

Calculation of Dipole Transition Matrix Elements and Expectation Values by Vibrational Coupled Cluster Method

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Abstract: An effective operator approach based on the coupled cluster method is described and applied to calculate vibrational expectation values and absolute transition matrix elements. Coupled cluster linear response theory (CCLRT) is used to calculate excited states. The convergence pattern of these properties with the rank of the excitation operator is studied. The method is applied to a water molecule. Arponen-type double similarity transformation in extended coupled cluster (ECCM) framework is also used to generate an effective operator, and the convergence pattern of these properties is compared to the normal coupled cluster (NCCM) approach. It is found that the coupled cluster method provides an accurate description of these quantities for low lying vibrational excited states. The ECCM provides a significant improvement for the calculation of the transition matrix elements.

1. Introduction

An accurate description of anharmonic molecular vibration is often necessary to account for the experimental results obtained from modern high resolution techniques of molecular spectroscopy. Several methods have been discussed in the literature over the past three decades. The vibrational self-consistence method (VSCF)^{1–5} and its generalizations to multiconfigurational reference functions (VMCSCF)^{6–10} has been developed and used extensively by several authors. The vibrational configuration interaction method (VCI)^{11–15} has also been developed and used for small molecules. The dimension of VCI matrix increases exponentially with the number of degrees of freedom. This makes VCI difficult to apply for large systems. Vibrational Moller–Plesset perturbation theory (VMP)^{16–18} has been used for the calculation of the vibrational spectra of many systems. Canonical van Vleck perturbation theory^{19–23} has been developed and applied extensively.

Recently, some attempts have been made to describe anharmonic molecular vibrations by the coupled-cluster

method (CCM).^{24–36} The CCM has been established as one of the most accurate techniques for the description of the many body systems.^{37–47} In this method, the ground-state wave function of a many body system is decomposed into a reference function and an exponential wave operator. The exact ground-state function in CCM is

$$|\psi_g\rangle = \exp(S)|\phi_{\text{ref}}\rangle \quad (1)$$

where $|\phi_{\text{ref}}\rangle$ is the reference wave function. The cluster operator S consists of connected singles, doubles, up to n -tuple excitation operators. The cluster matrix elements are determined from the equation

$$\langle\phi_e|e^{-S}He^S|\phi_{\text{ref}}\rangle = 0 \quad (2)$$

where $|\phi_e\rangle$ are the excited states. There are two advantages in the coupled cluster approach. First, the method is size consistent by virtue of the exponential ansatz. Second, again due to the exponential structure of the wave operator, the resulting wave function and energy are highly accurate in an approximate calculation even with a low order truncation of the cluster operator.

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There are two approaches to construct the Fock space required for the coupled cluster calculations for molecular vibrations. The first method is the basis set representation in which the Fock space is constructed as a union of all k -particle Hilbert spaces constructed as the tensor products of basis functions of the appropriate degrees of freedom. This is the route followed mainly by Christiansen and co-workers.^{24–30} The second approach is to construct the Fock space using harmonic oscillator (HO) ladder operators acting on an appropriate vacuum state.^{31–36} In this representation, the cluster operators are given by

$$S = \sum S_{n_1 n_2 \dots} a_1^{\dagger n_1} a_1^{\dagger n_2} \dots \quad (3)$$

The vacuum state is a variationally optimized multidimensional Gaussian state, and a_i^\dagger/a_i are the usual creation/annihilation operators of the harmonic oscillator algebra defined with respect to the vacuum state. We use this representation. Because the ladder a_i^\dagger/a_i satisfy the canonical commutation relations, we term this as the bosonic representation of the CCM.

There are two routes for calculation of excited-state energies in the coupled cluster approach. In the first approach, variously called the coupled cluster linear response theory (CCLRT) or the coupled cluster equation of motion method (EOMCC),^{48–51} the excited-state energies are obtained as the eigenvalues of the similarity transformed effective Hamiltonian H_{eff}^N

$$H_{\text{eff}}^N = e^{-S} H e^S \quad (4)$$

The second approach uses a multireference coupled cluster theory tailored to describe the excited states directly.^{52–56} All of the vibrational applications to date have used the CCLRT to obtain the excited-state energies.^{28,30,34–36} In an earlier work, we had studied the convergence trends of the CCM in the bosonic representation³⁶ in terms of the rank (the maximum number of creation operators used to define the truncation in eq 3) of the cluster operator.

