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**π -Electron Calculations using the Local
Linear-Response Coupled-Cluster Singles and Doubles Theory**

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ABSTRACT: Calculations of electronic excitation energies, electron charge distribution, and optical parameters for π -conjugated oligomeric systems are carried out with a new local semi-empirical π -electron variant of the coupled clusters (CC) theory involving single and double excitations. The results obtained in the calculations demonstrate adequate accuracy of the proposed linear-response generalization of the local semi-empirical π -electron CC approach employing covalently non-bonded molecules of ethylene as the basis set in the calculation. Limit values corresponding to the infinite system size for the lowest excitation energies for polyenes and for condensed and non-condensed polyfulvenes are obtained.

Key words: local theory, CCSD method, FCI method, linear response theory, semi-empirical theory.

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1. INTRODUCTION

The coupled cluster theory (CC)¹⁻⁵ has been widely applied approach in various *ab initio* quantum chemistry calculations. The size-extensivity and accurate accounting for the correlation effects have allowed for successful applications of the CC theory in studies of chemical problems related to structures and properties of molecular systems in ground electronic states. The various applications have demonstrated the efficiency of the method in describing the chemical behavior of moderate size molecules. At present, most important approaches within the CC theory are implemented at the *ab initio* level. Among them there are the most frequently used CC approach termed CCSD that includes all single and double excitations from the reference single-determinant wave function^{4,5} and a series of renormalized CC methods of Piecuch *et al*⁶. The standard approach in the CC theory for calculating electronically excited states of a molecule is the equation-of-motion method (EOM-CC)⁷⁻¹⁰. The method which includes all single and double excitations and its various modifications have been implemented in almost all main quantum chemistry program packages such as GAMESS¹¹ and Gaussian¹² packages. Conceptually similar to the EOM-CC approach is the time-dependent linear-response theory (LR-CC) which is implemented in the TURBOMOLE package¹³. Close to the LR approach is also the symmetry adapted cluster configuration interaction (SAC-CI) method developed by Nakatsuji¹⁴ (see also ref 15).

Test *ab initio* calculations for small molecules performed with the EOM-CCSD method demonstrated high accuracy of the method for calculating excited states whose wave functions are dominated by single excitations from the Hartree-Fock determinant representing the ground state. However, practical applications of EOM-CCSD are limited by a significant computational cost that the calculations using this method entail. Moreover, to accurately calculate excited states, the choice of the basis set is of great importance. Usually, the use of augmented basis sets with polarization and diffuse functions is required. It should be noted that the modification of the EOM-CCSD method by an additional transformation of the wave-function termed STEOM-CCSD¹⁶ allows for carrying out calculations of electronic spectra of larger systems (e.g. porphyrins¹⁷).

An approach that has potential of significantly decreasing the computational cost of the EOM-CCSD calculations involves the idea of treating the electron correlation as a local phenomenon⁴. The first working version of the local approach was introduced in early 1980's by Pulay and Saebo^{18,19} (see also references to their earlier articles). A local CCSD *ab initio* method was first proposed by Hampel and Werner²⁰. Further applications of the approach revealed its high efficiency (e.g. see ref 21). An implementation of an appropriate version of the local EOM-CCSD method was described in^{22,23}. That development has enabled describing the electronic structure of a wide series of small- and medium-sized systems. However, calculations of polymeric strong-correlated systems, which are of interest due to their unique optical properties, especially quasi-one-dimensional systems, still remain out of reach for the *ab initio* EOM-CCSD method due to an enormous computational cost involved in such calculations.

To solve this problem we proposed a semi-empirical π -electron variant (Pople-Parriser-Parr Hamiltonian, PPP²⁴⁻²⁶) of the local CCSD theory. A method, which was developed for calculating lengthy π -conjugated polymeric systems²⁷⁻²⁹, employs π -orbitals of ethylene (CCSD approach with covalent non-bonded molecules of ethylene as the basis set; or *cue*-CCSD for short) to construct the CCSD wave function. The local *cue* orbitals are arranged to effectively describe the double-bond structure of the molecule. Test calculations showed that the *cue*-CCSD results depend little on the double-bond arrangement of the basis-set ethylenes used in the calculation even for such a sensitive property as the molecular hyperpolarizability. The *cue*-CCSD approach enabled to estimate the infinite-size limit values of the static dipole (hyper)polarizabilities for a series of π -conjugated polymers^{28,29}. In the present work a further

generalization of the *cue*-CCSD method for calculating electronic transitions energies is developed in the framework of the linear response theory (the method is termed *cue*-LR-CCSD).

2. CUE-CCSD SEMI-EMPIRICAL THEORY OF π -CONJUGATED SYSTEMS

The standard CCSD theory and its generalization to calculate electronic excited states are well described in the literature, therefore we restrict ourselves here to only providing the most important information of the formalism. The wave-function is represented in the method in the form of the so-called exponential ansatz:

$$|\Psi_{\text{CCSD}}\rangle = e^T|0\rangle = \left(1 + T + \frac{1}{2}T^2 + \frac{1}{6}T^3 + \frac{1}{24}T^4 + \dots\right)|0\rangle, \quad (1)$$

where operator T generates a superposition of single ($|i^a\rangle$) and double excitations ($|ij^{ab}\rangle$) relatively to reference determinant $|0\rangle$. Indices i, j and a, b denote occupied and vacant spin-orbitals, respectively. In the language of the second quantization (i.e. with the use of creation and annihilation operators a_a^+ and a_i) the T operator has the following representation:

$$T = T_1 + T_2 = \sum_i t_i^a a_a^+ a_i + \sum_{ij} t_{ij}^{ab} a_a^+ a_b^+ a_i a_j. \quad (2)$$

In the above equation amplitudes t_i^a and t_{ij}^{ab} characterize the contributions of the corresponding determinants to the wave function. The exponential representation of wave function (1) results in generating higher-level excitations such as the triple ($T_1 T_2, T_1^3$), the quadruple ($T_1^2 T_2, T_2^2, T_1^4$), etc., excitations as components of the wave function. These excitations not only enable to more accurately account for the electron correlation effects, but also make the wave function and the corresponding total energy size-extensive.^{2,5}

Equations for calculating the energy of the system and for determining amplitudes t_1 and t_2 are usually obtained by projecting the Schrödinger equation with wave function (1) onto determinants $\langle\psi|$ obtained by acting with the T_1 and T_2 operators on the reference determinant:

$$\langle\psi|H - E_{\text{CCSD}}|\Psi_{\text{CCSD}}\rangle_C = 0, \quad \langle\psi| = \langle 0|, \langle i^a|, \langle ij^{ab}|. \quad (3)$$

Symbol “C” in the expression (3) means that in the work equations only the “connected” components are included (the disconnected components cancel out).

Due to the exponential form of expansion (1), the contributions of excitations of different levels in the wave function include non-linear components. Thus the coefficient $C_{k\mu}$ that defines the contribution of the μ k -fold excited configuration $\langle(k)_\mu|$ to the wave function $\langle\psi_{\text{CC}}|$ can be obtained as:

$$C_{k\mu} = \langle(k)_\mu|\Psi_{\text{CCSD}}\rangle. \quad (4)$$

At the same time, the contribution of reference determinant $|0\rangle$ is set equal to unity (i.e. the so-called “intermediate” normalization of the wave function is assumed)

$$C_0 = W_0 = \langle 0|\Psi_{\text{CCSD}}\rangle = 1. \quad (5)$$

Thus, overall weight of the k -fold excitations (W_k) is:

$$W_k = \sum_{\mu} C_{k\mu}^2. \quad (6)$$

As shown³⁰ the weights of the higher excitations obtained in the CCSD method qualitatively reproduce the exact values obtained with the full configuration interaction method (FCI). As a consequence of the intermediate normalization, the sum of all weights can be used to characterize the degree of “reorganization” of the reference state:

$$\Sigma_w = \sum_k W_k. \quad (7)$$

In the local *cue*-CCSD theory we introduced the ground-state reference determinant built using ethylene molecular orbitals (MOs). Every double bond in the system is represented by two ethylene molecular orbitals – an occupied one and a vacant one. Operators T_1 and T_2 (2) generate single and double excitations within each ethylene fragment (local excitation) or single and double excitations involving two different ethylene fragments (electron-transfer excitations). The amplitudes t_i^a and t_{ij}^{ab} corresponding to the latter excitations describe the correlation effects in the ground-state wave function in terms of inter-fragment electron transitions. In the diagram shown in Figure 1 V_1 corresponds to local excitations, V_2 corresponds to transitions between nearest fragments, V_3 corresponds to transitions between next nearest fragments, etc.

