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Stationary coupled cluster response: Role of cubic terms in molecular properties

NAYANA VAVAL, KEYA GHOSE, PRIYA NAIR and SOURAV PAL*
National Chemical Laboratory, Physical Chemistry Division, Pune 411 008, India

Abstract. We have demonstrated an application of a stationary coupled cluster response approach for molecular properties using an Euler functional. This involves terms which are of cubic power in cluster amplitudes. We have shown that these are important terms and have also discussed the convergence properties of the functional for higher order properties.

Keywords. Stationary coupled cluster response; Euler functional; cubic terms in molecular properties.

1. Introduction

The study of nonlinear molecular properties using *ab initio* quantum mechanical methods has recently been of great interest in electronic structure theory (Ratner 1992). The higher order properties are important in the realm of nonlinear materials. The *ab initio* accurate calculation of these properties critically depends on the use of proper basis sets and adequate treatment of electron correlation effects. For the incorporation of correlation effects coupled cluster (CC) based techniques (Cizek 1966, 1969) are well established in the area of electronic energies as well as molecular properties. The CC methods provide us with the size extensive values of energies and molecular properties. (For a discussion on size extensive values see Mukherjee and Pal 1989). Thus it is particularly attractive to use this method for higher order properties like polarizability, hyperpolarizability etc. where correlation effects are extremely pronounced.

Among different versions of CC methods, a nonvariational version is more traditional (Cizek 1966, 1969) and has been applied extensively to the electronic energies (Paldus *et al* 1972; Paldus and Cizek 1973; Bartlett and Purvis 1978; Bartlett 1981; Lee and Bartlett 1984). Application to properties has been done with a response approach (Monkhorst 1977; Mukherjee and Mukherjee 1979; Sekino and Bartlett 1984, 1986). On the other hand, a stationary version of CC is more difficult to implement and has not been popular for energy calculation either for ground or excited/ionized states, although such formalisms with pilot applications are available (Pal *et al* 1983, 1984). However, the stationary version of theory, using a response based approach, can compute the molecular properties efficiently because of the built-in generalised $(2n + 1)$ rule in theory (Handy and Schaefer 1984; Pal 1984;

*For correspondence
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Jörgenson and Helgaker 1988; Bartlett *et al* 1989; Koch *et al* 1990; Ghose *et al* 1993). There are associated problems in implementing a stationary CC theory (Noga and Urban 1988; Pal 1990; Pal and Ghose 1992). Various stationary approaches for properties using CC (Pal 1984; Bartlett *et al* 1989; Koch *et al* 1990; Ghose *et al* 1993) or CI (Handy and Schaefer 1984; Jorgensen and Helgaker 1988). Wave functions differ in structure from one another. In one novel stationary CC formulation for properties we started from a Euler expectation value functional and computed the amplitudes as well as the derivatives through a stationary principle (Pal 1984). Within the CC fremework there is a formulation by Koch *et al* (1990), which starts from a nonvariational energy expression and computes derivatives of this. However, this formulation was specially tailored to the calculation of energy gradients. With a nonvariational wave function and using intermediate variational Lagrangian, Helgaker and Jorgensen (1992) have shown simplications similar to stationary theory for time independent molecular properties. Then there is an approach by Arponen and coworkers (Arponen 1983; Arponen *et al* 1987) which starts from a biorthogonal expectation value and is adapted to the calculation of ground state energy and general expectation value functional. This functional has also been used for an alternative formulation of response approach by us (Pal 1986; Ghose and Pal 1987). Then there is a fixed perturbation order based expectation CC (XCC) and unitary CC (UCC) methods developed by Bartlett *et al* (1989) and applied for ground state energy and properties.