In this work, we turn our attention to the reliability of the CCM approach for the calculation of properties other than energies. Specifically, we study the convergence pattern of the CCM approach to the calculation of expectation values and transition matrix elements of the dipole moment operator. This is the first implementation of the coupled cluster method to study the expectation values and transition matrix elements in the context of molecular vibration. To the extent of our knowledge, no calculation on transition matrix elements is reported in the literature using the coupled cluster method even in electronic structure theory. The convergence pattern of the expectation values and the transition matrix elements are studied as a function of the rank of the excitation operator.

The similarity transformation of the Hamiltonian (eq 4) lies at the heart of the CCM. Consequently, the H_{eff} of eq 4 is not manifestly Hermitian. While this poses no problem in an exact calculation, in an approximate calculation where the basis set is truncated, the effective Hamiltonian can, and does on occasion, develop complex eigenvalues. One possibility of eliminating such complex eigenvalues is to use a unitary wave operator. The resulting equations, however,

generate an infinite series on the left-hand side of eq 2 and thus are subject to uncontrolled approximation.

An approximate way of treating such complex eigenvalues is to use a second similarity transformation inspired by the work of Arponen.^{57–59} The ground-state wave function is parametrized as

$$|\psi_g\rangle = e^S e^{-\sigma} |\phi_{\text{ref}}\rangle \quad (5)$$

Here, the generator of the second similarity transformation σ consists of the de-excitation operator alone. The effective Hamiltonian, H_{eff} , is now hermitized up to first order. We noted in our earlier study³⁶ that this modification of the wave operator eliminates some of the complex eigenvalues. According to the Lie algebraic decoupling theorem, the equation of motion for S is decoupled from the σ matrix elements in the exact limit.^{60,61} To distinguish the two approaches, we term them as normal coupled cluster method (NCCM) and extended coupled cluster method (ECCM) in the spirit of Arponen. The second goal of the present study is to see whether the ECCM approach offers any additional advantages over the NCCM approach for the calculations of expectation values and transition matrix elements.

The rest of this Article is organized as follows. In the next section, we describe the essential aspects of the calculation of expectation values and transition matrix elements from the CCM perspective. We have applied the formalism to water molecule and its isotopomers using an ab initio potential energy surface and dipole moment surface to understand the convergence properties of these quantities with respect to the truncation in the excitation operators. These results are presented in section III.

II. Theory

Within the Born–Oppenheimer approximation, the vibrational Hamiltonian for nonrotating molecules is given by

$$H = \sum_i \frac{P_i^2}{2} + V(Q) + V_c + V_w \quad (6)$$

Here, Q_i and P_i represent the mass weighted normal coordinates and their conjugate momenta. $V(Q)$ is the potential energy function. This is often approximated by a quartic polynomial in the Taylor series expansion

$$V = \frac{1}{2} \sum_i \omega_i^2 Q_i^2 + \sum_{i \leq j \leq k} f_{ijk} Q_i Q_j Q_k + \sum_{i \leq j \leq k \leq l} f_{ijkl} Q_i Q_j Q_k Q_l \quad (7)$$

V_c and V_w are the Coriolis coupling and the Watson's mass term, respectively.⁶² The formulation of CCM approach for molecular anharmonic vibration requires three steps. In the first step, Hartree approximation is invoked for the ground state. In this, a multi-dimensional Gaussian ansatz

$$\psi = N \exp[-(\sum_i \omega_i (Q_i - Q_i^0)^2/2)] \quad (8)$$

is optimized variationally with respect to ω_i and Q_i^0 . This optimized Gaussian function acts as vacuum state $|0\rangle$ for the

construction of Fock space of CCM. The harmonic oscillator ladder operators a_i^\dagger and a_i are defined with respect to this vacuum state

$$a_i = \sqrt{\frac{\omega_i}{2}} \left(Q_i - Q_i^0 + \frac{1}{\omega_i d(Q_i - Q_i^0)} \right) \quad (9)$$

$$a_i^\dagger = \sqrt{\frac{\omega_i}{2}} \left(Q_i - Q_i^0 - \frac{1}{\omega_i d(Q_i - Q_i^0)} \right) \quad (10)$$

