

Vibrational coupled cluster theory with full two-mode and approximate three-mode couplings: The VCC[2pt3] model

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Vibrational coupled cluster (VCC) calculations of molecular vibrational energy levels can be characterized by the number of modes coupled in the Hamiltonian operator and the number of modes simultaneously excited in the parameter space. We propose a VCC model which includes all two-mode couplings in the Hamiltonian and excitation space but only an approximate treatment of three-mode couplings. The approximation is based on a perturbational analysis and the introduced concepts can also be used for even more accurate treatments. The method is iterative and allows the use of VCC response theory to obtain excitation energies. Furthermore, the method is shown to scale with the number of vibrational modes to the third power which is no higher than the corresponding VCC model with only two-mode couplings. Encouraging benchmark calculations are given for a test set of three- and four-atomic molecules. The fundamentals of the larger ethylene oxide molecule have been calculated as well using a grid-based potential energy surface obtained from electronic coupled cluster theory with singles, doubles, and perturbative triples (CCSD(T)). © 2009 American Institute of Physics. [DOI: 10.1063/1.3158946]

I. INTRODUCTION

Within the Born–Oppenheimer approximation, the nuclei move on a potential energy surface (PES) set up by the electrons. By solving the nuclear Schrödinger equation for this potential, vibrational energies and wave functions are obtained. The solution of the nuclear Schrödinger equation is difficult since the PES generally couples all the nuclear degrees of freedom which results in correlated wave functions. Several different techniques have been used to approach this problem. In this paper, we consider the vibrational coupled cluster^{1,2} (VCC) method which is based on a vibrational self-consistent field (VSCF) reference state. Other methods based on the VSCF reference exist. These include vibrational configuration interaction (VCI) and vibrational Møller–Plesset (VMP) perturbation theory, see Refs. 3–6 for overviews. We further note that various improvements on the basic VCI method have been suggested^{3,7–11} as have various alternative perturbation theory corrections.^{12–14} In addition to this family of methods which has a clear analogy to electronic structure theory, a wealth of other methods exists. These include the simple harmonic approximation corrected using vibrational perturbation theory to various orders,¹⁵ the multiconfigurational time-dependent Hartree method,^{16,17} and specialized methods for high-accuracy calculations on small molecules.^{18–22}

An immediate concern in the solution of the nuclear motion problem is the availability of good PESs. The *ab initio*

generation of such surfaces is certainly not trivial and, in general, requires a large number of electronic calculations. Much research is going into finding ways to reduce the effort while retaining high accuracy. In this paper we will rely on a hierarchical approach of truncating the PES representation according to the number of interacting modes. This and related approaches are in widespread use under different names.^{23–28} Furthermore, we use a sum over products of one mode operators to represent each term in this hierarchy. This form has also been useful in other contexts.¹⁶ The specific implementation used in this paper is described in Ref. 27.

There are several possible strategies for obtaining excitation energies in the VCI and VCC methods. The one considered in this article is based on a VSCF optimization of the ground state. Given a set of optimized one-mode basis functions, often denoted modals, an excitation space is then set up, and both the ground and excited states are parametrized within this space. For VCI this corresponds to obtaining eigensolutions of the Hamiltonian matrix. For VCC, a two-step approach is used in which the ground state is first obtained followed by application of response theory to obtain the excited states. In Ref. 29 the VCC method was shown to be considerably more accurate than VCI when this so-called ground-state method was applied. An alternative to this strategy is a state-specific approach in which each state is optimized individually, i.e., a different basis is used for each state. This method was considered in Ref. 2 where VCC was also shown to be more accurate than VCI although the gain is not as general and large as in the simpler ground-state approach.

From a theoretical point of view, the above conclusions are in favor of VCC. However, the general VCC algorithm used for these studies was not efficient with respect to CPU

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time. In Ref. 30 it was shown that VCC at the two-mode-coupling level can be implemented very efficiently and made to scale as M^3 , where M is the number of vibrational modes. However, two-mode couplings often do not provide the desired accuracy. In this paper, we derive a new VCC model with an approximate inclusion of three-mode couplings. Remarkably, the extra couplings are included without increasing the overall computational scaling with respect to the number of modes which is still M^3 .

There is a clear analogy between our approach and electronic structure theory. In electronic structure theory it is well established that coupled cluster (CC) is significantly more accurate than the corresponding configuration interaction methods. This becomes increasingly true as the system size grows due to the size-extensive property of CC theory. Also, triple excitations are known to be important but expensive. Therefore, various approximate methods have been introduced. This includes the popular CCSD(T) model³¹ which generates a noniterative triple correction to the ground-state energy following a CCSD calculation. Alternatively, the triples may be only approximately included in the iterative solution of the CC equations. This is, for instance, necessary in response theory calculations and is done in the CCSDT-X ($X=1a, 1b, 2, 3$) (Refs. 32 and 33) and CC3 models.³⁴ See Refs. 5 and 35–40 for further reviews of approximate electronic CC methods. The method in this paper is based on an iterative approach following somewhat similar ideas as in CC3. As will become clear, however, the analogy cannot be taken too far. The nature of the vibrational Hamiltonian which in principle couples all degrees of freedom is completely different from the electronic one which only includes the two-body Coulomb interaction. Although we in this paper restrict ourselves to three-mode couplings in the Hamiltonian, a new analysis is still needed. Another difference from electronic theory is the distinguishability of the vibrational modes. As a result, small separate basis sets are used for each degree of freedom. Thus, the scaling properties of VCC cannot be compared to those of electronic CC theory.

The outline of this article is as follows. Section II contains the perturbational analysis necessary for deriving the new model. After a brief review of the implementation in Sec. III, a set of benchmark calculations on three- and four-atomic molecules is used to compare the new model to conventional ground-state based VCC and VCI methods. Also, the fundamentals of the larger ethylene oxide molecule have been calculated and compared to experiment.

II. THEORY

In this section, we first give a résumé of general VCC theory. Next, a perturbational analysis of the different terms in the VCC equations allows an identification of the most important contributions. This leads to the VCC[2pt3] model. The perturbation analysis is finally carried on to response theory in the following subsection where the expected relative accuracy of different excitation energies is determined.

A. General VCC theory

The VCC wave function is based on an exponential ansatz,

$$|\text{VCC}\rangle = \exp(T)|\Phi_i\rangle, \quad (1)$$

where T is the cluster operator and $|\Phi_i\rangle$ is the reference VSCF Hartree product for the state of interest. Using the second quantization formalism of Ref. 1, the reference state can be written as

$$|\Phi_i\rangle = \prod_{m=1}^M a_{i_m}^{m\dagger} |\text{vac}\rangle, \quad (2)$$

where the vector $\mathbf{i}=(i_1, i_2, \dots, i_M)$ is a vector specifying the excitation level of each mode. In this paper we adopt the convention that modal indices i, j, k, \dots correspond to modals occupied in the VCC reference, a, b, c, \dots correspond to unoccupied modals, and p, q, r, \dots correspond to any modal. The cluster operator is given as

$$T = \sum_{\mathbf{m} \in \text{MCR}[T]} \sum_{\mu^{\mathbf{m}}} t_{\mu^{\mathbf{m}}} \tau_{\mu^{\mathbf{m}}}. \quad (3)$$

In this definition $t_{\mu^{\mathbf{m}}}$ is the amplitude associated with the excitation operator $\tau_{\mu^{\mathbf{m}}}$ defined as

$$\tau_{\mu^{\mathbf{m}}} = \prod_{m \in \mathbf{m}} a_{a_m}^{m\dagger} a_{i_m}^m, \quad (4)$$

where \mathbf{m} is the mode combination (MC) for the operator, i.e., the set of modes on which it excites, and $\mu^{\mathbf{m}}$ is a compound index for the different possible excitations. The $\text{MCR}[T]$ in Eq. (3) is the MC range of the cluster operator, i.e., the set of MCs included in the excitation space. By restricting this MCR to include only MCs with size lower than or equal to n , a hierarchy of VCC[n] approximations is obtained. More elaborate MCRs may be constructed which is a subject of current research.

