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Lowest order perturbative approximation to vibrational coupled cluster method in bosonic representation

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Abstract. We propose a perturbative approximation to the vibrational coupled cluster method in bosonic representation to reduce the cost of calculating the cluster matrix elements by considering only the first order of S and σ for the construction of the effective Hamiltonian $e^{\sigma}e^{-S}He^{S}e^{-\sigma}$. With the systematic analysis of the results of two molecules, H_2O and 1,1-difluoroethylene, we find that the accuracy of the transition energies with such low order approximation is comparable to the fully converged VCCM.

Keywords. Vibrational coupled cluster method; perturbation theory; effective Hamiltonian.

1. Introduction

Development of efficient and accurate quantum mechanical method for the description of anharmonic vibrations in polyatomic molecules has been a key interest of many researchers. Within the Born-Oppenheimer approximation, the electronic Schrödinger equation generates the potential energy surface for the nuclear motion in the molecule. The Watson Hamiltonian describes the molecular vibrations in a simple and efficient way

$$H = \sum_i \frac{P_i^2}{2} + V(q) + V_W + V_C. \tag{1}$$

Here, q_i are the mass-weighted normal coordinates and P_i are the conjugate momenta. The terms V_W and V_C are the Watson's mass-dependent term and Coriolis coupling term, respectively. The potential $V(q)$ is usually approximated by the quartic polynomial of the Taylor series expansion

$$V(q) = \frac{1}{2}\sum_i \omega_i^2 q_i^2 + \sum_{i \leq j \leq k} f_{ijk}q_i q_j q_k + \sum_{i \leq j \leq k \leq l} f_{ijkl}q_i q_j q_k q_l. \tag{2}$$

Here, ω_i is the harmonic frequency of ith vibrational mode, f_{ijk} and f_{ijkl} are the third and fourth derivatives of the electronic energy with respect to the mass-weighted normal coordinates at equilibrium geometry.

The vibrational Hamiltonian with such quartic potential is a many-body Hamiltonian, and thus, the exact analytical solution of corresponding Schrödinger equation is not possible. Several approximate methods have been developed to solve the vibrational Schrödinger equation based on both variation principle and perturbation theory. The second order vibrational perturbation theory (VPT2[1–3]) has been developed, where the Hamiltonian with only quadratic potential is taken as the zeroth order Hamiltonian and the cubic and quartic terms are treated as perturbations. Although, such approach has been used extensively by many authors with successful interpretations of infrared spectra of numerous molecules, the failure of the VPT2 is well-known when the one encounters vibrational resonances like Fermi resonance. The vibrational self-consistent field (VSCF) theory[4–6] and its generalizations to multiconfigurational reference functions[7] are developed and used extensively to describe the experimental IR spectra of molecules with large number of vibrational modes. The vibrational configuration interaction (VCI)[8–10] method is also

developed and applied to small molecules. Here, one constructs and diagonalizes the vibrational Hamiltonian matrix in a configuration space generated by VSCF virtual orbitals, or distributed Gaussian functions. The VCI method is in principle exact. However, the dimension of the Hamiltonian matrix increases exponentially with the vibrational degrees of freedom, making it inapplicable for even medium size molecules.

The coupled cluster method[11–20] has been emerged as the most successful method for describing the quantum many-body problems, especially for electronic structures of atoms and molecules. The formulation of the coupled cluster method is inherently non-variational and non-perturbative, where the exact ground state wave function is parametrized with an exponential wave operator operating on a reference wave-function, $|0\rangle$

$$|\Psi_g\rangle = U|0\rangle, \tag{3}$$

with either

$$U = e^S \tag{4a}$$

or, $$U = e^S e^{-\sigma} \tag{4b}$$

Here, S, and σ are the cluster operators, consist of connected one-body, two-body up to n-body excitation and de-excitation operators, respectively. The working equations to determine the cluster matrix elements are given by

$$\langle e|U^{-1}HU|0\rangle = 0, \tag{5}$$

where, $|e\rangle$ are the excited states obtained by the excitation from the reference function $|0\rangle$. By virtue of the exponential wave operator, one can access the unlinked higher excited state functions, and as a result the energy and wave function are highly accurate even with a low order approximation of the cluster operator.