The Hamiltonian is written in terms of these ladder operators. By definition, the optimized Hartree product satisfies the relation

$$a_i |0\rangle = 0 \quad (11)$$

In the second step, the ground-state wave function is parametrized as

$$|\psi_g\rangle = e^S |0\rangle \quad (12)$$

The cluster operator is expanded as

$$S = \sum_i s_i a_i^\dagger + \sum_{i \leq j} s_{ij} a_i^\dagger a_j^\dagger + \sum_{i \leq j \leq k} s_{ijk} a_i^\dagger a_j^\dagger a_k^\dagger + \dots \quad (13)$$

The working equations for coupled cluster ground-state energy and cluster matrix elements are given by

$$\langle 0 | H_{\text{eff}}^N | 0 \rangle = E_g \quad (14)$$

$$\langle e | H_{\text{eff}}^N | 0 \rangle = 0 \quad (15)$$

Here,

$$H_{\text{eff}}^N = e^{-S} H e^S \quad (16)$$

Equation 15 represents a set of coupled nonlinear equations that has to be solved iteratively. The detailed procedure to solve this set of equations is described in ref 36.

In the last step, we invoke the CCLRT for the descriptions of excited states. The excited-state wave function is written as

$$|\psi_e\rangle = e^{\Omega} |0\rangle \quad (17)$$

Here, Ω is a linear excitation operator, which is given by

$$\Omega = \sum_i \Omega_i a_i^\dagger + \sum_{i \leq j} \Omega_{ij} a_i^\dagger a_j^\dagger + \sum_{i \leq j \leq k} \Omega_{ijk} a_i^\dagger a_j^\dagger a_k^\dagger + \dots \quad (18)$$

The working equation for CCLRT to get excitation energies is

$$[H_{\text{eff}}^N, \Omega] |0\rangle = \Delta E \Omega |0\rangle \quad (19)$$

We now turn to the calculation of expectation values transition matrix elements. A straightforward approach based on the CCM ansatz for the expectation values leads to a nonterminating series^{63,64}

$$\begin{aligned} \langle \hat{O} \rangle &= \frac{\langle 0 | \exp(S^\dagger) \hat{O} \exp(S) | 0 \rangle}{\langle 0 | \exp(S^\dagger) \exp(S) | 0 \rangle} \\ &= \langle 0 | \exp(S^\dagger) \hat{O} \exp(S) | 0 \rangle_L \end{aligned} \quad (20)$$

making it impractical for the numerical work. Prasad⁶⁰ has earlier suggested an alternative approach for the calculation of expectation values and transition matrix elements within the CCM framework that bypasses the need to evaluate such infinite series. Here, it is recognized that because the CCM approach involves the construction and diagonalization of an effective Hamiltonian via the similarity transformation in eq 16, it is possible to relate the left and right eigenvectors of H_{eff} to the eigenvectors of the original Hamiltonian.

$$H_{\text{eff}} |R_i\rangle = E_i |R_i\rangle \quad (21a)$$

$$\langle L_i | H_{\text{eff}} = \langle L_i | E_i \quad (21b)$$

$$|\psi_i\rangle = N_i e^S |R_i\rangle \quad (22a)$$

$$\langle \psi_i | = \langle L_i | e^{-S} M_i \quad (22b)$$

By choosing the normalization constants M_i and N_i such that $M_i N_i \langle L_i | R_i \rangle = 1$, the expectation value of any arbitrary operator O is given by

$$\langle O \rangle = \langle \psi_i | O | \psi_i \rangle = \langle L_i | O_{\text{eff}} | R_i \rangle \quad (23)$$

