for each mode m and all the others are 0. The state with no occupation is denoted as the *vacuum state* $|\text{vac}\rangle$. Further mathematical properties of ONVs are found in Ref. [17].

The fundamental operators in second quantization are the creation ($a_{p^m}^{m\dagger}$) and annihilation ($a_{p^m}^m$)

operators defined as,

$$a_{p^m}^{m\dagger} |\mathbf{k}\rangle = \sqrt{k_{p^m}^m + 1} |\mathbf{k} + \mathbf{1}_{m,p^m}\rangle . \quad (2)$$

$$a_{p^m}^m |\mathbf{k}\rangle = \begin{cases} \sqrt{k_{p^m}^m} |\mathbf{k} - \mathbf{1}_{p^m}^m\rangle & \text{if } k_{p^m}^m \geq 1 \\ 0 & \text{if } k_{p^m}^m = 0 \end{cases} . \quad (3)$$

The following commutation relations can be derived,

$$[a_{p^m}^{m\dagger}, a_{q^{m'}}^{m'\dagger}] = [a_{p^m}^m, a_{q^{m'}}^{m'}] = 0 , \quad (4a)$$

$$[a_{p^m}^m, a_{q^{m'}}^{m'\dagger}] = \delta_{mm'} \delta_{p^m q^{m'}} . \quad (4b)$$

The creation and annihilation operators are used to define all states as well as all other operators, e.g. a Hartree product is generated by applying a string of creation operators to the vacuum state. The one-mode shift operator $E_{p^m q^m}^m$ that moves occupation in mode m from modal q^m to p^m is defined as,

$$E_{p^m q^m}^m = a_{p^m}^{m\dagger} a_{q^m}^m . \quad (5)$$

A set of modes $\mathbf{m}$ is generally denoted a mode combination (MC) and may include from 1 to M modes. Occasionally we use a subscript to recall the dimensionality, i.e. $\mathbf{m}_n$ includes n modes. The generalized shift operator acting on n modes will accordingly be written as,

$$e_{\mathbf{p}^{\mathbf{m}_n} \mathbf{q}^{\mathbf{m}_n}}^{\mathbf{m}_n} = \prod_{m \in \mathbf{m}_n} E_{p^m q^m}^m = \left(\prod_{m \in \mathbf{m}_n} a_{p^m}^{m\dagger} \right) \left(\prod_{m' \in \mathbf{m}_n} a_{q^{m'}}^{m'} \right) \quad (6)$$

using commutativity between operators for different modes. Two special cases of shift operators are *number operators* $\hat{N}_{p^m}^m = E_{p^m p^m}^m$ and *excitation operators* $\tau_{\mu^{\mathbf{m}}} = \prod_{m \in \mathbf{m}} E_{a^m i^m}^m$. Because of the separation between occupied and virtual modal spaces, all excitation operators commute.

General Hermitian operators can be expressed in SQ by the following expansion,

$$\begin{aligned} \hat{\Omega} &= \Omega_0 + \sum_{m=1}^M \sum_{p^m q^m} \Omega_{p^m q^m}^m E_{p^m q^m}^m + \sum_{m_1 < m_2}^M \sum_{p^{m_1} p^{m_2} q^{m_1} q^{m_2}} \Omega_{p^{m_1} p^{m_2} q^{m_1} q^{m_2}}^{m_1 m_2} E_{p^{m_1} q^{m_1}}^{m_1} E_{p^{m_2} q^{m_2}}^{m_2} + \dots \\ &= \sum_{n=0}^M \sum_{\mathbf{m}_n} \sum_{\mathbf{p}_n \mathbf{q}_n} \Omega_{\mathbf{p}_n \mathbf{q}_n}^{\mathbf{m}_n} e_{\mathbf{p}_n \mathbf{q}_n}^{\mathbf{m}_n} \end{aligned} \quad (7)$$

where the sum over $\mathbf{m}_n$ runs over different sets only.

The exact nuclear Hamiltonian (under the Born-Oppenheimer approximation [29]) of the system can be expressed by such an expansion [17]. The exact PES of the system is not generally known and it is often computationally advantageous to express the Hamiltonian in an approximate *sum-over-products* (SOP) of one-mode operators $h^{mo^{tm}}$ [28, 30],

$${}^{\text{SQ}}H = \sum_t c_t \prod_{m \in \mathbf{m}_t} h^{mo^{tm}} = \sum_t c_t \prod_{m \in \mathbf{m}_t} \left(\sum_{r^m s^m} h_{r^m s^m}^{mo^{tm}} a_{r^m}^{m\dagger} a_{s^m}^m \right) \quad (8)$$

with $h_{r^m s^m}^{mo^{tm}} = \int (\phi_{r^m}^m(q_m))^* h^{mo^{tm}} \phi_{s^m}^m(q_m) dq_m$ being the one-mode integrals.

The kinetic energy operator is in the SOP form using normal coordinates [28] unless corrections from the Watson Hamiltonian are taken into account¹ [31]. The PES, however, is often given in the so-called *n-mode representation* [15] that needs to be fitted to the SOP form [28, 30]. We typically generate an *n-mode* coupled PES in SOP form directly from electronic-structure point calculations using either Taylor expansions [32] or iterative grid methods [33].

2.2. Density matrix

Considering a state expanded in ONVs,

$$|0\rangle = \sum_k c_{\mathbf{k}} |\mathbf{k}\rangle \quad (9)$$

we obtain expectation values of Hermitian operators as,

$$\langle 0 | \hat{\Omega} | 0 \rangle = \sum_{n=0}^M \sum_{\mathbf{m}_n} \sum_{\mathbf{p}_n \mathbf{q}_n} \Omega_{\mathbf{p}_n \mathbf{q}_n}^{\mathbf{m}_n} D_{\mathbf{p}_n \mathbf{q}_n}^{\mathbf{m}_n} \quad (10)$$

where

$$D_{\mathbf{p}_n \mathbf{q}_n}^{\mathbf{m}_n} = \langle 0 | e_{\mathbf{p}_n \mathbf{q}_n}^{\mathbf{m}_n} | 0 \rangle \quad (11)$$

are the elements of an *n-mode density matrix*.