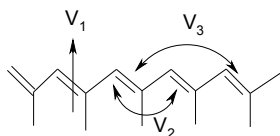


Figure 1. Symbolic description of excitations in a π -electron system in the *cue*-CCSD method.

The linear response operator corresponding to an external harmonic monochromatic perturbation in the dipole approximation has the following well-known representation³¹:

$$H' = \hat{\mu} (e^{i\omega t} + e^{-i\omega t}), \quad (8)$$

where ω is the emission frequency, $\hat{\mu}$ is the dipole moment operator, and t represents time. In the framework of the LR-CCSD theory the change of wave function (1) corresponding to (8) is described with the following cluster operators:

$$T_1(t) = T_1 + R_1 (e^{i\omega t} + e^{-i\omega t}), \quad (9)$$

$$T_2(t) = T_2 + R_2 (e^{i\omega t} + e^{-i\omega t}). \quad (10)$$

Using R_1 , R_2 , T_1 , and T_2 one can write the perturbed many-electron wave function in the following form:

$$|\Psi_{\text{LRCCSD}}\rangle = (r_0 + R_1 + R_2) e^T |0\rangle, \quad (11)$$

where r_0 characterizes the contribution of the reference function to (11). Operators R_1 and R_2 have second-quantization representation analogous to (2):

$$R_1 + R_2 = \sum r_i^a a_i^+ a_i + \sum r_{ij}^{ab} a_a^+ a_b^+ a_j a_i. \quad (12)$$

Both excitation operators, R and T , act onto the same reference state $|0\rangle$ and commute $[R, T] = 0$. This allows for expressing the working LR-CCSD equations in a CC-projection-like form as well as in a form of an eigenvalue problem. The working equations of the LR-CC theory for amplitudes r_i^a and r_{ij}^{ab} are obtained analogous to (3) by the projection method:

$$\langle 0 | H | R_1 + R_1 T_1 + R_2 | 0 \rangle = \omega r_0 \quad (13)$$

$$\langle_i^a | H | R_1 (1 + T_1 + T_2 + \frac{1}{2} T_1^2) + R_2 (1 + T_1) | 0 \rangle = \omega r_i^a, \quad (14)$$

$$\langle_{ij}^{ab} | H | R_1 (1 + T_1 + T_2 + \frac{1}{2} T_1^2 + T_1 T_2 + \frac{1}{6} T_1^3) + R_2 (1 + T_1 + T_2 + \frac{1}{2} T_1^2) | 0 \rangle = \omega r_{ij}^{ab}. \quad (15)$$

Thus, the problem becomes an eigenvalue problem. The value ω corresponds to the electronic excitation energy. A detailed description of the LR theory for different electronic-structure approaches can be found^{8,9} and in the works of Head-Gordon *et al.*^{32,33} For discussion on size-intensivity of LRCCSD models see refs 34, 35.

Implementation of the LR approach within the framework of the local *cue* method (*cue*-LR-CCSD) involves using the ground-state CC amplitudes and the corresponding one- and two-electron integrals. By solving equations (13-15) amplitudes r_0 , r_i^a and r_{ij}^{ab} are obtained. They,

unlike the t_i^a and t_{ij}^{ab} amplitudes, are normalized to unity. Using r_i^a and r_{ij}^{ab} the average excitation level (AEL) is determined as:

$$\eta = \sum_{i,a} (r_i^a)^2 + 2 \cdot \sum_{\substack{i>j \\ a>b}} (r_{ij}^{ab})^2. \quad (16)$$

In contrast to a local calculation of the ground state being only based on the structural characteristics of the system (as it will be shown below), it is impossible to formulate a principle based on which the most important r_i^a and r_{ij}^{ab} amplitudes can be selected. This is because the electronic excitations described by (8) may correspond to electron transitions between fragments separated by a significant distance from each other. Moreover, excitations may exist that cannot be classified according to the notation shown in Figure 1. Such excitations are those that alter the double-bond structure of the molecule. This is why in the current version of the *cue*-LR-CCSD approach no excitation preselection is done and the r_i^a and r_{ij}^{ab} sets include all possible amplitudes.

It should be emphasized that all *cue*-CCSD calculations, as well as all *cue*-LR-CCSD calculations, are performed using ethylenic orbitals which are not perturbed due to the presence of the electric field. Such a choice leads to a significant simplification of the calculation scheme. It should be noted that the use of the unperturbed ethylenic MOs gives quite accurate electric ground-state polarizabilities and hyperpolarizabilities (see refs 28 and 29).

In the present work we also calculate the elements of the one-particle reduced density matrix (RDM1; the RDM1 matrix elements are designated as $\rho_{\mu\nu}$), as it allows for better interpretation of the theoretical data. In the π -electron approximation, RDM1 can be simply calculated as the numerical derivative of the energy with respect to the matrix elements of the core Hamiltonian, $h_{\mu\nu}$, where μ and ν are orbital indices^{29,36}:

$$\rho_{\mu\nu} = \frac{1}{2 - \delta_{\mu\nu}} \frac{\partial E}{\partial h_{\mu\nu}}. \quad (17)$$

The results obtained in the *cue*-LR-CCSD and LR-CCSD calculations are compared with those obtained in the FCI calculations and the comparison is presented below.

In our previous work the *cue*-CCSD method was used to investigate non-linear optical properties of a series of π -conjugated polymers in the ground electronic states. With the present generalization of the method (*cue*-LR-CCSD) it is possible to estimate excitation energies and other electronic properties such as polarizabilities and hyperpolarizabilities for excited states for the earlier investigated systems. The calculations are based on the well-known Buckingham expansion of the energy of the system in external electro-static field F ^{37,38}:

$$E(\vec{F}) = E(0) - \mu_r F_r - \frac{1}{2} \alpha_{rs} F_r F_s - \frac{1}{3!} \beta_{rst} F_r F_s F_t - \frac{1}{4!} \gamma_{rstu} F_r F_s F_t F_u - \dots, \quad (18)$$

where $\{r, s, t, u\} = \{x, y, z\}$ and μ_r , α_{rs} , β_{rst} , and γ_{rstu} denote components of the dipole moment, the polarizability, and the first and second hyperpolarizabilities, respectively. These components can be calculated as the appropriate derivatives of the energy with respect to the coordinates of the field vector. To find the derivatives, it is necessary to determine the electric-field contribution corresponding to a particular field strength and for the field alignment along a particular coordinate axes of the molecule to the diagonal elements of the non-perturbed Hamiltonian. This contribution is:

$$H_{i,j,k} = H(0) + \xi(iX + jY + kZ), \quad (19)$$

where $H(0)$ is the non-perturbed Hamiltonian; X , Y , Z are the operators representing the coordinates of the dipole moment vector; ξ is a constant that characterizes the field strength; and integers $i, j, k = \dots \pm 3, \pm 2, \pm 1, 0$ define the grid of the field strengths for which the energy of the system is calculated³⁹. Thereby, the series of calculations of the perturbed system is performed

before the numerical differentiations leading to the determination of the polarizabilities and hyperpolarizabilities is carried out (for details see refs 28,29,40,41).

