

Approximate computations of linear and nonlinear polarizabilities for conjugated systems within a configuration interaction approach

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We propose a rather easily performed scheme for estimating static polarizabilities and hyperpolarizabilities for π -electron shells of carbon-containing conjugated networks. The scheme is based on the configuration interaction approach restricted to single and double excitations (CISD) with the Davidson size-consistency correction (or shortly CCSDr). We evaluate the accuracy of CCSDr for small systems and applied the method to several classes of conjugated π -structures (aromatic and pseudoaromatic compounds, cationic polymethine dyes etc.). In particular, the comparison is made between the polyacenes and the more stable circumacenes. Our results say that the circumacenes can be considered as more preferable nonlinear optic materials than the related acenes.

Keywords: polarizabilities and hyperpolarizabilities, conjugated networks, correlation energy, Davidson correction, aromatics and pseudoaromatics, polymethines.

Наближені обчислювання лінійних та нелінійних поляризованостей супряжених систем в рамках методу конфігураційної взаємодії. *А.В.Лузанов*

Запропоновано доволі легку схему оцінювання статичних поляризованостей та гіперполяризованостей π -електронних оболонок вуглецьмістких супряжених структур. Схему базовано на засадах методу конфігураційної взаємодії, котру обмежують однократними та двократними збудженнями (CISD) з поправкою Девідсона на розмірну узгодженість (скороченно CCSDr). Ми проаналізували точність CCSDr стосовно малих систем та запровадили метод до кількох класів супряжених π -структур (ароматичні та псевдоароматичні сполуки, катіонні поліметинові барвники тощо). Зокрема, зроблено порівняння поміж поліаценів та більш стабільних циркумаценових структур. З дослідження випливає, що як нелінійно-оптичні матеріали циркумацени більш придатні, аніж споріднені ацени.

1. Introduction

Electric properties of large conjugated molecules have been discussed in the literature for many years, at least starting from [1]; for recent works we refer the reader to reviews [2–5], selected papers [6–10] and references therein. It is not surprised that earlier very elementary approaches such as the topological Huckel model [1, 6], were frequently misleading due to strong influ-

ence of various electron interaction effects. The remarkable progress since the last thirty years was based on taking into proper account the electron correlation effects. Particularly, the coupled-cluster (CC) approaches are especially fruitful for estimating electric properties of small and medium-size molecules treated at ab initio levels of theory (e.g., see [11, 12]). The CC models (mainly coupled-cluster singles and doubles (CCSD) approach) are often employed for

assessing performance of more crude density functional theories (DFT) [13], and even for the recently developed machine learning algorithm for polarizabilities [14].

Among many others, π -conjugated systems have been extensively studied because of their great importance for both organic chemistry and material science. It is still common for researchers to treat the conjugated molecules by semiempirical electron correlation methods as it provides often the most feasible and comparably realistic framework for studying their electronic properties. Especially, this is valid for linear polarizabilities and nonlinear polarizabilities (hyperpolarizabilities) in large-scale conjugated systems (e.g., see review [4]). Indeed, many-electron π -shells, being most mobile in conjugated molecules, require a careful account for correlation effects which are beyond the simple second-order Moller-Plesset perturbation (MP2) theory. The complete account for π -electron correlation effects is achieved only in the full configuration interaction (FCI) method which, for π -shell electric properties, was earlier elaborated in [15, 16].

By using FCI (in fact available only for small size systems) one can evaluate the accuracy of conventional and any other approximate methods. Closely related to FCI is the noteworthy method based on the density matrix renormalization group (DMRG) scheme. Actually, DMRG produces the dipole polarizabilities [17, 18] almost of the same quality as the FCI method. As to approximate models whatsoever, it seems quite evident that generally there exist no universally working schemes for such rather nontrivial physical properties as molecular hyperpolarizabilities. In particular, in [19–21] one can find very effective models for the polarizabilities based on local MO and related considerations within the CCSD theory. However, the local description can be ineffective for certain types of molecular systems (charged ones, some high-symmetry structures and others). It motivated us to seek for alternative approximate π -schemes.

Thus, the main objective of the present work was to elaborate a sufficiently simple semiempirical correlated approach for estimating π -electron (hyper)polarizabilities (or, shortly, polarizabilities) in large conjugated systems. The elucidation of a realistic range of applicability of the proposed scheme is also an important part of the present study. The starting point of our consideration is the conventional variational CI theory at

the CISD level (CI limited to single and double excitations) with correcting the CISD energy for size-inconsistency effects.

