



Local configuration interaction single excitation approach: Application to singlet and triplet excited states structure for conjugated chains

Qingxu Li, Qikai Li, Zhigang Shuai*

Key Laboratory of Organic Solids, Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences, 100080 Beijing, China

ARTICLE INFO

Article history:

Received 1 February 2008

Received in revised form 7 February 2008

Accepted 8 February 2008

Available online 24 March 2008

Keywords:

Local configuration interaction

Excited states structure

Conjugated polymers

Singlet and triplet splittings

ABSTRACT

A local configuration interaction single (LCIS) excitations approach is implemented and applied to investigate the electronic excited states of extended conjugated polyenes up to 400 carbons within the semi-empirical Pariser–Parr–Pople (PPP) model. Numerical results show that the LCIS approach can reproduce well the canonical CIS results with much less computational costs. The dimension of the Hamiltonian matrix scales linearly in LCIS approach, comparing to quadratic scaling with canonical orbitals. Calculations for the lowest singlet excitation energy and the singlet–triplet splittings up to system with 400 carbons are demonstrated to saturate at about 100 carbons for polyene chain.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Understanding excited state structures of the conjugated systems is of great interest in organic electronics and photonics. There exist several quantum chemical tools for the treatment of the electronic excited states. The wave function-based tools include: single- or multi-reference configuration interaction (CI or MRCI), multi-reference perturbation theory (MRMP), multi-configuration self-consistent field (MCSCF) method, etc. Highly correlated equation-of-motion and linear-response coupled cluster (EOM-CC and LR-CC, respectively) [1–8] (or closely related symmetry-adapted cluster configuration interaction (SACCI) approach [9–13]) and density matrix renormalization approach (DMRG) [14] and its quantum chemistry realizations [15–19] have been used to investigate the nature of excited states. These are always found to be inadequate for extended conjugated systems at the first-principle level due to the huge computational costs.

In fact, time-dependent density functional theory (TDDFT) [20–22], CIS [23–26] and random-phase approximation (RPA) [27] are mostly applied due to computational considerations in this case. So far, DFT-based methods are found to fail to describe the charge localization versus delocalization situation: for extended system, either for long conjugated molecules or for molecular aggregates, the excited charges are always too much delocalized [22]. In studying the opto-electronic properties of conjugated polymers, the

charge separation characters are of great importance. For example, in the study of the exciton binding energies of conjugated polymer, which are generally believed to be around 0.5 eV [16], many commonly used functionals would give negative values [28]. The exciton binding energy characterizes the extent to which the electron and hole bound in the lowest excited state. This quantity is important for light-emitting and photovoltaic responses. Negative binding energy implies that the electron and hole interaction tends to be repulsive, which is nonphysical. Even for the well-studied small to medium-sized organic covalently bonded molecules, for calculating the lowest excited optically allowed state, Hutchison et al. found that ZINDO/CIS outperforms many first-principle methods for a set of 60 commonly found conjugated molecules, the mean-squared deviation between the calculations and the experiments for the first optically allowed state is ~ 0.35 eV for ZINDO/CIS and >0.5 eV for TDDFT [29]. Note that the charge delocalization problem of DFT is not present here. Thus, as far as excited state is concerned, post-Hartree–Fock can still play a role in a DFT-dominated quantum chemistry world.

As a simple and facile quantum chemical method that incorporated electron correlation, CIS is very useful to study the lowest-lying excited state structures [30–35]. Meanwhile, local correlation approach [36,37] developed earlier proves to be powerful to reproduce similarly accurate results of the corresponding canonical calculations with much less computational costs. Moreover, local CIS has been used as a starting point for local EOM-CC [38–40]. Saebø and Pulay reported their local CI approach [41,42]. Very recently, the fragmented orbital CIS, which is based on dividing molecule into fragments, has achieved great suc-

* Corresponding author. Tel.: +86 10 62521934; fax: +86 10 62525573.
E-mail address: zgshuai@iccas.ac.cn (Z. Shuai).

