

Local Approach to Coupled Cluster Evaluation of Polarizabilities for Long Conjugated Molecules

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Abstract: Electron correlation effect in conjugated polymer is a long-standing problem, especially for the nonlinear optical properties. We have implemented a spin-adapted Coupled Cluster with singles and doubles excitation with local molecular orbital approach. As a first application, we evaluate the static polarizability of conjugated polyene chains with finite field approach. It is found that the local molecular orbital approach can tremendously reduce the computational costs at sufficiently high accuracy. It is also found that the electron correlation can largely reduce the molecular polarizability with respect to the Hartree-Fock mean field results.

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Key words: local molecular orbital; coupled cluster; conjugated polymer; polarizability; linear scaling

Introduction

Conjugated polymers have great potentials in electronics and optoelectronics application. From the theoretical modeling point of views, the electron correlation effects have been found to play an essential role in conjugated chain for the optical properties as well as for nonlinear optical responses.^{1–4} In the context of quantum mechanical methods for studying the electrical and optical properties of conjugated polymers, Hartree-Fock mean-field theory,⁵ the Configuration Interaction (CI),⁶ the Random Phase Approximation (RPA) or time-dependent Hartree-Fock,⁷ Many-body Perturbation Theory,^{8,9} Coupled-Cluster (CC),¹⁰ Density Functional Theory (DFT),¹¹ and the Density Matrix Renormalization Group theory (DMRG)^{12–14} have been often employed to evaluate either the ground state property or the excitation energies or the linear and nonlinear optical responses. These methods have been developed with both *ab initio* and semi-empirical Hamiltonians. It has been established that the electron correlation play a key role in the molecular electronic structure. However, the highly demanding computational costs of traditional post-Hartree-Fock methods severely limit their application scopes. Many efforts have been devoted to developing various low-scaling methods in recent years.^{15–40}

We adopt the Pariser-Parr-Pople (PPP) model to describe conjugated hydrocarbon molecules.^{41–43} PPP model is an effective way to describe the π -electron properties for conjugated polymers. One of the present authors and his coworkers had first developed a numerical scheme for nearly exactly solving PPP

model with long-range Coulomb interaction for long conjugated chain by DMRG method.^{44,45} They have cautioned that for short-ranged Coulomb interaction, the methods based quasi-particle pictures such as 2nd and 3rd Green's function or RPA and second-order RPA could qualitatively deviate from the nearly exact solutions for the band gap and the lowest-lying excited state.⁴⁵ Even though the recent advances of DMRG for quantum chemistry have been quite impressive,^{46–48} for a general three-dimensional molecule, DMRG is still not yet a practical approach in terms of both accuracy and computational costs. DFT-based method has become an overwhelming computational tool in recent decade. Its intrinsic problem of empirical functional instead of exact, renders DFT to be still far from an all-purpose computational tool. For example, in the matters of $1B_u$ vs. $2A_g$ orderings, charge-transfer type excitation, and the charge localization, DFT gives qualitatively wrong answers.⁴⁹ Even worse, it has been shown that DFT fails to reproduce nonlinear optical (NLO) response for large system, due to the deficiency in the conventional exchange functional.⁵⁰ In this respect, Coupled Cluster might be a good choice to treat electron corre-

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lation, and to provide benchmarks for other approximate methods. As we have shown that for conjugated chain, Coupled Cluster with singles and doubles excitations (CCSD) can produce quite satisfactory results for the ground state and lowest-lying excited states,⁵¹ for instance, in terms of the excited state orderings⁵² as well as the singlet-triplet splitting.⁵³

Local molecular orbital was introduced to bridge the local chemical bonds concepts with the delocalized molecular orbitals.^{54–58} The local correlation approach was proposed in recent decades.^{15,59} It makes use of the spatial localization of localized molecular orbital (LMO) to reduce the computational cost in the electronic correlation calculation.^{15–40,60} Korona and Werner³⁹ and Crawford and King⁴⁰ combined CCSD and its Equation of Motion CCSD (EOM-CCSD) method with the local correlation approach. Their results show that great amounts of computational costs can be reduced. It should be noted that these studies have been carried out in the *ab initio* framework and the system treated are still limited to relatively small molecules or nonconjugated chains. The primary motivation of this work is to implement a local orbital CCSD to study the linear and nonlinear optical response for long conjugated chain molecules, specifically on the electron correlation effect, within a finite-field approach for the PPP model.