2. The renormalized CISD scheme

We first recall some basic facts about CISD (for detail see [11, 22]). The CISD ground state wave function is taken as a trial function of the conventional form

$$|\Psi^{CISD}\rangle = C_0|\Phi\rangle + \sum_i \sum_a C_{ai}|\Phi_{i\rightarrow a}\rangle + \sum_{i<j} \sum_{a<b} C_{ab,ij}|\Phi_{i\rightarrow a, j\rightarrow b}\rangle. \quad (1)$$

Here C_0 and other coefficients are linear variational parameters which determine respective contributions of individual Slater determinants to the total function $|\Psi^{CISD}\rangle$. In Eq. (1), $|\Phi\rangle$ is a reference (usually the Hartree-Fock determinant), $|\Phi_{i\rightarrow a}\rangle$ are single excitations, and $|\Phi_{i\rightarrow a, j\rightarrow b}\rangle$ are double excitations; indices i, j , etc. refer to occupied MOs, whereas a, b , etc. to virtual (vacant) ones. In practice, we made use of the superoperator algorithm of [22] united with the well-known Lanczos iteration technique such as given in [23].

Although the CISD model provides a good account for electron correlation in small molecules, it suffers from one typical drawback of most restricted CI models (except FCI, of course). It is the so-called size-inconsistency, that is a lack of the additive separability of the electronic energy E . More precisely, for any restricted CI, the energy E_{AB} of two noninteracting singlet molecules A and B is larger than a sum of energies of individual molecules (in their ground states): $E_{AB} > E_A + E_B$. This drawback leads to an abnormal repulsion of the isolated molecules (in their ground states). For CISD the relevant analysis was made in [24–26].

There is an easy way to appreciably diminish this defective size-inconsistency in E^{CISD} by the Davidson correction [24]. For this we make using a renormalized CISD model, or the CISDr approach, and define its energy, E^{CISDr} , as follows:

$$E^{CISDr} = E^{RHF} + (E^{CISD} - E^{RHF})/|C_0|^2, \quad (2)$$

where RHF signifies the restricted Hartree-Fock method which is the usual starting model for reference approximate singlet ground states. Below in this section, we will restrict only to few small-size molecular

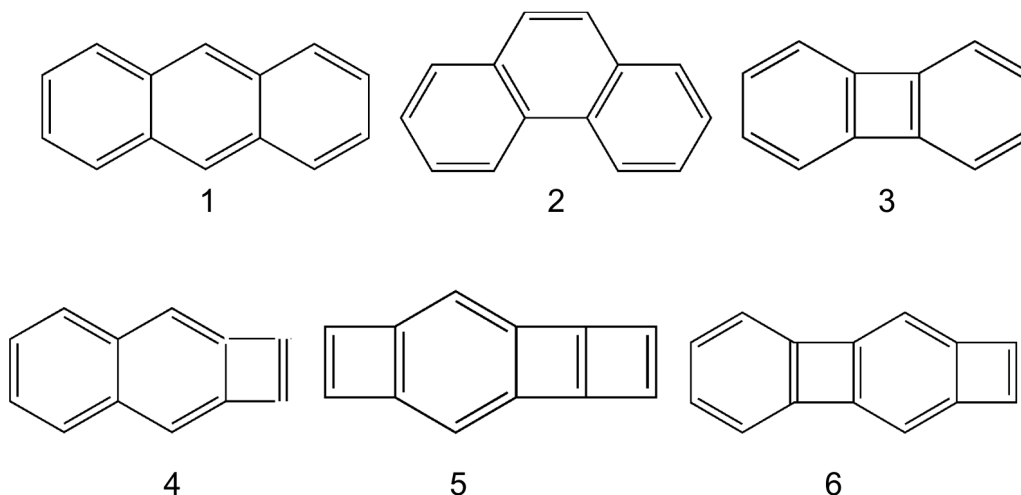


Fig.1. Small conjugated aromatic and pseudoaromatic molecules for testing approximate π -models.

systems that show us the capability of CISDr to reproduce the "exact" (at the FCI level) π -electron correlation energy, that is the quantity $\epsilon_{corr}^{FCI} = E^{FCI} - E^{RHF}$. Likewise, the CISD and CISDr correlation energies are defined as $\epsilon_{corr}^{CISD} = E^{CISD} - E^{RHF}$ and $\epsilon_{corr}^{CISDr} = (E^{CISD} - E^{RHF})/|C_0|^2$, respectively.