Two different representations have been developed to formulate the vibrational coupled cluster method (VCCM).[21–34] The fundamental difference between these formulations is the choice of the reference function and definition of excitation/de-excitation operators. In one representation, a set of orthonormal basis function is assigned to each vibrational degree of freedom. The VSCF calculation is carried out using these basis set and subsequently, the VSCF ground state wave function is used as the vacuum. The creation and annihilation operators are defined in a manner similar to the coupled cluster theory of Fermionic systems. This approach is known as the basis

set representation of VCCM.[21–24] The accuracy of the results with this method depends on the size and quality of single mode basis functions along with the truncation of the cluster operator. This approach was used by Latha and Prasad to describe the intramolecular vibrational relaxation dynamics,[35] and Christiansen and coworkers[21–24] to compute the IR spectra. The other representation is known as the bosonic representation, developed and implemented by Prasad and co-worker,[25–32,34] and, more recently by Hirata.[33] The vacuum here is an optimized multi-dimensional Gaussian product function and the cluster operator is constructed with simple harmonic oscillator (HO ladder operators that are defined with respect to the optimized vacuum state. In our earlier works, we used the bosonic representation to formulate the VCCM to calculate the vibrational excitation energies,[26] infra-red[27] and Raman intensities.[34]

The bosonic representation of VCCM offers several advantages over the basis set representation. Unlike the basis set representation, it is invariant to any arbitrary rotations and displacements in normal coordinate space. Secondly, since the excitation operators are the HO ladder operators, once can access, in principle, the full Hilbert space of the HO eigenfunctions. However, depending on the truncation of the cluster operator, the number of independent co-efficients in equation 5 is finite. In a previous study,[26,27] we found that the convergence is quite rapid, essentially by S_4, the ground state energy is converged.

Two different approaches have been developed to describe the excited state within the VCCM formulation in bosonic representation. One is the vibrational multi-reference coupled cluster method based on effective Hamiltonian formalism.[28] The second approach is the coupled cluster linear response theory (CCLRT), variously known as the equation of motion coupled cluster (EOMCC) method.[25,27,36] In this approach, one constructs a similarity transformed effective Hamiltonian

$$H_{eff} = U^{-1}HU, \tag{6}$$

in the space of zeroth-order excited states and diagonalizes it to get the excitation energies directly.

The equations to determine the cluster matrix elements (equation 5) are coupled non-linear equations, and they are solved iteratively in a self-consistent manner. The solution of these equations is one of the major computational bottleneck. When a four-body approximation of cluster cluster operator is used, the computational cost scales up to N^6 (here, N is the number of vibrational degrees of freedom) at each

iteration. Using the diagrammatic arguments it is realized that the coupled cluster wave function and energy can be decomposed in terms of infinite order of perturbation theory terms of selected excitation operators. In this work, we explore the possibility of using a low order perturbative approximation to the cluster operators for the VCCM. In other words, the effective Hamiltonian in equation 6 for the CCLRT is constructed using only the first order estimate of two-body, three-body and four-body S and σ operators. The motivation for doing so comes from two sources. The computation of the vibrational spectra consists of three steps. In the first step, the coupled nonlinear equations of the VCCM are to be solved. In the second step, H_{eff} has to be constructed. Finally, the H_{eff} has to be diagonalized in the manifold of excited states. By invoking the perturbative expansion, the computational burden of the first step reduces from iterative N^6 to a non-iterative N^4 scaling of CPU time. For a large molecular system, this itself is a desirable feature and hence worth exploring. The second source of motivation comes from a desire to understand the relative importance of changes in correlation and relaxation during the excitation process. Approximation to the cluster operator affect the computation of the changes in the ground state correlation energy, while the excitation manifold controls the accuracy of the relaxation effects. Thus, a perturbative approximation can give an insight in to the relative importance of these two quantities. We note that, in the context of electronic structure theory, Nooijen and Snijders,[37] Stanton and Gauss,[38] Pal and co-workers,[39] Bartlett and co-workers[40] have explored the possibility of expanding the cluster operator, S, in a perturbative manner. Numerical studies indicate that such perturbative truncation of S, within the CCLRT framework for the excited sates, gives satisfactory results, even when the perturbative expansion is kept as low as the first order for S. Several studies attempted to incorporate the effects of higher rank cluster operators within in the mathematical framework of lower rank approximation (such as the influence of T_3 operator with in the CCSD framework) by using perturbative approximations.[41–43] Our own goal is different. We are not looking to simulate the influence of higher rank cluster operator. We seek to understand the importance of different terms in the open part of H_{eff} on the approximate spectrum from a perturbation theory perspective. To that end, as a first step, we approximate the cluster matrix elements by their first order perturbative estimates.