The one-mode density matrix for mode m_1 is a Hermitian matrix with dimensions $N^{m_1} \times N^{m_1}$,

$$D_{p^{m_1} q^{m_1}}^{m_1} = \langle 0 | E_{p^{m_1} q^{m_1}}^{m_1} | 0 \rangle . \quad (12)$$

The diagonal elements of the one-mode density matrix are denoted *occupation numbers* [7],

$$\omega_{p^{m_1}}^{m_1} = D_{p^{m_1} p^{m_1}}^{m_1} = \langle 0 | \hat{N}_{p^{m_1}}^{m_1} | 0 \rangle . \quad (13)$$

For any normalized reference state we thereby have $\omega_{p^{m_1}}^{m_1} = \sum_{\mathbf{k}} k_{p^{m_1}}^{m_1} |c_{\mathbf{k}}|^2$. $\omega_{p^{m_1}}^{m_1}$ then represents the squared norm of the part of $|0\rangle$ where the modal $\phi_{p^{m_1}}^{m_1}(q_{m_1})$ is occupied in all ONVs. We note that,

$$0 \leq \omega_{p^{m_1}}^{m_1} \leq 1 \quad (14)$$

and that the sum of occupation numbers (equal to the one-mode trace of $\mathbf{D}^{m_1}$) gives,

$$\sum_{p^{m_1}} \omega_{p^{m_1}}^{m_1} = \text{Tr}_{m_1} \mathbf{D}^{m_1} = 1 . \quad (15)$$

It thereby follows that the sum of the traces of the set of one-mode density matrices $\mathbf{D}_1 = \{\mathbf{D}^{m_1}, \dots, \mathbf{D}^{m_M}\}$ is equal to the number of modes,

$$\sum_{m_1} \text{Tr}_{m_1} \mathbf{D}^{m_1} = \sum_{m_1} \sum_{p^{m_1}} \omega_{p^{m_1}}^{m_1} = M . \quad (16)$$

Equations (15) and (16) imply that the traces are independent of the choice of modals.

¹These correction terms can be fitted to the SOP form.

2.3. Natural modals

Since $\mathbf{D}^{m_1}$ is Hermitian it can be diagonalized by a unitary matrix,

$$\mathbf{D}^{m_1} = \mathbf{U}^{m_1} \boldsymbol{\eta}^{m_1} \mathbf{U}^{m_1 \dagger} \quad (17)$$

where $\boldsymbol{\eta}^{m_1}$ is a diagonal matrix containing the eigenvalues of $\mathbf{D}^{m_1}$. Note that $\text{Tr}_{m_1} \boldsymbol{\eta}^{m_1} = \text{Tr}_{m_1} \mathbf{D}^{m_1}$ since the trace is invariant under rotation of the basis.

The elements of $\boldsymbol{\eta}^{m_1}$ are denoted *natural modal occupation numbers* in analogy to the electronic natural occupations [3]. The eigenvectors define the corresponding *natural modals* analogous to electronic natural orbitals [7]. These modals have well-defined occupancy and have the same properties as electronic natural orbitals. In electronic-structure theory choosing the natural orbitals with the highest occupancies as basis functions is known to provide the fastest convergence towards the exact limit for FCI wave functions [3]. This convergence is not rigorously guaranteed for approximate wave functions, but nevertheless natural orbitals are often the best choice for ensuring fast basis-set convergence [8]. Thereby a correlated calculation using the natural modals with the highest occupation numbers as basis for each mode is expected to recover a larger amount of the total correlation energy. This is the idea behind *iterative natural modals* described in Section 2.7.

To be more concrete, the $\boldsymbol{\eta}^{m_1}$ matrix can be expressed in terms of transformed creation and annihilation operators $\tilde{a}_{p^{m_1}}^{m_1 \dagger}$ and $\tilde{a}_{q^{m_1}}^{m_1}$. From Eq. (17) we obtain,

$$\begin{aligned} \eta_{r^{m_1} s^{m_1}}^{m_1} &= \sum_{p^{m_1} q^{m_1}} (U^{m_1 \dagger})_{r^{m_1} p^{m_1}} \langle 0 | a_{p^{m_1}}^{m_1 \dagger} a_{q^{m_1}}^{m_1} | 0 \rangle U_{q^{m_1} s^{m_1}}^{m_1} \\ &= \langle 0 | \left(\sum_{p^{m_1}} a_{p^{m_1}}^{m_1 \dagger} U_{p^{m_1} r^{m_1}}^{m_1 *} \right) \left(\sum_{q^{m_1}} a_{q^{m_1}}^{m_1} U_{q^{m_1} s^{m_1}}^{m_1} \right) | 0 \rangle \\ &= \langle 0 | \tilde{a}_{r^{m_1}}^{m_1 \dagger} \tilde{a}_{s^{m_1}}^{m_1} | 0 \rangle . \end{aligned} \quad (18)$$

In the coordinate representation this corresponds to transforming the modals,

$$\tilde{\phi}_{r^{m_1}}^{m_1}(q_m) = \sum_{s^{m_1}} \phi_{s^{m_1}}^{m_1}(q_m) U_{s^{m_1} r^{m_1}}^{m_1 *} \quad (19)$$

due to the one-to-one correspondence between ONVs and Hartree products.

2.4. Reduced density matrix

The wave-function density can be obtained by computing reduced density matrices which can be viewed as the coordinate representation of the $\mathbf{D}^{m_n}$ matrices. The expectation value of a general FQ one-mode operator $f^c = \sum_{m_1} f^{cm_1}$ can be expressed as,

$$\langle 0 | f^c | 0 \rangle = \sum_{m_1} \langle 0 | f^{cm_1} | 0 \rangle = \sum_{m_1} \int [f^{cm_1}(q_{m_1}) \gamma_1^{m_1}(q_{m_1}, q'_{m_1})]_{q'_{m_1}=q_{m_1}} dq_{m_1} . \quad (20)$$

This defines the *first-order reduced density matrix* $\gamma_1^{m_1}(q_{m_1}, q'_{m_1})$ [3],

$$\begin{aligned} \gamma_1^{m_1}(q_{m_1}, q'_{m_1}) &= \int \Psi(q_1, q_2, \dots, q_{m_1}, \dots, q_M) \Psi^*(q_1, q_2, \dots, q'_{m_1}, \dots, q_M) \\ &\quad \times dq_1 dq_2 \dots dq_{m_1-1} dq_{m_1+1} \dots dq_M . \end{aligned} \quad (21)$$

For a normalized wave function the trace must be equal to $\int \gamma_1^{m_1}(q_{m_1}, q_{m_1}) dq_{m_1} = 1$ which constitutes the coordinate representation analog to equation (15).