Theoretical Methodology

PPP Model

We choose Pariser-Parr-Pople model^{41–43} to model the conjugated hydrocarbons. Hamiltonian in the PPP model reads as follows :

$$H = - \sum_{ij} t_{ij} C_{i,\sigma}^\dagger C_{j,\sigma} + U \sum_i n_{i,\uparrow} n_{i,\downarrow} + \frac{1}{2} \sum_{ij} V_{ij} (n_i - 1)(n_j - 1) \quad (1)$$

Here, $\langle ij \rangle$ means the summation are only made in the bonded sites. And in self-consistent field (SCF) level, one can obtain the single-particle Fock operator matrix:

$$F_{\mu\nu} = t_{\mu\nu} - \frac{1}{2} P_{\mu\nu} V_{\mu\nu}, \text{ for } \mu \neq \nu \quad (2)$$

$$F_{\mu\mu} = U_\mu + \sum_\nu P_{\nu\nu} V_{\nu\nu} - \frac{1}{2} P_{\mu\mu} U_\mu \quad (3)$$

where $P_{\mu\nu}$ is the density matrix, $t_{\mu\nu}$ is the transfer integral, and U_μ is the on-site repulsion energy.

Spin-Adapted Coupled-Cluster Singles and Doubles Approach (SA-CCSD)

Spin-adapted coupled cluster approach has been developed previously^{60,61} and we here only give a brief description for facilitating the subsequent discussions. The ground state wave function in CC theory is given based on the exponential ansatz:

$$|\psi_{cc}\rangle = e^T |0\rangle \quad (4)$$

where

$$e^T = 1 + T + \frac{1}{2!} T^2 + \frac{1}{3!} T^3 + \dots + \frac{1}{n!} T^n + \dots, \quad T = \sum_i T_i \quad (5)$$

The ket $|0\rangle$ represents the Hartree-Fock self-consistent-field Slater determinant. At the CCSD level, T includes only singles and doubles and the corresponding cluster operators are defined as follows:

$$T_1 = t_i^a E_{ai}, \quad T_2 = \frac{1}{2} t_{ij}^{ab} E_{ai} E_{bj}, \quad E_{ai} = a_\alpha^+ i_\alpha + a_\beta^+ i_\beta \quad (6)$$

Throughout this article, i, j, k, l are used for occupied molecular orbitals (MOs), a, b, c , for unoccupied ones, and p, q, r, s for generic orbitals. Hereafter, the Einstein summation convention is assumed unless specified. One can obtain the equations for the cluster expansion coefficients t_s and the total energy by projection as follows:

$$\begin{aligned} H \exp(T) |0\rangle &= E_{cc} |0\rangle, \\ \langle 0 | E_{ia} \exp(-T) H \exp(T) |0\rangle &= 0, \\ \langle 0 | E_{ia} E_{jb} \exp(-T) H \exp(T) |0\rangle &= 0. \end{aligned} \quad (7)$$

The explicit iteration equations can be found in literature.⁶⁰

Localized Molecular Orbitals and Domains

First, one needs localized molecular orbitals (LMOs) to replace canonical molecular orbitals (CMOs). We adopt the Pipek and Mezey's proposition to obtain LMOs,⁵⁴ though we have tested other propositions. Localization is done by two by two orbital rotations of CMOs till the required convergence criterion is reached. The molecular orbital $|p\rangle$ is expressed as the linear combinations of atomic orbitals (LCAO): $|p\rangle = C_{p\mu} \mu$, and the orbital rotation is of the form:

$$|p'\rangle = \cos \gamma |p\rangle + \sin \gamma |q\rangle, \quad |q'\rangle = -\sin \gamma |p\rangle + \cos \gamma |q\rangle \quad (8)$$