where

$$O_{\text{eff}} = e^{-S} O e^S \quad (24)$$

These equations are identical to the equations derived by the Z-vector^{65,66} or λ -vector⁶⁷ formalism by earlier workers because all of these methods use a linearly parametrized left vector to calculate the expectation values. Similarly, the transition matrix elements between two states $|\psi_i\rangle$ and $|\psi_j\rangle$ are given by

$$|\langle \psi_i | O | \psi_j \rangle|^2 = \langle L_i | O_{\text{eff}} | R_j \rangle \langle L_j | O_{\text{eff}} | R_i \rangle \quad (25)$$

and the phase of the transition matrix element $\phi(O_{ij} = |O_{ij}| e^{i\phi})$ is given by

$$\phi = \frac{1}{2} \text{Im} [\ln(\langle L_i | O_{\text{eff}} | R_j \rangle / \langle L_j | O_{\text{eff}} | R_i \rangle)] \quad (26)$$

We use this approach for the calculation of the expectation values and transition matrix elements of the dipole operator.

The structure of the equations remains unchanged in the case of ECCM. The only difference in the case of the ECCM is that the effective operators defined in eq 24 are replaced by

$$O_{\text{eff}} = e^\sigma e^{-S} O e^S e^{-\sigma} \quad (27)$$

and the σ matrix elements are given by

$$\langle \phi_{\text{ref}} | e^\sigma e^{-S} H e^S e^{-\sigma} | \phi_e \rangle = 0 \quad (28)$$

As mentioned in the Introduction, the equations for the S-matrix elements are decoupled from the σ matrix elements

in the exact limit. We assume that this holds even in approximate calculations and solve eqs 15 and 28 sequentially.

III. Results and Discussion

We have applied the above-discussed methodology of section II to study the vibrational corrections to dipole moments of different vibrational states and transition matrix elements between ground state and several excited states of water molecule and isotopic variants HDO and D₂O. Over the years, there have been extensive studies on the vibrational spectra of water molecule.^{68–70} It is an archetypical local mode molecule because of the large mass disparity between oxygen and hydrogen atoms. Moreover, the low barrier of inversion makes it highly anharmonic. Consequently, it is a very good test molecule for any theoretical method based on a normal coordinate system. There are several accurate quartic ab initio potential energy surfaces (PES) available for these systems in the literature. However, there are very few dipole moment surfaces (DMS) reported in the literature. We have taken both PES and DMS from ref 23. In addition to the calculation of the potential energy surface and dipole moment surface, these authors made extensive calculations to the dipole moment expectation values and transition matrix elements using perturbation theory. We choose both PES and DMS based on CISD calculations using STO basis for applying our methodology to H₂O, HDO, and D₂O molecules. Although the potentials presented here are old, we chose these for consistency between PES and DMS in terms of basis set and method used in electronic structure calculations. The PES does not contain Coriolis coupling terms. Because the goal of the present work is to study the reliability of the effective operator approach based on the coupled cluster linear response theory rather than attaining experimental accuracy, we compared our results to converged full CI results. As is well-known, the quartic force field provides a poor description for the H₂O molecule.⁷¹ Consequently, it does not give numbers that can be compared to experimental data even with full CI level. A higher order expansion in the potential is required to match experimental values. The present methodology can be easily expanded for higher order potential functions. It will only add more terms in eq 15. Among these three molecules, we found that the deviations between CCM and converged full CI are maximum in the case of the H₂O molecule. Here, we discuss the results for the H₂O molecule.

A. NCCM-Based Calculation. In our earlier work,³⁶ we presented extensive calculations on the convergence of state energies with respect to the variation of the rank of both cluster operator S and excitation operator Ω from four boson to six boson level in NCCM and CCLRT, respectively. In two illustrative examples of formaldehyde and water, we found that both the ground-state and the excited-state energies have converged with respect to cluster operator by S_4 in NCCM. However, in some cases, the results were not converged even with six boson rank of excitation operator Ω . On the basis of this, in the present work we study the convergence pattern of the dipole operator expectation values and transition matrix elements with respect to rank of excitation operator Ω only. In all calculations, we kept the