In SQ the form of the expectation value can be expressed in terms of the previously defined density matrices as in Eq. (10) which leads to,

$$\begin{aligned} \langle 0 | f^{m_1} | 0 \rangle &= \sum_{p^{m_1} q^{m_1}} D_{p^{m_1} q^{m_1}}^{m_1} \int (\phi_{p^{m_1}}^{m_1}(q_{m_1}))^* f^{cm_1} \phi_{q^{m_1}}^{m_1}(q_{m_1}) dq_{m_1} \\ &= \int \left[f^{cm_1} \sum_{p^{m_1} q^{m_1}} D_{p^{m_1} q^{m_1}}^{m_1} (\phi_{p^{m_1}}^{m_1}(q'_{m_1}))^* \phi_{q^{m_1}}^{m_1}(q_{m_1}) \right]_{q'_{m_1}=q_{m_1}} dq_{m_1} \\ &= \int [f^{cm_1} \gamma_1^{m_1}(q_{m_1}, q'_{m_1})]_{q'_{m_1}=q_{m_1}} dq_{m_1} \end{aligned} \quad (22)$$

and so we can make the identification,

$$\gamma_1^{m_1}(q_{m_1}, q'_{m_1}) = \sum_{p^{m_1} q^{m_1}} D_{p^{m_1} q^{m_1}}^{m_1} (\phi_{p^{m_1}}^{m_1}(q'_{m_1}))^* \phi_{q^{m_1}}^{m_1}(q_{m_1}) \quad (23)$$

which can be inverted to give,

$$D_{p^{m_1} q^{m_1}}^{m_1} = \langle 0 | E_{p^{m_1} q^{m_1}}^{m_1} | 0 \rangle = \int (\phi_{q^{m_1}}^{m_1}(q_{m_1}))^* \gamma_1^{m_1}(q_{m_1}, q'_{m_1}) \phi_{p^{m_1}}^{m_1}(q'_{m_1}) dq_{m_1} dq'_{m_1} . \quad (24)$$

Because the reduced density matrices constitute the coordinate representation of the density operator, the modal density can be obtained from the diagonal as,

$$\rho^{m_1}(q_m) = \gamma_1^{m_1}(q_{m_1}, q_{m_1}) = \sum_{p^{m_1} q^{m_1}} D_{p^{m_1} q^{m_1}}^{m_1} (\phi_{p^{m_1}}^{m_1}(q_{m_1}))^* \phi_{q^{m_1}}^{m_1}(q_{m_1}) . \quad (25)$$

This formalism can be generalized to n -mode reduced density matrices,

$$\begin{aligned} \gamma_n^{\mathbf{m}_n}(\{q\}_{\mathbf{m}_n}, \{q'\}_{\mathbf{m}_n}) &= \int \Psi(\{q\}_{\mathbf{m} \setminus \mathbf{m}_n}, \{q\}_{\mathbf{m}_n}) \Psi^*(\{q\}_{\mathbf{m} \setminus \mathbf{m}_n}, \{q'\}_{\mathbf{m}_n}) \prod_{m \notin \mathbf{m}_n}^M dq_m \\ &= \sum_{\mathbf{p}_n \mathbf{q}_n} (\Phi_{\mathbf{p}_n}^{\mathbf{m}_n}(\{q'\}_{\mathbf{m}_n}))^* D_{\mathbf{p}_n \mathbf{q}_n}^{\mathbf{m}_n} \Phi_{\mathbf{q}_n}^{\mathbf{m}_n}(\{q\}_{\mathbf{m}_n}) \end{aligned} \quad (26)$$

with $\Phi_{\mathbf{p}_n}^{\mathbf{m}_n}(\{q\}_{\mathbf{m}_n}) = \prod_{m \in \mathbf{m}_n} \phi_{p^m}^m(q_m)$. Here the subset of coordinates in the full coordinate set $\{q\}$ that correspond to the modes in $\mathbf{m}_n$ is denoted as $\{q\}_{\mathbf{m}_n}$.

2.5. Field operators

We may as an alternative to the above basis indexed by a set of quantum numbers choose to switch to a continuous basis indexed by a coordinate. Assuming a complete basis of $\hat{q}_m$ -eigenstates we obtain [34],

$$a_{p^m}^{m\dagger} |\text{vac}\rangle = |p^m\rangle = \int dq_m |q_m\rangle \langle q_m | p^m \rangle = \int dq_m \phi_{p^m}^m(q_m) |q_m\rangle . \quad (27)$$

This allows us to introduce *field operators* $\hat{\phi}^m(q_m)$ and $\hat{\phi}^{m\dagger}(q_m)$ to represent a given state in the coordinate representation of the quantized field [35]. Thus we have,

$$\hat{\phi}^{m\dagger}(q_m) |\text{vac}\rangle = |q_m\rangle . \quad (28)$$

Using Eq. (27) we obtain,

$$a_{p^m}^{m\dagger} = \int dq_m \phi_{p^m}^m(q_m) \hat{\phi}^{m\dagger}(q_m) . \quad (29)$$

Going back to the discrete basis representation enables us to write,

$$|q_m\rangle = \sum_{p^m} |p^m\rangle \langle p^m|q_m\rangle = \sum_{p^m} (\phi_{p^m}^m(q_m))^* |p^m\rangle \quad (30)$$

and thereby,

$$\hat{\phi}^{m\dagger}(q_m) = \sum_{p^m} (\phi_{p^m}^m(q_m))^* a_{p^m}^{m\dagger} . \quad (31)$$

The analogous relations for $\hat{\phi}^m(q_m)$ and $a_{p^m}^m$ are,

$$a_{p^m}^m = \int dq_m (\phi_{p^m}^m(q_m))^* \hat{\phi}^m(q_m) \quad (32)$$

and,

$$\hat{\phi}^m(q_m) = \sum_{p^m} \phi_{p^m}^m(q_m) a_{p^m}^m . \quad (33)$$

From equations (31) and (33) and the commutator relations for the creation and annihilation operators we obtain,

$$[\hat{\phi}^{m\dagger}(q_m), \hat{\phi}^{m\dagger}(q'_m)] = 0 , \quad (34a)$$

$$[\hat{\phi}^m(q_m), \hat{\phi}^m(q'_m)] = 0 , \quad (34b)$$

$$[\hat{\phi}^m(q_m), \hat{\phi}^{m\dagger}(q'_m)] = \delta(q_m - q'_m) . \quad (34c)$$

Introducing the field operators allows us to write the first-order reduced density matrices in second quantization as,

$$\gamma_1^m(q_m, q'_m) = \sum_{r^m s^m} D_{r^m s^m}^m (\phi_{r^m}^m(q'_m))^* \phi_{s^m}^m(q_m) = \langle 0 | \hat{\phi}^{m\dagger}(q'_m) \hat{\phi}^m(q_m) | 0 \rangle . \quad (35)$$

Comparing this to Eq. (12) again highlights the correspondence between the discrete-basis representation $D_{r^m s^m}^m$ and the coordinate representation $\gamma_1^m(q_m, q'_m)$.