The goal of the present study is to test the accuracy of the vibrational energy levels using similar low order

expansions to the cluster operator that is used to generate H_{eff}. The theoretical framework for this is presented in Section 2. Section 3 contains the computational results on two molecules, water and 1,1-difluoroethylene. The results indicates that perturbative expansion of S, correct up to first order, gives small errors compared to the full VCCM approach, about 5–10 cm^{-1}, while the computational cost is significantly reduced.

2. Theory

2.1 *Coupled Cluster Method in bosonic representation*

In the first step of the VCCM formalism, we invoke the effective harmonic oscillator (EHO) approximation,[25,44] to get an optimized reference state for the vibrational ground state. In EHO method, a product of N Gaussian functions

$$|0\rangle = exp\left(-\sum_i \omega_i(q_i - q_i^0)^2/2\right), \qquad (7)$$

is variationally optimized with respect to ω_i and q_i^0. Here, ω_i and q_i^0 are the harmonic frequency of the normal mode and origin of the normal coordinate i, respectively. The harmonic oscillator creation and annihilation operators are then defined with respect to this optimized state as

$$a_i = \sqrt{\frac{\omega_i}{2}}\left(q_i - q_i^0 + \frac{1}{\omega_i}\frac{d}{dq_i}\right) \qquad (8)$$

$$a_i^\dagger = \sqrt{\frac{\omega_i}{2}}\left(q_i - q_i^0 - \frac{1}{\omega_i}\frac{d}{dq_i}\right) \qquad (9)$$

The optimized function in equation 7 is, by definition, a vacuum state for the annihilation operator a_i as it satisfy the killer condition

$$a_i|0\rangle = 0. \qquad (10)$$

Unlike the traditional single reference coupled cluster formalism, where only the excitation operators are use to define the wave operator, we used both excitation and de-excitation cluster operators to parametrize the ground state wave function in the VCCM formalism in the spirit of extended coupled cluster method (ECCM) of Arponen.[45–47] However, we do not follow Arponen's bi-variational approach to determine the cluster matrix elements, as discussed below. The use of ECCM ansatz offers several advantages over the

traditional coupled cluster formalism. First, the ground state bra vector is also exponentially parametrized along with the ground state ket vector in the ECCM approach. The exponentially parametrized bra vector for the ground state gives a balanced description for the transition matrix elements.[27,32,36] Secondly, the excitation energies are obtained by the diagonalization of similarity transformed effective Hamiltonian within the CCLRT framework. The similarity transformed effective Hamiltonian is manifestly non-hermitian. Diagonalization of non-hermitian effective Hamiltonian occasionally generates spurious complex eigenvalues, when a low-order truncation of cluster operator S is used for the construction of H_{eff} matrix. In the ECCM, the effective Hamiltonian is now a double-similarity transformed Hamiltonian, with a de-excitation operator used for the second similarity transformation. Since the de-excitation operators are the adjoint of the excitation operators, the second similarity transformation eliminates substantial parts of the non-hermitian residue in the effective Hamiltonian. The reduction of the non-hermicity due to the second similarity transformation gives a better description for the excited states, eliminating some of the spurious complex eigenvalues.[26]

The ground state wave function for VCCM is thus written as,

$$|\Psi_g\rangle = e^S e^{-\sigma}|0\rangle. \tag{11}$$

Here, the cluster operators S and σ are consisting of one quanta, two quanta, etc., excitation and de-excitations operators, respectively.

