

Estimating spin gap in conjugated nanomolecules by spin-flip configuration-interaction-singles approach

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For solids and molecular structures, the spin gap, Δ_s , is usually defined as the lowest electronic transition energy with a minimal nonzero change of the ground-state total spin. Here we apply π -electron semiempirical schemes to estimate Δ_s in nanosized conjugated systems of graphene quantum-dot and chain-like types. Namely, the spin-flip configuration interaction singles (SF-CIS) and appropriately specified Heisenberg spin-Hamiltonian (HSH) models are employed. It is shown by comparison with results of the exact π -electron theory that the simplest version of SF-CIS reasonably reproduces Δ_s in small-size problems, thus providing a justification for using the method in related problems. A particular attention is given to ferromagnetic oligomeric systems based on phenalenyl and triangulene subunits. The conjunction of SF-CIS and HSH approaches gives an efficient numerical scheme for estimating Δ_s in very large chain-like magnetic structures.

Keywords: π -electrons, graphene molecules, polyradicals, organic ferromagnet, exchange integral, Heisenberg's spin Hamiltonian.

Оцінки спінової щілини в спряжених наномолекулах за методом однократних збуджень спин-фліп. *А.В.Лузанов*

Спінова щілина, Δ_s , стосовно твердих тіл та молекулярних структур зазвичай визначається як енергія найнижчого електронного переходу з мінімальною ненульовою зміною повного спіна основного стану. В даній роботі застосовано π -електронні напівемпіричні підходи для оцінок Δ_s у нанорозмірних супряжених системах за типом квантових ям та з ланцюгово-подібною структурою. Безпосередньо використовувались метод конфігураційної взаємодії SF-CIS (однократні збудження за типом спин-фліп) та спеціалізована модель на основі спин-гамільтоніану Гайзенберга (HSH). Порівняння з результатами точної π -електронної теорії для задач малого розміру демонструє прийнятність найпростішої версії SF-CIS стосовно оцінок Δ_s , що обґрунтовує цей метод для споріднених проблем. Особливу увагу приділено ферромагнітним олігомерним системам, котрі базуються на феналенілі та триангулені. Поєднання SF-CIS та HSH веде до ефективної схеми оцінки Δ_s у великих ланцюгоподібних магнітних структурах.

Спиновая щель, Δ_s , для твердых тел и молекулярных структур обычно определяется как энергия наименьшего электронного перехода с минимальным ненулевым изменением полного спина основного состояния. В данной работе применены π -электронные полуэмпирические подходы для оценок Δ_s в наноразмерных сопряженных системах типа квантовых ям или цепеобразных структур. Непосредственно использовались метод конфигурационного взаимодействия SF-CIS (однократные возбуждения по типу спин-флип) и специализированная модель на основе спин-гамильтониана Гайзенберга (HSH). Сравнение с результатами точной π -электронной теории для задач малого размера показывает приемлемость простейшей версии SF-CIS для оценок Δ_s , что оправдывает применение метода для задач родственного типа. Особенное внимание уделено ферромагнитным олигомерным системам, построенным на основе феналенила и триангулена. Сочетание SF-CIS и HSH приводит к эффективной схеме оценки Δ_s в больших цепеобразных магнитных структурах.

1. Introduction

Conjugated nanomolecules are an ample class of molecular systems for nanoelectronics, where, for instance, the well-known graphenic structures (carbon nanoribbons and quantum dots [1–3]) provide only the most popular examples of such type systems. As well known, unusual chemical and physical properties of conjugated molecules are due to mobile valence π -electron shells. Among their key physical characteristics are various energy gaps (charge gap, spin gap etc. [4, 5]). The main focus of the present article will be on the spin gap Δ_s (in usual notation). Here we will study the conventional spin triplet gap (the lowest singlet-triplet transition energy) as well as Δ_s in high-spin molecular systems of ferromagnetic type.

In the literature, one can find many interesting results for Δ_s in various nanomolecular and polymeric structures with π -electrons ([6–14] and many others). Most of the above cited works are based on the density matrix renormalization group (DMRG) technique for ground state properties of π -electron subsystems. The latter are normally considered within the many-electron semiempirical Pariser-Parr-Pople (PPP) approximation. While DMRG is a remarkable high-level approach for treating electron correlation effects, it is a highly specialized and rather difficult method to apply broadly. Therefore, it makes a sense to consider the gap problems within conventional approximations of quantum chemistry, such as not too complicated configuration interaction (CI) models. Thus, the main purpose of the paper is to explore and examine an easily-implemented CI-based method for obtaining practical estimates of spin gap Δ_s in large conjugated molecules.