2.6. *Density matrices for approximate vibrational wave functions*

We now consider the vibrational problem in more detail. The expectation value of the energy for an arbitrary state $|0\rangle$ and a SOP Hamiltonian is expressed as,

$$E = \langle 0 | H | 0 \rangle = \sum_t c_t \sum_{\mathbf{p}_t \mathbf{q}_t} D_{\mathbf{p}_t \mathbf{q}_t}^{\mathbf{m}_t} h_{\mathbf{p}_t \mathbf{q}_t}^{\mathbf{m}_t t} \quad (36)$$

with $h_{\mathbf{p}_t \mathbf{q}_t}^{\mathbf{m}_t t} = \prod_{m \in \mathbf{m}_t} h_{p^m q^m}^{m t}$, and the density-matrix elements defined as in Eq. (11). The terms in Eq. (36) include factors that are the trace of products of one-mode integrals and n -mode density matrices where n is the dimension of the mode combination $\mathbf{m}_t$.

The reference state for vibrational-structure calculations is often obtained from a VSCF calculation. Here the wave function is approximated by a single Hartree product where the modals are variationally optimized. Derivation of the VSCF equations in first and second quantization has been accounted for several times, see Refs. [13, 14, 17]. Here we shall solely discuss the density matrix before progressing to more advanced wave-function models employing VSCF as reference state. If we consider a single Hartree product, the one-mode density-matrix elements are,

$$D_{p^{m_1} q^{m_1}}^{m_1} = \langle \Phi_{\mathbf{i}} | E_{p^{m_1} q^{m_1}}^{m_1} | \Phi_{\mathbf{i}} \rangle = \delta_{p^{m_1} q^{m_1}} \delta_{p^{m_1} i^{m_1}} \quad (37)$$

where i^m is the occupied modal for mode m . Thereby the diagonal elements are equal to 1 for the occupied mode and all other elements are zero. Similar relations hold for high-order density matrices, with the two-mode example being,

$$D_{p^{m_1} p^{m_2} q^{m_1} q^{m_2}}^{m_1 m_2} = \langle \Phi_{\mathbf{i}} | e_{p^{m_1} p^{m_2} q^{m_1} q^{m_2}}^{m_1 m_2} | \Phi_{\mathbf{i}} \rangle = \delta_{p^{m_1} q^{m_1}} \delta_{p^{m_1} i^{m_1}} \delta_{p^{m_2} q^{m_2}} \delta_{p^{m_2} i^{m_2}} . \quad (38)$$

One consequence of this simple structure is that the density matrices factorize. Thus Eq. (36) leads to the simple expression for the VSCF energy,

$$E_{\text{VSCF}} = \sum_t c_t \prod_{m \in \mathbf{m}_t} h_{i^m}^{m t} . \quad (39)$$

2.6.1. Vibrational configuration interaction

VSCF theory is a mean-field theory for anharmonic vibrations and just like Hartree-Fock theory for electrons it does not include correlation effects between the degrees of freedom [7]. In order to describe correlation, a higher level of theory is needed. One way of including mode-correlation effects in the wave function is to add components of excited Hartree products to the reference state $|\Phi_{\mathbf{i}}\rangle$ using a linear parametrization. This is done in the VCI ansatz [14, 17–19, 36–39],

$$|\text{VCI}\rangle = C_{\mathbf{i}} |\Phi_{\mathbf{i}}\rangle + \sum_{\mu} C_{\mu} \tau_{\mu} |\Phi_{\mathbf{i}}\rangle . \quad (40)$$

The sum μ runs over the set of included excitations. If all excitations are included, the full VCI (FVCI) wave function is obtained which is exact for a given Hamiltonian and one-mode basis. Truncating the expansion after the n -mode excitations results in the VCI[n] hierarchy of methods analogous to CISD, CISDT, etc. from electronic-structure theory. The linear expansion parameters C_{μ} are optimized variationally by solving the VCI eigenvalue equations. VCI one-mode density matrices can be constructed as,

$$^{\text{VCI}} D_{p^{m_1} q^{m_1}}^{m_1} = \langle \text{VCI} | E_{p^{m_1} q^{m_1}}^{m_1} | \text{VCI} \rangle \quad (41)$$

and then diagonalized to obtain the VCI natural modals and occupations.

2.6.2. Vibrational coupled cluster

One of the most successful quantum-chemical methods is *coupled cluster* (CC) which is widely used in electronic-structure theory [7]. A formulation of CC theory for vibrational-structure calculations has been presented and implemented [17, 20, 21]. The *VCC variational Lagrangian* is defined as

[7, 40],

$$L(\mathbf{t}, \bar{\mathbf{t}}) = \langle \Phi_{\mathbf{i}} | H \exp(T) | \Phi_{\mathbf{i}} \rangle + \sum_{\mathbf{m} \in \text{MCR}[T]} \sum_{\mu^{\mathbf{m}}} \bar{t}_{\mu^{\mathbf{m}}} \langle \mu^{\mathbf{m}} | \exp(-T) H \exp(T) | \Phi_{\mathbf{i}} \rangle \quad (42)$$

where $\bar{t}_{\mu^{\mathbf{m}}}$ are the *Lagrangian multipliers* and T is the *cluster operator*. For an optimized VCC state the Lagrangian is equal to E_{VCC} . The cluster amplitudes and their multipliers are determined variationally by,

$$\frac{\partial L}{\partial \bar{t}_{\mu^{\mathbf{m}}}} = \langle \mu^{\mathbf{m}} | \exp(-T) H \exp(T) | \Phi_{\mathbf{i}} \rangle = 0, \quad (43)$$

$$\frac{\partial L}{\partial t_{\nu^{\mathbf{m}}}} = \langle \Phi_{\mathbf{i}} | H \tau_{\nu^{\mathbf{m}}} \exp(T) | \Phi_{\mathbf{i}} \rangle + \sum_{\mathbf{m}' \in \text{MCR}[T]} \sum_{\mu^{\mathbf{m}'}} \bar{t}_{\mu^{\mathbf{m}'}} \langle \mu^{\mathbf{m}'} | \exp(-T) [H, \tau_{\nu^{\mathbf{m}}}] \exp(T) | \Phi_{\mathbf{i}} \rangle = 0. \quad (44)$$

The first equation is simply the cluster-amplitude equation while the last equation determines the Lagrange multipliers. In order to calculate the VCC energy, the $\bar{t}_{\mu^{\mathbf{m}}}$ parameters are not necessary since this only requires the solution of the VCC amplitude equations. However, for calculating molecular properties and constructing VCC density matrices the Lagrange multipliers are of great importance [7, 40, 41].