Here, $|p\rangle$ and $|p'\rangle$ are initial and the updated MOs, respectively. The rotation angle γ is related to the quantities A_{pq} , B_{pq} as follows⁵⁴:

$$\sin 4\gamma = B_{pq} (A_{pq}^2 + B_{pq}^2)^{-\frac{1}{2}}, \quad \cos 4\gamma = -A_{pq} (A_{pq}^2 + B_{pq}^2)^{-\frac{1}{2}} \quad (9)$$

where

$$\begin{aligned} A_{pq} &= \sum_A \{ (P_A)_{pq}^2 - \frac{1}{4} [(P_A)_{pp}^2 - (P_A)_{qq}^2] \}, \\ B_{pq} &= \sum_A (P_A)_{pq} [(P_A)_{pp} - (P_A)_{qq}] \\ (P_A)_{pq} &= \frac{1}{2} \sum_\rho \sum_{\mu \in A} [C_{p\rho}^* S_{\rho\mu} C_{q\mu} + C_{p\mu}^* S_{\mu\rho} C_{q\rho}] \end{aligned} \quad (10)$$

Here, $S_{\rho\mu}$ is the overlap matrix and the summation in the second line of eq. (10) is restricted to atomic orbitals belonging to atom A.

For PPP model, zero differential overlap approximation is assumed and we have

$$(P_A)_{pq} = \sum_{\mu \in A} C_{p\mu}^* C_{q\mu}. \quad (11)$$

It should be pointed out here that localizations for occupied and virtual MOs are carried out separately, that is, the occupied and the virtual MOs will not be mixed. Since the resultant LMOs can be considered as a unitary transformation of original CMOs,⁵⁴ LMOs remain orthonormal each other, just like the CMOs: the unitary transformation keeps orthonormality.

After LMOs are obtained, the approach proposed by Boughton and Pulay⁵⁹ is used to determine the unoccupied local molecular orbitals (ULMO) assigned to the corresponding occupied orbitals and the pairs. The atoms are ordered according to their Mulliken charges for a given occupied LMO, and then the basis functions which contribute the most (Mulliken charge) to the orbital are used to expand the corresponding ULMO. If the expansion is as satisfied as expected, it is considered as important for the related OLMO.

For a given occupied LMO $|i\rangle$, firstly, atomic Mulliken charges ($\sum_{\mu \in A} P_{\mu\nu} S_{\nu\mu}$) are computed and the orbital domain $[i]$ is constructed by those atoms that contribute significantly to the Mulliken charge. The atoms with large Mulliken charge are added into the orbital domain until the sum of the charges reach a threshold, denoted as w_1 ($0 \leq w_1 \leq 2.0$). Secondly, we use this orbital domain to expand a ULMO $|a\rangle$:

$$|a'\rangle = \sum_{\mu \in [i]} C'_{a\mu} |\mu\rangle \quad (12)$$

The expansion coefficients are determined by minimizing the functional f^{59} :

$$f(C') = \langle a - a' | a - a' \rangle = \sum_{\mu, \nu} (C_{a\mu} - C'_{a\mu})(C_{a\nu} - C'_{a\nu}) S_{\mu\nu} \quad (13)$$

Minimizing the above functional, one can obtain linear equations for $C'_{a\mu}$ as follows:

$$\sum_{\nu \in [i]} S_{\mu\nu} C'_{a\nu} = \sum_{\sigma} S_{\mu\sigma} C_{a\sigma} \quad (14)$$

Then the minimum of $f(C')$ is calculated. If the minimum is less than a given criterion, denoted as w_2 , then the ULMO $|a\rangle$ is considered to be important for LMO $|i\rangle$ and is eventually kept as a correlation orbital for $|i\rangle$, and it is included eventually in a set denoted as $[I]$. Once all the ULMOs have been checked out and the domains for all the occupied LMOs are constructed, one starts to build orbital domains for LMO pairs $[IJ]$. This is simply done by assuming $[IJ]$ is the union of $[I]$ and $[J]$, or alternatively, one first constructs $[ij]$ as the union of $[i]$ and $[j]$, and then $[IJ]$ s are constructed.

Local Correlation in CCSD

After all the $[I]$'s and $[IJ]$'s are obtained, we can solve eq. (7). The CCSD amplitudes t_i^a and t_{ij}^{ab} equations are solved only for the locally correlated pairs of orbitals. Namely, $t_i^a = 0$, if $a \notin [I]$, and $t_{ij}^{ab} = 0$ if $a, b \notin [IJ]$.