It should be noted that the above-described scheme for calculating the energy derivatives may involve two possible variants of the CCSD method. In the first variant “unperturbed” HF orbitals are first generated for zero-field situation and used the CCSD calculation with the field turned on. This method is call *unrelaxed*-CCSD (u-CCSD). In the second variant the HF orbitals are generated with the field turned on and these orbitals are used in the subsequent field-dependent CCSD calculation. This approach is called *relaxed*-CCSD (r-CCSD).

The orbital relaxation effects can play an important role in the calculations of the molecular electric properties. This is why in our approach the restrictions due to the MO localization are only imposed on the double excitations, i.e. on the T_2 part of the wave function, and all possible one-electron excitations between the ethylene fragments are included. This leads to an adequate account of the relaxation of the reference determinant in the presence of the external electric field. Detailed information about the description of the relaxation effects in different π -electron CCSD approaches can be found in our articles^{28,41}.

3. NUMERICAL ILLUSTRATIONS

The present calculations of π -conjugated systems are carried out using the PPP model Hamiltonian²²⁻²⁴. For all systems under consideration we use an alternating form of the resonance integral corresponding to a pair of connected atoms:

$$\beta_{\pm} = (1 \pm t) \beta_0, \quad (20)$$

where «+» corresponds to a double bond and «-» – to a single bond. The value β_0 is set to equal -2.274 eV. The alternation parameter t equals 0.1. For the Coulomb integral we use well-known empirical Ohno formula⁴²:

$$[\mu\mu | \nu\nu] = \frac{1}{\sqrt{(1/\Gamma_0)^2 + R_{\mu\nu}^2}}, \text{ (in a.u.)} \quad (21)$$

The one-center Coulomb integral in the PPP parametrization equals $\Gamma_0 = [\mu\mu | \mu\mu] = 11.13$ eV. In the calculation idealized geometries of the studied systems are used where all bond lengths are equal 1.4 Å and all cyclic fragments of the systems are regular polygons. This parameterization was successfully used before in the polarizability and hyperpolarizability calculations of π -conjugated oligomers^{39,41}.

3.1. Polyenes

The calculation of the electronic structure of a polyene remains to be a complicated problem for quantum chemistry⁴³⁻⁴⁶. Let us first consider the ground-state wave function. Parameters W_k (6) clearly demonstrate the complicated nature of the problem. The W_k parameters are obtained using both the CCSD and *cue*-CCSD methods using the standard HF orbitals and the *cue* basis set, respectively. Three polyenes: $C_{10}H_{12}$, $C_{12}H_{14}$, and $C_{14}H_{16}$, are used as the test systems. The focus of the test is the dependence of the parameters of the wave function on the length of the oligomeric chain.

When the HF MOs are used the largest contribution to the CCSD wave function is made by the double excitations ($W_2 = 0.177$, 0.213, and 0.250 for the first, second, and the third polyene, respectively). The contribution is determined relative to the total value of W_{Σ} (7) which with the chain growing remains almost constant. The next largest contribution is of the 4-fold excitations (here $W_2 / W_4 \sim 10$). The contribution of the odd-electron excitations is found to be nearly three orders of magnitude smaller than of the contribution from the even-electron excitations. Noteworthy is the almost equal values of W_6 and W_1 for $C_{10}H_{12}$, while for $C_{14}H_{16}$ the values are significantly different. Apparently the importance of the six-fold excitations increases with the

growth of the chain length. The dominance of the even-electron excitations over the odd-electron excitations is easily explained considering the components of the W_k contributions. For example, let us examine the C_4 and C_5 configuration coefficients (4) obtained from the CC amplitudes of the CCSD wave function as:

$$C_4 = \frac{1}{2} t_2 t_2 + \frac{1}{2} t_2 t_1 t_1 + \frac{1}{24} t_1 t_1 t_1 t_1 \tag{22}$$

$$C_5 = \frac{1}{2} t_2 t_2 t_1 + \frac{1}{6} t_2 t_1 t_1 t_1 + \frac{1}{120} t_1 t_1 t_1 t_1 t_1. \tag{23}$$

The amplitude squared norms of the T_1 and T_2 operators are shown in the Table 1. It can be seen from the data that for the HF MO basis set the norm of the t_1 vector is almost by three orders of magnitude smaller than the norm of the t_2 vector. The C_k coefficients with even k 's contain only components that are products of t_2 amplitudes and no components that include any t_1 amplitude (i.e. t_2 , t_2^2 , and t_2^3 in the C_2 , C_4 , and C_6 coefficients, respectively). The C_k coefficients with odd k 's contain at least one t_1 amplitude.

Table 1. Squared norms of t_1 and t_2 amplitude vectors from CCSD and *cue*-CCSD calculations.

	C ₁₀ H ₁₂		C ₁₂ H ₁₄		C ₁₄ H ₁₆	
Basis	HF	cue	HF	Cue	HF	cue
$\sum (t_i^a)^2$	$4.9 \cdot 10^{-4}$	$3.8 \cdot 10^{-1}$	$6.6 \cdot 10^{-4}$	$4.8 \cdot 10^{-1}$	$8.4 \cdot 10^{-4}$	$5.8 \cdot 10^{-1}$
$\sum (t_{ij}^{ab})^2$	$1.8 \cdot 10^{-1}$	$2.1 \cdot 10^{-1}$	$2.1 \cdot 10^{-1}$	$2.5 \cdot 10^{-1}$	$2.5 \cdot 10^{-1}$	$3.0 \cdot 10^{-1}$

The use of the *cue* basis in the CCSD calculations is justified by the Thouless theorem⁴⁷, which states that a transformation between two non-orthogonal determinants is always possible by means of a T_1 operator. Thus, in the CCSD calculation the reference determinant can be improved by acting with the exponentiated T_1 operator on this determinant. Thus, when a “non-ideal” (non-Hartree-Fock) determinant is used as a reference determinant in the CC calculation the norm of the t_1 vector can be comparable with the t_2 norm or even larger. Larger norm of t_1 usually indicates that orbital relaxation happens in the calculation. This fact is illustrated with the data presented in Table 1.

For a better demonstration of the above-described trend, the individual contributions comprising C_k coefficients are presented in Table 2 for the C₁₀H₁₂, C₂₀H₂₂, and C₃₀H₃₂ polyenes. The analysis is limited to up-to the four-fold excitations.

From the data shown in Table 2 it can be seen that for the HF MO basis the main part of wave function corresponds to the combinations of the t_2 matrix elements (>99%). The wave function in the *cue*-CCSD method has a diverse structure which, with the growth of the chain length, becomes more complicated due to the increasing number of the cross-components (the number of possible combinations of t_1 and t_2 amplitudes increases). The overall contributions (in %) of the t_1 , t_2 , and cross components is determined as:

$$\Sigma_1 = t_1^1 + t_1^2 + t_1^3 + t_1^4, \tag{24}$$

$$\Sigma_2 = t_2 + t_2^2, \tag{25}$$

$$\Sigma_{1 \times 2} = t_1 t_2 + t_1^2 t_2. \tag{26}$$

In formulas (24-26) a symbolic way is used to denote different types of contributions. The results are presented in Table 2. The sum of contributions (7) is shown in the last row of the table as Σ_w . For the sake of comparability all values are renormalized to 100 %.

Table 2. Contributions (%) of different types of components to the CCSD wave-functions obtained in the calculations performed with HF MOs and with *cue* basis sets for polyenes C₁₀H₁₂, C₂₀H₂₂, and C₃₀H₃₂.