For the calculation of first-order properties in the presence of a perturbation the Hamiltonian is given as $H = H_0 + V_X \hat{X}$ where V_X is the strength of the perturbing field and $\hat{X}$ is the corresponding operator. The expectation value of this operator is given by the generalized Hellman-Feynman theorem,

$$\langle \hat{X} \rangle = \left. \frac{dE_{\text{VCC}}}{dV_X} \right|_{V_X=0} = \left. \frac{dL}{dV_X} \right|_{V_X=0} = \left. \frac{\partial L}{\partial V_X} \right|_{V_X=0} = \langle \Lambda | \hat{X} | \text{VCC} \rangle \quad (45)$$

where the third equality comes from the variational criteria on the Lagrangian. The second equality comes from the definition,

$$\langle \Lambda | = \langle \Phi_{\mathbf{i}} | + \sum_{\mathbf{m} \in \text{MCR}[T]} \sum_{\mu^{\mathbf{m}}} \bar{t}_{\mu^{\mathbf{m}}} \langle \mu^{\mathbf{m}} | \exp(-T). \quad (46)$$

Equation (45) defines the expectation value of a Hermitian operator (Eq. (7)) with the VCC wave function,

$$\langle \hat{\Omega} \rangle = \langle \Lambda | \hat{\Omega} | \text{VCC} \rangle = \sum_{n=0}^M \sum_{\mathbf{m}_n} \sum_{\mathbf{p}_n \mathbf{q}_n} \Omega_{\mathbf{p}_n \mathbf{q}_n}^{\mathbf{m}_n} \bar{D}_{\mathbf{p}_n \mathbf{q}_n}^{\mathbf{m}_n}. \quad (47)$$

where $\bar{\mathbf{D}}^{\mathbf{m}_n}$ is the n -mode VCC Lagrangian density matrix defined as,

$$\bar{D}_{\mathbf{p}_n \mathbf{q}_n}^{\mathbf{m}_n} = \langle \Lambda | e_{\mathbf{p}_n \mathbf{q}_n}^{\mathbf{m}_n} | \text{VCC} \rangle. \quad (48)$$

These matrices differ from the ones in Eq. (11) because of the different bra and ket states. One consequence of this is that the VCC Lagrangian density matrices are not Hermitian and may give complex eigenvalues upon diagonalization.

In order to avoid complex natural modal occupation numbers (which would be unphysical), we divide the one-mode density matrices into real (Hermitian) and imaginary (skew-Hermitian)

contributions,

$$\bar{\mathbf{D}}^{m_1} = {}^R\bar{\mathbf{D}}^{m_1} + {}^I\bar{\mathbf{D}}^{m_1} = \left(\frac{\bar{\mathbf{D}}^{m_1} + \bar{\mathbf{D}}^{m_1\dagger}}{2} \right) + \left(\frac{\bar{\mathbf{D}}^{m_1} - \bar{\mathbf{D}}^{m_1\dagger}}{2} \right). \quad (49)$$

For the calculation of the VCC energy and many other molecular properties we only consider the real, symmetric one with elements,

$${}^R\bar{D}_{p^{m_1}q^{m_1}}^{m_1} = \frac{1}{2} \left(\langle \Lambda | E_{p^{m_1}q^{m_1}}^{m_1} | \text{VCC} \rangle + \langle \Lambda | E_{p^{m_1}q^{m_1}}^{m_1} | \text{VCC} \rangle^* \right). \quad (50)$$

This matrix can be diagonalized by a unitary transformation in order to obtain the VCC natural modals and their occupation numbers.

2.7. Iterative natural modals

The idea behind iterative natural modals is to obtain the best possible set of modals to describe the wave function of the system. This is done for a given vibrational wave-function model by first calculating a set of reference modals using VSCF. Then correlated calculations are carried out repeatedly, replacing the input modals with the natural modals after each calculation. This is repeated until the change in the natural modals weighted by their natural modal occupations is below a given threshold. Algorithm 1 shows the structure of our pilot implementation in the case of VCC. The VCI implementation is similar using Eq. (41) instead of the VCC Lagrangian density matrix.

Algorithm 1: Iterative natural modal calculation

Input: VSCF modals, $\{\phi_i^m, \{\phi_a^m\}\}$
Maximum ItNaMo iterations, $N_{maxiter}$
ItNaMo convergence threshold, T_{ItNaMo}
Output: Iterative natural modals, $\{\tilde{\phi}_i^m, \{\tilde{\phi}_a^m\}\}$
Natural occupations, $\{\eta_p^m\}$
Cluster amplitudes and Lagrange multipliers, $\{\mathbf{t}_{\mu^m}, \bar{\mathbf{t}}_{\mu^m}\}$
VCC energy, E_{VCC} , calculated in the ItNaMo basis

```

1 repeat
2   Solve for the VCC amplitude equations,  $\mathbf{t}_{\mu^m}$  (Eq.(43))
3   Solve for the Lagrange multipliers,  $\bar{\mathbf{t}}_{\mu^m}$  (Eq.(44))
4   Calculate the one-mode VCC Lagrangian density matrices,  $\bar{\mathbf{D}}^m$  (Eq.(50))
5   Diagonalize the (real) density matrices,  $\boldsymbol{\eta}^m = \mathbf{U}^{m\dagger} {}^R\bar{\mathbf{D}}^m \mathbf{U}^m$  (Eq.(17))
6   Transform the modals,  $\tilde{\boldsymbol{\phi}}^m = \mathbf{U}^{m\dagger} \boldsymbol{\phi}^m$ 
7   if  $\eta_{p^m}^m ||\phi_{p^m}^m - \tilde{\phi}_{p^m}^m|| > T_{\text{ItNaMo}}$  for any  $p^m$  then  $\boldsymbol{\phi}^m \leftarrow \tilde{\boldsymbol{\phi}}^m \forall m$ 
8 until  $\eta_{p^m}^m ||\phi_{p^m}^m - \tilde{\phi}_{p^m}^m|| < T_{\text{ItNaMo}} \forall p^m$ 