The CCSD correlation energy is now expressed as follows:

$$E_{CC}^{corr} = 2 \sum_{a \in [I]} t_i^a f_{ia} + \sum_{a, b \in [IJ]} (t_{ij}^{ab} + t_i^a t_j^b) L_{iajb}, \quad (L_{iajb} = 2(i a | j b) - (i b | j a)) \quad (15)$$

Further reduction of computational costs can be achieved through the following procedure suggested by Li et al.²⁵ Defining a quantity:

$$\Omega(i, j) = (C_{\nu}^i C'_{\nu}^j S_{\mu\nu})^2 \quad (16)$$

If $\Omega(i, j)$ is less than a given threshold, denoted by w_3 , then the pair (i, j) are considered to be unimportant and all the relevant t_{ij}^{ab} are set to be zero.

Computational Details

We take polyenes $C_{2n}H_{2n+2}$ as example. The PPP parameters are: $b_1 = 1.48 \text{ \AA}$ and transfer integral $t_1 = -2.2 \text{ eV}$ for single bond; $b_2 = 1.35 \text{ \AA}$ and -2.6 eV for double bond. The on-site repulsion for π -orbital is $U = 11.13 \text{ eV}$ and the Ohno-Klopman parameterization for Coulomb integrals is $V_{\mu\nu} = 14.397 \times (1.673 + r_{\mu\nu}^2)^{-1/2}$. The electric field F is included by adding an additional term: $-eFx_{\mu}$ to the diagonal Fock matrix elements: the electric field is assumed to be along the chain direction. The e is the electron charge and x_{μ} is the position of μ -th atom. The longitudinal polarizability is evaluated at zero electric field by numerical derivations of total energies with respect to the electric field strength:

$$\alpha = \left(\frac{\partial^2 E}{\partial F^2} \right)_{F=0} = - \frac{E(\delta F) + E(-\delta F) - 2E(0)}{(\delta F)^2} \quad (17)$$

The values of electric field are chosen to be $0, \pm 4 \times 10^{-4} \text{ a.u.}$ for the purpose of finite differentiation calculations. The direct inversion in the iterative subspace (DIIS) method is employed both in SCF and CCSD iterations⁶²⁻⁶⁴ to improve the convergence of the nonlinear iterations.

Results and Discussions

For all the molecules studied here, we find that each LMO is typically localized within one double bond. That is, there are only two atomic orbitals contribute much more than others to LMO. This makes the local correlation approach highly efficient. The number of important atoms for a given occupied LMO is typically less than 10. The numbers of virtual LMOs included in all $[IJ]$ is usually less than 23 for all the systems studied here.

We first discuss the threshold parameters w_1 , w_2 , and w_3 , which are key to make a balance between accuracy and efficiency. The optimal set with $w_1 = 1.998$, $w_2 = 10^{-4}$, $w_3 = 10^{-6}$ are found to satisfy the requirements for the computational cost reduction and the precision of the numerical differentiation with respect to the electric field strength. We give in Table 1 the comparison of thresholds vs. the number of double excitation

Table 1. The Number of Amplitude Coefficients to be Optimized and the Corresponding Correlation Energy Obtained by LCCSD for Polyene $C_{30}H_{32}$ for Different Threshold Cutoffs.

N_{loc}	$-E_{loc}$ (eV)	w_1	w_2	w_3
13,465	4.2659	1.9998	1.0d-4	1.0d-6
10,343	4.2658	1.998	1.0d-4	1.0d-6
8420	4.2654	1.98	1.0d-4	1.0d-6
6441	4.2634	1.98	1.0d-3	1.0d-6
5255	4.2546	1.998	1.0d-4	1.0d-4
4076	4.2542	1.98	1.0d-4	1.0d-4
2724	4.2211	1.998	1.0d-3	1.0d-3

The canonical coefficients number is 25,425 corresponding to a correlation energy $E_{corr} = -4.2663$ eV, to be compared with.

amplitudes to be optimized as well as the correlation energies for $C_{30}H_{32}$. Compared with double excitation amplitudes, the single excitation amplitudes do not cost much computational costs for evaluation. It is seen from the Table that the local approach works quite satisfactory. Namely, for all cases listed in the Table, more than 98% of correlation energy is retained. At the same time, the number of coefficients to be optimized is reduced from 25,425 to only 2724.