2. Models within the spin-flip methodology

As familiar from quantum chemistry of large systems, the normal truncated CI models for ground state wave functions are relatively inefficient due to lacking size consistency and related important features (asymptotic additive separability of energy etc.) [15]. However, there is a set of limited CI models for which the size consistency requirement is satisfied in a certain special sense. Particularly, the configuration interaction singles (CIS) method for excited state is of this type. For excited states, the size consistency can be naturally understood as the

size intensive property in the following meaning: asymptotically (with a full separation into fragments) low-lying excitation energies of the combined system must be the same as those of individual fragments [15, 16]. The fact that the variational CIS is size-consistent for excitation energy, was suitably used in Ref. [17] where the so-called spin-flip CIS (SF-CIS) method was proposed as a convenient scheme for estimating molecular excitations [18]. The state-of-art overview of SF models and their generalizations is given in [19].

In the SF-CIS approach, when considering excitations from a singlet ground state, one must start from the Hartree-Fock spin-triplet reference determinant. Then appropriate CIS-like computations are carried out in such a way that in each singly excited electron configuration one azimuthal spin-up convert to a spin-down, thus making spin flip. Notice that similar spin-flip procedures were known long ago in the quantum theory of magnetism where a ferromagnetic ground state (all spins up) was taken as the reference state resulting in the famous Bethe ansatz for an antiferromagnetic state [20]. In quantum chemistry, the spin-flip techniques were employed previously for special semiempirical π -electron models in [21]. Recently we studied by SF-CIS, excitation spectra in several high-spin nanosized π -structures of a ferromagnetic type [22].

Now we revisit the spin transition problem at the traditional π -electron level of treatment, providing a wider set of issues. We need not recapitulate here in detail our earlier discussion of the SF-CIS basic points in [22, 23]. Recall only that for closed-shell molecular systems the simplest SF-CIS scheme is based on wave functions of the compact form

$$|\Psi^{SF-CIS}\rangle = \sum_{1 \leq k \leq N} \tau(k) |\Phi\rangle. \quad (1)$$

Here $|\Phi\rangle$ is an N -electron reference determinant, and one-electron operator τ transforms $|\Phi\rangle$ into a superposition of virtual excitations (singly excited configurations). The spin-flip context is specified by putting $|\Phi\rangle = |\Phi_{S=1}^{ROHF}\rangle$ where the abbreviation ROHF (restricted open-shell Hartree-Fock) shows the type of the chosen reference determinant, and $S=1$ specifies its spin triplet value. Together with this, τ is taken as follows:

$$\tau = ts_-, \quad (2)$$

Table 1. Spin gap Δ_s (in eV) in typical medium-size PAHs by FCI (or DMRG), SF-CIS and EHF. The FCI and DMRG spin gaps are taken from [26]

PAH	FCI (DMRG)	SF-CIS	EHF
Naphthalene	2.55	2.77	2.68
Diphenylene	1.95	2.11	2.14
Anthracene	1.71	1.72	2.03
Tetracene	1.22	1.27	1.62
Pyrene	1.86	1.95	2.16
Chrysene	2.34	2.52	2.39
Perylene	1.58	1.63	1.92

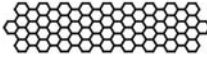
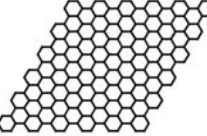

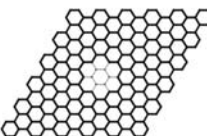
with t being a spin-free transition operator and s the spin-flip (lowering spin) operator. In term of standard single-electron spin eigenkets $|\alpha\rangle$ and $|\beta\rangle$ we have the dyadic representation: $s = |\beta\rangle\langle\alpha|$. Transition operator t and corresponding transition energies can be easily obtained from an appropriate eigenvalue matrix equation expressed in terms of atomic orbital (AO) quantities (for detail see Eq. (A1) in [21]). It is significant that our computational scheme can be implemented using these one-electron matrices in AO basis sets, thus economizing π -calculations (no four-index arrays, no AO to MO transformation, etc.).