	C ₁₀ H ₁₂		C ₂₀ H ₂₂		C ₃₀ H ₃₂	
	HF	CUE	HF	CUE	HF	CUE
t ₁	0.26	52.87	0.34	39.16	0.34	28.54
t ₂	94.24	29.15	86.87	19.42	80.49	13.72
t ₁ ²	≈0	8.31	≈0	15.77	≈0	18.59
t ₂ t ₁	0.02	6.34	0.09	13.42	0.16	16.23
t ₁ ³	≈0	0.71	≈0	3.87	≈0	7.63
t ₂ ²	5.48	1.99	12.70	3.45	19.01	3.97
t ₂ t ₁ ²	≈0	0.59	≈0	4.27	≈0	9.11
t ₁ ⁴	≈0	0.04	≈0	0.65	≈0	2.22
Σ ₁	0.26	61.93	0.34	59.45	0.34	56.98
Σ ₂	99.71	31.14	99.57	22.86	99.50	17.69
Σ _{1x2}	0.02	6.93	0.09	17.67	0.16	25.33
Σ _W	0.188	0.746	0.413	2.392	0.672	5.205

The structure of the wave function in the *cue*-CCSD method can be analyzed in terms of weights of different orders of excitations that belong to certain *cue* layers (see Figure 1). We shall represent by V_ℓ the sum of single, double, triple, and quadruple excitations:

$$V_\ell \approx V_\ell[1] + V_\ell[2] + V_\ell[3] + V_\ell[4] \quad (27)$$

$$\Sigma_V = \sum_\ell V_\ell. \quad (28)$$

It should be stressed that V_k 's are different from W_k 's (eq. 6). W_k characterizes the contribution of the k^{th} excitation level to the CCSD wave function, while V_ℓ characterizes the contribution of the ℓ^{th} *cue* layer to the wave function. In the CI method W_k is equal to C_k because there are no non-linear components in the CI wave function.

For polyenes the structure of the *cue* reference state corresponds to a high level of localization. Therefore it is interesting to compare the V_ℓ values obtained in the *cue*-CCSD calculations with those obtained in the CCSD calculations that use localized MOs (LMOs) obtained from the HF orbitals (the approach is denoted as LCCSD). To localize the MOs in the π -electron approximation it is convenient to use the Pipek-Mezey procedure⁴⁸ applied separately to the occupied and vacant orbital blocks. The procedure allows for minimization of the average number of atoms where MOs are located by the sequence of unitary pair-rotations of the delocalized orbitals. Considering that the *cue* basis set has the highest level of localization let us hypothetically assume that a basis set of orbitals exists that cannot be obtained by any unitary transformation inside the occupied MO block or inside the vacant MO block.

The V_ℓ values obtained in the *cue*-CCSD and LCCSD calculations for polyenes C₁₀H₁₂, C₂₀H₂₂, and C₃₀H₃₂ are presented in Table 3. In the third column of the table the average numbers of atoms (average localization index; ALI) where the MOs are localized are shown (naturally, in the *cue*-CCSD case these values are all equal 2 for any system). ALIs show the lowest possible level of localization for the studied systems that can be achieved by the unitary transformation of the HF MOs.

Table 3. Relative contributions of excitations in the *cue*-CCSD and LCCSD wave function representing the ground state for polyenes by *cue* layers (V_ℓ values are renormalized to 1; the values of sum (27) is shown in column Σ_v)

polyene	basis	ALI	V_1	V_2	V_3	V_4	V_5	V_6	Σ_v
$C_{10}H_{12}$	LMO	2.16	0.672	0.235	0.061	0.022	0.010	–	0.188
	CUE	2.00	0.202	0.589	0.109	0.066	0.034	–	0.746
$C_{20}H_{22}$	LMO	2.19	0.585	0.233	0.072	0.033	0.023	0.018	0.413
	CUE	2.00	0.125	0.423	0.095	0.076	0.070	0.064	2.392
$C_{30}H_{32}$	LMO	2.20	0.532	0.220	0.071	0.035	0.025	0.021	0.672
	CUE	2.00	0.086	0.304	0.071	0.061	0.060	0.059	5.205

For the LCCSD method the relative contribution of each excitation type decreases with the number of excitations of that type. In the case of *cue*-CCSD the V_2 values dominate over the V_1 values. This can be explained by the fact that the local t_1 excitations are identically equal zero and the main part of the t_1 norm originates from the excitations between the nearest ethylene fragments (i.e. inside the $\ell = 2$ *cue* layer). As in the case of LCCSD, with the *cue* excitation length increasing a decrease of the V_ℓ values is observed. This behavior enables to formulate a hierarchy of local approximations that allows for estimating the size-limit values of the second hyperpolarizability for π -conjugated polymers that contain hundreds of atoms. The t_2 matrix in the LCCSD method in terms of the inter-fragment excitations has a very similar form as that in the *cue*-CCSD method. Therefore no separate consideration is needed. A detailed analysis of the t_2 amplitudes in the *cue*-CCSD method can be found in our previous works^{27,28}.

Let us start the analysis of the LR-CCSD calculations with comparing the R_1 and R_2 amplitudes. The average excitation level of the $A_g \rightarrow B_u^+$ excitation for polyenes is close to unity, indicating that the wave function of the B_u^+ state is almost completely dominated by configurations which are single excitations from the ground state reference determinant.

Let us now analyze the configurational composition of the wave function of the B_u^+ state using the $C_{20}H_{22}$ polyene as an example. In the HF MO basis set let us use the standard convention and denote the highest occupied orbital as $1 \equiv \text{HOMO}$, the next highest as $2 \equiv \text{HOMO}-1$, the next after that as $3 \equiv \text{HOMO}-2$, etc. The vacant orbitals are marked with *prime* and numbered as $1' \equiv \text{LUMO}$, $2' \equiv \text{LUMO}+1$, $3' \equiv \text{LUMO}+2$, etc. The enumeration of the MOs in the *cue* basis follows the numbering of the consecutive ethylene fragments and, as in the HF MO case, the vacant orbitals are marked with *prime*.

The B_u^+ state in the LR-CCSD calculation is dominated by a single singly-excited configuration ($\text{HOMO} \rightarrow \text{LUMO}$; the contribution of the reference determinant to the wave function of this state is equal to zero due to its different spatial symmetry):

$$|\Psi'_{\text{LR-CCSD}}\rangle \approx -0.61|1'\rangle - 0.25|2'\rangle + 0.12|3'\rangle. \tag{29}$$

With the growth of the polyene chain the coefficient of the dominant configuration, $|1'\rangle$, decreases (for polyene $C_{30}H_{32}$ the value is equal 0.56), while the contributions of other configurations increase (for polyene $C_{30}H_{32}$: $0.29|2'\rangle$, $0.17|3'\rangle$, $0.11|4'\rangle$, etc.). This demonstrates that the electron correlation effects in polyenes become more complicated as the chain length increases.

In the *cue* representation all occupied orbitals among themselves, as well as all vacant orbitals among themselves, are degenerate and this fundamentally affects the configuration composition of the wave-function. In the *cue*-LR-CCSD calculation the singly-excited configurations have

very similar contributions to the wave function (the proper symmetry of the wave function relative to the center of inversion is explicitly implemented in the expression):

$$|\Psi'_{\text{cue-LR-CCSD}}\rangle \approx 2 \cdot \left(0.17 \begin{vmatrix} 5' \\ 5 \end{vmatrix} + 0.16 \begin{vmatrix} 4' \\ 4 \end{vmatrix} - 0.14 \begin{vmatrix} 6' \\ 5 \end{vmatrix} + 0.13 \begin{vmatrix} 3' \\ 3 \end{vmatrix} \right) - 2 \cdot \left\{ 0.14 \begin{vmatrix} 5' \\ 4 \end{vmatrix} + 0.12 \begin{vmatrix} 4' \\ 3 \end{vmatrix} \right\}. \quad (30)$$

With the growth of the polymeric chain the configuration coefficients become even more similar and the domination of the maximum coefficient becomes even less pronounced. In Figure 2 this trend is illustrated through plots of the R_l amplitude vectors obtained in the *cue*-LR-CCSD calculations (for polyene $C_{30}H_{32}$ – solid line, for $C_{26}H_{28}$ – dotted line). For clearness, the amplitudes belonging to the same *cue* layer are marked with the same symbol. Along the horizontal axis the centroids representing the excitations are plotted. The plots reveal the above noted significant decrease of the r_i^a amplitude values with the growth of the chain (the difference in chain length between $C_{26}H_{28}$ and $C_{30}H_{32}$ polyenes is less than 5 Å).