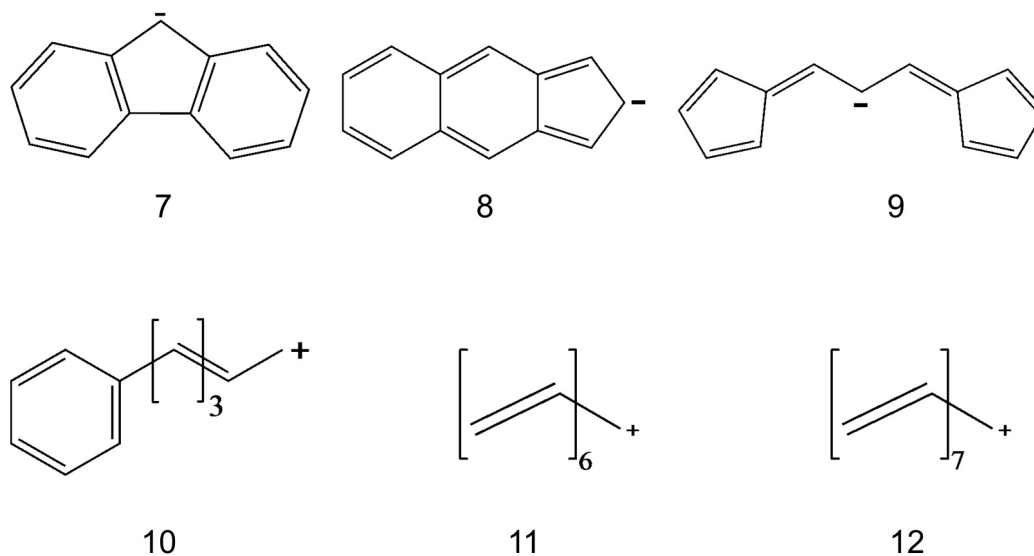
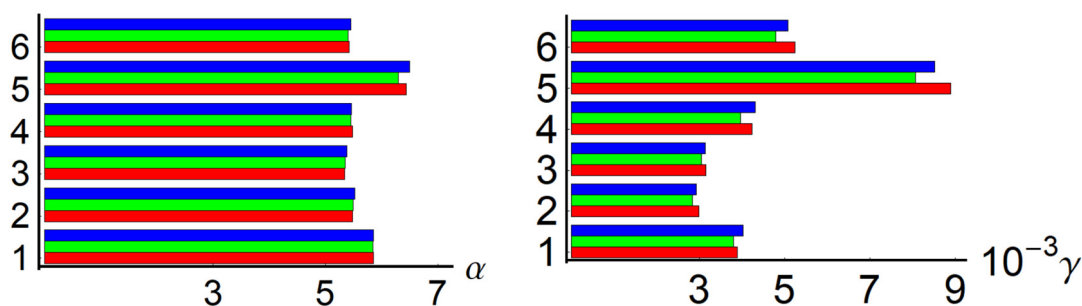
In the computations performed in this work, we apply, unless specified otherwise, the same conventional π -parametrization scheme as previously in [27–29]: all nonzero resonance integrals $\beta_{\mu\nu}$ are equal to -2.4 eV, and the Ohno approximation is used for two-electron two-center integrals $\gamma_{\mu\nu}$ with all $\gamma_{\mu\mu} = 11.13$ eV. Moreover, we define "specific" correlation π -energies, $\bar{\epsilon}_{corr}^{FCI} = \epsilon_{corr}^{FCI}/N$, $\bar{\epsilon}_{corr}^{CISD} = \epsilon_{corr}^{CISD}/N$, and $\bar{\epsilon}_{corr}^{CISDr} = \epsilon_{corr}^{CISDr}/N$, with N being a number of π -electrons. In particular, we find that the anthracene and phenanthrene molecules have, in eV, the following values of $\bar{\epsilon}_{corr}^{FCI}$: -0.1409 and -0.1336 , respectively, whereas the $\bar{\epsilon}_{corr}^{CISDr}$ values in the same examples are equal to -0.1401 and -0.1324 , respectively. The markedly poor results, -0.1230 and -0.1179 , respectively, are obtained if using the standard (unrenormalized) $\bar{\epsilon}_{corr}^{CISD}$. A similar picture is observed for other studied π -structures. For instance, in the 14π -electron system **6** (the cyclobutadienediphenylene molecule) $\bar{\epsilon}_{corr}^{FCI} = -0.1550$ eV, and the CISD and CISDr methods recover, respectively, 85 % and 99 % of this energy.