Table 1. Variation of Expectation Values of Dipole Moment of H₂O with Varying Excitation Operator from Four Boson to Six Boson^a

state	4 boson	5 boson	6 boson	full CI	PT2 ^b
000	0.88	0.88	0.88	0.87	0.90
010	-2.09	-2.10	-2.10	-2.09	-1.93
020	-5.39	-5.62	-5.71	-5.87	4.80
100	2.26	2.26	2.26	2.26	2.32
030	-7.07	-9.17	-10.36	-11.43	-7.71
110	-0.31	-0.28	-0.29	-0.26	-0.47
120	-2.44	-2.81	-2.82	-3.41	-3.30
200	3.24	3.38	3.36	3.42	3.69
002	6.57	6.65	6.65	6.87	7.12
210	0.25	0.54	0.67	1.41	0.95
012	1.70	2.06	2.07	4.53	4.35
300	3.04	4.20	4.58	4.34	5.02
102	4.75	6.98	7.72	7.00	8.38
001	3.93	3.93	3.92	3.93	4.03
011	1.28	1.34	1.34	1.40	1.23
021	-1.72	-1.64	-1.55	-1.66	-1.61
101	4.67	4.84	4.83	4.88	5.37
111	1.32	2.35	2.63	2.60	2.61
201	3.90	5.48	5.87	5.52	6.66
003	6.83	9.13	9.59	9.75	10.17

^a The tabulated values are the vibrational corrections to the dipole moments ($\mu_{vv} - \mu_e$). Units are in 10^{-2} debye. ^b Reference 23.

cluster operator of NCCM fixed at six boson level. We compare our results with the converged full CI results. For full CI, we used 10–18–10 harmonic oscillator basis. Comparisons have also been made with the second-order perturbation results of ref 23.

1. Expectation Values of Dipole Operator. In Table 1, we present the variation of expectation values of dipole operator with respect to truncation levels of excitation operator Ω , keeping the cluster operator fixed at six boson level. The values presented in the table are vibrational corrections to the dipole moment. The Z axis is taken as the molecular axis. The states with maximum three quanta excitations are reported here. We find that for the ground state and fundamentals, CCM results are in excellent agreement with the converged full CI results. The values are converged even with as low as four boson excitation operator. For all states with two quanta of excitations, the dipole moment expectation values are very close to the full CI values. In 200, 002, and 011 states, the values are nearly converged with the rank of excitation operator. In case of 020, 030, 003 states, we find that dipole moment is monotonically converging with respect to excitation operator but has not saturated even at six boson level. For most of the three quantum states, the error is about 5% except for three states (120, 210, and 012) for which the maximum error is as high as 50%. As can be seen, the expectation values are not converged with respect to Ω even at the six boson level. We find dramatic improvements in the dipole moment expectation values on increasing the rank of excitation operator from four boson to five boson to six boson in some cases. For example, the dipole moment of 030 state changes from -7.07×10^{-2} to -10.36×10^{-2} debye from four boson to six boson rank of excitation operator. The converged full CI value for this state is -11.43×10^{-2} debye. As we noted in our earlier work,³⁶ lower lying states like fundamentals, first overtones, etc., are well represented by the CCLRT method because of its

Table 2. Variation of Absolute Transition Matrix Elements of H₂O with Varying Excitation Operator from Four Boson to Six Boson^a

state	4 boson	5 boson	6 boson	full CI	PT2 ^b
010	14.75	14.75	14.76	14.75	14.6
020	0.58	0.57	0.57	0.73	0.93
100	3.59	3.59	3.59	3.59	3.50
030	0.16	0.18	0.19	0.07	
110	0.10	0.10	0.10	0.06	0.22
200	0.44	0.44	0.44	0.35	0.44
002	0.08	0.07	0.08	0.01	0.08
012	0.13	0.13	0.13	0.02	
300	0.02	0.01	0.03	0.09	
102	0.11	0.11	0.11	0.03	
001	6.27	6.27	6.27	6.26	6.60
011	1.62	1.62	1.62	1.64	3.10
021	0.06	0.06	0.05	0.07	
101	0.94	0.94	0.94	0.78	1.10
111	0.34	0.35	0.35	0.32	
201	0.08	0.10	0.11	0.07	
003	0.14	0.14	0.13	0.07	

^a Values greater than 0.01 are reported. ^b Reference 23.

bivariational nature. However, truncation of the linear excitation operator at six boson level does not describe the wave functions of higher states adequately. The convergence pattern of states energies also reflects these improper descriptions of the higher excited-state wave functions.