We then keep the optimal threshold parameters (w_s) and investigate the scalability of computational cost vs. the system size. The results are presented in Table 2. For the longest chain ($C_{100}H_{102}$) investigated here, the largest deviation is only 0.0026 eV, namely 0.02% for the correlation energy. The corresponding number of coefficients to be optimized is vastly reduced from 3.13×10^6 to 56,000 only. These results are also depicted in Figure 1. The canonical CCSD doubles coefficients scales as M^4 (M is a measure of the size of the system, e.g., the number of the double bonds), whereas for LCCSD it scales linearly as showed in the inset of Figure 1.

The comparison of the computational costs in CPU time for LCCSD and conventional CCSD are displayed in Figure 2. It is noted that even though the number of optimized amplitudes scales linearly with the system size, the CPU time does not scale linearly in the present LCCSD implementation. This is due to the iteration procedure for solving the LCCSD equation is not linearly scaled. Still, the CPU savings are very remarkable for long chain systems.

As a first application of the LCCSD, finite field method is used to obtain the numerical derivatives of the energies with

respect to electric field, and the derivatives at zero fields are calculated according to eq. (17).

We gather recently reported *ab initio* polarizabilities⁶⁵ and our results in Table 3. Polarizabilities (column B in CCSD/PPP part) obtained from the geometry given in part III are a bit less than the *ab initio* counterparts. The CCSD/PPP polarizabilities are improved (column A in CCSD/PPP part) when the same geometry as in *ab initio* calculations are taken (though still smaller than *ab initio* values: $\alpha_{PPP}/\alpha_{ab\text{initio}} = 0.66 \sim 0.78$). From the Table, it is obvious that the CCSD/PPP polarizabilities are seriously affected by the geometry. For example, Champagne et al. reported their MP2 polarizabilities for $C_{12}H_{14}$ and $C_{20}H_{22}$.⁶⁶ They obtained values of 357 and 778 a.u. in RHF/6-31G geometry with BLA (bond length alternation) = 0.112 Å, and 388 a.u. and 917 a.u. for B3LYP/6-311G* geometry with BLA = 0.065 Å, respectively, see Table 3. The difference between PPP model and the *ab initio* is understood that PPP parameters adopted here were obtained mostly through spectroscopy, not based on total energy geometry optimization. The finite-field approach is based on total energy. It is thus not surprised to find such 20–30% deviation.

In Figure 3 we compare polarizabilities per unit cell (only correlation contribution considered here) calculated by CCSD and LCCSD. It is clearly seen that LCCSD reproduces almost the same results as the CCSD. And LCCSD can be extended for much larger system. One can also find in Figure 3 that the polarizability obtained by LCCSD is discontinuous for some systems, e.g., systems with 35, 54, 77 unit cells. We owe this discontinuity to numerical instability, because the second order derivative of energy with respect to the field requires rather high precision.

We finally assess the role of electron correlation from LCCSD calculations by extracting the Hartree-Fock contribution, see Figure 4. It is found that electron correlation always contributes negatively. For example, for chain length of 78 unit cells ($C_{156}H_{158}$), the Hartree-Fock result is 113.2 a.u., and the correlation contribution is -47.2 a.u., making the final result to be 66 a.u. This is in sharp contradictory to the general result calculated from DFT, which in general gave the polarizability value much larger than Hartree-Fock,⁵⁰ namely, the electron correlation contributes positively to polarizability from DFT.

A final remark should be made on the comparison between local approaches between *ab initio* and semi-empirical model. In the state-of-the-art *ab initio* local CCSD approach,²³ several more techniques have been employed such as matrix sparsity, classifications of spatial domains for two-electron terms as well

Table 2. Comparison of LCCSD (N_{loc} , E_{loc}) with Canonical CCSD (N , E) for the Number of Optimized Double Excitation Coefficients and the Correlation Energies, for Elongating the Chain Lengths (with the Optimal Parameters: $w_1 = 1.998$, $w_2 = 1.0d-4$, $w_3 = 1.0d-6$).