$$S = \sum_i s_i a_i^\dagger + \sum_{i \leq j} s_{ij} a_i^\dagger a_j^\dagger + \sum_{i \leq j \leq k} s_{ijk} a_i^\dagger a_j^\dagger a_k^\dagger + \cdots$$
$$\sigma = \sum_i \sigma_i a_i + \sum_{i \leq j} \sigma_{ij} a_i a_j + \sum_{i \leq j \leq k} \sigma_{ijk} a_i a_j a_k + \cdots \tag{12}$$

The working equations for cluster operator S, ground state energy E_g, and cluster operator σ are obtained from,

$$\langle e|e^{-S}He^S|0\rangle = 0, \tag{13}$$

$$E_g = \langle 0|e^{-S}He^S|0\rangle, \tag{14}$$

$$\langle 0|e^\sigma e^{-S}He^S e^{-\sigma}|e\rangle = 0, \tag{15}$$

respectively. Note that, the original formulation of ECCM by Arponen invokes a variational solution for the cluster matrix elements σ.[45–47] However, we use the method of moment approach of equation 15 in the spirit of conventional coupled cluster solutions, as

suggested by Prasad,[48] and implemented in several of our earlier studies.[26–31,34] Within this framework, the equations for S are decoupled from the equations for σ. Such decoupling can be shown to be exact in the exact limit of both S and σ using Lie algebraic decoupling theory,[48] and by looking at the coupled cluster method as a similarity transformed effective Hamiltonian theory and relating the eigenfunctions of the Hamiltonian to the left and right eigenfunctions of the transformed Hamiltonian. Since these two vectors are constructed separately, the left eigenvector (represented by $e^{-\sigma}$) does not affect the construction of the right eigenvector (e^S by construction). However, it carries the burden of normalization of the coupled cluster ansatz for the ket state.[36] Hence, σ depends on S, but not vice versa. Both equations 13 and 15 are sets of coupled non-linear equations that are solved consecutively in a self-consistent manner to get converged sets of S and σ matrix elements respectively. The ground state energy is independent of σ matrix elements. Thus, the second similarity transformation keeps the ground state unaltered, but affects the description of the excited states. The similarity transformed Hamiltonians of equations 13 and 15 are written in terms of Hausdorff expansion,

$$H_{eff}^1 = e^{-S}He^S = H + [H,S] + \frac{1}{2!}[[H,S],S]$$
$$+ \frac{1}{3!}[[[H,S],S],S] + \cdots, \tag{16}$$

and,

$$H_{eff}^2 = e^\sigma H_{eff}^1 e^{-\sigma} = H_{eff}^1 + [\sigma, H_{eff}^1] + \frac{1}{2!}[\sigma, [\sigma, H_{eff}^1]]$$
$$+ \frac{1}{3!}[\sigma, [\sigma, [\sigma, H_{eff}^1]]] + \cdots \tag{17}$$

The commutator structure of the above expressions ensure that diagrammatically only the connected terms will survive. Since the Hamiltonian has a maximum four-body operator, the series in equation 16 terminates after fourth commutator term, irrespective of the truncation used for the S cluster operator. Note that the operators in the effective Hamiltonian H_{eff}^1 are many more and the number depends on the truncation of cluster operator S. For example, for a four-body truncation of S, the maximum number of operators in H_{eff}^1 is twelve. Similar situation holds for the double-similarity transformed effective Hamiltonian H_{eff}^2. In the implementation of VCCM, both H_{eff}^1 and H_{eff}^2 are approximated with maximum of four boson operators.

The excited states are described using CCLRT. Here, the excited state wave functions are obtained by the action of a linear operator on the ground state CCM wave function

$$\Psi_e = X_e U |0\rangle. \tag{18}$$

Generally, X_e requires both excitations and de-excitation operators to define it both from operator completeness requirements,[49–51] and the physical requirement to describe the population changes in various zeroth order states from ground state to the excited state. However, in the present case, it is not necessary.