In Table 1, we have compared the CCM dipole moment values with the second-order perturbation theory results presented in ref 23 also. We found that for almost all states the CCM results are better than the second-order perturbation results.

2. Transition Matrix Elements. The absolute values of the transition matrix elements of H₂O from the ground state to different excited states are presented in Table 2. Like state energies and dipole moment expectation values, here also we find excellent agreement between converged full CI and CCM with as low as four boson excitation operator for the fundamentals. Even for lower lying two quanta excited state 011 and three quanta excited state 111, we find that converged full CI values are reached by NCCM with four boson excitation operator. For two quanta states, the results are converged with the truncation of excitation operator, and they are close to converged full CI values except in the cases where the transition matrix element is very small. In our earlier study on energetics,³⁶ we found that the ground-state ket vector is well represented by as low as four body cluster operator S_4 . So the errors in transition matrix elements must be due to an inadequate description of the ground-state bra vector within the NCCM approach. In the NCCM approach, the ground-state bra vector is linearly parametrized. Parametrizing the ground-state bra vector by an exponential ansatz as is done in the ECCM approach should improve the transition matrix elements.

Finally, NCCM generally gives a better description for transition matrix elements than does the second-order perturbation theory.

B. ECCM-Based Calculation. In this section, we compare the results of different levels of truncation of Ω operator after Arponen-type double similarity transformation. In all calculations, both cluster operator S and σ are kept at the six boson level.

Table 3. Variation of Expectation Values of Dipole Moment of H₂O with Varying Excitation Operator from Four Boson to Six Boson after Arponen-Type Double Similarity Transformation^a

state	4 boson	5 boson	6 boson	full CI	PT2 ^b
000	0.88	0.88	0.88	0.87	0.90
010	-2.03	-2.04	-2.04	-2.09	-1.93
020	-5.46	-5.58	-5.60	-5.87	-4.80
100	2.25	2.25	2.25	2.26	2.32
030	-7.10	-9.42	-10.18	-11.43	-7.71
110	-0.28	-0.29	-0.29	-0.26	-0.47
120	-2.44	-2.76	-2.87	-3.41	-3.30
200	3.37	3.37	3.38	3.42	3.69
002	6.62	6.64	6.64	6.87	7.12
210	0.26	0.69	0.73	1.41	0.95
012	1.71	2.11	2.18	4.53	4.35
300	3.03	4.41	4.49	4.34	5.02
102	4.66	7.19	7.69	7.00	8.38
001	3.90	3.90	3.90	3.93	4.03
011	1.32	1.35	1.35	1.40	1.23
021	-1.71	-1.64	-1.62	-1.66	-1.61
101	4.79	4.82	4.83	4.88	5.37
111	1.33	2.51	2.63	2.60	2.61
201	4.04	5.70	6.01	5.52	6.66
003	6.65	9.24	9.44	9.75	10.17

^a The tabulated values are the vibrational corrections to the dipole moments ($\mu_{vv} - \mu_e$). Units are in 10^{-2} debye. ^b Reference 23.**Table 4.** Variation of Absolute Transition Matrix Elements of H₂O after Arponen-Type Double Similarity Transformation with Varying Excitation Operator from Four Boson to Six Boson^a

state	4 boson	5 boson	6 boson	full CI	PT2 ^b
010	14.81	14.81	14.81	14.75	14.6
020	0.75	0.75	0.75	0.73	0.93
100	3.63	3.63	3.63	3.59	3.50
030	0.02	0.02	0.02	0.07	
110	0.04	0.04	0.04	0.06	0.22
200	0.34	0.34	0.34	0.35	0.44
002	0.01	0.01	0.01	0.01	0.08
012	0.03	0.03	0.03	0.02	
300	0.09	0.09	0.09	0.09	
102	0.00	0.02	0.02	0.03	
001	6.32	6.32	6.32	6.26	6.60
011	1.61	1.61	1.61	1.64	3.10
021	0.08	0.08	0.08	0.07	
101	0.78	0.78	0.78	0.78	1.10
111	0.32	0.32	0.32	0.32	
201	0.07	0.08	0.09	0.07	
003	0.10	0.08	0.08	0.07	

^a Values greater than 0.01 are reported. ^b Reference 23.