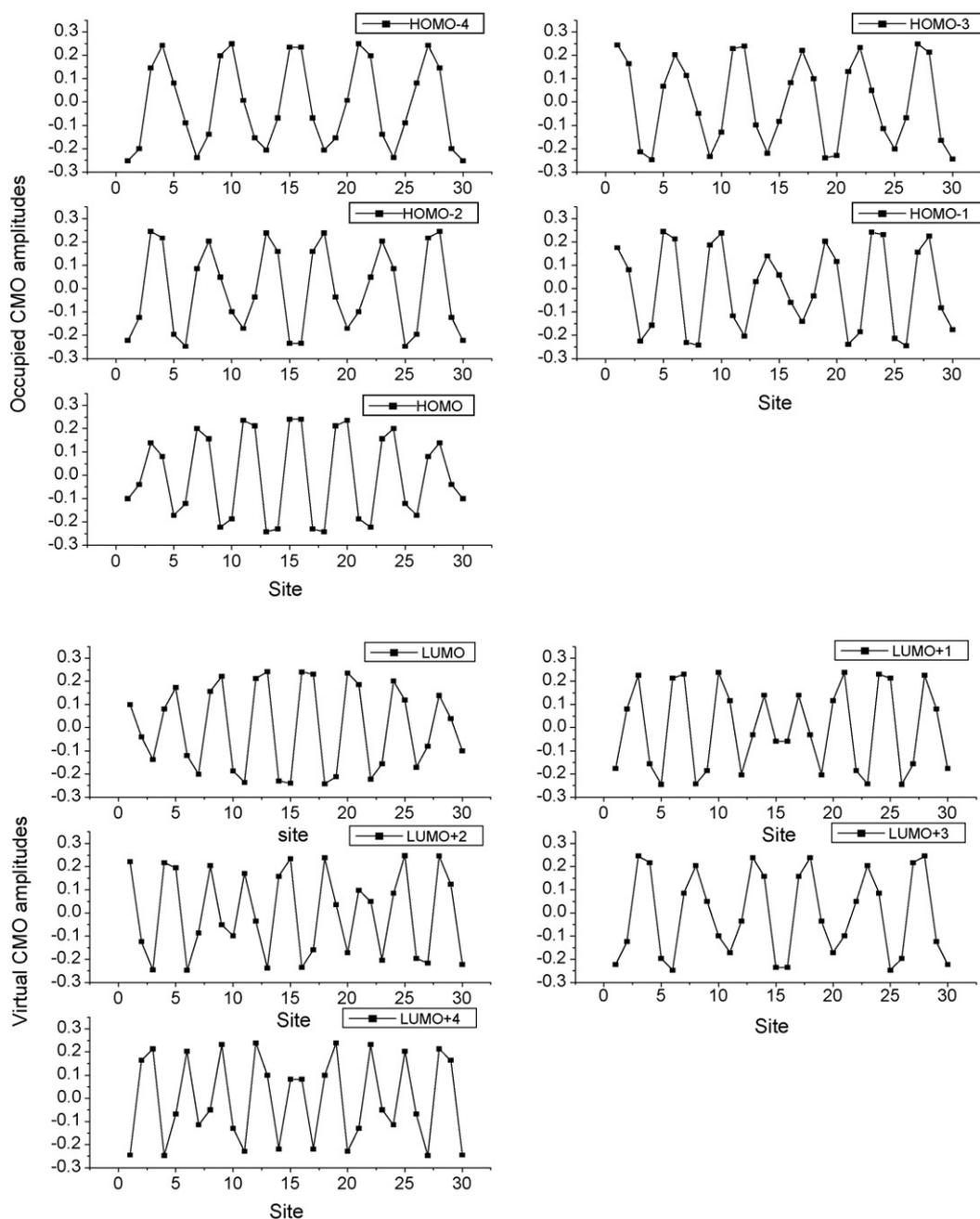


Fig. 1. Canonical molecular orbital wavefunction amplitude for $C_{30}H_{32}$.

cess [43,30,44,45]. This approach is closely related to but still different with the local configuration interaction single (LCIS) excitations. Both of them can handle the lowest-lying excited states for very large molecules. The motivation of this work is to implement the LCIS approach as developed by Sæbø and Pulay in the context of conjugated polymers to study the excited state structure, in particular, to look at how the lowest singlet and triplet excited states evolve and saturate with the polyene chain length.