Equation 18 can be rewritten as

$$|\Psi_e\rangle = UU^{-1}X_e U|0\rangle = UX_e^{eff}|0\rangle. \tag{19}$$

The operator X_e^{eff} now acts on the vacuum, and hence requires excitation operators only. The general expression for the X_e^{eff} can be written as,

$$X_e^{eff} = \sum_i X_{e,i}^{eff} a_i^\dagger + \sum_{i \le j} X_{e,ij}^{eff} a_i^\dagger a_j^\dagger + \sum_{i \le j \le k} X_{e,ijk}^{eff} a_i^\dagger a_j^\dagger a_k^\dagger + \cdots \tag{20}$$

The working equation for the excitation energies is,

$$[H_{eff}^2, X_e^{eff}] = \Delta E_e X_e^{eff}. \tag{21}$$

If equations 13, 14 and 15 are not exactly satistfied, X_e^{eff} can have a constant component as well. However, we ignore it in the present study, since it is expected to be quite small. This statement applies to the conventional coupled cluster equation of motion based approaches as well, since most of them truncate the cluster operator at some low order. The solutions of equation 21 are obtained directly by diagonalization of effective Hamiltonian H_{eff}^2 in the configuration space constructed by the manifold of excitation operator X_e^{eff}. Since the similarity transformations leave the eigen spectrum of an operator unchanged, the eigenvalues of H_{eff}^2 are the same as of the original Hamiltonian. It may be noted that by virtue of equations 13 and 15, the matrix elements of H_{eff}^2 between the vacuum state and the zeroth order excited states are zero. We restrict the excited state space to all states with at most four quanta excitations from all modes.

2.2 *Lowest order perturbative approximation to VCCM*

As mentioned in the introduction, the solutions of the nonlinear equations in equations 13 and 15 are among

major computational bottlenecks for the VCCM. For a four boson approximation of the cluster operator S, the most expensive contribution in equation 13 comes from the quadratic term $[[H, S_4], S_4]$. Since in the bosonic representation the number of vibrational modes (N) plays the role of basis set in the computation of the cluster matrix elements, the calculation of this term scales up to N^6 for each iteration of the solution of equation 13 (considering the proper intermediate storage is done during the computations). Similar situation arises for the determination of the σ matrix elements with equation 15. We use perturbative approximations to reduce the expensive computations of the cluster matrix elements.

There exists a fundamental relation between the coupled-cluster method and perturbation theory. Using this connection, one can construct any finite-order perturbative corrections to energy and effective Hamiltonian through iterations of the coupled cluster equations. To reduce the computational cost of the evaualion of the cluster matrix elements, we approximate both the cluster operators S and σ only up to first order. Since the reference function in our formulation is a variationally optimized Hartree product function, there is no contribution of S_1 operator to the first order. Thus, in the first order approximation of the cluster operator, only S_2, S_3 and S_4 terms will contribute. Essentially, one has to evaluate only the diagonal part of the linear terms $[H, S_2]$, $[H, S_3]$ and $[H, S_4]$. The computational scaling to evaluate these terms are N^2, N^3 and N^4, respectively. Thus, the computational cost to calculate the cluster matrix elements with the present approximation scales as non-iterative N^4, instead of iterative N^6 in the full VCCM with four boson S. Moreover, such approximation also eliminates the effort to compute the cluster matrix elements σ. The excitation operator S and de-excitation operator σ are equal up to first order in perturbation.

In the lowest order approximation, the H_{eff}^1 in equation 16 is constructed with only the first order of the cluster operator S,

$$H_{eff}^1 = H + [H, S^{(1)}] + \frac{1}{2!}[[H, S^{(1)}], S^{(1)}]$$
$$+ \frac{1}{3!}[[[H, S^{(1)}], S^{(1)}], S^{(1)}] + \ldots \tag{22}$$

Following our previous implementation, we consider H_{eff}^1 has at most four boson operator in it. The double similarity transformation effective Hamiltonian H_{eff}^2 is then constructed using only the first order σ

$$H_{eff}^2 = e^\sigma H_{eff}^1 e^{-\sigma} = H_{eff}^1 + [\sigma^{(1)}, H_{eff}^1]$$
$$+ \frac{1}{2!}[\sigma^{(1)}, [\sigma^{(1)}, H_{eff}^1]] + \cdots$$

The H_{eff}^2 is also approximated with a maximum of four boson operators.

Thus, the H_{eff}^2 is correct up to first order with respect to both S and σ due to the linear terms of S and σ in the above equation. However, the presence of the non-linear terms leads to the partial infinite summation of the lower order corrections. We note that the construction of the effective Hamiltonian H_{eff}^1 and H_{eff}^2 scales as N^6.