3. Accuracy evaluation of spin gap within SF-CIS

As usual, in order to test accuracy of approximate π -electron models we will compare between spin gaps of the exact π -method (π -electron full CI scheme, or simply FCI) and those of the SF-CIS method. The FCI results are available only for relatively small π -systems (in fact, having less than 20 π -centers). For larger polycyclic aromatic hydrocarbons (PAHs), we can rely on high-quality DMRG π -results from [7, 8, 12]. Furthermore, for a more complete account we add here the Δ_s results obtained by the extended Hartree-Fock method (EHF) [24, 25]. For the numerical EHF calculations we used the appropriate matrix algorithm from [25]. In this section all our SF-CIS and EHF π -electron data are related to the same PPP π -parametrization scheme which was used in [7, 8, 12, 26] for finding the FCI and DMRG values of Δ_s .

A summary of obtained information is presented in Table 1. As it follows from the

Table 2. Spin gap Δ_s [TB] and Δ_s [SF-CIS] (in eV) in the Clar-types PAHs and associated hole (antidot) structures; N is a number of carbon atoms

№	Structure	N	Δ_s [TB]	Δ_s [SF-CIS]
1		168	1.08	1.99
2		216	0.94	1.65
3		210	1.14	2.13
4		210	0.77	1.12

table, SF-CIS and EHF provide in whole the results which are quite close to those in FCI or DMRG approaches. At the same time, EHF can be not so good for large-scale systems, and the tetracene and perylene molecules are of this kind. Our supplementary computations confirm a low quality of the EHF estimations for Δ_s in extended conjugated molecules.

For instance, consider one π -structure related to the modeled zigzag graphene nanoribbons (ZGNRs). This is the 34-center [3]ZGNR system with 5 subunits which was carefully examined within DMRG in [8] (see therein Table 2). Together with our data we have the following Δ_s values in this [3] ZGNR problem:

$$\Delta_s[\text{DMRG}] = 0.293, \Delta_s[\text{SF-CIS}] = 0.383, \quad (3)$$

$$\Delta_s[\text{EHF}] = 1.034.$$

In above, the too poor Δ_s [EHF] value reflects the mentioned drawback of EHF, namely, its size-inconsistency which occurs for all EHF electronic energies, including excitation energies. By this [3] ZGNR example we can also suggest that just the size consistency in SF-CIS (recall Section 2) allows to obtain the sufficiently reasonable Δ_s estimates.

As an additional check of the SF-CIS calculations, we as well report $\Delta_s[\text{SF-CIS}]$ for two polymeric systems, and compare them with the respective DMRG results from [7, 12]. In the cited papers, the extrapolated estimates of Δ_s were obtained from calculations of large-scale oligomers associated with linear polyacenes (LPA) [7] and armchair polyacenes (APA) [12]. We have calculated the spin gaps for oligomers of the same structural types with a various number of acene subunits (up to 15 subunits), and found the extrapolated values to be 0.56 eV (in LPA) and 2.69 eV (in APA). It should be compared with the extrapolated DMRG values 0.52 eV [7] and 2.55 eV [12], respectively. We see that in the considered large-scale π -structures, the simplest SF-CIS scheme produces quite realistic spin-gap values, and this result brings certain hope that the SF-CIS technique will be realistic in case of more complex structures for which the DMRG approach cannot be practically executed.

3. SF-CIS computations for conjugated nanomolecules

As the first type of the large systems studied in this section we consider the so-called Clar type PAHs. They correspond to the fully-benzoid conjugated systems investigated in the vast number of papers; for more detail see the original review article [27] dedicated to the "clarology" (the term is from [27]) for these and related structures. Simply speaking, the Clar PAHs as extremal fully-benzoid systems are the PAHs which have a maximal number of benzene subunits; the latter are linked with all adjacent benzene subunits only by simple π -bonds. The most trivial examples are polyphenyls. By their condensation, one can produce the two-dimensional structures such as systems 1, 2 and 3 displayed in Table 2. Notice that much efforts are directed to synthesize the real large PAHs of this type [2, 3, 28–31]. In Table 2 we also include the modified Clar-type megamolecule having a hole in the carbon backbone (systems 3 and 4). The "antidot" structures of this kind had been known to experimentalists [32].