2. Methodological approach

We choose Pariser–Parr–Pople model to model the conjugated linear chain systems in this study. The Hamiltonian in the

Pariser–Parr–Pople (PPP) model can be expressed as

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

Here $\langle ij \rangle$ means the summation for chemical bonds, $C_{i,\sigma} (C_{i,\sigma}^\dagger)$ is the annihilation (creation) operator for electron, $n_{i\uparrow} = C_{i\uparrow}^\dagger C_{i\uparrow}$ is the particle number operator, and V_{ij} is the parameterized Coulombic potential. At the Hartree–Fock self-consistent field (SCF) level, one can obtain the one-particle Fock operator matrix as

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

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

Table 1

Ratio of the LCIS dimension (N_{loc}) with respect to the full CIS dimension (N) and the LCIS deviations for the calculated lowest three excited state energies, as a function of cut-off parameters for $C_{100}H_{102}$

N_{loc}/N	1st (δE^{ex})	2nd (δE^{ex})	3rd (δE^{ex})	w_1	w_2
0.1352	0.1733	0.1665	0.1567	0.99	10^{-3}
0.1724	0.0665	0.0635	0.0588	0.999	10^{-3}
0.2424	0.0102	0.0096	0.0085	0.999	10^{-4}
0.2776	0.0040	0.0036	0.0030	0.9999	10^{-4}
1	0	0	0	1.0	0

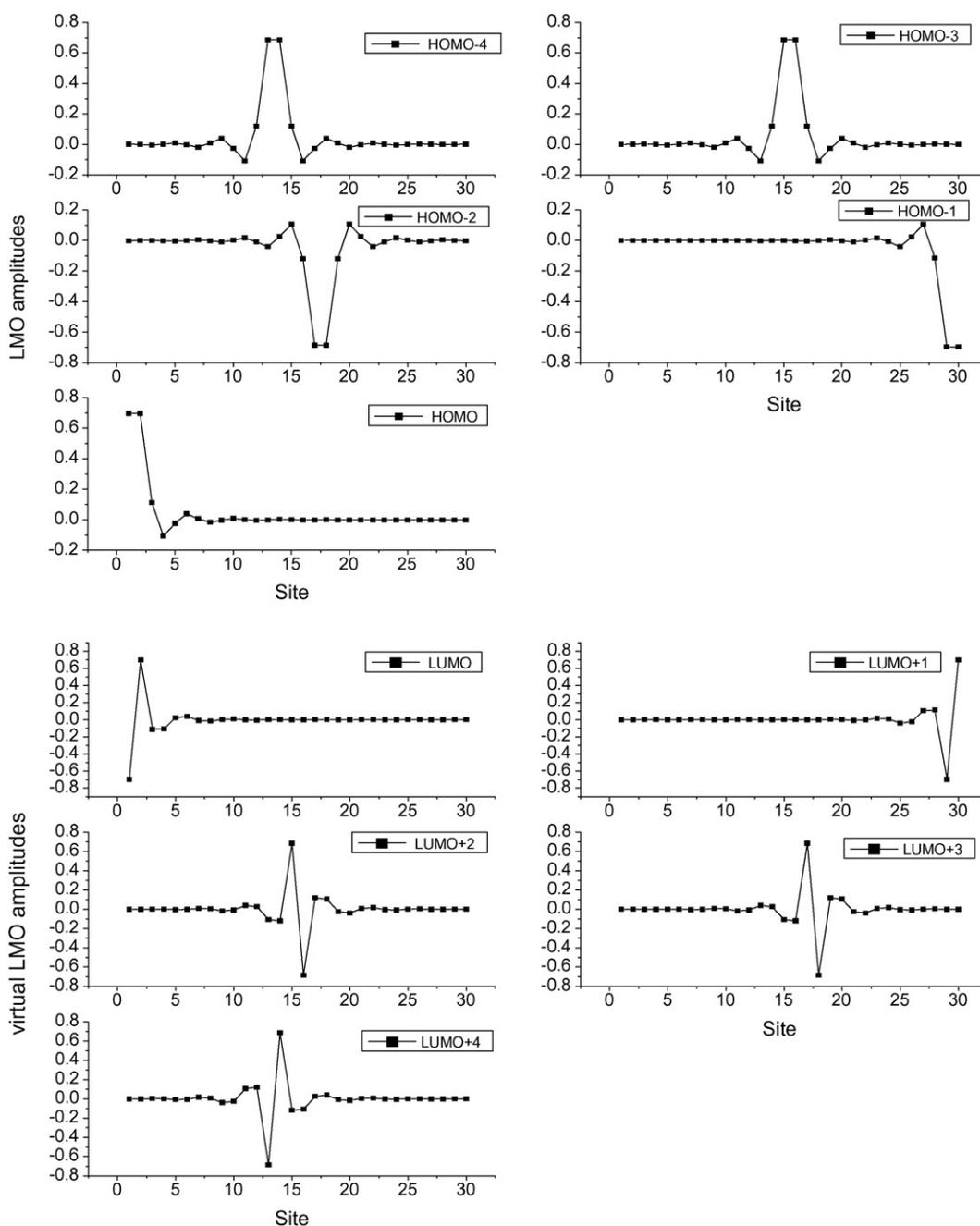
Here $P_{\mu\nu}$ is the density matrix, $t_{\mu\nu}$ is the transfer integral, and U_{μ} is the on-site repulsion Coulomb integral.

