



Extended coupled cluster method for potential energy surface: A decoupled approach



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ABSTRACT

Extended coupled cluster (ECC) method has been implemented extensively for the calculation of molecular properties. In this Letter we report the potential energy surface (PES) study using coupled and a decoupled approximation of ECC. HF, N₂ and C₂ are studied as test systems. N₂ and C₂ being doubly and triply bonded, are considered to be interesting systems for PES study. We compare our results with full CI (FCI) results wherever available. Decoupled approach within ECC framework shows good convergence for all the molecules.

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1. Introduction

Study of potential energy surface (PES) provides a key to understand various chemical reactions [1], kinetics, dynamics [2–4] and spectroscopic properties. In recent years, there have been a lot of studies on PES [2–5]. Hartree Fock [6,7] is used as a zeroth order approximation for the correlated calculations. Among the correlated methods, single reference coupled cluster (SRCC) method [8–12] has been accepted as the most accurate method even in its approximate form. SRCC has been extensively used for the calculation of energy [13–15] and energy derivatives [16–21] as well as for potential energy surface calculations. Application of SRCC for the PES calculations at the bond breaking region is one of the most challenging problems. Though SRCC is suitable at the ground state geometry, it fails completely at the dissociation limit in particular when RHF does not dissociate correctly, where the non-dynamical correlation dominates [22–24]. To overcome this problem higher order terms like triples and quadruples are included [25] or multi reference methods are used [26,27]. Various studies have been performed for the calculation of PES using variational coupled cluster method [28–31]. Being variational it has upper bound in energy and does not collapse like standard SRCC method. Expectation values coupled cluster (XCC) [32], unitary coupled cluster (UCC) [33], extended coupled cluster (ECC) [34–37], improved coupled cluster (ICC) [30] and quadratic coupled cluster (QCC) [31] are some of the variants of the variational coupled cluster approach. However, all the variational methods suffer from the

problem of non-terminating series and needs to be truncated for practical application. Various truncation schemes are available in the literature. Energy functional in variational CC theory includes connected diagrams, however, when differentiated leads to disconnected diagrams giving loss of size extensivity. ECC functional due to the double linked nature always maintains linked diagrams even after differentiation and therefore the size extensivity is maintained [37]. However, this has double the number of amplitudes and hence twice the number of equations to be solved. Decoupled approximation has been proposed to solve this problem. Decoupled approximation was implemented for electric properties at the equilibrium geometry and is successfully tested for closed shell systems [38].

Last decade has witnessed a wide variety of study on potential energy surfaces. The incorrect convergence of RHF based studies makes it challenging for any SRCC method to study PESs. Musial and Bartlett [25] have shown that the Λ CCSD(TQ_f) approximation, based on Λ^2 CCSD(TQ_f) method, gives improvement in the PESs due to the inclusion of the connected factorized quadruples. Knowles and co-workers [30,31] used different approximations of the variational coupled cluster method for the study of potential energy surfaces. Piecuch and co-workers [26] used renormalized non-iterative coupled cluster method for the study of PESs. Current Letter emphasizes on the study of extended coupled cluster (ECC) method along with promising decoupled approximation for the potential energy surface. We have studied close shell molecules like HF, N₂ and C₂ in bond breaking region. All the three systems are very well studied in the literature before, due to the challenges they possess.

The Letter is organized in the following manner. In Section 2 we briefly discuss the extended coupled cluster (ECC) method along

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with the decoupled approximation. Results and discussion on them is done in Section 3. Conclusions on the results are presented in Section 4.

2. Theory

We briefly discuss the extended coupled cluster (ECC) functional, that we have used for PES study. The ECC functional uses different ket and bra vectors.

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

$$|\Psi\rangle = e^T |\Phi\rangle \quad (2)$$

$$\langle \Psi' | = \langle \Phi | e^{\Sigma} e^{-T} \quad (3)$$

Here \sum is a hole particle de-excitation operator while T is hole particle excitation operator.

They can be defined as

$$T = \sum_i t_i C_i^\dagger \quad (4)$$

$$\sum = \sum_i \sigma_i C_i \quad (5)$$

Here Ψ' and Ψ are bi-orthogonal to each other and they are differently parameterized. Arponen [34] and Bishop et al. [35] first time proposed the functional for calculating energy and is popularly known as ECC.