To treat the above structures we make use of the standard π -parametrization applied in most our recent works ([22] and others): all resonance integrals $\beta_{\mu\nu}$ for CC bonds are equal to $\beta_0 = -2.4$ eV, and two-center Coulomb integrals $\gamma_{\mu\nu}$ are due to Ohno, with the one-center integral $\gamma_0 \equiv \gamma_{\nu\nu} = 11.13$ eV. This π -para-

metrization and the normal regular geometry of carbon backbones (with 1.4 Å for all CC bond lengths) differ insignificantly from the scheme applied in the above cited papers on DMRG calculations.

Table 2 summarizes the computed data for $\Delta_s[\text{SF-CIS}]$ together with the simplistic TB estimations $\Delta_s[\text{TB}]$ (i.e., the Hueckel HOMO-LUMO orbital gaps with using the above defined β_0). It should be noted that TB still remains in use for elementary evaluations of UV spectra in large PAHs [33]. Nevertheless, TB should be used very restrictively, that is, only for π -systems with small correlation effects. The Clar structures in Table 2 are just of this type, and that is why we observe that the qualitative picture in TB is practically the same as in SF-CIS. Of course, the quantitative results are markedly different in SF-CIS and TB.

Next, we consider examples extracted from two families of well-known armchair carbon nanotubes (ACNTs). Short ACNTs are close cousins to the so-called nanobelts [34]. As established in [35, 36], the TB energy gap in finite-length ACNTs depends crucially on nanotube length L . This L can be identified with a number of cis-polyene cycles (lossing hydrogen atoms) which are transverse to the tube axis in ACNT. According to [35, 36], in ACNTs the TB orbital energy gap (and thus Δ_s) is zero if $L = 3k - 1$, where k is a positive integer. This family will be categorized here as $[3k-1]$ ACNT. If L takes another values, say $L = 3k$ (ACNT family in our notation), then the TB gap is generally not zero while the gap disappears all the same in the large k limit. In other words, at the TB level the spin gap vanishes for any infinite length ACNT.

Turn now to SF-CIS as a more advanced and reliable approach. For definiteness, take (4,0) CNTs, that is the ACNT produced by a condensation of L cyclohexadecaene moieties. For instance, when $L = 2$ the cyclohexadecaene(16-cyclopolyene) is formed, and $L = 3$ gives [4]cycloparaphenylene. In the case $L = 4$ we have the structure of the cyclo[10]phenacene (nanobelt) synthesized recently in [37].

The results for $\Delta_s[\text{SF-CIS}]$ (in eV) are presented in Fig. 1. The upper plot line is related to the more stable $[3k]$ ACNT family, and the lower plot line shows corresponding data for the less stable ACNT family. Nevertheless, in the both cases the spin gap reaches practically the same nonzero asymptotic limit at large L (at zero limit of

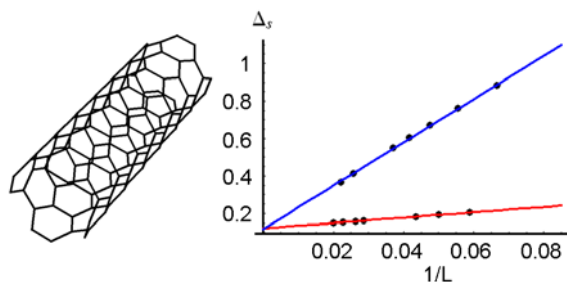


Fig. 1. The representative small [4]ACNT (the left panel) and spin gap dependences as a function of the ACNT inverse length $1/L$ for [3k] ACNT family (in blue) and [3k-1] ACNT (in red) family.

$1/L$), namely, $\Delta_s[\text{SF-CIS}] \cong 0.12$ eV, in evident contrast to the above given $\Delta_s[\text{TB}] = 0$. We see again that one cannot fully rely on the TB estimation even at the qualitative level if large-scale (or infinite) systems are involved.

4. Spin gaps and excitations in conjugated polyradicals

Now we turn to various organic structures possessing a high-spin ground state. Such systems are often named single-molecule ferromagnets [38], and this topic keeps actively developing (see recent review works [39–41]). In the last years, the systems based on phenalenyl (PhNal) radical and triangulene (TrGl) biradical (Fig. 2), have attracted special attention [22, 29, 42–46]. Notice also that within the context of organic ferromagnet materials, the structures of similar type have first appeared in seminal papers [47, 48].