The LCIS consists of the following steps: first, a conventional SCF calculation is performed to get conventional canonical molecular orbitals (CMOs). Then the population localization scheme of

Pipek and Mezey is applied to obtain localized occupied and virtual molecular orbitals (LMOs) [46]. After that, the local correlation approach is used to select important virtual LMOs for each occupied LMO. For a given occupied LMOs i , the chosen virtual “important” LMO set is denoted as $[I]$. $[I]$ can be considered as the correlation space of the occupied LMO i . Then single excitation configuration from occupied orbital i is only allowed to $[I]$, instead of running over all the virtual orbitals. Doing this can tremendously reduce the number of configurations.

The canonical molecular orbital $|p\rangle$ is expressed as a linear combination of atomic orbitals (LCAO) $|p\rangle = \sum_{\mu} C_{p\mu}|\mu\rangle$. The LMOs are obtained by consecutive two by two orbital rotations of the form:

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

**Fig. 2.** Localized molecular orbitals for $C_{30}H_{32}$.

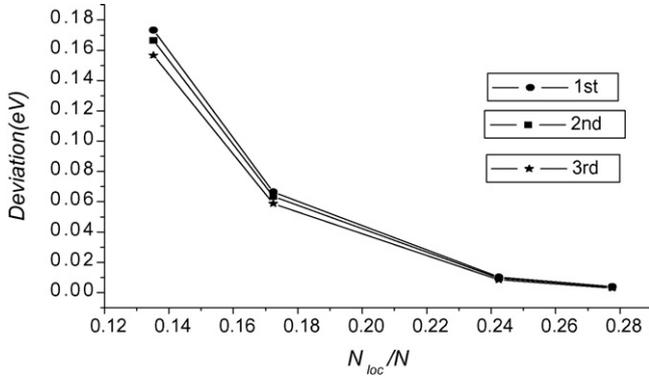


Fig. 3. Deviations (in eV) of the lowest three excited state energies from LCIS to conventional CIS as a function of the ratio of LCIS dimensions with respect to the full dimension.

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

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

and A_{pq} , B_{pq} are defined as

$$A_{pq} = \sum_A \left\{ (P_A)_{pq}^2 - \frac{1}{4} [(P_A)_{pp}^2 - (P_A)_{qq}^2] \right\},$$

$$B_{pq} = \sum_A (P_A)_{pq} [(P_A)_{pp} - (P_A)_{qq}],$$

$$(P_A)_{pq} = \frac{1}{2} \sum_{\rho} \sum_{\mu \in A} [C_{p\rho}^* S_{\rho\mu} C_{q\mu} + C_{p\mu}^* S_{\mu\rho} C_{q\rho}] \quad (10)$$

Here, $S_{\rho\mu}$ is the overlap matrix and $C_{p\mu}$ is the expansion coefficient of μ th atomic orbital for the p th MO and the second summation is restricted to atomic orbitals belonging to atom A.

Zero differential overlap approximation is assumed for PPP model, and $(P_A)_{pq}$ can be simplified in this case as

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

Rotations between occupied and virtual MOs are frozen. So, localization procedure is done for occupied and virtual MOs separately. The final LMOs can be considered as consecutive unitary transformation from the original CMOs. Thus, the LMOs remain ortho-normal each other, just like CMOs: unitary transformation maps an ortho-normal basis to another ortho-normal basis. Once LMOs are obtained, they are re-ordered according to their diagonal Fock matrix elements.

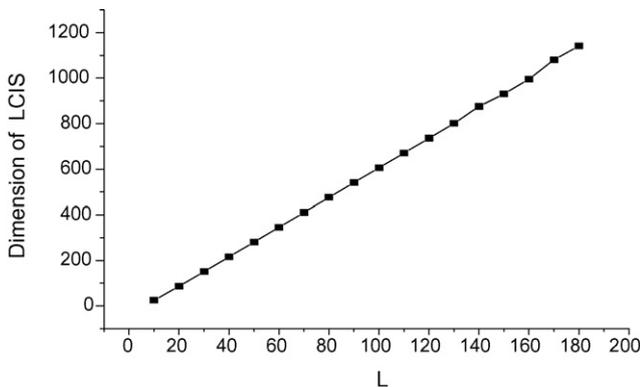


Fig. 4. Linear scaling of matrix dimension of LCIS with the chain length.