In our theory using Euler functional (Pal 1984; Ghose *et al* 1993), we truncated the functional to total of quadratic power in cluster amplitudes. The Euler functional $\langle\psi|H|\psi\rangle/\langle\psi|\psi\rangle$ can be written in terms of only the linked part of the numerator in CC approach and is identical to the one based on unitarized CC (Kutzelnigg 1987). The series is normally a non-terminating series and so it needs to be truncated for practical computations. For nonlinear properties, the truncation to quadratic power is not so good and the properties (like first hyperpolarizability) are not even correct up to second order in electron correlation. To obtain more accurate values of molecular properties, it is important to include the cubic terms. Results of this study will be presented in this paper. There is yet another aspect i.e. the convergence of the expansion of the Euler series. We will address this aspect as well in this paper. In a related work Kutzelnigg (1991) discussed the error analysis of an expectation value and an improvement of coupled cluster theory.

In this paper we have calculated the properties up to first hyperpolarizability for a prototype molecule HF and compared with benchmark full configuration interaction (FCI) or large CI values (Bauschlicher and Taylor 1987). We have also studied the changes in the values from quadratic power to cubic power in the expansion. In the next section we give a brief overview of our stationary CC principle explicitly highlighting the cubic terms of the functional and their importance and in § 3 we present results for HF and discussion of these results.

2. Theory

The perturbed Hamiltonian $H(\lambda)$, in the presence of an external electric field is written as

$$H(\lambda) = H_0 + \lambda\hat{O}, \tag{1}$$

where λ denotes the field strength, H_0 is the unperturbed (zeroth order) Hamiltonian and $\hat{O}$ is the dipole operator. In a variational response approach we construct a functional $\mathbb{E}(\lambda)$ and relate properties with various derivatives of it with respect to λ evaluated at $\lambda = 0$. These are, in turn, related to the derivatives of wave function. The eigen functions of $H(\lambda)$ and the expectation values may be written in terms of linked series (Pal *et al* 1983)

$$\psi(\lambda) = e^{T(\lambda)}|\phi_0\rangle, \tag{2a}$$

$$\mathbb{E}(\lambda) = \langle\phi_0|e^{T(\lambda)\dagger}H(\lambda)e^{T(\lambda)}|\phi_0\rangle_L. \tag{2b}$$

The subscript L denotes (connected terms only) that $\mathbb{E}(\lambda)$ and $T(\lambda)$ can be expanded as power series in λ

$$\mathbb{E}(\lambda) = \mathbb{E}^{(0)} + \lambda\mathbb{E}^{(1)} + \lambda^2\mathbb{E}^{(2)} + \ldots\ldots \tag{2c}$$

$$T(\lambda) = T^{(0)} + \lambda T^{(1)} + \lambda^2 T^{(2)} + \ldots\ldots \tag{2d}$$

such that the nth order property can be identified as $n!\,\mathbb{E}^{(n)}$.

In the variational response approach the functional $\mathbb{E}(\lambda)$ is stationary with respect to the first order change in the wave function. Hence, the generalized Hellmonn–Feynmann (GHF) theorem is satisfied. More generally a $(2n+1)$ rule is built in the stationary approach, by which higher order properties can be calculated using lower order derivative amplitudes. More extensive discussion on this subject may be found in our recent review article (Pal and Ghose 1992). But the Euler type expectation value functional is nonterminating in nature and the use of this leads to disconnected terms in the equation for amplitudes when different n-body T's are used. For example, if T_1 is connected exclusively to a $T_2^\dagger$ vertex, then the differentiation of $T_2^\dagger$ vertex leads to disconnected terms. One may note in passing that in XCC/UCC based methods the equations are derived on the basis of terms, which contribute at least to a fixed nth order, and subsequently disconnected diagrams do not appear. A response approach based on this functional has not been attempted but one can speculate such an approach (Bartlett *et al* 1989). In our approach we use a stationary principle to derive a family of equations e.g.

$$\partial\mathbb{E}^{(m)}/\partial t^{\dagger(n)} = 0, \quad \vee\, m \geqslant n, \tag{3}$$

where $t^{(n)}$ is the nth order derivative of t amplitude. We have shown (Pal 1990) that if the amplitudes and their derivatives are truncated to a uniform degree, then (3) provides an identical set of equations for a fixed value of $(m-n) = 0, 1, 2, 3, \ldots$. and there is only one unique set of equations (Pal 1984) given by

$$\partial\mathbb{E}^{(m)}/\partial T^{\dagger(0)} = 0, \quad \vee\, m. \tag{4}$$