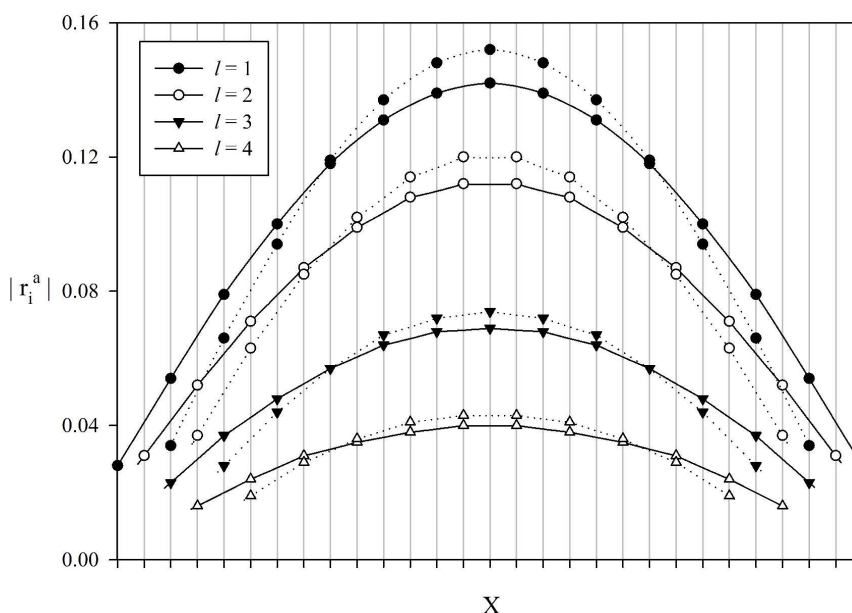


Figure 2. r_i value distribution along the polyene chain for different *cue* layers. (solid line corresponds to polyene $C_{30}H_{32}$ and dotted line to $C_{26}H_{28}$)

The *cue*-LR-CCSD wave functions of the B_u^+ state for polyenes can also be analyzed in terms of the V_ℓ quantities (see Table 4).

Table 4. Analysis of the structure of the *cue*-LR-CCSD wave function of the B_u^+ in terms of V_ℓ values renormalized to unity.

polyene	η	V_1	V_2	V_3	V_4	V_5	V_6	Σ_V
$C_{10}H_{12}$	1.042	0.307	0.408	0.187	0.078	0.020	–	1.111
$C_{20}H_{22}$	1.054	0.251	0.341	0.165	0.094	0.062	0.042	1.136
$C_{30}H_{32}$	1.056	0.235	0.316	0.147	0.081	0.056	0.045	1.178

In general, the descriptions of the electron correlation in the ground (A_g) and excited (B_u^+) states in the *cue* terms are similar. However, upon arranging the contributions to the wave functions of the two states in terms of layers, differences in the values of amplitudes that belong to each particular *cue* type appear. This can be illustrated using polyene $C_{30}H_{32}$ as an example (see Table 5). The maximal values, the mean values, the standard deviations, and the number of

unique elements are shown in the table for six *cue* layers for the amplitude vectors of the T_2 and R_2 operators.

Table 5. Maximal values, mean values, standard deviation, and number of unique elements in the amplitude vectors of the two-electron excitation operators in the wave functions of the ground and excited states (1÷6 *cue* layers) of polyene $C_{30}H_{32}$.

ℓ	T_2			R_2			N_e
	$\max(t^{(\ell)})$	$\langle t^{(\ell)} \rangle$	σ_t	$\max(r^{(\ell)})$	$\langle r^{(\ell)} \rangle$	σ_r	
1	$1.74 \cdot 10^{-1}$	$1.73 \cdot 10^{-1}$	$3.08 \cdot 10^{-4}$	0	0	0	15
2	$3.92 \cdot 10^{-2}$	$2.46 \cdot 10^{-2}$	$9.45 \cdot 10^{-3}$	$1.62 \cdot 10^{-2}$	$7.11 \cdot 10^{-3}$	$5.17 \cdot 10^{-3}$	112
3	$9.20 \cdot 10^{-3}$	$4.46 \cdot 10^{-3}$	$2.96 \cdot 10^{-3}$	$8.95 \cdot 10^{-3}$	$3.10 \cdot 10^{-3}$	$2.39 \cdot 10^{-3}$	338
4	$2.44 \cdot 10^{-3}$	$1.24 \cdot 10^{-3}$	$7.74 \cdot 10^{-4}$	$4.16 \cdot 10^{-3}$	$1.66 \cdot 10^{-3}$	$1.09 \cdot 10^{-3}$	672
5	$1.16 \cdot 10^{-3}$	$4.52 \cdot 10^{-4}$	$3.09 \cdot 10^{-4}$	$2.81 \cdot 10^{-3}$	$8.94 \cdot 10^{-4}$	$6.42 \cdot 10^{-4}$	1078
6	$6.29 \cdot 10^{-4}$	$1.80 \cdot 10^{-4}$	$1.60 \cdot 10^{-4}$	$1.68 \cdot 10^{-3}$	$4.76 \cdot 10^{-4}$	$4.02 \cdot 10^{-4}$	1520

As can be seen from Table 5, for the ground state there is a well-defined separation between the layers by the amplitude values: the maximum $t^{(\ell)}$ value (except the last one) is significantly smaller than the mean value for the previous one. The R_2 distribution demonstrates strong overlap of the $r^{(\ell)}$ values for neighboring ℓ . This indicates that the local-approximation hierarchy good for the wave function of the ground state is not suitable for the excited state. Despite the sparse structure of the *cue*-CCSD amplitude vector for the ground state, the development of an efficient algorithm for describing the correlation effects in excited states is a rather difficult problem. However the *cue*-structures of the amplitude vector and of the corresponding matrix of the two-electron integrals are helpful in creating the most efficient computational algorithm.

The energies of the singlet electron $A_g \rightarrow B_u^+$ transition for the studied polyenes are presented in Table 6. The results obtained with approximate methods are compared with the results obtained with CIS approach (Configuration Interaction Singles) often used for calculating excited states, with the available experimental data, and with the results obtained with the formally-exact FCI method. Our FCI calculations have been performed employing method based on the so-called “wave operator” approach⁴⁹.

Table 6. Transition energies corresponding to the $A_g \rightarrow B_u^+$ electronic excitation (eV) for polyenes (C_NH_{N+2}), obtained with different π -electron approaches.

N	CIS	<i>cue</i> -LR-CCSD	LR-CCSD	FCI	experimental ^a
4	5.39	5.75	5.75	5.76	6.25, 5.92, 5.74
6	4.58	4.97	4.99	5.01	4.93, 4.95, 5.13
8	4.06	4.49	4.50	4.55	4.41
10	3.72	4.17	4.18	4.24	4.02, 4.21
12	3.48	3.95	3.95	4.02	3.85
14	3.31	3.79	3.78	3.86	3.46 ^b

As can be seen from Table 6, LR-CCSD and *cue*-LR-CCSD values differ little. Moreover, they are close to those obtained in the FCI calculations. With the growth of the chain length, however, the discrepancies increase (it is known that the CC methods underestimate transition energies). We attribute this behavior to the complexity of the correlation effects in strongly correlated systems (as the length of the system increases, the importance of high-level excitations becomes more noticeable). The dependence of the transition energy of the lowest

^a From refs 50 and 51.

^b From ref 52.

allowed transition on the number of π -electrons in the polymeric chain is presented in Figure 3. Near the point where the increase of the chain length starts to have negligible effect on the results (the stabilization point; $N > 30$) the difference between cue-LR-CCSD and LR-CCSD results becomes more pronounced but still does not exceed 5%.