For each occupied LMO $|i\rangle$, we construct an “orbital domain” $[i]$. The Mulliken charge for each atom is calculated as $\sum_{\mu \in A} P_{\mu\nu} S_{\nu\mu}$. And

atoms are now re-ordered with descending Mulliken charge. The atoms with the largest Mulliken charge are added to the orbital domain $[i]$ until the sum of the charges reach a threshold, denoted as w_1 ($0 \leq w_1 \leq 1.0$) for pi-orbital only and without consideration of spin degeneracy). According to Hampel and Werner, these atoms along with their atomic orbitals can be used to construct the correlation virtual LMO [47]. Thus, we use this orbital domain $[i]$ to expand any virtual LMO $|a\rangle$:

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

The expansion coefficient C_s are determined by minimizing the functional suggested by Boughton and Pulay [37]:

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

Minimizing above functional by variation technique, one can obtain linear equations for $C'_{a\mu}$:

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

Then the minimum of $f(C')$ is computed. If the minimum is less than a given parameter, denoted as w_2 , the virtual LMO $|a\rangle$ is believed to be “important” for the occupied LMO $|i\rangle$ and is eventually selected as “correlation orbitals” for $|i\rangle$, and is included/appended to orbital set $[I]$.

For CIS approach, the CIS wave functions for singlet and triplet are expressed as

$$|\text{CIS}\rangle_S = \frac{1}{\sqrt{2}} C_i^a E_{ai} |0\rangle, \quad E_{ai} = a_{\uparrow}^+ i_{\uparrow} + a_{\downarrow}^+ i_{\downarrow}$$

$$|\text{CIS}\rangle_T = \frac{1}{\sqrt{2}} C_i^a E_{ai}^- |0\rangle, \quad E_{ai}^- = a_{\uparrow}^+ i_{\uparrow} - a_{\downarrow}^+ i_{\downarrow}$$

and the Hamiltonian matrix elements in this CIS configuration space are

$$(H)_{ia,jb}^S = \frac{1}{2} \langle E_{ia} E_{bj} \rangle = \delta_{iajb} E_{\text{HF}} + \delta_{ijfb} - \delta_{abfj} + L_{aijb}$$

$$(H)_{ia,jb}^T = \frac{1}{2} \langle E_{ia}^- E_{bj}^- \rangle = \delta_{iajb} E_{\text{HF}} + \delta_{ijfb} - \delta_{abfj} - g_{ijab}$$

where

$$g_{ijab} = (ij|ab) = \int d\vec{r}_1 d\vec{r}_2 \varphi_i^*(\vec{r}_1) \varphi_j(\vec{r}_1) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \varphi_a^*(\vec{r}_2) \varphi_b(\vec{r}_2)$$

and $L_{aijb} = 2g_{aijb} - g_{ijab}$. Here the superscript S(T) corresponds to singlet(triplet) case. Throughout this paper, i, j , etc. are used for occupied orbitals and a, b , etc. for virtual ones. To get CIS excited states energies and wave functions, one can either fully diagonalize the CIS Hamiltonian Matrix of dimension $N_{\text{occ}} \times N_{\text{vir}}$ (N_{occ} and N_{vir} are the number of the occupied and virtual orbitals, respectively) if full spectra are needed, or use the iterative Davidson technique to obtain a few low-lying excited states [48]. For LCIS, the wave function is defined as:

$$|\text{LCIS}\rangle_S = \frac{1}{\sqrt{2}} \sum_i \sum_{a \in [I]} C_i^a E_{ai} |0\rangle$$

$$|\text{LCIS}\rangle_T = \frac{1}{\sqrt{2}} \sum_i \sum_{a \in [I]} C_i^a E_{ai}^- |0\rangle$$

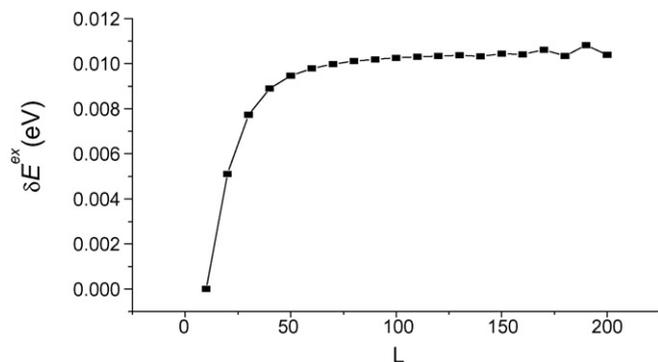


Fig. 5. Evolution of the truncation errors (the difference between the local CIS and canonical CIS) for the lowest excitation energies (δE^{ex}) for $10 \leq N \leq 200$.