After performing double similarity transformation the functional is written in the following form:

$$E = \langle \Phi_0 | e^{\Sigma} (H e^T)_L | \Phi_0 \rangle_{DL} \quad (6)$$

DL implies that the right operator must be connected to the Hamiltonian H . The subscript DL (double linked) signifies the left vector Σ is either connected to the Hamiltonian H or to two different T operators. Thus, DL conforms that the series is naturally terminating and thus gives size extensive energy and properties [33]. Double linking also ensures that we have only connected diagrams.

The form of the functional used in this Letter is as follows:

$$\begin{aligned} E = \langle \Phi_0 | & \hat{V} t_2 + \sigma_2 \hat{V} + \sigma_1 \hat{V} t_1 + \sigma_2 \hat{V} t_2 + \sigma_1 \hat{V} t_2 + \sigma_2 \hat{V} t_1 + \sigma_1 \hat{F} t_1 \\ & + \sigma_2 \hat{F} t_2 + \frac{1}{2} \sigma_1 \sigma_1 \hat{V} + \frac{1}{2} \hat{V} t_1 t_1 + \frac{1}{2} \sigma_1 \hat{V} t_1 t_1 + \frac{1}{2} \sigma_2 \hat{V} t_1 t_1 + \frac{1}{2} \sigma_1 \sigma_1 \hat{V} t_1 \\ & + \sigma_1 \sigma_2 \hat{V} t_2 + \sigma_1 \hat{V} t_2 t_1 + \sigma_2 \hat{V} t_2 t_1 + \frac{1}{2} \sigma_2 \hat{V} t_2 t_2 + \frac{1}{2!} \sigma_2 \hat{V} t_2 t_1^2 \\ & + \frac{1}{3!} \sigma_2 \hat{V} t_1^3 + \frac{1}{4!} \sigma_2 \hat{V} t_1^4 + \frac{1}{3!} \sigma_1^3 \hat{V} t_2 + \frac{1}{2!} \sigma_2 \hat{V} t_1 t_1 | \Phi_0 \rangle \end{aligned} \quad (7)$$

It can be seen that, the contribution of the right operator is taken full within CCSD approximation; also the terms we use are double linked within CCSD model. The initial implementation was based on the cubic truncation of the left and right vector. Thus, the extra terms compared to the cubic approximation are $\sigma_2 V t_2 t_1^2$, $\sigma_2 V t_1^3$, $\sigma_2 V t_1^4$, $\sigma_1 V t_2$. However, we have not included terms like $\sigma_2^2 V t_2^2$ and some other terms like this.

The amplitude equations are obtained by differentiating energy expression with respect to cluster amplitudes i.e.

$$\frac{\partial E}{\partial t_i^{(0)}} = 0 \quad i = 1, 2, \dots \quad (8a)$$

$$\frac{\partial E}{\partial \sigma_i^{(0)}} = 0 \quad i = 1, 2, \dots \quad (8b)$$

Differentiation with respect to t amplitudes gives equation for σ amplitudes, while differentiation with respect to σ amplitudes gives equation for t amplitudes. The superscript (0) denotes that the amplitudes are unperturbed.

Equations for $t_2^{(0)}$ and $t_1^{(0)}$ amplitudes are given below

$$\begin{aligned} \frac{\partial E}{\partial \sigma_2^{(0)}} = \langle \Phi_{ab}^{pq} | & \hat{V} + \hat{V} t_1^{(0)} + (\hat{F} + \hat{V}) t_2^{(0)} + \frac{1}{2!} \hat{V} t_1^{(0)} t_1^{(0)} + \hat{V} t_1^{(0)} t_2^{(0)} \\ & + \frac{1}{2!} \hat{V} t_2^{(0)} t_2^{(0)} + \sigma_1^{(0)} \hat{V} t_2^{(0)} + \frac{1}{2!} \hat{V} t_2^{(0)} (t_1^{(0)})^2 + \frac{1}{3!} \hat{V} (t_1^{(0)})^3 \\ & + \frac{1}{4!} \hat{V} (t_1^{(0)})^4 | \Phi_0 \rangle = 0 \end{aligned} \quad (9a)$$

$$\begin{aligned} \frac{\partial E}{\partial \sigma_1^{(0)}} = \langle \Phi_a^p | & \sigma_1^{(0)} \hat{V} + (\hat{F} + \hat{V}) t_1^{(0)} + \hat{V} t_2^{(0)} + \frac{1}{2!} \hat{V} t_1^{(0)} t_1^{(0)} \\ & + \hat{V} t_1^{(0)} t_2^{(0)} + \sigma_1^{(0)} \hat{V} t_1^{(0)} + \sigma_2^{(0)} \hat{V} t_2^{(0)} + \frac{1}{2!} (\sigma_1^{(0)})^2 \hat{V} t_2^{(0)} | \Phi_0 \rangle = 0 \end{aligned} \quad (9b)$$