The VCC amplitudes and subsequently the energy are obtained by inserting the ansatz (1) into the Schrödinger equation followed by transformation with $\exp(-T)$ and projection onto the excited Hartree products and the reference,

$$0 = \langle \mu^{\mathbf{m}} | \exp(-T) H \exp(T) | \Phi_i \rangle = e_{\mu^{\mathbf{m}}}, \quad (5)$$

$$E_{\text{VCC}} = \langle \Phi_i | H \exp(T) | \Phi_i \rangle. \quad (6)$$

The equations (5) for the amplitudes are solved iteratively as described in Ref. 2 and the time consuming step is the evaluation of the error vector $e_{\mu^{\mathbf{m}}}$ given a set of trial amplitudes.

Two strategies can be used to evaluate the error vector. The first one, used in the initial general implementations,^{2,29} is based on a Taylor expansion of the $\exp(\pm T)$ operators. This strategy was chosen for its simplicity compared to the second method which is based on a Baker–Campbell–Hausdorff (BCH) expansion of the similarity transformed Hamiltonian, $\exp(-T) H \exp(T)$,

$$e_{\mu^{\mathbf{m}}} = \langle \mu^{\mathbf{m}} | H + [H, T] + \frac{1}{2} [[H, T], T] + \frac{1}{6} [[[[H, T], T], T], T] + \dots | \Phi_i \rangle. \quad (7)$$

The latter approach is usually employed in electronic struc-

ture theory and also in the specific two-mode implementation of Ref. 30.

In Sec. II B, we use the BCH expansion to perform a perturbation analysis of the importance of the different commutators for different excitation levels. This will allow us to select the most important contributions and discard some of the presumably less important, but most time consuming terms.

B. Perturbational analysis

The correlation of the vibrational motions is due to the coupling of these in the Hamiltonian. As mentioned in Sec. I, the Hamiltonian can be represented using a hierarchy of terms coupling more and more modes. In this article we will consider the case where only up to three-mode couplings are included,

$$H = H_1 + H_2 + H_3. \quad (8)$$

We now introduce a partitioning similar to that of VMP perturbation theory and divide the Hamiltonian into a mean-field part and a fluctuation operator. The mean-field operator can, in second quantization, be written as

$$F = \sum_{m=1}^M \sum_{p_m q_m} \langle \Phi_i | a_{i_m}^{m\dagger} a_{p_m}^m H a_{q_m}^{m\dagger} a_{i_m}^m | \Phi_i \rangle a_{p_m}^{m\dagger} a_{q_m}^m. \quad (9)$$

This is in one-to-one correspondence with the first quantization operator, $F = \sum_m \langle \Phi_i^{-m} | H | \Phi_i^{-m} \rangle$, where $\langle \Phi_i^{-m} | \dots | \Phi_i^{-m} \rangle$ indicates that the integration over mode m is neglected. Similarly to the Hamiltonian in Eq. (8), we can write the mean-field operator as

$$F = F_1 + F_2 + F_3, \quad (10)$$

where F_i is given by Eq. (9) with the substitutions $F \rightarrow F_i$ and $H \rightarrow H_i$. The fluctuation operator is the difference between the true Hamiltonian and the mean-field operator. Note that $F_1 = H_1$.

We now split the fluctuation operator in two parts based on the mode-coupling level,

$$H = F + U_2^{(1)} + U_3^{(2)}, \quad (11)$$

where

$$U_2^{(1)} = H_2 - F_2, \quad (12)$$

$$U_3^{(2)} = H_3 - F_3. \quad (13)$$

The one-mode part of the Hamiltonian H_1 is treated exact at the VSCF level and is therefore included fully in the zeroth order mean-field operator F . From Eq. (11) it is seen that the two-mode couplings are treated as first order, whereas the three-mode couplings are second order since they are expected to be less important. This assumption is based on the hierarchical form of the PES discussed in Sec. I. In fact, the relative strength of the U_2 and U_3 operators is not defined *a priori*. One possible approach is therefore to carry out a

double perturbation analysis with U_2 and U_3 as independent perturbations. However, in the end a decision must be made on their relative importance to arrive at a well defined set of final equations. For simplicity, we have in this presentation opted to define the relative strength from the beginning. In the following we derive the VCC equations in terms of orders in the fluctuation operators. Nowadays, this is textbook material for electronic CC theory, see, for instance, Secs. 14.3 and 14.6 of Ref. 35 and Ref. 36. However, in this context the details are different due to the three-mode couplings and the splitting in two fluctuation operators.

Before we proceed, we note that the commutator between the mean-field operator in the canonical representation and an excitation operator is given by

$$[F, t_{\mu^m} \tau_{\mu^m}] = \varepsilon_{\mu^m} t_{\mu^m} \tau_{\mu^m}, \quad (14)$$

where

$$\varepsilon_{\mu^m} = \sum_{m \in \mathbf{m}} (E_{a_m}^{(0)} - E_{i_m}^{(0)}) \quad (15)$$

is a sum of VSCF modal energy differences. From Eq. (14) we conclude that a BCH expansion of the similarity transformed mean-field operator gives

$$\exp(-T) F \exp(T) = F + \sum_{\mathbf{m} \in \text{MCR}[T]} \sum_{\mu^m} \varepsilon_{\mu^m} t_{\mu^m} \tau_{\mu^m}. \quad (16)$$

The VCC equations (5) can now be expressed as

$$0 = \varepsilon_{\mu^m} t_{\mu^m} + \langle \mu^m | \exp(-T) (U_2^{(1)} + U_3^{(2)}) \exp(T) | \Phi_i \rangle, \quad (17)$$

and the energy is given by

$$\begin{aligned} E_{\text{VCC}} = & E_{\text{VSCF}} + \langle \Phi_i | [U_2^{(1)}, T_1] + [U_3^{(2)}, T_1] + [U_2^{(1)}, T_2] \\ & + [U_3^{(2)}, T_2] + \frac{1}{2} [[U_2^{(1)}, T_1], T_1] + \frac{1}{2} [[U_3^{(2)}, T_1], T_1] \\ & + [U_3^{(2)}, T_3] + [[U_3^{(2)}, T_1], T_2] \\ & + \frac{1}{6} [[[U_3^{(2)}, T_1], T_1], T_1] | \Phi_i \rangle. \end{aligned} \quad (18)$$

We want initially to carry out a perturbation analysis of the amplitudes and therefore expand these in orders of the fluctuation operators,

$$T = T^{(0)} + T^{(1)} + T^{(2)} + T^{(3)} + \dots \quad (19)$$

Using this definition in Eq. (17), we can collect terms to identical orders and obtain a set of equations,

$$\varepsilon_{\mu^m} t_{\mu^m}^{(0)} = 0, \quad (20)$$

$$- \varepsilon_{\mu^m} t_{\mu^m}^{(1)} = \langle \mu^m | U_2^{(1)} | \Phi_i \rangle, \quad (21)$$

$$- \varepsilon_{\mu^m} t_{\mu^m}^{(2)} = \langle \mu^m | U_3^{(2)} + [U_2^{(1)}, T^{(1)}] | \Phi_i \rangle, \quad (22)$$

$$\begin{aligned} - \varepsilon_{\mu^m} t_{\mu^m}^{(3)} = & \langle \mu^m | [U_2^{(1)}, T^{(2)}] + \frac{1}{2} [[U_2^{(1)}, T^{(1)}], T^{(1)}] \\ & + [U_3^{(2)}, T^{(1)}] | \Phi_i \rangle, \end{aligned} \quad (23)$$

TABLE I. The orders to which the amplitudes and the energy are correct for the different VCC models discussed in this paper. The order in which the amplitude enter is given in the last column.