The corresponding reduced Hilbert space dimensional is

$$d = \sum_i d_i$$

Here d_i is the number of the important virtual LMOs for occupied LMOs i . For d_i is always much less than N_{vir} , and is independent on system size. Thus, the computational costs can be reduced tremendously in this local correlation approach.

3. Computational details and results

As an example of applying this LCIS implementation, we study the lowest-lying singlet and triplet excited state for the prototypical-conjugated polymer, the polyacetylene chain. The parameters of PPP model for polyene are for single bond, bond length $b_1 = 1.45 \text{ \AA}$ and transfer integral $t_1 = -2.26 \text{ eV}$; for double bond, $b_2 = 1.35 \text{ \AA}$ and $t_2 = -2.58 \text{ eV}$, and the angle between the neighboring single bond and double bond is fixed at 120° . The on-site repulsion for pi-orbital is $U = 11.13 \text{ eV}$ and the Ohno-Klopman parameterization for Coulomb integrals is used: $V_{\mu\nu} = 14.397(1.673 + r_{\mu\nu}^2)^{-1/2}$.

For the sake of clarity, we give orbital contours plots for both CMO (Fig. 1) and LMO (Fig. 2) for trans-polyene $\text{C}_{30}\text{H}_{32}$. It is seen that the CMOs extend for the whole chain while LMOs are typically localized within one covalent bond. Note that there are two important cut-off parameters in the LCIS approach, namely, the Mulliken charge criterion w_1 and the minimum of functional Eq. (13) w_2 . This pair of values controls the balance between accuracy and efficiency. In fact, in all the local approaches, cut-off control is the central issue [49]. In Table 1, we made a comparative test on the cut-off and accuracy for $\text{C}_{100}\text{H}_{102}$. The conventional CIS result is given in the last

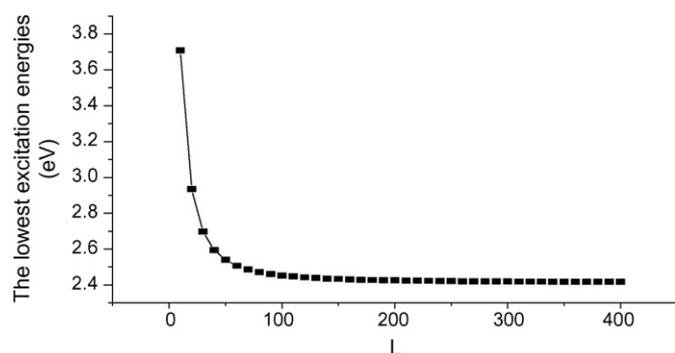


Fig. 6. The lowest singlet excitation energies (E^{ex}) as calculated by LCIS for ($10 \leq N \leq 400$).

Table 2

The lowest excitation energies of polyenes: evolution with conjugated chain length

L	Dim	E (eV)	ΔE
10	25	3.7089	0
20	86	2.9353	0.0051
30	151	2.6980	0.0077
40	216	2.5946	0.0089
50	281	2.5399	0.0095
60	346	2.5073	0.0098
70	411	2.4862	0.0100
80	476	2.4716	0.0101
90	541	2.4611	0.0102
100	606	2.4534	0.0103
110	671	2.4474	0.0103
120	736	2.4427	0.0104
130	801	2.4389	0.0103
140	876	2.4358	0.0104
150	931	2.4334	0.0104
160	996	2.4312	0.0106
170	1081	2.4296	0.0106
180	1142	2.4278	0.0104

L, Dim and E are the chain length (sites), dimension of the LCIS matrix, and the lowest excitation energies from LCIS calculations, respectively. $\Delta E = E - E_{\text{cmo}}$ is the difference between the energies obtained by LCIS (E) and the canonical CIS (E_{cmo}).