Size-limit values are estimated based on the linear behavior of the excitation energy near the stabilization points:

$$E = E^\infty + E^0/N. \quad (31)$$

Earlier, such extrapolation was successfully employed to estimate the limit values of the (hyper)polarizability^{28,29}.

Thus, by extrapolating the dependence of the $A_g \rightarrow B_u^+$ transition energy pass the stabilization point one can obtain a value corresponding to a quasi-infinite chain. The transition energies for some extended polyenes and the extrapolated values for infinite chains are presented in Table 7.

Table 7. Calculated $A_g \rightarrow B_u^+$ transition energies (eV) for some extended polyenes and extrapolated value for the infinite chain.

N	20	30	40	50	∞
CIS	2.995	2.774	2.678	2.627	2.40
cue-LR-CCSD	3.532	3.357	3.283	3.240	3.07
LR-CCSD	3.477	3.263	3.170	3.121	2.90

These estimates are close to those obtained in ref 43.

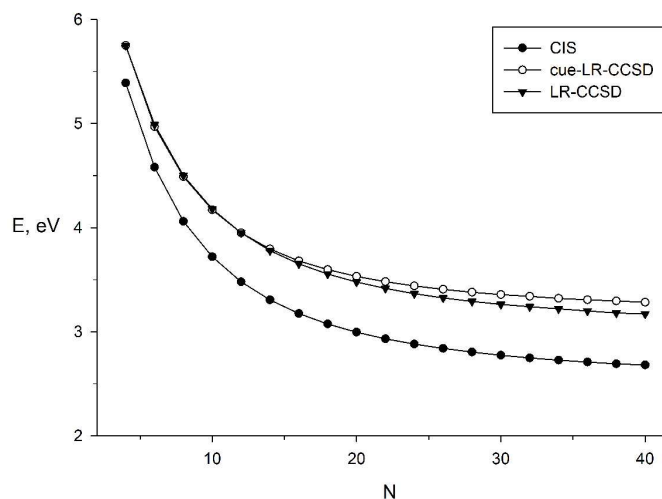


Figure 3. $A_g \rightarrow B_u^+$ transition energy of polyenes as a function of the number of π -electrons.

The goal of this work is the development of a π -electron approach for calculating optically intensive transitions. Our main interest is in a comparative description of optical excitations of long polymers. This is why we mainly mention allowed transitions. In principle, the LR-CCSD method can be also applied to describe the forbidden $A_g \rightarrow A_g$ transitions in polyenes. However, it is well known that the CCSD-based methods are unable to describe correctly the electronically excited states with significant contributions from doubly excited configurations (see refs 54, 55). For such states more sophisticated methods, which explicitly include higher excited configurations, have to be used. However for the completeness sake we show in Table 8 the results obtained for the lowest forbidden $A_g \rightarrow A_g$ transition in some short polyenes.

Table 8 Energies of the lowest electronic (λ , eV) $A_g \rightarrow A_g$ excitations in some short polyenes C_nH_{n+2} . For the CCSD-based methods the contribution of the reference state, r_0 , and the average excitation level, η , are shown.

		n = 4	n = 6	n = 8	n = 10	n = 12	n = 14	n = 16
LRCCSD	λ	5.18	4.41	3.97	3.70	3.54	3.44	3.38
	r_0	0.090	0.117	0.129	0.136	0.142	0.148	0.153
	η	1.57	1.61	1.63	1.64	1.65	1.65	1.66
cue-LRCCSD	λ	5.09	4.51	4.17	3.98	3.87	3.81	3.76
	r_0	0.270	0.352	0.390	0.424	0.455	0.487	0.518
	η	1.71	1.74	1.74	1.74	1.74	1.74	1.73
FCI	λ	5.17	4.29	3.75	3.41	3.19	3.04	N/A
Exp ⁵⁰	λ	5.40 ^a	4.22 ^a , 5.21	3.59 ^a , 3.97	3.48	N/A	N/A	N/A

The table illustrates how difficult the electron correlation problem is to describe even for methods based on the simple PPP model Hamiltonian. It is worth noting that according to our calculations the π -electron FCI results are rather close to the experimental values for the excitation energies while all LRCCSD calculations reveal rather poor accuracy.

3.2 Polyfulvenes

To test the applicability of the proposed *cue*-CCSD generalization, one needs to test the method in the calculations of excited states of alternant polymeric systems, as well as in the calculations of non-alternant molecules. In the latter systems the electronic structures can be significantly distinct from the alternant systems. First we examine non-alternant systems with AEL (15) of about one because the excitation energies for such systems are usually described fairly accurately in the CCSD calculations.

In the earlier work²⁹ we studied non-linear optical properties of the following two types of π -conjugated polymers that fit the above-mentioned criteria, i.e. the condensed and non-condensed polyfulvenes. In Figure 4 (A and B) some systems representing the two types of polymers are presented (structure A – dimer of non-condensed polyfulvene $C_{12}H_{10}$ and structure B – dimer of condensed polyfulvene $C_{10}H_8$).

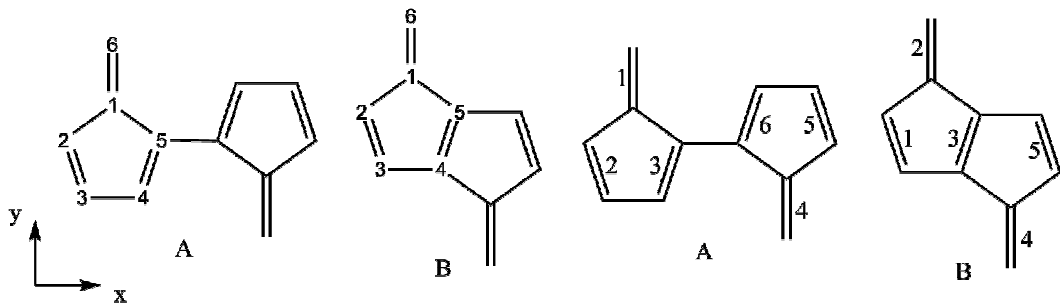


Figure 4. Structure of non-condensed (system A) and condensed (system B) polyfulvene dimers. The numbering on the left is used in the charge distribution analysis described below, numbering on the right is used in the configuration analysis (in the *cue* basis).

As in the case of polyenes, let us first examine the structure of the ground-state wave function. The calculated weights of different levels of excitations are presented in Table 9. The data show that the weight distribution does not fundamentally differ from that of polyenes. In the HF MO basis the odd-fold excitations contribute less to the CCSD wave function due to the

^a From ref 53.

small value of the norm of the t_1 amplitude vector. In the *cue* basis, a decrease of the norms of the excitation amplitudes with the increase of the excitation level is observed. The Σ_w values for systems A and B differ by less than 5%, indicating that the configurational composition of the wave functions of the two systems is equally complicated.

Table 9. Weights corresponding to different excitation level for the CCSD ground-state wave functions of systems A and B.

Basis	(A) $C_{12}H_{10}$		(B) $C_{10}H_8$	
	HF	<i>cue</i>	HF	<i>cue</i>
W_1	$2.47 \cdot 10^{-3}$	$6.99 \cdot 10^{-1}$	$1.65 \cdot 10^{-3}$	$5.92 \cdot 10^{-1}$
W_2	$1.84 \cdot 10^{-1}$	$4.91 \cdot 10^{-1}$	$1.53 \cdot 10^{-1}$	$3.74 \cdot 10^{-1}$
W_3	$2.83 \cdot 10^{-4}$	$1.61 \cdot 10^{-1}$	$1.45 \cdot 10^{-4}$	$9.50 \cdot 10^{-2}$
W_4	$1.17 \cdot 10^{-2}$	$5.39 \cdot 10^{-2}$	$7.27 \cdot 10^{-3}$	$2.80 \cdot 10^{-2}$
W_5	$1.00 \cdot 10^{-5}$	$9.41 \cdot 10^{-3}$	$3.34 \cdot 10^{-6}$	$3.34 \cdot 10^{-3}$
W_6	$3.21 \cdot 10^{-4}$	$1.95 \cdot 10^{-3}$	$1.36 \cdot 10^{-4}$	$6.31 \cdot 10^{-4}$
Σ_w	$1.99 \cdot 10^{-1}$	1.42	$1.62 \cdot 10^{-1}$	1.09

The V_i values for the ground and the lowest excited states are presented in Table 10 for systems A and B. Generally, these distributions determined for the different *cue* layers for polyfulvenes are similar to the case of polyenes. The contribution from the reference-state determinant, c_0 , is equal zero for symmetry reasons. The main difference between polyfulvenes and polyenes lies in the structure of the ethylene fragments. This difference leads to different weights of single excitations within each *cue* layer. For polyenes, in contrast to both types of polyfulvenes, all ethylene fragments are always separated by an odd number of bonds. This, unfortunately, leads to partial blurring of the layers' boundaries and requires more careful selection of the excitation set.