	VCC[2]	VCC[2pt3]	VCC[3]	Enters in
T_1	2	3	4	1
T_2	2	3	3	1
T_3	1	2	3	2
T_4	2	2	2	3
E_{VCC}	3	4	4	

$$\begin{aligned}
 -\varepsilon_{\mu\mathbf{m}l} \mu_{\mu\mathbf{m}}^{(4)} &= \langle \mu^{\mathbf{m}} | [U_2^{(1)}, T^{(3)}] + [[U_2^{(1)}, T^{(1)}], T^{(2)}] \\
 &\quad + \frac{1}{6} [[U_2^{(1)}, T^{(1)}], T^{(1)}], T^{(1)}] + [U_3^{(2)}, T^{(2)}] \\
 &\quad + \frac{1}{2} [[U_3^{(2)}, T^{(1)}], T^{(1)}] | \Phi_{\mathbf{i}} \rangle. \quad (24) \\
 &\vdots
 \end{aligned}$$

Based on these equations, we can analyze to what order in the fluctuation operators different VCC models are correct. The results we are about to derive are collected in Table I. From Eq. (21) we see that both the T_1 and T_2 amplitudes enter to first order. In electronic theory the T_1 operator enters only to second order due to the Brillouin theorem. Because of the separation of the fluctuation operator into U_2 and U_3 , the vibrational case is different.

Equation (22) shows that the T_3 amplitudes enter to second order. However, this does not change the second order correction to the T_1 and T_2 amplitudes since $T^{(2)}$ itself is not present on the right-hand side of Eq. (22). Instead, these amplitudes are corrected to third order by Eq. (23) where the commutator $[U_2^{(1)}, T^{(2)}]$ can generate one- and two-mode excitations. From this we infer that the VCC[2] model is correct through second order in the T_1 and T_2 amplitudes. From the energy expression, Eq. (18), we see that in VCC[2] all terms will be correct to at least third order.

Equation (23) is the first equation containing commutators that can generate four-mode excitations. Thus, the T_4 amplitudes enter to third order. These third order T_4 amplitudes in turn enter in the first commutator, $[U_2^{(1)}, T^{(3)}]$, of Eq. (24). This commutator can, for the case of a T_4 operator, generate from two- to five-mode excitations. Thus, the T_2 and T_3 amplitudes are modified to fourth order. The T_1 amplitudes, however, are not affected to fourth order by the inclusion of T_4 . Instead, these are corrected to fifth order as can be seen by writing out the equation for $t^{(5)}$ explicitly ($[U_3^{(2)}, T_4^{(3)}]$ generates from one to six excitations). In summary, we have that the T_1 , T_2 , T_3 , and T_4 amplitudes in the VCC[3] model are correct to orders 4, 3, 3, and 2, respectively. Considering the energy, Eq. (18), we see that all terms are correct to at least fourth order.

As expected, the VCC[3] model is correct to higher orders in the fluctuation operators than VCC[2]. However, the correctness comes at a price of much higher complexity. Before we discuss this further, we introduce the T_1 transformed Hamiltonian,

$$\tilde{H} = \exp(-T_1) H \exp(T_1), \quad (25)$$

and similarly for the fluctuation operators. As discussed in Ref. 30, this transformation can be realized simply by a transformation of the integrals over the one-mode operators. The practical result of this is that the T_1 amplitudes are taken care of once and for all, i.e., they will not enter our equations explicitly. Additionally, there is a theoretical motivation: In the following, we will count the T_1 amplitudes as zeroth order. This is conveniently incorporated using the T_1 transformation. The zeroth order treatment of one-mode excitations is important, especially for response theory and thereby excited states, since the T_1 transformation provides approximate modal relaxation as is well known from electronic CC theory.³⁹ More precisely, response theory is derived by introducing a formal external one-mode perturbation. The order of this perturbation is counted separately from that of the fluctuation operators. In keeping a fixed (unrelaxed) reference state, the one-mode amplitudes will respond to this perturbation to zeroth order in the fluctuation operators. In other words, for a balanced description of the system with and without external perturbations, which is necessary for obtaining good response functions, it is appropriate to treat the one-mode amplitudes as zeroth order.

Using the T_1 transformed Hamiltonian, the VCC[3] equations projected on the two-mode space can be explicitly written as

$$\begin{aligned}
 e_{\mu_2} &= \langle \mu_2 | \tilde{U}_2^{(1)} + \tilde{U}_3^{(2)} + [F, T_2]^{(1)} + [\tilde{U}_2^{(1)}, T_2]^{(2)} \\
 &\quad + [\tilde{U}_3^{(2)}, T_2]^{(3)} + [\tilde{U}_2^{(1)}, T_3]^{(3)} + [\tilde{U}_3^{(2)}, T_3]^{(4)} \\
 &\quad + \frac{1}{2} [[\tilde{U}_2^{(1)}, T_2], T_2]^{(3)} + \frac{1}{2} [[\tilde{U}_3^{(2)}, T_2], T_2]^{(4)} \\
 &\quad + [[\tilde{U}_3^{(2)}, T_2], T_3]^{(5)} | \Phi_{\mathbf{i}} \rangle, \quad (26)
 \end{aligned}$$

where the orders n in which the different commutators enter have been written as $[\dots]^{(n)}$. The corresponding VCC[2] equation is identical except for the terms containing T_3 which are not present. The VCC[3] equations projected on the three-mode space are

$$\begin{aligned}
 e_{\mu_3} &= \langle \mu_3 | [F, T_3]^{(2)} + \tilde{U}_3^{(2)} + [\tilde{U}_2^{(1)}, T_2]^{(2)} + [\tilde{U}_3^{(2)}, T_2]^{(3)} \\
 &\quad + [\tilde{U}_2^{(1)}, T_3]^{(3)} + [\tilde{U}_3^{(2)}, T_3]^{(4)} + \frac{1}{2} [[\tilde{U}_2^{(1)}, T_2], T_2]^{(4)} \\
 &\quad + \frac{1}{2} [[\tilde{U}_3^{(2)}, T_2], T_2]^{(4)} + [[\tilde{U}_2^{(1)}, T_2], T_3]^{(4)} \\
 &\quad + [[\tilde{U}_3^{(2)}, T_2], T_3]^{(5)} + \frac{1}{2} [[\tilde{U}_3^{(2)}, T_3], T_3]^{(6)} \\
 &\quad + \frac{1}{6} [[[\tilde{U}_3^{(2)}, T_2], T_2], T_2]^{(5)} | \Phi_{\mathbf{i}} \rangle. \quad (27)
 \end{aligned}$$

We propose in this paper that some of the higher order terms included in VCC[3] but not present in VCC[2] can be

discarded resulting in a significantly lower computational cost without dramatically affecting the accuracy of the results. In the two-mode equations, the commutators $[\tilde{U}_3^{(2)}, T_3]^{(4)}$ and $[[\tilde{U}_3^{(2)}, T_2], T_3]^{(5)}$ are discarded. The remaining fourth order commutator, $1/2[[\tilde{U}_3^{(2)}, T_2], T_2]^{(4)}$, is already present in the VCC[2] model and is therefore retained. In the three-mode equations, Eq. (27), all terms of third or higher order are discarded, leaving only the first three terms on the right-hand side. We denote this new model VCC[2pt3] because all two-mode couplings are explicitly included, but only the most important three-mode couplings are included based on the perturbation theory analysis. Using the definitions in Eqs. (11)–(13), the explicit equations for the VCC[2pt3] model can be written in terms of the Hamiltonian and mean-field operators as

$$e_{\mu_2}^{2pt3} = \langle \mu_2 | \tilde{H} + [\tilde{H}, T_2] + [\tilde{H}_1 + \tilde{H}_2 + F_3, T_3] + \frac{1}{2}[[\tilde{H}, T_2], T_2] | \Phi_i \rangle, \quad (28)$$

$$e_{\mu_3}^{2pt3} = \langle \mu_3 | \tilde{H} + [\tilde{H}_2, T_2] + [F, T_3] | \Phi_i \rangle. \quad (29)$$

The expected accuracy of the model can once again be analyzed in terms of order in the fluctuation operators. We start by noting that the three-mode equation (29) is equivalent to the second order equation (22). In VCC[3], we know that the T_3 amplitudes are correct through third order. However, the third order corrections provided by Eq. (23) are among the commutators discarded to arrive at Eq. (29). In the VCC[2pt3] model, the T_3 amplitudes are therefore only correct through second order, i.e., the lowest nonvanishing order. Regarding the T_2 amplitudes, these are still correct to third order since none of the commutators in Eqs. (21)–(23) are discarded from Eq. (26) and the fourth order correction was not fully correct even in VCC[3]. Finally, in the one-mode equations we make no approximations. However, the fourth order contribution $[U_2^{(1)}, T^{(3)}]$ depends on the T_3 amplitudes which are not correct to third order in this model. Therefore, the T_1 amplitudes are correct only through third order. The energy can once again be analyzed using Eq. (18) and is seen to be correct to fourth order like for VCC[3]. This analysis confirms the expectation that VCC[2pt3] is intermediate between the VCC[2] and VCC[3] models. This will be validated further by benchmark calculations in Sec. IV.