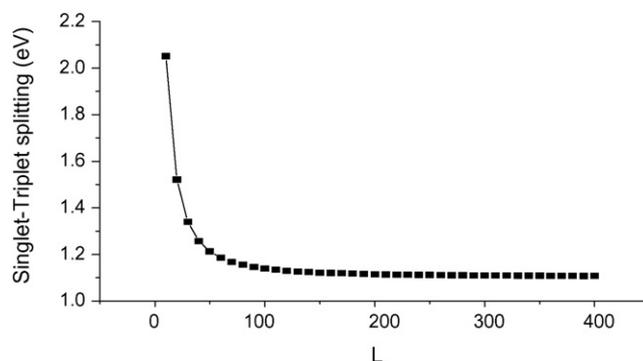


Fig. 7. Local CIS calculated exchange energy (gap between the lowest singlet and triplet) for ($10 \leq N \leq 400$).

row. We find that the choice of $w_1 = 0.999$ and $w_2 = 10^{-4}$ is quite satisfactory and is adopted for the subsequent application.

We plot in Fig. 3 the difference for the lowest three excitation energies between CIS and LCIS as a function of the ratio of LCIS dimension with respect to the full CIS dimension. It is seen that deviation as small as 0.004 eV is obtained with only about a quarter of full dimension of Hamiltonian matrix. Table 2 offers a more detailed comparison between LCIS and the canonical CIS approaches for different chain lengths at fixed cut-off ($w_1 = 0.999$, $w_2 = 10^{-4}$). Traditional CIS Hamiltonian is of a quadratic scaling for the dimension, while the local CIS dimension scales linearly, as shown in Fig. 4. From Table 2, the error introduced by the local correlation in the order of 0.01 eV, and the evolution of the deviation with chain length is plotted in Fig. 5.

Thus, we have shown that LCIS can reproduce well the canonical CIS results. We have computed the lowest singlet excitation energy and the lowest singlet-triplet gap for ($N \leq 400$)-site trans-polyenes with LCIS approach, see Figs. 6 and 7, respectively. It is found that both quantities approach the polymer limit at $N \sim 100$.

4. Summary

We have implemented a local CIS approach in combined with semi-empirical PPP model, and applied it to study the excited state properties of the conjugated polyenes. The balance of accuracy

and efficiency can be well tailored by the cut-off parameter w_1 and w_2 . We find that for long polyene, the optimal parameters are $w_1 = 0.999$ and $w_2 = 10^{-4}$. It is found that LCIS is a linear scaling approach with high efficiency and accuracy. Tremendous computational costs can be reduced. The lowest excited energies and the singlet–triplet splittings and their evolution with the chain length are reported and we found that these values saturate at about 100 carbons.

Acknowledgements

This work is supported by NSFC (grant Nos. 10425420 and 20433070) and the Chinese Academy of Sciences.