To get the T amplitudes we need to solve (4) hierarchically. In our stationary coupled cluster theory we have implemented the above equations. If we solve (4) for $m = 0$ and 1 then we get the cluster amplitudes for the ground state as well as the first derivatives. The stationary values may be used to compute energy derivatives up to third order. Stationary energies and their derivatives will be denoted by the symbol E (with appropriate superscripts), $E^{(1)}$ depends only on $T^{(0)}$ amplitudes.

$$E^{(1)} = \langle\phi_0|\exp(T^{(0)\dagger})\hat{O}\exp(T^{(0)})|\phi_0\rangle_L. \tag{5}$$

Similarly stationary $E^{(2)}$ and $E^{(3)}$ expressions depend nonlinearly on $T^{(0)}$ and $T^{(1)}$ only. One can easily derive that

$$E^{(2)} = \langle\phi_0|\exp(T^{(0)\dagger})\hat{O}\,T^{(1)}\exp(T^{(0)})|\phi_0\rangle_L, \tag{6}$$

$$\begin{aligned} E^{(3)} = {} & \langle\phi_0|\exp(T^{(0)\dagger})\{T^{(1)\dagger}\hat{O}T^{(1)}\}\exp(T^{(0)}|\phi_0\rangle_L \\ & + \langle\phi_0|\exp(T^{(0)\dagger})\{1/3!\hat{H}T^{(1)}T^{(1)}T^{(1)} + 1/2!(T^{(1)\dagger}\hat{H} + \hat{O})T^{(1)}T^{(1)}\} \\ & \times \exp(T^{(0)})|\phi_0\rangle_L + \langle\phi_0|\exp(T^{(0)\dagger})\{1/3!\,T^{(1)\dagger}T^{(1)\dagger}T^{(1)\dagger}\hat{H} \\ & + 1/2! \\ & T^{(1)\dagger}T^{(1)\dagger}(\hat{H}T^{(1)} + \hat{O})\}\exp(T^{(0)}|\phi_0\rangle_L. \end{aligned} \tag{7}$$

The expressions for $\mathbb{E}^{(0)}$, $\mathbb{E}^{(1)}$ as well as the stationary values of $E^{(1)}$, $E^{(2)}$, and $E^{(3)}$ are truncated up to cubic at a singles and doubles approximation. Only for $\mathbb{E}^{(0)}$, where some of the cubic terms start to contribute at a very high order, we have included the cubic terms contributing at least at the fourth order in perturbation. In $\mathbb{E}^{(1)}$ as wel' as the stationary $E^{(1)}$, the contributions of the cubic terms start at a lower perturbation order. It may easily be seen that the T_1 and T_2 contributions are at least at the second and first order respectively. One can find the perturbation order analysis of the T amplitudes and their derivatives in stationary CC response (Ghose and Pal 1993). Let us investigate the nature of (4) for $m = 1$, i.e.

$$\partial\mathbb{E}^{(1)}/\partial T_1^{(0)\dagger} = 0, \tag{8a}$$

and

$$\partial\mathbb{E}^{(1)}/\partial T_2^{(0)\dagger} = 0. \tag{8b}$$

There are the defining equations for $T_1^{(1)}$ and $T_2^{(1)}$ containing terms. $\mathbb{E}^{(1)}$ contains the terms of the type $T_1^{\dagger}\hat{O}$, which yields an inhomogeneous term $\hat{O}$ (one body) giving rise to $T_1^{(1)}$ containing terms with zeroth order dependence on V. This means that these are fairly significant. $\mathbb{E}^{(1)}$ series, however, can contain only a $T^{(1)}$ operator and infinite summations come from $T^{\dagger}$, T contributions. Thus it is expected to be still convergent. The argument can be extended to higher order $\mathbb{E}^{(n)}$ or any stationary $E^{(n)}$. If we check $\partial\mathbb{E}^{(1)}/\partial T_2^{\dagger} = 0$ equations, we find that the important inhomogeneous term is $\hat{O}T_2$ which is first order in V. Hence we conclude that $T_2^{(1)}$ depends at least on first order in V.