The VCC[2pt3] model differs in some aspects from related ones in electronic CC theory, e.g., CCSDT-X ($X = 1b, 2, 3$) (Refs. 32 and 33) and CC3.³⁴ Contrary to these models, in VCC[2pt3] we introduce approximations not only in the equations for the highest excitation level but also in lower levels (as is also the case in CCSTD-1a). This is motivated by the order analysis and is necessary to obtain a low scaling that can justify the model relative to VCC[3]. Also, it should be noted that the approximations in the two-mode equations are only related to the U_3 terms. Such three-body interactions are alien to electronic structure theory. If we neglect U_3 completely, identical one- and two-mode equations are obtained for VCC[2pt3] and VCC[3]. The three-mode equations in VCC[2pt3] will, however, simplify to $\langle \mu_3 | [F, T_3] + [\tilde{U}_2, T_2] | \Phi_i \rangle = 0$. This is in exact analogy to the

electronic CC3 model. This is not so surprising since CC3 was also derived with a particular emphasis on obtaining good response functions. We note that the simplifications in VCC[2pt3] give a significant reduction in computational time, *vide infra*.

C. Response theory excitation energies

CC excitation energies may be obtained from response theory, see Ref. 41 and references therein, for details on CC response theory and related methods. The application to VCC (Ref. 29) is completely analogous to the electronic case, and here we simply quote the result that excitation energies are given as the eigenvalues of the VCC error vector Jacobian,

$$A_{\mu^m, m'} = \frac{\partial}{\partial t_{j, m'}} \langle \mu^m | \exp(-T) H \exp(T) | \Phi_i \rangle. \quad (30)$$

In approximate models, the Jacobians of the truncated expressions for the error vectors are used. The aim of this section is to analyze the expected accuracy of the VCC[2], VCC[2pt3], and VCC[3] models.

The Jacobian is asymmetric and therefore has different right and left eigenvectors,

$$\mathbf{A} \mathbf{R}_i = \omega_i \mathbf{R}_i, \quad (31)$$

$$\mathbf{L}_i \mathbf{A} = \omega_i \mathbf{L}_i. \quad (32)$$

The eigenvalues ω_i are, however, identical and, furthermore, the left and right eigenvectors may be chosen to fulfill the biorthogonality condition,

$$\mathbf{L}_i \mathbf{R}_j = \delta_{ij}. \quad (33)$$

The excitation energies may thus be obtained from

$$\omega_i = \mathbf{L}_i \mathbf{A} \mathbf{R}_i. \quad (34)$$

By considering to which orders in the fluctuation operators different blocks of \mathbf{L}_i , \mathbf{A} , and \mathbf{R}_i enter, we may analyze the expected accuracy of ω_i . The following analysis is similar to previous works^{34,42} but repeated here since there is some variation due to the somewhat different context.

We first consider the blocks of the Jacobian matrix. The exact VCC Jacobian can be expressed as a BCH expansion,

$$\begin{aligned} A_{\mu^m, m'} = & \langle \mu^m | [F, \tau_{j, m'}] + [U_2^{(1)}, \tau_{j, m'}] + [U_3^{(2)}, \tau_{j, m'}] \\ & + [[U_2^{(1)}, \tau_{j, m'}], T] + [[U_3^{(2)}, \tau_{j, m'}], T] \\ & + [[[U_2^{(1)}, \tau_{j, m'}], T], T] + [[[[U_3^{(2)}, \tau_{j, m'}], T], T], T] \\ & + \dots | \Phi_i \rangle. \end{aligned} \quad (35)$$

By considering to which order different levels of T enter, it can be determined to what orders the different blocks enter in the Jacobian,

$$\begin{pmatrix}
 & 1 & 2 & 3 & 4 & 5 & \dots \\
 1 & d(0) + O(1) & O(1) & O(1) & O(2) & 0 & \\
 2 & O(1) & d(0) + O(1) & O(1) & O(1) & O(2) & \\
 3 & O(2) & O(1) & d(0) + O(1) & O(1) & O(1) & \\
 4 & O(3) & O(2) & O(1) & d(0) + O(1) & O(1) & \\
 5 & O(4) & O(3) & O(2) & O(1) & d(0) + O(1) & \\
 \vdots & & & & & &
 \end{pmatrix}. \quad (36)$$

In this notation the column headings refer to excitation levels and $d(0)$ are the diagonal terms arising from the commutator with the mean-field operator in Eq. (35).

To analyze the blocks of the eigenvectors, we expand \mathbf{A} , \mathbf{R}_i , \mathbf{L}_i , and ω_i in orders of the fluctuation operators analogously to Eq. (19). We then insert these expansions into Eqs. (31) and (32) and collect terms of identical order. For the right-hand eigenvector, we obtain

$$(\mathbf{A}^{(0)} - \omega^{(0)}\mathbf{I})\mathbf{R}^{(k)} = \sum_{l=1}^k (\omega^{(l)}\mathbf{R}^{(k-l)} - \mathbf{A}^{(l)}\mathbf{R}^{(k-l)}), \quad \forall k > 0, \quad (37)$$

where $\mathbf{A}^{(0)}$ is simply a diagonal matrix of mean-field energy differences,

$$A_{\mu m, \nu m'}^{(0)} = \varepsilon_{\mu m} \delta_{\mu m, \nu m'}, \quad (38)$$

see Eqs. (14)–(16). Note that for simplicity, we have discarded the i subscript on the eigenvectors and eigenvalues here and in the following. Consider now some state dominated by a one-mode excitation relative to the reference. In this case the zeroth order eigenvector $\mathbf{R}^{(0)}$ will have a single nonzero element in the one-mode block. The first order correction is obtained from

$$\mathbf{R}^{(1)} = (\mathbf{A}^{(0)} - \omega^{(0)}\mathbf{I})^{-1}(\omega^{(1)}\mathbf{R}^{(0)} - \mathbf{A}^{(1)}\mathbf{R}^{(0)}). \quad (39)$$

The interesting term in this expression is $\mathbf{A}^{(1)}\mathbf{R}^{(0)}$. It states that we are only multiplying first order blocks of the Jacobian onto the zeroth order eigenvector. From the structure of $\mathbf{A}^{(1)}$ derived from Eq. (36), we see that the $\mathbf{R}^{(1)}$ vector is only modified in the one- and two-mode blocks, i.e., only the two-mode block enters to first order. The second order correction can be obtained from

TABLE II. The order in the fluctuation operators in which different blocks of the response eigenvectors enter.