Table 10. Relative contributions of excitations to the *cue*-CCSD wave-functions of the ground and the lowest excited states of the A and B dimers. (the V_i values are renormalized to unity)

	V_1	V_2	V_3	V_4	Σ_v
A ($\eta=1.22$, $c_0=0$, $E=2.733$ eV)					
Ground	0.1199	0.6286	0.1761	0.0753	1.404
Excited	0.1658	0.5751	0.1972	0.0619	1.301
B ($\eta=1.22$, $c_0=0$, $E=2.617$ eV)					
Ground	0.1282	0.6936	0.1782	—	1.089
Excited	0.1846	0.6558	0.1596	—	1.218

The configuration composition of the excited-state wave function of polyfulvene is notably different from that of polyene. In the LR-CCSD wave function the dominant singly excited HOMO \rightarrow LUMO configuration is still present, but among the most significant configurations, a doubly excited configuration appears (with contribution ~ 0.1 ; the orbital numbering is similar as used for polyenes). The most important configurations for the excited state wave functions of systems A and B are:

$$|\Psi'_{\text{LR-CCSD}}\rangle \approx -0.58 \left| \begin{smallmatrix} 1' \\ 1 \end{smallmatrix} \right\rangle + 0.18 \left| \begin{smallmatrix} 2' \\ 2 \end{smallmatrix} \right\rangle - 0.16 \left| \begin{smallmatrix} 2' \\ 4 \end{smallmatrix} \right\rangle + 0.11 \left| \begin{smallmatrix} 1' & 1' \\ 4 & 1 \end{smallmatrix} \right\rangle \quad (32)$$

$$|\Psi'_{\text{LR-CCSD}}\rangle \approx -0.62 \left| \begin{smallmatrix} 1' \\ 1 \end{smallmatrix} \right\rangle - 0.14 \left| \begin{smallmatrix} 1' & 1' \\ 1 & 4 \end{smallmatrix} \right\rangle + 1.3 \left| \begin{smallmatrix} 1' & 2' \\ 2 & 1 \end{smallmatrix} \right\rangle + 0.11 \left| \begin{smallmatrix} 1' & 1' \\ 3 & 1 \end{smallmatrix} \right\rangle + 0.11 \left| \begin{smallmatrix} 2' \\ 3 \end{smallmatrix} \right\rangle \quad (33)$$

With increase of the number of the monomeric units the weight of the doubly excited configurations decreases leading to the average excitation level of $\eta \approx 1.1$. The weight of the dominant configuration, $\left| \begin{smallmatrix} 1' \\ 1 \end{smallmatrix} \right\rangle$, for non-condensed polyfulvenes changes on average by 2.5 % for

any additional monomeric unit added to the system, while for the condensed polymer it remains almost constant.

According to the *cue*-LR-CCSD calculation the contribution of the most significant doubly excited configuration is found to be 2÷3 times smaller than that obtained in the LR-CCSD calculation, and the wave function is almost fully described by the following singly excited determinants (the numbering of the *cue* orbital in Figure 4 is used):

$$|\Psi'_{\text{cue-LR-CCSD}}\rangle \approx 2 \cdot \left(-0.19 \left| \begin{smallmatrix} 1' \\ 3 \end{smallmatrix} \right\rangle + 0.18 \left| \begin{smallmatrix} 1' \\ 2 \end{smallmatrix} \right\rangle + 0.18 \left| \begin{smallmatrix} 3' \\ 3 \end{smallmatrix} \right\rangle + 0.15 \left| \begin{smallmatrix} 2' \\ 2 \end{smallmatrix} \right\rangle - 0.14 \left| \begin{smallmatrix} 3' \\ 2 \end{smallmatrix} \right\rangle - 0.14 \left| \begin{smallmatrix} 2' \\ 3 \end{smallmatrix} \right\rangle + 0.12 \left| \begin{smallmatrix} 6' \\ 3 \end{smallmatrix} \right\rangle \right) \quad (34)$$

$$|\Psi'_{\text{cue-LR-CCSD}}\rangle \approx -0.26 \left| \begin{smallmatrix} 3' \\ 3 \end{smallmatrix} \right\rangle + 2 \cdot \left(-0.21 \left| \begin{smallmatrix} 2' \\ 3 \end{smallmatrix} \right\rangle + 0.19 \left| \begin{smallmatrix} 2' \\ 1 \end{smallmatrix} \right\rangle + 0.17 \left| \begin{smallmatrix} 3' \\ 1 \end{smallmatrix} \right\rangle - 0.15 \left| \begin{smallmatrix} 1' \\ 1 \end{smallmatrix} \right\rangle + 0.14 \left| \begin{smallmatrix} 1' \\ 3 \end{smallmatrix} \right\rangle \right), \quad (35)$$

for systems A and B, respectively. For the polyene case the distribution of the r_1 elements is uniform for all ethylene fragments with largest values corresponding to the fragments located closer to the middle of the polymer.

Table 11. Charges on atoms (in the units of the electron charge) for A and B dimers obtained with different variants of the CCSD method and with the FCI method (atom numbering according to Figure 4). Charges corresponding to the ground state are presented with regular font and for the lowest excited state in bold.

$q_i \cdot 10^{-2}$	1	2	3	4	5	6
A						
cue-CCSD	1.8 / -6.8	-4.2 / 4.5	-0.2 / -2.2	-2.0 / -0.5	-2.5 / 4.4	7.0 / 0.6
u-CCSD	1.9 / -6.8	-4.1 / 4.6	-0.1 / -2.7	-1.9 / -0.4	-2.4 / 4.3	6.6 / 0.9
r-CCSD	1.7 / -7.1	-4.0 / 4.8	-0.2 / -2.9	-1.8 / -0.4	-2.4 / 4.2	6.7 / 1.4
FCI	1.8 / -6.6	-4.1 / 4.2	-0.1 / -2.7	-1.9 / -0.2	-2.4 / 3.9	6.7 / 1.4
B						
cue-CCSD	2.2 / -7.7	-4.3 / 8.8	0.1 / -1.3	-3.9 / 3.5	-3.9 / 3.5	5.8 / -3.3
u-CCSD	2.3 / -7.7	-4.3 / 9.2	0.2 / -1.9	-3.8 / 3.7	-3.8 / 3.7	5.6 / -3.2
r-CCSD	2.2 / -8.1	-4.2 / 9.4	0.2 / -2.3	-3.8 / 3.7	-3.8 / 3.7	5.7 / -2.7
FCI	2.3 / -7.6	-4.3 / 8.7	0.2 / -2.0	-3.8 / 3.4	-3.8 / 3.4	5.7 / -2.5

All variants of the CCSD method correctly describe the charge distribution for both the ground and the lowest excited state (as compared to the FCI values). The calculated charges on atoms (see eq. (16)) for the A and B systems are presented in Table 11. The average error in the charge distribution obtained with the *cue*-LR-CCSD method does not exceed 5%.

