



Multipole moments using extended coupled cluster method

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ABSTRACT

Using analytic extended coupled cluster (ECC) response approach quadrupole moments, dipole–quadrupole polarizabilities and dipole polarizabilities are studied. In the current implementation of the functional we have included all the double linked terms within (CCSD) approximation. These terms will be important for the accurate description of properties at the stretched geometries. We report the properties for carbon monoxide and hydrogen fluoride molecules, as a function of bond distance and compare our results for carbon monoxide with the full CI results. We have also reported the properties of methane, tetrafluoromethane, acetylene, difluoroacetylene, water and ammonia.

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1. Introduction

Among various *ab initio* methods single reference coupled cluster method (SRCC) [1] is best suited for the accurate calculation of energy [2] and energy derivatives [3–5] of the molecules in their ground state. The success of the theory lies in its ability to introduce electron correlation accurately even in its approximate form. Various forms of the SRCC method have enabled the accurate calculation of molecular properties, gradients, geometry optimization and potential energy surfaces at equilibrium or near equilibrium geometry.

First order properties, i.e dipole moment, quadrupole moment can be obtained using expectation value method. A more general approach is the response approach [3] which is used for the calculation of higher order properties. With the help of Z vector technique [6,7], SRCC method can be used for the calculation of properties. However, this approach is difficult to extend for higher order properties. Constrained variation approach of Jørgensen and co-workers [8] is based on Lagrange multipliers and can be easily extended for higher order properties. The resulting equations using constrained variational approach are same as the one obtained by non-variational Z-vector technique for the first order properties.

Pal et al. [9] developed a stationary response approach. In a variational/stationary approach a suitable energy functional is chosen, which is made stationary with respect to the cluster amplitudes. This method is most suitable for the calculation of energy derivatives, in particular higher order derivatives because of the inbuilt $(2n + 1)$ rule. In this approach, the choice of the energy functional is very crucial. Pal and co-workers [10,11] used different energy functionals namely, expectation value coupled cluster (XCC), unitary coupled cluster (UCC) and extended coupled cluster (ECC)

for the calculation of properties. Among the various functionals, ECC [12,13] was found to be most suitable for the calculation of molecular properties due to its double linked nature resulting in a naturally terminating series. This functional was used for the calculation of electric [11,14] as well as magnetic properties [15,16] of small molecules. The initial implementation was based on the cubic truncation scheme. In the current implementation we have used the right as well as left vector all the terms within singles and doubles approximation which are double linked. We denote them as cubic-ECCSD and ECCSD throughout the Letter. The terms included are expected to be important for the property calculations at the stretched geometry.

Electric properties in particular have been studied very extensively due to their role in the design of non-linear optical materials [17–21]. On the other hand dipole–quadrupole polarizabilities [22] and dipole–octupole polarizabilities [23,24] have recently received attention. They are important for the Raman scattering studies as well as interaction induced light scattering spectra. The gradient of the dipole–quadrupole polarizability are important for the determination of vibrational Raman optical activity (VROA) intensities.

Study of multipole moments [23,24] is important due to their applicability in predicting long range interactions [25] in atoms and molecules. Unlike the dipole moments which can be experimentally measured, experimental measurement of quadrupole moments depends on various parameters. High quality *ab initio* calculations is the best way to obtain accurate values of quadrupole moments. In this Letter we report the study of basis set and electron correlation on quadrupole moment, dipole–quadrupole polarizability and dipole polarizability, of small molecules. We report the properties of carbon monoxide and hydrogen fluoride as a function of bond length to emphasize the importance of the terms newly added in the functional. We have also studied methane, tetrafluoromethane, acetylene, difluoroacetylene, water, and

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ammonia as a case study. The Letter is organized as follows. Section 2 gives brief theory of the ECC response properties. Results and discussion on them will be presented in Section 3. Section 4 contains conclusions.

2. Theory

To obtain the properties of our interest, we have used the ECC functional. The ECC functional uses different ket and conjugate vectors.

$$\langle H \rangle = \langle \Psi | H | \Psi \rangle \quad (1)$$

where $|\Psi\rangle$ and $\langle\Psi|$ are parametrized differently and are bi-orthogonal to each other. This functional also known as the ECC functional, was first proposed by Arponen and Bishop [12,13]. After double similarity transformation the form of the functional is given as follows

$$\langle H \rangle = \langle \phi_0 | e^{\Sigma} (He^T)_L | \phi_0 \rangle_{DL} \quad (2)$$

Here subscript L denotes the T operator to the right of Hamiltonian, which is linked/connected to H, subscript DL (double linked) means the left operator Σ is either connected to the Hamiltonian H or to two different T operators. Double linking ensures that the series is naturally terminating and hence gives size-extensive properties [11]. ECC method differs from the standard SRCC due to presence of left exponential, which includes several higher order terms. In this Letter, the contribution of the right exponential is taken full within CCSD approximation, i.e. $(He^T)_L$ and all the double linked higher order terms within CCSD approximation are included in the left vector. The extra terms that are included in the energy functional are $\Sigma_2 VT_2 T_1^2$, $\Sigma_2 VT_1^3$, $\Sigma_2 VT_1^4$, $\Sigma_1^3 VT_2$.