Excitation vector block		1M	2M	3M	4M
One-mode dominated	R	0	1	2	3
	L	0	1	1	2
Two-mode dominated	R	1	0	1	2
	L	1	0	1	1

$$\mathbf{R}^{(2)} = (\mathbf{A}^{(0)} - \omega^{(0)}\mathbf{I})^{-1}(\omega^{(1)}\mathbf{R}^{(1)} + \omega^{(2)}\mathbf{R}^{(0)} - \mathbf{A}^{(1)}\mathbf{R}^{(1)} - \mathbf{A}^{(2)}\mathbf{R}^{(0)}). \quad (40)$$

In this expression both the $\mathbf{A}^{(1)}\mathbf{R}^{(1)}$ and $\mathbf{A}^{(2)}\mathbf{R}^{(0)}$ terms will modify the one-, two-, and three-mode blocks of $\mathbf{R}^{(2)}$, i.e., the three-mode blocks enter to second order. Analysis of higher orders is carried out by continuing in this fashion. If the state of interest is dominated by a two-mode excitation, the analysis proceeds in the same way but the results will be different since now the two-mode block of $\mathbf{R}^{(0)}$ is nonzero. Similarly, the orders in which different excitation levels enter the left-hand eigenvector may be obtained by expanding Eq. (32). In this case the results will be different since the Jacobian is asymmetric. The outcome of the full analysis is summarized in Table II.

The excitation energy, Eq. (34), can be expressed using the block structure of the eigenvectors and the Jacobian. For instance, the VCC[2] excitation energies are obtained from

$$\omega = \mathbf{L}_1\mathbf{A}_{11}\mathbf{R}_1 + \mathbf{L}_1\mathbf{A}_{12}\mathbf{R}_2 + \mathbf{L}_2\mathbf{A}_{21}\mathbf{R}_1 + \mathbf{L}_2\mathbf{A}_{22}\mathbf{R}_2, \quad (41)$$

where the subscripts refer to the excitation levels in the different blocks. This is summarized in Table III where different excitation levels are separated by horizontal lines. Along with each contribution is the order to which it enters in the cases of one- and two-mode dominated excitations.

Now consider the VCC[2] response energy, Eq. (41). In VCC[2] all three-mode and higher blocks are discarded from the Jacobian. From Table III we see that the corresponding contributions to the excitation energies are of third and

TABLE III. Orders in which different contributions to the response excitation energies enter.

	One-mode dominated	Two-mode dominated
$\mathbf{L}_1\mathbf{A}_{11}\mathbf{R}_1$	0	2
$\mathbf{L}_1\mathbf{A}_{12}\mathbf{R}_2$	2	2
$\mathbf{L}_2\mathbf{A}_{21}\mathbf{R}_1$	2	2
$\mathbf{L}_2\mathbf{A}_{22}\mathbf{R}_2$	2	0
$\mathbf{L}_1\mathbf{A}_{13}\mathbf{R}_3$	3	3
$\mathbf{L}_3\mathbf{A}_{31}\mathbf{R}_1$	3	4
$\mathbf{L}_2\mathbf{A}_{23}\mathbf{R}_3$	4	2
$\mathbf{L}_3\mathbf{A}_{32}\mathbf{R}_2$	3	2
$\mathbf{L}_3\mathbf{A}_{33}\mathbf{R}_3$	3	2
4M and higher	$O(5)$	$O(3)$

TABLE IV. Orders to which response excitation energies are correct for different VCC models.

	VCC[2]	VCC[2pt3]	VCC[3]
One-mode dominated	2	3	4
Two-mode dominated	1	2	2

higher orders for one-mode dominated excitations and of second and higher orders for the two-mode dominated excitations. Therefore, in VCC[2], one-mode dominated excitations are correct through second order, while two-mode dominated excitations are correct through only first order. For VCC[3], one-mode excited states will be correct through fourth order and two-mode excited states through second order.

For VCC[2pt3], the situation is slightly more complicated. In this case the full two- and three-mode equations, Eqs. (26) and (27), of VCC[3] are only approximated. However, this is sufficient to include the lowest order three-mode blocks of the Jacobian. This makes the one-mode dominated excitation energies correct through third order. The reason they are not correct to fourth order like the full VCC[3] energies can be explained by considering, e.g., the A_{33} block. In VCC[2pt3] only the zeroth order diagonal is included and the $L_3 A_{33} R_3$ contribution can therefore only be correct to third order. In VCC[3] higher order contributions to this block are also included. For completeness we note that the A_{21} and A_{22} blocks are also modified relative to VCC[3]. However, they are still correct to sufficient high order and do not influence the analysis. By similar arguments the two-mode dominated excitations are seen to be correct through second order. These results are summarized in Table IV.

III. IMPLEMENTATION AND COMPUTATIONAL SCALING

In Sec. II, we have discussed the general expressions for the VCC[2pt3] error vector and the associated Jacobian in terms of commutators. To implement the model, these commutators must be expanded into expressions depending only on amplitudes and integrals. Furthermore, intermediates must be identified to lower the computational scaling. In a previous publication, this was done by hand for the commutators arising in the VCC[2] model.³⁰ However, for more advanced models, this derivation becomes tedious and error prone. To overcome this difficulty, an algorithm for automatic derivation, manipulation, and evaluation of the required expressions has been developed and implemented in the MIDASCPP (Ref. 43) program package. The details of this algorithm are postponed to a future publication. However, we note that the resulting expressions for the VCC[2pt3] model have a formal scaling of M^3 . Due to technical issues related to addressing of amplitudes and intermediates in memory, certain logical steps in the implementation may scale as $M^3 \log M$. This will all be discussed further along with the full account of the general algorithm and may possibly be avoided. For now we merely note that the observed scaling turns out to be quite satisfactory and reflect the expected M^3 behavior, see Sec. IV A.

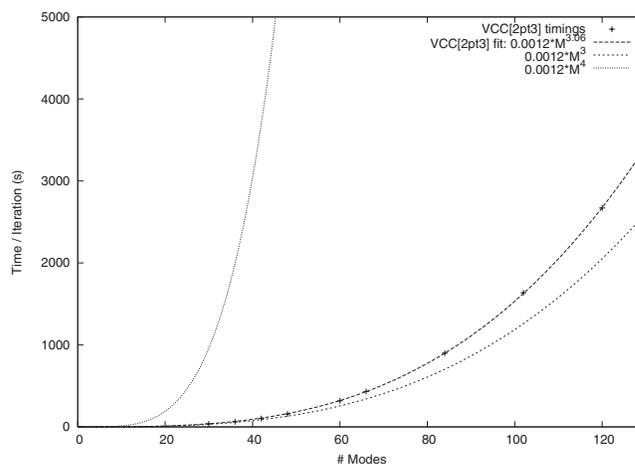


FIG. 1. Scaling of the VCC[2pt3] algorithm with respect to the number of modes. The timings are per iteration in VCC[2pt3] ground-state calculations on artificial PESs of increasing size.

An important prerequisite for the low scaling is that the Hamiltonian is expressed as a sum over products of one-mode operators as already mentioned in Sec. I. Presently, the PES generation module of MIDASCPP only works in normal coordinates with the possibility of using the full Watson Hamiltonian. However, VCC theory and the present implementation can be applied with other coordinates and kinetic energy operators as long as the Hamiltonian is provided numerically in the basic sum over products form.

IV. RESULTS

A. Computational scaling

To test the scaling of our new algorithm, we have produced a set of artificial quartic force fields with up to three-mode couplings. The size ranges from 30 to 120 modes. For the largest PES, this corresponds to 1 166 801 terms. The test calculations were carried out using eight modals per mode. For a 120 mode system this corresponds to 96 678 820 amplitudes demonstrating that the algorithm is capable of handling very large excitation spaces. The timings are obtained on a 2.3 GHz Quadcore AMD Opteron model 2356 and are shown in Fig. 1 together with a fit and theoretical M^3 and M^4 curves. The prefactor in these curves is chosen identical to the one obtained from the fitting. It is seen that the observed scaling is very close to the theoretical M^3 . This result should be compared with the scaling of other VCC[n] and VCI[n] methods. VCC[2] and VCI[2] also come with a M^3 scaling although with smaller prefactors. However, VCC[3] and VCI[3] to which the accuracy of this model can be compared (see below) scale as M^4 .

