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# Electron correlation effects on the nonlinear optical properties of conjugated polyenes

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ABSTRACT

We employ the coupled cluster method to calculate the nonlinear optical coefficients for conjugated polyenes and their push–pull forms. We find that the electron correlation always reduces the nonlinear optical responses. While MP2 can predict correct trend for properties like dipole moment and polarizability, it gives completely wrong trend for the hyperpolarizabilites for long polyenes. It is highly cautioned to use MP2 when benchmarking computational methods for nonlinear properties such as improving exchange-correlation functionals in DFT.

## 1. Introduction

Intense research efforts have been devoted to the nonlinear optical (NLO) properties of conjugated polymers in recent decades, and abundant knowledge are gained till now [1–3]. Previous studies show that electron correlation play a very important role in describing correctly NLO properties of conjugated polymers [1,4–9]. The electron correlation effect is evaluated through comparison with the mono-electronic Hartree–Fock self-consistent-field (HF-SCF) results by more advanced quantum chemical methods. Density functional theory (DFT) has been found to fail to describe the NLO behavior for long chain systems with the commonly used xc-functionals [10–12]. Many efforts have been devoted to develop new functionals to properly correct the self-interaction problems [13–15]. And the general way to validate DFT results is to compare with MP2 for relative large systems.

In this work, we present our calculations based on coupled cluster method with single and double excitations (CCSD), using finite field method, for NLO properties of polyenes and push–pull conjugated polyenes. CCSD is known to give better description of electron correlation. As a matter of fact, in the nonlinear iteration procedure to solve CCSD amplitude equations, MP2 solutions serve as the zeroth order approximation [16]. We will point out that the trends of chain length dependent NLO coefficients produced from MP2 can be misleading in some cases for long conjugated molecules.

## 2. Theoretical methodology

We choose the semi-empirical Pariser–Parr-Pople model [17] to describe the linear polyenes. The Fock matrix reads

$$F_{\mu\nu} = H^{\mathrm{core}}_{\mu\nu} - \frac{1}{2} P_{\mu\nu} V_{\mu\nu}, \quad \mathit{for} \quad \mu \neq \nu$$
$$F_{\mu\mu} = H^{\mathrm{core}}_{\mu\mu} + \sum_{\nu} P_{\nu\nu} V_{\mu\nu} - \frac{1}{2} P_{\mu\mu} U \qquad (1)$$

Here, $P_{\mu\nu}$ is density matrix, and $H^{\mathrm{core}}_{\mu\mu} = U, H^{\mathrm{core}}_{\mu\nu} = t_{\mu\nu}$ are site energy and transfer integral, respectively. Electric field $F$ is included in the Hückel approximation, by adding an additional term: $-eFx_{\mu}$ to the diagonal Fock matrix elements, where $x_{\mu}$ is the longitudinal-component of the nuclear position. The electric filed direction is assumed to be along the chain. Parameters required to specify the model are gathered here: for single bond, bond length $b_1 = 1.48$ Å and transfer integral $t_1 = -2.2$ eV; and for double bond length $b_2 = 1.35$ Å and $t_2 = -2.6$ eV. The on-site Coulomb repulsion energy for carbon pi-orbital is $U = 11.13$ eV and the Ohno-Klopman parameterization [18,19] is used for Coulomb integrals: $V_{\mu\nu} = 14.397(1.673 + r^2_{\mu\nu})^{-\frac{1}{2}}$. The CCSD ground state energy is obtained through standard numerical scheme, see Refs. [20,21] for PPP model.

The longitudinal NLO coefficients are calculated by the finite field method through numerical derivatives of the ground state energies with respect to the applied electric field

$$\mu = -\left(\frac{\partial E}{\partial F}\right)_{F=0} = -\frac{E(F) - E(-F)}{2F}$$
$$\alpha = -\left(\frac{\partial^2 E}{\partial F^2}\right)_{F=0} = -\frac{E(F) + E(-F) - 2E(0)}{F^2}$$

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$$\beta = -\left(\frac{\partial^3 E}{\partial F^3}\right)_{F=0} = -\frac{E(2F) - 2E(F) + 2E(-F) - E(-2F)}{2F^3} \qquad (2)$$

$$\gamma = -\left(\frac{\partial^4 E}{\partial F^4}\right)_{F=0} = -\frac{E(2F) - 4E(F) + 6E(0) - 4E(-F) + E(-2F)}{F^4}$$

The electric field strengths are chosen to be $F = 0$, ±4, $\pm 8 \times 10^{-4}$ a.u. for the finite differentiations. These should be neither too small nor too big for the sake of numerical stability.