The cluster amplitudes are obtained using following equations

$$\frac{\partial E}{\partial t^{(0)}} = 0; \quad \frac{\partial E}{\partial \sigma^{(0)}} = 0 \quad (3)$$

Similarly, the derivative energy functional $E^{(1)}$ is obtained by replacing either the Hamiltonian by derivative Hamiltonian, i.e. dipole operator/ quadrupole operator or one of the cluster operator by its derivative.

$$E^{(1)} = \langle \phi_0 | e^{\Sigma} (H^{(1)} e^T)_L | \phi_0 \rangle_{DL} + \langle \phi_0 | e^{\Sigma} [\Sigma^{(1)} (He^T)_L + (He^T T^{(1)})_L] | \phi_0 \rangle_{DL} \quad (4)$$

where, the T and its derivative $T^{(1)}$, are explicitly connected to the Hamiltonian derivative or to the Hamiltonian. Similarly, the Σ or its derivative $\Sigma^{(1)}$, will either be connected to the Hamiltonian derivative or to the Hamiltonian or to two different T operators. To obtain the derivative amplitudes, the derivative functional is made stationary with respect to the amplitudes of Σ and T operators. For example, the first derivative amplitudes of Σ and T operators are obtained by the solution of the following set of equations.

$$\frac{\partial E^{(1)}}{\partial t^{(0)}} = 0; \quad \frac{\partial E^{(1)}}{\partial \sigma^{(0)}} = 0 \quad (5)$$

Eqs. (3) and (5) define the amplitude and derivative amplitude equations. With the help of them we can obtain the properties up to third order using Hellmann–Feynman theorem. The dipole and quadrupole moments are obtained as the expectation values of the dipole and quadrupole moment operator. However, second order properties like the dipole polarizability, dipole–quadrupole polarizability are obtained using analytic response approach.

3. Results and discussion

We report the quadrupole moment, dipole–quadrupole polarizability and dipole polarizability using ECCSD method.

Dipole–quadrupole polarizability is evaluated for methane, tetrafluoromethane, water, ammonia, carbon monoxide, hydrogen fluoride while quadrupole moments of acetylene, difluoroacetylene, water, ammonia and carbon monoxide are calculated. Dipole polarizability is calculated and reported for all the molecules. We have used cc-pVDZ and aug-cc-pVDZ basis [26] for all the molecules except for carbon monoxide we have used DZ (dunning) basis set. Water molecule has also been studied using Sadlej basis set [27] to compare our analytical values with the other correlated methods. All the calculations are done at the equilibrium geometry except for carbon monoxide and hydrogen fluoride molecule. We compare our results with the available experimental values and/or with time dependent Hartree–Fock (TDHF) results wherever available. We also report analytic CCSD values for dipole polarizability obtained using DALTON software [28] and quadrupole moment using GAMESS [29]. For dipole–quadrupole polarizability we compare our results with finite field CCSD values obtained using GAMESS [29].

3.1. Comparison between cubic-ECCSD and ECCSD

As mentioned in the previous section, the initial implementation of the functional was based on the cubic approximation, i.e. total of three cluster amplitudes in the functional. In the current Letter we have considered all the terms that appear within CCSD approximation. At the equilibrium geometry, these terms are not expected to contribute much in the property calculations. However, at the stretched geometry we expect them to improve the results. In particular, higher order properties should show improvement. To confirm our point we have calculated the properties for carbon monoxide and hydrogen fluoride at different geometries. Carbon monoxide molecule was studied using double zeta basis at R_e , $1.25R_e$ and $1.4R_e$. We compare our results with finite field FCI and CCSD values obtained using GAMESS [29]. We also compare our quadrupole value for carbon monoxide with the experimental value [30]. For hydrogen fluoride molecule we have used cc-pVDZ basis set. We report the values for R_e , $1.25R_e$, $1.5R_e$, $1.75R_e$ and $2.0R_e$. For hydrogen fluoride molecule, we compare our results with the finite field CCSD values obtained using GAMESS [29]. In Table 1 we report the properties of carbon monoxide at different geometries using the cubic truncation and CCSD approximation. We have frozen two core orbitals in our calculations. At the equilibrium as well as at $1.25R_e$, the difference between the cubic-ECCSD and ECCSD is marginal. However, effect can be seen that at $1.4R_e$ for dipole polarizability and dipole–quadrupole polarizability. The quadrupole moment has marginal effect of the ECCSD terms. Dipole polarizability values along the molecular axis approaches the CCSD value with ECCSD approximation. Full CI is slightly low compared to ECCSD as well as CCSD value. Dipole–quadrupole polarizability along the molecular axis approaches the Full CI as well as CCSD value with ECCSD values. The effect is prominent for the polarizability α_{zz} at $1.4R_e$. Similar trend is observed for the dipole–quadrupole polarizability of along the molecular axis. Carbon monoxide molecule is also studied by Maroulis et al. [31] and the results obtained for the properties show similar trend using different basis sets.

We have also carried out similar study of comparison between cubic-ECCSD and ECCSD for hydrogen fluoride molecule at R_e , $1.25R_e$, $1.5R_e$, $1.75R_e$ and $2.0R_e$. We compare our results with the finite field CCSD results using GAMESS [29]. We compare our results at the equilibrium geometry with the experimental values [32–34]. In Table 2 we report the dipole polarizability and dipole–quadrupole polarizability along the molecular axis. It can be seen that till $1.5R_e$ the difference between the cubic-ECCSD and ECCSD is marginal. At $1.75R_e$ and $2.0R_e$ the dipole polarizability values along the molecular axis differ. Similarly cubic-ECCSD and ECCSD

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