Systems	$C_{30}H_{32}$	$C_{40}H_{42}$	$C_{50}H_{52}$	$C_{60}H_{62}$	$C_{70}H_{72}$	$C_{80}H_{82}$	$C_{90}H_{92}$	$C_{100}H_{102}$
N_{loc}	10,343	17,066	23,791	30,516	37,241	43,966	50,691	57,416
$-E_{loc}$ (eV)	4.2658	5.6924	7.1189	8.5454	9.9720	11.3985	12.8250	14.2515
N	25,425	80,200	1.96E5	4.05E5	7.51E5	1.28E6	2.05E6	3.13E6
$-E$ (eV)	4.2663	5.6931	7.1199	8.5468	9.9736	11.4004	12.8272	14.2541

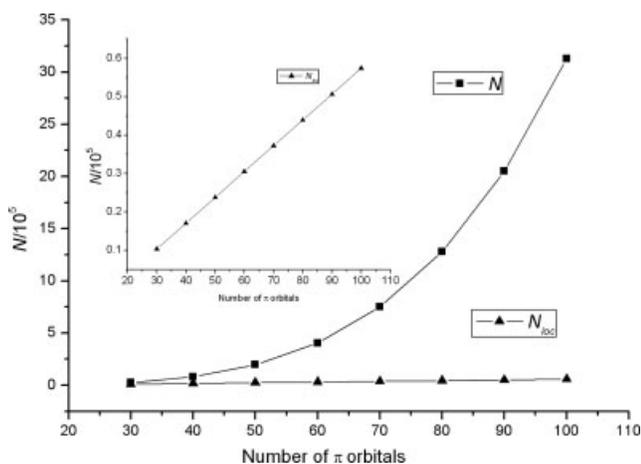


Figure 1. Numbers of the doubles coefficients required to be optimized versus the system size for LCCSD and CCSD. The inset plot is enlarged for LCCSD. N_{loc} and N are the double coefficient number for LCCSD and canonical CCSD, respectively.

as the direct integral transformation for two-electron integrals, which eventually result in a linear scaling, as shown in the example of $(\text{Gly})_n$. We note that Schutz and Werner concluded that their approach does not work well for conjugated system.²³ In our work, we only applied the local MOs for the study of scalability. Even though the method is not fully linear scaling, tremendous computational costs have been reduced. Most interestingly, we find that the local MO scheme works quite well for conjugated system, especially for very long conjugated polyenes, the accuracy is found to be very satisfactory, since the evaluation of finite field is very accuracy-demanding. We conjectured that maybe it is the further approximations beyond the bare local treatments worsen the accuracy for conjugated systems. This deserves further more careful studies.

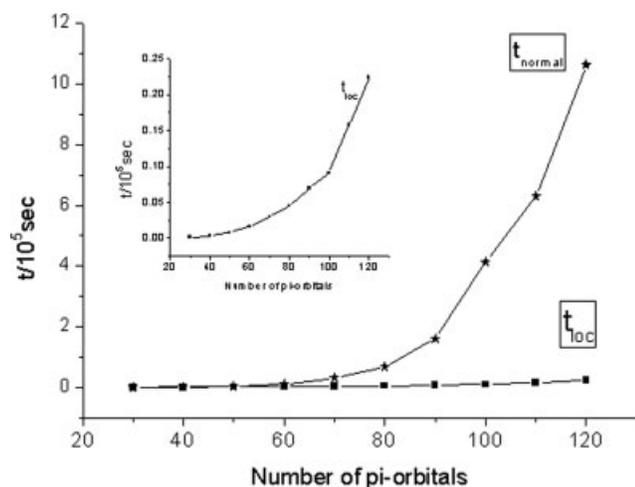


Figure 2. CPU time consumption versus system size: t_{normal} is for canonical CCSD calculations and t_{loc} is for LCCSD.

Table 3. Longitudinal Polarizabilities of Polyenic Systems (in a.u.).