3. Results and Discussion

We implemented the lowest order perturbative approximation to the VCCM as described above. The vibrational transition energies of water, and 1,1-difluoroethylene $(1,1\text{-}C_2F_2H_2)$ molecule are calculated using the proposed approximation (VCCM(pt)). The numerical performance with such low order VCCM are analyzed in comparison to the full VCCM results.

3.1 H_2O

Our first case study is on water molecule. We compared the transition energies from the lowest order perturbative VCCM method (VCCM(pt)) with full VCCM and converged full VCI results (FVCI) in Table 1. The FVCI calculations were carried out using 8 harmonic oscillator basis (HO) functions for the stretching modes and 16 HO basis functions for the bending mode. The convergence of the VCI transition energies were found with this basis set. The quartic potential energy surface was calculated using Gaussian09 software suit,[52] using MP2 method with cc-pVTZ basis sets.

We find that the VCCM(pt) approximation gives results comparable to the full VCCM. For the fundamentals and two quanta excitations, the deviations between these two methods are usually less than 3 cm^{-1}. The maximum deviation among these excitations is only about 5 cm^{-1} for 2_2 state. The VCCM results are close to the FVCI values, except for the transitions 1_2 and $1_1 3_1$. The difference between the FVCI and full VCCM results for these two transitions are 11 cm^{-1} and 24 cm^{-1}, respectively. Despite of such discrepancy between the VCCM and FVCI results, the perturbative approximation does not bring any substantial changes for the VCCM transition

Table 1. Transition energies (in cm^{-1}) of H_2O.

State	FVCI	VCCM(full)	VCCM(pt)
2_1	1566	1566	1568
2_2	3090	3094	3100
1_1	3675	3674	3672
3_1	3755	3752	3750
2_3	4556	4602	4611
$1_1 2_1$	5198	5199	5200
$2_1 3_1$	5252	5252	5253
2_4	6238	6244	6252
$1_1 2_2$	6694	6710	6714
$2_2 3_1$	6717	6742	6746
1_2	7327	7316	7313
$1_1 3_1$	7397	7373	7372
3_2	7486	7479	7474
$1_2 2_1$	8777	8808	8807
$1_1 2_1 3_1$	8814	8857	8858
$2_1 3_2$	8905	8944	8943
1_3	10992	11029	11022
$1_2 3_1$	11075	11135	11129
$1_1 3_2$	11155	11462	11447
3_3	11210	11257	11247

energies of these states. Even for the three quanta excitations, where the differences between the FVCI and converged VCCM values are substantially large, the VCCM(pt) results are close to the converged VCCM results. For instance, the full VCCM transition energy for higher excited state $1_1 3_2$ differ by 307 cm^{-1} from the FVCI value. The difference between the VCCM(pt) and full VCCM values for this transition is only 15 cm^{-1}. The standard deviation of VCCM(pt) results from the full VCCM values for all the states reported here is only 6 cm^{-1}.

We note that the VCCM(pt) transition energies are higher than the full VCCM transition energies for most of the lower lying transitions. Thus, the perturbative approximation overestimates the VCCM for the transition energies. We note that a correlated transition energy can be decomposed in to three components

$$\Delta E = \Delta E^0 + \epsilon_{ex} + \epsilon_g^{corr} \quad (23)$$

Here, ΔE^0 is the zeroth order transition energy obtained from the EHO approximation, ϵ_{ex} is the correlation effect for the excited states, and ϵ_g^{corr} is the ground state correlation correction. The excited state correlation energy, ϵ_{ex}, will have two parts

$$\epsilon_{ex} = \epsilon_{mix} + \epsilon_{rel}. \quad (24)$$

The ϵ_{mix} arises due to mixing among the zeroth order excited states, and ϵ_{rel} is the relaxation effect. It can be shown that the ϵ_{mix} energy partially cancels out the

ground state correlation energy ϵ_g^{corr} for the fundamentals. Thus, the transition energy is dominated by the relaxation term ϵ_{rel}. The over estimation of the VCCM results with the lowest order perturbative approximations indicates that the relaxation effect is underestimated by this approximation.