We start our study from the phenalenyl polyradicals. The monomeric PhNal has been previously studied experimentally and computationally at various theoretical levels. For the lowest optical (doublet-doublet) transition energy λ_{opt} , the experimental value $\lambda_{opt}[\text{exp}] = 2.3$ eV and the ab initio value $\lambda_{opt}[\text{theor}] = 2.1$ eV were given in [49]. It can be compared with our semiempirical computations here: $\lambda_{opt}[\text{FCI}] = 2.22$ eV and $\lambda_{opt}[\text{SF-CIS}] = 2.11$ eV. So, we hope that SF-CIS will provide reliable results for related phenalenyl-based oligomeric structures.

First, we directly treat linear (chain-like) oligomer systems $(\text{PhNal})_n$ ($n = \pm 7$) at the SF-CIS level and then juxtapose the results with those of a pertinent spin model of the well known Heisenberg type. Let us begin with the dimer $(\text{PhNal})_2$. Because the ground state of the pristine PhNal is spin-

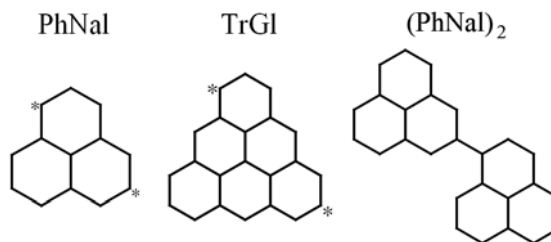


Fig. 2. Magnetic molecular subunits phenalenyl and triangulene, and phenalene dimer $(\text{PhNal})_2$. The star signs in PhNal and TrGl indicate the position via which the subunits are linked to produce oligomeric high-spin chains.

doublet ($S = 1/2$), possible electronic states of $(\text{PhNal})_2$ are singlet, triplet and other high-spin (very excited) electronic states. Due to the Lieb-Mattis-Ovchinnikov rule [48, 50] for alternant (bipartite) PAHs, the ground state of the dimer (see Fig. 2) is the triplet state, so that the lowest singlet state lies above the ground triplet one. In the case of two weakly coupled fragments (as in our dimer), the energy difference between these states is but the usual exchange integral $J_{eff} = E_{S=1} - E_{S=0}$. Specifically, we naturally predict the negative $J_{eff} = -0.1709$ eV at the SF-CIS level.

The next point that is needed to discuss is the SF-CIS results obtained for not so long oligomer chains $(\text{PhNal})_n$ with $n = 2 \div 7$. Equipped with the results we will show below the usefulness of J_{eff} and the related spin chain models (even with larger n). As to the latter, we make a quite reasonable assumption that owing to a weak coupling between PhNal fragments, the involved polyatomic chain $(\text{PhNal})_n$ can be approximately reduced to the standard (nearest-neighbor) spin $1/2$ linear chain with n spins. The chain can be treated by the isotropic Heisenberg's spin Hamiltonian (HSH) of the same normal kind which is typically used; e.g., see [51]. In our case, all nonzero exchange integrals in the associated HSH are identified to the above given J_{eff} . The relevant HSH results together with the direct SF-CIS data are displayed in Table 3. In the second column of this table we present the model analytic expressions, and compare numerical HSH and SF-CIS data in the two last column of the table. It is clearly seen that the HG model leads to quite satisfactory results for the spin gap in phenalenic ferromagnetic chains. This fact allows one to treat $(\text{PhNal})_n$ with a large n by the more

Table 3. Comparison between ferromagnetic spin gaps (in eV) obtained in the spin-flip approach SF-CIS for $(\text{PhNal})_n$ and in the HSH model for open linear spin 1/2 chain with $J_{\text{eff}} = -0.1709$ eV

$n = 2S$	$\Delta_s[\text{HSH}]$ (analyt.)	$\Delta_s[\text{HSH}]$ (numb.)	$\Delta_s[\text{SF-CIS}]$
2	$-J_{\text{eff}}$	0.1709	0.1709
3	$-J_{\text{eff}}/2$	0.0854	0.0812
4	$(\sqrt{2} - 2)J_{\text{eff}}/2$	0.0501	0.0477
5	$(\sqrt{5} - 3)J_{\text{eff}}/4$	0.0326	0.0319
6	$(\sqrt{3} - 2)J_{\text{eff}}/2$	0.0229	0.0231
7	$(\cos[\pi/7] - 1)J_{\text{eff}}$	0.0169	0.0176

simple (at least in this case) HSH technique, and invoke also the appropriate general results of the quantum theory of magnetism (e.g., see review [52]).