N	MP2 ^a	CCSD ^a	CCSD/PPP	
			A ^b	B ^c
2	72.07 (66.41)	70.38 (64.47)	46.35 (50.94)	41.21 (41.53)
3	138.48 (88.36)	134.85 (80.17)	97.30 (65.80)	82.74 (50.75)
4	226.84 (109.46)	215.02 (98.06)	163.10 (77.51)	133.49 (57.07)
5	336.30 (127.98)	313.08 (108.19)	240.60 (86.21)	190.56 (61.20)
6	464.28 (186.29)	421.27 (/)	326.81 (92.36)	251.76 (63.83)
10	1128.3 (/)		715.37 (101.44)	514.86 (67.15)

Experimental value for C_4H_6 is 58.31 a.u. ref. [65]. N is the number of unit cells, $\Delta\alpha_N = \alpha_{N+1} - \alpha_N$ are given in parentheses.

^aReference 66.

^bObtained by our method with geometry used in ref. 67, and the related PPP parameters are $b_1 = 1.428 \text{ \AA}$, $t_1 = -2.500 \text{ eV}$, $b_2 = 363 \text{ \AA}$, $t_2 = -2.709 \text{ eV}$; $U = 11.13 \text{ eV}$.

^cResults reported in this study.

Conclusions

To conclude, a local correlation approach combined with semi-empirical Hamiltonian is implemented in the framework of CCSD/PPP, which was shown to be highly efficient and accurate for conjugated molecules. Much lower scaling for CPU costs has been achieved. The test calculations have been performed to evaluate the polarizability as a function of chain length. It is found that (i) LCCSD gives almost the same results as the canonical CCSD for all the molecular sizes; (ii) the local correlation approach works very well even for conjugated systems; and (iii) the electron correlation plays an essential role in determin-

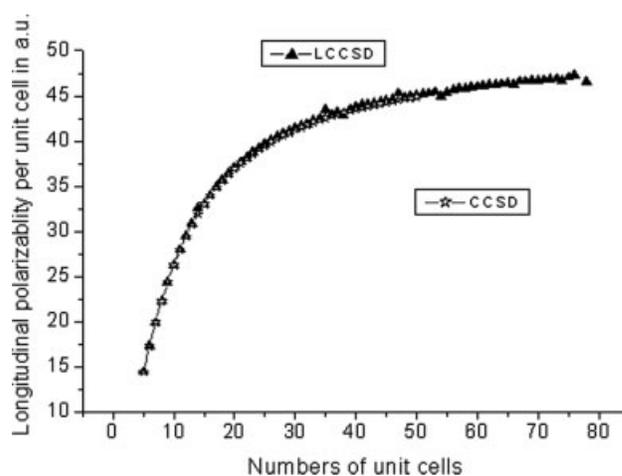


Figure 3. Correlation contributions to longitudinal polarizabilities per unit cell (absolute amplitudes are given here) for polyenes: comparisons between CCSD and LCCSD results. CCSD calculations are carried out up to 50 unit cells.

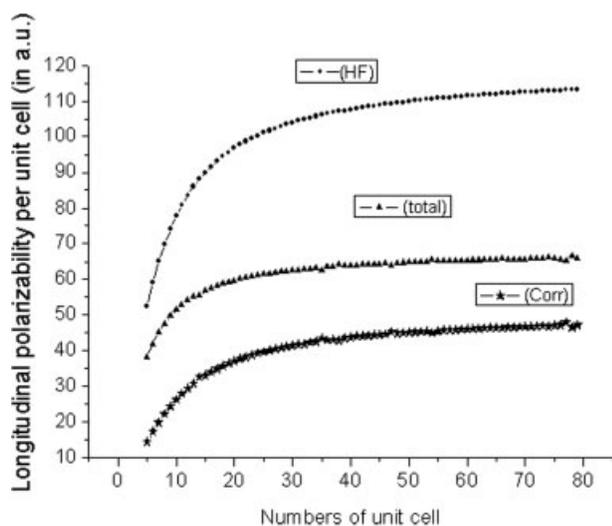


Figure 4. Longitudinal polarizabilities per unit cell calculated by LCCSD. (Electron correlation contributions are given in absolute value and denoted as Corr in the figure).

ing the molecular electronic polarizability and it tends to reduce the polarizability, in sharp contrast to DFT.

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