3.2 *1,1-Difluoroethylene*

Our second case study is $1,1$-$C_2F_2H_2$ molecule. The quartic PES for this molecule was calculated using B3LYP density functional method along with 6-311G(2d,2p) basis set. We present the VCCM(pt), full VCCM along with the zeroth order Hartree energies for the fundamental transitions in Table 2. The results are compared with the experimental values.[53]

Like H_2O molecule, here also, the VCCM(pt) results are comparable with the full VCCM results. For the most of the states, the difference between these two methods are less than 10 cm^{-1}. The largest difference in the transition energies is found to be only 20 cm^{-1} for the fundamental transitions 3_1. The standard deviations between these two methods is about 10 cm^{-1} for all the fundamental.

Both the VCCM and VCCM(pt) give results close to the experimental results. The standard deviations for the VCCM and VCCM(pt) results with respect to the experimental values are 20 cm^{-1} and 19 cm^{-1}, respectively.

For $1,1$-$C_2F_2H_2$ molecule also, we find that the VCCM(pt) overestimates the transition energy compared to full VCCM, except for the 3_1 and 9_1 transitions. The relaxation of frequencies causes the changes in the transition energies (other than Fermi coupling). These relaxation energies have the most significant contributions to the transition energies. The VCCM(pt) underestimates these relaxation energies.

Both the 3_1 and 9_1 states mix strongly with several other states. The transition energies for these strongly coupled states along with their weight of mixing in the VCCM descriptions are presented in Table 3. We find that the perturbative approximation affects the mixing of states significantly. Consequently, the transition energies deviate from the full VCCM. For example, 3_1 fundamental mixes strongly with two quanta states 6_2, $11_1 12_1$, and $7_1 8_1$. In the full VCCM description, the fundamental 3_1 has 0.49 weight of zeroth order 3_1 state and 0.27 weight of zeroth order combination state $7_1 8_1$. In the perturbative approximation VCCM(pt), the weight of zeroth order 3_1 state decreases to 0.44. Here, the second major contribution comes from the zeroth order $11_1 12_1$ state (weight equal to 0.29). The transition energy for 3_1 state is found to be 1357 cm^{-1} with full VCCM and 1337 cm^{-1} with VCCM(pt) approximation. Similarly, in the full VCCM description of the 6_2 state, the zeroth order 3_1 state has weight 0.25, which becomes only 0.15 in the VCCM(pt) method. The weight of zeroth order 6_2 state increases from 0.47 for the full VCCM to 0.61 for the VCCM(pt) approximation for this 6_2 transition. We find an increase of 73 cm^{-1} in the transition energy for this 6_2 transition from the full VCCM to VCCM(pt) method.

The perturbative approximation of the VCCM, i.e. VCCM(pt) estimates the state mixing according to the perturbative analysis. Lower the gap in the zeroth

Table 2. Transition energies (in cm^{-1}) of $F_2C_2H_2$ molecule.

State	Hartree energy	VCCM(full)	VCCM(pt)	Exp[53]
1_1	3107	3016	3025	3058
2_1	1757	1729	1734	1728
3_1	1400	1357	1337	1359
4_1	933	923	923	926
5_1	546	544	544	550
6_1	784	682	696	Inactive
7_1	881	782	795	802
8_1	633	625	626	609
9_1	3196	3154	3142	3176
10_1	1302	1279	1281	1301
11_1	972	930	936	954
12_1	462	428	432	437

Table 3. A comparison of some strongly coupled state of $F_2C_2H_2$ with VCCM approaches. (Transition energies are in cm^{-1}).