In our study when calculating polarizabilities, the standard (Pople-like) finite-field perturbation technique for molecular electric properties [30] is used. The basic definitions allow to identify the dipole polarizability component α_{ii} ($i = x, y, z$) with an negative second derivative of the total electronic energy at zero external electric field along the i th axis. Likewise, the second hyperpolarizabilities γ are computed as the negative forth-order derivatives (for additional detail see [16, 21]).

For neutral alternant (bipartite) π -structures possessing no odd-membered rings, the first π -hyperpolarizability, β , as an negative third-order field derivative of the total energy, vanishes, but β is generally nonzero in ionic π -structures and nonalternant systems. However, in the present paper we restrict ourselves by studying α and γ only, reserving the right to revise the problem in a future work. Throughout the paper, the atomic units (a.u.) are used for α and γ quantities. Furthermore, with the aim of comparing results among related structural classes, the specific (hyper)polatizability values are suitably applied instead of the initial α and γ . That is, we make using the α and γ quantities per π -electron (α/N and γ/N), and retain for them the same notation α and γ .

3. Evaluations of the accuracy of the applied approximations

In order to verify the accuracy of the used approaches (the above considered CISDr modification of CISD and the conventional CCSD) we inspect the static

Fig.2. Structures of conjugated ions for testing approximate π -models.Fig. 3. The bar chart for average π -polarizabilities α and γ computed within FCI, CCSD, and CISDr models. The red, green and blue bars represent, respectively, FCI, CCSD, and CISDr values of α (the left panel) and γ (the right panel); on the ordinates, integers 1-6 correspond to numbers assigned to the structures given in Fig. 1.

(hyper)polarizability results for several medium-size π -structures of two types (Figs. 1 and 2). The first type (Fig. 1) includes the small acenes molecules (anthracene and phenanthrene) along with biphenylene-type structures involving fused cyclobutadiene rings. The second type (Fig. 2) contains aromatic ions and polymethine cations.

For the first type systems, the results are shown graphically by the clustered bar charts in Fig. 3. We see that both, CCSD and CISDr, models describe well the electric properties of the medium-size π -systems, particularly the average dipole polarizability α (with errors within fractions of percentages). The results of somewhat lesser accuracy are obtained for the average hyperpolarizability γ (usually within a percent or so). Notice that for γ CISDr can produce even better results than CCSD, as it is the case of

moderately correlated π -systems (see the bar charts for molecules 5 and 6 in Fig. 3).

Numerical data for the second type systems are condensed in Table 1 (in this case the clustered bar charts are not suitable due to large changes in the polarizability quantities). Clearly, for the closed-shell π -electron ions we obtained somewhat less accurate CCSD and CISDr results in respect to the FCI reference data (errors about 3 % for α , and 10 % for γ in average). Nevertheless, CCSD as well as CISDr provide very good order-of-magnitude estimates of nonlinear polarizabilities even in this difficult case of strongly delocalized extended π -systems. Draw attention to quite large magnitudes in systems 11 and 12 (almost one order of magnitude higher than for other systems in the table). Of course, such an increase is a result of the above-mentioned extended delocalization.

Table 1. FCI, CCSD & CISDr date for average π -polarizabilities α and γ (both per π -electron) in the ionic π -systems from Fig. 2 (γ -values in 10^6 a.u.).

No.	α^{FCI}	α^{CCSD}	α^{CISDr}	γ^{FCI}	γ^{CCSD}	γ^{CISDr}
7	6.16	6.11	6.14	1.07	0.95	1.06
8	6.64	6.52	6.56	2.80	2.09	2.43
9	15.45	15.54	15.71	168	159	147
10	19.8	20.9	21.1	-139	-144	-139
11	40.5	41.2	41.7	-900	-967	-988
12	50.1	51.5	51.4	-1860	-1970	-1930