In a similar manner, more complex triangulene ferromagnetic chains can be studied. In this case the monomeric triangulene molecule (see Fig. 2) possesses the triplet ground state in concordance with the Lieb-Mattis-Ovchinnikov rule. With the adopted topology of linking monomers (see Fig. 2) the same rule guarantees the polymeric $(\text{TrGl})_n$ to be a ferromagnetic spin 1 chain (with local spin $s = 1$ for each monomeric unit TrGl).

We start with the monomer TrGl and dimer $(\text{TrGl})_2$. The good-quality ab initio computation of the pristine triangulene molecule gives the following lowest triplet-singlet gap: $\Delta_s = 0.703$ eV [53], and again in our semiempirical computations we obtain a quite comparable value: $\Delta_s[\text{SF-CIS}] = 0.815$ eV. For estimating J_{eff} in the investigated ferromagnetic spin 1 chain we take the dimer $(\text{TrGl})_2$ and compute for it the half-difference $(E_{S=1} - E_{S=2})/2 \equiv J_{\text{eff}}$. Within SF-CIS we find $J_{\text{eff}} = -0.04218$ eV.

The relevant results of the comparison between the direct SF-CIS computations of $(\text{TrGl})_n$ ($n = 2+$) and the model HSH treatment are displayed in Table 4. In this table analytic expressions for Δ_s are omitted since in our open spin 1 chains all Δ_s are doubled in respect to those of the relevant spin 1/2 chains. For instance, $\Delta_s = -J_{\text{eff}}$ in the spin 1 chains with $n = 3$, and $\Delta_s = (\sqrt{2} - 2)J_{\text{eff}}$ for $n = 4$. This fact is in conformity with the known results [54, 55] concerning one-magnon transitions (the magnon energy is proportional to a local spin value s).

Table 4. Comparison ferromagnetic spin gaps (in eV) obtained in the spin-flip approach SF-CIS for $(\text{TrGl})_n$ and in the HSH model for open linear spin 1 chain with $J_{\text{eff}} = -0.0422$ eV

$n = S$	$\Delta_s[\text{HSH}]$	$\Delta_s[\text{SF-CIS}]$
2	0.0842	0.0842
3	0.0422	0.0419
4	0.0247	0.0251
5	0.0161	0.0169
6	0.0113	0.0122
7	0.0083	0.0093

From Table 4 we see that for the spin 1 chains the predictions of Δ_s by HSH are also sufficiently close to those by SF-CIS. Thus, the practical upshot of the above calculations is that one can avoid computations on long oligomeric chains, and instead must calculate by quantum chemistry only a certain dimer to estimate J_{eff} for the given chain. Then, simple HSH computations provide all needed lowest excitation energies of the given chain composed of weakly coupled local spins. In particular,

$$\Delta_s[\text{HSH}] = (\cos[\pi/n] - 1)J_{\text{eff}}, \quad (4)$$

for open linear spin 1/2 chains, and

$$\Delta_s[\text{HSH}] = (\cos[2\pi/n] - 1)J_{\text{eff}} \quad (5)$$

for cyclic (closed) spin 1/2 chains. Naturally, Eq. (5) is exactly the energy of the lowest one-magnon transition (see again Eq. (16) in [54]); for more details how to simply compute the magnon spectrum see Appendix to the present paper. We add also that by modifying spin-flip CI methods we can directly generate $\Delta_s[\text{HSH}]$ for rather general ferromagnetic spin 1/2 networks, but algorithmic details are beyond the scope of our discussion.

5. Conclusion

Summing up, we stress again that currently developed techniques for synthesizing organic materials allow to fabricate complex nanomolecules and oligomeric structures with unusual electronic and spin properties. In the present paper we have investigated the structures of this type by the spin-flip quantum chemical machinery which was applied previously for similar purposes in [22]. Now we have demonstrated that SF-CIS permits to reasonably describe conjugated nanomolecular struc-

tures containing up to several hundreds carbon atoms.