B. Benchmarks against FVCI

The accuracy of the VCC[2pt3] model has been tested on a set of 11 molecules: F_2O , Cl_2O , FNO , O_3 , H_2S , $CINO$, H_2O , H_2CO , $SOCI_2$, $HFCO$, and CCl_2O . These small molecules allow the full hierarchy of VCC and VCI methods to be applied all the way up to full VCI (FVCI) which gives the exact results within our modal basis and given a concrete

PES. Thus, a comparison of VCC[2pt3] with other methods as well as the exact solution can be performed.

Note that our focus is to benchmark the response approach. It is not unlikely that some of the states considered here can be calculated more accurately by a state-specific approach, particularly in the case of VCI. Testing the response approach is, however, in line with the theoretical discussions and derivations in the previous sections. Furthermore, the state-specific approach has other problems such as the nonorthogonality of different states which complicates the evaluation of transition properties.

For each molecule, previously reported²⁸ semiglobal representations of the PESs including up to three-mode couplings have been used. The representations are expressed analytically using normal coordinates. The construction is based on the grid method described in Ref. 27 with coarse grid definitions $64_1 32_{3/4} 8_{3/4}$ for the triatomics and $32_1 16_{3/4} 8_{3/4}$ for the tetra-atomics. These coarse grids are refined to a higher resolution using the modified Shepard interpolation technique⁴⁴ with up to second order derivatives. Finally, the grids are fitted to a 12th order polynomial suitable for the wave function method implementations. The electronic energy point was calculated using density functional theory with the B3LYP functional^{45,46} and the Dunning cc-pVTZ basis sets.⁴⁷⁻⁴⁹ The kinetic energy operator employed is simply a sum of second derivatives of each normal coordinate, $T = -1/2 \sum_m \partial^2 / \partial Q_m^2$.

All vibrational structure calculations use a primitive basis set consisting of the first 11 harmonic oscillator wave functions to expand each VSCF modal. The functions correspond to the frequencies obtained from the coefficients of the quadratic terms in the one-dimensional parts of the PESs. The six modals with lowest energy are retained in the VCC and VCI calculations. VCI[2], VCC[2], VCC[2pt3], and FVCI calculations have been performed for the triatomic molecules. For the tetra-atomics, also VCI[3], VCI[4], VCC[3], and VCC[4] calculations have been done. Note that the VCI[2] and VCC[2] calculations still include the three-mode couplings in the PES. The supplementary information to this article⁵⁰ contains tables with all calculated energies as well as the weights of one-, two-, and three-mode excitations in the different states obtained using the VCC[2pt3] method. Below we only present the numbers graphically to illustrate the general accuracy and behavior of the methods.

Figure 2 shows the errors of the different wave function methods relative to FVCI for the fundamental, overtone, and combination bands of the triatomic molecules on a logarithmic scale. For the fundamentals, there is a clear improvement in going from VCI[2] to VCC[2] where all errors are below 1 cm^{-1} . The VCC[2pt3] method improves the accuracy even further. The same picture is seen for the overtones although the accuracy is generally lower. This should come as no surprise since the higher energy of these states increases the possibility of resonances which will introduce other configurations into the description of a given state and hence complicate the wave function representation. Turning to the combination bands, these are, in general, much less accurate than the first two kinds with VCC[2] errors as high as 69.9 cm^{-1} for the $\nu_1 \nu_3$ state of H_2S and 113.0 cm^{-1} for

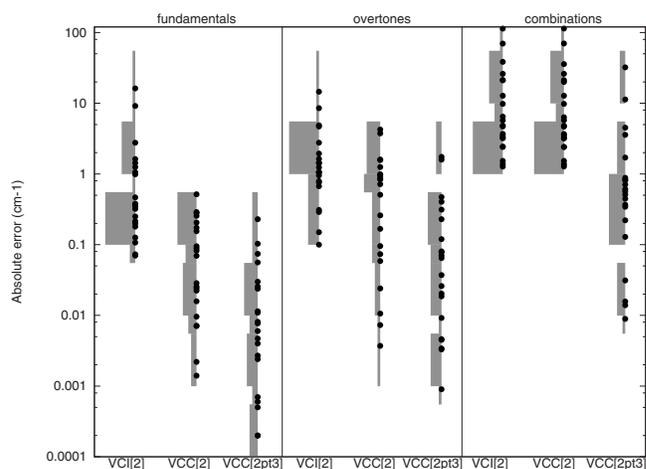


FIG. 2. Errors of the different wave function methods relative to FVCI for the fundamental, overtone, and combination bands of the triatomic molecules. Each dot represents one state. The gray boxes indicate the density of dots in a given interval. The intervals are divided at 0.0001, 0.0005, 0.001, 0.005, 0.01, etc.

the $\nu_1 \nu_3$ state of H_2O . The VCC[2pt3] method reduces these errors significantly to -11.9 and -33.7 cm^{-1} . These errors are, however, still large on an absolute scale and much larger than for any other states. Investigation of the tables provided in the supplementary information⁵⁰ shows that these two specific states have relatively large weights of three-mode excited Hartree products (2.16% and 2.63%). The poor accuracy is thus consistent with the fact that three-mode excitations are only approximately described in VCC[2pt3] and not at all included in VCC[2]. There are other states also having errors above 10 cm^{-1} for VCC[2], but these errors are all reduced to below 5 cm^{-1} in the VCC[2pt3] model. This agrees with the lower three-mode weights observed in these cases. At the end of this section we will discuss further how the amounts of one-, two-, and three-mode excitations may be used as a diagnostic for the accuracy of the VCC[2pt3] method. In addition, we note that the observed errors are consistent with the perturbation theory analysis performed in Sec. II C and summarized in Table IV: The one-mode dominated configurations are correct through second order for VCC[2] and third order for VCC[2pt3]. This is reduced to first and second orders for the two-mode dominated excitations.

The results for the fundamentals, first overtones, and combinations of the tetraatomic molecules are collected in Figs. 3–5. In the figures, the wave function methods are ordered according to the computational cost. The general picture of the accuracy is that the magnitudes of the errors are ordered as $\text{VCI}[2] > \text{VCC}[2] > \text{VCC}[2\text{pt}3] \approx \text{VCI}[3] > \text{VCC}[3] > \text{VCI}[4] > \text{VCC}[4]$. In the following we only discuss the relation between VCC[2pt3], VCI[3], and VCC[3] since these offer comparable accuracy for these small molecules. Considering the fundamentals in Fig. 3, we see that the VCC[2pt3] results are better than the more expensive VCI[3] results and almost as good as the VCC[3] results. The only VCC[2pt3] error larger than 1 cm^{-1} is the well-known resonance between the antisymmetric stretch and the CH_2 bending+rock combination in H_2CO . This res-

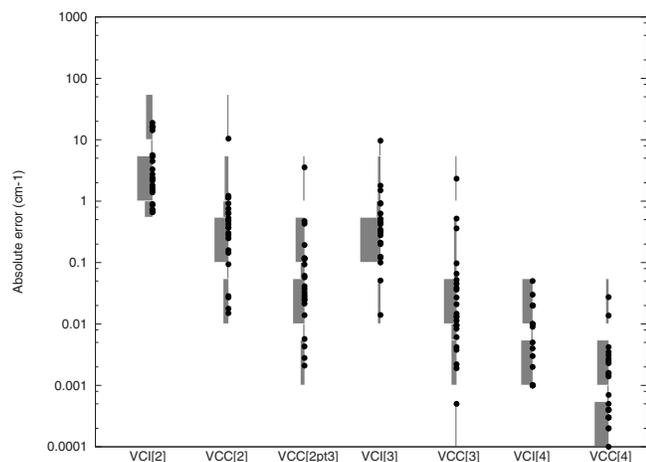


FIG. 3. Errors of different wave function methods relative to FVCI for the fundamentals of the tetra-atomic molecules. See Fig. 2 for details.

nance results in a two-mode excitation weight of 47% and a correspondingly large error of 3.7 cm^{-1} . For the overtones in Fig. 4, VCC[2pt3] is slightly better than VCI[3] with the exception of two states. These are overtones of H_2CO and exhibit three-mode weights of 5.29% and 11.41%. The poorer performance is thus not surprising. With the exception of the few outliers, the accuracy of VCC[2pt3] is generally higher than that of VCI[3] and comparable but not quite as good as VCC[3]. The combination band errors shown in Fig. 5 are generally larger than for the fundamentals and overtones. Once again we note that this is as predicted by the perturbation theory analysis. Both VCC[2pt3], VCI[3], and VCC[3] give errors larger than 10 cm^{-1} in a few cases. For higher accuracy it is therefore desirable to include four-mode or even higher excitations. The relative accuracy is similar to that observed for the overtones, i.e., VCC[2pt3] is intermediate between VCI[3] and VCC[3].