## 3. Results and discussion

We first look at the results for pristine polyenes. The static longitudinal linear polarizabilities ($\alpha$) and second hyperpolarizabilities ($\gamma$) of polyenes obtained by different methods are presented in Figs. 1 and 2 , respectively. For $\alpha$, one can see that both CCSD and MP2 lead to a reduction, when compared with HF results. This is fully consistent with previous *ab initio* results [14,15]. In fact, Soos et al. argued that the polarizability is determined by the transition dipole moment between the ground state and the excited state. The most important contribution comes from the first dipole-allowed $1B_u$ state, which is an ionic state, namely, the major contribution in configuration space to this state is a charge separated configuration in real space. For the ground state, without electron correlation, the ionicity defined as the average electron double-occupation number at half-filling is 0.25, namely, the orbital could be empty, spin-up, spin-down, or doubly occupied. The probability for double occupation is 25%. When the electron correlation is turned on, the energy of doubly occupied configuration largely increases (Hubbard U). Thus the ionicity becomes less than 0.25. Soos et al. showed that this reduces the transition dipole moment between the ground state and the dipole-allowed ionic $1B_u$ state [22].

While for the second hyperpolarizabilities as the polyene length increases, two methods go in fully opposite directions: MP2 leads to larger values than HF, while CCSD predicts smaller values (except for $N < 4$), see Fig. 2. When compared with nearly exact density matrix renormalization group (DMRG) study [23], we found that CCSD still underestmates the $\gamma/N$ for long polyenes. However, qualitatively, DMRG is below Hartree–Fock, namely, correlation induces reduction of hyperpolarizability. This indicates that the dynamic correlation is very important in determining the nonlinear response, as pointed out by Yaron [24]. In fact, DMRG contains all the dynamic correlation effect, because it is basically an exact theory for 1-d model [23].

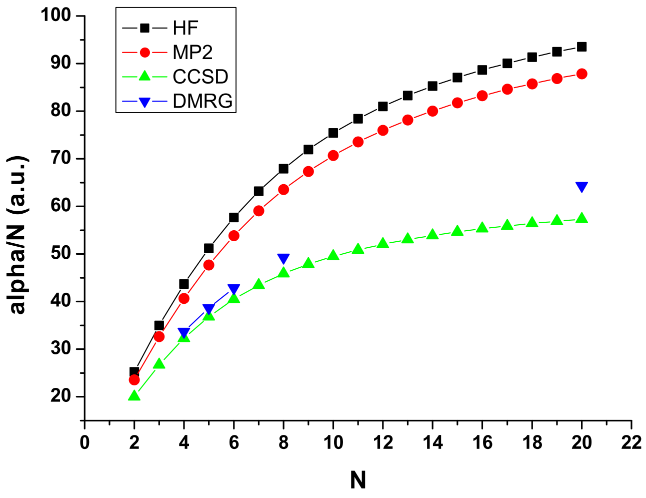

**Fig. 1.** Longitudinal linear polarizabilities ($\alpha/N$) of polyenes. $(CH{=}CH)_N$, $N$ is the number of the unit cells.

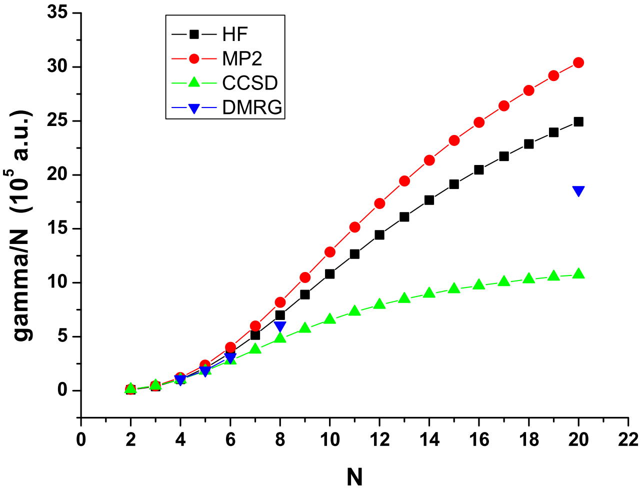

**Fig. 2.** Second hyperpolarizabilities ($\gamma/N$) calculated by different methods for polyenes $(CH{=}CH)_N$, $N$ is the number of the unit cells.