1. Dipole Moment Expectation Values. We present the variation of dipole moment expectation values for H₂O with different levels of truncation of excitation operator with ECCM in Table 3. Like energetics of the states, here also we find the improvement due to double similarity transformation over NCCM is marginal.

2. Transition Matrix Elements. Variation of the transition matrix elements with rank of excitation operator for H₂O is given in Table 4. Here, we find significant improvements due to the double similarity transformation of ECCM approach over NCCM. For fundamentals, the NCCM results are very close to converged full CI. So improvements due to ECCM over NCCM are marginal. Beyond the fundamental states, we find dramatic improvements with ECCM-based

calculations. For example, with the NCCM-based method, the converged transition matrix element value for the 020 state is 0.57×10^{-2} debye, whereas the full CI value is 0.73×10^{-2} debye. With the ECCM-based calculation, it improves to 0.75×10^{-2} debye. Similarly, for the 002 state, the full CI value is 0.01×10^{-2} debye. NCCM-based calculation gives 0.08×10^{-2} debye, whereas ECCM gives the exact full CI value. Similarly, for 300, 101, 111 states, we find exact full CI values with the ECCM-based method. In all of the cases, the errors by the ECCM-based method are negligible. As we stated earlier, in the NCCM-based method, the ground-state bra vector is not properly described. In the ECCM, the ground-state bra vector is parametrized with an exponential operator. This makes the ECCM approach significantly superior over NCCM in calculating transition matrix elements.

We find a similar convergence pattern of expectation values and transition matrix elements in HDO and D₂O molecules. For low energy states, particularly states with two quanta excitations (in some cases with three quanta excitations, e.g., 030, 300, etc.), the results are converged with respect to full CI even with four boson operator rank. Some higher energy excited values have not reached the converged full CI values, but they are monotonically converging toward full CI results. Like the H₂O molecule, ECCM does not give any significant improvement over the NCCM approach in calculating the expectation values. However, transition matrix elements are better represented by the ECCM-based approach than by the NCCM-based approach.

IV. Conclusion

In this work, we presented an effective operator approach within the framework of CCM to calculate expectation values of operators and absolute transition matrix elements. We conclude that these properties can be calculated very accurately using CCLRT. We studied the convergence pattern of these properties with respect to truncations of excitation operator in CCLRT. We found that for fundamentals and most of the states with two quanta excitations, these properties are converged with the rank of excitation operator and reached full CI limit by Ω_4 . For higher states, the values tend to approach full CI values on going from four boson to six boson rank of excitation operator.

Next, we turn to the utility of Arponen-type double similarity transformation. We found that the ECCM does not offer any significant advantage over NCCM as far as state energies and expectation values are concerned. However, the story is quite different in case of transition matrix elements. Here, the ECCM fares far better than the NCCM, particularly when the transition matrix elements are small.

The CCLRT approach with a low rank excitation operator does not appear to be suitable for the description of highly excited states. As the number of quanta of excitation in a molecule increases, the wave function samples a larger region of coordinate space and, consequently, is affected to a greater extent by the anharmonicity. This has some intriguing consequences on the wave functions. For example, in a system described by quartic potential, the centroid of the wave functions would move away from the origin in the

energy regime dominated by cubic terms of the potential, but would return toward the origin as the quartic term becomes significant at higher energies. Thus, a proper description of the shifting of the wave function centroids and changes in their effective frequencies is necessary to describe such states. The CCLRT, with its linear structure, is perhaps not the best way to parametrize such changes. A multireference CCM for the excited states that describes the shifts in the centroids and frequencies in a state-specific manner might provide a better description. Efforts in this direction are in progress and will be presented in due course.

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