In similar way, equations for $\sigma_2^{(0)}$ and $\sigma_1^{(0)}$ are given as

$$\begin{aligned} \frac{\partial E}{\partial t_2^{(0)}} = \langle \Phi_0 | & \hat{V} + \sigma_1^{(0)} \hat{V} + \sigma_2^{(0)} (\hat{F} + \hat{V}) + \frac{1}{2!} \sigma_1^{(0)} \sigma_1^{(0)} \hat{V} \\ & + \sigma_1^{(0)} \sigma_2^{(0)} \hat{V} + \sigma_1^{(0)} \hat{V} t_1^{(0)} + \sigma_2^{(0)} \hat{V} t_1^{(0)} + \sigma_2^{(0)} \hat{V} t_2^{(0)} \\ & + \frac{1}{2!} \sigma_2^{(0)} \hat{V} (t_1^{(0)})^2 + \frac{1}{3!} (\sigma_1^{(0)})^3 \hat{V} | \Phi_{ab}^{pq} \rangle = 0 \end{aligned} \quad (10a)$$

$$\begin{aligned} \frac{\partial E}{\partial t_1^{(0)}} = \langle \Phi_0 | & \hat{V} t_1^{(0)} + \sigma_1^{(0)} (\hat{F} + \hat{V}) + \sigma_2^{(0)} \hat{V} + \frac{1}{2!} \sigma_1^{(0)} \sigma_1^{(0)} \hat{V} \\ & + \hat{V} t_1^{(0)} t_2^{(0)} + \sigma_1^{(0)} \hat{V} t_1^{(0)} + \sigma_2^{(0)} \hat{V} t_2^{(0)} + \sigma_2^{(0)} \hat{V} t_1^{(0)} \\ & + \sigma_1^{(0)} \hat{V} t_2^{(0)} + \sigma_2^{(0)} \hat{V} t_2^{(0)} t_1^{(0)} + \frac{1}{2!} \sigma_2^{(0)} \hat{V} (t_1^{(0)})^2 \\ & + \frac{1}{3!} \sigma_2^{(0)} \hat{V} (t_1^{(0)})^3 | \Phi_a^p \rangle = 0 \end{aligned} \quad (10b)$$

For cluster amplitude calculations, we solve equations (9a) and (9b) along with (10a) and (10b). These equations are solved iteratively to get the accurate energy. It can be seen that ECC method contains double the number of terms and hence amplitude equations compared to the SRCC approximation. This at times gives problem in convergence. Decoupled approximation is used as an alternative to eliminate this problem. The discussion on it is done in next section.

2.1. Decoupled scheme

The ECC functional behaves very well at equilibrium and stretched geometries around equilibrium. However, near bond breaking region ECCSD possess problem of convergence. To overcome this problem we have used a decoupled scheme for the study of PES.

Current decoupled scheme separates the left and right cluster operators. Eq. (8b), in detail Eqs. (9a) and (9b) give the amplitudes within singles and doubles approximations and they are very similar to non-variational coupled cluster (NVCC) equation. Thus, initially we determine the t amplitudes eliminating σ amplitudes. Once t amplitudes are known, we treat them as constant. We then solve the equation for σ amplitudes i.e. Eq. (8a) and Eqs. (10a) and (10b) i.e. detail expression. Then we come back to the t amplitude equation. This time we consider all the terms including σ amplitudes, however, σ amplitudes are treated as constant. Again, we go back to the σ amplitude equation. Thus, in the decoupled approximation we have both the amplitudes but we treat the other amplitude as a constant and hence every time only half the numbers of cluster amplitudes are included. Using these left and right cluster amplitudes we evaluate the potential energy surface

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