In part, the electron correlation-induced reduction of hyperpolarizability can be similarly rationalized by the argument of Soos et al. [22] made for the polarizability. In fact, Wang and Mukamel has also pointed out that the electron correlation reduces largely $\gamma$ [25]. Their argument is that in a single electron picture, the electron and hole are independent coherent band particles. They can separate freely, which causes large susceptibility. Once electron is correlated, then electron and hole form bound state. This causes a reduction in susceptibility. By comparing Hückel model and PPP model, their numerical calculation confirms this trend [25].

It is thus intriguing to rationalize why MP2 gives opposite trend, as shown both from our results of PPP model and from the literature of *ab initio*. We should point out that the finite field method is completely different from the sum-over-state approach. Even at the Hartree–Fock level, if coupled with finite-field, it is equivalent to the time-dependent formalism for nonlinear response. At the linear response level, it is equivalent to the random-phase-approximation. Even though the ground state energy is not correlated, the polarizability and hyperpolarizability evaluation contains electron correlation effects.

Now we look at the case for push–pull substituted polyenes, which is modeled by adding a site-energy $+\delta$ at one end and $-\delta$ at another end so that the correlation effects on the dipole moments ($\mu$) and the first hyperpolarizabilities ($\beta$) for long push–pull polyene chain can be revealed. We have checked different values for $\delta$ and found that the general trend holds for values ranging from 0.25 to 3.0 eV and here we present results for $\delta = 0.5$ eV. Our calculated longitudinal dipole moments, polarizabilities, first and second hyperpolarizabilities are given Figs. 3–6. Note that all the results here can reproduce well the previous one in the cases of HF and MP2 [12]. For the longitudinal dipole moment and the linear polarizability, we can observe the correlation-induced reduction effect, which is fully consistent with the electron correlation picture, see Figs. 3 and 4.

However, the situation becomes different for nonlinear optical properties. For the first hyperpolarizability $\beta$ (Fig. 5) and the second hyperpolarizability $\gamma$ (Fig. 6), we can observe that for short chains, both MP2 and CCSD give values larger than HF. But for longer chains ($N > 6$), CCSD results go below the HF while MP2 is always above HF.

For large molecular systems, DFT is probably the only choice at the first-principles level. We note that the DFT benchmark has been always made in comparison with MP2. Our results suggest that for linear optical properties, MP2 is quite reasonable, but for

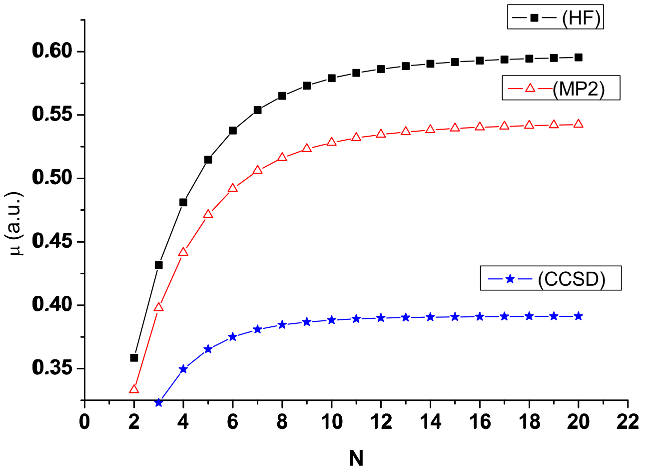

**Fig. 3.** Evolution of longitudinal dipole moments ($\mu$) of push–pull polyenes ($\delta$ = 0.5 eV) as a function of the number of the polyene unit cells for different methods.