```

The VSCF and VCC calculations can be set to target specific states, i.e. the ground state or a given excited state. Thereby excitation energies can be calculated using ItNaMos and the values can be compared to standard calculations. This is denoted the *state-specific* (ss) approach. When doing state-specific calculations the VCC and VCI hierarchies of methods are labeled VCC[ss,2], VCC[ss,3], etc. to avoid confusion. A different way of calculating excitation energies is the response-function approach described in Refs. [41, 42] where excitation energies are obtained as eigenvalues of the CC Jacobian. However, in this work the state-specific approach is taken in order to obtain a set of ItNaMos for each state instead of describing excited states using a basis optimized for the ground state.

3. Implementation and computational details

All calculations have been performed using the MidasCpp chemistry program package [43] which includes implementations of all mentioned vibrational-structure methods, i.e. VSCF, VCI, VCC, etc. Furthermore the program interfaces with many popular electronic-structure programs for PES generation.

We have made a pilot implementation of VCI and VCC densities and the ItNaMo method. Although the operation count of the implementation has not been analyzed in detail, the major computational effort of the VCC density calculation is the solution of the $\mathbf{t}$ and $\bar{\mathbf{t}}$ equations as it should be. Constructing the density-matrix elements is carried out by multiple calculations of the VCC transformations of Ref. [21] with 'unit' operators of the form $E_{r^m s^m}^m$. Having available $\langle \Phi_{\mathbf{i}} | E_{r^m s^m}^m \exp(T) | \Phi_{\mathbf{i}} \rangle$ and $e_{\mu^{\mathbf{m}}}^{E_{r^m s^m}^m} = \langle \mu^{\mathbf{m}} | \exp(-T) E_{r^m s^m}^m \exp(T) | \Phi_{\mathbf{i}} \rangle$ the density matrix is easily constructed as $\bar{D}_{r^m s^m}^m = \langle \Phi_{\mathbf{i}} | E_{r^m s^m}^m \exp(T) | \Phi_{\mathbf{i}} \rangle + \sum_{m \in \text{MCR}[T]} \sum_{\mu^{\mathbf{m}}} \bar{t}_{\mu^{\mathbf{m}}} e_{\mu^{\mathbf{m}}}^{E_{r^m s^m}^m}$. This implementation is general with respect to excitation levels in the VCC wave function.

Details about the PESs for the test calculations on water, formaldehyde, and ethylene can be found in Refs. [44], [45], and [46], respectively. In all calculations harmonic-oscillator (HO) functions are used as basis sets. In the case of formaldehyde and ethylene the basis sets from Refs. [20] and [46] are used, while in the case of water the basis functions are generated automatically from the harmonic part of the PES.

All calculations use an ItNaMo convergence threshold of $T_{\text{ItNaMo}} = 10^{-8}$ and convergence is typically achieved in 3 to 4 iterations. In more difficult cases like the $[0, 0, 0, 0, 1, 0]$ state of formaldehyde up to 8 iterations are needed. Although the ItNaMo method does not change the computational scaling with respect to system size, it does result in a pre-factor on the computation time corresponding to the number of iterations which makes the VCC-it[ss,n] models roughly 3-4 times as expensive as a standard VCC[ss,n] calculation. This could be optimized by e.g. using adaptive convergence thresholds and solving for $t_{\mu^{\mathbf{m}}}$ and $\bar{t}_{\mu^{\mathbf{m}}}$ simultaneously, but here the focus is primarily on the properties of natural modals rather than absolute timings of the current implementation.

4. Results

4.1. Water

The smallest test system is H_2O with 3 vibrational modes. The total energies of the ground state and the three fundamental excitations of water are shown in Table I. Here the VCI[ss,2] and VCC[ss,2] energies with and without iterative natural modals are compared to the FVCI results. The ItNaMos do not change the errors significantly, but for the second excited state the energies are lowered a little. It must be emphasized, however, that the errors are very small without ItNaMos since only the three-mode coupling is not explicitly accounted for in the VCI[ss,2] and VCC[ss,2] wave-function ansätze. Therefore there is not too much to be gained by optimizing the basis functions. Since FVCI[ss] provides the exact wave function within the given modal space, the energy should be invariant with respect to the choice of modal basis. This is clearly seen in the results since the FVCI-it[ss] energies are identical to the FVCI[ss] energies for all states.

The vibrational ground state and first excited state of the water molecule have been optimized using normal coordinates and ground-state optimized coordinates. Normal coordinates are the standard choice for many vibrational-structure calculations. They diagonalize the mass-weighted molecular Hessian and thereby reduce the system to a set of uncoupled harmonic oscillators in the case where the PES is a quadratic form. However, accurate vibrational calculations require a PES of higher order than quadratic and in those cases normal coordinates are not necessarily the best choice. One approach to obtaining better coordinates is to minimize the VSCF energy with

State	FVCI[ss]	FVCI-it[ss]	VCI[ss,2]	VCI-it[ss,2]	VCC[ss,2]	VCC-it[ss,2]
[0, 0, 0]	4703.60	0.00	0.02	0.02	0.02	0.02
[1, 0, 0]	6282.45	0.00	0.08	0.08	0.08	0.08
[0, 1, 0]	8446.13	0.00	0.18	0.11	0.13	0.11
[0, 0, 1]	8545.09	0.00	0.07	0.07	0.07	0.07

Table I. FVCI total energies and errors of VCI[ss,2], VCC[ss,2] and the corresponding ItNaMo methods in normal coordinates using the 4 lowest VSCF modals for the correlated calculations. All units are in cm^{-1} .

respect to Jacobi rotations of the normal coordinates. These resulting coordinates are denoted *optimized coordinates* [47–50]. These coordinates tend to localize the vibrations as described in Refs. [47–49]. In the case of H_2O , this means that the individual O-H stretches are represented by two separate coordinates instead of the symmetric and anti-symmetric normal coordinates. Optimized coordinates facilitate a more accurate description of the wave function, and it is therefore expected that fewer basis functions are needed in order to describe the mode correlation. This is confirmed by looking at the results in Tables II and III where the natural occupations for the different modals of the three modes converge faster towards zero for optimized coordinates. Furthermore the occupations are identical for modes 1 and 2 when using optimized coordinates. This is due to the symmetry of the water molecule where the natural modals of the two equivalent localized O-H stretches are identical. The occupation numbers do not change significantly when going from VCC-it[ss,2] to VCC-it[ss,3] (VCC-it[ss,3] being the exact wave function for the given set of modals). Note that in the ItNaMo method the modals are ordered by the size of the natural occupation numbers instead of modal energies. Thus for the excited state in Table III the 0th modal in mode 0 is dominated by the $n = 1$ HO basis function.