For larger molecules, the full hierarchy of wave function methods will not be available due to their high cost. Thus, it would be of great utility if the expected quality of different results obtained from VCC[2pt3] could be estimated. Motivated by the above discussion and the perturbation theory arguments in Sec. II C, we propose to use the VCC[2pt3]

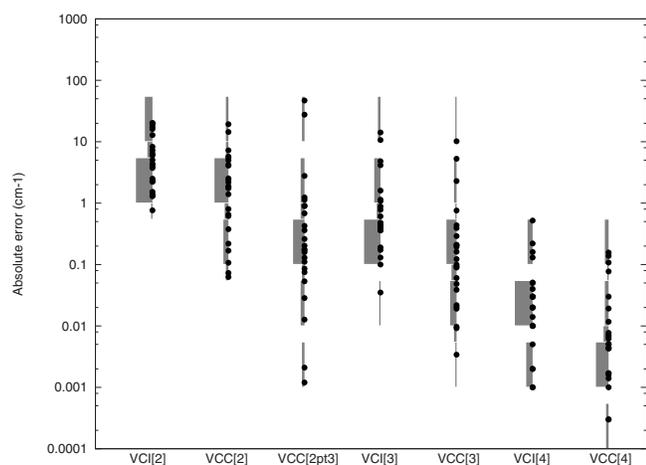


FIG. 4. Errors of different wave function methods relative to FVCI for the overtones of the tetra-atomic molecules. See Fig. 2 for details.

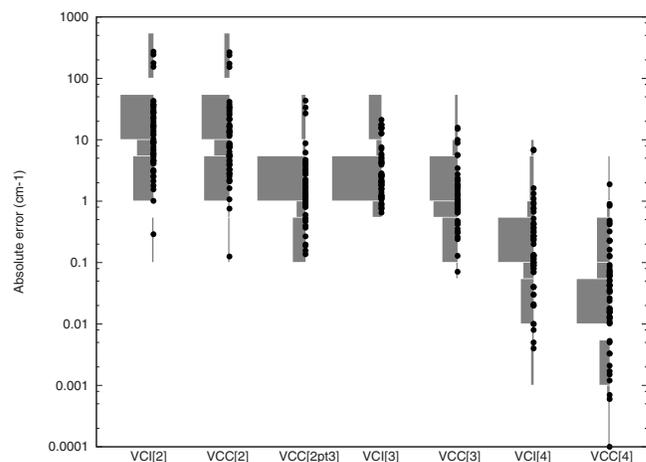


FIG. 5. Errors of different wave function methods relative to FVCI for the combination bands of the tetra-atomic molecules. See Fig. 2 for details.

excitation level weights as diagnostics for the quality of different states. Figure 6 shows the absolute error as a function of the one-mode excitation weight in the excited state wave functions. It is seen that a weight above 94% consistently results in an error below 1 cm^{-1} . Similarly, Fig. 7 shows the absolute error as a function of the combined one- and two-mode excitation weights. In this case, a weight above 98% (less than 2% three-mode excitations) results in errors below 5 cm^{-1} . It should be noted that a large weight of two- or three-mode excitations does not necessarily imply a large error but only that the accuracy cannot be expected to be high.

C. Ethylene oxide

In this subsection we report all fundamental excitation energies for ethylene oxide calculated using VCC[2pt3]. Previously, this molecule has been studied by Begue *et al.*⁵¹ using the parallel multiple window configuration interaction^{8,9} (P-VMWCI) and vibrational mean-field configuration interaction¹⁰ (VMFCI) variants of VCI in combination with a quartic force field.

A PES with up to three-mode couplings has been generated using the grid-based method implemented in

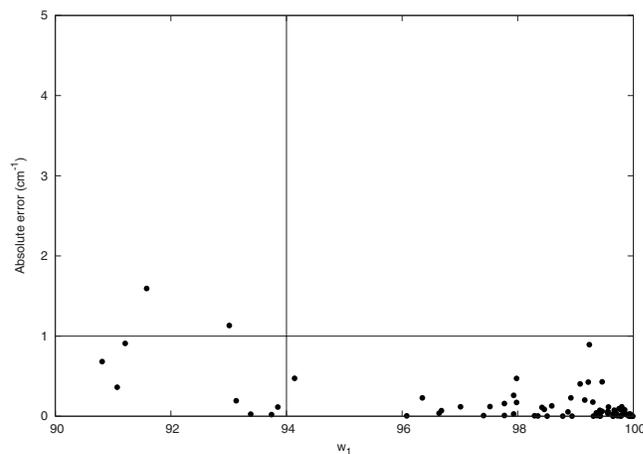


FIG. 6. The absolute error as a function of the one-mode excitation weight.

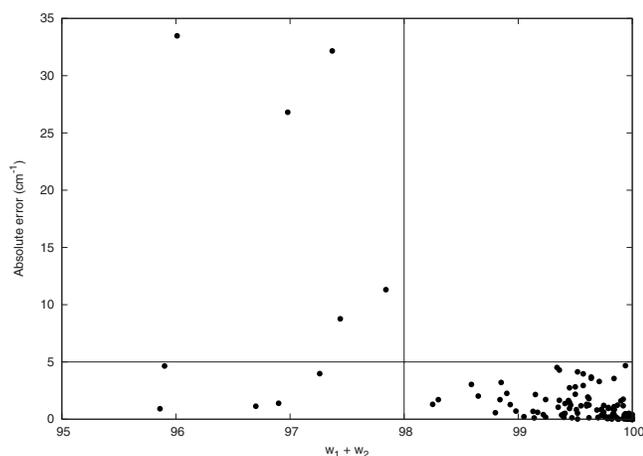


FIG. 7. The absolute error as a function of the sum of the one- and two-mode excitation weights.

MIDASCPP.²⁷ The coarse grid parameters are given as $32_1 16_{3/4} 8_{1/2}$. The coarse grid points are interpolated on a finer grid (no derivative information used) and fitted to a polynomial in the normal coordinates. The polynomial order is 12 for the one-mode part, 8 for the two-mode part, and 6 for the three-mode part. The electronic calculations have been performed using ACESII (Ref. 52) at the CCSD(T) level with cc-pVTZ basis sets and frozen cores. Thus the PES is expected to be quite accurate. As in Sec. IV B, the kinetic energy operator is simply a sum of second derivatives with respect to the normal coordinates.

The vibrational calculation is based on a primitive basis of 11 harmonic oscillator functions in the VSCF optimization. The six lowest VSCF modals have then been used in the

VCC[2pt3] calculation. The ground state was optimized in 20 iterations with each iteration requiring approximately 1.6 s on a 2.3 GHz quadcore AMD Opteron model 2356 CPU. The excited states are obtained using response theory. Each transformation with the VCC[2pt3] Jacobian requires approximately 4.1 s. Since the higher lying states are known to have resonances with other excited states, the flexible targeting strategy reported elsewhere⁵³ has been used to obtain the resonant states. This is done by converging all states found which have an overlap squared larger than 0.05 with the Hartree product representing a simple fundamental. In total, 62 iterations are needed to converge all excited states. The total CPU time for the entire vibrational calculation is 1h40m.