References

- [1] J. Geertsen, M. Rittby, R.J. Bartlett, *Chem. Phys. Lett.* 164 (1989) 57.
- [2] J.F. Stanton, R.J. Bartlett, *J. Chem. Phys.* 98 (1993) 7029.
- [3] D.C. Comeau, R.J. Bartlett, *Chem. Phys. Lett.* 297 (1993) 414.
- [4] R.J. Rico, T.J. Lee, M. Head-Gordon, *Chem. Phys. Lett.* 218 (1994) 139.
- [5] H. Koch, P. Jorgensen, *J. Chem. Phys.* 93 (1990) 3333.
- [6] H. Koch, H.J. Jensen, P. Jorgensen, T. Helgaker, *J. Chem. Phys.* 93 (1990) 3345.
- [7] R.J. Rico, M. Head-Gordon, *Chem. Phys. Lett.* 213 (1993) 224.
- [8] H.J. Monkhorst, *Int. J. Quantum Chem.* 11 (1977) 421.
- [9] H. Nakatsuji, *Chem. Phys. Lett.* 59 (1978) 362.
- [10] H. Nakatsuji, *Chem. Phys. Lett.* 67 (1979) 329.
- [11] H. Nakatsuji, K. Hirao, *J. Chem. Phys.* 68 (1978) 2053.
- [12] H. Nakatsuji, K. Hirao, *J. Chem. Phys.* 68 (1978) 4279.
- [13] H. Nakatsuji, *Int. J. Quantum Chem.* 17 (1983) 241.
- [14] S.R. White, R.M. Noack, *Phys. Rev. Lett.* 68 (1992) 348.
- [15] Z. Shuai, J.L. Brédas, S.K. Pati, S. Ramasesha, *Proc. SPIE* 3145 (1997) 293.
- [16] Z. Shuai, S.K. Pati, W.P. Su, S. Ramasesha, J.L. Brédas, *Phys. Rev. B* 55 (1997) 15368.
- [17] D. Yaron, E.E. Moore, Z. Shuai, J.L. Brédas, *J. Chem. Phys.* 108 (1998) 7451.
- [18] J. Hachmann, W. Cardoen, G.K.L. Chan, *J. Chem. Phys.* 125 (2006) 144101.
- [19] S. Ramasesha, S.K. Pati, H.R. Krishnamurthy, Z. Shuai, J.L. Brédas, *Phys. Rev. B* 54 (1996) 7598.
- [20] M.E. Casida, in: J.M. Seminario (Ed.), *Theoretical and Computational Chemistry*, vol. 4, Elsevier Science, Amsterdam, 1996.
- [21] M.A.L. Marques, C. Ullrich, F. Nogueira, A. Rubio, K. Burke, E.K.U. Gross (Eds.), *Time-dependent Density Functional Theory*, Lecture Notes in Physics, vol. 706, Springer, Berlin, 2006.
- [22] A. Dreuw, Martin Head-Gordon, *Chem. Rev.* 105 (2005) 4009.
- [23] J.B. Foresman, M. Head-Gordon, J.A. Pople, M. Frisch, *J. Phys. Chem.* 96 (1992) 135.
- [24] M. Head-Gordon, A.M. Grafiá, D. Maurice, C.A. White, *J. Phys. Chem.* 99 (1995) 14261.
- [25] A. Tomlinson, D. Yaron, *J. Comput. Chem.* 24 (2003) 1782.
- [26] J.L. Brédas, J. Cornil, D. Beljonne, D.A. Dos Santos, Z. Shuai, *Acc. Chem. Res.* 32 (1999) 267.
- [27] J. Oddershede, P. Jorgensen, D.L. Yeager, *Comput. Phys. Rep.* 2 (1984) 33.
- [28] (a) S. Tretiak, K.I. Igumenshchev, V.Y. Chernyak, *Phys. Rev. B* 71 (2005), 033201; (b) K.I. Igumenshchev, S. Tretiak, V.Y. Chernyak, *J. Chem. Phys.* 127 (2007) 114902.
- [29] G.R. Hutchison, M.A. Ratner, T.J. Marks, *J. Phys. Chem.* 106 (2002) 10596.
- [30] Y. Mochizuki, S. Koikegami, S. Amari, K. Segawa, K. Kitaura, T. Nakano, *Chem. Phys. Lett.* 406 (2005) 283.
- [31] S. Hirata, M. Head-Gordon, R.J. Bartlett, *J. Chem. Phys.* 111 (1999) 10774.
- [32] L. Meissner, *Mol. Phys.* 104 (2006) 2073.
- [33] I. Mayer, *Chem. Phys. Lett.* 437 (2007) 284.
- [34] Y.M. Rhee, M. Head-Gordon, *J. Phys. Chem. A* 111 (2007) 5314.
- [35] J.S. Sears, C.D. Sherrill, A.I. Krylov, *J. Chem. Phys.* 118 (2003) 9084.
- [36] S. Saebø, P. Pulay, *Ann. Rev. Phys. Chem.* 44 (1993) 213.
- [37] J.W. Boughton, P. Pulay, *J. Comput. Chem.* 14 (1993) 736.
- [38] T.D. Crawford, R.A. King, *Chem. Phys. Lett.* 366 (2002) 611.
- [39] T. Korona, H.J. Werner, *J. Chem. Phys.* 118 (2003) 3006.
- [40] Q. Li, Y. Yi, Z. Shuai, *J. Comput. Chem.* 29 (2008) 1650.
- [41] P. Pulay, *Chem. Phys. Lett.* 100 (1983) 151.
- [42] S. Saebø, P. Pulay, *Chem. Phys. Lett.* 113 (1985) 13.
- [43] M. Chiba, D.G. Fedorov, K. Kitaura, *J. Chem. Phys.* 127 (2007) 11.
- [44] Y. Mochizuki, Y. Komeiji, T. Ishikawa, T. Nakano, H. Yamataka, *Chem. Phys. Lett.* 437 (2007) 66.
- [45] D.G. Fedorov, K. Kitaura, *J. Phys. Chem. A* 111 (2007) 6904.
- [46] J. Pipek, P.G. Mezey, *J. Chem. Phys.* 90 (1989) 4916.
- [47] C. Hampel, H.J. Werner, *J. Chem. Phys.* 104 (1996) 6286.
- [48] E.R. Davidson, *J. Comput. Phys.* 17 (1987) 87.
- [49] B. Kirtman, C.E. Dykstra, *J. Chem. Phys.* 85 (1986) 2791.