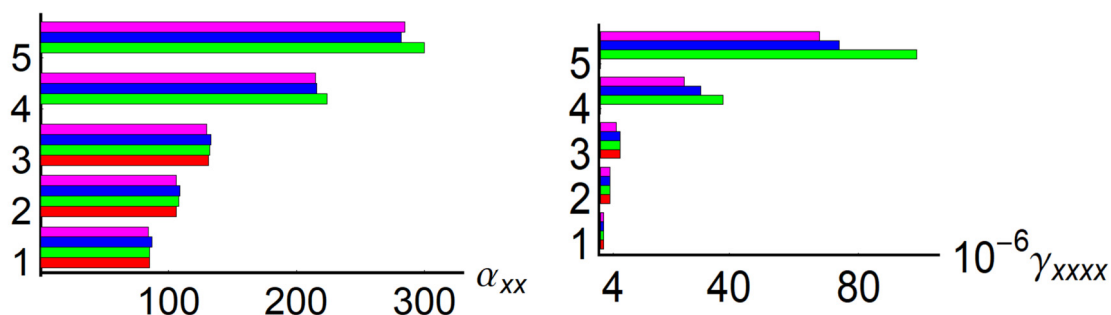


Fig. 4. The bar charts for longitudinal π -polarizabilities α_{xx} and γ_{xxx} (per π -electron) in polymethines at the FCI (in red), CCSD (in green), CISDr (in blue), and DMRD (in magenta) levels. In the both graphs, the ordinate labels 1, 2, 3, 4, and 5 correspond to the polymethine $\text{C}_{2n-1}\text{H}_{2n-1}^+$ with $n = 6$, $n = 7$, $n = 8$, $n = 11$ and $n = 13$, respectively. The α_{xx} -values and γ_{xxx} -values are given in a.u. The FCI results are available for $n = 6$, 7 and 8 only.

4. Applications of CISDr to some oligomers

4.1 Polymethine dyes

There is an additional possibility for comparing the CISDr results against other high-quality approaches. As mentioned in the introduction, DMRG is one of the most suitable and effective numerical methods for describing electron correlation effects. In particular, in [17] one can find the detailed DMRG study of longitudinal π -electron (hyper)polarizabilities α_{xx} and γ_{xxx} in cationic polymethine dyes of the form $\text{C}_{2n-1}\text{H}_{2n-1}^+$ with large n . In Fig. 4 we compare the specific α_{xx} and γ_{xxx} quantities from [17] with ours which are computed at the CCSD and CISDr levels with the same molecular geometry and π -electron parametrization as in the cited paper. The obtained FCI results for the polymethines with $n = 7$ and $n = 8$ are also included in Fig. 4.

From Fig. 4. we see that for small n the DMRG results are practically the same as the FCI results. For the larger polymethine systems, all the α_{xx} data are also suffi-

ciently close between themselves. Somewhat another matter is the γ_{xxx} data displayed on the right panel of the figure. They are very close between themselves only for the first three (rather small) polymethines. For the medium-size systems, the γ_{xxx} magnitudes in CISDr and DMRG deviate markedly from those in CCSD.

In order to estimate which results are more valid, we will analyze in detail the available data for $n = 7$ and $n = 8$ (polymethines $\text{C}_3\text{H}_{15}^+$ and $\text{C}_{15}\text{H}_{17}^+$). For them, the γ_{xxx} specific values within FCI, CCSD, CISDr, and DMRG are as follow (in 10^6 a.u.):

36.2, 37.3, 36.7, 30.8, and 86.3, 89.7, 84.2, 68.3,

respectively. Clearly, in the polymethines CCSD overestimates γ_{xxx} whereas CISDr and DMRG slightly underestimate it. We can suggest that for the hyperpolarizabilities of large-scale polymethines and similar ionic systems, CCSD provides more crude estimations than in the case of the related polyene structures where CCSD is quite successful [4, 19]. This fact can be simply understood

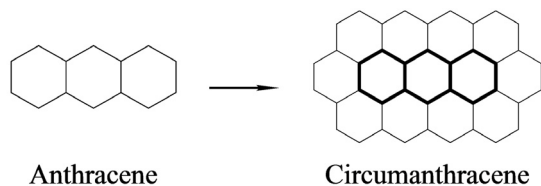


Fig. 5. The circumacene example.

in terms of HOMO-LUMO orbital gap. The gap is noticeably lower in the long polymethine than in the related polyene system with strong bond alternation, and this effect drastically influences the polymethine electronic structure, thus leading to a strong radical character of large ionic carbon chains. As a result the single-reference CCSD model (based on the Hartree-Fock determinant) can lose validity and accuracy. Apparently, the range of applicability of CISD and CISDr is somewhat more wide due to a variational nature of the CISD scheme.