Importantly, in the case of long ferromagnetic chains with weakly coupled fragments, one can invoke a combined computational scheme in which only the selected high-spin fragments (monomers and dimers) are quantum-chemically computed (at the SF-CIS level), so that a subsequent analysis of long oligomeric or polymeric structures is easily performed by the conventional Heisenberg spin-Hamiltonian theory. Furthermore, we hope that the spin-flip approach we used may be further improved, without being too complicated, thus providing even more accurate estimates of large-scale molecular spin properties.

Appendix. Computations of one-magnon gap

Here we give convenient expressions for computing one-magnon spectra of the ferromagnetic Heisenberg spin 1/2 model. The corresponding Hamiltonian, H , can be put into the customary form [51] as follows:

$$H = \sum_{1 \leq a, b \leq n} J_{ab} (\mathbf{S}_a \mathbf{S}_b - 1/4), \quad (6)$$

where \mathbf{S}_a is a spin operator localized on the site a of the given molecule or lattice; J_{ab} is defined as a two-site exchange integral for the specified pair (a, b) . Generally all J_{ab} are nonzero (and $J_{aa} = 0$ by definition).

As an initial state, the Bethe-like reference state $|0\rangle \equiv |\uparrow \dots \uparrow\rangle$ (with all spins up) is taken, so that $\langle 0 | H | 0 \rangle = 0$ is the energy of the ground ferromagnetic state. To obtain magnon excitations, one generates basis vectors $\{|a_\downarrow\rangle\}_{1 \leq a \leq n}$ with a single spin-down electron at each site a . In this basis the Hamiltonian $n \times n$ matrix

$$H^{[1]} = \|H_{ab}\|_{1 \leq a, b \leq n}, \quad (7)$$

and $H_{ab} = \langle a_\downarrow | H | b_\downarrow \rangle$ can be computed by the simple recipe:

$$H_{aa} = -\sum_{c \neq a} J_{ac}/2, \quad H_{ab} = J_{ab}/2, \quad a \neq b. \quad (8)$$

Note in passing that in Eq. (8) the requirement $c \neq a$ is in fact redundant because $J_{aa} = 0$.

Eq. (8) is a suitable form of more or less known expressions; e.g., Eq. (8) is implicitly contained in Eq. (12) from [55] and in Eq. (11) from [56]. In addition, we note that $H^{[1]}$ is the matrix which row sums (or

column sums) are all equal to zero. It provides the minimum (zero) eigenvalue of $H^{[1]}$ that is naturally related to the ground state, so that the second eigenvalue of $H^{[1]}$ should be identified with $\Delta_s[\text{HSH}]$.

In practice, the most applicable is a counterpart of the tight-binding approximation for exchange integrals J_{ab} when only nearest-neighbor site interactions are taken into account. Typically, in this scheme each nonzero J_{ab} is equal to a single prescribed value J_{eff} , so we must set

$$J_{ab} = J_{eff} A_{ab}, \quad (9)$$

with $A = \|A_{ab}\|$ being the ordinary adjacency matrix of a topological graph for the studied structure. In graph-theoretic terms, H_{aa} in Eq. (8) is, within a constant factor, identical to d_a , that is degree (valence) of vertex a . Then, Eq. (7) can be rewritten:

$$H_{[1]} = -J_{eff} L/2, \quad (10)$$

where $L = \|d_a \delta_{ab} - A_{ab}\|$ is the combinatorial Laplacian of the given graph. Seemingly, representation (10) was not noted before, while some useful applications can be made of this equation.

Indeed, the graph Laplacians are well investigated, and many results concerning L , and thereby $H^{[1]}$, may be simply borrowed from a rich literature, especially the results about spectral properties of L ([57–60] and many others). Special attention deserves the Laplacian second eigenvalue λ_2 which plays an important role for describing graph. In our context this λ_2 is actually the spin gap

$$\Delta_s[\text{HSH}] = -J_{eff} \lambda_2/2. \quad (11)$$

In particular, Eq. (4) in the form of $\lambda_2 = 2(1 - \cos[\pi/n])$ is presented in [57] and others; within quantum communication problems, the one-magnon spectrum of the open linear chain is also presented in [61]. It is remarkable fact that $\lambda_2 = 0$ if and only if the graph is disconnected (no isolated subgraphs) [57, 59]. It means that in normal (connected) structures $\Delta_s[\text{HSH}]$ cannot be the strict zero (unlike $\Delta_s[\text{TB}]$). Another interesting inferences pertinent to studying magnon Δ_s can be drawn from graph theory, but we will not dwell on these issues here.

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