States	ν^{VCCM}	State description	$\nu^{VCCM(pt)}$	State description	$\nu^{Hartree}$
3_1	1357	$0.49 * 3_1 + 0.27 * 7_1 8_1$	1337	$0.44 * 3_1 + 0.29 * 11_1 12_1$	1400
6_2	1309	$0.47 * 6_2 + 0.25 * 3_1$	1382	$0.61 * 6_2 - 0.15 * 3_1$	1568
$7_1 8_1$	1427	$0.69 * 7_1 8_1 - 0.22 * 3_1$	1436	$0.74 * 7_1 8_1 - 0.17 * 3_1$	1514
$11_1 12_1$	1351	$0.68 * 11_1 12_1 + 0.27 * 6_2$	1366	$0.63 * 11_1 12_1 + 0.20 * 3_1$	1434
9_1	3154	$0.24 * 9_1 + 0.30 * 6_1 7_1 11_1 12_1$	3142	$0.37 * 9_1 - 0.32 * 10_1 11_2$	3196
$2_1 6_1 7_1$	3157	$0.63 * 2_1 4_1 7_1 - 0.10 * 9_1$	3192	$0.76 * 2_1 6_1 7_1 + 0.04 * 6_1 7_2 8_1$	3240

order energy levels, greater is the coefficient. Again, we consider the example of mixing of 6_2, $11_1 12_1$, and $7_1 8_1$ states with 3_1 fundamental. The zeroth order Hartree energy difference between 3_1 state and $11_1 12_1$ state is only 34 cm^{-1}. Such small difference in Hartree energy leads to strong mixing of these two states in the VCCM(pt) description. The 3_1 state has 0.29 weight of zeroth order $11_1 12_1$ state and the $11_1 12_1$ state has 0.20 weight of zeroth order 3_1 state. The differences in the Hartree energy of $7_1 8_1$ and 6_2 states from the Hartree energy of 3_1 are 114 and 168 cm^{-1}, respectively. The weight of zeroth order 3_1 state in the $7_1 8_1$ and 6_2 states are 0.17 and 0.15, respectively.

The transition energies for the two quanta states with the VCCM methods are presented in Table S1 of the supplementary materials. Trend of the transition energies with the VCCM(pt) approximation is similar to the fundamentals for the two quanta excitations, where the mixing of states is not very significant. The VCCM(pt) values are higher than the full VCCM results for almost all the states. Thus, for the two quanta excitations also, the perturbative approximation underestimates the relaxation corrections. However, the deviations between the VCCM and VCCM(pt) transition energies are not very large. In about forty two quanta excited states, the transition energy difference between the VCCM(pt) and full VCCM results are less than 10 cm^{-1}. The standard deviation between these two methods is about 14 cm^{-1} for two quanta states.

4. Conclusions

In this work, we implemented the lowest order perturbative approximations to the VCCM in bosonic representation, by considering only the first order of both the excitation (S) and de-excitation (σ) cluster matrix operators for the construction of the effective Hamiltonian. We made a systematic comparison between the converged VCCM and perturbative approximation with the example of two molecules, H_2O and $1, 1\text{-}C_2F_2H_2$. We find that such low order perturbative approximation to the VCCM gives transition energies close the full VCCM method.

The VCCM(pt) usually overestimates the transition energies compared to the full VCCM. The major contribution to the transition energy arises from the relaxation of the excitations, due to the cancellations of excited state correlation and ground state correlation energies. The overestimated transition energies in the perturbative approximation implies that such lowest order perturbation underestimates the

relaxation effect. However, such underestimation of the relaxation effects does not affect the accuracy of the transition energies significantly.

The present lowest order perturbative approximation to the cluster operator reduces the computational cost significanly, as the scaling of computation of the S matrix elements reduces from iterative N^6 to non-iterative N^4. The computation of σ matrix elements are avoided by equating them with the S matrix elements, since the S and σ operators are identical up to first order.

The mixing of states differs significantly with the perturbative approximation compared to the full VCCM. As a results, we get large deviations for the states which coupled strongly with one or more states. The VCCM(pt) transition energies for such strongly coupled states are found to be even smaller than the full VCCM results. The coefficients of mixing of states in the perturbative approximation are determined by the perturbation analysis. Smaller the difference in the zeroth order Hartree energies, greater is the mixing weight.

Overall, we find good accuracy for the transition energies with the VCCM(pt) approach. The results are comparable with the FVCI results or the experimental results. Such approximations will reduce the computational cost to calculate the converged cluster matrix elements significantly without compromising much of the resultant accuracy.

Supplementary Information (SI)

The transition energies for the two quanta states of 1,1-diflouroethylene with VCCM calculations are available at www.ias.ac.in/chemsci.

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