4.2 Acenes and circumacenes

We also discuss another interesting classes of conjugated systems, linear polyacenes $[n]$ acenes and $[n]$ circumacenes. The last are obtained as circumscribed linear $[n]$ acenes (the example for $n = 3$ is given on Fig. 5). The electric properties of the acene molecules were considered previously, e.g. in [4, 31]. The circumacene structures being closely related to the parental acenic structures are more stable as follows from the analysis of their radical character [32, 33]. Therefore, the comparison of polarizability values of these systems has a certain practical usefulness. To make the comparison more consistent we juxtapose the data for the circumacene and acene molecules having a commensurable longitudinal length. Namely, we will compare $[n]$ circumacenes $C_{8n+16}H_{2n+10}$, and the associated linear $[n+2]$ acenes $C_{4n+10}H_{2n+8}$. As

example, for $n = 2$ we compare between the [2]circumacene (ovalene $C_{32}H_{14}$) and [4]acene (tetracene $C_{18}H_{12}$) data.

The relevant polarizability data are presented in Fig. 6. We see that for the lengthy acenes and circumacenes (with sufficiently large n) their specific π -electron (hyper)polarizability values become approximately equal. At the same time, the average radical character of these two type of networks is markedly different [32, 33] as this also shows below our simple computations within the main adopted π -parametrization (turn to Section 2).

In Fig. 7 we display, for the same structures, the specific index $\bar{N}_{eff} = N_{eff}/N$, with N_{eff} being the hole-particle index from [27–29], which for ground singlet states is in fact the same as the well-known radical character index due to Head-Gordon [34]. Here, our computations of \bar{N}_{eff} were based on easy going but reasonable calculations within the quasi correlated tight-binding model [27–29]. We see that indeed linear polyacenes possess a higher radicaloid character (a larger number of effectively unpaired electrons N_{eff}) — the magnitude \bar{N}_{eff} in the acene series is nearly 1.2 times more than that of the circumacene series.

5. Conclusion

In present paper we proposed a not complicated technique for approximate computations of π -electron (hyper)polarizabilities α and γ in large carbon-containing networks with conjugated double bonds. By using the specified CISDr model (CISD approximation with the renormalized energy due to Davidson) we obtained reasonable almost size-consistent estimates of α and γ for large cationic polymethine dyes, polyacenes and related circumacenes. In particular, it is founded that for the large circumacenes the

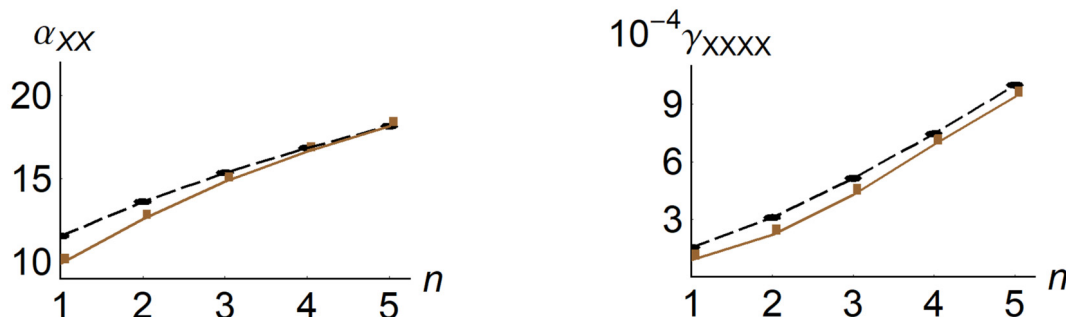


Fig. 6. Longitudinal polarizability α_{xx} and γ_{xxxx} (both per π -electron) in $[n]$ circumacenes (in brown) and $[n+2]$ acenes (in dashed black) for $n = 1+5$.

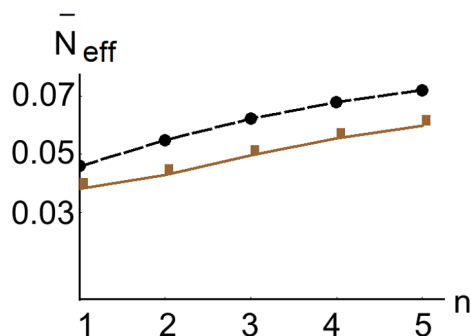


Fig. 7. Magnitude of effectively unpaired electrons N_{eff} in $[n]$ circumacenes (in brown) and $[n+2]$ acenes (in dashed black).

longitudinal hyperpolarizability γ_{xxx} per π -electron differs little from that of the parental acene structures. This fact can be employed when making design and synthesis of new nonlinear optic materials since the circumacenes are chemically more stable than the related acenes. Furthermore, we can expect that the CISDr model can be usefully extended to all-valence semiempirical schemes and, possibly, to ab initio quantum chemistry approaches.

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