Table V displays the calculated fundamental energies. The aforementioned targeting finds three additional states corresponding to resonances with ν_1 and $2\nu_2$ in the VCC[2pt3] calculations. Actually, it turns out that no state is found which is dominated by ν_1 . Instead, the following three states, primarily mixed with $2\nu_{10}$ and $2\nu_2$, are obtained:

$$|\nu_1\rangle \approx 0.62\Phi_{2\nu_{10}} - 0.60\Phi_{\nu_1} + 0.46\Phi_{2\nu_2} + \dots, \quad (42)$$

$$|2\nu_{10}\rangle \approx 0.76\Phi_{2\nu_{10}} + 0.58\Phi_{\nu_1} + 0.21\Phi_{2\nu_2} + \dots, \quad (43)$$

$$|2\nu_2\rangle \approx 0.80\Phi_{2\nu_2} - 0.47\Phi_{\nu_1} + 0.17\Phi_{\nu_2+2\nu_{12}} + 0.15\Phi_{2\nu_{10}} + 0.14\Phi_{\nu_2+2\nu_{15}} + \dots. \quad (44)$$

We have chosen to denote the state in Eq. (42) as $|\nu_1\rangle$ since that state has the largest overlap with the target Hartree prod-

TABLE V. Fundamental excitation energies for ethylene oxide along with some important resonances.

		Expt. ^a	VCC[2pt3]	w(1)	w(2)	w(3)	P-VMWCI ^b
A ₁	ν_1	3005	2965.9	96.8	2.0	1.1	2922
	$2\nu_{10}$		2924.3	97.8	1.3	0.9	
	$2\nu_2$		3014.0	90.7	7.8	1.5	
	ν_2	1497	1498.2	99.1	0.7	0.1	1499
	ν_3	1270	1267.3	99.5	0.5	0.1	1271
	ν_4	1120	1129.5	98.9	0.8	0.3	1120
	ν_5	877	875.6	99.4	0.6	0.0	881
A ₂	ν_6	3050–3073 ^c	3038.7	60.9	9.5	29.6	3027
	ν_7	1043–1046 ^c	1152.8	99.2	0.6	0.2	1152
	ν_8	807–851 ^c	1023.1	99.0	0.7	0.3	1024
B ₁	ν_9	2978	2921.1	60.5	37.7	1.8	2908
	$\nu_2 + \nu_{10}$		3018.6	28.5	70.6	1.0	
	ν_{10}	1470	1470.3	99.1	0.7	0.1	1474
	ν_{11}	1151 ^d	1124.6	98.9	0.9	0.3	1130
	ν_{12}	822	819.4	98.5	1.4	0.1	820
B ₂	ν_{13}	3065	3051.6	82.5	12.2	5.3	3041
	ν_{14}	1147	1147.8	99.2	0.6	0.2	1151
	ν_{15}	808	802.0	98.8	0.9	0.3	800

^aFrom Ref. 54 (gas phase) unless otherwise indicated.

^bBegue *et al.*, Ref. 51.

^cRange of values obtained in various condensed phase experiments, see Refs. 56, 58, and 59.

^dGas phase, Ref. 57.

uct. Furthermore, the ν_9 state has a resonance with the $\nu_2 + \nu_{10}$ combination,

$$|\nu_9\rangle \approx -0.78\Phi_{\nu_9} + 0.55\Phi_{\nu_2+\nu_{10}} - 0.12\Phi_{\nu_4+\nu_{11}} + \dots, \quad (45)$$

$$|\nu_2 + \nu_{10}\rangle \approx 0.79\Phi_{\nu_2+\nu_{10}} + 0.53\Phi_{\nu_9} - 0.15\Phi_{\nu_{10}+2\nu_{12}} - 0.13\Phi_{\nu_{10}+2\nu_{15}} + \dots. \quad (46)$$

The energies for these resonant states are shown in the table as well. From the table it is seen that all energies below 1500 cm^{-1} agree very well with the experimental values except the ν_{11} state. Also, all these states have three-mode excitation weights below 0.5%. The source of error for the ν_{11} state is thus not obvious. The four CH stretches around 3000 cm^{-1} do not reproduce the experimental values as convincingly. These four states are all characterized by relatively low one-mode and large two- or three-mode weights, especially for the ν_6 , ν_9 , and ν_{13} states. The larger error is thus consistent with the diagnostics proposed in Sec. III.

Another issue is of course the quality of the experimental values. The IR spectrum of ethylene oxide appears very complex⁵⁴ with many overlapping bands. The literature contains a number of studies all reporting different results. These include gas phase⁵⁴⁻⁵⁷ as well as various condensed phase^{58,59} experiments. The experimental values for symmetry species A_1 , B_1 , and B_2 given in the table are, with exception of ν_{11} , from Ref. 54 as these appear to be the most accurate. The A_2 fundamentals are IR inactive and various condensed phase experiments have been used to obtain these as indicated in the table. For this reason the discrepancy between theory and experiment for these states is not alarming. We also note that Begue *et al.*⁵¹ have obtained results similar to ours for these cases and also for the ν_{11} state using the P-VMWCI and VMFCI methods. For ease of comparison, the P-VMWCI results are also listed in Table V.

As is evident from the above discussion, the cause of the discrepancy between experimental and theoretical values is not obvious. In a future publication this will be investigated further by applying higher quality wave function methods as well as possibly higher mode couplings in the PES. The primary purpose of this subsection is to prove that fundamental excitation energies can be obtained from high quality PESs using moderate computational effort.

V. SUMMARY AND OUTLOOK

The VCI and VCC methods have an advantage over perturbative methods due to their hierarchical construction and guaranteed convergence: There is a well defined route toward the FVCI result. However, in practice this hierarchy is limited by the rapid increase in cost of successively more accurate methods. The VCC[2pt3] method is intended as an extra step in this hierarchy. In benchmark calculations on three- and four-atomic molecules, the accuracy of VCC[2pt3] is intermediate between VCI[3] and VCC[3]. This is noteworthy since the new method only scales as M^3 while the other two methods exhibit an M^4 scaling, where M is the number of modes. VCC[2pt3] is furthermore significantly more accurate than the M^3 scaling VCC[2] and

VCI[2] methods. While the VCC[2pt3] method as any other approximate method has its limitations, we have suggested to use the weights of different excitation levels as a hint to predict when this happens. We believe that such diagnostics are important since they can help in assessing the quality of predictive calculations.

As a real world example, the fundamental excitation energies of ethylene oxide have been calculated using a high quality CCSD(T) PES. The 11 lowest fundamentals are expected to be well described according to the above diagnostics and, with one exception, agree with experiment. The remaining four CH stretches have larger three-mode weights and may therefore require higher levels of theory. Although we cannot assume the accuracy for these states to be high in VCC[2pt3], the discrepancy with experiment may, however, also be partly attributed to limitations in the PES construction and maybe even insufficient experimental data.

From a theoretical point of view, we have in this paper suggested a particular way of doing perturbational analysis in vibrational structure theory and pointed out important differences relative to electronic theory. The basic concepts should be straightforwardly transferable to more accurate treatments. While the accuracy of VCC[2pt3] is good relative to what one can reasonably expect from comparison with VCC[2] and VCC[3], higher level VCC[n] would be systematically more accurate and less sensitive to larger weights of higher mode couplings. The agreement between the theoretical analysis and the numerical results combined with the major reduction in computational scaling suggests that there is certainly perspective in pursuing development of other VCC[n pt($n+1$)] models.

In future research we will explore the hierarchy of wave function methods further. This includes especially a perturbative treatment of four-mode couplings. Also, the VCC implementation allows flexible excitation spaces. For instance, not all mode couplings need to be included at a given level. This may allow higher accuracy methods to be used without the penalty of a much higher cost. Methods for selecting only the important couplings are under development. Finally, we stress that the basic VCC method as well as the present implementation is not restricted to normal coordinates but only relies on a sum of products over one-mode operator representation of the Hamiltonian. A very interesting perspective is therefore to test the method using other coordinates than normal coordinates.

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