VCC-it[ss,2]	Mode \ Modal	0	1	2	3
Normal	0	0.99983	0.00012	0.00005	0.00000
	1	0.99873	0.00124	0.00001	0.00000
	2	0.99878	0.00122	0.00000	0.00000
gs-Optimized	0	0.99984	0.00012	0.00004	0.00000
	1	0.99987	0.00010	0.00003	0.00000
	2	0.99987	0.00010	0.00003	0.00000
VCC-it[ss,3]	Mode \ Modal	0	1	2	3
Normal	0	0.99983	0.00012	0.00005	0.00000
	1	0.99873	0.00125	0.00001	0.00000
	2	0.99878	0.00122	0.00000	0.00000
gs-Optimized	0	0.99983	0.00012	0.00005	0.00000
	1	0.99985	0.00012	0.00003	0.00000
	2	0.99985	0.00012	0.00003	0.00000

Table II. Natural modal occupation numbers of the ground state of H_2O in VCC-it[ss,2] and VCC-it[ss,3] using normal coordinates and ground-state-optimized coordinates.

4.2. Formaldehyde

In order to test the ItNaMos on a slightly larger system than H_2O where the errors of low-order VCC and VCI models are expected to be more significant, a series of calculations on formaldehyde (6 modes) are performed. Table IV shows the state-specific FVCI energies and the errors of the approximate models. The results show that for high-order models such as VCI[ss,4] and VCC[ss,4] the iterative natural modals result in smaller energy errors. Though for the lowest states the behavior is similar to the case of water, the trend is not entirely clear for the lower-order models generally. As described in Ref. [20] the $[0,0,0,0,1,0]$ state has multi-reference character containing large components of two states which are triple-excited with respect to the VSCF

VCC-it[ss,2]	Mode \ Modal	0	1	2	3
Normal	0	0.99923	0.00048	0.00029	0.00000
	1	0.99819	0.00176	0.00005	0.00000
	2	0.99846	0.00154	0.00000	0.00000
gs-Optimized	0	0.99928	0.00047	0.00025	0.00000
	1	0.99959	0.00028	0.00013	0.00000
	2	0.99959	0.00028	0.00013	0.00000
VCC-it[ss,3]	Mode \ Modal	0	1	2	3
Normal	0	0.99922	0.00049	0.00029	0.00000
	1	0.99818	0.00177	0.00005	0.00000
	2	0.99845	0.00155	0.00000	0.00000
gs-Optimized	0	0.99921	0.00049	0.00030	0.00000
	1	0.99953	0.00034	0.00013	0.00000
	2	0.99953	0.00034	0.00013	0.00000

Table III. Natural modal occupation numbers of the first excited (H-O-H bend) state of H₂O in VCC-it[ss,2] and VCC-it[ss,3] using normal coordinates and ground-state-optimized coordinates.

reference. The coefficients of these configurations in the VCC[ss,4] wave function are $> 50\%$ and $> 25\%$ of the reference coefficient, respectively, which makes it a case of strong resonance. The VCI[ss,2]/VCC[ss,2] and VCI[ss,3]/VCC[ss,3] models are not able to account for correlation in these important configurations which gives rise to large energy errors. Including higher-order excitations solves the problem, although the errors are still larger than for all other states. Using ItNaMos does not improve the lower-order VCC and VCI results. Changing the modal basis cannot circumvent the fact that important configurations are missing in the reference state. This includes both the resonance configurations and low-order excitations out of those which are needed for relaxation. The latter are not included in the VCC[ss,2] and VCC[ss,3] models. For the models that include all important configurations in the wave-function ansatz, the ItNaMos do make a significant difference by improving the description of the mode-correlation. Therefore using the ItNaMo method within a multi-reference context could be an interesting future application [12]. However, there is no reason to expect that the ItNaMos can fundamentally improve on a single reference description in a true multiconfigurational case as the numerical data also show.

4.3. Ethylene

The largest system to be looked at is ethylene (12 modes) where the energy errors of all models compared to FVCI are calculated for the ground state and the 8 lowest fundamental excitations. This excludes the C-H stretches that are hard to target with a state-specific single-reference VCC method. Since there are strong resonances similar to the [0,0,0,0,1,0] state of formaldehyde there is also no reason to expect the ItNaMos to provide any general improvements and we therefore do not consider these states here.

The results in Table V show small improvements in the ItNaMo energies compared to the standard procedure. Note that in this case we consider total energies. The errors in the excitation energies are somewhat smaller meaning that the errors cancel out to significant extent. The major trends between methods are, however, the same. The benefits of VCC compared to VCI are more pronounced because of the larger number of vibrational modes. For both VCI and VCC we see that the difference between ItNaMos and standard calculations is small compared to the size of the error at the given level. Thus, while the natural modals may be usefull from an analysis perspective, the gain in using them is modest.