3. Results and discussions

We have chosen HF as a model system for which full CI as well as related nonvariational coupled cluster results are available. In an earlier study we used the stationary coupled cluster theory with the Euler functional truncated to a total of quadratic power in amplitudes. As explained earlier, in this paper we have incorporated the terms containing cubic powers in amplitudes, except that for $\mathbb{E}^{(0)}$ those cubic terms whose initial contributions appear at the fourth order but *not any higher*, have not been included. The stationary expressions for $E^{(1)}$, $E^{(2)}$, and $E^{(3)}$ are simplified using the $(2n+1)$ rule in terms of $T^{(0)}$, $T^{(1)}$ amplitudes. We have presented results up to first hyperpolarizability of HF in DZP basis. We have used two models, one with disconnected terms ($n_{\text{dis}} = 0$) and another without them ($n_{\text{dis}} = 1$). The results of these

Table 1. (Meunter 1972) Properties of hydrogen fluoride (DZP basis[a]). All values are in atomic units; HF distance = 1·733 a.u.

		Variational						
		$n_{dis}=0$		$n_{dis}=1$				
Property	SCF	Quad.	Cubic	Quad.	Cubic	Non-variational[b]	Full[c] CI	Experiment
μ_z	0·812	0·760	0·768	0·755	0·765	0·756	0·765	0·707[d]
α_{zz}	4·261	4·597	3·798	4·930	4·049	4·4	4·4	6·40[e]
α_{xx}	1·516	1·696	1·429	1·734	1·463	1·638	—	5·08[e,f]
β_{zzz}	−14·633	−23·268	−11·510	−25·788	−12·042	−15·360	—	—

[a]Double zeta basis from Bauschlicher *et al* (1986), $\alpha_p = 0{\cdot}75$, $\alpha_d = 1{\cdot}60$; [b]Salter *et al* (1987). Exponents used are $\alpha_p = 0{\cdot}70$ & $\alpha_d = 1{\cdot}58$, $n_{dis} = 0$ means disconnected terms have been included in the cluster amplitudes equations, $n_{dis} = 1$ means disconnected terms have not been included in the cluster amplitudes equations; [c]Bauschlicher and Taylor 1987; [d]Muenter and Klemperer (1970); [e]Werner and Meyer (1976); [f]Muenter 1972

two models are presented in table 1. We find a large contribution of the cubic terms in both the models. In particular, the change in the value of β_{zzz} is dramatic. Although it is expected that the calculation of the higher order properties is more sensitive to the electron correlation, such a large change in the first hyperpolarizability was surprising. Benchmark FCI results quoted here were carried out with five 3*d* functions, while ours contained six 3*d* functions. However, this may still serve as a useful guide to the trends of the calculation. No nonvariational results are available exactly in this basis. But we have presented in the tables the available nonvariational results in a slightly different basis (same DZP level, but the exponents of the polarization function differ only slightly). One can still say that the cubic corrections with either $n_{dis} = 0$ or $n_{dis} = 1$ are towards the FCI results. It may be pointed out that the model neglecting the disconnected terms ($n_{dis} = 1$) furnishes results closer to the FCI numbers as compared to the other model. Comparing the two models, the absolute values of polarizability and the first hyperpolarizability are higher when the disconnected terms are neglected. The improvement of the dipole moment with the cubic terms can be readily seen from the table 1.

The saturation of the dipole moment with the addition of the cubic terms is evident from table 1. However, for α_{xx}, α_{zz}, and in particular β_{zzz}, the cubic corrections are relatively larger and it seems that these values have not saturated with the addition of the cubic terms. To get accurate values of this, clearly still higher order terms are needed. This, in itself, is a problem of the stationary coupled cluster response approach that may be addressed separately.

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