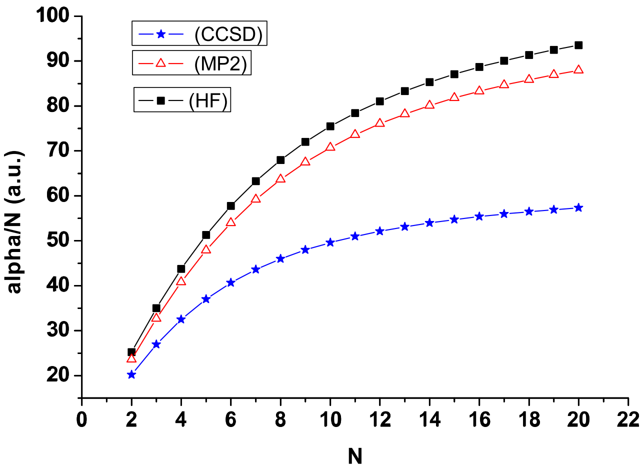

**Fig. 4.** Longitudinal linear polarizabilities ($\alpha/N$) of push–pull polyenes $(CH{=}CH)_N$, $N$ is the number of the unit cells ($\delta$ = 0.5 eV).

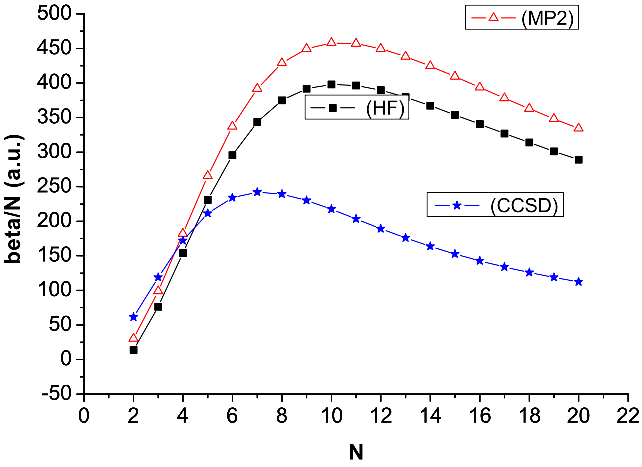

**Fig. 5.** Longitudinal first hyperpolarizabilities ($\beta/N$, in a.u.) of push–pull polyenes $(CH{=}CH)_N$, $N$ is the number of the unit cells ($\delta$ = 0.5 eV).

nonlinear case, the trend predicted from MP2 can be fully wrong. Thus this should be highly cautioned in developing new functionals.

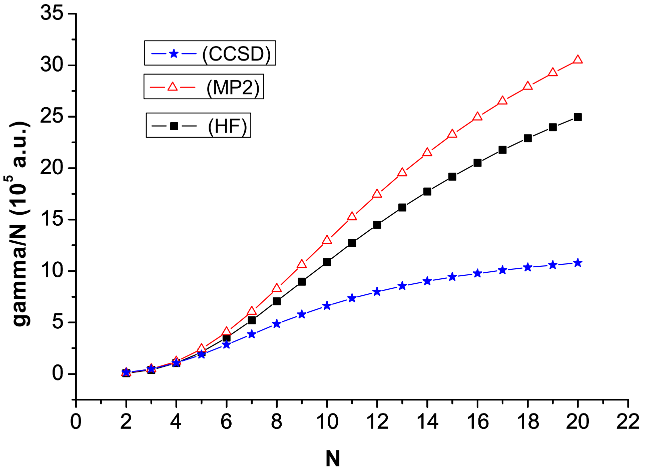

**Fig. 6.** Longitudinal second hyperpolarizabilities ($\gamma/N$) of push–pull polyenes. $(CH{=}CH)_N$, $N$ is the number of the unit cells ($\delta$ = 0.5 eV).

## 4. Summary

To summarize, we have carried out CCSD with PPP model for the proto-typical conjugated polymer, polyene and push–pull polyenes to investigate linear and nonlinear optical responses from $N = 2$ to 20 double bonds, and we have made comparisons against Hartree–Fock and MP2 in order to assess the electron correlation effects. It has been known that electron correlation causes electron localization, and tends to decrease NLO responses. This is confirmed by the CCSD calculations. To our surprise, MP2 gives fully different trends, namely, for long polyenes, MP2 predicts that the electron correlation tends to enhance the nonlinear optical responses. Thus, it should be highly cautioned to use MP2 to benchmark the DFT developments for nonlinear optical properties.

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