Order	[0,0,0,0,0,0]	[0,0,0,1,0,0]	[0,0,0,0,0,1]	[0,0,1,0,0,0]	[0,1,0,0,0,0]	[1,0,0,0,0,0]	[0,0,0,0,1,0]
FVCI[ss]	5778.3401	6924.5255	7020.1866	7277.4246	7524.6787	8558.5020	8612.7783
FVCI-it[ss]	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
VSCF[ss]	17.9485	23.2472	24.5618	25.5352	22.1226	52.0836	27.2884
VCI[ss,2]	1.4262	1.7221	5.0525	4.5765	3.2807	2.9719	-12.8424
VCI[ss,3]	0.3349	0.3619	1.1044	1.1260	0.5760	1.4018	-42.5337
VCI[ss,4]	0.0032	0.0076	0.0133	0.0158	0.0126	0.0384	0.5502
VCI[ss,5]	0.0001	0.0003	0.0003	0.0004	0.0008	0.0001	0.0041
VCC[ss,2]	1.4219	1.7154	5.0471	4.5010	3.2358	2.6198	-12.8683
VCC[ss,3]	0.3283	0.3482	1.0886	1.0354	0.5173	1.3079	-45.4199
VCC[ss,4]	0.0022	0.0042	0.0086	0.0108	0.0078	0.0295	0.3789
VCC[ss,5]	0.0001	0.0001	0.0001	0.0000	0.0001	0.0001	0.0007
VCI-it[ss,2]	1.4272	1.7273	5.0557	4.5557	3.2913	2.6950	-12.8535
VCI-it[ss,3]	0.3342	0.3597	1.0961	1.1209	0.5744	1.4368	-48.3158
VCI-it[ss,4]	0.0030	0.0072	0.0126	0.0151	0.0122	0.0373	0.4450
VCI-it[ss,5]	0.0001	0.0003	0.0003	0.0004	0.0008	0.0002	0.0032
VCC-it[ss,2]	1.4222	1.7175	5.0482	4.4886	3.2399	2.5995	-12.8754
VCC-it[ss,3]	0.3280	0.3470	1.0840	1.0314	0.5168	1.3221	-105.9165
VCC-it[ss,4]	0.0021	0.0041	0.0084	0.0106	0.0078	0.0294	0.2925
VCC-it[ss,5]	0.0001	0.0001	0.0001	0.0000	0.0001	0.0001	0.0005

Table IV. FVCI total energies and errors in VSCF, VCI, VCC, VCC-it, and VCI-it energies for the state-specific vibrations of formaldehyde with 3 correlated modal basis functions, units are cm^{-1} .

5. Summary and outlook

The second-quantization formulation of the molecular vibrational problem has been used to derive expressions for vibrational density matrices. The connection between density matrices in second quantization and reduced density matrices in the coordinate representation originally introduced by Löwdin has been described in terms of field operators. The diagonal representations of the one-mode density matrices have been used to define sets of natural modals with well-defined natural occupation numbers for each vibrational mode.

We have introduced iterative calculation of natural modals (ItNaMo) and energy calculations on water, formaldehyde, and ethylene have been presented. It has been shown that using optimized coordinates for the water molecule lowers the natural modal occupation numbers of the excited modals compared to normal coordinates. This highlights the benefits of using optimized coordinates since fewer basis functions are needed for obtaining an accurate description of the wave function. This is an example of natural occupation numbers being useful in the context of wave-function analysis. The formaldehyde and ethylene results show that the ItNaMos are able to lower the absolute energy errors of approximate wave-function models as long as the wave-function ansatz includes the most important configurations. Since both the ground-state and excited-state energies are lowered, the effect on state-specific excitation energies was found to be minor compared to other errors. While ItNaMos may improve on basis-set convergence in many cases, it cannot be expected to correct major deficiencies in the wave functions, such as when a strong multi-configurational wave function is described with a single-reference state. However, the effect of ItNaMos is quite significant for VCC[ss,4] on the [0,0,0,0,1,0] state of formaldehyde which shows strong multi-reference character. Therefore introducing ItNaMos in vibrational MCSCF would be an interesting future application [51, 52]. In this context, natural modals can also be used to choose relevant active spaces, which has also been done in electronic-structure theory [10].

In this paper the iterative natural modals have only been used in simple energy calculations, but there are other interesting applications. For instance using the first few ItNaMos from a low-order VCC model as basis for a more accurate calculation could improve the basis-set convergence and thereby facilitate accurate calculations on larger systems with smaller basis sets. Furthermore,

Order	Ground state	μ_8	μ_7	μ_1	μ_4	μ_3	μ_6	μ_9	μ_{11}
FVCI[ss]	11139.08	11967.04	12075.99	12096.85	12183.09	12361.01	12494.21	12578.00	12775.29
VSCF[ss]	68.78	87.91	92.13	92.20	90.35	84.49	79.79	89.00	85.26
VCI[ss,2]	39.57	60.19	63.66	64.01	61.48	54.90	46.73	59.39	50.95
VCI[ss,3]	1.32	2.33	2.48	2.50	2.33	2.24	2.42	3.33	4.15
VCI[ss,4]	0.59	1.16	1.35	1.36	1.29	1.16	1.15	1.74	2.11
VCC[ss,2]	39.55	60.17	63.64	63.99	61.36	54.87	46.57	59.37	50.07
VCC[ss,3]	1.01	1.80	1.85	1.86	1.75	1.69	1.65	2.46	2.57
VCC[ss,4]	0.34	0.68	0.78	0.78	0.77	0.68	0.54	0.87	0.64
VCI-it[ss,2]	39.58	60.21	63.67	64.02	61.49	54.90	46.72	59.40	50.92
VCI-it[ss,3]	1.28	2.27	2.41	2.43	2.27	2.17	2.36	3.24	4.10
VCI-it[ss,4]	0.59	1.16	1.35	1.35	1.29	1.16	1.15	1.74	2.12
VCC-it[ss,2]	39.55	60.18	63.64	63.99	61.36	54.87	46.57	59.37	50.01
VCC-it[ss,3]	1.00	1.78	1.83	1.84	1.74	1.66	1.63	2.43	2.55
VCC-it[ss,4]	0.34	0.67	0.77	0.78	0.77	0.67	0.54	0.86	0.63

Table V. FVCI energies and errors in VCI, VCI-it, VCC, and VCC-it for the ground state and the lowest fundamental vibrations of C_2H_4 , units are cm^{-1} . The state names refer to the excited mode, e.g. $\mu_3 = [0, 0, 1, 0, 0, 0, 0, 0, 0, 0, 0]$.

the application of ItNaMos in VCC response theory will be a way of avoiding the complicated, non-linear optimization of the VCC wave function for each excited state. However, this introduces a whole new set of non-trivial problems since the ItNaMos are currently optimized for a specific state. One future possibility is to introduce a state-average extension where the ItNaMos are optimized for at set of states simultaneously [7]. This will for example make the calculation of transition moments and other properties much easier in an ItNaMo context. A final example of a future application is time-dependent theory where wave-packet propagation in natural modals has been reported (see Ref. [11] and references therein). Defining natural modals in a VCC context provides a part of the foundation for extending the VCC ansatz to time-dependent theory using natural modal occupation numbers instead of modal energies to define a reference state. This will be a topic for future research.

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