In the calculations we use the relaxed (r-LR-CCSD) and unrelaxed (u-LR-CCSD) variants of the HF orbitals. No orbital localization is used. The calculated components of the polarizability for the ground and the excited state are presented in Table 12. As noted earlier^{28,29}, the *cue*-CCSD method has performed well in estimating the non-linear optical characteristics of π -conjugated polymers. However, in the description of the hyperpolarizability the components corresponding to excited states in the *cue*-LR-CCSD method occasionally acquire values that are different from those obtained with FCI by an order of magnitude. For example, the discrepancy in the values obtained with different CCSD approaches is within 5% while, relatively to FCI, the error is about 80%. This effect is not due to the use of the HF MO or *cue* basis, but likely results from imperfection of the LR generalization of the CCSD method. A more correct estimation of higher-order optical characteristics usually requires more exact description of higher excited states relative to the state under consideration. Usually, the main contribution to the α , β , and γ properties is made by the lowest-energy excitations. For the ground state such excitations are included at the CCSD level. In estimating the hyperpolarizability corresponding to an excited state significantly higher-level excitations are required. Such excitations are not included at the CCSD level. One needs to resort to such methods as CCSDT, CCSDTQ, *etc.* to include the needed higher excitations.

Table 12. Calculated components of the static polarizability (a.u.) of the A and B dimers. The values for the ground state are shown with regular font and for the lowest excited state in bold.

	cue-LR-CCSD	u-LR-CCSD	r-LR-CCSD	FCI
A				
α_{xx}	60.9 / 330	60.2 / 355	58.4 / 355	59.9 / 465
α_{yy}	116 / 227	118 / 220	118 / 211	118 / 290
B				
α_{xx}	36.8 / 127	36.6 / 118	36.0 / 117	36.5 / 113
α_{yy}	127 / 190	127 / 178	126 / 171	125 / 162

In Figures 5 and 6 the dependency of the lowest transition energy on the number of π -electrons is shown for non-condensed and condensed polyfulvenes. One can see that the *cue*-LR-CCSD and LR-CCSD methods show similar dependence (the correlation coefficient is higher than 0.999) and differ only in the size-limit values (Table 13). The CIS method provides a qualitatively incorrect picture of the dependence and significantly underestimates the energy of the electron transition. The size-limit values presented in Table 13 are obtained using similar (as for polyenes) extrapolation procedures. The correlation coefficients corresponding to the extrapolation by a linear function is about 0.999.

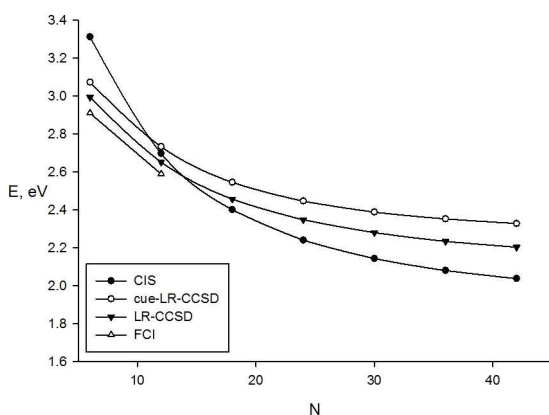


Figure 5. Dependence of the lowest transition energy on the number of π -electrons for non-condensed polyfulvene

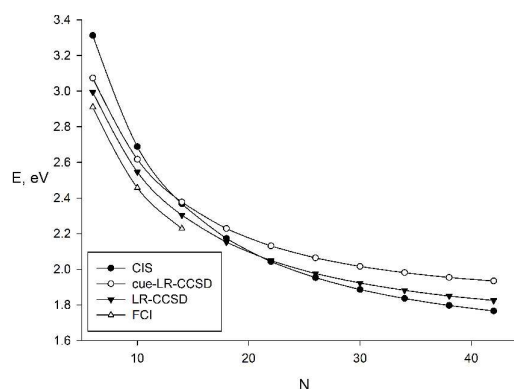


Figure 6. Dependence of the lowest transition energy on the number of π -electrons for condensed polyfulvene

Table 13. Extrapolated limit values of the lowest transition energy (eV) for condensed and non-condensed polyfulvenes.

	CIS	cue-LR-CCSD	LR-CCSD
non-condensed	1.76	2.16	2.01
condensed	1.46	1.72	1.58

In addition to the energies of spectral transitions we also estimate the average polarizabilities corresponding to the lowest excited state. It can be expected that with the growth of the chain length the accuracy of the $\langle\alpha\rangle$ calculation should increase due to decrease of the average excitation level (i.e. due to decrease of the contribution of doubly excited determinants). The $\langle\alpha\rangle$ value is defined as follows:

$$\langle\alpha\rangle = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}). \quad (36)$$

In Figure 7 the dependence of the calculated average polarizability on the number of π -electrons is shown for condensed polyfulvenes (solid line – ground state, dashed line – excited state). For the ground state all variants of the CC method give very similar results. However the HF method noticeably overestimates the polarizability. In the case of the excited state the values obtained with the *cue*-LR-CCSD method reveal insignificant deviation from those obtained with the u-LR-CCSD and r-LR-CCSD methods. Interestingly, the simple CIS approach unexpectedly correctly describes the values of the average polarizabilities. However, as the calculations have shown, such a coincidence does not guarantee an accurate estimation of the optical characteristics for other π -conjugated systems.

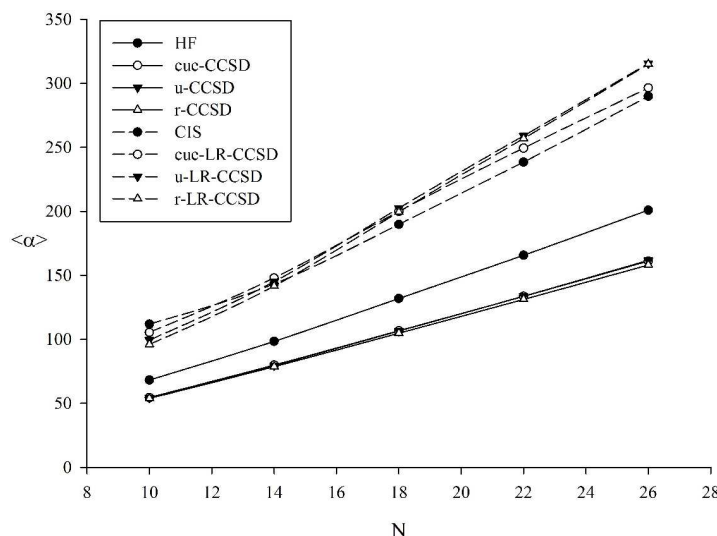


Figure 7. Dependence of the average polarizabilities (in a.u.) of the ground (solid line) and the lowest excited (dashed line) state for condensed polyfulvenes on the number of π -electrons.

4. CONCLUSION

The problem of reliably calculating optical and non-linear optical properties of π -conjugated systems still remains challenging for modern theoretical chemistry. Increasing application of such materials as carbon nanotubes, nanofibers, graphene, fullerenes, *etc.* in the nanostructure technology requires the development of reliable theoretical approaches for investigating the electronic properties of these systems. Such approaches have to account for a significant part of the electron correlation effects due to extreme sensitivity of the hyperpolarizabilities to these effects particularly for the π -shell electrons. The coupled cluster theory, which has established itself as very accurate method in the field of *ab initio* quantum chemistry calculations, cannot be directly applied to investigate systems that contain hundreds of atoms. In this context the semi-empirical approach we proposed (the *cue*-CCSD method) is a viable alternative because it allows for calculating the important optical (spectral) and non-linear parameters of conjugated π -electron systems with the use of the present-day computational resources. The test calculations performed in this work show that an adequate level of accuracy in accounting for the electron correlation effects is achieved with the *cue*-CCSD approach as compared with the results of the FCI calculations and with the available experimental data.

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Notes

The authors declare no competing financial interest.

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